

Project Summary



Field Validation of the DNPH Method for Aldehydes and Ketones

Gerald S. Workman, Jr. and Joette Steger

Two field validation studies were conducted to evaluate and validate the proposed 2,4-dinitrophenylhydrazine (DNPH) method for sampling aldehydes and ketones. The sampling trains were similar to the train described in SW-846 Draft Method 0011, except that the first impinger contained 200 mL of reagent to increase sample capacity, and an additional impinger containing DNPH was added to evaluate breakthrough. The nine compounds evaluated in the first field test were formaldehyde, acetaldehyde, quinone, acrolein, propionaldehyde, methyl isobutyl ketone, methyl ethyl ketone, acetophenone, and isophorone. Laboratory studies indicated that formaldehyde and isophorone are efficiently recovered from the first impinger. When formaldehyde and isophorone compounds are present in the source at high levels, the capacity of DNPH to capture and derivatize may be exceeded and low compound recoveries result. By doubling the amount of DNPH reagent in the first impinger, recoveries doubled for formaldehyde and quadrupled for isophorone.

To validate the proposed DNPH method, ten field test runs were performed using quadruplicate sampling trains. Two of the four trains during each run were dynamically spiked with the aldehydes and ketones. The test results were evaluated statistically using the procedures described in EPA Method 301. Precision and bias were calculated using all four impingers for the first field test. Two-impinger data are reported for the first field test to demonstrate that formaldehyde and ac-

etophenone met acceptance criteria with only two impingers. For the second field test, data are reported for only two impingers because breakthrough levels were low with little difference in total recovery whether two- and four-impinger data sets were used.

Based on the EPA Method 301 criteria for method precision ($\leq \pm 50\%$ relative standard deviation) and bias (correction factor of 1.00 ± 0.30) the proposed DNPH method for sampling aldehydes and ketones was validated for formaldehyde, acetaldehyde, propionaldehyde, acetophenone, and isophorone. Quinone, acrolein, methyl isobutyl ketone, and methyl ethyl ketone did not meet the validation criteria for the method as used in the field validation studies.

This Project Summary was developed by the National Exposure Research Laboratory's Air Measurements Research Division, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

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*. Bias is established by comparing the method's results with a reference value. The data obtained from the validation test is used to determine if the bias is statistically significant, and to calculate a correction factor, which eliminates the bias. Methods that have correction factors out-

side the 0.7 to 1.3 range are unacceptable. 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 differ-

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

Table 1. Results of the EPA Method 301 Statistical Evaluation

Parameter	Formaldehyde	Acetaldehyde	Propionaldehyde	Acetophenone	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	Pass	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	Fail	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	ND	ND	ND	ND	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	NT

NR = Not Reported

NT = Not Tested

RSD = Relative Standard Deviation

CF = Correction Factor

ND = Native Compound Not Detected

^aStatistics calculated from 4-impinger results in Field Test 1.

^bStatistics calculated from 2-impinger results in Field Test 1.

^cStatistics calculated from 2-impinger results in Field Test 2.

ence 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 0011² 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 2-chloroacetophenone can be determined by Method 0010,³ there was no need to include it in the Method 0011² validation study.

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 determine acrolein. 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 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.

Conclusions and Recommendations

Based on the work performed in the laboratory studies and the field evaluation of the aldehydes and ketones, and using Method 301¹ 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, waterpurgeable 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 0011² to stabilize acrolein. Potential modifications to Method 0011² include using hexane to recover the sample trains instead of methylene chloride.
- Method 0011² 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 0011² 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 0011² for these compounds.

2U.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, DC November 1986.

3U.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, DC November 1986.

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

Gerald S. Workman, Jr. and Joette Steger are with Radian Corp., Research Triangle Park, NC 27709

Joseph E. Knoll is the EPA Project Officer (see below).

The complete report, entitled "Field Validation of the DNPH Method for Aldehydes and Ketones," (Order No. PB96-168398; Cost: \$41.00, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Air Measurements Research Division
National Exposure Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

United States
Environmental Protection Agency
National Risk Management Research Laboratory (G-72)
Cincinnati, OH 45268

Official Business
Penalty for Private Use \$300

EPA/600/SR-96/050

BULK RATE
POSTAGE & FEES PAID
EPA
PERMIT No. G-35