

Dynamic Spiking Studies Using the DNPH Sampling Train

Joette L. Steger,
Radian Corporation, P. O. Box 13000, Research Triangle Park, N.C. 27709

Joseph E. Knoll,
National Exposure Research Laboratory, U. S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

The proposed aldehyde and ketone sampling method using aqueous 2,4-dinitrophenylhydrazine (DNPH) was evaluated in the laboratory and in the field. The sampling trains studied were based on the train described in SW-846 Method 0011. Nine compounds were evaluated: formaldehyde, acetaldehyde, quinone, acrolein, propionaldehyde, methyl isobutyl ketone, methyl ethyl ketone, acetophenone, and isophorone. In the laboratory, the trains were spiked both statically and dynamically. Laboratory studies indicated that formaldehyde and isophorone are efficiently recovered from the first impinger. Laboratory studies also investigated potential interferences to the method. Based on their potential to hydrolyze in acidic solution to form formaldehyde, dimethylolurea, saligenin, s-trioxane, hexamethylenetetramine, and paraformaldehyde were investigated. Dimethylolurea, hexamethylenetetramine, and paraformaldehyde all interfered with formaldehyde analysis. The sampling train containing 200 mL of reagent in the first impinger followed by two impingers containing 100 mL of reagent was then evaluated at a plywood veneer manufacturing plant. Ten runs were performed using quadruplicate sampling trains. Two of the four trains were dynamically spiked with the nine aldehydes and ketones. The test results were evaluated using the EPA Method 301 criteria for method precision ($< \pm 50\%$ relative standard deviation) and bias (correction factor of 1.00 ± 0.30). Formaldehyde, acetaldehyde, propionaldehyde, and acetophenone passed the requirements for accuracy and precision.

INTRODUCTION

Radian, while assisting the Method Branch of the National Exposure Research Laboratory (NERL), has evaluated a multiple pollutant sampling and analytical method for aldehydes and ketones in gaseous 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 Title III of the Clean Air Act Amendments of 1990. Test methods for these analytes are needed to determine risk to the public and to support the regulatory process.

The sampling method in the present study employs an impinger train containing a saturated solution of acidified 2,4-dinitrophenylhydrazine (DNPH) to capture and derivatize aldehyde and ketone compounds. The proposed method was first evaluated in the laboratory; then the method was evaluated in the field at a plywood veneer dryer vent at a pressboard manufacturing plant.

The method was evaluated for precision and bias using procedures described in EPA Method 301¹ in which bias is determined by spiking sampling trains and precision is determined by collocating sampling trains. Spiking was carried out by a dynamic method in which measured quantities of analyte were introduced into the flue gas being sampled for the duration of the sampling run.

INTERFERENCE STUDIES

Because of the low pH reagent used, a potential exists for some compounds to be collected in the impingers and hydrolyzed to form formaldehyde, biasing the results. Five compounds with the potential to hydrolyze under acidic conditions to form formaldehyde were studied using duplicate aliquots of DNPH at pH 4. Blank DNPH was used as a control. The results are reported in Table 1. 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.

SPIKING STUDIES

Two approaches were considered for spiking an aqueous solution of the nine compounds. Static spiking of an aqueous solution, and dynamic spiking of an aqueous solution using a syringe pump. The dynamic and static spiking procedures were compared in the laboratory. Two trains were spiked statically by directly adding the solution to the first impinger. Another two trains were spiked dynamically using a syringe pump. For quality control purposes, a reference spike and method blank sample were also analyzed.

Table 2 compares the average results for static and dynamic spiking. 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. Although total recoveries for acetaldehyde were equivalent by the two spiking methods 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.

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. 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.

LABORATORY TRAIN STUDIES

In the initial laboratory evaluation studies, low recoveries of the spiked carbonyl compounds from the sampling trains were obtained. The effect of the amount of reagent in the first impinger and impinger temperature were evaluated in the laboratory before the first field test to determine if spiked compound recoveries could be improved by changing these parameters. The effect of reagent volume was studied to determine if the low recoveries were caused by insufficient reagent rather than by the compounds breaking through the train. The impinger temperature was studied to see if raising the impinger temperature would increase the rate of the derivatization reaction and improve recoveries of methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK), which appeared to be breaking through the train.

Four trains were dynamically spiked with 14 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.

Results

Results for comparison of the amount of reagent in the first impinger are reported in Table 3. 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 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 levels of aldehydes and ketones above 10 ppmv, using 200 mL of reagent in the first impinger appears necessary to obtain quantitative recoveries.

Results for comparison of the temperature of the first impinger reagent solution are presented in Table 4. 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 (6% versus 16% in the warm impingers). For MEK and MIBK, the two cold impingers recovered more compound. Interestingly, the breakthrough of MEK and MIBK into the second impinger was also higher when the impingers were cold. In general, for all of the compounds, higher recoveries, with less breakthrough and greater compound stability, are achieved when the impingers are kept cold. Based on the laboratory evaluation, the field validation study used iced impingers with 200 mL of reagent in the first impinger.

FIELD EVALUATION

For the field test, flue gas samples for carbonyl analysis were collected at a pressboard manufacturing plant from a plywood veneer dryer stack. The sampling ports were 6-inch (152 mm) diameter pipe nipples located approximately 2.6 meters (m) above the sampling platform. The ports were located at least 4 stack diameters downstream and 1 stack diameter upstream of the nearest flow disturbances.

Gas was extracted from the source duct through a glass nozzle/probe system as shown in Figure 1. Four collocated sampling trains, referred to as a “quad-train”, were used to collect four independent samples simultaneously under identical stack conditions. Two of the trains were dynamically spiked with an aqueous solution of aldehydes and ketones at a level from two to five times higher than the levels measured in the source gas. Flue gas samples were collected isokinetically from a single sampling point identified from a preliminary velocity traverse. The aldehyde/ketone sample was recovered from the train in two fractions.

The first and second impinger contents, water and methylene chloride rinses from the nozzle/probe liner and first and second impingers were Fraction 1. The contents and methylene chloride rinses from the third and fourth impingers were Fraction 2. The two fractions were analyzed separately. Before statistical analysis, all compound quantities from the analytical reports were normalized using the gas volume sampled by each train.

Results

According to Method 301, methods that have bias correction factors between 0.70 and 1.30 are acceptable when the precision of the method at the level of the emission standard is less than or equal to 50% relative standard deviation. Method 301 assumes that the bias and standard deviation of the data remain constant over the test period.

Formaldehyde, acetaldehyde, and acetophenone were evaluated two ways: using the data from the first two impingers only and using the data from all four impingers. Methyl ethyl ketone, methyl isobutyl ketone, acrolein, propionaldehyde, isophorone, and quinone were evaluated using the data from all four impingers only. Precision and bias calculations were completed using all four impingers because of the high breakthrough that occurred during Runs 3, 4, 6 and 7. Two-impinger data also was reported to demonstrate that formaldehyde and acetophenone met the acceptance criteria for bias and precision with only two impingers. Tables 5 and 6 show results of the statistical evaluation of the test data for the spiked compounds using Method 301 using four impingers and two impingers, respectively.

Bias and Precision

Formaldehyde and acetophenone showed acceptable precision and bias with two impingers. There was significant breakthrough of acetaldehyde and propionaldehyde into the third impinger in four of the ten runs. The breakthrough on these runs prevented the method from being validated for two reagent impingers. No satisfactory explanation for the high breakthrough in the four runs was discovered. Acrolein, quinone, MEK, and MIBK did not meet bias criteria. In addition, MEK also did not meet precision criteria for the unspiked samples. Low levels of MEK are challenging to identify because low levels of other four-carbon carbonyl compounds can interfere with the identification and quantification of MEK by HPLC. Isophorone failed the precision criteria for the unspiked samples. One of the unspiked samples contained approximately 200 µg of isophorone while all the other unspiked samples contained 40 µg or less. Because the native isophorone is very low, isophorone performed acceptably using this method.

CONCLUSIONS AND RECOMMENDATIONS

Based on the laboratory and field evaluation of the aldehydes and ketones, the following conclusions may be drawn:

- Based on Method 301 criteria, the sampling method with 200 mL of DNPH reagent in the first impinger and 100 mL of DNPH reagent in the second impinger performs acceptably for the determination of formaldehyde, isophorone, and acetophenone. The method with 200 mL of reagent in the first impinger followed by two impingers with 100 mL of reagent performs acceptably for acetaldehyde and propionaldehyde.
- The test method is not appropriate for the measurement of quinone, acrolein, MEK, and MIBK, due either to poor collection efficiency or analytical problems.
- Dimethylolurea, hexamethylenetetramine, and paraformaldehyde interfere with the determination of formaldehyde.

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

- 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, isophorone, acetaldehyde, and propionaldehyde, use 200 mL of DNPH in the first impinger followed by two impingers containing 100 mL of DNPH and keep the impingers iced.
- Alternate pollutant-specific methods should be developed for measuring emissions of quinone, acrolein, MEK, and MIBK from stationary sources.

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Contracts 68-D1-0010 to Radian Corporation. It has been subjected to Agency review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ACKNOWLEDGEMENTS

The authors wish to thank the pressboard manufacturing facility and the contributions of the following individuals to the success of these evaluations: Merrill Jackson, Mike Hartman, Joan Bursey, Danny Harrison, Mark Owens, Phyllis O'Hara, Donna Tedder, and Linh Nguyen.

REFERENCES

1. U.S. Environmental Protection Agency. Method 301--Field Validation of Pollutant Measurement Methods from Various Waste Media, in Code of Federal Regulations, Title 40, Part 63, Appendix A. Washington, D.C. Office of the Federal Register, July 1, 1987.

Table 1. Results of Interference Study at pH 4.0

Interferant	Formaldehyde Measured			
	Sample 1		Sample 2	
	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

Table 2. 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 ^b	<1	5	114	266 ^b
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
Isopherone	86	80	68	6	16	92	78

^aAverage of two trials

^bResults biased high due to contamination of the spiking apparatus with methanol (methanol contains traces of formaldehyde).

BQL = Below the Quantitation Limit.

NA = Not Applicable.

Table 3. Spike Train Recoveries Using pH 0 Reagent and Spiking at a Nominal 14 mg for Each Compound

Compound	Percent of Spike Recovered (based on spiking solution concentration)						
	Reference Spike ^a	100 mL in First Impinger			200 mL in First Impinger (Train 12)	Difference ^c	% Difference ^d
		Train 5	Train 6	Mean ^b			
Formaldehyde	74	45.5	53.8	49.6	106	+56.4	114
Acetaldehyde	82	27.0	37.9	32.4	61.8	+29.4	90.7
Quinone	25	50.5	57.9	54.2	54.5	+0.3	0.6
Acrolein	41	30.1	39.9	35.0	49.9	+14.9	42.6
Propionaldehyde	70	24.3	33.7	29.0	59.9	+30.9	107
Methyl Ethyl Ketone	91	4.57	6.88	5.72	13.0	+7.28	127
Acetophenone	171	34.4	49.4	41.9	54.7	+12.8	30.5
Methyl Isobutyl Ketone	67	5.26	8.88	7.07	14.6	+7.53	107
Isophorone	86	15.4	14.0	14.7	79.9	+65.2	444

^aReference Spike = Static liquid spike into 200 mL of reagent.

^bMean = (Train 5 + Train 6) / 2.

^cDifference = Train 12 - Mean.

^d%Difference = Difference / Mean x 100.

Table 4. Spike Train Recoveries Using pH 0 Reagent and Spiking at a Nominal 14 mg for Each Compound

Compound	Percent of Spike Recovered (based on spiking solution concentration)							
	Impingers at Room Temperature (Train 13)				Impingers in Ice Bath (Train 12)			
	Impinger 1	Impinger 2	Total	First Impinger Breakthrough ^a (%)	Impinger 1	Impinger 2	Total	First Impinger Breakthrough ^a (%)
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

^aFirst Impinger Breakthrough = Impinger 2 / Total x 100.

Table 5. EPA Method 301 Statistical Evaluation Results Using Four Impingers

Parameter	Form- aldehyde	Acet- aldehyde	Quinone	Acrolein	Propion- aldehyde	Aceto- phenone	Methyl Ethyl Ketone	Methyl Isobutyl Ketone	Isophorone
RSD Spiked (%)	7.36	7.18	40.0	12.1	7.20	7.94	26.1	17.2	7.94
RSD Unspiked (%)	10.2	10.6	39.7	17.3	21.0	42.5	74.3	32.2	211
Bias CF	1.11	1.26	1.84	2.00	1.25	1.08	2.55	2.22	1.08
Disposition	Pass	Pass	Fail	Fail	Pass	Pass	Fail	Fail	Fail

RSD = Relative Standard Deviation
 CF = Correction Factor

Table 6. EPA Method 301 Statistical Evaluation Results Using Two Impingers

Parameter	Formaldehyde	Acetaldehyde	Acetophenone
RSD Spiked (%)	7.32	8.15	7.79
RSD Unspiked (%)	9.95	10.3	43.5
Bias CF	1.10	1.34	1.11
Disposition	Pass	Fails	Pass

RSD = Relative Standard Deviation
 CF = Correction Factor

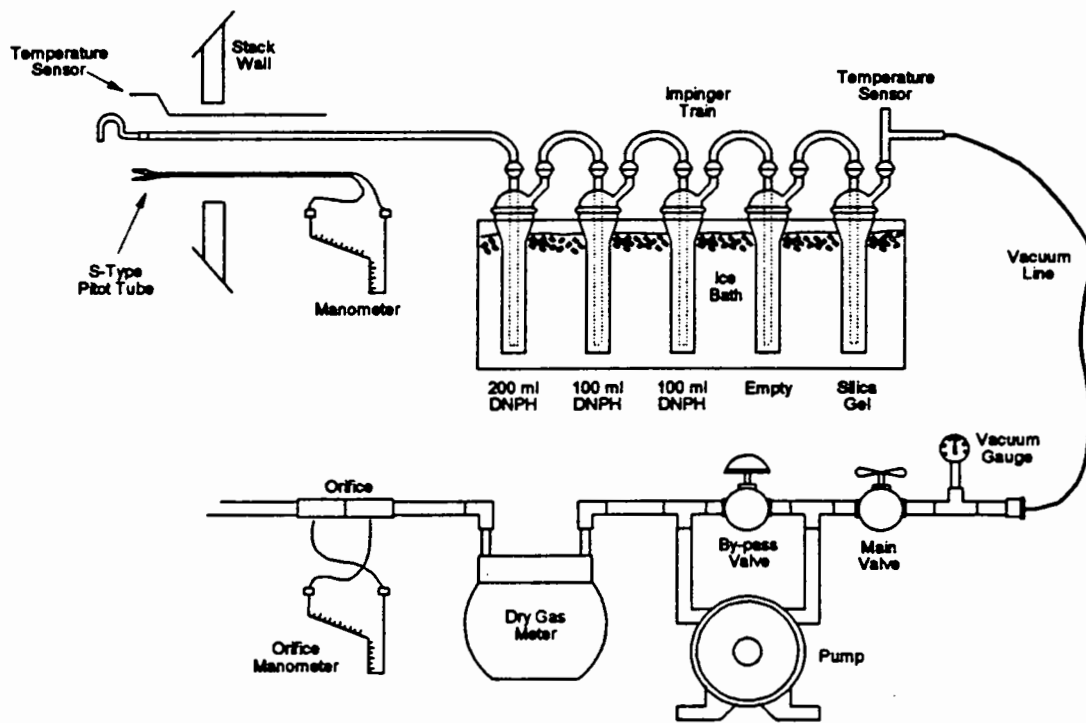


Figure 1. Sampling Train for Aldehydes and Ketones

TECHNICAL REPORT DATA



PB97-122873

1. REPORT NO. EPA/600/A-96/085		2.	3. RECIPIE
4. TITLE AND SUBTITLE Dynamic Spiking Studies Using the DNPH Sampling Train		5. REPORT DATE	
		6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) Joette L. Steger^a and Joseph E. Knoll^b		8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS a. Radian Corporation, P.O. Box 13000, Research Triangle Park, NC 27709 b. National Exposure Research Laboratory U.S. Environmental Protection Agency Research Triangle Park, NC 27711		10. PROGRAM ELEMENT NO.	
		11. CONTRACT/GRANT NO. 68-D4-0022	
12. SPONSORING AGENCY NAME AND ADDRESS National Exposure Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Project Report	
		14. SPONSORING AGENCY CODE EPA/600/09	
15. SUPPLEMENTARY NOTES			
16. ABSTRACT <p>The proposed aldehyde and ketone sampling method using aqueous 2,4-dinitrophenylhydrazine (DNPH) was evaluated in the laboratory and in the field. The sampling trains studied were based on the train described in SW 846 Method 0011. Nine compounds were evaluated: formaldehyde, acetaldehyde, quinone, acrolein, propionaldehyde, methyl isobutyl ketone, methyl ethyl ketone, acetophenone, and isophorone. In the laboratory, the trains were spiked both statically and dynamically. Laboratory studies indicated that formaldehyde and isophorone are efficiently recovered from the first impinger. Laboratory studies also investigated potential interferences to the method. Based on their potential to hydrolyze in acid solution to form formaldehyde, dimethylolurea, saligenin, s-trioxane, hexamethylenetetramine, and paraformaldehyde were investigated. Dimethylolurea, hexamethylenetetramine, and paraformaldehyde all interfered with formaldehyde analysis. The sampling train containing 200 ml of reagent in the first impinger followed by two impingers containing 100 mL of reagent was then evaluated at a plywood veneer manufacturing plant. Ten runs were performed using quadruplicate sampling trains. Two of the four trains were dynamically spiked with the nine aldehydes and ketones. The test results were evaluated using the EPA method 301 criteria for method precision (<math>\pm 50\%</math> relative standard deviation) and bias (correction factor of 1.00 ± 0.30). Formaldehyde, acetaldehyde, propionaldehyde, and acetophenone passed the requirements for accuracy and precision.</p>			
17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS	b. IDENTIFIERS/ OPEN ENDED TERMS	c. COSATI	
18. DISTRIBUTION STATEMENT <u>RELEASE TO PUBLIC</u>	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES	
	20. SECURITY CLASS (This Page) UNCLASSIFIED	22. PRICE	