FIELD VALIDATION OF THE DNPH METHOD FOR ALDEHYDES AND KETONES

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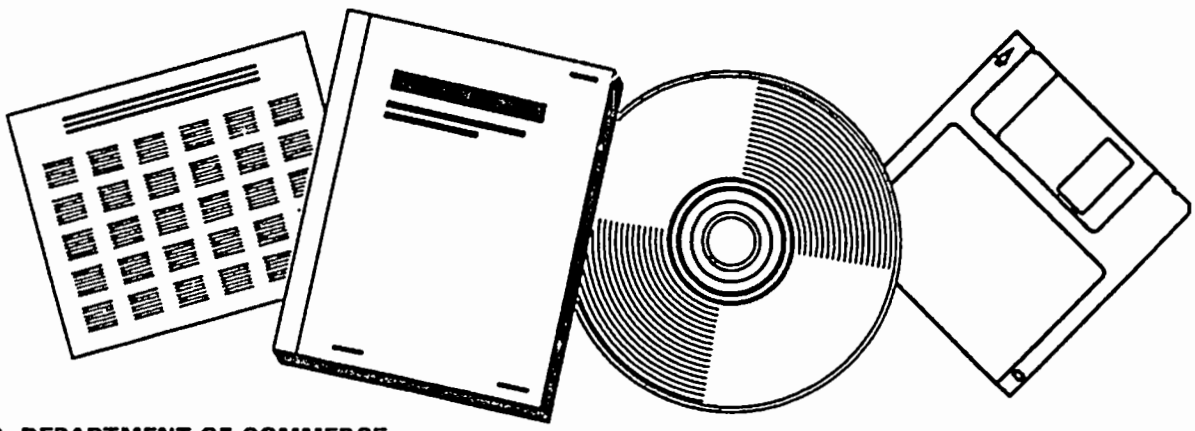

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Field Validation of the DNPH Method for Aldehydes and Ketones

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16. ABSTRACT

A stationary source emission test method for selected aldehydes and ketones has been validated. The method employs a sampling train whith impingers containing 2,4-dinitrophenylhydrazine (DNPH) to derivatize the analytes. The resulting hydrazones are recovered and analyzed by high performance liquid chromatography. Nine analytes were studied: formaldehyde, acetaldehyde, propionaldehyde, methyl ethyl ketone, methyl isobutyl ketone, acetophenone, isophorone, and quinone. The study employed the validation techniques described in EPA method 301, which uses train spiking to determine bias, and collocated sampling trains to determine precision. The studies were carried out at a plywood veneer dryer and a polyester manufacturing plant.

On the basis of the Method 301 criteria for precision (±50% relative standard deviation) and bias (correction factor of 1.00 ±0.30) the method was validated for formaldehyde, acetaldehyde, propionaldehyde, acetophenone and isophorone. Acrolein, methyl ethyl ketone, methyl isobutyl ketone, and quinone did not meet the validation criteria.

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SECTION 1.0
INTRODUCTION

Radian Corporation, while assisting the Method Branch of the National Exposure Research Laboratory (NERL), has evaluated and validated a multiple pollutant sampling and analytical method for aldehydes and ketones in emissions from stationary sources. This study is part of an EPA program to develop stationary source emission test methods for the 189 hazardous air pollutants listed in the Clean Air Act Amendments of 1990, and which are needed to determine risk to the public and to support the regulatory process.

The method in the present study employs an impinger train containing acidified 2,4-dinitrophenylhydrazine (DNPH) to capture and derivatize aldehyde and ketone compounds. Validation of the test method was needed to demonstrate applicability to different source types. Test sites known to emit relatively low concentrations of both acetaldehyde and formaldehyde were selected. Under Work Assignment 67 of EPA Contract 68-D1-0010, the method was evaluated at a plywood veneer dryer vent at a pressboard manufacturing plant; under Work Assignment 12 of EPA Contract 68-D4-0022, method evaluation was conducted at a spinning machine exhaust vent at a polyester fiber manufacturing plant. Site parameters and aldehyde concentrations were confirmed with information gathered during pretest site surveys. The present report covers both of these field validation studies.

The method was evaluated using procedures described in EPA Method 301,[1] *Protocol for the Field Validation of Emission Concentrations from Stationary Sources*, in which bias is determined by spiking sample trains and precision is determined by collocating sampling trains. In the present study, spiking was carried out by a dynamic method in which measured quantities of analyte were introduced into the flue gas being sampled.

Precision and bias of the test method for each compound tested are summarized in Table 1. For Field Test I data is shown for both two and four impingers. Precision and bias calculations were completed using all four impingers for Field Test I because of the high breakthrough values that occurred during Runs 3, 4, 6, and 7. Two-impinger data also was reported for Field Test I to demonstrate that formaldehyde and acetophenone passed with only two impingers. For Field Test II, data is shown for two impingers only because breakthrough levels for all of the trains were low and there was little difference in total amounts recovered between the two- and four-impinger data sets.

For Field Test I and Field Test II, four sampling trains were operated simultaneously (quadruplicate sampling train) to collect flue gas samples. The configuration of each sampling train was the same as that described in SW-846 Method 0011[2] for formaldehyde, except that the first impinger contained 200 mL of reagent to increase sample capacity, and an additional impinger containing DNPH was added to check for breakthrough. The actual method evaluated is included in Appendix B. In this sampling method, gaseous and particulate pollutants are collected from an emission source in aqueous, acidic DNPH. Aldehydes and ketones present in the stack gas stream react with the DNPH to form dinitrophenylhydrazones. Samples are then extracted with organic solvent. The resulting organic extract is concentrated as necessary and exchanged into an appropriate solvent for analysis by high performance liquid chromatography (HPLC).

Ten aldehydes and ketones listed in Title III of the Clean Air Act were studied as part of this project. These compounds are listed in Table 2. Nine of the ten compounds listed in Table 2—formaldehyde, acetaldehyde, quinone, acrolein, propionaldehyde, methyl ethyl ketone, acetophenone, methyl isobutyl ketone, and isophorone—were spiked into the sampling trains during sample collection as part of the method evaluation procedure at the first field test site. The compound 2-chloroacetophenone was excluded from the list of compounds quantifiable by this method because a purified DNPH derivative of this compound could not be successfully made during the initial laboratory studies. Furthermore, because

Table 1. Results of the EPA Method 301 Statistical Evaluation

Parameter	Form-aldehyde	Acet-aldehyde	Propion-aldehyde	Aceto-phenone	Methyl Ethyl Ketone	Methyl Isobutyl Ketone	Isophorone	Quinone	Acrolein
Field Test 1[a]									
RSD Spiked (%)	7.36	7.18	7.20	7.94	26.1	17.2	7.94	40.0	12.1
RSD Unspiked (%)	10.2	10.6	21.0	42.5	74.3	32.2	211	39.7	17.3
Bias CF	1.11	1.26	1.25	1.08	2.55	2.22	1.08	1.84	2.00
Disposition	Pass	Pass	Pass	Pass	Fail	Fail	Fail	Fail	Fail
Field Test 1[b]									
RSD Spiked (%)	7.32	8.15	NR	7.79	NR	NR	NR	NR	NR
RSD Unspiked (%)	9.95	10.3	NR	43.5	NR	NR	NR	NR	NR
Bias CF	1.10	1.34	NR	1.11	NR	NR	NR	NR	NR
Disposition	Pass	Fails	NR	Pass	NR	NR	NR	NR	NR
Field Test 2[c]									
RSD Spiked (%)	8.8	16.7	12.9	10.4	18.8	21.2	9.0	NT	NT
RSD Unspiked (%)	20.7	12.4	48.5	--	--	--	--	NT	NT
Bias CF	1.10	1.24	1.29	1.09	2.45	4.33	0.93	NT	NT
Disposition	Pass	Pass	Pass	Pass	Fail	Fail	Pass	NT	NT

NR = Not Reported
NT = Not Tested
RSD = Relative Standard Deviation
CF = Correction Factor

[a]Statistics calculated from 4-impinger results in Field Test 1.
[b]Statistics calculated from 2-impinger results in Field Test 1.
[c]Statistics calculated from 2-impinger results in Field Test 2.

2-chloroacetophenone can be determined by Method 0010,[3] there was no need to include it in the Method 0011[2] validation study.

Table 2. Aldehydes and Ketones Included on the Clean Air Act Title III List

Formaldehyde
Acetaldehyde
Quinone
Acrolein
Propionaldehyde
Methyl Ethyl Ketone
Acetophenone
Methyl Isobutyl Ketone
2-Chloroacetophenone
Isophorone

For Field Test II, acrolein and quinone were not included in the spiking solution. Acrolein is chemically unstable under the acidic reaction conditions because of its double bond. Acrolein is a highly reactive substance and is known to dimerize by the Diels-Alder reaction. Acrolein may also react with other aldehydes, causing their recoveries to be low. Therefore, acrolein was considered inappropriate to study as part of a multiple pollutant aldehyde and ketone method test. A pollutant-specific method may be required to measure acrolein emissions. Quinone appears to be collected in the impingers but does not react well with the DNPH under the conditions specified in the method. Quinone is also a strong oxidizing agent having the potential to oxidize formaldehyde, and its addition to the spiking solutions may have caused low recoveries of some aldehydes during the first field test. For these reasons, quinone was also excluded from the second field study. Of the compounds that were spiked, the laboratory studies indicated the method would perform satisfactorily for five: formaldehyde, acetaldehyde, propionaldehyde, acetophenone, and isophorone. Methyl ethyl ketone and methyl isobutyl ketone in the impingers and do not react rapidly enough with the

DNPH to be quantitatively collected. The two compounds are volatile and are swept through the sampling train before they have time to react.

This test report is divided into seven sections. Section 2 is a summary of the validation test results including the conclusions and recommendations based on the results of the field validation tests and laboratory studies. Sections 3 and 4 present the results of Field Test I and Field Test II, respectively. Sampling and analytical procedures are detailed in Section 5. Quality assurance/quality control (QA/QC) data are described in Section 6 and references are provided in Section 7.

SECTION 2.0
CONCLUSIONS AND RECOMMENDATIONS

Based on the work performed in the laboratory studies and the field evaluation of the aldehydes and ketones, and using Method 301[1] criteria as revised in December, 1994, the following conclusions may be drawn regarding the proposed sampling method.

- **Acetophenone, Formaldehyde, Isophorone, Acetaldehyde, and Propionaldehyde** Using the criterion of 70-130% recovery for the dynamically spiked compounds, acetophenone, formaldehyde, isophorone, acetaldehyde, and propionaldehyde meet the minimum recovery criterion.

- **Quinone, Acrolein, Methyl ethyl ketone, and Methyl isobutyl ketone** The test method is not appropriate for the measurement of quinone, acrolein, methyl ethyl ketone, and methyl isobutyl ketone, due either to poor collection efficiency or analytical problems.

- **Formaldehyde, Acetaldehyde, Propionaldehyde, Methyl Ethyl Ketone, Acetophenone, and Methyl isobutyl ketone** are all stable in the aqueous spiking solution for up to 62 days.

- **All Compounds Except Formaldehyde** Dynamic spiking allowed the collection efficiency of the train to be more adequately evaluated than static spiking and is the preferred spiking technique especially when very volatile, water-purgeable compounds are being tested.

- **All Compounds** Keeping the first two impingers in an ice bath results in higher compound recoveries with less breakthrough into the second impinger and less tautomer formation than when the first two impingers are kept warm.

Based on work performed in the laboratory and in the field evaluation, the following recommendations are made:

- Subject to the number of impingers used for various compounds (as stated below), the sampling and analytical method tested is recommended for adoption as a standard EPA method for the determination of formaldehyde,

acetophenone, isophorone, acetaldehyde, and propionaldehyde emissions from stationary sources.

- To obtain quantitative recoveries of formaldehyde, acetophenone, and isophorone, use 200 mL of DNPH reagent in the first impinger followed by one impinger containing 100 mL and keep the impingers iced. To obtain quantitative recoveries of acetaldehyde and propionaldehyde, use 200 mL of DNPH reagent in the first impinger followed by two impingers containing 100 mL and keep the impingers iced.

- Recoveries for acrolein in the laboratory studies were low, probably due to the reactive nature of the double bond. Alternative sampling and analytical methods should be pursued for acrolein or modifications should be made to Method 0011[2] to stabilize acrolein. Potential modifications to Method 0011[2] include using hexane to recover the sample trains instead of methylene chloride.

- Method 0011[2] yields inconsistent results when used to determine quinone. Alternative sampling and analytical methods should be investigated for quinone.

- Methyl isobutyl ketone and methyl ethyl ketone are not efficiently collected by the aqueous DNPH reagent. Alternative sampling and analytical methods, possibly using sorbents, should be investigated for these compounds. Alternatively, modifications to Method 0011[2] such as using five or more reagent impingers, sampling at lower flow rates, using a lower pH reagent (>2N HCl), may improve the performance of Method 0011[2] for these compounds.

SECTION 3.0
FIELD TEST I

The first Method 0011[2] field evaluation study was conducted at a plywood veneer manufacturing plant during the weeks of July 26 and August 1, 1994. Ten runs were performed using quadruplicate aldehyde and ketone sampling trains. The sampling train that was evaluated is shown in Figure 1. Dynamic analyte spiking was used for method evaluation. The dynamic spiking apparatus and procedure are described in detail in Section 5.

Samples were analyzed and the analysis results were used to determine the method precision and bias for each of the spiked compounds by EPA Method 301.[1] Two fractions from each individual sampling train were recovered and used to detect and quantify the amount of breakthrough of the nine test compounds through the DNPH solution in the first two impingers. Laboratory results in total micrograms of each compound were summed for the probe rinse, first impinger contents, and second impinger contents (Fraction 1) and for the third impinger and knockout rinse (Fraction 2). Breakthrough was calculated as the percentage of the total that was found in Fraction 2. Recovery efficiency of the sampling and analytical method for the aldehyde and ketone compounds was determined using the data from the 20 dynamically spiked trains.

Details of the sampling runs and results of the laboratory and statistical analyses are presented in the following subsections.

FIELD SAMPLING

Flue gas samples for carbonyl analysis were collected at a plywood veneer manufacturing plant from a dryer used to dry the plywood veneer before shipping. Samples were collected from the first dryer stack. The sampling ports were 6-inch (152 mm) diameter

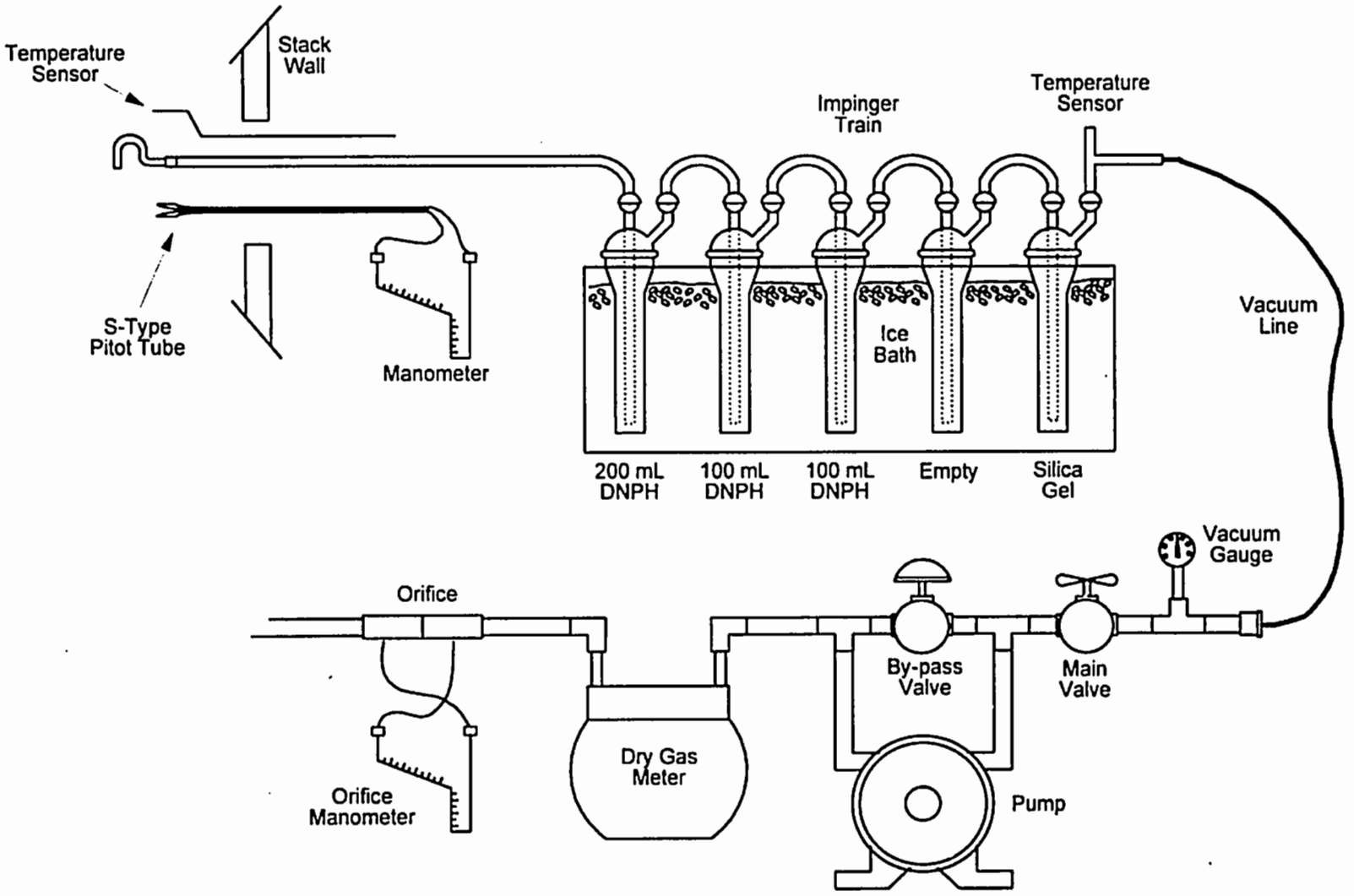


Figure 1. Sampling Train for Aldehydes and Ketones

pipe nipples located approximately 2.6 meters above the sampling platform. The sampling platform was approximately 12 meters above ground level. Figure 2 is a diagram of the sampling location. The ports were located at least 4 stack diameters downstream and 1 stack diameter upstream of the nearest flow disturbances. Preliminary samples were collected from the dryer stack during a pretest site survey. Formaldehyde, acetaldehyde, propionaldehyde, and acrolein were all detected in the dryer stack gas at levels over 10 times the method detection limit. Other aldehydes and ketones, including methyl ethyl ketone and methyl isobutyl ketone, were also identified and determined to be present at low concentrations in the samples.

Ten quad train runs were completed at the test site. The quad-train probe is described in detail in Section 5. Trains A and D were spiked and Trains B and C were unspiked. Table 3 summarizes the sampling parameters recorded for each run. The diameter of all the sampling nozzles was 5.72 mm. The static pressure in the stack was positive, and remained constant at approximately 15 mm of water during all test runs. The target sample volume for each run was 0.85 cubic meters. The sampling time was 75 minutes.

Because of the additional liquid spiked into Trains A and D, only Trains B and C were used to calculate the percentage of moisture in the stack gas. Moisture values were in the range of 19 to 28% by volume because of the high level of moisture expelled from the product.

The stack temperature and velocity for each run were measured using a single thermocouple and S-Type pitot tube on the sampling probe assembly. Individual stack gas temperature and pitot tube differential pressure measurements were taken for each of the four trains at the time the other sampling data were recorded. This measurement scheme resulted in some slightly different temperature and velocity data associated with individual trains for the same run, even though measurements were made with a common probe. These temperature and differential pressure measurement differences did not affect the test data because the

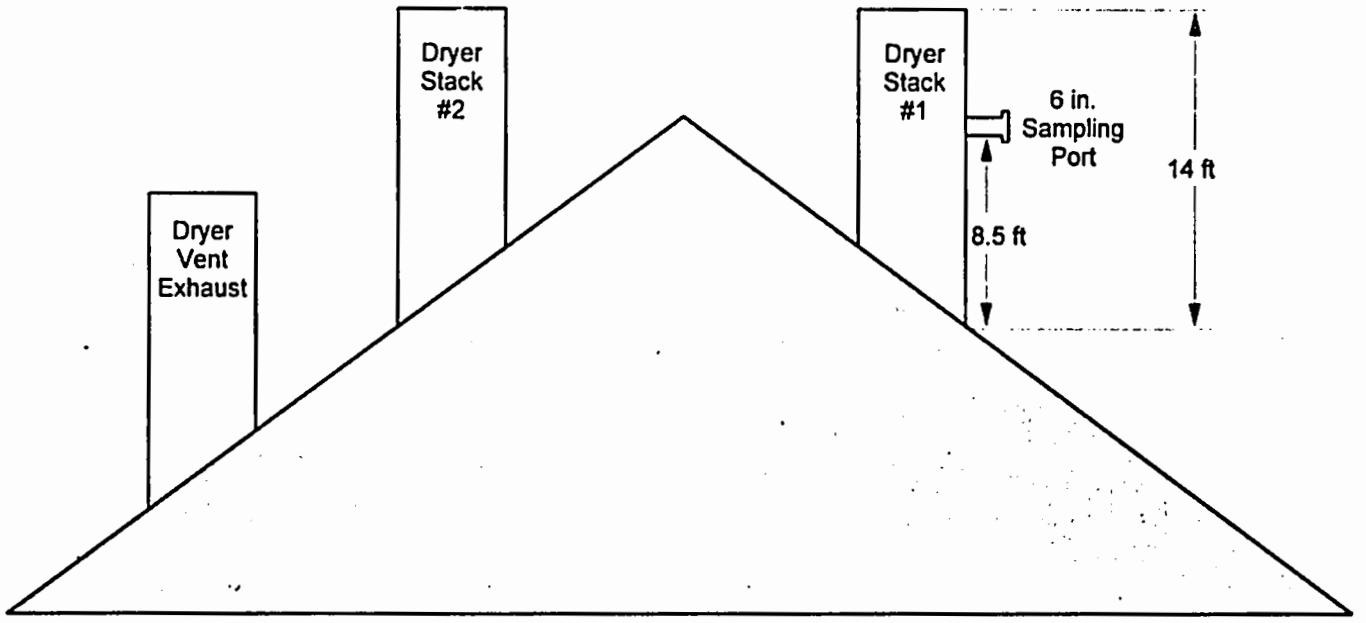


Figure 2. Sampling Location for the First Aldehyde and Ketone Method Development Field Test

Table 3. Sampling Parameters, Field Test I (August 1994)

Run	Sampling Duration (min	Moisture (%)	Standard Meter Volume (dscm)	Stack Temperature (°C)	Stack Gas Velocity (mpm)	Percent Isokinetic
1A	75	--	0.871	160	881.0	98.97
1B	75	27.4	0.820	160	887.4	97.09
1C	75	25.8	0.924	160	884.6	107.4
1D	75	--	0.864	160	881.5	98.70
2A	75	--	0.944	194	1014	101.9
2B	75	26.6	0.904	194	1018	99.60
2C	75	26.2	0.906	194	1017	99.27
2D	75	--	0.932	194	1015	101.1
3A	75	--	1.00	197	1042	107.0
3B	75	27.7	0.908	197	1046	99.19
3C	75	27.2	0.926	197	1045	100.5
3D	75	--	0.914	197	1043	98.40
4A	75	--	0.849	189	980.4	97.52
4B	75	28.4	0.830	189	982.4	96.47
4C	75	27.7	0.849	189	980.9	97.78
4D	75	--	0.837	189	978.9	95.30
5A	75	--	0.889	189	986.0	97.53
5B	75	26.0	0.852	189	989.2	95.21
5C	75	25.2	0.852	189	987.4	94.19
5D	75	--	0.872	189	985.3	95.34
6A	75	--	0.919	191	988.5	104.3
6B	75	29.4	0.860	191	993.7	100.5
6C	75	29.0	0.858	191	992.7	99.70
6D	75	--	0.862	191	990.6	99.01
7A	75	--	0.912	203	1022	95.21
7B	75	22.7	0.885	203	1026	93.89
7C	75	21.6	0.892	203	1023	93.61
7D	75	--	0.873	203	1020	90.15

Table 3. (Continued)

Run	Sampling Duration (min	Moisture (%)	Standard Meter Volume (dscm)	Stack Temperature (°C)	Stack Gas Velocity (mpm)	Percent Isokinetic
8A	75	–	0.978	204	1049	98.09
8B	75	23.6	0.924	204	1057	96.47
8C	75	20.9	0.943	204	1051	95.62
8D	75	–	0.954	204	1050	96.09
9A	75	–	0.931	204	988.8	96.98
9B	75	20.3	0.891	204	993.3	95.02
9C	75	19.7	0.868	204	992.1	91.91
9D	75	–	0.882	204	989.2	92.11
10A	75	–	0.859	203	980.8	91.11
10B	75	19.7	0.852	203	981.8	90.81
10C	75	19.5	0.863	203	981.4	91.83
10D	75	–	0.856	203	982.1	91.42

sample for all four trains was collected from the same point, the volumes collected were recorded, and the data was corrected for the slight differences in sample volume.

The spiking system was operated to inject approximately equal quantities of spiking solution into Trains A and D during each sampling run. The actual amounts spiked varied from train to train because the syringe pumps used did not always deliver exactly the same amount of spiking solution. The results of the laboratory study indicated that dynamic spiking was preferable to static spiking even though it resulted in variable spike amounts. Table 4 shows the quantity of each compound spiked into Trains A and D during each run. Spiked quantities were determined by weighing the spiking syringes before and after each test run. Spike weights were recorded in a field notebook.

ANALYSIS

The samples from each train were collected and analyzed in two fractions. The first fraction contained the probe rinse and contents of the first two impingers. The second fraction contained the contents of the third and fourth impingers. Table 5 shows the results of the analysis of the first fraction from each run.

Table 6 shows cumulative analytical results for both fractions combined (all impingers) of each sampling train. Table 7 shows the percentage of each spiked compound recovered in all four impingers. The recovery is calculated as follows:

$$R = 100\% \times \frac{S - M}{CS}$$

where:

R = percent recovery,

S = measured quantity in the spiked sample,

M = mean value of the unspiked samples in the run, and

CS = calculated spike quantity.

Table 4. Spike Quantities for First Field Test (August 1994)

	Quantity Spiked (μg)							
Run	Formaldehyde	Acetaldehyde	Acrolein	Propionaldehyde	Acetophenone	MEK	MIBK	Isophorone
1A	20,700	12,500	4,220	4,420	8,900	5,310	7,100	9,650
1D	18,700	11,300	3,820	4,000	8,050	4,810	6,430	8,730
2A	20,400	12,400	4,180	4,370	8,810	5,260	7,030	9,550
2D	22,400	13,600	4,580	4,800	9,660	5,770	7,710	10,500
3A	22,900	13,900	4,690	4,910	9,880	5,900	7,890	10,700
3D	23,800	14,400	4,850	5,080	10,200	6,110	8,180	11,100
4A	22,400	13,600	4,580	4,800	9,660	5,770	7,710	10,500
4D	21,900	13,300	4,470	4,680	9,430	5,630	7,530	10,200
5A	20,300	12,300	4,160	4,350	8,760	5,230	7,000	9,510
5D	21,400	13,000	4,370	4,570	9,210	5,500	7,350	9,990
6A	23,500	14,200	4,790	5,020	10,100	6,030	8,070	11,000
6D	26,000	15,700	5,300	5,550	11,200	6,680	8,920	12,100
7A	23,500	14,200	4,790	5,020	10,100	6,030	8,070	11,000
7D	22,000	13,300	4,490	4,710	9,480	5,660	7,570	10,300
8A	21,700	13,100	4,430	4,640	9,340	5,580	7,460	10,100
8D	22,100	13,400	4,520	4,730	9,520	5,690	7,600	10,300
9A	21,600	13,100	4,410	4,620	9,300	5,550	7,430	10,100
9D	22,400	13,600	4,580	4,800	9,660	5,770	7,710	10,500
10A	21,300	13,000	4,350	4,550	9,160	5,470	7,320	9,940
10D	21,200	12,800	4,320	4,530	9,120	5,450	7,280	9,890

Table 5. Analytical Results for First Two Impingers for Field Test I (August 1994)

	Quantity Measured (μg)								
Run	Formaldehyde	Acetaldehyde	Quinone	Acrolein	Propion-aldehyde	Acetophenone	MEK	MIBK	Isophorone
1A	24,400	14,400	6,850	5,250	4,020	7,740	2,110	4,400	8,250
1B	11,900[c]	6,340	2,320	1,900	614	150	183	307	42.3
1C	11,800	6,670	2,390	1,860	503	180[b]	228[b]	282[b]	ND
1D	27,100	14,850	3,640	5,100	4,400	8,530	1,500	2,960	8,550
2A	24,500	16,000	7,370	2,980	3,900	8,730	1,330	2,690	9,190
2B	6,290	6,740	2,360	457	231	20.2[a,b]	46.4[a]	61.8	11.4[b]
2C	5,480	5,500	427[b]	396	217[b]	<0.84	260[b]	45.5[b]	ND
2D	27,100	17,400	6,480	3,030	4,140	9,280	2,030	2,990	7,770
3A	24,500	13,200	6,690	1,680	2,800	8,200	518	1,110	9,220
3B	4,950	5,060	2,300	230	106[a]	39.5	13.3[a,b]	88.8	8.46[b]
3C	4,020	4,030	1,220	195	111[a]	20.5[a,b]	21.6[a]	<0.23	ND
3D	29,800	17,000	7,920	2,440	3,830	10,600	702	1,900[b]	10,800
4A	27,000	16,200	5,240	2,660	4,060	9,010	850[a]	1,940	9,250
4B	5,780[c]	4,670	1,630[c]	490	143	12.3[a,b]	34.6[a]	<0.12	8.16[b]
4C	5,420[c]	4,260	3,010	452	182	51.6	27.2[a]	<0.12	8.14[b]
4D	29,200	16,100	7,650	2,050	3,450	9,580	696	1,720[b]	9,460
5A	25,100	15,800	6,290	2,220	3,850	8,310	1,400	3,020	8,300
5B	5,350	4,280	1,240	289	182	<0.84	25.9[a]	<0.23	ND
5C	5,750	4,530	993	318	219	46.2	28.9[a]	<0.23	9.46[b]
5D	26,200	15,700	10,800	2,200	3,810	8,900	763	2,360	9,300
6A	18,400	10,700	8,110	1,270	2,700	7,190	832	1,580	7,650
6B	4,420[c]	3,000	1,500	98.6	77.5[a]	43.8	15.6[a,b]	285	8.14
6C	4,530	2,860	1,690	98.3	65.5[a]	45.6	13.8[a,b]	274	11.7
6D	24,200[c]	9,800	5,890	2,920	2,410	8,070	419	1,050	9,280
7A	18,500	9,780	3,690	1,310	2,530	6,630	837[c]	1,350	7,430

Table 5. (Continued)

	Quantity Measured (μg)								
Run	Formaldehyde	Acetaldehyde	Quinone	Acrolein	Propion-aldehyde	Acetophenone	MEK	MIBK	Isophorone
7B	3,330	3,150	1,180	128	132	7.60[a,b]	20.4[a]	38.4	13.4[b]
7C	3,900	3,590	1,290	116	117	13.4[a,b]	18.8[a,b]	31.2	15.6[b]
7D	18,200	10,100	7,580	1,360	2,640	7,080	834	1,280	7,820
8A	25,000	14,600	6,440	2,070	3,510	8,380	1,060	2,510	9,240
8B	3,230	4,290	1,380	183	174	11.6[a,b]	30.4[a]	34.7	8.12[b]
8C	3,340	3,990	785	158	132	11.2[a,b]	18.6[a,b]	34.1	9.27[b]
8D	26,700	15,700	6,500	1,870	3,450	8,920	771	2,140	9,810
9A	26,800	13,800	4,830	1,990	3,730	8,830	1,510	2,890	9,560
9B	3,010	2,940	1,410	136	136	9.21[a,b]	21.7[a]	26.6	9.24[b]
9C	3,140	3,230	1,550	141	160	12.1[a,b]	20.7[a]	33.9	8.91[b]
9D	27,700	14,400	2,160	2,470	3,720	9,300	1,450	2,530	10,700
10A	24,200	12,600	869[b]	1,650	3,370	8,200	1,370	2,050	9,490
10B	3,230	3,630	893	158	212	20.1[a,b]	51.2[a]	38.1	166
10C	2,850	3,180	725	154	189	15.0[a,b]	53.3[a]	36.4	8.87[b]
10D	24,400	14,400	7,220	1,760	3,480	8,860	1,130	2,650	10,100

NOTE: Final values are not corrected for the field train blank.

ND = Not Detected.

[a] Less than 10 times the field train blank.
[b] Below calibration curve, quantified by extrapolation.
[c] Above calibration curve, quantified by extrapolation.

Table 6. Analytical Results for All Fractions (Field Test I, August 1994)

	Quantity Measured (μg)								
Run	Formaldehyde	Acetaldehyde	Quinone	Acrolein	Propion-aldehyde	MEK	Aceto-phenone	MIBK	Isophorone
1A	24,500	15,000	6,870	5,410	4,250	2,640	7,860	5,090	8,520
1B	12,100	6,730	2,370	1,940	638	202	155	314	42.3
1C	11,800	7,090	2,390	1,860	503	228	180	282	ND
1D	27,100	15,500	3,640	5,250	4,620	2,310	8,680	3,910	8,800
2A	24,500	16,900	7,410	3,090	4,250	2,400	8,890	3,880	9,610
2B	6,300	7,640	2,370	469	279	60.9	20.2	61.8	11.4
2C	5,510	6,200	427	396	273	304	ND	45.5	ND
2D	27,100	18,200	6,550	3,130	4,450	2,970	9,430	3,850	8,270
3A	24,500	16,900	6,730	1,820	3,720	2,180	8,560	2,710	9,740
3B	4,990	6,460	2,330	242	158	28.3	39.5	105	8.46
3C	4,040	5,420	1,220	207	166	30.8	24.9	ND	ND
3D	29,900	19,500	7,940	2,600	4,480	1,880	11,000	3,150	11,500
4A	27,100	18,000	5,250	2,780	4,520	1,960	9,220	3,180	9,750
4B	5,800	5,790	1,630	504	189	47.6	12.3	ND	8.16
4C	5,450	5,660	3,020	488	245	45.8	53.7	ND	8.14
4D	29,300	19,900	7,680	2,240	4,370	2,200	9,990	3,490	10,100
5A	25,200	16,300	6,310	2,310	4,040	2,200	8,430	3,170	8,610
5B	5,380	4,770	1,240	310	210	39.4	ND	ND	0.32
5C	5,760	4,960	998	334	243	40.6	46.2	8.41	9.46
5D	26,200	16,800	10,800	2,290	4,120	15,900	9,060	3,230	9,720
6A	18,400	13,200	8,130	1,380	3,330	2,080	7,500	2,910	8,240
6B	4,440	4,510	1,500	108	131	30.0	43.8	299	8.14

Table 6. (Continued)

Run	Quantity Measured (μg)								
	Formaldehyde	Acetaldehyde	Quinone	Acrolein	Propion-aldehyde	MEK	Aceto-phenone	MIBK	Isophorone
6C	4,560	5,690	1,690	110	128	27.1	45.6	293	11.7
6D	24,300	14,900	5,940	3,090	3,610	1,240	8,660	2,240	10,200
7A	18,500	10,900	3,710	1,390	2,860	1,620	6,820	2,190	7,860
7B	3,340	3,750	1,180	137	176	35.6	7.60	53.9	13.4
7C	3,910	4,470	1,290	126	170	29.6	13.4	46.9	15.6
7D	18,200	12,100	7,610	1,460	3,300	2,280	7,340	2,560	8,260
8A	25,000	15,300	6,470	2,150	3,760	1,900	8,530	3,260	9,670
8B	3,240	4,810	1,390	190	199	46.0	11.6	34.7	8.12
8C	3,350	4,570	785	167	159	30.6	11.2	34.1	9.27
8D	26,700	17,200	6,520	1,980	3,910	1,920	9,140	3,340	10,400
9A	26,800	14,200	4,860	2,060	3,890	2,360	8,950	3,580	9,880
9B	3,020	3,370	1,410	144	163	33.0	9.21	26.6	9.24
9C	3,140	3,590	1,550	148	183	31.8	15.8	33.9	8.91
9D	27,800	15,000	2,190	2,550	3,940	2,270	9,450	3,300	11,100
10A	24,200	13,200	900	1,710	3,590	2,090	8,330	2,760	9,860
10B	3,240	4,090	893	166	249	65.2	21.6	38.1	166
10C	2,860	3,600	725	162	228	70.8	15.0	36.4	8.87
10D	24,500	14,900	7,230	1,800	3,680	1,930	8,960	3,240	10,500

NOTE: Final values are not corrected for the field train blank.

Table 7. Spike Recovery for Field Test I (August 1994)[a]

Run	Percent Recovered								
	Form-aldehyde	Acetaldehyde	Quinone	Acrolein	Propion-aldehyde	Acetophenone	MEK	MIBK	Isophorone
1A	60.0	66.4	54.4	82.3	81.8	86.6	45.9	67.3	87.8
1D	82.1	74.7	16.8	88.6	103	106	43.2	56.4	101
2A	89.2	75.0	61.4	62.7	90.7	101	44.4	54.3	100
2D	96.3	88.4	68.1	59.7	87.0	97.7	46.2	49.3	79.0
3A	85.1	75.2	47.9	33.7	72.6	86.3	36.4	33.0	90.8
3D	109	97.7	70.5	49.4	84.9	107	30.3	38.6	104
4A	94.8	89.6	40.3	49.6	90.2	95.3	33.2	41.2	93.0
4D	109	107	53.1	39.1	88.0	105	38.3	46.3	98.8
5A	97.2	93.7	62.1	48.1	88.1	96.2	41.2	45.3	90.6
5D	95.6	91.7	114	44.9	84.7	97.9	28.2	43.8	97.2
6A	59.5	61.5	70.5	26.5	63.8	73.8	33.9	32.4	75.1
6D	76.1	58.7	40.8	56.3	62.8	77.1	18.2	21.9	83.8
7A	64.8	50.3	26.9	26.1	53.6	67.4	26.2	26.4	71.6
7D	65.0	57.5	71.6	29.6	66.4	77.3	39.8	33.2	80.2
8A	101	79.6	58.4	44.1	76.8	91.2	33.2	43.2	95.4
8D	106	94.3	64.8	40.2	79.3	95.9	33.2	43.5	100
9A	110	82.7	39.8	43.5	80.6	96.1	41.9	47.8	97.8
9D	110	84.0	7.09	52.5	78.3	97.7	38.8	42.4	106
10A	98.5	70.3	0.09	35.6	73.4	90.7	37.0	37.1	97.5
10D	102	88.4	76.7	37.9	76.2	98.1	34.2	44.1	106

Table 7. (Continued)

Run	Percent Recovered								
	Form-aldehyde	Acetaldehyde	Quinone	Acrolein	Propion-aldehyde	Acetophenone	MEK	MIBK	Isophorone
Minimum	59.5	50.3	0.09	26.1	53.6	67.4	18.2	21.9	71.6
Maximum	110	107	114	88.6	103	106	46.2	67.3	106
Average	90.5	79.3	52.2	47.5	79.1	92.2	36.2	42.4	92.8

[a]Based on the analysis of all impingers.

Recovery of quinone, acrolein, MEK, and MIBK was poor, as expected. The average recovery of the other five compounds was acceptable.

Analysis of the second fractions enabled examination of breakthrough of individual compounds into third and fourth impingers. Any amount of compound detected in the second fraction was classified as having broken through the first two impingers. Breakthrough for each compound is shown in Table 8. Average breakthrough of the spiked MEK and MIBK was over 30 percent. Average breakthrough of the acetaldehyde and propionaldehyde was greater than 10 percent. Average measured breakthrough of the other five spiked compounds was less than 10 percent. Except for formaldehyde and quinone, the compounds follow a consistent trend with high breakthroughs for Runs 3, 4, 6 and 7. The high breakthroughs do not appear to correlate to moisture levels in the source, source temperature, or sampling rate. These results indicate that some of the compounds, especially MEK and MIBK, may be carried beyond the fourth impinger, especially at high flow rates. Measured breakthrough in the unspiked samples is also shown in Table 8, but many of the values have a wide margin of error because the concentration of these compounds was close to the detection limit.

STATISTICAL ANALYSIS

Data using all impingers from all ten runs were used to generate the method validation statistics. Two-impinger data for formaldehyde, acetaldehyde, and acetophone were also evaluated. Before statistical analysis, all compound quantities from the analytical reports were normalized using the gas volume sampled by each train, using the equation below:

$$m' = m \times \frac{V}{V_m}$$

where:

m' = normalized quantity;

m = measured quantity;

Table 8. Breakthrough Analysis

Run	Percent Breakthrough								
	Form-aldehyde	Acet-aldehyde	Quinone	Acrolein	Propion-aldehyde	MEK	Aceto-phenone	MIBK	Isophorone
1A	0.13	4.29	0.29	3.10	5.46	20.2	1.56	13.7	3.10
1B	1.18	5.78	2.13	2.12	3.75	9.06	3.30	2.19	0.00
1C	0.33	5.91	0.00	0.00	0.00	0.00[a]	0.00[a]	0.00[a]	ND
1D	0.21	4.49	0.00	2.78	4.74	34.9	1.72	24.2	2.85
2A	0.17	5.57	0.44	3.32	8.01	44.7	1.79	30.6	4.33
2B	0.24	11.8	0.22	2.54	17.4	23.8	0.00[a]	0.00	0.00[a]
2C	0.55	11.2	0.00[a]	0.00	20.7[a]	14.4[a]	ND	0.00[a]	ND
2D	0.14	4.53	1.00	3.14	6.79	31.7	1.64	22.4	6.07
3A	0.15	22.0	0.48	7.60	24.8	76.2	4.20	59.2	5.35
3B	0.68	21.7	0.98	4.86	32.9	53.2[a]	0.00	15.3	0.00[a]
3C	0.50	25.7	0.40	5.79	33.3	29.7	17.8[a]	ND	ND
3D	0.18	12.9	0.20	6.15	14.5	62.8	3.64	39.6[a]	6.47
4A	0.15	10.0	0.26	4.36	10.1	56.6	2.27	39.1	5.18
4B	0.26	19.3	0.15	2.79	24.2	27.3	0.00[a]	ND	0.00[a]
4C	0.50	24.7	0.44	7.36	25.7	40.6	3.92	ND	0.00[a]
4D	0.22	18.9	0.41	8.43	20.9	68.4	4.10	50.6[a]	6.60
5A	0.14	3.27	0.28	3.81	4.86	36.2	1.47	4.61	3.63
5B	0.47	10.3	0.38	6.65	13.2	34.3	ND	ND	100
5C	0.21	8.65	0.52	4.77	9.96	28.9	0.00	100.	0.00[a]
5D	0.13	6.55	0.06	3.88	7.43	52.0	1.83	26.9	4.33
6A	0.23	19.4	0.26	7.71	19.1	60.0	4.10	45.7	7.21
6B	0.46	33.4	0.12	8.83	41.0	48.1[a]	0.00	4.62	0.00
6C	0.61	49.7	0.37	10.8	48.9	48.9	0.00	6.31	0.00
6D	0.29	34.3	0.76	5.47	33.4	66.4	6.79	53.3	8.72
7A	0.16	10.3	0.60	5.80	11.7	48.2	2.77	38.0	5.45
7B	0.44	16.0	0.13	6.57	24.8	42.7	0.00[a]	28.7	0.00[a]

Table 8. (Continued)

Run	Percent Breakthrough								
	Form-aldehyde	Acet-aldehyde	Quinone	Acrolein	Propion-aldehyde	MEK	Aceto-phenone	MIBK	Isophorone
7C	0.23	19.7	0.00	7.48	31.0	36.6	0.00[a]	33.5	0.00[a]
7D	0.19	16.8	0.40	6.93	20.0	63.5	3.47	49.8	5.31
8A	0.14	4.52	0.43	3.61	6.55	43.8	1.75	22.9	4.50
8B	0.43	10.8	0.15	4.14	12.7	33.9	0.00[a]	0.00	0.00[a]
8C	0.29	12.6	0.00	5.37	17.1	39.2	0.00[a]	0.00	0.00[a]
8D	0.20	8.89	0.34	5.54	11.7	59.8	2.45	35.8	5.46
9A	0.11	3.03	0.66	3.44	4.09	36.0	1.29	19.2	3.22
9B	0.32	12.8	0.00	5.64	16.8	34.1	0.00[a]	0.00	0.00[a]
9C	0.21	10.2	0.00	5.07	12.9	34.9	23.6[a]	0.00	0.00[a]
9D	0.12	3.88	1.52	3.10	5.60	36.1	1.58	23.3	3.65
10A	0.15	4.32	3.47	3.87	6.13	34.3	1.56	25.5	3.83
10B	0.25	11.1	0.00	5.12	14.7	21.6	6.87[a]	0.00	0.00
10C	0.28	11.7	0.00[a]	4.63	16.9	24.7	0.00[a]	0.00	0.00[a]
10D	0.12	3.76	0.19	2.34	5.39	41.4	1.04	18.2	3.08
Spike Average	0.17	10.1	0.60	4.72	11.6	48.7	2.55	32.1	4.92
Maximum	0.29	34.3	3.47	8.43	33.4	76.2	6.79	59.2	8.72
Minimum	0.11	3.03	0.00	2.34	4.09	20.2	1.04	4.61	2.85
Unspiked Average	0.42	16.6	0.30	5.02	20.9	31.3	2.77	9.53	5.00
Maximum	1.18	49.7	2.13	10.8	48.9	53.2	23.6	100	100
Minimum	0.21	5.78	0.00	0.00	0.00	0.00	0.00	0.00	0.00

ND = Component not detected in either fraction.

[a]Levels measured were below the calibration curve.

V = sample volume; and

V_m = mean sample volume (all runs).

Normalization of the data was required because each train collected slightly different sample volumes.

Results for the statistical analysis for each compound are shown in Table 9. The RSD and bias correction factor were calculated using the EPA Method 301[1] with the typographical errors corrected as posted on the EPA bulletin board. Using the criteria of 50% maximum for the RSD and 1.00 ± 0.30 for the bias correction factor, the method validation test was successful for formaldehyde, acetaldehyde, propionaldehyde, and acetophenone. Quinone, acrolein, MEK, and MIBK did not meet the bias criterion, so the method was shown to be invalid for these four compounds. MEK and isophorone did not meet the relative standard deviation criterion for the unspiked samples. Low levels of MEK are challenging to identify and quantitate because low levels of other four-carbon carbonyl compounds can interfere with the identification and quantification of MEK by HPLC. For isophorone, one of the unspiked samples contained approximately 200 μg of isophorone while all the other unspiked samples contained 40 μg or less. However, when analyte concentrations in the stack effluent are very low, the relative standard deviation criterion is unrealistic. Because the native isophorone concentration was very low, isophorone is judged to have performed acceptably using this method.

Table 9. Summary of Method 301 Statistical Analysis (Field Test I, August 1994)

Parameter	Form-aldehyde	Acet-aldehyde	Quinone	Acrolein	Propion-aldehyde	MEK	Aceto-phenone	MIBK	Isophorone
Statistics Calculated from Compounds Collected in Impingers 1 through 4									
RSD Spiked (%)	7.36	7.18	40.0	12.1	7.20	26.1	7.94	17.2	7.94
RSD Unspiked (%)	10.2	10.6	39.7	17.3	21.0	74.3	42.5	32.2	211
Bias CF	1.11	1.26	1.84	2.00	1.25	2.55	1.08	2.22	1.08
Disposition	Passes	Passes	Fails	Fails	Passes	Fails	Passes	Fails	Fails
Statistics Calculated from Compounds Collected in First Two Impingers									
RSD Spiked (%)	7.32	8.15	NR	NR	NR	NR	7.79	NR	NR
RSD Unspiked (%)	9.95	10.3	NR	NR	NR	NR	43.5	NR	NR
Bias CF	1.10	1.34	NR	NR	NR	NR	1.11	NR	NR
Disposition	Passes	Fails	NR	NR	NR	NR	Passes	NR	NR

RSD = Relative Standard Deviation
CF = Correction Factor
NR = Not Reported

SECTION 4.0
FIELD TEST II

Ten test runs were completed during testing at a polyester fiber manufacturing plant during the week of April 24 through April 28, 1995. The sampling trains were each recovered into two sample fractions.

Samples were analyzed for seven target compounds. Results were reported for the two sample fractions from each test run; the first two impingers and all four impingers. Results were normalized by the sample gas volumes before statistical analysis, in order to remove variability attributable to the small differences in the volume of gas extracted from the stack through each train. Statistical analysis was performed according to the latest revisions to EPA Method 301.[1]

Details of the sampling runs and results of the laboratory and statistical analyses are presented in the following subsections.

FIELD SAMPLING

Flue gas samples were collected from a spinning machine exhaust stack at a polyester fiber manufacturing plant. Sampling was performed from a concrete slab roof surface, approximately 22 meters above ground level. The sampling port was a 4-inch (102 mm) diameter pipe nipple, 1.4 meters above the sampling platform. Figure 3 is a diagram of the sampling location. Preliminary samples were collected from the spinning machine exhaust duct in a pre-test site survey. Formaldehyde, acetaldehyde, and propionaldehyde were all detected in the preliminary and validation test samples.

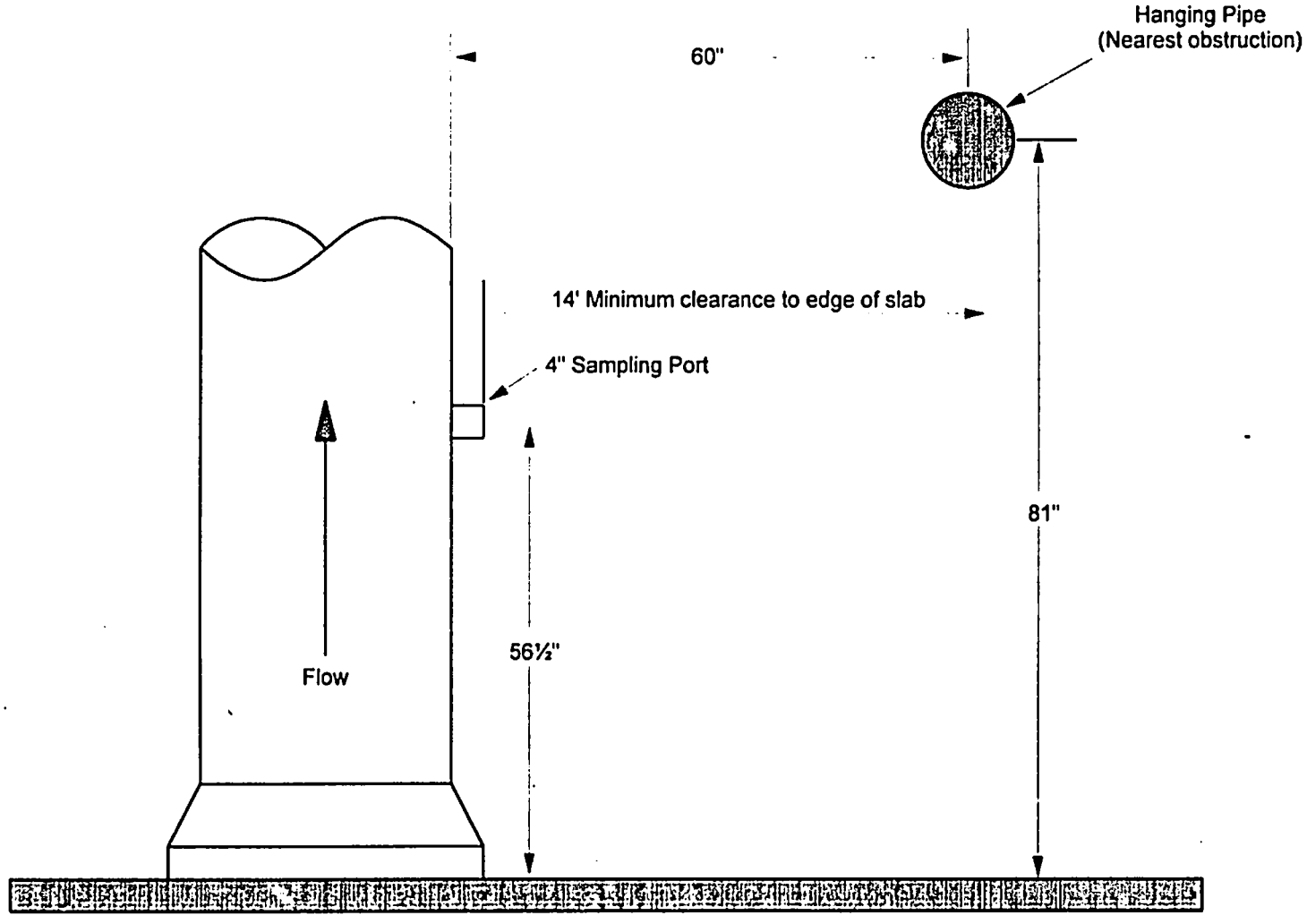


Figure 3. Diagram of Sampling Location for Second Carbonyl Field Test

Ten quad train runs were completed at the test site. The quad-train probe is described in detail in Section 5. Trains A and D were spiked and Trains B and C were unspiked. Table 10 summarizes the sampling parameters recorded for each run. The diameter of all the sampling nozzles was 6.30 mm. The static pressure in the stack was negative, and remained constant at approximately -130 mm of water during all test runs.

The target sample volume for each run was 0.85 cubic meters. The sampling time was normally 100 minutes. However, some runs were extended to allow collection of the full 0.85 cubic meters when the stack gas velocity dropped slightly.

Because of the additional liquid spiked into trains A and D, only trains B and C were used to calculate the percentage of moisture in the stack gas. Moisture values were generally in the range of 4-5 percent by volume. The average moisture content indicated by trains B and C was used in subsequent calculations for trains A and D.

The stack temperature and velocity for each run were measured using a single thermocouple and S-Type pitot tube on the sampling probe assembly. Individual stack gas temperature and pitot tube differential pressure measurements were taken for each of the four trains at the time the other sampling train data were recorded. This measurement scheme resulted in some slightly different temperature and velocity data associated with individual trains for the same run, even though measurements were made with a common probe. These temperature and differential pressure measurement differences did not affect the test data because the sample for all four trains was collected from the same point, the volumes collected were recorded, and the data was corrected for the slight differences in sample volume.

The spiking system was operated to inject approximately equal quantities of spiking solution into trains A and D during each sampling run. The dynamic spiking apparatus and procedure are described in detail in Section 5. Table 11 shows the quantity of each compound spiked into Trains A and D during each run. Spiked quantities were determined by weighing the spiking syringes before and after each test run. Spike weights were recorded in a

Table 10. Sampling Parameters, Field Test II (April 1995)

Run	Sampling Duration (min)	Moisture (%)	Standard Metered Volume (dscm)	Stack Temperature (deg. C)	Stack Gas Velocity (mpm)	Percent Isokinetic
1A	100	-	0.891	34.4	295	108.6
1B	100	5.21	0.877	34.4	293	107.8
1C	100	4.82	0.861	34.4	294	105.2
1D	100	-	0.861	34.4	294	105.3
2A	100	-	0.858	36.1	293	109.0
2B	100	5.11	0.846	36.7	293	104.6
2C	100	5.02	0.824	36.1	293	101.7
2D	100	-	0.821	36.7	293	101.4
3A	100	-	0.876	36.7	304	102.5
3B	100	4.01	0.872	37.2	305	102.0
3C	100	4.20	0.873	36.1	304	102.0
3D	100	-	0.853	37.2	305	99.8
4A	100	-	0.879	37.2	302	103.9
4B	100	4.32	0.860	37.2	302	101.6
4C	100	4.26	0.867	36.7	302	102.4
4D	100	-	0.845	37.2	302	99.8
5A	100	-	0.823	36.7	259	103.1
5B	100	4.85	0.831	36.7	259	104.5
5C	100	3.83	0.842	36.7	261	104.3
5D	100	-	0.807	36.7	261	100.3
6A	100	-	0.816	37.2	289	101.4
6B	100	4.79	0.851	36.7	289	105.8
6C	100	4.82	0.847	37.2	289	105.2
6D	100	-	0.844	37.2	289	105.0
7A	100	-	0.861	37.8	302	101.6
7B	100	4.00	0.868	37.2	302	102.4
7C	100	4.20	0.859	37.2	302	101.5
7D	100	-	0.853	37.2	302	100.6
8A	110	-	0.892	37.8	283	102.4
8B	110	4.19	0.906	37.8	283	104.1
8C	110	4.24	0.880	37.2	283	101.0
8D	110	-	0.874	37.2	283	100.4

Table 10. (Continued)

Run	Sampling Duration (min)	Moisture (%)	Standard Metered Volume (dscm)	Stack Temperature (deg. C)	Stack Gas Velocity (mpm)	Percent Isokinetic
9A	106	-	0.855	37.2	286	102.1
9B	106	5.18	0.858	37.2	285	102.5
9C	106	5.05	0.866	36.7	285	103.3
9D	106	-	0.849	37.2	286	101.4
10A	100	-	0.799	37.8	284	101.6
10B	101	4.97	0.832	37.8	284	104.9
10C	102	4.60	0.840	37.8	283	104.5
10D	103	-	0.824	37.2	283	101.7

Table 11. Spike Quantities

Run	Form-aldehyde (µg)	Acet-aldehyde (µg)	Propion-aldehyde (µg)	Acetophenone (µg)	Methyl Ethyl Ketone (µg)	Methyl Isobutyl Ketone (µg)	Isophorone (µg)
1A	1621.2	6006.9	2945	6483.4	3773.4	5267.1	7375.4
1D	1707.7	6327.3	3102	6829.2	3974.6	5548	7768.7
2A	1372.6	5085.8	2493.4	5489.3	3194.8	4459.5	6244.5
2D	1426.7	5286.1	2591.6	5705.4	3320.6	4635	6490.3
3A	1750.9	6487.5	3180.5	7002.1	4075.3	5688.5	7965.4
3D	843	3123.6	1531.4	3371.4	1962.2	2738.9	3835.2
4A	1329.4	4925.7	2414.9	5316.4	3094.2	4319	6047.8
4D	1242.9	4605.3	2257.8	4970.6	2892.9	4038.1	5654.4
5A	1405	5206	2252.3	5619	3270.3	4564.8	6392
5D	1513.1	5606.4	2748.6	6051.2	3521.8	4916	6883.7
6A	1437.5	5326.1	2611.2	5748.7	3345.7	4670.2	6539.5
6D	1351	5005.8	2454.1	5402.9	3144.5	4389.2	6146.1
7A	1437.5	5326.1	2611.2	5748.7	3345.7	4670.2	6539.5
7D	1405	5206	2552.3	5619	3270.3	4564.8	6392
8A	1523.9	5646.5	2738.3	6094.4	3547	4951.1	6932.8
8D	1599.6	5926.8	2905.7	6397	3723.1	5196.9	7277
9A	1448.3	5366.2	2630.8	5791.9	3370.9	4705.3	6588.6
9D	1491.5	5526.3	2709.4	5964.8	3471.5	4845.7	6785.3
10A	1351	5005.8	2454.1	5402.9	3144.5	4389.2	6146.1
10D	702.5	2603	1276.1	2809.5	1635.1	2282.4	3196

field notebook. Review of the spiking data indicated that there may have been a spiking error associated with runs 3 and 10. Recorded weights from both of these runs show a discrepancy between the amounts spiked in the A and D trains.

ANALYSIS

The samples from each train were collected and analyzed in two fractions. The first fraction contained the probe rinse and contents of the first two impingers. The second fraction contained the contents of the third and fourth impingers. Table 12 shows the results of the analysis of the first fractions from each run. This sample is the fraction intended for analysis using Method 0011.[2] Acetaldehyde and formaldehyde were present in the unspiked samples, along with trace amounts of propionaldehyde.

Table 13 shows the percentage of each spiked compound recovered in the first two impingers. The recovery is calculated as follows:

$$R = 100\% \times \frac{S-M}{CS}$$

where:

R = percent recovery;
S = measured quantity in the spiked sample;
M = mean value of the unspiked samples in the run; and
CS = calculated spike quantity.

Recovery of methyl ethyl ketone and methyl isobutyl ketone was poor, as expected. The average recovery levels of the other five compounds were acceptable. The recovery level of all compounds calculated for runs 3 and 10 are inconsistent with the values calculated for the other runs. These are the same two runs for which a spiking error is suspected. These two runs, therefore, were eliminated from subsequent statistical analysis for method validation.

Table 12. Analytical Results, Impingers 1 and 2

Run	Form-aldehyde (µg)	Acet-aldehyde (µg)	Propion-aldehyde (µg)	Aceto-phenone (µg)	Methyl Ethyl Ketone (µg)	Methyl Isobutyl Ketone (µg)	Isophorone (µg)
1A	1656.9	6343.4	2730.8	6791.2	1478.4	1068[a]	9128.6
1B	15.51[b]	463.2	5.97[b,d]	<4.40	<1.27	<1.39	<3.01
1C	12.02[b]	433	5.47[b,d]	<4.40	<1.27	<1.39	<3.01
1D	1592.2	5412.2	2222	5690.1	1284.7	1055[a]	7680.2
2A	1149.6	5077.3	1886.8	4653.6	1570.4	1136[a]	6552.8
2B	19.8[b]	836.8	9.84[b,d]	<8.80	<2.55	<2.79	<6.02
2C	16.43[b]	834.3	5.21[b,d]	<4.40	<1.27	<1.39	<3.01
2D	1168.6	4971.1	1854.2	4872.1	1089.9	837[a]	6385.5
3A	970.7	4361	1662.3	4291.2	1120.8	336[a]	5486.2
3B	19.63[b]	849.7	4.52[b,d]	<8.80	<2.55	<2.79	<6.02
3C	13.14[b]	739.7	2.96[b,d]	<4.40	<1.27	<1.39	<3.01
3D	1398.5	5439.1	2051.3	5635.3	1093	623[a]	7341
4A	1532.3	6453.5	1736.1	5839.6	1423.9	964[a]	7693.5
4B	10.5[b]	449.4	<1.12	<4.40	<1.27	<1.39	<3.01
4C	22.7[b]	839.7	3.12[b,d]	<4.40	<1.27	<1.39	<3.01
4D	1280.7	5025.1	1916.3	4854.9	1341.5	956[a]	6305.6
5A	1401.2	5670.9	2133.9	5502.5	1474	1170[a]	7382.6
5B	20.32[b]	908.9	<1.12	<4.40	<1.27	<1.39	<3.01
5C	27.4[b]	898.9	<2.24	<8.80	<2.55	<2.79	<6.02
5D	1218	4583.6	2031.6	5263.4	1440.8	1691[a]	7040.6
6A	1232.8	4801.9	2009.5	5009.5	1293.8	812[a]	6751.4
6B	18.55[b]	1013.4	<1.12	<4.40	<1.27	<1.39	<3.01
6C	16.29[b]	860.7	3.01[b,d]	<4.40	<1.27	<1.39	<3.01
6D	1379.3	5176.8	2122	5552.7	1136.3	764[a]	7329.7
7A	1335.3	5061.7	2016.1	5310.9	1267.4	977[a]	6868.5
7B	19.9[b]	1003.3	3.77[b,d]	<4.40	<1.27	<1.39	<3.01
7C	17.99[b]	982	3.33[b,d]	<4.40	<1.27	<1.39	<3.01
7D	1249.8	2544.1	2019.9	5022.3	1327.6	1041[a]	6665.1
8A	1205.9	5361.1	1967.8	5246	1478.1	1181[a]	7171.3
8B	16.52[b]	1060.8	3.87[b,d]	<4.40	<1.27	<1.39	<3.01
8C	17.97[b]	973.4	3.44[b,d]	<4.40	<1.27	<1.39	<3.01
8D	1296.2	5690.1	1990.1	5143.4	1483.2	1339[a]	7081.9

Table 12. (Continued)

Run	Form-aldehyde (µg)	Acet-aldehyde (µg)	Propion-aldehyde (µg)	Aceto-phenone (µg)	Methyl Ethyl Ketone (µg)	Methyl Isobutyl Ketone (µg)	Isophorone (µg)
9A	1286.4	4937.1	1859.7	4860.9	1646.2	1191[a]	6438.3
9B	17.48[b]	987.4	2.5[b,d]	<4.40	<1.27	<1.39	<3.01
9C	18.04[b]	967.8	2.79[b,d]	<4.40	<1.27	<1.39	<3.01
9D	1459.7	5830.1	2141.9	6048.5	1344.4	1170[a]	7355.9
10A	1312.1	1520	1766.27	4990	1821.6	1448[a]	6919.5[e]
10B	17.22[b]	840.7	2.21[b,d]	<4.40	<1.27	<1.39	<3.01
10C	16.24[b]	825.3	2.47[b,d]	<4.40	<1.27	<1.39	<3.01
10D	1129.69	4423.37	1510.8	4058.4	1503	1106[a]	5808.6[e]

NOTE: Final values are not corrected for the field train blank.

[a]Method spike recoveries outside acceptable range.
[b]Less than 10 times field train blank.
[c]Calibration check standard outside acceptable range.
[d]Below calibration curve.
[e]Above calibration curve.

Table 13. Spike Recovery

Run	Form-aldehyde (%)	Acetaldehyde (%)	Propion-aldehyde (%)	Acetophenone (%)	Methyl Ethyl Ketone (%)	Methyl Isobutyl Ketone (%)	Isophorone (%)
1A	101	98	93	105	39	20[a]	124
1D	92	78	71	83	32	19[a]	99
2A	82	83	75	85	49	25[a]	105
2D	81	78	71	85	33	18[a]	98
3A	55	55	52	61	28	6[a]	69
3D	164	149	134	167	56	23[a]	191
4A	114	118	72	110	46	22[a]	127
4D	102	95	85	98	46	24[a]	112
5A	98	92	95	98	45	26[a]	115
5D	79	66	74	87	41	34[a]	102
6A	85	73	77	87	39	17[a]	103
6D	101	85	86	103	36	17[a]	119
7A	92	76	77	92	38	21[a]	105
7D	88	30	79	89	41	23[a]	104
8A	78	77	72	86	42	24[a]	103
8D	80	79	68	80	40	26[a]	97
9A	88	74	71	84	49	25[a]	98
9D	97	88	79	101	39	24[a]	108
10A	96	98	72	92	58	33[a]	113[b]
10D	158	138	118	144	92	48[a]	182[b]
Maximum*	114	118	95	110	49	34	127
Minimum*	78	30	68	80	32	17	97
Average*	91	81	78	92	41	23	108

*Does not include Runs 3 and 10 (see text).

[a]Method spike recoveries outside acceptable range.
[b]Calibration check standard outside acceptable range.

Table 14 shows analytical results for both fractions (all impingers) of each sampling train combined. Analysis of the second fractions enabled examination of breakthrough of individual compounds into third and fourth impingers. Breakthrough for each compound is shown in Table 15. Breakthrough of the spiked MEK and MIBK was over 20 percent. Breakthrough of all other spiked compounds in the spiked samples was less than 10 percent. Measured breakthrough in the unspiked samples is also shown in Table 15, but values for formaldehyde and especially propionaldehyde have a wide margin of error since the concentration of these compounds was close to the detection limit.

STATISTICAL ANALYSIS

Data from eight of the ten runs were used to generate the method validation statistics. Runs 3 and 10 were eliminated from the data set because of suspected spiking errors. Before statistical analysis, all compound quantities from the analytical reports were normalized using the gas volume sampled by each train. This was done using the equation

$$m' = m \times \frac{V}{V_m}$$

where:

m'	=	normalized quantity;
m	=	measured quantity;
V	=	sample volume; and
V_m	=	mean sample volume (all runs).

Table 14. Analytical Results, All Fractions

Run	Form-aldehyde (µg)	Acet-aldehyde (µg)	Propion-aldehyde (µg)	Aceto-phenone (µg)	Methyl Ethyl Ketone (µg)	Methyl Isobutyl Ketone (µg)	Isophorone (µg)
1A	1656.9	6639.2	2866.1	6969.2	2245.5	1875.2[b]	9445.2
1B	17.56[a]	506.8	10.25[a]	ND	ND	ND	ND
1C	14.48[a]	471.6	10.53[a]	ND	ND	ND	ND
1D	1630.9	5673.8	2359.25	5878.5	1980.1	1699.2[b]	7927.9
2A	1183.7	5215.5	1960.2	4782.3	1931.7	1378.5[b]	6718.5
2B	22.36[a]	886.7	14.37[a]	ND	ND	ND	ND
2C	17.62[a]	903.6	10.16[a]	ND	ND	ND	ND
2D	1168.6	5119	1913.3	4985.5	1386.6	1047.1[b]	6630.9
3A	970.7	4620.1	1791.2	4423.4	1583.2	723.6[b]	5679.1
3B	22.14[a]	906.9	4.52[a]	ND	ND	ND	ND
3C	17.71[a]	805	4.9[a]	ND	ND	ND	ND
3D	1398.5	5690.8	2176.4	5814.6	1610.9	1164.2[b]	7820.6
4A	1557.8	6669.7	1818.3	5983.9	1807.1	1246.5[b]	7986.1
4B	12.93[a]	503.6	ND	ND	ND	ND	ND
4C	25.03[a]	910.2	3.12[a]	ND	ND	ND	ND
4D	1280.7	5163.3	2020.1	4854.9	1692	1198.7[b]	6471.2
5A	1423.7	5845.8	2205.9	5625.9	1946.3	1576.8[b]	7625
5B	23.01[a]	967.7	ND	ND	ND	ND	ND
5C	31.52[a]	952.9	ND	ND	ND	ND	ND
5D	1218	4673.3	2141.9	5263.4	1794.4	1981.8[b]	7040.6
6A	1232.8	4956.7	2110.3	5137.8	1675.2	1080.1[b]	6751.4
6B	21.62[a]	1077.6	ND	ND	ND	ND	ND
6C	19.39[a]	930.3	3.01[a]	ND	ND	ND	ND
6D	1379.3	5361.4	2210.1	5662	1448.9	968.2[b]	7488.9
7A	1356.5	5243.6	2134.1	5452.4	1692.3	1336.4[b]	7103.1
7B	22.5[a]	1060.5	3.77[a]	ND	ND	ND	ND
7C	20.24[a]	1049.7	5.27[a]	ND	ND	ND	ND
7D	1249.8	2691.9	2118.7	5147.3	1674.4	1313.4[b]	6812.4
8A	1227.2	5505.7	2063.2	5363	1794.3	1444.5[b]	7415.8
8B	18.79[a]	1116.3	5.86[a]	ND	ND	ND	ND
8C	20.29[a]	1039.1	5.42[a]	ND	ND	ND	ND
8D	1321.6	5841.4	5052.7	5280.4	1874.9	1692.6[b]	7242

Table 14. (Continued)

Run	Form-aldehyde (μg)	Acet-aldehyde (μg)	Propion-aldehyde (μg)	Aceto-phenone (μg)	Methyl Ethyl Ketone (μg)	Methyl Isobutyl Ketone (μg)	Isophorone (μg)
9A	1309.1	5120.6	1970	5028.1	2040	1519.2[b]	6712.6
9B	19.76[a]	1036.1	4.13[a]	ND	ND	ND	ND
9C	20.2[a]	1025.3	5.97[a]	ND	ND	ND	ND
9D	1486.3	5935.6	2259.6	6190.6	1572.7	1394.3[b]	7594[c]
10A	1312.1	5844.27	1570	5102.4	2163	1731.5[b]	7089.7[c]
10B	19.04[a]	882.9	4.27[a]	ND	ND	ND	ND
10C	19.26[a]	865.8	4.04[a]	ND	ND	ND	ND
10D	1153.3	4560.8	1582.3	4162.9	1860.7	1371.2[b]	5946.2[c]

NOTE: Final values are not corrected for the field train blank.

ND = Not Detected

[a]Less than 10 times field train blank.
[b]Method spike recoveries outside acceptable range.
[c]Calibration check standard outside acceptable range.

Table 15. Breakthrough Analysis

Run	Form-aldehyde (%)	Acet-aldehyde (%)	Propion-aldehyde (%)	Aceto-phenone (%)	Methyl Ethyl Ketone (%)	Methyl Isobutyl Ketone (%)	Isopborone (%)
1A	0.0	4.5	4.7	2.6	34.2	43.1	3.4
1B	11.7	8.6	41.8	ND	ND	ND	ND
1C	17.0	8.2	48.1	ND	ND	ND	ND
1D	2.4	4.6	5.8	3.2	35.1	37.9	3.1
2A	2.9	2.7	3.7	2.7	18.7	17.6	2.5
2B	11.4	5.6	31.5	ND	ND	ND	ND
2C	6.8	7.7	48.7	ND	ND	ND	ND
2D	0.0	2.9	3.1	2.3	21.4	20.1	3.7
3A	0.0	5.6	7.2	3.0	29.2	53.5	3.4
3B	11.3	6.3	0.0	ND	ND	ND	ND
3C	25.8	8.2	39.6	ND	ND	ND	ND
3D	0.0	4.4	5.7	3.1	32.2	46.5	6.1
4A	1.6	3.2	4.5	2.4	21.2	22.7	3.7
4B	18.8	10.8	ND	ND	ND	ND	ND
4C	9.3	7.7	0.0	ND	ND	ND	ND
4D	0.0	2.7	5.1	0.0	20.7	20.3	2.6
5A	1.6	3.0	3.3	2.2	24.3	25.8	3.2
5B	11.7	6.1	ND	ND	ND	ND	ND
5C	13.1	5.7	ND	ND	ND	ND	ND
5D	0.0	1.9	5.2	0.0	19.7	14.7	0.0
6A	0.0	3.1	4.8	2.5	22.8	24.8	0.0
6B	14.2	6.0	ND	ND	ND	ND	ND
6C	16.0	7.5	0.0	ND	ND	ND	ND
6D	0.0	3.4	4.0	1.9	21.6	21.1	2.1
7A	1.6	3.5	5.5	2.6	25.1	26.9	3.3
7B	11.6	5.4	0.0	ND	ND	ND	ND
7C	11.1	6.4	36.8	ND	ND	ND	ND
7D	0.0	5.5	4.7	2.4	20.7	20.8	2.2
8A	1.7	2.6	4.6	2.2	17.6	18.3	3.3
8B	12.1	5.0	34.0	ND	ND	ND	ND

Table 15. (Continued)

Run	Form-aldehyde (%)	Acet-aldehyde (%)	Propion-aldehyde (%)	Aceto-phenone (%)	Methyl Ethyl Ketone (%)	Methyl Isobutyl Ketone (%)	Isophorone (%)
8C	11.4	6.3	36.5	ND	ND	ND	ND
8D	1.9	2.6	60.6	2.6	20.9	20.9	2.2
9A	1.7	3.6	5.6	3.3	19.3	21.6	4.1
9B	11.5	4.7	39.5	ND	ND	ND	ND
9C	10.7	5.6	53.3	ND	ND	ND	ND
9D	1.8	1.8	5.2	2.3	14.5	16.1	3.1
10A	0.0	2.0	3.1	2.2	15.8	16.4	2.4
10B	9.6	4.8	48.2	ND	ND	ND	ND
10C	15.7	4.7	38.9	ND	ND	ND	ND
10D	2.0	3.0	4.5	2.5	19.2	19.3	2.3
Average Spiked	1.1	3.2	8.2	2.2	22.4	23.3	2.6
Maximum	2.9	5.6	60.6	3.3	35.1	53.5	6.1
Minimum	0.0	1.8	3.1	0.0	14.5	14.7	0.0
Average Unspiked	12.4	6.7	23.1	ND	ND	ND	ND
Maximum	25.8	10.8	53.5	ND	ND	ND	ND
Minimum	6.8	4.7	0.0	ND	ND	ND	ND

Averages, maximums, and minimums do not include Runs 3 and 10 (see text).

ND = Not Detected

Results of the statistical analysis for each compound collected in the first two impingers are shown in Table 16. Statistical analysis results for Impingers 1 through 4 are not reported because they did not significantly differ from the results with two impingers. The RSD and bias correction factor were calculated using the EPA Method 301[1] with the typographical errors corrected as posted on the EPA bulletin board. Using the criteria of 50% maximum for the RSD and 1.00 ± 0.30 for the bias correction factor, the method validation test was successful for formaldehyde, acetaldehyde, propionaldehyde, acetophenone, and isophorone. Collection of MEK and MIBK did not meet the bias criterion, and therefore the method was not shown to be valid for these two compounds.

Table 16. Statistical Analysis Using First Two Impingers

Parameter	Form-aldehyde	Acet-aldehyde	Propion-aldehyde	Aceto-phenone	Methyl Ethyl Ketone	Methyl Isobutyl Ketone[a]	Isophorone
RSD Spiked (%)	8.8	16.7	12.94	10.43	18.75	21.17	8.99
RSD Unspiked (%)	20.71[b]	12.35	48.54[b]	--	--	--	--
Bias CF	1.1	1.24	1.29	1.09	2.45	4.33	0.93
Disposition	Pass	Pass	Pass	Pass	Fail	Fail	Pass

[a]Method spike recoveries were outside acceptable range.
[b]Measured amounts were less than 10 times the field train blank.

SECTION 5.0
FIELD TEST PROCEDURES

The purpose of the sampling programs was to evaluate the proposed aldehyde and ketone sampling and analytical methods and to determine the performance (precision and accuracy) of the methods. Replicate, independent flue gas samples were collected simultaneously from an aldehyde/ketone emission source to determine precision. For bias determination, known concentrations of aldehydes and ketones were dynamically spiked only into Trains A and D. Various blank samples were collected and analyzed to identify sources of contamination in the method.

Both field tests consisted of 10 quadruplicate sampling runs. Each test run used four independent sampling trains to collect four samples from essentially the same location during each test run.

The nozzle and probe rinse and the contents of the first two impingers comprised the first of two samples collected from each sampling train. The contents of the third and fourth impingers made up the second sample collected from each train. Samples were processed and analyzed at Radian's PPK laboratory following procedures detailed in this section of this document. Both samples collected from each of the four trains were analyzed to determine carryover into the third impinger.

Sample collection during both field validation field tests was performed using procedures similar to those detailed in SW-846 Method 0011,[2] "Sampling for Formaldehyde Emissions from Stationary Sources." The method that was evaluated was modified based on the results of the laboratory studies (reported in Appendix A) and to enable information on compound breakthrough to be collected. This sampling method is a modification of the EPA stationary source test Method 5. Gas was extracted isokinetically from the source through a heated glass nozzle and probe system as shown earlier in Figure 1. The gas was passed through a five-bottle impinger train, a sample pump, a dry gas meter and an orifice differential pressure meter. The following modifications were made to the SW-846 Method 0011[2] for the aldehyde and ketone sampling method validation tests:

- Four co-located sampling trains were used per Method 301[1] to allow determination of precision and bias of the proposed sampling and analytical method.
- The trains were dynamically spiked with a solution of aldehydes and ketones.
- The first impinger contained 200 mL of DNPH reagent to increase the sample capacity.
- The second impinger contained 100 mL of DNPH.
- A third reagent impinger containing 100 mL of DNPH was added to the train between the second reagent impinger and the empty impinger to enable compound breakthrough to be determined.

EQUIPMENT

Probe

A special probe assembly was required to allow simultaneous sampling at essentially the same point with four independent sampling trains. Proposed Method 301[1] describes field evaluation procedures and details the criteria for the quadruple sampling probe tip arrangement. The quad-probe arrangement is designed to minimize velocity variations at the nozzles of the four sampling probes.[4]

Figures 4 and 5 illustrate the configuration of the sampling probe used during the aldehyde and ketone test program. Note that the probe inlets are in the same plane perpendicular to the gas stream, allowing the probe tip openings to be exposed to the same gas conditions.

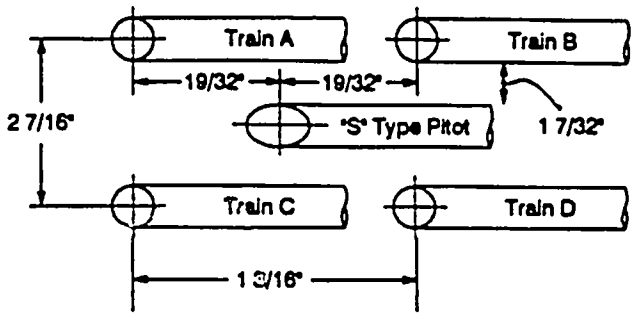
EPA Method 301 specifies that the inside edge of sampling probe tips shall be situated in a 6.0 cm x 6.0 cm square area, and that the area encompassed by the probe tip arrangement should occupy less than 5% of the stack cross-sectioned area. If this criterion is met, then the flow at each of the four probe tips can be considered similar. Radian used a probe tip assembly with a cross-sectional area of 19 square centimeters as measured from the probe/nozzle centerlines. The criterion that the probe tip area not exceed 5% of the stack area was met at both field test sites.

Sampling Trains

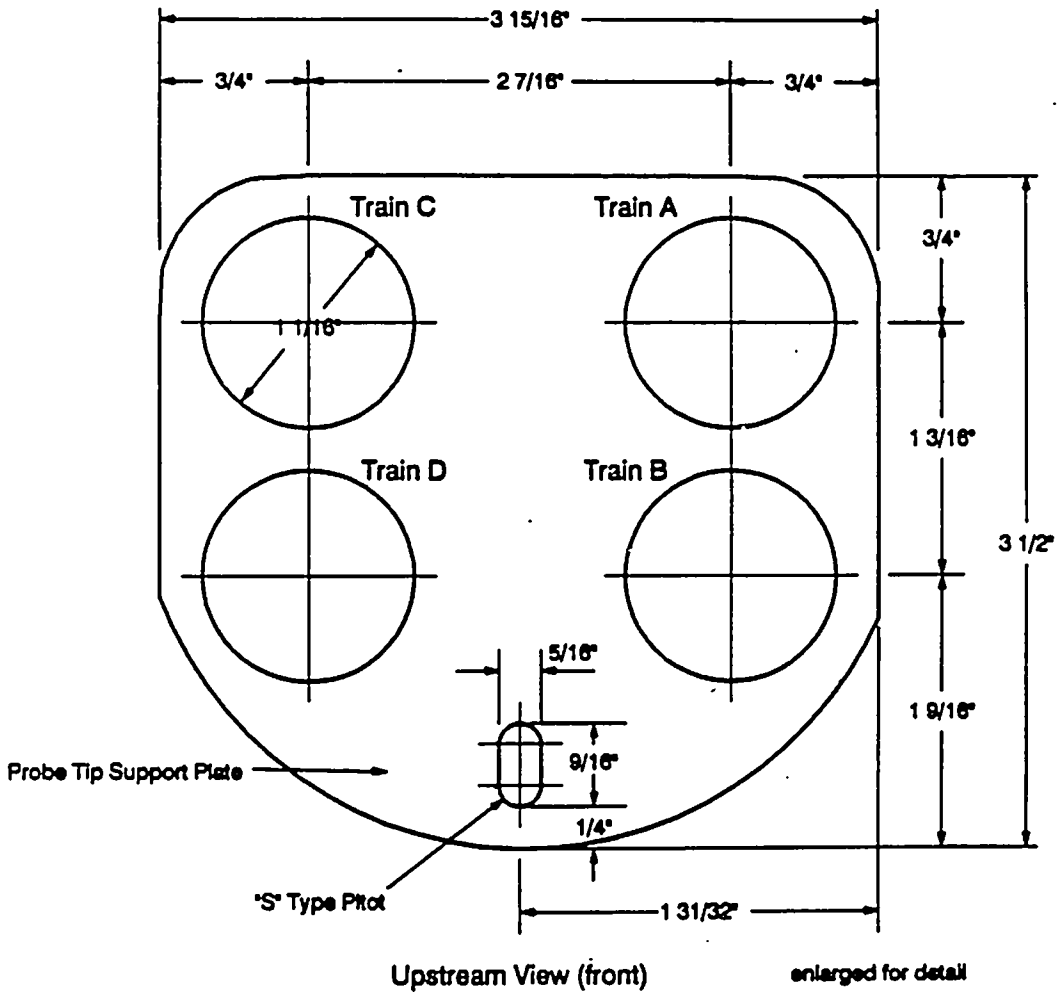
Four independent impinger trains comprised the quad-train assembly. Each train used five glass impingers. Each train had its own meter box and pump. The trains were designated "A," "B," "C," and "D." Spiking compounds were dynamically added to trains A and D in the field for bias determination.

Dynamic Spiking Apparatus

Spiked compounds were introduced to the sampling system in gaseous form using liquid syringe injection through a heated glass elbow mounted at the outlet of the probe as shown in Figure 6. The Teflon® line from the syringe pump was connected to a piece of glass-lined stainless steel tubing with a beveled tip. The liquid spike was maintained as a droplet at the tip of the glass-lined stainless steel tubing, from which point the spike volatilized and became a gaseous spike as it entered the heated gas stream. The spiking liquid was not allowed to drip into the sampling line. Liquid feed rates of the spiking solution were metered



Upstream View (bottom)



Upstream View (front) enlarged for detail

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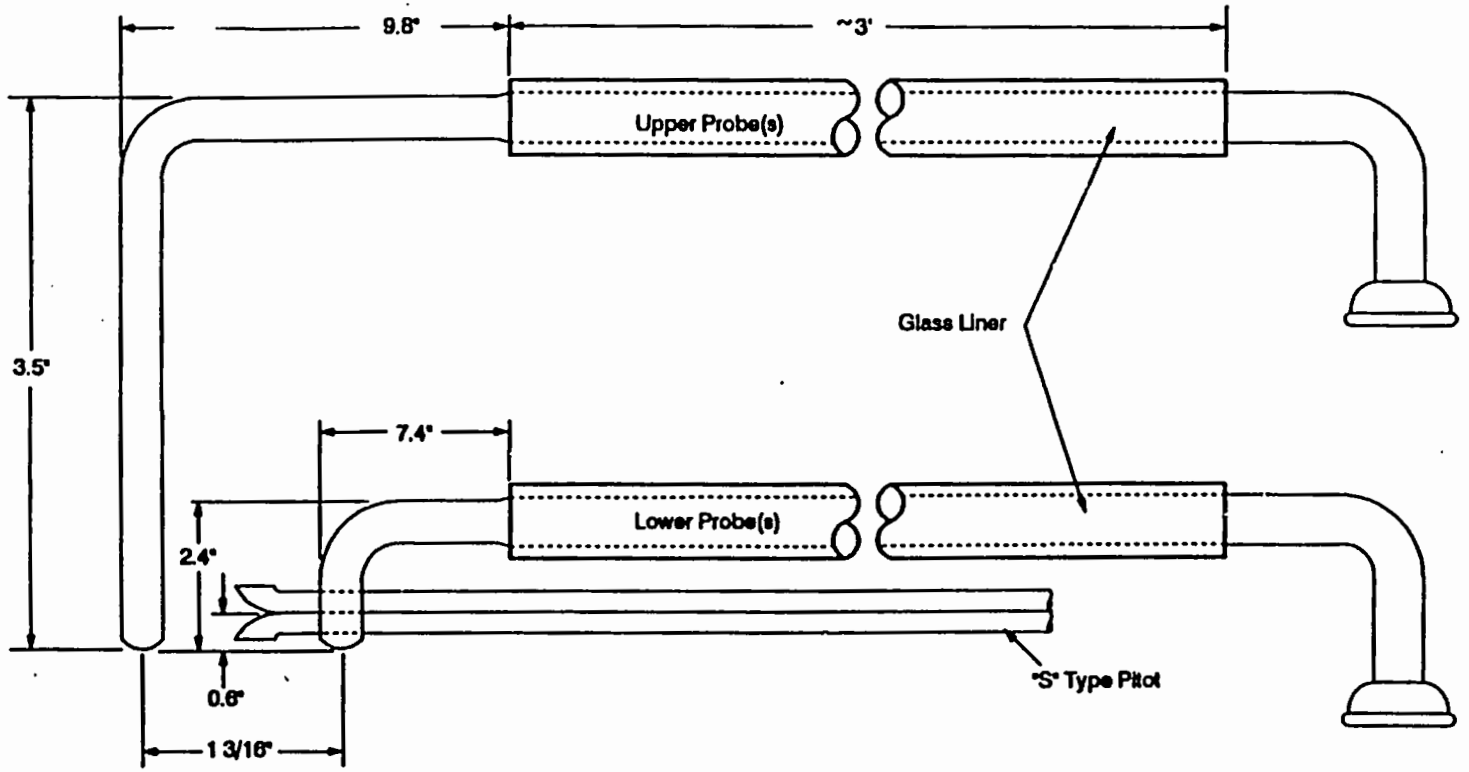
Figure 4. Quad-Train Probe and Pitot Arrangement



Drawing not to scale. For clarity, probe detail is exaggerated.

Figure 5. Upper and Lower Sampling Probes (Side View)

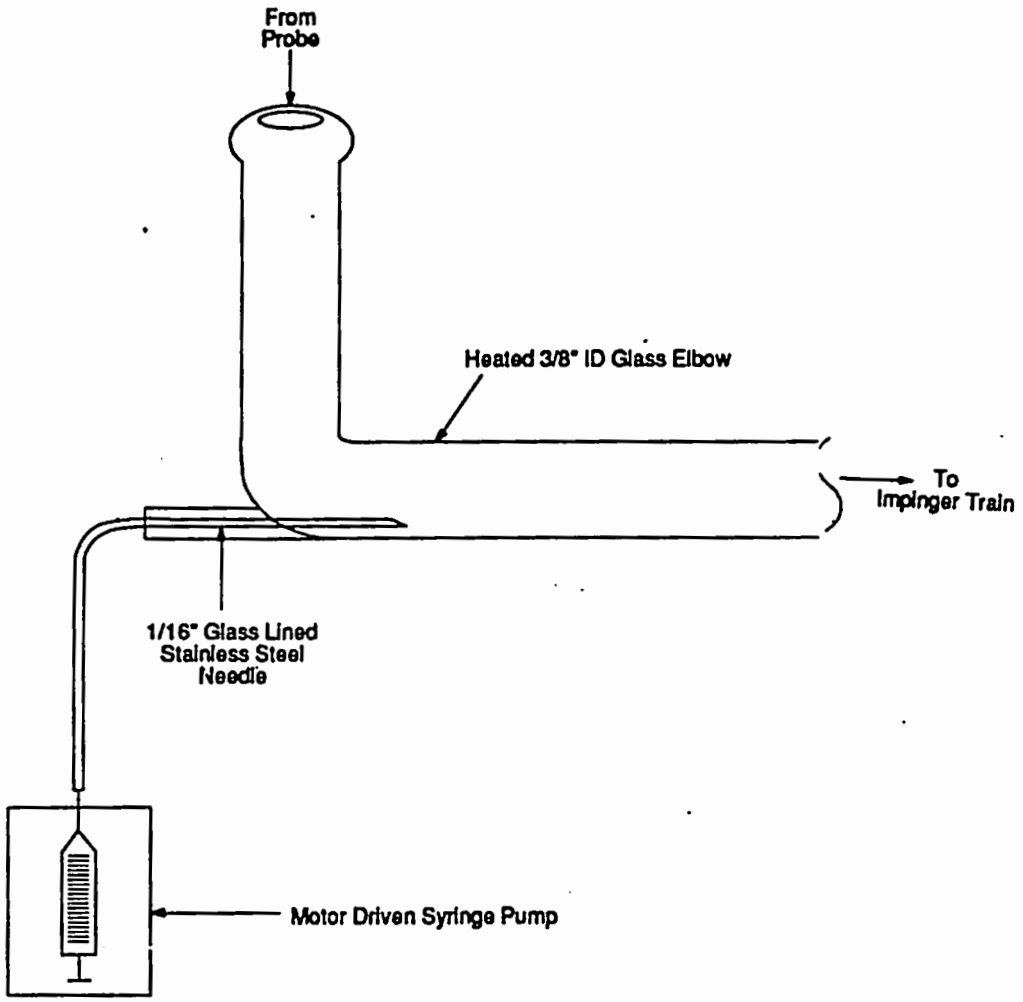


Figure 6. Dynamic Spiking Apparatus

by means of motor driven syringe pumps. The quantity of liquid spiked was measured gravimetrically by recording the syringe weights before and after each test run.

PREPARATION

Glassware Preparation

All glassware used for sampling, including the probe, impingers, all sample bottles, and all utensils used during sample recovery, was thoroughly cleaned prior to use. All glassware was washed with hot soapy water, rinsed with hot tap water, rinsed with distilled water, and dried. The glassware was triple rinsed with methanol followed by triple rinsing with methylene chloride ($MeCl_2$). No acetone was used in glassware preparation.

Reagent bottles used for the storage of DNPH derivatizing solution were rinsed with acetonitrile and dried before use.

DNPH Preparation

The DNPH reagent was prepared and purified within five days of sampling. The reagent was prepared at Radian's Perimeter Park (PPK) laboratory in North Carolina using the procedure described in the test plan. Each reagent container was properly labeled, tightly capped, and sealed with Teflon® tape. The reagent was delivered directly to the test locations via Radian vehicle. Once a container of prepared DNPH was opened in the field, the contents were used within 48 hours to minimize the possibility of the reagent becoming contaminated from the ambient air.

Method 0011[2] Equipment Preparation

Reference calibration procedures were followed when available for all the train equipment, including meterboxes, nozzles, pitot tubes, and thermocouples. The results were

properly documented and retained. A discussion of the techniques used to calibrate this equipment is presented in Section 7 of this document.

SAMPLING OPERATIONS

Flue gas samples were collected isokinetically from a single sampling point identified from a preliminary velocity traverse. Preliminary information obtained during the pre-site survey was used for selecting the proper nozzle size. Prior to testing, a leak check of pitot lines was performed according to EPA Method 2.[5]

Preparation of Sampling Trains

Impingers for the four sampling trains were filled and assembled in the recovery trailer. The impinger buckets were clearly marked as Train A, B, C, or D. All impingers used were tared to obtain the initial weight. Approximately 200 mL of purified DNPH reagent were transferred into the first impinger of each train, and 100 mL of reagent were added to the second and third impingers. The fourth impingers remained empty, and 200 to 300 grams (g) of silica gel were placed in the fifth impingers. Openings were covered with Teflon® film or aluminum foil.

Final assembly of the sampling trains took place at the sampling location, as shown in Figure 1. Thermocouples were attached to measure the stack, probe outlet, and impinger outlet temperatures. Crushed ice was added to each impinger bucket, and the probe heaters were turned on and allowed to stabilize at 120 ±14°C (248°F ±25°F).

The sampling trains were leak checked before and after sampling. To leak check the assembled train, the nozzle end was capped off and a vacuum was pulled in the system. With the system evacuated, the volume of gas flowing through the system was timed for 60 seconds.

The leak rate is required to be less than 0.566 L/min (0.02 acfm), or 4% of the average sampling rate, whichever is less. After the leak rate was determined, the cap was slowly removed from the nozzle end until the pressure equalized, and then the pump was turned off.

The leak rates and sampling start and stop times were recorded on the sampling task log. Also, any other events that occurred during sampling were recorded on the task log (such as pitot cleaning, thermocouple malfunctions, heater malfunctions, and any other unusual occurrences).

A checklist for aldehyde/ketone sampling is included in Appendix B-1. Sampling train data were recorded every five minutes on standard data forms. Actual data forms are provided in Appendix B-2. With the single-pitot arrangement used in the quad-test, the pitot tube was connected to only one of the four DGM boxes (Box A).

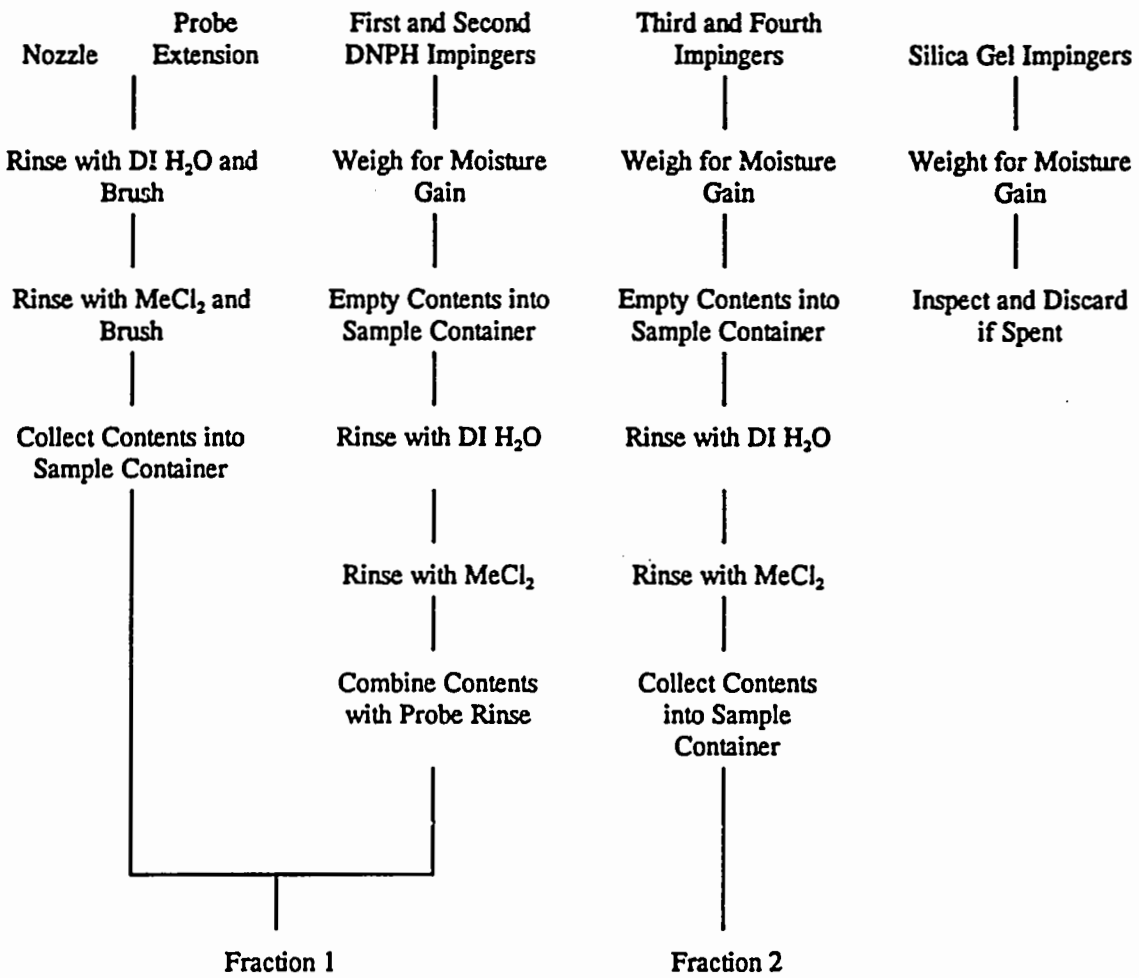
Sample Recovery

Recovery of the sampling trains is summarized in Table 17. The sample bottles containing the probe and nozzle washings and each of the sampling trains were moved to the recovery trailer. Each impinger was carefully removed from the impinger bucket, the outside was wiped dry, and the final impinger weight was measured and recorded. The aldehyde/ketone sample was collected in the following fractions:

- First and second impinger contents, water and $MeCl_2$ rinses from the nozzle/probe liner and the first and second impingers; and
- Contents and $MeCl_2$/water rinses from the third and fourth impingers.

No methanol or acetone was used in the field.

Table 17. Sample Recovery Scheme



Container 1 - Probe Rinse, First and Second Impinger Contents--

The contents of each of the first two impingers and first two impinger connectors were included with the probe/nozzle rinse solution. A small portion of $MeCl_2$ was used to rinse the impingers and connectors three times. Exposed glassware surfaces were brushed to ensure recovery of fine particulate matter. A final rinse of the impinger and Teflon® brush with $MeCl_2$ was also necessary as the two-phase DNPH/$MeCl_2$ mixture does not pour well, and a significant amount of impinger catch was left on the impinger wall.

Container 2 - Third and Fourth Impinger Contents--

The contents of the third and fourth impingers of each train were recovered in the same manner as described in Table 17. The contents of these impingers were analyzed separately from the contents collected in the first and second impingers to check for breakthrough. Care was taken to avoid physical carryover from the first and second impingers to the third and fourth.

Field Train Blank(s)

Two sets of field train blanks were prepared. A sampling train was assembled in the staging area, taken to the sampling location, and leak-checked before and after the test period. No gaseous sample passed through the sampling train. The blank sampling trains were recovered into two containers in the same manner as the other trains. These samples were returned to the laboratory, processed, and analyzed with the flue gas samples collected.

Field Reagent Blank(s)

Aliquots of each lot of DNPH, $MeCl_2$, and deionized water were collected for analysis as field reagent blanks. These samples were returned to the laboratory, processed, and analyzed with the flue gas samples collected.

Sample Storage and Shipping

Sample containers were checked to ensure that complete labels were affixed. The labels identified Trains A, B, C, or D as appropriate. Teflon®-lined lids were tightened and secured with Teflon® tape. The sample bottles were stored in a cooler on ice, and returned to the Radian PPK laboratory.

ANALYTICAL PROCEDURES

All analyses were performed at Radian's PPK laboratory. This section describes the procedures that were used.

Sample Preparation

The samples were received in the laboratory in screw-capped glass bottles with Teflon®-lined caps, and stored in coolers on ice. Samples were extracted within 12 days of collection and analyzed within 30 days of extraction. Actual times between sample collection and extraction are provided in Table 18.

All labware was washed with detergent and tap water and rinsed with organic-free water, followed by a methanol and methylene chloride solvent rinse prior to use. Because acetone is an analytical interferant, glassware was not rinsed with acetone, and care was taken to minimize acetone contamination. Methanol and methylene chloride used were HPLC grade or equivalent.

Table 18. Hold Time Between Sample Collection and Sample Extraction

Field Test	Samples	Hold Time (Days)
1	MS 3, 4, 8 and 9; MB 3, 4, 8 and 9; Run 4; Run 5 Train A	1
1	Runs 1, 6 and 7; Run 5 Trains B, C, and D; MS 5-7; MB 5-7; Run 8 Trains A and B, FTB A	2
1	MS 1 and 10; MB 1 and 10; Run 8 Trains C and D; Run 9	3
2	MB 7 and 8; MS/MSD 7 and 8	
1	Runs 2 and 10; MS 2; MB 2; Run 3 Trains A and B; FTB B; FRB 2	4
2	MB 1 and 2; MS/MSD 1 and 2	
1	Run 3 Trains C and D; FRB 1	5
2	MB 3 and 4; MS/MSD 3 and 4	
2	Runs 1-3; Run 4 Trains A and B; Run 4 Train C P/I; FTB B ; MB 5, 6 and 9; MS/MSD 5, 6 and 9	6
2	Run 4 Train C I/K; Run 4 Train D; Runs 5-7, and 9; MB 10; MS/MSD 10	7
2	Runs 8 and 10; FTB A	8
2	$MeCl_2$ Bl; DNPH Bl 2; H_2O Bl 2	11
2	DNPH Bl 1; H_2O Bl 1	12

MS/MSD = Method Spike/Method Spike Duplicate
MB = Method Blank
FTB = Field Train Blank
FRB = Field Reagent Blank

Extraction

The samples were extracted into methylene chloride using separatory funnels. The separatory funnel was shaken for at least three minutes. Three separatory funnel extractions were performed. The methylene chloride extracts were added to a volumetric flask (100, 250, or 500 mL), which was then filled to the line with methylene chloride. The organic extract was then transferred to a bottle for storage at 4°C.

Solvent Exchange

The samples were solvent exchanged into acetonitrile before HPLC analysis. Table 19 summarizes the solvent exchange ratios used for the samples. To solvent exchange the samples, an aliquot of the methylene chloride extract was evaporated to near dryness at room temperature under a stream of pure nitrogen. Eight milliliters of acetonitrile was added when the sample just reached dryness. For some of the train samples, a 1:5 solvent exchange was performed by transferring a 1 mL aliquot of the methylene chloride extract into a graduated test tube, evaporating the solvent until only 0.5 mL remained, and bringing the solvent volume back up to 8 mL with acetonitrile. This step was repeated a second time, followed by a third evaporation step. The solvent volume was brought up to a final volume of 5 mL. For most of the samples and all of the blanks, a 15:4 solvent exchange was performed by transferring a 15 mL aliquot of the methylene chloride extract to a graduated test tube and following the sample procedures as for the spiked samples, except that the final solvent volume was brought up to 4 mL. The exchanged samples were transferred to vials with Teflon®-lined screw caps and stored at 4°C until analysis.

Table 19. Solvent Exchange and Dilution Procedures

Samples	Solvent Exchange Ratio
Field Test 1 Run 1 Trains A and B; Run 2 Trains A, B, and D; Runs 3-10; MB 1-10; FTB A and B; FRBs Field Test 2 Runs 1-10 Trains B and C; FTB A and B; FRBs; MB 1-10	15 mL $MeCl_2$:4 mL ACN
Field Test 1 Run 1 Trains C and D; Run 2 Train C Field Test 2 Run 1, 4 and 10 Trains A and D; Runs 2, 5, 7 and 8 Trains A and D I/K; Runs 3, 6 and 9 Train A I/K; Runs 3, 6 and 9 Train D;	1 mL $MeCl_2$:5 mL ACN
Field Test 1 MS 1-10 Field Test 2 MS/MSD 1-7	1 mL $MeCl_2$:1 mL ACN
Field Test 2 Runs 2, 5, 7 and 8 Trains A and D P/I; Runs 3, 6 and 9 Train A P/I;	2 mL $MeCl_2$:5 mL ACN
Field Test 2 MS/MSD 8-10	1 mL $MeCl_2$:2 mL ACN

MS/MSD = Method Spike/Method Spike Duplicate
MB = Method Blank
FTB = Field Train Blank
FRBs = Field Reagent Blanks
P/I = Fraction 1 (Probe Rinse and First Two Impinger Contents)
I/K = Fraction 2 (Third and Fourth Impinger Contents)
$MeCl_2$ = Methylene Chloride
ACN = Acetonitrile

Chromatographic Analyses

Standard Preparation--

A multicomponent stock aldehyde derivative standard was prepared at a concentration of 200 ng/μL by weighing 40 mg ($\pm$ 0.01 mg) of purified derivatized aldehyde crystals into small vials, dissolving the crystals in acetonitrile, quantitatively transferring the solutions to a 200-mL volumetric flask and diluting to the line with acetonitrile. This stock solution was aliquoted into 1-mL glass ampules, sealed and stored at 0°C.

Calibration standards were prepared by diluting 12.5, 25, 150, 300, and 500 μL of the multicomponent stock solution to 5 mL with acetonitrile to provide a standard curve with calibration points at 0.5, 1.0, 6, 12, and 20 ng/μL of derivative.

A check standard was prepared at 5 ng/μL of derivative by taking 125 μL of the 200 ng/μL multicomponent stock standard and diluting to 5 mL with acetonitrile. The check standard was used to check the instrument response and the calibration curve.

The HPLC system operating parameters for analysis of standards and samples were as follows:

Instrument:	Varian 5000 LC with autosampler
Data System:	Nelson 2600 or Turbochrome
Column:	Zorbax ODS (4.6 mm ID x 25 cm), or equivalent with pellicular ODS (2 mm ID x 2 cm) guard column, or equivalent
Mobile Phase:	Acetonitrile/Water/Methanol
Gradient:	Table 20
Detector:	Perkin Elmer LC 95, ultraviolet at 360 nm
Flow Rate:	0.9 mL/min
Injection Volume:	25 μL
Retention Time:	See Table 21

Table 20. HPLC Gradient for Analysis of DNPH-Derivatized Aldehydes

Time (min)	Acetonitrile (%)	Water (%)	Methanol (%)
0	20	40	40
12	5	25	70
18	5	23	72
28	10	15	75
35	10	15	75
37	20	40	40
47	20	40	40

Table 21. Retention Times of Aldehyde Derivatives

Component	Retention Time (min)
Formaldehyde	8.38
Acetaldehyde	11.48
Quinone	13.86
Acrolein	15.08
Propionaldehyde	16.41
Methyl ethyl ketone	21.40
Acetophenone	28.99
Methyl isobutyl ketone	30.51
Isophorone	38.22

Instrument Calibration--

Calibration standards were prepared at five levels as described earlier. Each calibration standard was injected in duplicate. Linear regression analysis of peak area response vs. concentrations of derivatized aldehyde or ketone was used to prepare a calibration curve, and the linearity was confirmed by visual inspection and a correlation coefficient to be at least 0.995. After an initial calibration curve was obtained, the calibration check standard described

earlier was analyzed. The standard was injected periodically throughout the analysis of samples (i.e., after every six to eight samples), and was used for daily calibration.

Sample Analysis--

Samples were analyzed by HPLC. An acetonitrile blank was analyzed at least once per day to ensure that the system was not contaminated. A check standard was analyzed prior to sample analysis, after 6-8 samples, and at the end of the sample analysis. Samples were diluted as necessary to keep concentrations within the calibration range.

Analytes were identified by retention time. The width of the retention time window used for identification was based on the standard deviation in retention time for multiple injections of a standard.

Laboratory Method Blanks

After DNPH preparation was completed, an aliquot of the solution was retained at the laboratory and analyzed with the samples, as an indicator of any aldehyde/ketone contributions attributable to laboratory procedures.

QUANTITATION

A least squares linear regression analysis of the calibration standards data was used to calculate a correlation coefficient, slope, and intercept. Concentrations were used as the X-variable, and response was used as the Y-variable.

The concentration of aldehyde in the samples was calculated as follows:

$$\text{Concentration Aldehyde in Sample} = \frac{\text{Sample Response} - \text{Intercept}}{\text{Slope}} \times \frac{\text{MW aldehyde}}{\text{MW derivative}}$$

where:

MW aldehyde = the molecular weight of the aldehyde or ketone; and

MW derivative = the molecular weight of the derivative.

The total weight of aldehyde in the sample was calculated from the concentration, the volume of methylene chloride into which the derivative was originally extracted, the volume of methylene chloride that was used for the solvent exchange, and the final volume of acetonitrile into which the sample was solvent exchanged.

$$\text{Total ACN in Sample } (\mu g) = \text{Concentration ACN in Sample } (\mu g/mL) \times \text{Total Volume of } MeCl_2 \text{ Extract } (mL) \times \frac{\text{mL of ACN (after solvent exchange)}}{\text{mL of } MECl_2 \text{ (before solvent exchange)}}$$

SPIKING

Two of the four trains making up the quad assembly were dynamically spiked during each test run. Ten complete runs resulted in a total of 20 spiked and 20 unspiked trains. For the first field test, nine different spiking compounds were used: formaldehyde, acetaldehyde, quinone, acrolein, propionaldehyde, methyl ethyl ketone, acetophenone, methyl isobutyl ketone, and isophorone. For the second field test, quinone and acrolein were excluded. Spiking compounds were added at a level indicated in Table 22. Spiking compounds were added at a level approximately five times that determine in the site survey samples (Appendix C) of the flue gas stream or at 2 ppmv for compounds that were present at 0.4 ppmv or less.

Table 22. Compounds Spiked and Nominal Spike Concentrations

Compound	Nominal Concentration Spiked			
	Field Test I		Field Test II	
	ppmv	total mg	ppmv	total mg
Formaldehyde	20	21	2.0	2.1
Acetaldehyde	8.6	13	4.4	6.4
Quinone	2.1	8.1	NT	NT
Acrolein	2.1	4.2	NT	NT
Propionaldehyde	2.1	4.4	2.1	4.4
Methyl ethyl ketone	2.1	5.3	2.1	5.3
Acetophenone	2.1	8.9	2.1	8.9
Methyl isobutyl ketone	2.0	7.1	2.0	7.1
Isophorone	2.1	10	2.1	10

NT = Not Tested

The compounds dynamically spiked into the designated trains were prepared from neat materials in water at a nominal concentration of 0.2 to 1 mg/mL. The concentrations were verified in the laboratory and an aliquot removed and stored in the laboratory at 4°C. During each run, the spiking solution was introduced to two of the four Method 0011[2] trains through glass-lined stainless steel tubing via motor-driven syringe pumps. The flow rate of the liquid spike into each train was set to 0.25 mL/min to allow the collection of a nominal 2 to 20 mg of each compound in each Method 0011[2] train over a 1-hour sampling period. The spike was introduced to each train at a point immediately after the probe and before the first impinger. The probe and glass tubing leading to each train was maintained at a temperature of 130°C (266°F).

PRECISION AND ACCURACY ASSESSMENT

Precision is defined as the estimate of variability in the data obtained from the entire system (i.e., sampling and analysis). At least two paired samples are needed to establish precision.

Accuracy (bias) is defined as any systematic positive or negative difference between the measured value and the true value. Percent recovery is defined as any gain or loss of a given compound compared to a known spiked value.

Ten quadruplicate sampling runs (i.e., 40 sampling trains) were conducted during each testing program. Acceptability criteria for the runs are detailed in Section 6 of the test plan. Completion of at least six quad runs (24 independent trains) is required for statistical analysis by Method 301.[1] For the second field test, two runs were eliminated from the data set because of suspected spiking errors. The following data treatment approach is written based on the completion of all 10 quad runs. Adjustments to calculations were made based on the number of runs actually performed and accepted.

The latest version of the Method 301[1] describes the data analysis method necessary to evaluate both the bias and the precision of emission concentration data from stationary sources. Method 301[1] was used for the statistical evaluation of the test data for this work assignment.

Method 301[1] assumes that the spike amounts for each train are equal. A problem encountered in this study was that the calculated value of the spiked level was not constant for every train. In order to complete the Method 301[1] statistical analysis, the variability of the spiked data was calculated from Equation 1:

$$d_i = Y_{iA} - Y_{iB} + S_{iB} - S_{iA}$$

where:

d_i = the difference for Run i;

Y_{iA} = the measured concentration of spiked sample A for Run i;

Y_{iB} = the measured concentration of spiked sample B for Run i;

S_{iB} = the amount spiked into sample B for Run i; and

S_{iA} = the amount spiked into Sample A for Run i.

Assessment of Precision According to Method 301

Precision of the spiked compounds was calculated using the difference between the measured concentration, d_i, of each spiked compound for each spiked train as calculated in Equation 1. Precision is reported as the standard deviation between the paired measurements of spiked compounds, SD_s, given by the following equation:

$$SD_s = \sqrt{\frac{\sum d_i^2}{2n}}$$

where:

SD_s = the standard deviation between the paired measurements of each spiked compound;

n = the number of paired samples used in the calculation (n = 8 or 10); and

d_i = the difference of paired sampling train measurements as calculated in Equation 1.

The percent relative standard deviation (%RSD) of the proposed spiked method was calculated as:

$$\%RSD = \frac{SD_s}{S_m} * 100$$

where:

S_m = measured mean of the spiked samples.

The proposed method is acceptable if the %RSD is not greater than 50 percent.

Precision of the unspiked compounds was calculated using the difference between the measured concentration, d_i, of each spiked compound for each unspiked train. Precision (SD_u) is reported as the standard deviation of the differences between the paired measurements of unspiked compounds, given by the following equation:

$$SD_u = \sqrt{\frac{\sum d_i^2}{2n}}$$

where:

SD_u = the standard deviation between the paired measurements of unspiked compounds;

n = the number of paired samples used in the calculation (n = 10); and

d_i = the difference of paired unspiked sampling train measurements.

The %RSD of the unspiked trains was calculated as:

$$\%RSD = \frac{SD_u}{M_m} * 100$$

where:

M_m = measured mean of the unspiked samples.

The proposed method is acceptable if the %RSD is not greater than 50 percent.

Assessment of Bias According to Method 301[1]

The experimental design allows for the determination of bias for each spike compound. Bias for each spike compound was calculated using 16 or 20 spiked field samples, 16 or 20 unspiked field samples, and the calculated value of each spike. Because of differing spiked amounts, the equation as given in Method 301[1] was modified to calculate bias for each spiked train. Bias, b, of the method for each spiked compound for each spiked train of each run is defined as:

$$b_{ij} = S_{ij} - \left(\frac{M_{i1} + M_{i2}}{2} \right) - CS_{ij}$$

where:

i = run number (i.e., 1, 2, 3, ...);

j = 1 or 2 (to indicate the first sample or the second sample);

b_{ij} = bias for the j^{th} spiked sample of the i^{th} run;

S_{ij} = reported amount of the compound in the j^{th} spiked sample of the i^{th} run; and

M_{i1} = reported amount of the compound in the first unspiked sample for the i^{th} run;

M_{i2} = reported amount of the compound in the second unspiked sample for the i^{th} run; and

CS_{ij} = calculated (or theoretical) value of the spiked compound in the j^{th} spiked sample of the i^{th} run.

The overall bias was then defined as:

$$B = \frac{\sum\sum b_{ij}}{n}$$

where:

b^{ij} = bias for the j^{th} spiked sample of the i^{th} run; and

n = the number of samples used in the calculation (i.e., 2*the number of runs).

The standard deviation of the bias was then calculated as follows:

$$SD = \sqrt{\frac{\sum\sum b_{ij}^2 - \frac{(\sum\sum b_{ij})^2}{n}}{n-1}}$$

The bias, B, calculated above was tested to determine if it was statistically different from 0.0. A *t*-test was used to make this determination. The *t*-test compared the calculated *t*-statistic of the test data with the critical *t* value for the degrees of freedom in the test data and the desired level of significance. For the test matrices in this plan, there were 8 or 10 data points, which were tested using a two-tailed *t*-distribution at the 95% confidence level. The *t*-statistic was calculated as shown below:

$$t = \frac{|B|}{\frac{SD}{\sqrt{n}}}$$

This *t*-test evaluates the hypothesis that the bias is not equal to zero. If the calculated absolute value of the *t*-statistic is greater than the two-tailed critical value for the specified degrees of freedom and level of significance, then there is significant bias. If the calculated absolute value of the *t*-statistic is less than the critical value for the specified degrees of freedom and level of significance, then the average difference of the concentration between paired sampling trains is assumed to be zero and the measured concentration can be pooled for statistical tests. The critical value of the *t*-statistic for the two-tailed *t*-distribution at a 0.05 level of significance (95% confidence level) with 18 degrees of freedom is 2.101.

When the *t*-test showed that the bias was statistically significant, the correction factor (CF) was calculated as follows:

$$CF = \frac{1}{1+\frac{B}{CS}}$$

where:

CF = the correction factor;

B = the bias; and

CS = the average calculated (or theoretical) spiked amount.

When the CF was within the range of 0.70 to 1.30, the data and method were considered acceptable.

SECTION 6.0
QUALITY ASSURANCE/QUALITY CONTROL

The quality assurance/quality control (QA/QC) activities for the sampling and analytical procedures are presented in this section.

QUALITY CONTROL

The quality control procedures for field and laboratory activities are described in this section. In addition to sampling and analytical QA/QC procedures, the project staff was organized to allow review of project activities and provide QC coordination throughout the term of the evaluation program.

Sampling QA/QC Procedures

The sampling QA/QC program for this project included data quality objectives, manual method sampling performance criteria, field equipment calibrations, field spiking consistency, sampling and recovery procedures, representative sampling, complete documentation of field data and abnormalities, and adequate field sample custody procedures.

Data Quality Objectives--

Precision, bias, and completeness objectives were determined for manual sampling operations and are listed in Table 23. The completeness objective was met with sampling runs completed in the field. The precision and bias objectives were met for five of the seven compounds tested. As expected from previous testing, MEK and MIBK did not pass the method bias tests.

Table 23. Field Sampling Quality Control Objectives

	Precision (%RSD)[a]	Accuracy (%)	Completeness (%)
Aldehyde/Ketone Concentration	50[b]	70-130%[c]	100
Flue Gas Temperature	±1°C	±3°C	100

[a]Relative standard deviation.
[b]Method 301,[1] Section 1.2.2, precision objectives for method validation.
[c]Method 301[1] bias objectives for method validation.

Manual Method Performance Criteria--

Acceptance criteria, control limits and corrective actions for sample collection using the Method 0011[2] sampling train are provided in Table 24.

Table 24. Summary of Acceptance Criteria, Control Limits, and Corrective Action

Criteria	Control Limits[a]	Corrective Action
Final Leak Rate	≤0.00057 acmm or 4% of sampling rate, whichever is less	None: Results are questionable and should be reviewed and compared with other (3) train results
Dry Gas Meter Calibration	Post average factor (λ) agree ±5% of pre-factor	Adjust sample volumes using the factor that gives smallest volume
Individual Correction Factor (λ)	Agree within 2% of average factor	Redo correction factor
Average Correction Factor	1.00 ±1%	Adjust the dry gas meter and recalibrate
Intermediate Dry Gas Meter	Calibrated every six months against EPA standard	--
Analytical Balance (top loader)	0.1 g of NBS Class Weights	Repair balance and recalibrate
Barometric Pressure	Within 2.5 mm Hg of mercury-in-glass barometer	Recalibrate

[a]Control limits are established based on previous test programs conducted by the EPA.

Field Equipment Calibrations--

S-Type Pitot Tube Calibration--The EPA has specified guidelines concerning the construction and geometry of an acceptable S-Type pitot tube. Information pertaining to the design and construction of the Type-S pitot tube is presented in detail in Section 3.1.1 of the Quality Assurance Handbook.[6] Pitot tubes were inspected and documented as meeting EPA specifications prior to field sampling. A pitot tube coefficient of 0.84 was used for velocity calculations.

Sampling Nozzle Calibration--Glass nozzles were used for isokinetic sampling. All nozzles were thoroughly cleaned, visually inspected, and calibrated according to the procedure outlined in Section 3.4.2 of EPA's Quality Assurance Handbook.[6]

Dry Gas Meter Calibration--Dry gas meters (DGMs) were used in the aldehyde/ketone sample trains to measure the sample volume. All DGMs were calibrated to document the volume correction factor prior to the departure of the equipment to the field. Post-test calibration checks were performed after the equipment was returned to Radian's PPK laboratory. All dry gas meters met the acceptance criteria listed in Table 24.

Dry gas meter calibrations were performed at Radian's PPK laboratory using an American® wet test meter as an intermediate standard. The intermediate standard is calibrated every six months against the EPA spirometer at EPA's Emission Measurement Laboratory in Research Triangle Park (RTP), North Carolina.

Prior to calibration a positive pressure leak check of the system was performed using the procedure outlined in Section 3.3.2 of EPA's Quality Assurance Handbook.[6] The system was placed under approximately 250 mm of water pressure and a gauge oil manometer demonstrated that no decrease in pressure occurred over a one-minute period.

After the sampling console was assembled and leak checked, the pump was allowed to run for 15 minutes to allow the pump and DGM to warm up. The valve was then adjusted to

obtain the desired flow rate. For the pre-test calibrations, data were collected at the orifice manometer settings (ΔH) of 13, 25, 38, 51, 76, and 102 mm H_2O. Gas volumes of 0.14 m^3 were used for the two lower orifice settings, and volumes of 0.28 m^3 were used for the higher settings. The individual gas meter correction factors (γ_i) were calculated for each orifice setting and averaged. The method requires that each of the individual correction factors fall within ±2% of the average correction factor or the meter will be cleaned, adjusted, and recalibrated. In addition, Radian requires that the average correction factor be within 1.00 ±1 percent. For the post-test calibration, the meter was calibrated three times at the average orifice setting and vacuum which were used during the actual test.

Sampling Operation/Recovery Procedures--

To ensure consistency between trains/runs, two individuals conducted the manual sampling, and one person was assigned to clean up, recover, and reassemble the glassware. This protocol serves to eliminate propagation of multiple operator variance. All team members were familiar with the procedures detailed in the test plan. Sampling trains were leak checked before and after each run. The leak rate of each train was within the specified limits. The recorded leak rates for each train are presented in Tables 25 and 26. All samples were withdrawn at a rate within 10 percent of isokinetic with the stack gas velocity. Isokinetic rate data are presented with the sampling parameters in Tables 3 and 10.

Representative Sampling--

The uniformity of sampling between trains was verified by comparing gas volumes and moisture content values. Velocity head and flue gas temperature were compared between runs to assess the variability in stack gas conditions.

Table 25. Leak Rates, Field Test I

	Pre-Test		Post-Test	
Run	Leak Rate (m^3/min)	Vacuum (mm Hg)	Leak Rate (m^3/min)	Vacuum (mm Hg)
1A	0.00017	203	0.00017	127
1B	0.00023	203	0.00028	102
1C	0.00034	203	0.00023	178
1D	0.00011	203	0.00023	152
2A	0.00017	229	0.00017	127
2B	0.00040	203	0.00025	127
2C	0.00014	178	0.00014	152
2D	0.00011	203	0.00037	127
3A	0.00017	178	0.00031	152
3B	0.00028	203	0.00037	203
3C	0.00025	178	0.00037	152
3D	0.00017	203	0.00011	279
4A	0.00011	229	0.00008	127
4B	0.00023	203	0.00028	178
4C	0.00008	178	0.00011	152
4D	0.00020	305	0.00011	305
5A	0.00011	152	0.00011	127
5B	0.00042	178	0.00034	203
5C	0.00017	178	0.00023	203
5D	0.00017	305	0.00025	279
6A	0.00040	152	0.00031	127
6B	0.00040	178	0.00028	178
6C	0.00011	203	0.00008	127
6D	0.00023	203	0.00025	152
7A	0.00023	152	0.00011	152
7B	0.00023	178	0.00042	203
7C	0.00017	203	0.00011	127
7D	0.00008	178	0.00014	178
8A	0.00006	152	0.00017	203
8B	0.00025	178	0.00037	152

Table 25. (Continued)

Run	Pre-Test		Post-Test	
	Leak Rate (m^3/min)	Vacuum (mm Hg)	Leak Rate (m^3/min)	Vacuum (mm Hg)
8C	0.00008	178	0.00011	178
8D	0.00020	203	0.00011	178
9A	0.00011	203	0.00006	152
9B	0.00040	254	0.00045	254
9C	0.00023	178	0.00008	127
9D	0.00025	178	0.00011	229
10A	0.00008	152	0.00014	203
10B	0.00034	254	0.00028	305
10C	0.00028	178	0.00113	152
10D	0.00014	254	0.00011	127

Table 26. Leak Rates, Field Test II

Run	Pre-Test		Post-Test	
	Leak Rate (m^3/min)	Vacuum (mm Hg)	Leak Rate (m^3/min)	Vacuum (mm Hg)
1A	0.00028	254	0.00017	203
1B	0.00017	254	0.00014	203
1C	0.00028	254	0.00025	229
1D	0.00040	254	0.00031	178
2A	0.00023	203	NR	NR
2B	NR	NR	0.00014	178
2C	0.00020	254	0.00025	178
2D	0.00017	254	0.00011	127
3A	0.00031	178	0.00020	203
3B	0.00011	178	0.00008	127
3C	0.00025	203	0.00017	178
3D	0.00034	203	0.00025	203
4A	0.00014	127	0.00006	127
4B	0.00023	178	0.00020	178
4C	0.00020	178	0.00020	203
4D	0.00031	178	0.00017	254
5A	0.00020	203	0.00031	203
5B	0.00020	203	0.00031	203
5C	0.00017	152	0.00000*	203
5D	0.00011	203	0.00025	178
6A	0.00014	152	0.00025	178
6B	0.00028	178	0.00011	152
6C	0.00023	178	0.00017	152
6D	0.00020	127	0.00020	178
7A	0.00031	229	0.00025	203
7B	0.00017	203	0.00011	127
7C	0.0014	127	0.00017	178
7D	0.00020	152	0.00011	152
8A	0.00014	178	0.00011	127
8B	0.00008	178	0.00017	178
8C	0.00017	178	0.00000*	178
8D	0.00031	254	0.00025	178

Table 26. (Continued)

Run	Pre-Test		Post-Test	
	Leak Rate (m^3/min)	Vacuum (mm Hg)	Leak Rate (m^3/min)	Vacuum (mm Hg)
9A	0.00025	203	0.00017	178
9B	0.00020	178	0.00011	178
9C	0.00023	152	0.00008	127
9D	0.00020	203	0.00008	178
10A	0.00017	178	0.00011	178
10B	0.00017	178	0.00023	229
10C	0.00011	152	0.00017	229
10D	0.00017	254	0.00020	203

NR = Not recorded.

*Leak check performed after tightening impinger clamp which was knocked loose during removal of probe assembly from stack.

Documentation–

Field data sheets were completed and checked after each test run. Test progress and any notable events affecting the sampling or process were recorded in the field log notebook. Documentation of pre- and post-test calibrations and inspections was maintained.

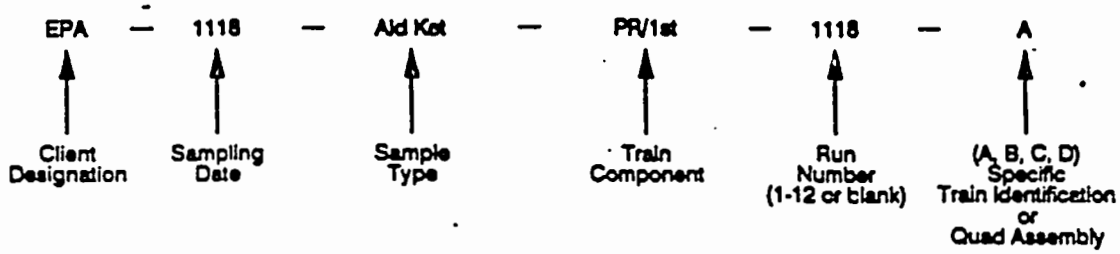
Sample Custody–

Sample custody procedures for this program are based on EPA-recommended procedures. The custody procedures emphasize careful documentation of sample collection and field analytical data and the use of chain-of-custody records for samples being transferred. These procedures are discussed below.

The sample recovery task leader was responsible for ensuring that all samples taken were accounted for and that proper custody and documentation procedures were followed for the field sampling efforts. A master sample logbook was maintained by the recovery task leader to provide a hard copy of all sample collection activities. Manual flue gas sampling data were also maintained by the recovery task leader.

Following sample collection, all samples were given a unique alphanumeric sample identification code as shown in Figure 7. Sample labels and integrity seals, similar to those shown in Figure 8, were completed and affixed to the sample containers. The sample volumes were determined and recorded and the liquid levels were marked on each bottle. The sample identification code was recorded on the sample label and in the sample logbook. The samples were stored in a secure area until they were packed.

As the samples were packed for travel, chain-of-custody forms (Figure 9) were completed for each shipment container. The chain-of-custody forms and written instructions specifying the treatment of each sample were enclosed in the sample shipment container. Shipping containers were labeled with "up arrows" to clearly indicate the upright position of sample bottles.



PR/1st	combined probe rinse and first impinger contents
2nd/3rd	combined contents of second and third impingers

Figure 7. Sample Identification Code

RADIAN
CORPORATION

900 Perimeter Park
Morrisville, NC 27560
(919)481-0212

PRELIM. NO: _____

SAMPLE TYPE: _____

LOCATION: _____

DATE: _____ CONTRACT: _____

REMARK: _____ FINAL WT: _____

TARE: _____

SAMPLE WT: _____

8-84-17483

ATTENTION:
BEFORE OPENING
NOTE IF BOTTLE WAS
TAMPERED WITH.

RADIAN
CORPORATION

900 Perimeter Park
Morrisville, NC 27560
(919)481-0212

SAMPLE CODE _____

FIELD NO. _____ CONTAINER NO. ____

ATTENTION:
BEFORE OPENING
NOTE IF BOTTLE WAS
TAMPERED WITH.

Figure 8. Example of Sample Label and Integrity Seal

RADIAN CORPORATION

Chain of Custody Record

Page___ of___

PROJECT			NO. OF CONTAINERS	ANALYSES								REMARKS	SAM ID NO. (for lab use only)
SITE:													
COLLECTED BY (Signature)													
FIELD SAMPLE I.D.	SAMPLE MATRIX	DATE/TIME											

REMARKS										RELINQUISHED BY:	DATE	TIME
RECEIVED BY:	DATE	TIME	RELINQUISHED BY:	DATE	TIME	RECEIVED BY:			DATE	TIME	RELINQUISHED BY:	DATE	TIME

LAB USE ONLY

RECEIVED FOR LABORATORY BY:	DATE	TIME	LOG NO.	CONDITION	TEMP	SEALS	CUSTODY
REMARKS:							

1 95-30337

Figure 9. Chain-of-Custody Record

Laboratory QA/QC Procedures

The laboratory QA program for this project included proper handling, logging and tracking of incoming samples, procedure validations including calibration curves, daily QC checks, and collection and/or analysis of field train and field reagent blanks, and method spikes as well as laboratory spikes. A summary of Radian's laboratory QC procedures is provided in Table 27.

Table 27. Laboratory Quality Control Procedures

Parameter	Analytical Method	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Linearity Check	HPLC	Run 5-point curve	At setup or when check std. is out-of-range	Correl. coeff. ≥0.995	Check integ., reinteg. If necessary, recalibrate
Retention Time	HPLC	Analyze check standard	1/6-8 injections	±15% day-to-day; ±5% within one day	Check instr. funct. for plug, etc. Heat column; Adjust gradient
Calibration Check	HPLC	Analyze check standard	1/6-8 injections min. 2/set	±15% of calibration curve	Check integ., remake std. or recalib.
System Blank	HPLC	Analyze acetonitrile	1/day	≤0.1 level of expected analyte	Locate source of contam.; reanalyze
Method Spikes	HPLC	Analyze spiked DNPH	1/10 samples or 1/set	±20% of spiked amount	Check integ., check instr. function, reanalyze, reprepare if possible

Sample Custody/Tracking--

Upon receipt of samples at Radian's PPK laboratory, the chain-of-custody forms and sample bottle labels were compared to verify receipt of samples. A copy of the sample log notebook was provided to the laboratory representative. After logging the samples into the Radian tracking system, they were stored at 4°C to prevent decomposition of derivatives.

Calibration Curve--

A five-point calibration curve as described in Section 5 was prepared and analyzed after initially setting up the instrument. The calibration data are presented in Table 28. All of the calibration curves used for both field tests had correlation coefficients greater than 0.998.

Daily QC Checks--

A check standard as described in Section 5 was prepared and used to check instrument response and the calibration curve. The check standard was analyzed before and after all sample analyses and after each sixth to eighth sample. The check standard recoveries are presented in Tables 29 and 30 for Field Tests I and II, respectively. All of the check standard responses fell within the 85 to 115% of known value criterion for Field Test I. Two MEK and most of the isophorone check standard responses fell outside the 85 to 115% criterion for Field Test II because of a calculation error during sample analysis. In some cases the data were not affected by the high check standard responses because only diluted samples were being analyzed for acetaldehyde.

System Blanks--

Neat acetonitrile (system blank) was analyzed at least once per day to ensure that the analytical instrument was not contaminated. None of the analytes were detected in the system blanks.

Table 28. Calibration Data[a]

Compound	Date	Slope	Intercept	Correlation Coefficient	Meets Acceptance Criteria
Formaldehyde	4/94	8.14×10^{-6}	0.0422	0.9999	Yes
	5/95	8.44×10^{-6}	0.0916	0.9989	Yes
Acetaldehyde	4/94	7.98×10^{-6}	-0.00133	0.9999	Yes
	5/95	8.18×10^{-6}	0.0529	0.9989	Yes
Quinone	4/94	1.30×10^{-5}	-0.191	0.9997	Yes
Acrolein	4/94	7.08×10^{-6}	-0.00088	0.9998	Yes
Propionaldehyde	4/94	8.37×10^{-6}	0.00642	0.9999	Yes
	5/95	8.46×10^{-6}	0.0690	0.9987	Yes
Methyl Ethyl Ketone	4/94	8.91×10^{-6}	0.0809	0.9996	Yes
	5/95	9.66×10^{-6}	0.0669	0.9989	Yes
Acetophenone	4/94	9.96×10^{-6}	0.0158	0.9999	Yes
	5/95	1.12×10^{-5}	0.165	0.9987	Yes
Methyl Isobutyl Ketone	4/94	9.75×10^{-6}	0.00486	0.9999	Yes
	5/95	9.79×10^{-6}	0.0585	0.9989	Yes
Isopherone	4/94	1.13×10^{-5}	-0.0108	0.9999	Yes
	5/95	1.23×10^{-5}	0.104	0.9988	Yes

[a] Concentration of Derivative (μg/mL) = Area x Slope + Intercept

Table 29. Calibration Check Standard Recoveries for Field Test I

Sample ID	File #	Date	Time	Percent of Target*								
				Form-aldehyde	Acet-aldehyde	Quinone	Acrolein	Propion-aldehyde	MEK	Aceto-phenone	MIBK	Isophor-one
QC 1	T4HA004	080194	16:53	90.3	91.4	97.3	99.8	96.9	90.0	92.9	92.2	93.4
QC 2	T4HA014	080294	00:53	96.5	98.7	97.7	102.	102.	97.9	99.5	98.1	101.
QC 3	T4HA025	080294	09:40	96.2	98.6	97.8	101.	94.7	97.7	101.	100.	104.
QC 1	T4HB001	080294	14:52	98.4	101.	104.	104.	103.	98.7	100.	101.	102.
QC 2	T4HB012	080294	23:40	97.8	97.8	97.8	101.	102.	95.6	100.	97.9	102.
QC 3	T4HB020	080394	06:03	88.8	95.6	99.5	102.	102.	95.8	96.6	97.3	100.
QC 1	T4HC001	080394	16:30	95.9	97.4	101.	100.	98.3	97.0	101.	99.1	102.
QC 2	T4HC013	080494	02:06	97.3	96.2	94.1	98.7	95.1	94.9	95.8	96.2	101.
QC 3	T4HC019	080494	06:53	96.6	99.5	100.	102.	101.	98.2	101.	98.5	101.
QC 1	T4HD010	080494	17:12	97.3	97.9	97.8	100.	99.1	98.6	97.3	98.3	101.
QC 2	T4HD022	080594	02:47	98.2	97.7	96.6	101.	99.5	98.3	99.3	98.2	100.
QC 3	T4HD027	080594	06:47	93.6	95.7	95.3	101.	99.2	93.9	95.2	96.0	99.9
QC 1	T4HE001	080594	17:24	93.6	95.3	96.1	99.0	99.7	92.6	94.6	94.1	101.
QC 2	T4HE013	080694	02:59	94.9	96.7	95.9	99.2	98.1	96.4	98.6	97.2	98.1
QC 3	T4HE020	080694	08:35	96.4	99.6	98.6	104.	102.	98.4	102.	99.8	101.
QC 1	T4HH001	080794	16:04	98.5	98.1	96.5	101.	101.	98.4	103.	100.	102.
QC 2	T4HH013	080894	01:40	99.4	100.	98.0	103.	102.	97.9	98.4	98.8	103.
QC 3	T4HH022	080894	08:51	94.6	98.8	95.5	99.6	99.0	96.4	98.6	99.1	100.
QC 4	T4HH022H	080894	15:21	96.3	97.1	101.	103.	106.	94.3	97.4	98.5	100.
QC 1	T4HI007	080894	20:44	94.4	93.6	93.9	98.0	98.6	94.0	93.2	94.1	96.6
QC 2	T4HI019	080994	06:19	99.1	98.5	97.1	99.9	98.5	99.2	96.6	99.6	100.
QC 3	T4HI031	080994	15:55	95.3	97.3	93.5	99.1	99.5	98.4	96.1	93.9	101.
QC 4	T4HI041	080994	23:58	98.4	97.0	97.8	104.	104.	95.6	100.	100.	101.
QC 5	T4HI046	081094	03:58	97.7	100.	93.4	100.	99.0	97.0	100.	96.6	101.
QC 6	T4HI046K	081094	12:46	95.1	96.0	94.6	100.	102.	96.3	95.5	96.3	100.

Table 29. (Continued)

Sample ID	File #	Date	Time	Percent of Target[a]								
				Form-aldehyde	Acet-aldehyde	Quinone	Acrolein	Propion-aldehyde	MEK	Aceto-phenone	MIBK	Isophor-one
QC 1	T4HK001	081094	14:00	95.8	97.2	96.6	103.	103.	97.1	94.9	98.0	99.2
QC 2	T4HK013	081094	23:35	97.7	97.9	95.8	100.	99.2	97.0	96.7	100.	100.
QC 3	T4HK022	081194	06:47	96.5	98.3	95.0	99.2	98.6	99.5	97.6	100.	102.
QC 1	T4HO002	081394	10:35	94.5	99.4	97.6	100.	99.6	97.0	95.2	97.3	101.
QC 2	T4HO014	081394	20:11	95.3	98.3	95.9	99.4	100.	97.0	94.0	99.8	101.
QC 3	T4HO026	081494	05:46	99.0	98.8	96.3	101.	101.	97.1	95.0	96.7	102.
QC 4	T4HO036	081494	13:46	95.7	98.3	98.6	102.	106.	98.1	93.7	97.9	99.4
QC 1	T4HY001	082594	10:55	99.5	99.1	101.	103.	101.	99.7	95.8	98.8	101.
QC 2	T4HY009	082594	17:18	97.6	97.2	97.0	101.	98.2	96.6	93.3	95.0	99.3

MEK = Methyl ethyl ketone
MIBK = Methyl isobutyl ketone

[a] Acceptable range is 85 to 115 percent.

Table 30. Calibration Check Standard Recoveries for Field Test II

Sample ID	File #	Date	Time	Percent of Target[a]						
				Form-aldehyde	Acet-aldehyde	Propion-aldehyde	MEK	Aceto-phenone	MIBK	Iso-phorone
QC 1	J5EC001	04-May-95	05:59 am	102.	112.	108.	109.	109.	104.	116.[b]
QC 2	J5EC015	04-May-95	05:11 pm	93.5	98.0	99.3	101.	102.	96.0	110.
QC 1	T5ED002	04-May-95	07:12 pm	104.	106.	109.	110.	105.	102.	114.
QC 2	T5ED014	05-May-95	04:48 am	92.3	101.	101.	106.	102.	97.9	109.
QC 3	T5ED024	05-May-95	12:47 pm	96.2	101.	102.	108.	101.	96.5	109.
QC 1	J5EH001	06-May-95	01:04 pm	98.4	108.	107.	110.	107.	104.	116.[b]
QC 2	J5EH016	07-May-95	02:49 am	98.1	103.	102.	110.	100.	99.4	118.[b]
QC 3	J5EH028	07-May-95	12:25 pm	96.8	105.	104.	108.	102.	100.	116.[b]
QC 4	J5EH040	07-May-95	10:00 pm	103.	107.	109.	112.	104.	103.	116.[b]
QC 5	J5EH051	08-May-95	06:48 am	90.8	98.3	95.6	102.	94.0	91.0	104.
QC 1	T5EJ001	08-May-95	01:02 pm	101.	108.	107.	111.	104.	103.	116.[b]
QC 2	T5EJ013	09-May-95	12:17 am	97.4	104.	106.	109.	101.	100.	117.[b]
QC 3	T5EJ025	09-May-95	09:53 am	88.1	103.	98.8	107.	97.7	98.0	116.[b]
QC 1	T5EO001	15-May-95	11:09 am	100.	108.	111.	116.[c]	106.	106.	119.[c]
QC 2	T5EO010	15-May-95	07:08 pm	97.3	101.	101.	105.	97.9	96.8	114.
QC 3	T5EO019	16-May-95	02:20 am	87.6	95.8	96.9	97.5	97.7	89.9	99.8
QC 4	T5EO031	16-May-95	11:56 am	94.7	103.	105.	104.	97.0	98.3	117.[c]
QC 5	T5EO043	17-May-95	12:36 am	96.1	107.	109.	113.	102.	103.	116.[b]
QC 6	T5EO055A	17-May-95	01:08 pm	97.2	111.	111.	112.	102.	105.	116.[b]
QC 7	T5EO068	17-May-95	11:31 pm	100.	111.	108.	111.	99.3	101.	115.

Table 30. (Continued)

Sample ID	File #	Date	Time	Percent of Target[a]						
				Form-aldehyde	Acet-aldehyde	Propion-aldehyde	MEK	Aceto-phenone	MIBK	Iso-phorone
QC 8	T5EO082	18-May-95	10:43 am	97.7	105.	106.	113.	98.4	98.7	117.[b]
QC 9	T5EO084C	18-May-95	02:42 pm	96.4	112.	109.	117.[c]	97.5	104.	118.[c]
QC 1	T5ED002A	22-May-95	11:33 am	94.6	103.	105.	108.	97.1	99.5	119.[b]
QC 2	T5EV006	22-May-95	03:37 pm	94.2	103.	104.	109.	96.6	101.	115.

MEK = Methyl ethyl ketone
MIBK = Methyl isobutyl ketone

[a] Acceptable range is 85 to 115 percent.
[b] Outside range, data flagged.
[c] Outside range, data not affected.

Laboratory Method Blanks--

One method blank (MB) was prepared for every quad run for both field tests. The MBs indicated contamination that occurred in the laboratory during the sample preparation process. The MB data is presented in Tables 31 and 32 for Field Tests I and II, respectively.

Laboratory Method Spikes and Method Spike Duplicates--

For the first field test, one method spike (MS) for every quad train was prepared. For the second field test, one MS and method spike duplicate (MSD) for every quad train were prepared. Thus, for both field tests a total of 30 MS samples were prepared and analyzed. The recovery criterion for MS and MSDs was 100±20 percent. The MS recovery data are presented in Tables 33 and 34 for Field Tests I and II, respectively.

Formaldehyde MS/MSD recoveries were within the acceptable range in every case. One isophorone MSD recovery during the second field test was just barely outside the upper limit (121 versus 120). Two acetophenone MSD recoveries during the second field test were also outside the upper limit. For these three compounds the MS/MSD recovery criteria were achievable greater than 90% of the time.

During the first field test, acetaldehyde and propionaldehyde MS recoveries were within the acceptable range for 9 of the 10 samples. MEK and MIBK MS recoveries were within the acceptable range for 8 of the 10 samples and 7 of the 10 samples, respectively. However, during the second field test, acetaldehyde MS/MSD recoveries were within range for only 14 out of the 20 samples; propionaldehyde was within the acceptable range for 3 of the 20 samples; MEK was within the acceptable range for 6 of the 20 samples; and MIBK was out of the acceptable range for all 20 samples. The poorer performance of these compounds during the second field test may have resulted from the longer time that the samples were stored between being spiked and extracted.

Table 31. Laboratory Method Blank Results for Field Test I

	Total micrograms								
Sample	Form-aldehyde	Acet-aldehyde	Quinone	Acrolein	Propion-aldehyde	MEK	Aceto-phenone	MIBK	Iso-phorone
MB 1	1.03	ND	ND	ND	ND	1.90	ND	0.86	ND
MB 2	1.05	0.19	ND	ND	ND	ND	ND	ND	ND
MB 3	1.21	ND	ND	ND	0.76	1.33	ND	ND	ND
MB 4	0.70	0.28	ND	0.22	0.47	1.11	ND	ND	ND
MB 5	1.01	0.26	ND	ND	ND	ND	ND	ND	ND
MB 6	1.13	ND	ND	ND	0.46	1.30	ND	ND	ND
MB 7	0.70	0.31	ND	0.70	0.24	1.28	ND	ND	ND
MB 8	10.6	0.28	4.26	0.51	0.51	2.83	ND	ND	ND
MB 9	1.95	ND	ND	ND	ND	ND	ND	ND	ND
MB 10	2.96	ND	0.39	0.59	2.29	1.31	ND	ND	ND
Average	2.23	0.13	0.47	0.20	0.47	1.106	0.00	0.09	0.00
Standard Deviation	3.03	0.14	1.34	0.29	0.69	0.91	NA	0.27	NA
Relative Standard Deviation	135%	108%	285%	145%	147%	82%	NA	300%	NA

Table 32. Laboratory Method Blank Results for Field Test II

	Total micrograms						
Sample	Formaldehyde	Acetaldehyde	Propionaldehyde	Methyl Ethyl Ketone	Acetophenone	Methyl Isobutyl Ketone	Isophorone
MB 1 RERUN	0.82	0.89	2.07	ND	ND	ND	ND
MB 2	0.92	0.64	1.27	ND	ND	ND	ND
MB 3	0.99	0.50	ND	ND	ND	ND	ND
MB 4	1.09	0.28	ND	ND	ND	ND	ND
MB 5	1.95	0.61	ND	ND	ND	2.12	ND
MB 6	1.34	0.58	ND	ND	ND	1.43	ND
MB 7	0.81	0.28	ND	ND	ND	ND	ND
MB 8	1.18	0.59	ND	ND	ND	ND	ND
MB 9	1.09	0.73	ND	ND	ND	ND	ND
MB 10	1.12	0.58	ND	ND	ND	ND	ND
Average	1.13	0.57	1.67	ND	ND	1.78	ND
Standard Deviation	0.33	0.19	0.57	NA	NA	0.49	NA
Relative Standard Deviation	29.31%	32.91%	34.03%	NA	NA	27.40%	NA

Note: Final values are not Method Blank corrected.

ND = Not Detected

Table 33. Percent Recovery[a] for Method Spike Samples for Field Test I

Sample	Form-aldehyde	Acet-aldehyde	Quinone	Acrolein	Propion-aldehyde	MEK	Acetophenone	MIBK	Isophorone
MS 1	97.3	91.3	93.1	81.0	97.3	92.6	102	81.4	107
MS 2	95.2	89.4	85.5	80.0	101	74.6[b]	93.8	73.8[b]	99.2
MS 3	101	92.4	68.6[b]	71.4[b]	93.6	97.5	102	90.5	105
MS 4	98.1	90.9	57.4[b]	64.5[b]	90.1	80.9	98.1	80.0	105
MS 5	110	100	68.3[b]	71.8[b]	107	74.6[b]	110	78.9[b]	115
MS 6	113	99.3	39.9[b]	83.2	102	94.7	104	92.2	112
MS 7	108	97.4	56.6[b]	85.4	108	102.8	107	97.5	115
MS 8	99.0	92.9	81.6	65.2[b]	94.5	95.5	104	94.6	111
MS 9	83.4	76.8[b]	46.6[b]	48.3[b]	73.4[b]	81.4	82.3	69.9[b]	86
MS 10	101	89.0	36.0[b]	59.9[b]	90.1	95.5	98.8	82.4	104
Maximum	113	100	93.1	85.4	108	102.8	107	97.5	115
Minimum	83.4	76.8	36.0	48.3	73.4	74.6	82.3	69.9	86
Average	101	92.0	63.4	71.1	95.8	89.0	100	84.1	106
Standard Deviation	8.45	6.69	19.5	11.8	10.2	10.2	7.79	9.18	8.53
Relative Standard Deviation	8.40%	7.27%	30.8%	16.6%	10.7%	11.4%	7.78%	10.9%	8.06%

MEK = Methyl ethyl ketone
MIBK = Methyl isobutyl ketone

$$\text{Percent Recovery} = \frac{\text{Total } \mu\text{g Recovered}}{\text{Total } \mu\text{g Spiked}} \times 100$$

[a] Acceptable range is 80 to 120 percent.
[b] Outside range, data flagged.

Table 34. Percent Recovery[a] for Method Spike Samples for Field Test II

Sample	Formaldehyde	Acetaldehyde	Propionaldehyde	MEK	Acetophenone	MIBK	Isophorone
MS 1	96.6	91.8	79.5[b]	86.0	118	54.2[b]	112[c]
MSD 1	87.2	89.0	77.4[b]	72.4[b]	114	36.5[b]	112[c]
MS 2	92.4	92.8	84.5	93.1	119	47.3[b]	117[c]
MSD 2	89.7	88.0	77.9[b]	86.5	114	39.8[b]	106[c]
MS 3	91.6	84.3	77.9[b]	78.4[b]	119	43.2[b]	110[c]
MSD 3	93.8	82.6	77.1[b]	78.9[b]	121[b]	40.1[b]	109[c]
MS 4	94.2	81.2	82.1	85.5	119	37.6[b]	107[c]
MSD 4	91.2	93.9	76.9[b]	80.0	117	35.1[b]	121[b,c]
MS 5	87.2	91.0	73.4[b]	65.1[b]	113	38.2[b]	114[c]
MSD 5	95.4	90.3	84.2	69.4[b]	124[b]	41.9[b]	115[c]
MS 6	88.0	82.3	74.6[b]	79.7[b]	111	30.2[b]	107[c]
MSD 6	82.5	82.4	69.9[b]	77.8[b]	104	30.5[b]	104[c]
MS 7	82.8	79.2[b]	67.6[b]	70.5[b]	108	30.0[b]	106[c]
MSD 7	91.7	81.5	73.6[b]	72.1[b]	114	28.6[b]	108[c]
MS 8	84.1	76.8[b]	68.8[b]	80.6	98.0	43.3[b]	103[c]
MSD 8	87.5	78.6[b]	71.7[b]	77.9[b]	99.5	45.5[b]	104[c]
MS 9	90.8	81.6	73.7[b]	72.4[b]	104	30.0[b]	109[c]
MSD 9	82.3	71.8[b]	58.7[b]	67.8[b]	89.7	35.6[b]	98.4[c]
MS 10	88.2	78.4[b]	69.9[b]	75.6[b]	99.0	30.7[b]	105[c]
MSD 10	86.2	76.2[b]	67.3[b]	70.5[b]	97.3	30.0[b]	104[c]

Table 34. (Continued)

Sample	Formaldehyde	Acetaldehyde	Propionaldehyde	MEK	Acetophenone	MIBK	Isophorone
Maximum	96.6	93.9	84.5	93.1	124	54.2	121
Minimum	82.3	71.8	58.7	65.1	89.7	28.6	98.4
Average	89.2	83.7	74.3	77.0	110	37.4	109
Standard Deviation	4.29	6.23	6.30	7.16	9.65	7.05	5.55
%RSD	4.81%	7.44%	8.48%	9.30%	8.77%	18.8%	5.11%

MEK = Methyl ethyl ketone
MIBK = Methyl isobutyl ketone

$$\text{Percent Recovery} = \frac{\text{Total } \mu g \text{ Recovered}}{\text{Total } \mu g \text{ Spiked}} \times 100$$

[a] Acceptable range is 80 to 120 percent.
[b] Outside range, data flagged.
[c] Calibration check standard outside range (116%, 117%).

Quinone and acrolein were only included during the first field test. The MS recoveries were usually outside of the acceptable limits. Quinone seems to react with the DNPH reagent at a slower rate than the other carbonyl compounds and acrolein, because of its reactive double bond, tends to tautomerize.

Field Train and Field Reagent Blanks--

Two field train blanks were collected as described in Section 5. These field train blanks were collected on the first and fourth day of sampling and were processed in the same manner as collected samples. One field train blank was collected using a spiked train (Train A) and the other field train blank was collected using an unspiked train (Train B). The field train blank results are reported in Tables 35 and 36 for Field Tests I and II, respectively.

Formaldehyde and acetaldehyde were detected in all four field train blanks. MIBK and isophorone were not detected in any of the field train blanks.

Field reagent blanks of recovery solvents and unused DNPH reagent were collected in the field and shipped to Radian's PPK laboratory. The field reagent blank results are reported in Tables 37 and 38 for Field Tests I and II, respectively. Field train and field reagent blank analytical results serve as indicators of contamination that may have occurred during sampling and recovery operations.

Table 35. Field Train Blank Results in Total Micrograms of Carbonyl for Field Test I

Compound	Field Train Blank A			Field Train Blank B			Average
	Probe, Impingers 1 and 2	Impinger 3 and 4	Total	Probe, Impingers 1 and 2	Impinger 3 and 4	Total	
Formaldehyde	6.90[a]	2.08[a,b]	8.98	5.61[a,b]	2.14[a,b]	7.75	8.36
Acetaldehyde	2.69[a,b]	1.82[a,b]	4.51	3.55[a,b]	1.40[a,b]	4.95	4.73
Quinone	2.88[b]	ND	2.88	ND	ND	ND	1.44
Acrolein	0.97[a,b]	1.68[a,b]	2.65	ND	ND	ND	1.32
Propionaldehyde	1.07[a,b]	2.19[a,b]	3.26	7.36[a,b]	4.11[a,b]	11.5	7.36
Methyl ethyl ketone	2.77[b]	2.88[b]	5.65	15.5[b]	<1.54	15.5	10.6
Acetophenone	2.26[b]	<0.42	2.26	<0.84	<0.42	<0.84	1.13
Methyl isobutyl ketone	<0.58	<0.58	<0.58	<1.16	<0.58	<1.16	<0.87
Isophorone	ND	ND	ND	ND	ND	ND	ND

Note: Final values are not corrected for the Field Reagent Blank.

ND = Not Detected

[a]Less than 10 times the level measured in the Field Reagent Blank.
[b]Below calibration curve.

Table 36. Field Train Blank Results in Total Micrograms of Carbonyl for Field Test II

Compound	Field Train Blank A			Field Train Blank B			Average
	Probe, Impingers 1 and 2	Impinger 3 and 4	Total	Probe, Impingers 1 and 2	Impinger 3 and 4	Total	
Formaldehyde[a]	3.56[c,d]	3.36[c,d]	6.92	4.23[c,d]	3.95[c,d]	8.18	5.82
Acetaldehyde[b]	3.37[c,d]	1.60[c,d]	4.98	2.96[c,d]	2.61[c,d]	5.58	4.03
Propionaldehyde[a]	<1.12	<1.12	<1.12	1.41[c,d]	1.68[c,d]	3.09	1.54
Methyl ethyl ketone	<1.27	<1.27	<1.27	<1.27	<1.27	<1.27	<1.27
Acetophenone	<4.40	<4.40	<4.40	<4.40	<4.40	<4.40	<4.40
Methyl isobutyl ketone	<1.39	<1.39	<1.39	<1.39	<1.39	<1.39	<1.39
Isophorone	<3.01	<3.01	<3.01	<3.01	<3.01	<3.01	<3.01

Note: Final values are not corrected for the Field Reagent Blank.

ND = Not Detected

[a] More than 10% of the lowest sample value, data flagged.
[b] Less than 10% of the lowest sample value, meets criterion.
[c] Less than 10 times the level measured in the field reagent blank.
[d] Below calibration curve.

Table 37. Field Reagent Blank Results for Methylene Chloride Blank (Field Test I, August 1994)

	Total micrograms		
Compound	WIL-85	WIL-86	Average
Formaldehyde	1.94	1.95	1.95
Acetaldehyde	1.67	0.57	1.12
Quinone	ND	ND	ND
Acrolein	0.78	ND	0.39
Propionaldehyde	1.18	1.96	1.57
Methyl ethyl ketone	ND	ND	ND
Acetophenone	ND	ND	ND
Methyl isobutyl ketone	ND	ND	ND
Isophorone	ND	ND	ND

Table 38. Field Reagent Blank Results in Total Micrograms of Carbonyl for Field Test II

Compound	Methylene Chloride Blank	DNPH Blank			Water Blank		
	4/28/95	4/27/95	4/28/95	Average	4/27/95	4/28/95	Average
Formaldehyde	1.34[a,b]	3.25[a]	1.58[a,b]	2.41	0.96[a,b]	1.21[a,b]	1.08
Acetaldehyde	<0.69	1.05[a,b]	1.25[a,b]	1.15	0.77[a,b]	0.50[a,b]	0.63
Propionaldehyde	1.54[b]	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45
Methyl ethyl ketone	<1.27	<0.51	<0.51	<0.51	<0.51	<0.51	<0.51
Acetophenone	<4.40	<1.76	<1.76	<1.76	<1.76	<1.76	<1.76
Methyl isobutyl ketone	3.65[b]	1.11[b]	1.28[b]	1.20	1.00[b]	1.21[b]	1.10
Isopherone	<3.01	<1.20	<1.20	<1.20	<1.20	<1.20	<1.20

Note: Final values are not Laboratory Method Blank corrected.

[a]Less than 10 times the level measured in the method blank.
[b]Below calibration curve.

SECTION 7.0

REFERENCES

1. U. S. Environmental Protection Agency. Method 301, in Code of Federal Regulations. Title 40, Part 63. Washington, D.C. Office of the Federal Register, July 1, 1987.

2. U.S. Environmental Protection Agency, Method 0011, in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846 Manual, 3rd ed." Document No. 955-001-0000001. Washington, D.C. November 1986.

3. U.S. Environmental Protection Agency, Method 0010, in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846 Manual, 3rd ed." Document No. 955-001-0000001. Washington, D.C. November 1986.

4. Mitchell, William J., Midgett, M. Rodney. "Means to Evaluate Performance Stationary Source Test Methods." Environmental Science and Technology. 10:85, January 1976.

5. U.S. Environmental Protection Agency. Method 2, in Code of Federal Regulations. Title 40, Part 60, Appendix A.

6. U.S. Environmental Protection Agency. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Staionary Source Specific Methods (EPA 600/4-77-027b).

Appendix A

Results from Preliminary Laboratory Study

APPENDIX A

This appendix provides a description of the technical activities and results obtained for the laboratory studies conducted on Work Assignment No. 67 on Contract No. 68-D1-0010, entitled "Improvement and Testing of the DNPH Method for Aldehydes & Ketones," for the period of performance between August 1993 and September 1994.

CONCLUSIONS AND RECOMMENDATIONS

Based on the work performed in the laboratory, the following conclusions may be drawn from the results:

- Formaldehyde, acetaldehyde, propionaldehyde, methyl ethyl ketone, acetophenone, and methyl isobutyl ketone are all stable in the aqueous spiking solution for up to 62 days.
- Because 5% or less of the recovered formaldehyde was found in the second impinger regardless of whether the trains were dynamically or statically spiked, the spiking procedure used does not significantly affect the results obtained for formaldehyde.
- For all of the compounds studied other than formaldehyde, dynamic spiking allowed the collection efficiency of the train to be more adequately evaluated than static spiking and is the preferred spiking technique especially when very volatile, water-purgeable compounds are being tested.
- Keeping the first two impingers in an ice bath generally resulted in higher compound recoveries with less breakthrough into the second impinger and less tautomer formation than when the first two impingers were kept warm.

Based on work performed in the laboratory, the following recommendations are made:

- Recoveries for acrolein were low probably due to the reactive nature of the double bond. Alternate sampling and analytical methods should be pursued for acrolein or modifications should be made to Method 0011[1] to stabilize acrolein. Potential modifications to Method 0011[1] include using hexane to recover the sample trains instead of methylene chloride.

- Quinone performs inconsistently by Method 0011[1]. Alternate sampling and analytical methods should be investigated for quinone.

- Methyl isobutyl ketone and methyl ethyl ketone are not efficiently collected by the aqueous reagent. Alternate sampling and analytical methods, possibly using sorbents should be investigated for these compounds. Alternatively, modifications to Method 0011[1] such as using five or more reagent impingers, sampling at lower flow rates, using a lower pH reagent (>2N HCl), etc., may improve the performance of Method 0011[1] for these compounds.

- To obtain quantitative recoveries use 200 mL of reagent in the first impinger followed by two impingers containing 100 mL when sampling high levels (above 10 ppmv) of aldehydes and ketones and keep the impingers iced.

INTRODUCTION

Title I of the Clean Air Act (CAA) identifies 189 substances as toxic air pollutants which must be monitored under several provisions of the CAA Amendments. Title I identifies several members of the class of organic compounds consisting of aldehydes and ketones as toxic compounds emitted from stationary sources. No test method for aldehydes and ketones is currently validated to perform the required stationary source monitoring under 40 CFR Part 60.

Radian Corporation is assisting the Methods Branch of the National Exposure Research Laboratory (NERL) in evaluating sampling and analytical methods for measuring aldehyde and ketone emissions from stationary sources. All aldehydes and ketones listed in Title I of the CAA have been studied as part of this project.

Sampling and analytical methods that were evaluated in the laboratory were based on the SW-846 Method 0011 for formaldehyde. SW-846 Method 0011 uses the EPA Method 5[2] sampling trains modified to collect gaseous and particulate pollutants from an emission source in aqueous acidic 2,4-dinitrophenylhydrazine (DNPH). Aldehydes and ketones present in the stack gas stream react with DNPH to form the dinitrophenylhydrazone derivative. Samples

are then extracted with organic solvent, dried, concentrated, and exchanged into an appropriate solvent for analysis by high performance liquid chromatography (HPLC).

Background

Prior activities on the aldehyde/ketone sampling and analysis program include the following efforts:

- Synthesis of all of the hydrazone derivatives for the aldehydes and ketones listed in the CAA, as well as the analytes listed in SW-846 Method 0011;[1]
- Study of the effect of pH on hydrazone derivative formation efficiency in DNPH solution, at a pH of 0, 0.5, 1.0, and 2.0;
- Optimization of the HPLC analytical method to effectively separate the hydrazones from one another for accurate quantification and to select an internal standard for the analysis; and
- Confirmation of the chemical composition and purity of the hydrazone derivatives which had been synthesized.

The following conclusions could be drawn from the previous studies:

- The 2-chloroacetophenone hydrazone was not readily purified following the standard derivatization and recrystallization procedures. However, 2-chloroacetophenone has shown acceptable performance in laboratory validation studies using the SemiVOST method,[3] and in one field validation study using the semiVOST method where 2-chloroacetophenone was dynamically spiked in the field.[4]
- The acrolein hydrazone derivative converted to another form (referred to as "x-acrolein", possibly a tautomer) during recrystallization using ethanol and in contact with O_2 in the air. This conversion also occurred during pH dependent reaction rate studies.
- Three pairs of carbonyl compounds coeluted under the analytical conditions chosen for the HPLC analysis: butyraldehyde and isobutyraldehyde, acetophenone and o-tolualdehyde, and methyl isobutyl ketone (MIBK) and p-tolualdehyde.

- The solubility of the DNPH reagent in hydrochloric acid solution decreases rapidly as the pH is increased.

- At pH 0 (2N HCl), formaldehyde, acetaldehyde, acetone, propionaldehyde, methyl ethyl ketone, valeraldehyde, m-tolualdehyde, p-tolualdehyde, MIBK, hexaldehyde, and 2,5-dimethylbenzaldehyde average recoveries were between 80 and 120 percent.

- Average recoveries for formaldehyde, acetaldehyde, propionaldehyde, valeraldehyde, m-tolualdehyde, p-tolualdehyde, MIBK, hexaldehyde, and 2,5-dimethylbenzaldehyde were not changed when the pH was increased to 0.5 (0.3N HCl).

- The average recoveries for quinone and acrolein increased when the pH was increased from 0 to 0.5.

- The average recoveries for acetone and methyl ethyl ketone decreased when the pH was increased from 0 to 0.5.

- At pH 1 and 2 where the DNPH reagent was exhausted as indicated by the lack of a DNPH peak in the HPLC chromatogram, the recoveries of the aromatic aldehydes--benzaldehyde, m-tolualdehyde, and 2,5-dimethylbenzaldehyde--were greater than 80%, indicating that the aromatic aldehydes effectively competed with the more reactive aldehydes (formaldehyde and acetaldehyde) for DNPH reagent, probably because the aromatic aldehydes are more stable in solution than the other compounds studied.

Information on the reaction of aldehydes and ketones to form hydrazones under different pH conditions is available, and information on the ability of the various aldehydes and ketones listed in Title I of the CAA to form hydrazone derivatives is also available. Under Work Assignment 13 (Contract No. 68-D1-0010), a successful field study was completed at a fiberglass coating plant. However, during the laboratory and field studies, several problems were observed:

- Ketones are not collected as efficiently as aldehydes. Also, ketones are more likely to tautomerize than aldehydes.

- Certain polymeric substances containing formaldehyde are reported to decompose in the absorbing solution and react with the DNPH.

These questions were addressed in controlled laboratory studies and another field test was conducted to provide a validated stationary source test method. Other laboratories have encountered difficulties in the application of SW-846 Method 0011[1] to extensive lists of analytes.

Objectives

The EPA Methods Branch is developing a test method for aldehydes and ketones in emissions from stationary sources for use by the Office of Air Quality Planning and Standards (OAQPS) in the regulatory process. The object of Work Assignment 67 was to provide a fully validated source test method.

To achieve this goal, Radian carried out the following tasks:

- Determined the collection efficiency of the SW-846 Method 0011[1] sampling train for the aldehydes and ketones listed in Title I of the CAA and studied the effect of changing sampling conditions, including pH of the DNPH solution and volume and temperature of the DNPH solution.
- Studied the stability of the DNPH solution and the derivatives in the DNPH solution and in the methylene chloride extract.
- Studied the potential for interference from formaldehyde-containing polymeric substances, including hexamethylenetetramine, paraformaldehyde, and trioxane.

Project Description

Studies have been performed to establish the purity of the hydrazone derivatives that have been synthesized. The purity information is summarized in Table A-1. The purity of the hydrazone derivatives was confirmed by melting point, HPLC analysis, GC analysis, and GC/MS analysis. Melting points were determined for all the hydrazone derivatives. Most of the hydrazones melted within one to four degrees of the values reported in the literature. Hydrazones of 21 aldehydes and ketones were analyzed by HPLC to check purity. Seventeen

Table A-1

Aldehyde/Ketone Hydrazone Derivative Purity Data

Hydrazone	Carbonyl Compound Formula	Analyzed Purity (%)	Melting Point (°C)		HPLC Retention Time (min)
			Measured	Literature	
Acetaldehyde	CH_3CHO	>99.5	150	147	12.6
Acetone	CH_3COCH_3	>99.5	121	126	17.5
Acetophenone	$C_6H_5COCH_3$	>99.5	243	NA	25.5
Acrolein	$CH_2=CHCHO$	>99.5	162	165	14.8
Benzaldehyde	C_6H_5CHO	>99.5	235	237	23.0
Butyraldehyde	$CH_3CH_2CH_2CHO$	>99.5	117	122	21.6
Crotonaldehyde	$CH_3CH=CHCHO$	>99.5	183	190	19.5
2,5-Dimethylbenzaldehyde	$C_6H_4(CH_3)_2CHO$	>99.5	250	NA	28.1
Formaldehyde	$HCHO$		162	166	
Heptaldehyde	$C_6H_{13}CHO$	>99.5	99	108	28.4
Hexaldehyde	$CH_3(CH_2)_4CHO$	>99.5	100	104	26.5
Isobutyraldehyde	$(CH_3)_2CHCHO$	>99.5	171	182	20.6
Isophorone	$C_9H_{14}O$	>99.5	140	NA	29.9
Methyl ethyl ketone	$CH_3COCH_2CH_3$	97.5	110	117	21.4 22.0
4-Methyl-2-pentanone (methyl isobutyl ketone, MIBK)	$CH_3COCH_2CH(CH_3)_2$	>99.5	81	95	26.4
Propionaldehyde	CH_3CH_2CHO	>99.5	149	154	23.5
Quinone	$C_6H_4O_2$	92.9			16.2
m-Tolualdehyde	C_8H_8O	>99.5	212	211	26.0
o-Tolualdehyde	C_8H_8O	>99.5	189	195	16.2
p-Tolualdehyde	C_8H_8O	>99.5	241	239	26.0
Valeraldehyde	$CH_3(CH_2)_3CHO$	>99.5	104	106	24.4

Note: Data from Shriner, R.L., Fuson, R.C., Curtin, D.Y., Morrill, T.C. The Systematic Identification of Organic Compounds. Sixth Edition. John Wiley & Sons, Inc., New York, New York. 1980.

of the derivatives are 99% pure based on HPLC analysis at 360 nm. Because the hydrazone of 2-chloroacetophenone could not be purified to a level of more than 66% and because 2-chloroacetophenone shows acceptable performance in the semiVOST method,[1,2] we recommend that this compound be omitted from further study by SW-846 Method 0011[1] sampling methods.

A further check of the purity of the hydrazones was performed by gas chromatography with flame ionization detection. Ten of the hydrazones (formaldehyde, butyraldehyde, benzaldehyde, valeraldehyde, acetaldehyde, hexaldehyde, acetone, methyl ethyl ketone, and propionaldehyde) were greater than 86% pure. The tolualdehydes, 2,5-dimethylbenz-aldehyde, and acetophenone did not elute from the chromatographic column. The rest of the aldehydes and ketones were less than 76% pure.

Several aldehyde/ketone hydrazones were synthesized in Radian's Specialty Chemicals Group in Austin. The compounds shown in Table A-2 are currently available. In the Specialty Chemicals Group, all hydrazones derivatives are purified by multiple recrystallization and analyzed by HPLC, GC, GC/MS, NMR, IR, and melting point; all standards are >99% pure.

Studies have also been performed to establish the optimum pH for reaction of aldehydes/ketones to produce the hydrazone derivatives. From the pH studies, pH 0.5 appeared to be the best for most of the compounds studied. Raising the pH from 0 to 0.5 did not appear to significantly affect the recoveries for formaldehyde, acetaldehyde, propionaldehyde, valeraldehyde, m-tolualdehyde, p-tolualdehyde, MIBK, hexaldehyde, and 2,5-dimethylbenzaldehyde. Raising the pH from 0 to 0.5 appeared to increase the recovery of butyraldehyde, acetophenone, o-tolualdehyde, benzaldehyde, quinone, and acrolein. Only the recoveries of acetone and MEK decreased when the pH was raised to 0.5. In the laboratory experiments which were performed, pH was 0.5 based on previous studies.

Table A-2

Crystalline Aldehyde/Ketone-DNPH Derivatives

			Purity (%)
Acetaldehyde-DNPH CAS No. 1019-57-4	$C_8H_8N_4O_4$	M.W. 224.18	99
Acetone-DNPH CAS No. 1567-89-1	$C_9H_{10}N_4O_4$	M.W. 238.20	99
Acrolein-DNPH CAS No. 888-54-0	$C_9H_8N_4O_4$	M.W. 236.19	99
Benzaldehyde-DNPH CAS No. 1157-84-2	$C_{13}H_{10}N_4O_4$	M.W. 286.25	99
2-Butanone (MEK)-DNPH CAS No. 958-60-1	$C_{10}H_{12}N_4O_4$	M.W. 252.23	99
n-Butyraldehyde-DNPH CAS No. 1527-98-6	$C_{10}H_{12}N_4O_4$	M.W.252.23	99
Crotonaldehyde-DNPH CAS No. 1527-96-4	$C_{10}H_{10}N_4O_4$	MW 250.21	99
Formaldehyde-DNPH CAS No. 1081-15-8	$C_7H_6N_4O_4$	MW 210.15	99
Hexanal-DNPH CAS No. 1527-97-5	$C_{13}H_{14}N_4O_4$	M.W. 280.28	99
Methacrolein-DNPH CAS No. 5077-73-6	$C_{10}H_{10}N_4O_4$	M.W. 250.21	99
Propionaldehyde-DNPH CAS No. 725-00-8	$C_9H_{10}N_4O_4$	M.W. 238.20	99
m-Tolualdehyde-DNPH CAS No. 2880-05-9	$C_{14}H_{12}N_4O_4$	M.W. 300.27	99
o-Tolualdehyde-DNPH CAS No. 1773-44-0	$C_{14}H_{12}N_4O_4$	M.W. 300.27	99
p-Tolualdehyde-DNPH CAS No. 2571-00-8	$C_{14}H_{12}N_4O_4$	M.W. 300.27	99
Valeraldehyde-DNPH CAS No. 2057-84-3	$C_{11}H_{14}N_4O_4$	M.W. 266.26	99

The following activities were performed for Work Assignment 67:

- DNPH stability and derivative stability tests;
- Interference study; and
- Method 0011 train studies.

The following sections summarize the experimental results. The experimental procedures are described in at the end of this appendix.

PRELIMINARY STUDIES

The preliminary studies included a reverse stability study and an interference study. The stability study will be discussed first.

Stability Study

A reverse time study was conducted to evaluate the stability of pH 0.5 DNPH over time. A test solution consisting of nine of the CAA aldehydes and ketones was used to test reactivity: 2-chloroacetophenone was omitted from the list of carbonyl compounds in the CAA. The reaction of 2-chloroacetophenone with DNPH appears to yield multiple products and a pure derivative could not be obtained in derivatization studies. In addition, the compound has shown acceptable results in laboratory and field studies using Method 0010.[5]

Table A-3 shows the experimental design of the stability study. In the reverse time study, DNPH reagent was prepared. On Day 30, 8 aliquots of the DNPH solution were selected. Four aliquots were designated as blanks; two were refrigerated and two were held at room temperature. Four aliquots were spiked with the test solution and refrigerated. The spiking procedure was repeated at Day 15, Day 7, Day 4, and Day 0. All samples were then extracted, solvent-exchanged, and analyzed by HPLC to determine the effect of time upon the reactivity of DNPH.

Table A-3

Experimental Design for Studying the Stability of DNPH Solution and Derivatives in the DNPH Solution

	Number of Aliquots		
Day	Spiked[a]	Unspiked[b]	
	4°C	Ambient	4°C
30	4	2	2
15	4	2	2
7	4	2	2
4	4	2	2
0	4	2	2

[a]All spiked samples will be stored in 500 mL wide-mouth amber bottles with Teflon®-lined caps and sealed with Teflon® tape.

[b]All unspiked aliquots will be stored in 250 mL narrow-neck amber bottles with Teflon®-lined caps and sealed with Teflon® tape. (Reagent is generally stored in 1L bottles with minimal headspace.)

The results of the DNPH stability test allowed the evaluation of the amount of time that DNPH solution which has been prepared can be held until used, as well as the amount of time that the collected samples can be held before extraction.

The spiked samples were solvent exchanged using the 15:4 method. The unspiked samples were solvent exchange using the 1:1 method. Half of the spiked samples and half of the unspiked samples were analyzed 3 times to allow for a statistical evaluation of the data. Only half of the samples were analyzed in triplicate to save time and money. The results for spiked sample results are presented as percent recovered in Table A-4. The results for the unspiked samples are presented in total μg in Table A-5.

Table A-4

Results of the Stability Study of the Derivatives in pH 0.5 DNPH

	Average Recovery (%)				
Compound	Day 0	Day 4	Day 7	Day 15	Day 30
Formaldehyde	86	78	72	80	70
Acetaldehyde	94	89	88	86	68
Quinone	<1	2	3	13	51
Acrolein	31	26	29	28	45
Propionaldehyde	73	69	75	71	66
MEK	11	5	4	6	4
Acetophenone	38	102	106	101	99
MIBK	16	15	10	16	11
Isophorone	3	22	26	44	47

Table A-5

Results of the Stability Study of the DNPH Reagent at pH 0.5

	Total Micrograms									
	Stored at Ambient Temperature					Stored Refrigerated at 4°C				
Compound	Day 0	Day 4	Day 7	Day 15	Day 30	Day 0	Day 4	Day 7	Day 15	Day 30
Formaldehyde	16	7	9	46	19	4	28	1	6	30
Acetaldehyde	<1	2	2	14	25	ND	<1	<1	2	7
Quinone	18	ND	<1	ND	<1	17	ND	ND	ND	<1
Acrolein	ND	ND	1	<1	ND	<1	ND	ND	ND	ND
Propionaldehyde	ND	ND	ND	ND	ND	1	ND	ND	ND	ND
MEK	<1	ND	19	6	ND	ND	ND	ND	ND	ND
Acetophenone	ND	ND	ND	ND	1	ND	ND	ND	ND	ND
MIBK	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Isophorone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND = Not Detected

Interference Study

Duplicate aliquots of DNPH at pH 4 were challenged with potential interferences such as hexamethylenetetramine, trioxane, and paraformaldehyde. The DNPH aliquots were then extracted, solvent-exchanged, and analyzed by HPLC. Blank DNPH was used as a control for laboratory interferences. The results are reported in Table A-6. Saligenin and s-trioxane did not interfere under the conditions tested. Dimethylolurea created a slight interference and hexamethylenetetramine and paraformaldehyde significantly interfere with the determination of formaldehyde. No other potential interferences were studied.

Table A-6

Results of Interference Study at pH 4.0

	Formaldehyde Measured			
	Sample 1		Sample 2	
Interferant	Area	Bias (μg)	Area	Bias (μg)
Dimethylolurea	88277	+6.4	82328	+5.6
Hexamethylenetetramine	331391	+36	382432	+42
Paraformaldehyde	315908	+34	534753	+61
Saligenin	ND	0	ND	0
s-Trioxane	ND	0	ND	0

ND = Not Detected

Spiking Solution Stability Studies

Recoveries from the sample trains using pH 4 reagent were consistently low. Several explanations were possible: the spiking solution could be deteriorating, the dynamic spiking apparatus could be failing to properly deliver the spiked aldehydes and ketones to the impingers, or the reagent could be ineffective at efficiently converting the aldehydes and

ketones to the hydrazones. To determine the cause for the low recoveries, an investigation into the stability of the spiking solution was initiated and additional train experiments were conducted.

Stability of the spiking solution was evaluated in two ways. First, a freshly prepared and a two-month-old spiking solution were analyzed by GC/FID and the relative peak areas for each component were compared. The results are shown in Table A-7. The percent bias ranged from -9 for MIBK to +12% for acetaldehyde.

Second, the recoveries of reference spike samples using the old spiking solution at 41, 55, and 62 days were compared with reference spike sample recoveries of the new spiking solution prepared at Day 0. These results are shown in Table A-8. Except for quinone and acrolein, the recoveries on day 62 were equal or larger than the recoveries on Day 0. Quinone was only detected on Day 0 and acrolein recoveries decreased by 40% after 62 days. Thus, formaldehyde, acetaldehyde, propionaldehyde, methyl ethyl ketone, acetophenone, and methyl isobutyl ketone derivatives were all stable in the aqueous spiking solution for up to 62 days.

Comparison of Dynamic and Static Spiking

To perform train studies for SW-846 Method 0011,[1] a dynamic spiking system for aldehydes/ketones was developed, constructed, and evaluated. Two approaches were considered for spiking of an aqueous solution of the nine compounds: static spiking of an aqueous solution, and dynamic spiking of an aqueous solution using a syringe pump. Dynamic spiking was performed immediately after the probe.

After the dynamic spiking apparatus was constructed and installed in the SW-846 Method 0011[1] train, dynamic and static spiking procedures were compared using the experimental design shown in Table A-9. Two trains were spiked statically by directly adding the spiking solution to the first impinger. Another two trains were spiked dynamically using a

Table A-7

Spiking Solution Stability Based on GC/FID Analysis[a]

Compound	Peak Area[b]			
	Old Spiking Solution (WA67-CDK-113093)	New Spiking Solution (WA67-DST-013194)	Bias[c]	%Bias[d]
Acetaldehyde	1794557.3 ± 400405.8	1608230.7 ± 207361.6	+186,326.6	11.59
Propionaldehyde	1653741.0 ± 272985.3	1512187.7 ± 317168.8	+141,553.3	9.36
Acrolein	1855555.0 ± 380143.2	1833751.7 ± 188208.0	+21,803.3	1.19
Methyl Ethyl Ketone Formaldehyde	3246638.3 ± 691584.8	2985691.7 ± 334098.6	+260,946.6	8.74
Methyl Isobutyl Ketone	2672018.3 ± 481260.3	2929719.3 ± 229216.3	-257,701.0	-8.80
Acetophenone Isophorone	3610432.7 ± 525417.9	3900593.0 ± 246395.9	-290,160.3	-7.44

[a] Quinone did not chromatograph under the conditions used.
[b] Average of triplicate analyses.
[c] Bias = Old Peak Area - New Peak Area
[d] %Bias = Bias/New Peak Area x 100

Table A-8

Comparison of Spiking Solution Recoveries with Time

Compound	Old Spiking Solution (WA67-CDK-113093)									New Spiking Solution (WA67-DST-013194)
	41 Days			55 Days			62 Days			
	Recovery (%)	Bias[a]	%Bias[b]	Recovery (%)	Bias[a]	%Bias[b]	Recovery (%)	Bias[a]	%Bias[b]	Day 0
Formaldehyde	86-106	-12 to +8	-12 to +8	102	+4	+4	101	+3	+3	98
Acetaldehyde	89-112	-2 to +21	-2 to +23	104	+13	+14	103	+12	+13	91
Quinone	ND	-35	-100	ND	-35	-100	ND	-35	-100	35
Acrolein	44-54	-33 to -23	-43 to -30	49	-28	-36	46	-31	-40	77
Propionaldehyde	81-99	+10 to +28	+14 to +39	84	+13	+18	91	+20	+28	71
Methyl Ethyl Ketone	10-20	-1 to +9	-9 to +82	6	-5	-45	11	0	0	11
Acetophenone	16-36	-21 to -1	-57 to -3	25	-12	-32	43	+6	+16	37
Methyl Isobutyl Ketone	7-14	-4 to +3	-36 to +27	7	-4	-36	14	+3	+27	11
Isophorone	ND	0	NA	ND	0	NA	ND	0	NA	ND

[a] Bias = Day X - Day 0
[b] %Bias = Bias/Day 0 x 100

NA = Not Applicable

Table A-9

Experimental Design for the Comparison of Dynamic and Static Spiking Procedures Using pH 0 Reagent Prepared with HCl

Sample Name	Temperature (°C)	Spike Amount (mg)	Spiking Procedure
Train 1	0	1.5	Static
Train 2	0	1.5	Static
Train 3	0	1.5	Dynamic
Train 4	0	1.5	Dynamic
Reference Spike	RT	1.5	Static
Blank	RT	0.0	NA

RT = Room Temperature (approximately 20°C)
NA = Not Applicable

syringe pump. For quality control purposes, a reference spike and method blank sample were also analyzed.

Results for static spiking are presented in Table A-10. Recoveries based on the concentration of the spiking solution and volume of solution spiked were above 50% for formaldehyde, acetaldehyde, propionaldehyde, acetophenone, MIBK, and isophorone. Quinone was either not detected or detected at levels that were too low to quantitate. Only 30% of the MEK was recovered and just slightly less than 50% of the acrolein. Over 94% of the compounds recovered were recovered in the first impinger. When percent recoveries are calculated versus the reference spike, recoveries range from 70 to 120% for formaldehyde, acetaldehyde, acrolein, propionaldehyde, acetophenone, MEK and isophorone.

Results for dynamic spiking are presented in Table A-11. Recoveries based on the concentration of the spiking solution and volume of solution spiked were above 50% and less

Table A-10

Static Spike Train Recoveries Using pH 0 Reagent and Spiking at a Nominal 1.4 mg for Each Compound

	Percent of Spike Recovered (based on spiking solution concentration)						
		Train 1			Train 2		
Compound	Reference Spike	Impinger 1	Impinger 2	Total	Impinger 1	Impinger 2	Total
Formaldehyde	74	82	<1	82	86	<1	86
Acetaldehyde	82	73	3	76	79	4	83
Quinone	25	BQL	ND	BQL	ND	BQL	BQL
Acrolein	41	46	ND	46	49	ND	49
Propionaldehyde	70	66	<1	66	68	1	69
Methyl Ethyl Ketone	91	30	1	31	31	2	33
Acetophenone	171	137	BQL	137	135	BQL	135
Methyl Isobutyl Ketone	67	55	BQL	55	56	BQL	56
Isophorone	86	72	4	76	78	5	83

BQL = Below the quantitation Limit
ND = Not Detected

Table A-11

Dynamic Spike Train Recoveries Using pH 0 Reagent and Spiking at a Nominal 1.4 mg for Each Compound

Compound	Reference Spike	Percent Recovered (based on spiking solution concentration)					
		Train 1			Train 2		
		Impinger 1	Impinger 2	Total	Impinger 1	Impinger 2	Total
Formaldehyde	74	257	13	270	118	6	124
Acetaldehyde	82	57	24	81	48	22	70
Quinone	25	BQL	BQL	BQL	BQL	BQL	BQL
Acrolein	41	30	7	38	23	7	30
Propionaldehyde	70	40	18	58	38	17	55
Methyl Ethyl Ketone	91	14	20	34	8	11	19
Acetophenone	171	114	27	141	170	17	187
Methyl Isobutyl Ketone	67	6	14	20	7	9	16
Isophorone	86	57	11	68	57	10	67

BQL = Below the quantitation Limit

than 150% for acetaldehyde, propionaldehyde, and isophorone. Formaldehyde and acetophenone had recoveries greater than 150% for one train out of the pair. Quinone was detected at levels too low to be quantitated. Less than 40% of the acrolein, MEK, and MIBK was recovered. Significant quantities of all of the compounds except for formaldehyde were detected in the second impinger. For MEK and MIBK over 50% of the compound recovered was recovered in the second impinger. When recoveries were calculated compared to the reference spike, 73 to 99% of the acetaldehyde, acrolein, propionaldehyde, acetophenone, and isophorone were recovered. Formaldehyde recoveries were greater than 150% and quinone, MEK, and MIBK recoveries were less than 40 percent.

Table A-12 compares the average results for static and dynamic spiking. When dynamically spiking the trains, a large positive bias in formaldehyde was observed. There are at least two possible sources for this high bias--contamination of the sample during spiking, sampling, recovery, preparation, or analysis and decomposition of one or more of the other compounds into formaldehyde. If decomposition of one or more of the other compounds into formaldehyde was occurring, a high positive bias would also be expected to be present for the static trains. Because the static trains did not exhibit a high positive bias for formaldehyde, the high positive bias for the dynamic trains was contributed to contamination. For the remaining dynamic spiking trials, the glassware and spiking apparatus was cleaned thoroughly with methylene chloride to eliminate any possible traces of methanol which can be contaminated with formaldehyde. Regardless of the spiking procedure used, 5% or less of the recovered formaldehyde was found in the second impinger, indicating that the spiking procedure does not significantly affect the results obtained for formaldehyde.

Total recoveries for acetaldehyde were equivalent by the two spiking methods. Interestingly, the distribution of the acetaldehyde in the train shifted. When dynamic spiking was used, 30% of the recovered acetaldehyde was present in the second impinger versus only 4% when static spiking was used. Thus, although the spiking procedure does not affect the overall performance of the train in recovering acetaldehyde, it does affect any conclusions regarding breakthrough of acetaldehyde.

Table A-12

Comparison of Dynamic and Static Spike Train Recoveries Using pH 0 Reagent and Spiking at a Nominal 1.4 mg for Each Compound

Compound	Percent Recovered (based on spike amount)			Percent of Total Recovered in Second Impinger		Percent Recovered (based on reference spike)	
	Reference Spike	Static Trains[a]	Dynamic Trains[a]	Static Trains[a]	Dynamic Trains[a]	Static Trains[a]	Dynamic Trains[a]
Formaldehyde	74	84	197	<1	5	114	266
Acetaldehyde	82	80	76	4	30	97	92
Quinone	25	BQL	BQL	NA	NA	BQL	BQL
Acrolein	41	48	34	0	20	116	83
Propionaldehyde	70	68	56	<2	31	96	81
Methyl Ethyl Ketone	91	32	26	4	58	35	29
Acetophenone	171	136	164	0	14	80	96
Methyl Isobutyl Ketone	67	56	18	0	63	83	27
Isophorone	86	80	68	6	16	92	78

[a] Average of two trials
BQL = Below the quantitation Limit
NA = Not Applicable

Quinone was not detected at this spike level by either spiking procedure although it was detected in the reference spike. Additional tests were done at higher spike levels to determine whether there was a threshold level at which quinone would react.

For acrolein, propionaldehyde, MIBK, and isophorone, the total recoveries were less with dynamic spiking than with static spiking and significant quantities of the recovered compounds were found in the second impinger. For these compounds, static spiking would overestimate the performance of the train and could lead to false conclusions that the sampling procedure is adequate for these compounds when in reality significant quantities of the compound would not be recovered. Thus, for acrolein, propionaldehyde, MIBK, and isophorone, dynamic spiking should be used for any evaluation and validation activities.

For MEK the overall recoveries for the dynamically spiked train varied from 19% to 34% so the recoveries were equivalent to or less than the recoveries for the statically spiked trains and much more variable. Most of the recovered MEK (58%) was found in the second impinger for the dynamically spiked trains, indicating that the impingers and DNPH reagent do not collect MEK efficiently. The variability in the overall recoveries for the dynamically spiked trains also indicate a lack of precision of this sampling method for MEK.
The acetophenone results were biased high in all of the samples. Interestingly, higher recoveries were obtained for acetophenone when using dynamic spiking rather than static spiking. However, with dynamic spiking 14% of the recovered acetophenone was found in the second impinger, indicating that breakthrough occurs.

Because different results were obtained with some of the compounds when dynamic spiking was used and dynamic spiking is more representative of what occurs in an actual sampling situation, dynamic spiking was used for the remaining studies.

Evaluation of Reagent Amount in First Impinger and Impinger Temperature on Carbonyl Recoveries

The effect of the amount of reagent in the first impinger and impinger temperature were evaluated using the experimental design shown in Table A-13. Four trains were dynamically spiked with 15 mg of each carbonyl compound. For two of the trains, the first impinger contained 100 mL of reagent and was kept in an ice bath during the entire sampling period. For the other two trains, the first impinger contained 200 mL of reagent. For one of these trains the first impinger was kept at room temperature during sampling and for the other train the impinger was maintained in an ice bath. For quality control purposes, a reference spike and method blank sample were also analyzed.

Table A-13

Experimental Design for the Evaluation of the Amount of Reagent in the First Impinger and the Impinger Temperature Using pH 0 Reagent Prepared with HCl and Spiking 15 mg of Each Carbonyl

Sample Name	Temperature of First Impinger (°C)	Reagent Amount in the First Impinger (mL)
Train 5	0	100
Train 6	0	100
Train 11	RT	200
Train 12	0	200
Reference Spike	RT	100
Blank	RT	100

RT = Room Temperature (approximately 20°C)

Results for comparison of the amount of reagent in the first impinger are reported in Table A-14. Recoveries based on the concentration of the spiking solution and volume of solution spiked improved for all of the compounds except quinone when the volume of reagent

Table A-14

Spike Train Recoveries Using pH 0 Reagent and Spiking at a Nominal 14 mg for Each Compound

	Perecent of Spike Recovered (based on spiking solution concentration)					
	100 mL in First Impinger			200 mL in First Impinger		
Compound	Train 5	Train 6	Mean	Train 12	Bias	%Bias
Formaldehyde	45.5	53.8	49.6	106	+56.4	114
Acetaldehyde	27.0	37.9	32.4	61.8	+29.4	90.7
Quinone	50.5	57.9	54.2	54.5	+0.3	0.6
Acrolein	30.1	39.9	35.0	49.9	+14.9	42.6
Propionaldehyde	24.3	33.7	29.0	59.9	+30.9	107
Methyl Ethyl Ketone	4.57	6.88	5.72	13.0	+7.28	127
Acetophenone	34.4	49.4	41.9	54.7	+12.8	30.5
Methyl Isobutyl Ketone	5.26	8.88	7.07	14.6	+7.53	107
Isophorone	15.4	14.0	14.7	79.9	+65.2	444

BQL = Below the quantitation Limit
ND = Not Detected

in the first impinger was increased from 100 to 200 mL. The recovery for isophorone quadrupled. Recoveries for formaldehyde, acetaldehyde, propionaldehyde, MEK, and MIBK doubled. The recoveries for acrolein and acetophenone increased by 40 and 30%, respectively. Thus, for sampling high levels (above 10 ppmv) of aldehydes and ketones, using 200 mL of reagent in the first impinger is recommended.

Results for comparison of the temperature of the first impinger reagent solution are presented in Table A-15. Recoveries based on the concentration of the spiking solution and volume of solution spiked were above 70% in the first impinger for formaldehyde and

acetophenone regardless of whether the impinger was kept warm or cold. Recoveries and breakthrough into the second impinger were unaffected by impinger temperature for acetophenone, formaldehyde, and quinone. For isophorone the recoveries were unaffected by impinger temperature but the breakthrough into the second impinger was lower when the impingers were kept cold. For acetaldehyde and propionaldehyde the recoveries were higher and the breakthrough was less when the impingers were kept cold. For acrolein, cold impingers resulted in slightly better recoveries. In addition, less tautomer formed in the cold impingers (5.78% versus 15.8% in the warm impingers). For MEK and MIBK the two cold impingers recovered more compound. Interestingly, the breakthrough into the second impinger was also higher when the impingers were cold. In general, for all of the compounds, the train performs better (higher recoveries, less breakthrough, higher compound stability) with the impingers cold.

EXPERIMENTAL PROCEDURES

This section focuses on the preparation, sampling and analysis procedures used during the laboratory studies. The procedures will be discussed in an order consistent with the order they would be performed in an actual situation: reagent preparation, sampling, sample preparation, and finally analysis.

Preparation of 0.5 pH Reagent

To prepare the DNPH reagent used for the pH 0.5 laboratory studies, a 4 liter container is placed under a fume hood on a magnetic stirrer. A large stir bar is added and the container is filled half full with organic-free reagent water. A pipet is used to measure 6.5 mL of concentrated sulfuric acid, which should be added to the stirring water slowly. Fumes may be generated and the water may become warm. Approximately 15 to 20 g of DNPH crystals are weighed on a one-place balance and added to the stirring acid solution. The 4 liter container is filled with organic-free reagent water and allowed to stir overnight. If all the

Table A-15

Spike Train Recoveries Using pH 0 Reagent and Spiking at a Nominal 14 mg for Each Compound

	Percent of Spike Recovered (based on spiking solution concentration)							
	Impingers at Room Temperature				Impingers in Ice Bath			
Compound	Impinger 1	Impinger 2	Total	Breakthrough (%)	Impinger 1	Impinger 2	Total	Breakthrough (%)
Formaldehyde	95.9	2.9	98.80	2.94	106	2.5	108.5	2.3
Acetaldehyde	33.2	14.1	47.30	29.81	61.8	14.2	76.0	18.7
Quinone	55.3	2.2	57.50	3.83	54.5	1.7	56.2	3.0
Acrolein	40.3	0.2	40.50	0.49	49.9	0.6	50.5	1.2
Propionaldehyde	42.5	13.4	55.90	23.97	59.9	14.7	74.6	19.7
Methyl Ethyl Ketone	4.4	3.7	8.10	45.68	13.0	16.9	29.9	56.5
Acetophenone	52.7	13.1	65.80	19.91	54.7	11.6	66.3	17.5
Methyl Isobutyl Ketone	6.2	6.1	12.30	49.59	14.6	19.2	33.8	56.8
Isophorone	74.5	15.7	90.20	17.41	79.9	10.2	90.1	11.3

DNPH crystals have dissolved overnight, additional DNPH is added and the solution is stirred for two more hours. The process of adding DNPH is continued with additional stirring until a saturated solution is formed. The DNPH solution is filtered using gravity filtration and set aside for the next step.

Approximately 1.6 liters of the DNPH reagent is placed in a 2 liter separatory funnel. Approximately 200 mL of cyclohexane was added to the funnel. The stopper is then placed in the funnel. The stopper is wrapper with paper towels to absorb any leakage. The funnel is inverted and vented. The funnel is shaken vigorously for three minutes, venting initially every 10-15 seconds and then irregularly. After the layers have separated, the upper (organic) layer is discarded.

The DNPH is extracted a total of three times. The clean DNPH solution is stored in amber bottles that have been rinsed with acetonitrile and allowed to dry. The top of the amber bottle has been capped with a teflon lined top and then sealed around the edges with teflon tape.

Sample Preparation

The samples were prepared using the same method as the reagent preparation with a few modifications. The sample was placed into an appropriate size separatory funnel (a 250-mL sample would be placed into a 500-mL separatory funnel). A small amount of methylene chloride was added to the funnel. The funnel was stoppered. Paper towels were wrapped around the stopper to absorb leakage. The funnel was inverted and vented. The funnel was shaken vigorously for three minutes, venting initially every 10-15 seconds and then irregularly. After the layers separated, the lower (organic) layer was placed into a volumetric flask. The sample was extracted a total of three times. The extract solution was brought to volume with methylene chloride and stored in an amber bottle rinsed with methylene chloride and allowed to dry.

The samples were then solvent exchanged. Fifteen milliliters of sample were placed into a graduated centrifuge tube. The tube was placed on an N-evap and the solvent was evaporated under nitrogen at room temperature to a volume of 0.5 mL. Volume was adjusted with acetonitrile to a preordained volume. The solvent was again evaporated under nitrogen at room temperature to a volume of 0.5 mL. Volume was readjusted with acetonitrile to a preordained volume. This volume depended on the type of solvent exchange being performed. The usual solvent exchange technique was abbreviated as 15:4. One starts with 15.0 mL sample evaporates to 0.5 mL, adjusts volume to 8.0 mL, evaporates to 0.5 mL, and adjust volume to 4.0 mL. Another technique is abbreviated as 1:1. One starts with 15.0 mL sample, evaporates to 0.5 mL, adjusts volume to 15.0 mL, evaporates to 0.5 mL, and adjusts to 15.0 mL.

Sample Analysis

The samples were analyzed by HPLC components consisting of a Rainin HPLX solvent delivery system, a Waters autosampler, and a Rainin Dynamax absorbance detector. The mobile phase gradient is shown in Table A-16. The HPLC operating parameters are shown in Table A-17. The analytes were located using retention times found in Table A-18.

REFERENCES

1. Test Methods for Evaluating Solid Waste-Physical/Chemical Methods, EPA SW-846, 3rd Edition, Method 0011, U.S. Environmental Protection Agency, Washington, DC.

2. Method 5 —Determination of Particulate Emissions from Stationary Sources, Federal Register, Part 60, Appendix A, 742-766, July 1, 1991.

3. Laboratory Validation of VOST and Semi-VOST for Halogenated Hydrocarbons from the Clean Air Act Amendments List, Volumes 1 and 2, U.S. Environmental Protection Agency, 600/4-93/123a and b. NTIS PB93-227163 and PB93-227171, July 1993.

4. McGaughey, J.F., J.T. Bursey, and R.G. Merrill. "Field Test of Generic Method for Halogenated Hydrocarbons." Prepared for the Atmospheric Research and Exposure Assessment Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, EPA-600/SR-93/101, September 1993, NTIS PB93-212181.

5. Test Methods for Evaluating Solid Waste-Physical/Chemical Methods, EPA SW-846, 3rd Edition, Method 0010, U.S. Environmental Protection Agency, Washington, DC.

Table A-16

HPLC gradient for analysis of DNPH-derivatized aldehydes

Time (min)	Acetonitrile (%)	Water (%)	Methanol(%)
0	20	40	40
25	5	25	70
40	5	15	80
62	5	15	80
64	20	40	40
74	20	40	40

Table A-17

HPLC operating parameters

Instrument	Rainin HPLX solvent delivery system
Data System	Nelson 2600
Column	Zorbax ODS (4.6 mm ID x 25 cm), or equivalent with pellicular ODS (2 mm ID x 2 cm) guard column, or equivalent
Mobile Phase	Acetonitrile/Water/Methanol
Gradient	See Table A-16
Detector	Rainin Dynamax Absorbance Detector UV at 360 nm
Flow Rate	0.8 mL/min
Retention Time	See Table A-18

Table A-18

Retention Times for the Analytes

Analyte	Retention Time (min)
Formaldehyde	11.3
Acetaldehyde	15.9
Quinone	19.5
Acrolein	21.6
Propionaldehyde	23.5
Methyl Ethyl Ketone	31.8
Acetophenone	41.7
Methyl Isobutyl Ketone	43.0
Isophorone	52.7

Appendix B - Sampling and Analytical Methods

B.1 Aldehyde and Ketone Sampling Checklist

Table B.1-1. Aldehyde and Ketone Sampling Checklist

Before test starts:

1. Check impinger sets to verify the correct order, contents, orientation, and number of impingers.

2. Check that the correct pieces of glassware are available and in good condition. Have at least one spare probe liner, probe sheath, and meterbox ready to go at location.

3. Verify that a sufficient number of appropriate data sheets are available. Complete required preliminary information including ambient temperature, barometric pressure, and static pressure.

4. Examine meter boxes - level as necessary, zero the manometers and confirm that pumps are operational.

5. Clean the stack access port to eliminate the chance of sampling deposited material.

6. Add probes to quad-train. Verify that the pitot tube and probes are properly positioned.

7. Check thermocouples - make sure they are reading correctly.

8. Perform initial leak checks; record leak rate and vacuum on sampling log.

9. Turn on variacs/heaters and check to see that the heat is increasing.

10. Add ice to impinger buckets.

11. Record the initial dry gas meter reading.

During test:

1. Notify crew chief of any sampling problems ASAP. Train operator should fill in sampling log and document any abnormalities.

Table B.1-1. Aldehyde and Ketone Sampling Checklist

6. Probe recovery (use 500-mL amber flint glass bottles)

   a) Move the probes to a clean area, protected from wind to reduce chances of contamination or losing sample. Recover sample probe using care to segregate the four probes and trains.

   b) Wipe the exterior of the probe to remove any loose material that could contaminate the sample.

   c) Carefully remove the nozzle/probe liner and cap it off with aluminum foil or Teflon® tape.

   d) Recover samples from each train as follows:

      - Rinse the inside surface of the probe/nozzle assembly with deionized water (DI H_2O). Brush with a Teflon® bristle brush until rinse shows no visible particles or yellow color. Make a final rinse of the inside surface.
      - Recover DI H_2O into a pre-weighed, pre-labelled sample container.
      - With recovery bottle positioned at end of probe, wet all sides of probe interior with DI H_2O.
      - While holding the probe in an inclined position, put pre-cleaned Teflon® brush down into probe and brush it in and out.
      - Rinse the brush, while in the probe, with DI H_2O.
      - Rinse at least 3 times until all the particulate has been recovered.
      - Rinse the brush with DI H_2O and collect these washings in the sample bottle.
      - After brushing, make a final rinse of the probe with DI H_2O.

Table B.1-1. Aldehyde and Ketone Sampling Checklist

e) Rinse the nozzle/probe liner thoroughly with methylene chloride ($MeCl_2$).

- With recovery bottle positioned at end of probe, wet all sides of probe interior with $MeCl_2$.
- Rinse the brush with $MeCl_2$ and collect these washings in the sample bottle.

7. Cap both ends of nozzle/probe liner for the next test, and store in a dry safe place.

8. Make sure data sheets are completely filled out legibly and give them to the Crew Chief.

Appendix B - Sampling and Analytical Methods

B.2 Aldehyde and Ketone Sampling Method

METHOD XXXX - SAMPLING AND ANALYSIS FOR ALDEHYDE AND KETONE EMISSIONS FROM STATIONARY SOURCES

1.0 SCOPE AND APPLICATION.

1.1 Method XXXX is applicable to the collection and analysis of the aldehydes and ketones listed in Table XXXX-1. This method has been validated for these pollutant compounds at wood pressboard and polyester fiber manufacturing processes and is believed to be applicable to other processes where these aldehydes and ketones may be emitted.

TABLE XXXX-1. LIST OF ANALYTES, CAS NUMBERS RETENTION TIMES, AND DETECTION LIMITS

Compound Name	CAS No.[a]	Retention Time (minutes)[b]	Method Detection Limits (MDL) (ppbv)[c]
Acetaldehyde	75-07-0	11.48	40
Acetophenone	98-86-2	28.99	10
Formaldehyde	50-00-0	8.38	90
Isophorone	78-59-1	38.22	10
Propionaldehyde	123-38-6	16.41	60

[a] Chemical Abstract Services Registry Number

[b] HPLC conditions: Reverse phase C18 column, 4.6 x 250 mm; gradient elution using acetonitrile/methanol/water (20:40:40, v/v/initial); flow rate 0.9 mL/min.; UV detector 360 nm, injector volume 25 μL.

[c] For an 849 Liter (30 cubic foot) sample, based on 10 times the levels detected in field train blanks, or 10 times the instrument detection limit.

1.2 When this method is used to analyze unfamiliar sample matrices, compound identification should be supported by at least one additional qualitative technique. A gas

The conditions permit the separation and measurement of aldehydes and ketones in the extract by absorbance detection at 360 nanometers (nm).

3.0 DEFINITIONS. Reserved

4.0 INTERFERENCES.

4.1 A decomposition product of DNPH, 2,4-dinitroaniline, can be an analytical interferant if the concentration is high. 2,4-Dinitroaniline can coelute with the 2,4-dinitrophenylhydrazone of formaldehyde under the HPLC conditions used for the analysis. High concentrations of highly-oxygenated compounds, especially acetone, that have the same retention time or nearly the same retention time as the dinitrophenylhydrazone of formaldehyde, and that also absorb at 360 nm, will interfere with the analysis. Formaldehyde, acetone, and 2,4-dinitroaniline contamination of the aqueous acidic 2,4-dinitrophenylhydrazine (DNPH) reagent is frequently encountered. The reagent must be prepared within five days of use in the field and must be stored in an uncontaminated environment both before and after sampling in order to minimize blank problems. Some acetone contamination is unavoidable, because background levels of acetone are widespread in laboratory and field operations. In spite of these background levels, the acetone contamination must be minimized.

4.2 Dimethylolurea creates a slight interference. Hexamethylenetetramine and paraformaldehyde significantly interfere with the determination of formaldehyde. O-Tolualdehyde interferes with the determination of acetophenone because their hydrazones coelute under the analytical conditions used. Acetone can interfere with the determination of propionaldehyde if the hydrazones of the two compounds are not well resolved. High levels of nitrogen dioxide can interefere by consuming all of the reagent.

4.3 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing laboratory reagent blanks.

4.3.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This rinse should be followed by washing with hot water and detergent, and rinsing with tap water and distilled water. Glassware should then be drained and heated in a laboratory oven at 130°C (266°F) for several hours before use. Solvent rinses using acetonitrile may be substituted for the oven heating. After drying and cooling, glassware should be stored in a clean environment to prevent any accumulation of dust or other contaminants.

4.3.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

4.4 Formaldehyde analysis is expecially complicated because, like acetone, background levels are constantly encountered in laboratory and field operations.

4.5 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the matrix being sampled. If interferences occur in subsequent samples, some additional cleanup may be necessary.

4.6 The extent of interferences that may be encountered using liquid chromatographic techniques has not been fully assessed. Although the HPLC conditions described allow for a

resolution of the specific compounds covered by this method, other matrix components may interfere.

5.0 SAFETY.

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means are available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety & Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available.

5.2 Formaldehyde has been tentatively classified as a known or suspected human or mammalian carcinogen.

6.0 EQUIPMENT AND SUPPLIES.

6.1 A schematic diagram of the sampling train is shown in Figure XXXX-1. This sampling train configuration is adapted from EPA Method 4 procedures. The sampling train consists of the following components: Probe Nozzle, Pitot Tube, Differential Pressure Gauge, Metering System, Temperature Sensor, Barometer, and Gas Density Determination Equipment.

6.1.1 Probe Nozzle. Quartz or glass with sharp leading edge at a tapered 30° angle. The taper shall be on the outside to preserve a constant inner diameter.

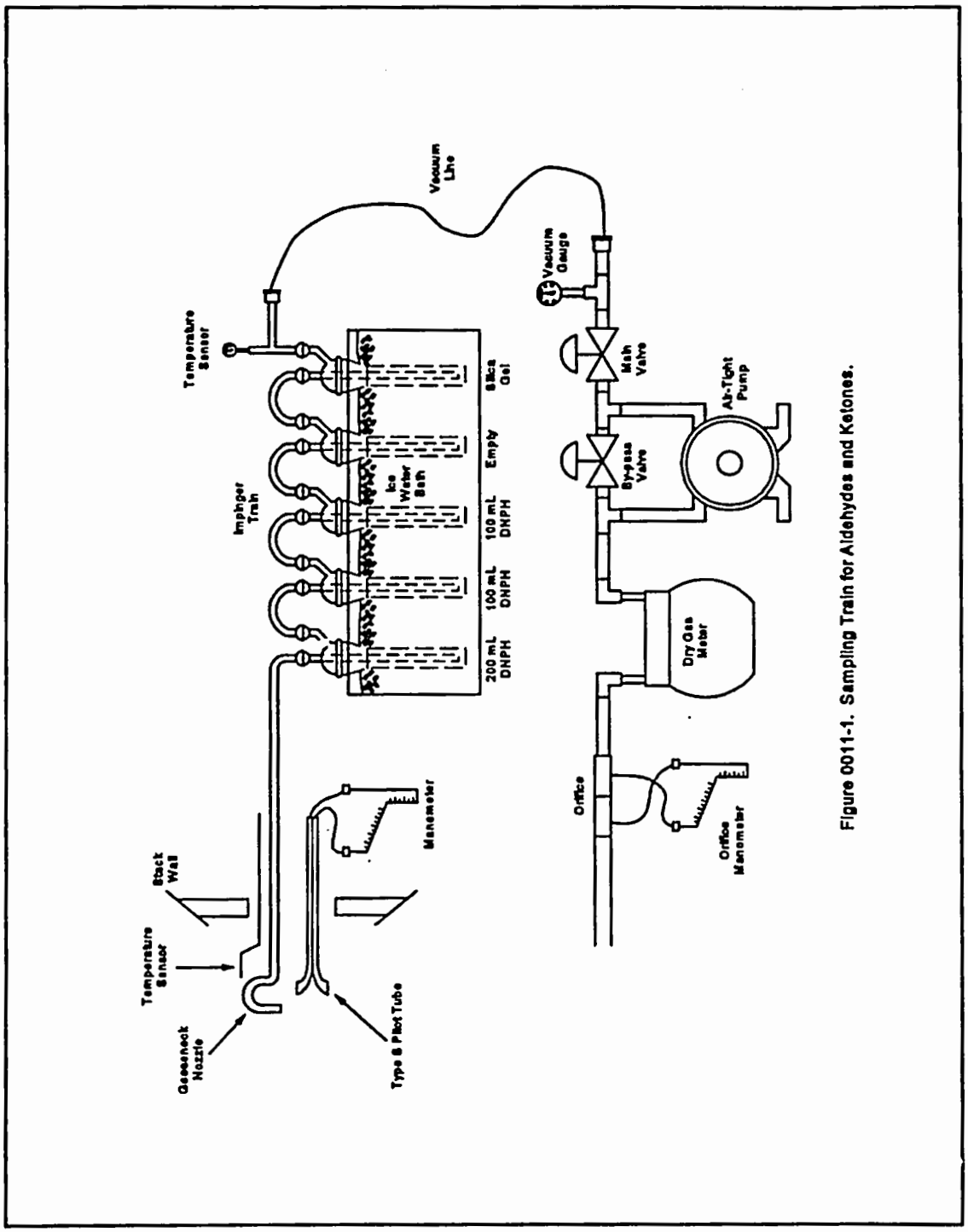


Figure XXXX-1. Sampling Train for Aldehydes and Ketones

The nozzle shall be of a buttonhook or elbow design. A range of nozzle sizes suitable for isokinetic sampling should be available in increments of 0.16 cm (1/16 in), e.g., 0.32 to 1.27 cm (1/8 to 1/2 in), or larger if higher volume sampling trains are used. Each nozzle shall be calibrated according to the procedures outlined in Section 10.1.

6.1.2 Probe Liner. Borosilicate or quartz glass shall be used for the probe liner. The tester should maintain the temperature in the probe at 120 ± 14°C (248 ± 25°F).

6.1.3 Pitot Tube. Type S, as described in Section 2.1 of Promulgated EPA Method 2 (Section 6.1 of Reformatted EPA Method 2), or other device approved by the Administrator. The pitot tube shall be attached to the probe to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see EPA Method 2, Figure 2-6b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 4 of Promulgated EPA Method 2 (Section 10.0 of Reformatted EPA Method 2).

6.1.4 Differential Pressure Gauge. Two inclined manometers or equivalent devices as described in Section 2.2 of Promulgated EPA Method 2 (Section 6.2 of Reformatted EPA Method 2). One manometer shall be used for velocity-head readings and the other for orifice differential pressure readings.

6.1.5 Temperature Sensor. A temperature sensor capable of measuring temperature to within ± 3°C (± 5.4°F) shall be installed so that the temperature at the impinger outlet can be regulated and monitored during sampling.

6.1.6 Impinger Train. The sampling train requires a minimum of five impingers, connected as shown in Figure XXXX-1, with ground glass (or equivalent) vacuum-tight fittings. For the first, third, fourth, and fifth impingers, use the Greenburg-Smith design, modified by replacing the tip with a 1.27 cm (1/2 in.) inside diameter glass tube extending to 1.27 cm (1/2 in.) from the bottom of the flask. For the second impinger, use a Greenburg-Smith impinger with the standard tip.

6.1.7 Metering System. The necessary components are a vacuum gauge, leak-free pump, temperature sensors capable of measuring temperature within 3°C (5.4°F), dry gas meter (DGM) capable of measuring volume to within 1%, and related equipment as shown in Figure XXXX-1. At a minimum, the pump should be capable of 4 cubic feet per minute (cfm) free flow, and the DGM should have a recording capacity of 0-999.9 cubic feet with a resolution of 0.005 cubic feet. Other metering systems may be used which are capable of maintaining sample rates within 10 percent of isokinetic and of determining sample volumes to within 2%, subject to the approval of the Administrator. The metering system may be used in conjunction with a pitot tube to enable checks of isokinetic sampling rates.

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

NOTE: The barometric pressure reading may be obtained from a nearby National Weather Service Station. In this case, the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point be made at a rate of minus 2.5 mm (0.1 in.) Hg per 30 meters (100 ft.) elevation increase or plus 2.5 mm (0.1 in.) Hg per 30 meters (100 ft.) elevation decrease.

6.1.9 Gas Density Determination Equipment. Temperature sensor and pressure gauge (as described in Sections 2.3 and 2.4 of Promulgated EPA Method 2 as well as Sections 6.3 and 6.4 of Reformatted Method 2), and gas analyzer, if necessary, as described in EPA Method 3. The temperature sensor shall, preferably, be permanently attached to the pitot tube or sampling probe in a fixed configuration so that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot openings (as illustrated in Promulgated EPA Method 2, Figure 2-7, as well as Reformatted Method 2, Figure 2-4). As a second alternative, if a difference of no more than 1% in the average velocity measurement is to be introduced, the temperature sensor need not be attached to the probe or pitot tube (This alternative is subject to the approval of the Administrator).

6.1.10 Viton A O-ring.

6.1.11 Heat Resistant Tape.

6.1.12 Teflon tape.

6.2 Sample Recovery. The following items are required for sample recovery.

6.2.1 Probe Liner and Probe Nozzle Brushes. Teflon bristle brushes with stainless steel wire handles are required. The probe brush must have extensions of stainless steel, Teflon, or inert material at least as long as the probe. The brushes must be properly sized and shaped to brush out the probe liner, the probe nozzle, and the impingers.

6.2.2 Wash Bottles. Three wash bottles are required. Teflon or glass wash bottles are recommended; polyethylene wash bottles should not be used because organic contaminants may be extracted by exposure to organic solvents used for sample recovery.

6.2.3 Graduated Cylinder and/or Balance. These will be used to measure condensed water to the nearest 1 mL or 0.5 g. Graduated cylinders must have divisions not >2 mL. Laboratory balances capable of weighing to $\pm$0.5 g are required.

6.2.4 Amber Flint Glass Storage Containers. One-liter wide-mouth amber flint glass bottles with Teflon-lined caps are required to store impinger water samples. The bottles must be sealed with Teflon tape.

6.2.5 Rubber Policeman and Funnel. To aid in the transfer of material into and out of containers in the field.

6.2.6 Cooler. To store and ship sample containers.

6.3 Reagent Preparation.

6.3.1 Bottles/Caps. Amber 1- or 4-L bottles with Teflon-lined caps are required for storing cleaned DNPH solution. Additional 4-L bottles are required to collect waste organic solvents.

6.3.2 Large Glass Container. At least one large glass container (8 to 16 L) is required for mixing the aqueous acidic DNPH solution.

6.3.3 Stir Plate/Large Stir Bars/Stir Bar Retriever. A magnetic stir plate and large stir bar are required to mix the aqueous acidic DNPH solution. A stir bar retriever is needed for removing the stir bar from the large container holding the DNPH solution.

6.3.4 Büchner Filter/Filter Flask/Filter Paper. A large filter flask (2-4 L) with a büchner filter, appropriate rubber stopper, filter paper, and connecting tubing are required for filtering the aqueous acidic DNPH solution prior to cleaning.

6.3.5 Separatory Funnel. At least one large separatory funnel (2 L) is required for cleaning the DNPH prior to use.

6.3.6 Beakers. Beakers (150 mL, 250 mL, and 400 mL) are useful for holding/measuring organic liquids when cleaning the aqueous acidic DNPH solution and for weighing DNPH crystals.

6.3.7 Funnels. At least one large funnel is needed for pouring the aqueous acidic DNPH into the separatory funnel.

6.3.8 Graduated Cylinders. At least one large graduated cylinder (1 to 2 L) is required for measuring organic-free reagent water and acid when preparing the DNPH solution.

6.3.9 Top-Loading Balance. A top loading balance readable to the nearest 0.1 g is needed for weighing out the DNPH crystals used to prepare the aqueous acidic DNPH solution.

6.3.10 Spatulas. Spatulas are needed for handling DNPH crystals when preparing the aqueous DNPH solution.

6.4 Crushed Ice. Quantities ranging from 10-15 lb may be necessary during a sampling run, depending upon ambient temperature. Samples must be stored and shipped cold; sufficient ice for this purpose must be allowed.

6.5 Analysis.

6.5.1 Separatory Funnel. 250 mL, with Teflon stopcock.

6.5.2 Concentrator Tube. 15 mL graduated or equivalent. A ground glass stopper may be used to prevent evaporation of extracts.

6.5.3 Vials. 10, 25 mL, glass with Teflon lined screw caps or crimp tops.

6.5.4 Analytical Balance. Capable of accurately weighing to the nearest 0.1 mg.

6.5.5 Glass Ampules. 1 mL in size. Used for storing stock aldehyde derivative standard.

6.5.6 High Performance Liquid Chromatograph (modular).

6.5.6.1 Pumping system. Gradient with constant flow control capable of 0.9 mL/min.

6.5.6.2 High Pressure Injection Valve with 25 μL loop.

6.5.6.3 Column. 250 mm x 4.6 mm ID, 5 μm particle size, C18 (or equivalent).

6.5.6.4 Ultra-Violet (UV) Absorbance detector. 360 nm.

6.5.6.5 Strip Chart Recorder Compatible With Detector. Use of a data system for measuring peak areas and retention times is recommended.

6.5.7 Volumetric Flasks. 250 or 500 mL.

6.5.8 Nitrogen blow down apparatus.

7.0 REAGENTS AND STANDARDS.

7.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided that the reagent is of sufficiently high purity to use without jeopardizing accuracy.

7.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One of SW-846 (see Reference 2 in Section 16.0).

7.3 Silica Gel. Indicating type, 6-16 mesh. If the silica gel has been used previously, dry at 180°C (350°F) for 2 hours before using. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.

7.4 2,4-Dinitrophenylhydrazine (DNPH), $[2,4]\text{-}(O_2N)_2C_6H_3]NHNH_2$ - The moisture content may vary from 10 to 30%.

7.4.1 The DNPH reagent must be prepared in the laboratory within five days of sampling use in the field. DNPH can also be prepared in the field, with consideration of appropriate procedures required for safe handling of solvent in the field. When a container of prepared DNPH reagent is opened in the field, the contents of the opened container should be used within 48 hours. All laboratory glassware must be washed with detergent and water and rinsed with water, methanol, and methylene chloride prior to use.

NOTE: DNPH crystals or DNPH solution should be handled with plastic gloves at all times with prompt and extensive use of running water in case of skin exposure.

7.4.2 Preparation of Aqueous Acidic DNPH Derivatizing Reagent: Each batch of DNPH reagent should be prepared and purified within five days of sampling, according to the procedure described below.

NOTE: Reagent bottles for storage of cleaned DNPH derivatizing solution must be rinsed with acetonitrile and dried before use. Baked glassware is not essential to prepare DNPH reagent. The glassware must not be rinsed with acetone or methanol or an unacceptable concentration of acetone or formaldehyde contamination will be introduced. If DNPH is prepared in the field, exercise caution to avoid acetone contamination.

7.4.2.1 Place an 8 L container under a fume hood on a magnetic stirrer. Add a large stir bar and fill the container half full of organic-free reagent water. Save the empty bottle from the organic-free reagent water. Start the stirring bar

and adjust it to stir as fast as possible. Using a graduated cylinder, measure 1.4 L of 12N hydrochloric acid. Slowly pour the acid into the stirring water. Fumes may be generated and the water may become warm. Weigh the DNPH crystals on a one-place balance (see Table XXXX-2 for approximate amounts) and add to the stirring acid solution. Fill the 8-L container to the 8-L mark with organic-free reagent water and stir overnight. If all of the DNPH crystals have dissolved overnight, add additional DNPH and stir for two more hours. Continue the process of adding DNPH with additional stirring until a saturated solution has been formed. Filter the DNPH solution using vacuum filtration. Gravity filtration may be used, but a longer time is required to filter the DNPH solution. Store the filtered solution in an amber bottle at room temperature.

TABLE XXXX-2. APPROXIMATE AMOUNT OF CRYSTALLINE DNPH USED TO PREPARE A SATURATED SOLUTION

Amount of Moisture in DNPH	Weight Required per 8 L of Solution
10 weight percent	36 g
15 weight percent	38 g
30 weight percent	46 g

7.4.2.2 Within five days of proposed use, place about 1.6 L of the DNPH reagent in a 2-L separatory funnel. Add approximately 200 mL of methylene chloride and stopper the funnel. Wrap the stopper of the funnel with paper towels to absorb any leakage. Invert and vent the funnel. Then shake vigorously for 3 minutes. Initially, the funnel should be vented frequently (every 10-15 sec). After the layers have separated, discard the lower (organic) layer.

7.4.2.3 Extract the DNPH a second time with methylene chloride and finally with cyclohexane. When the cyclohexane layer has separated from the DNPH reagent, the cyclohexane layer will be the top layer in the separatory funnel. Drain the lower layer (the cleaned extract DNPH reagent solution) into an amber bottle that has been rinsed with acetonitrile and allowed to dry.

7.4.3 Shipment to the Field: Tightly cap the bottle containing extracted DNPH reagent using a Teflon-lined cap. Seal the bottle with Teflon tape. After the bottle is labeled, the bottle may be placed in a friction-top can (paint can or equivalent) containing a 1-2 inch layer of granulated charcoal and stored at 4°C until use.

7.4.3.1 If the DNPH reagent has passed the Quality Control criteria in Section 9.2.4, the reagent may be packaged to meet necessary shipping requirements and sent to the sampling area. If the Quality Control criteria are not met the reagent solution may be re-extracted; or, the solution may be re-prepared and the extraction sequence repeated.

7.4.3.2 If the DNPH reagent is not used in the field within five days of extraction, an aliquot may be taken and analyzed as described in Section 11.3. If the reagent meets the Quality Control requirements in Section 9.2.4, the reagent may be used. If the reagent does not meet the Quality Control requirements in Section 9.2.4, the reagent must be discarded and new reagent must be prepared and tested.

7.5 Field Spike Standard Preparation. To prepare a formaldehyde field spiking standard at 4.01 mg/mL, use a 500 μL syringe to transfer 0.5 mL of 37% by weight of formaldehyde (401 mg/mL) to a 50 mL volumetric flask containing approximately 50 mL of water. Dilute to 50 mL with water.

7.6 Hydrochloric Acid, HCl. Reagent grade hydrochloric acid (approximately 12N) is required for acidifying the aqueous DNPH solution.

7.7 Methylene Chloride, CH_2Cl_2. Methylene chloride (suitable for residue and pesticide analysis, GC/MS, HPLC, GC Spectrophotometry or equivalent) is required for cleaning the aqueous acidic DNPH solution, rinsing glassware, recovery of sample trains, and extracting samples.

7.8 Cyclohexane, C_6H_{12}. Cyclohexane (HPLC grade) is required for cleaning the aqueous acidic DNPH solution.

NOTE: Do not use spectroanalyzed grades of cyclohexane if this sampling methodology is extended to aldehydes and ketones with four or more carbon atoms.

7.9 Methanol, CH_3OH. Methanol (HPLC grade or equivalent) is required for the HPLC analysis.

7.10 Acetonitrile, CH_3CN. Acetonitrile (HPLC grade or equivalent) is required for rinsing glassware, solvent exchanging of the samples, and the HPLC analysis.

7.11 Purified derivatized aldehyde crystals are required for preparation of standards.

7.12 Ethanol (absolute), CH_3CH_2OH. HPLC grade or equivalent.

7.13 2,4-Dinitrophenylhydrazine (DNPH) (70% (W/W)), $[2,4\text{-}(O_2N)_2C_6H_3]NHNH_2]$, in organic-free reagent water.

7.14 Formalin [37.6 percent (w/w)], formaldehyde in organic free reagent water.

7.15 Stock standard solutions.

7.15.1 Preparation of Calibration Standards for Chromatographic Analyses.

7.15.1.1 Stock Aldehyde Derivative Standard. Prepare a multi-component stock aldehyde derivative standard at a concentration of 200 ng/μL by weighing 40 mg ($\pm$ 0.01 mg) of purified derivatized aldehyde crystals into small vials, dissolving the crystals in acetonitrile, quantitatively transferring the solution to a 200 mL volumetric flask and diluting to the line with acetonitrile. From this stock solution, prepare 1-mL aliquots using 1-mL glass ampules. Seal and store the aliquots at 0°C (32°F).

7.15.1.2 Calibration Standards. Prepare calibration standards by diluting 12.5, 25, 150, 300, and 500 μL of the multi-component stock solution to 5 mL with acetonitrile to provide a standard curve with calibration points at 0.5, 1.0, 6, 12, and 20 ng/μL of derivative.

7.15.1.3 Check Standard. Prepare a check standard of 5 ng/μL of derivative by taking 125 μL of the 200 ng/μL multi-component stock standard and diluting to 5 mL with acetonitrile.

7.15.2 Standard solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE AND TRANSPORT.

8.1 Because of the complexity of this method, field personnel should be trained in and experienced with the test procedures in order to obtain reliable results.

8.2 Laboratory Preparation.

8.2.1 All the components must be maintained and calibrated according to the procedure described in APTD-0576 (Reference 3 in Section 16.0), unless otherwise specified.

8.2.2 Weigh several 200 to 300 g portions of silica gel in airtight containers to the nearest 0.5 g. Record on each container the total weight of the silica gel plus containers. As an alternative to preweighing the silica gel, it may be weighed directly in the impinger or sampling holder just prior to train assembly.

8.3 Preliminary Field Determinations.

8.3.1 Select the sampling site and the minimum number of sampling points according to EPA Method 1 or other relevant criteria. Determine the stack pressure, temperature, and range of velocity heads using EPA Method 2. Check the pitot lines for leaks according to Promulgated EPA Method 2, Section 3.1 (Reformatted EPA Method 2, Section 8.1). Determine the stack gas moisture content using EPA Approximation Method 4 or its alternatives to establish estimates of isokinetic sampling-rate settings. Determine the stack gas dry molecular weight, as described in Promulgated EPA Method 2, Section 3.6 (Reformatted EPA Method 2, Section 8.6). If integrated EPA Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the sample run.

8.3.2 Based on the range of velocity heads, select a nozzle size that will maintain isokinetic sampling rates below 28 L/min (1.0 cfm). Do not change the nozzle during the run. Ensure that the proper differential pressure gauge is chosen for

the range of velocity heads encountered (as described in Section 2.2 of Promulgated EPA Method 2, as well as Section 8.2 of Reformatted EPA Method 2).

8.3.3 Select a suitable probe liner and probe length so that all traverse points can be sampled. Consider sampling from opposite sides of large stacks so a shorter probe can be used.

8.3.4 Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry. A total sampling time must be selected so that (l) the sampling time per point is not less than 2 minutes (or some greater time interval as specified by the Administrator), and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume. The latter is based on an approximate average sampling rate.

8.3.5 The sampling time at each point shall be the same. It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to avoid timekeeping errors.

8.3.6 In some circumstances (*e.g.*, batch cycles) it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas-volume samples. In these cases, careful documentation must be maintained in order to allow accurate concentration calculation.

8.4 Preparation of Collection Train.

8.4.1 During preparation and assembly of the sampling train, keep all openings where contamination can occur covered with Teflon film or aluminum foil until just prior to assembly or until sampling is about to begin.

8.4.2 Place 200 mL of purified DNPH reagent in the first impinger and 100 mL of reagent in the second and third impingers. Leave the fourth impinger empty. Transfer approximately 200 to 300 g of pre-weighed silica gel from its container to the fifth impinger. Be careful to ensure that the silica gel is not entrained and carried out from the impinger during sampling. Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded. For moisture determination, weigh all of the impingers after filing them with reagent.

8.4.3 With a glass or quartz probe liner, install the selected nozzle using a Viton A O-ring when stack temperatures are <260°C (500°F) and a woven glass-fiber gasket when temperatures are higher. See Reference 3 in Section 16.0 for details. Other connection systems utilizing either 316 stainless steel or Teflon ferrules may be used. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

8.4.4 Assemble the train as shown in Figure XXXX-1. During assembly, do not use any silicone grease on ground-glass joints upstream of the impingers. Use Teflon tape, if required. A very light coating of silicone grease may be used on ground-glass joints downstream of the impingers, but the silicone grease should be limited to the outer portion [see APTD-0576 (Reference 3 in Section 16.0)] of the ground-glass joints to minimize silicone grease contamination. If necessary, Teflon

(1 in. Hg) vacuum. Alternatively, leak-check the probe with the rest of the sampling train in one step at 381 mm Hg (15 in. Hg) vacuum. Leakage rates in excess of (a) 4% of the average sampling rate or (b) >0.00057 m^3/min (0.020 cfm), are unacceptable.

8.5.1.3 The following leak check instructions for the sampling train described in APTD-0576 and APTD-0581 (References 3 and 4 of Section 16.0, respectively) may be helpful. Start the pump with the fine-adjust valve fully open and coarse-adjust valve completely closed. Partially open the coarse-adjust valve and slowly close the fine-adjust valve until the desired vacuum is reached. Do not reverse direction of the fine-adjust valve, as liquid will back up into the train. If the desired vacuum is exceeded, either perform the leak check at this higher vacuum or end the leak check, as shown below, and start over.

8.5.1.4 When the leak check is completed, first slowly remove the plug from the inlet to the probe. When the vacuum drops to 127 mm (5 in. Hg) or less, immediately close the coarse-adjust valve. Switch off the pumping system and reopen the fine-adjust valve. Do not reopen the fine-adjust valve until the coarse-adjust valve has been closed to prevent the liquid in the impingers from being forced backward in the sampling line and silica gel from being entrained backward into the fourth impinger.

8.5.2 Leak Checks During Sampling Run.

8.5.2.1 If, during the sampling run, a component change (i.e., impinger) becomes necessary, a leak check shall be conducted immediately after the interruption of sampling and before the change is made. The leak check

tape may be used to seal leaks. Connect all temperature sensors to an appropriate potentiometer/display unit. Check all temperature sensors at ambient temperatures.

8.4.5 Place crushed ice around the impingers.

8.4.6 Turn on and set the probe heating system at the desired operating temperature. Allow time for the temperature to stabilize.

8.5 Leak-Check Procedures.

8.5.1 Pre-test Leak Check.

8.5.1.1 After the sampling train has been assembled, turn on and set the probe heating system to the desired operating temperature. Allow time for the temperature to stabilize. If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 381 mm Hg (15 in. Hg) vacuum.

NOTE: A lower vacuum pressure may be used, provided that the lower vacuum pressure is not exceeded during the test.

8.5.1.2 If a heat resistant string is used, do not connect the probe to the train during the leak check. Instead, leak-check the train by first attaching a carbon-filled leak check impinger to the inlet and then plugging the inlet and pulling a 381 mm Hg (15 in. Hg) vacuum. (A lower vacuum pressure may be used if this lower vacuum pressure is not exceeded during the test.) Next connect the probe to the train and leak-check at approximately 25 mm Hg

shall be performed according to the procedure described in Section 8.5.1, except that it shall be performed at a vacuum greater than or equal to the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.020 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable. If a higher leakage rate is obtained, the tester must void the sampling run.

NOTE: Any correction of the sample volume by calculation reduces the integrity of the pollutant concentration data generated and must be avoided.

8.5.2.2 Immediately after a component change and before sampling is reinitiated, a leak check similar to a pre-test leak check must also be conducted.

8.5.3 Post-test Leak Check.

8.5.3.1 A leak check of the sampling train is mandatory at the conclusion of each sampling run. The leak check shall be performed in accordance with the same procedures as the pre-test leak check, except that the post-test leak check shall be conducted at a vacuum greater than or equal to the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.020 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable. If, however, a higher leakage rate is obtained, the tester shall record the leakage rate and void the sampling run.

8.6 Sampling Train Operation.

8.6.1 During the sampling run, maintain an isokinetic sampling rate to within 10% of true isokinetic, below 28 L/min (1.0 cfm). Maintain a temperature around the probe of 120° ± 14°C (248° ± 25°F).

8.6.2 For each run, record the data on a data sheet such as the one shown in Figure XXXX-2. Be sure to record the initial DGM reading. Record the DGM readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak check, and when sampling is halted. Take other readings indicated by Figure XXXX-2 at least once at each sample point during each time increment and additional readings when significant adjustments (20% variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

8.6.3 Clean the stack access portholes prior to the test run to eliminate the chance of collecting deposited material. To begin sampling, remove the nozzle cap, verify that the probe heating systems are at the specified temperature, and verify that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations, are available. These nomographs are designed for use when the Type S pitot tube coefficient is 0.84 ± 0.02 and the stack gas equivalent density (dry molecular weight) is equal to 29 ± 4. APTD-0576 (Reference 3 in Section 16.0) details the procedure for using the nomographs. If the stack gas molecular weight and the pitot tube

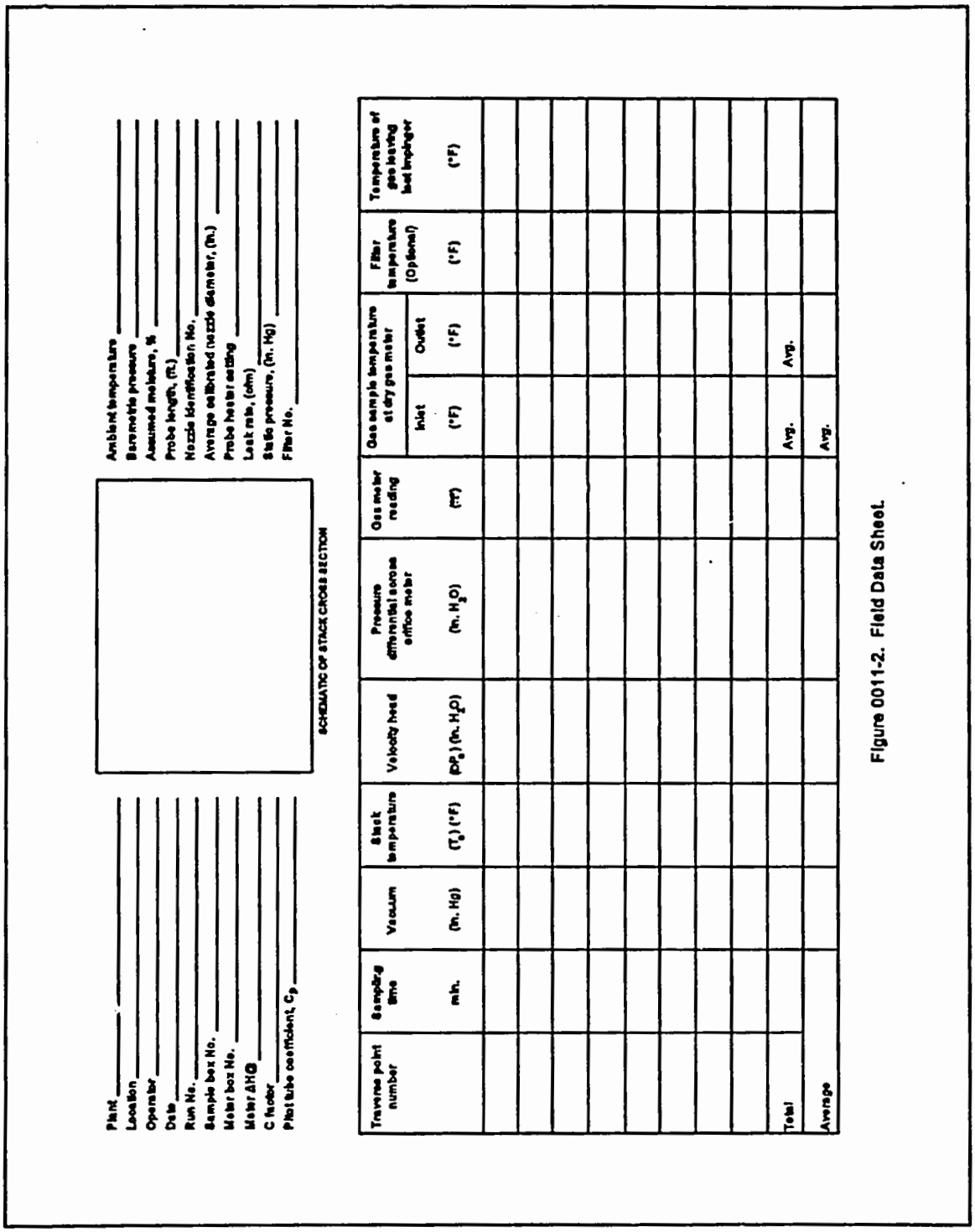


Figure XXXX-2. Field Data Sheet

coefficient are outside the above ranges, do not use the nomographs unless appropriate steps are taken tc compensate for the deviations.

8.6.4 When the stack is under significant negative pressure (equivalent to the height of the impinger stem), take care to close the coarse-adjust valve before inserting the probe into the stack in order to prevent liquid from backing up through the train. If necessary, the pump may be turned on with the coarse adjust valve closed.

8.6.5 When the probe is in position, block off the openings around the probe and stack access porthole to prevent unrepresentative dilution of the gas stream.

8.6.6 Traverse the stack cross-section, as required by EPA Method 1. To minimize the chance of extracting deposited material be careful not to bump the probe nozzle into the stack walls when sampling near the walls when removing or inserting the probe through the access porthole.

8.6.7 During the test run, make periodic adjustments to keep the temperature around the probe at the proper levels. Add more ice and, if necessary, salt, to maintain a temperature of $<20°C$ (68°F) at the silica gel outlet. Also, periodically check the level and zero of the manometer.

8.6.8 A single train shall be used for the entire sampling run, except in cases where simultaneous sampling is required in two or more separate ducts; at two or more different locations within the same duct; or, in cases where equipment failure necessitates a change of trains. Additional train(s) may also be used for sampling when the capacity of a single train is exceeded.

8.6.9 When two or more trains are used, components from each train shall be analyzed. If multiple trains have been used because the capacity of a single train would be exceeded, first impingers from each train may be combined, and second impingers from each train may be combined.

8.6.10 At the end of the sampling run, turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak check as outlined in Section 8.5.3. Also, leak check the pitot lines as described in EPA Method 2 (Section 8.1 of Reformatted Method 2). The lines must pass this leak check in order to validate the velocity-head data.

8.6.11 Calculate percent isokineticity (as described in Section 6.11 of Method 5, as well as see Section 12.11 of Reformatted Method 5) to determine whether the run was valid or another test should be performed.

8.7 Sample Recovery.

8.7.1 Preparation.

8.7.1.1 Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. When the probe can be handled safely, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over the tip to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling because a vacuum will be created drawing liquid from the impingers back through the sampling train.

8.7.1.2 Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet, being careful not to lose any condensate that might be present. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used, let any condensed water or liquid drain into the impingers. Cap off any open impinger inlets and outlets. Ground glass stoppers, Teflon caps, or caps of other inert materials may be used to seal all openings.

8.7.1.3 Transfer the probe and impinger assembly to an area that is cleaned and protected from wind so that the chances of contaminating or losing the sample are minimized.

8.7.1.4 Inspect the train before and during disassembly, and note any abnormal conditions.

8.7.1.5 Save a portion of all washing solutions (methylene chloride, water) used for cleanup as a blank. Transfer 200 mL of each solution directly from the wash bottle and place each in a separate prelabeled sample "blank" container (see Section 8.7.2.2).

8.7.2 Sample Containers.

8.7.2.1 Container 1: Probe and Impinger Catches. Using a graduated cylinder, measure to the nearest mL, and record the volume of the solution in the first four impingers. Alternatively, the solution may be weighed to the nearest 0.5 g. Include any condensate in the probe in this determination. Transfer the impinger solution from the graduated cylinder into the amber flint glass bottle. Taking care that dust on the outside of the probe or other exterior

surfaces does not get into the sample, clean all surfaces to which the sample is exposed (including the probe nozzle, probe fitting, probe liner, all impingers, and impinger connectors) with methylene chloride. Use less than 500 mL for the entire wash. Add the washing to the sample container.

8.7.2.1.1 Carefully remove the probe nozzle and rinse the inside surface with methylene chloride from a wash bottle. Brush with a Teflon bristle brush, and rinse until the rinse shows no visible particles or yellow color. Make a final rinse of the inside surface. Brush and rinse the inside parts of the Swagelok fitting with methylene chloride the same way.

8.7.2.1.2 Rinse the probe liner with methylene chloride. While squirting the methylene chloride into the upper end of the probe, tilt and rotate the probe so that all inside surfaces will be wetted with methylene chloride. Let the methylene chloride drain from the lower end into the sample container. The tester may use a funnel (glass) to aid in transferring the liquid washes to the container. Follow the rinse with a Teflon brush. Hold the probe in an inclined position, and squirt methylene chloride into the upper end as the probe brush is being pushed with a twisting action through the probe. Hold the sample container underneath the lower end of the probe, and catch any methylene chloride, water, and particulate matter that is brushed from the probe. Run the brush through the probe three times or more. Rinse the brush with methylene chloride or water, and quantitatively collect these washings in the sample container. After the brushing, make a final rinse of the probe as described above.

NOTE: Two people should clean the probe in order to minimize sample losses. Between sampling runs, brushes must be kept clean and free from contamination.

8.7.2.1.3 Rinse the inside surface of each of the first three impingers (and connecting tubing) three separate times. Use a small portion of methylene chloride for each rinse, and brush each surface to which the sample is exposed with a Teflon bristle brush to ensure recovery of fine particulate matter. Water will be required for the recovery of the impingers in addition to the specified quantity of methylene chloride. There will be at least two phases in the impingers. This two-phase mixture does not pour well and a significant amount of the impinger catch will be left on the walls. The use of water as a rinse makes the recovery quantitative. Make a final rinse of each surface and of the brush, using both methylene chloride and water.

8.7.2.1.4 After all methylene chloride and water washings and particulate matter have been collected in the sample container, tighten the lid so the solvent, water, and DNPH reagent will not leak out when the container is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Seal the container with Teflon tape. Label the container clearly to identify its contents.

8.7.2.2 Container 2: Sample Blank. Prepare a blank by using an amber flint glass container and adding a volume of DNPH reagent and methylene chloride equal to the total volume in Container 1. Process the blank in the same manner as Container 1.

8.7.2.3 Container 3: Silica Gel. Note the color of the indicating silica gel to determine whether it has been completely spent, and make a notation of its condition. The impinger containing the silica gel may be used as a sample transport container with both ends sealed with tightly fitting caps or plugs. Ground-glass stoppers or Teflon caps may be used. The silica gel impinger should then be labeled, covered with aluminum foil, and packaged on ice for transport to the laboratory. If the silica gel is removed from the impinger, the tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall that are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use water or other liquids to transfer the silica gel. If a balance is available in the field, the spent silica gel (or silica gel plus impinger) may be weighed to the nearest 0.5 g.

8.7.2.4 Sample containers should be placed in a cooler, cooled by (although not in contact with) ice at a temperature not to exceed 4°C. Sample containers must be placed vertically and, because they are glass, protected from breakage during shipment. Samples should be cooled during shipment so they will be received at the laboratory at 4°C. It is recommended that samples be extracted within 30 days of collection and that extracts be analyzed within 30 days of extraction.

8.8 Alternative Procedure.

8.8.1 Addition of a Filter to the Sampling Train. As a check on the survival of particulate material through the impinger system, a filter can be added to the impinger

train either after the second impinger or after the third impinger. Since the impingers are in an ice bath there is no reason to heat the filter at this point.

NOTE: Any suitable medium (e.g., paper, organic membrane) may be used for the filter if the material conforms to the following specifications.

1) The filter has at least 95% collection efficiency (<5% penetration) for 3 μm dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D2986-71. Test data from the supplier's quality control program are sufficient for this purpose.

2) The filter has a low aldehyde blank value (<0.015 mg formaldehyde/cm^2 of filter area). Before the test series, determine the average formaldehyde blank value of at least three filters (from the lot to be used for sampling) using the applicable analytical procedures.

8.8.2 Recover the exposed filter into a separate clean container and return the container over ice to the laboratory for analysis. If the filter is being analyzed for formaldehyde, the filter may be recovered into a container or DNPH reagent for shipment back to the laboratory. If the filter is being examined for the presence of particulate material, the filter may be recovered into a clean dry container and returned to the laboratory.

9.0 QUALITY CONTROL.

9.1 Sampling. Sampling quality control procedures are listed in Table XXXX-3. See Reference 5 in Section 16.0 for additional Method 5 quality control.

TABLE XXXX-3. SAMPLING QUALITY CONTROL PROCEDURES

Criteria	Control Limits[a]	Corrective Action
Final Leak Rate	≤0.00057 acmm or 4% of sampling rate, whichever is less.	None: Results are questionable and should be compared with other (3) train results.
Dry Gas Meter Calibration	Post average factor γ agree ±5% of pre-factor.	Adjust sample volumes using the factor that gives the smallest volume.
Individual Correction Factor (γ)	Agree within 2% of average factor.	Redo correction factor.
Average Correction Factor	1.00 ± 1%.	Adjust the dry gas meter and recalibrate.
Intermediate Dry Gas Meter	Calibrated every six months against EPA standard.	---
Analytical Balance (top loader)	0.1 g of NBS Class Weights.	Repair balance and recalibrate.
Barometer	Within 2.55 mm Hg of mercury-in-glass barometer.	Recalibrate.

[a]Control limits are established based on previous test programs conducted by the EPA.

9.2 Analysis. The quality assurance program required for this method includes the analysis of the field and method blanks, procedure validations, and analysis of field spikes. The assessment of combustion data and positive identification and quantitation of formaldehyde are dependent on the integrity of the samples received and the precision and accuracy of the analytical methodology. Quality assurance procedures for this method are designed to monitor the performance of the analytical methodology and to provide the required information to take corrective action if problems are observed in laboratory operations or in field sampling activities. Table XXXX-4 lists laboratory quality control procedures.

TABLE XXXX-4. LABORATORY QUALITY CONTROL PROCEDURES

Parameter	Analytical Method	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Linearity Check	HPLC	Run 5-point curve.	At setup or when check standard is out-of-range.	Correlation coefficient ≥0.995.	Check integ., reinteg. If necessary recalibrate.
Retention Time	HPLC	Analyze check standard.	1/10 injections.	Within three standard deviations of average calibration relative retention time.	Check instr. funct. for plug, etc. Heat column: Adjust gradient.
Calibration Check	HPLC	Analyze check standard.	1/10 injections min. 2/set.	±15% of calibration curve.	Check integ., remake std. or recalib.
System Blank	HPLC	Analyze acetonitrile .	1/day.	≤0.1 level of expected analyte.	Locate source of contam.; reanalyze.
Method Spike/ Method Spike Duplicate	HPLC	Analyze spiked DNPH.	1/set or 1/20 samples .	±20% of spiked amount.	Check integ., check instrument function, reanalyze, reprepare if possible.
Replicate Analyses	HPLC	Re-inject sample.	1/10 samples or 1/set	±15% of first injection	Check integ., check instrument function, reanalyze.
Method Blank	HPLC	Analyze DNPH	1/set or 1/20 samples	≤0.1 level of expected analyte	Locate source of contamination, reanalyze, reprepare if possible.

9.2.1 Field Train Blanks. Field blanks must be submitted with the samples collected at each sampling site. The field blanks include the sample bottles containing aliquots of sample recovery solvents, methylene chloride and water, and unused DNPH reagent. At a minimum, one complete sampling train will be assembled in the field staging area, taken to the sampling area, and leak-checked at the beginning and end of the testing (or for the same total number of times as the actual sampling train). The probe of the blank train must be heated during the sample test. The train will be recovered as if it were an actual test sample. No gaseous sample will be passed through the blank sampling train.

9.2.2 Laboratory Method Blanks. A method blank must be prepared for each set of analytical operations, to evaluate contamination and artifacts that can be derived from glassware, reagents, and sample handling in the laboratory.

9.2.3 Field Spike. A field spike is performed by introduction of 200 μL of the Field Spike Standard into an impinger containing 200 mL of DNPH solution. Standard impinger recovery procedures are followed and the spike is used as a check on field handling and recovery procedures. An aliquot of the field spike standard is retained in the laboratory for derivatization and comparative analysis.

9.2.4 Preparation of DNPH Reagent. Take two aliquots of the extracted DNPH reagent. The size of the aliquots depends on the exact sampling procedure used, but 100 mL is reasonably representative. To ensure that the background in the reagent is acceptable for field use, analyze one aliquot of the reagent according to the procedure in Section 11. Save the other aliquot of aqueous acidic DNPH for use as a laboratory method blank when the analysis is performed.

10.0 CALIBRATION AND STANDARDIZATION.

NOTE: Maintain a laboratory log of all calibrations.

10.1 Probe Nozzle. Probe nozzles must be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make measurements at three separate places across the diameter and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When the nozzles become nicked, dented, or corroded, they must be replaced. Each nozzle must be permanently and uniquely identified.

10.2 Pitot Tube Assembly. The Type S pitot tube assembly must be calibrated according to the procedure outlined in Section 4 of Promulgated EPA Method 2 (Section 10.1 of Reformatted Method 2), or assigned a nominal coefficient of 0.84 if it is not visibly nicked or corroded, and, if it meets design and intercomponent spacing specifications.

10.3 Metering System.

10.3.1 Calibration Prior to Use. Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576 (see Reference 3 of Section 16.0). Instead of physically adjusting the DGM dial readings to correspond to the wet-test meter readings, calibration factors may be used to correct the gas meter dial readings mathematically to the proper values. Before calibrating the metering system, a leak check procedure may not detect leaks with the pump. For these cases, the following leak check procedure will apply. Make a ten-minute calibration run at 0.00057 m^3/min (0.020 cfm). At the end of the run, take the difference of the measured wet-test and dry-gas meter volumes and divide the

difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.020 cfm).

10.3.2 Calibration After Use. After each field use, check the calibration of the metering system by performing three calibration runs at a single intermediate orifice setting (based on the previous field test). Set the vacuum at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet-test meter and the inlet of the metering system. Calculate the average value of the calibration factor. If the value has changed by more the 5%, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576 (Reference 3 of Section 16.0).

10.3.3 Leak check of metering system. The portion of the sampling train from the pump to the orifice meter (see Figure XXXX-1) should be leak checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. Use the following procedure. Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 - 18 cm (5 - 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for 1 minute. A loss of pressure on the manometer indicates a leak in the meter box. Leaks must be corrected.

NOTE: If the DGM coefficient values obtained before and after a test series differ by >5%, either the test series must be voided or the test series must be calculated using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

10.4 Probe Heater. The probe heating system must be calibrated before its initial use in the field according to the procedure outlined in APTD-0576 (Reference 3 of Section 16.0). Probes constructed according to APTD-0581 (Reference 4 of Section 16.0) need not be calibrated if the calibration curves in APTD-0576 (Reference 3 of Section 16.0) are used.

10.5 Temperature Sensors. Each temperature sensor must be permanently and uniquely marked on the casting. All mercury-in-glass reference thermometers must conform to ASTM E-1 63C or 63F specifications. Temperature sensors should be calibrated in the laboratory with and without the use of extension leads. If extension leads are used in the field, the temperature sensor readings at the ambient air temperatures, with and without the extension lead, must be noted and recorded. Correction is necessary if using an extension lead produces a change $>1.5\%$.

10.5.1 Impinger and DGM Temperature Sensors. For the temperature sensors used to measure the temperature of the gas leaving the impinger train, a three-point calibration at ice water, room air, and boiling water temperatures is necessary. Accept the temperature sensors only if the readings at all three temperatures agree to $\pm$ 2°C ($\pm$ 3.6°F) with those of the absolute value of the reference thermometer.

10.5.2 Probe and Stack Temperature Sensor. For the temperature sensors used to indicate the probe and stack temperatures, a three-point calibration at ice water, boiling water, and hot oil bath temperatures must be performed. Use of a point at room air temperature is recommended. The thermometer and thermocouple must agree to within 1.5% at each of the calibration points. A calibration curve (equation) may be constructed (calculated) and the data extrapolated to cover the entire temperature range suggested by the manufacturer.

10.6 Barometer. Adjust the barometer initially and before each test series to agree to within ±2.5 mm Hg (0.1 in. Hg) of the mercury barometer or the correct barometric pressure value reported by a nearby National Weather Service Station (same altitude above sea level).

10.7 Triple-Beam Balance. Calibrate the triple-beam balance before each test series, using Class S standard weights. The weights must be within ±0.5% of the standards, or the balance must be adjusted to meet these limits.

10.8 Analytical Calibration.

10.8.1 Establish liquid chromatographic operating parameters to produce a retention time equivalent to that indicated in Table XXXX-1. Suggested chromatographic conditions are provided in Section 11.2. Prepare derivatized calibration standards according to the procedure in Section 7.15.1. Calibrate the chromatographic system using the external standard technique (Section 10.8.2).

10.8.2 External Standard Calibration Procedure.

10.8.2.1 Analyze each derivatized calibration standard using the chromatographic conditions listed in Section 11.2, and tabulate peak area against concentration injected. The results may be used to prepare calibration curves for each analyte listed in Table XXXX-1.

10.8.2.2 The working calibration curve must be verified on each working day by the measurement of one or more calibration standards. If the response for any analyte varies from the previously established responses by more than 15% (see Section 12.8), the test must be repeated using a fresh calibration standard, but only after it is verified that the analytical system is in

control. Alternatively, a new calibration curve may be prepared for that compound. If an autosampler is available, it is convenient to prepare a calibration curve daily by analyzing standards along with test samples.

10.8.2.3 Periodically use the check standard prepared in Section 7.15.1.3 to check the instrument response and calibration curve.

11.0 PROCEDURES.

11.1 Extraction of Stack Gas Samples.

11.1.1 Pour the sample into a separatory funnel, rinse the bottle three times with methylene chloride, adding the rinses to the separatory funnel, and drain the methylene chloride into a volumetric flask.

11.1.2 Extract the aqueous solution with two or three aliquots of methylene chloride depending on the initial volume of methylene chloride present. If more than 100 mL of methylene chloride is present in the sample, use two aliquots, otherwise use three. Add the methylene chloride extracts to the volumetric flask.

11.1.3 Fill the volumetric flask to the line with methylene chloride. Mix well and remove an aliquot.

11.1.4 If high levels of formaldehyde (>2000 μg/mL, derivatized) are present, the extract can be diluted with mobile phase, otherwise the extract must be solvent exchanged as described in Section 11.1.5. If low levels of formaldehyde are present (<0.5 μg/mL, derivatized), the sample should be concentrated during the solvent exchange procedure.

11.1.5 Solvent exchange the methylene chloride to acetonitrile for analysis.

11.1.5.1 Evaporate an aliquot of the methylene chloride extract to near dryness (≤0.5 mL) at room temperature under a stream of pure nitrogen.

11.1.5.2 Add acetonitrile when the sample just reaches dryness. Add 3 mL more than the final sample volume.

11.1.5.3 Evaporate the sample to near dryness again.

11.1.5.4 Repeat Steps 11.1.5.2 and 11.1.5.3. After the third evaporation step, bring the volume up to the final volume with acetonitrile.

11.1.6 Transfer the organic extract to a bottle and store at 4°C (39°F).

11.2 Chromatographic Conditions.

Column:	C18, 250 mm x 4.6 mm ID, 5 μm particle size
Mobile Phase:	Acetonitrile/methanol/water
Gradient:	See Table XXXX-5
Flow Rate:	0.9 mL/min.
UV Detector:	360 nm
Injector Volume:	25 μL

TABLE XXXX-5. HPLC GRADIENT FOR ANALYSIS OF DNPH-DERIVATIZED ALDEHYDES

Time (min)	Acetonitrile (%)	Water (%)	Methanol (%)
0	20	40	40
12	5	25	70
18	5	23	72
28	10	15	75
35	10	15	75
37	20	40	40
47	20	40	40

11.3 Analysis.

11.3.1 Analyze samples by HPLC, using conditions established in Section 11.2. Table XXXX-1 lists the retention times and MDLs that were obtained under these conditions. Other HPLC columns, chromatographic conditions, or detectors may be used if the requirements for Section 9.2. are met, or if the data are within the limits described in Table XXXX-1.

11.3.2 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of the chromatograms.

11.3.3 If the peak area exceeds the linear range of the calibration curve, a smaller sample volume should be used. Alternatively, the final solution may be diluted with acetontrile and reanalyzed.

11.3.4 If the peak area measurement is prevented by the presence of observed interferences, further cleanup is required. However, no method has been evaluated for this procedure.

12.0 DATA ANALYSIS AND CALCULATIONS.

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

12.1 Nomenclature:

ACN	=	Volume of acetonitrile after solvent exchange (mL)
AIC	=	Acceptable Impurity Concentration (μg/mL),
ALD_C	=	Concentration of aldehyde in sample (μg/mL)
ALD_T	=	Total aldehyde in sample (μg)
C_f	=	Concentration of aldehydes in stack gas (mg/dscm)
EAC	=	Expected Analyte Concentration (ppbv)
FW	=	Formula weight of analyte (g/mole)
$MeCl_2$	=	Volume of methylene chloride before solvent exchange (mL)
MVOL	=	Total volume of $MeCl_2$ extract (mL)
RVOL	=	Volume of DNPH reagent that will be used in the impingers (mL)
SVOL	=	Volume of air sampled at standard conditions (L)
V	=	Organic extract volume (mL)
$V_{m(std)}$	=	volume of gas sample a measured by dry gas meter, corrected to standard conditions, dscm (dscf)

12.2 Concentration of Aldehyde in Sample. A least squares linear regression analysis of the calibration standards shall be used to calculate a correlation coefficient, slope, and intercept. Concentrations are the X-variable, and response is the Y-variable.

12.3 Calculation of Total Weight of Aldehydes in the Sample. To determine the total aldehyde in μg, use the following equation:

$$ALD_T = ALD_C \times MVOL \times \frac{(ACN)}{(MeCl_2)} \qquad \textbf{Eq. XXXX-1}$$

12.4 Aldehyde concentration in stack gas. Determine the aldehyde concentration in the stack gas using the following equation:

$$C_f = \frac{K\ (\text{total formaldehyde, mg})}{V_{m(std)}} \qquad \textbf{Eq. XXXX-2}$$

where:

$K = 35.31\ ft^3/m^3$ if $V_{m(std)}$ is expressed in English units
$= 1.00\ m^3/m^3$ if $V_{m(std)}$ is expressed in metric units

12.5 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop are obtained from the data sheet.

12.6 Dry Gas Volume: Calculate $V_{m(std)}$ and adjust for leakage, if necessary, using the equation in Section 6.3 of EPA Method 5.

12.7 Volume of Water Vapor and Moisture Content: Calculate the volume of water vapor and moisture content from equations 5-2 and 5-3 of EPA Method 5.

12.8 Calculate the Acceptable Concentrations of Impurities in DNPH Reagent as follows.

$$IC = 0.1 \times \frac{EAC \times SVOL \times \frac{FW}{22.4} \times (FW+180)}{FW} \times (RVOL \times 1{,}000 \qquad \textbf{Eq. XXXX-3}$$

where:

0.1 is the acceptable contaminant concentration,
22.4 is a factor relating ppbv to g/L,
180 is a factor relating underivatized to derivatized analyte,
1,000 is a unit conversion factor.

13.0 METHOD PERFORMANCE.

13.1 Method performance evaluation: The expected method performance parameters for precision, accuracy, and detection limits are provided in Table XXXX-6.

13.2 The MDL concentrations listed in Table XXXX-1 were obtained using field train blank sample results (formaldehyde, acetaldehyde, propionaldehyde) or instrument detection limits (acetophenone and isophorone).

14.0 POLLUTION PREVENTION. Reserved

TABLE XXXX-6. EXPECTED METHOD PERFORMANCE BASED ON EPA METHOD 301 VALIDATION TESTS

Compound	Precision (% RSD)[a]	Bias (Correction Factor)[b]	Detection Limit (ppbv)[c]	Concentration Level (ppmv)	Test Matrix
Formaldehyde	±8	1.11	90	20	Plywood Dryer Vent
	±9	1.10	70	2	Polyester Spinner Vent
Acetaldehyde	±9	1.26	40	9	Plywood Dryer Vent
	±17	1.24	40	4	Polyester Spinner Vent
Propionaldehyde	±8	1.25	60	2	Plywood Dryer Vent
	±13	1.29	20	2	Polyester Spinner Vent
Acetophenone	±8	1.11	10	2	Plywood Dryer Vent
	±11	1.09	10	2	Polyester Spinner Vent
Isophorone	±8	1.08	10	2	Plywood Dryer Vent
	±9	0.93	10	2	Polyester Spinner Vent

[a] Relative Standard Deviation (%) for dual spiked trains as calculated by EPA Method 301.

[b] Bias Correction Factor for dual spiked trains as calculated by EPA Method 301.

[c] Based on ten times the levels measured in the field train blank samples for a 849 L (30 cubic foot) sample.

15.0 WASTE MANAGEMENT.

15.1 Disposal of Excess DNPH Reagent. Excess DNPH reagent may be returned to the laboratory and recycled or treated as aqueous waste for disposal purposes. 2,4-Dinitrophenylhydrazine is a flammable solid when dry, so water should not be evaporated from the solution of the reagent.

16.0 REFERENCES.

1. Federal Register, 1986, 51, 40643-40652; November 7.

2. EPA Methods 6010, 7000, 7041, 7060, 7131, 7421, 7470, 7740, and 7841, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846, Third Edition. September 1988, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C. 20460.

3. Rom, Jerome J. Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment. Environmental Protection Agency. Research Triangle Park, NC., 27711. APTD-0576. March 1972.

4. Martin, Robert M. Construction Details of Isokinetic Source-Sampling Equipment. Environmental Protection Agency. Research Triangle Park, NC., 27711. APTD-0581. April 1971.

5. Quality Assurance Handbook for Air Pollution Measurement Systems. Volume III: Stationary Sources of Specific Methods (Interim Edition). U.S.

Environmental Protection Agency. Office of Research & Development, Washington D.C., 20460. EPA/600/R-94-038c. April 1994.

6. U. S. Environmental Protection Agency. Method 301-Protocol for the Field Validation of Emission Concentrations from Stationary Sources. Code of Federal Regulations, Title 40, Part 63. Washington, D.D. Office of the Federal Register, July 1, 1987.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA.

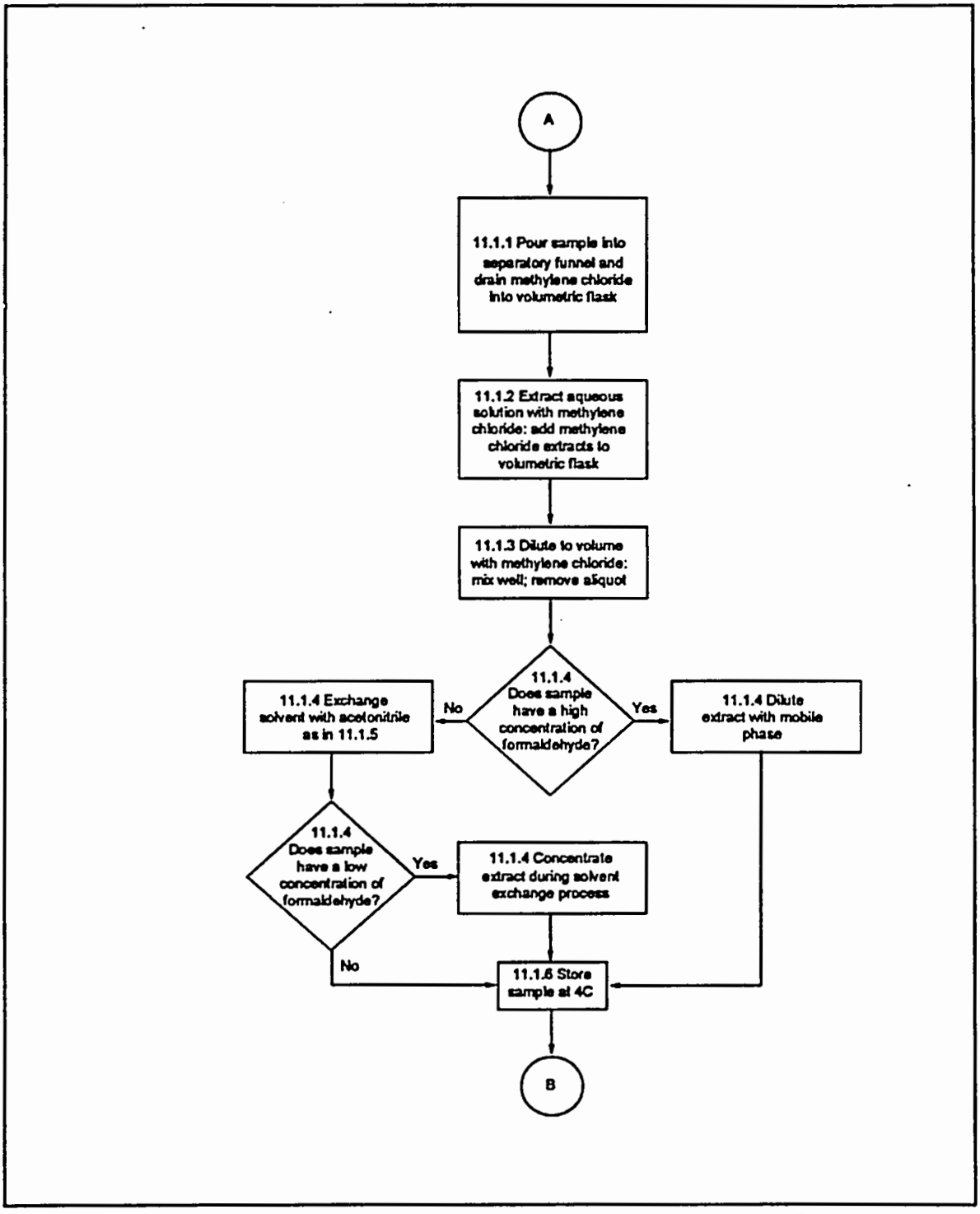


Figure XXXX-3. **Aldehydes and Ketones by High Performance Liquid Chromatography (HPLC)**

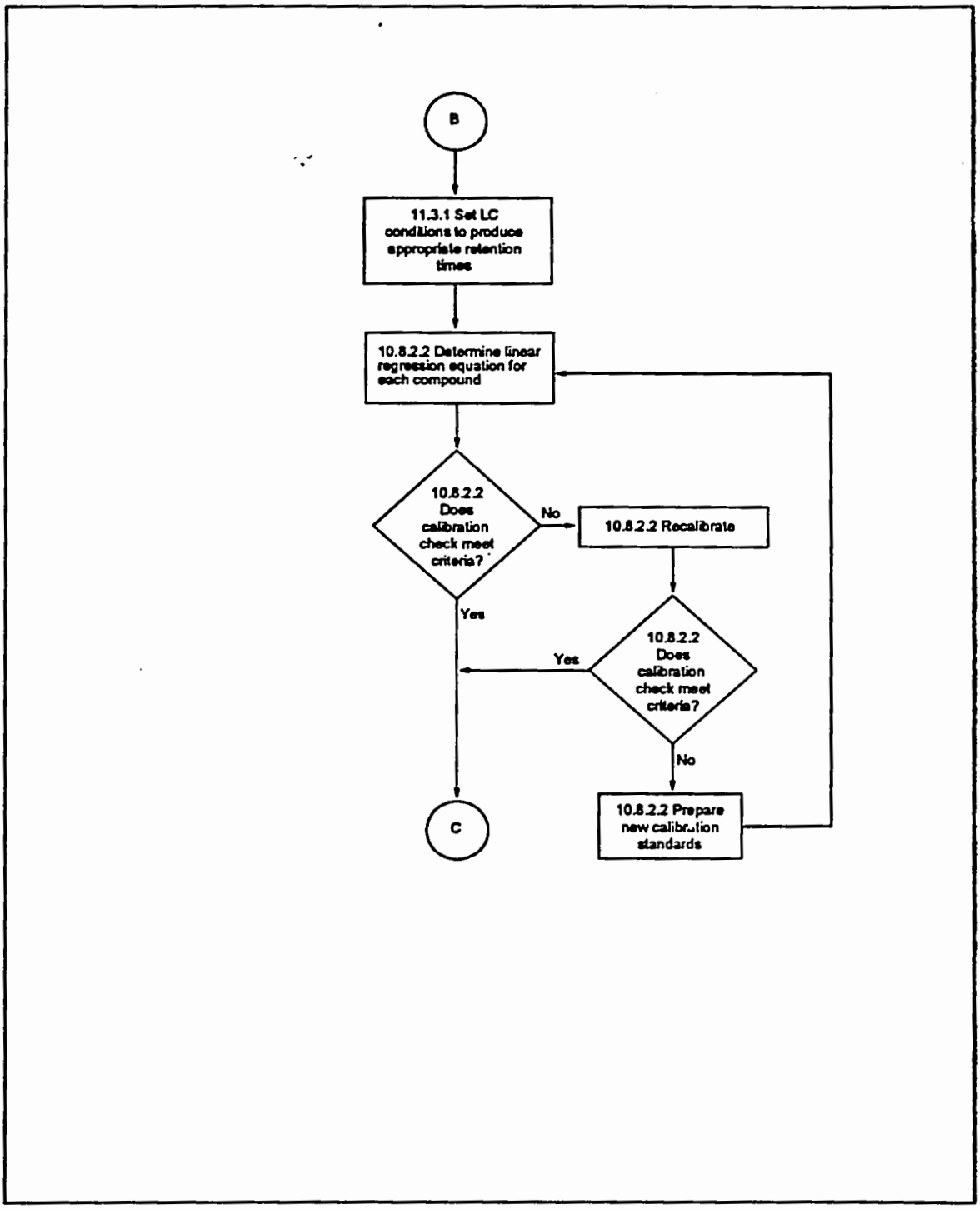


Figure XXXX-3. Aldehydes and Ketones by High Performance Liquid Chromatography (HPLC) (continued).

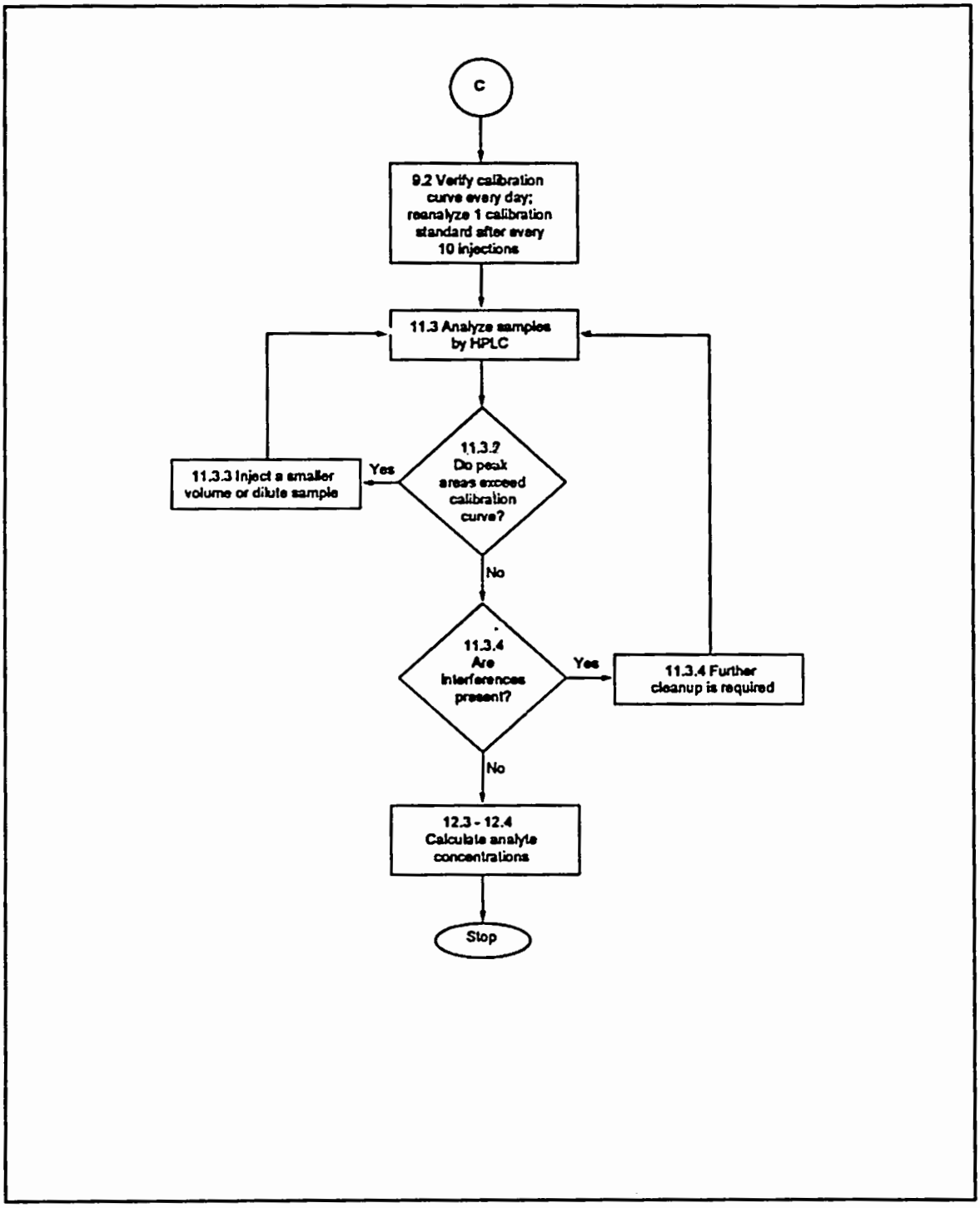


Figure XXXX-3. Aldehydes and Ketones by High Performance Liquid Chromatography (HPLC) (continued)

Appendix C

Site Survey Analysis Results

APPENDIX C

SITE SURVEY ANALYSIS RESULTS

This appendix provides the analysis results of the site survey samples collected on Work Assignment No. 67 on Contract No. 68-D1-0010 and on Work Assignment No. 12 on Contract No. 68-D4-0022.

FIELD TEST SITE 1

Flue gas samples for aldehyde/ketone analysis were collected at a plywood veneer manufacturing plant. The unit tested at this facility is a plywood veneer dryer used to dry the product veneer before shipping. Preliminary sampling was performed during the pre-test site survey. Formaldehyde, acetaldehyde, propionaldehyde, and acrolein were all detected in the dryer stack gas at levels over ten times the method detection limit. Low concentrations of other aldehydes and ketones, including methyl ethyl ketone and methyl isobutyl ketone were also identified. Average concentrations of these compounds in the pre-test samples are shown in Table C-1. Method detection limits and reagent blank analysis results are also shown, for comparison.

Table C-1. Average Aldehyde and Ketone Concentrations in Pretest Samples for Site 1

Compound	Run 1 Concentration (ppbv)[a]	Run 2 Concentration (ppbv)[a]	Reagent Blank Concentration (ppbv)[a]	Method Detection Limit (ppbv)[a]
Acetaldehyde	1400	1700	0.5	2.1
Acrolein	120	120	ND	2.0
Formaldehyde	2800	3500	0.5	2.20
Methyl Ethyl Ketone	13	14	ND	1.9
Methyl Isobutyl Ketone	8.6	4.7	ND	1.7
Propionaldehyde	62	71	ND	2.0
Quinone	100	130	ND	1.6

[a]Concentrations shown are for a 30 ft^3 gas sample.
ND = Not Detected

FIELD TEST SITE 2

Flue gas samples for aldehyde/ketone analysis were collected at a polyester fiber manufacturing plant. The emission source tested is a duct which carries air exhausted from two fiber spinning machines. Preliminary samples were collected from the spinning machine exhaust duct in a pre-test site survey. Formaldehyde, acetaldehyde, and propionaldehyde were all detected in the samples. Average concentrations of these compounds in the pre-test samples are shown in Table C-2.

Table C-2. Average Aldehyde and Ketone Concentrations in Pretest Samples for Site 2

Compound	Run 1 Concentration (ppbv)[a]	Run 2 Concentration (ppbv)[a]	Reagent Blank Concentration (ppbv)[a]	Method Detection Limit (ppbv)[a]
Acetaldehyde	120	100	ND	2.1
Formaldehyde	14	13	2	2.2
Propionaldehyde	8	7	2	2.0

[a]Concentrations shown are for a 30 ft^3 gas sample.
ND = Not Detected