ERG
www.erg.com

0143.04.003

September 8, 2005

Mr. James Homolya
Emissions, Monitoring and Analysis Division (C339-02)
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dear Mr. Homolya:

We found a clerical error in Table 3 from the Final Report for *Carbonyl Recovery and Stability Study in Canisters* (Task 2 in Work Assignment No. 5-03, for EPA Contract No. 68-D-00-264). A revised report is enclosed.

If you have any questions or comments, please call me at (919) 468-7924.

Sincerely,

Julie L. Swift

Julie L. Swift
Senior Program Manager

cc: M. Dougherty, EPA (C304-02)
B. Barbour, EPA (E105-02)
S. Lewis, ERG/AUS

601 Keystone Park Drive, Suite 700, Morrisville, NC 27560 • Phone (919) 468-7800 • Fax (919) 468-7803
Arlington, VA • Atlanta, GA • Austin, TX • Boston, MA • Chantilly, VA • Chicago, IL • Fairfield, CT
Harrisburg, PA • Kansas City, KS • Lexington, MA • Nashua, NH • Research Triangle Park, Morrisville, NC • Sacramento, CA

ERG No.: 0143.04.003
EPA No.: 68-D-00-264

Carbonyl Recovery and Stability Study in Canisters

Final Report
Work Assignment 5-03

Prepared for:

Mr. James Homolya
Emissions, Monitoring and Analysis Division (C339-02)
Office of Air Quality Planning and Standards
US Environmental Protection Agency
Research Triangle Park, NC 27711

Prepared by:

Eastern Research Group, Inc.
1600 Perimeter Park Drive
Morrisville, NC 27560

July 19, 2005

Table of Contents

List of Tables

Executive Summary

This is the final report for the Carbonyl Recovery and Stability in Canisters, Task 2 for Work Assignment 5-03 on EPA contract 68-D-00-264.

The initial phase of this work evaluated the performance of a carbonyl calibration standard prepared in SUMMA canisters. The study was performed to determine the feasibility on analyzing acrolein from 6L summa canisters. The study also evaluated canisters as a means to collect and measure other highly profiled carbonyls (i.e., formaldehyde, acetaldehyde, etc.). The cost efficiency for using one method for TO-15 compounds and carbonyls makes use of canisters a preferable approach.

A stability study was performed using standards prepared in four types of canisters. The canisters used in this study include Entech, Restek, AeroSphere and SUMMA. Compendium Method TO-15 compounds[1] were also spiked into the canisters to simulate a "real world" sample matrix and to check for possible interferences.

Acceptable calibration was demonstrated for carbonyls using the gas chromatograph with mass spectrometer (GC/MS) FULL SCAN and SIM methods. Daily continuing calibrations for acrolein at concentrations of 5.00 ppbv passed method quality objectives. TO-15 sampler certification recoveries for acrolein also passed quality objectives, however other carbonyl compounds were not as stable.

Based on the analysis results during this study, there is no clear trend or general reduction in concentration for acrolein relative to the canister manufacture or manufacturing process. However, at least one canister per manufacture showed significant loss of acrolein recovery over the study period.

Laboratories wishing to analyze acrolein following TO-15 should demonstrate analysis procedures that meet detection limits near or below these risk thresholds. It is recommended that any laboratory using this method should demonstrate that they can analyze acrolein with the consistency and accuracy described in the attached Standard Operating Procedure (SOP in Appendix A).

1.0 BACKGROUND

There are currently 188 hazardous air pollutants (HAPs), or Air Toxics (AT), regulated under the Clean Air Act (CAA) that have been associated with a wide variety of adverse health effects, including cancer, neurological, reproductive and developmental effects, as well as eco-system effects. These air toxics are emitted from multiple sources, including major stationary, area, and mobile sources, resulting in population exposure to these air toxics as they occur in the environment. While in some cases the public may be exposed to an individual HAP, more typically people experience exposures to multiple HAPs and from many sources. Exposures of concern result not only from the inhalation of these HAPs, but also, for some HAPs, from multi-pathway exposures to air emissions.

Current Government Performance Results Act (GPRA) commitments specify a goal of reducing air toxics emissions by 75% from 1993 levels to significantly reduce the risk to Americans of cancer and other serious adverse health effects caused by airborne toxics. Because of the limited tools to assess the impacts of these emissions on public health and the environment, reducing emissions is the focus used to meet GPRA goals. However, as new assessment tools are developed and begin to address the risk associated with these emissions as required by the CAA, the GPRA goal may be modified to one that focuses on risk reductions associated with exposure to AT.

2.0 INTRODUCTION

EVALUATION OF SELECTED CARBONYL COMPOUND RECOVERY AND STABILITY IN CANISTERS

There are sampling and analytical problems when acrolein is determined using Compendium Method TO-11A[2] (2, 4-Dinitrophenylhydrazine cartridges). Samples collected by this method have shown low recovery and chemical reaction that interferes with accurate acrolein measurement. New methods have been proposed following Method TO-15 with collection in canisters. Due to its toxicological effects, acrolein is receiving more attention as one of EPA's toxic substances. Highly industrialized areas can expect higher population exposure exposed to acrolein. Therefore, improved monitoring techniques need to be developed.

Recent work with Compendium Method TO-15 and SUMMA treated stainless steel canisters for carbonyl sampling and analysis shown promising results as an alternative to TO-11A for volatile carbonyl compounds. Additional recovery and stability testing were needed to determine the bias and precision of using method TO-15 for formaldehyde, acrolein and acetaldehyde.

The MQOs that must be met for all data from EPA's National Ambient Air Toxic Trends Study (NATTS) are:

- Relative Percent Difference should not exceed ± 25 percent.
- Coefficient of Variation should not exceed ± 15 percent.

These quality objectives for the carbonyl study are necessary to obtain the high degree of consistency and quality data required for the NATTS program.

To generate the quality of data needed for NATTS carbonyl monitoring in canisters, the MDL must be low enough to allow risk assessment studies. The bias, percent recovery, precision, selectivity, and MDLs were derived from the study.

3.0 EXPERIMENTAL DESIGN

Additional experiments were designed to evaluate the stability of the carbonyls in canisters and to develop a canister sampling and analysis SOP. The analytical detection method required to meet the detection limit quality objective was GC/MS with SIM. Key elements to complete the acrolein validation included:

- Evaluating recovery of carbonyls (acrolein, formaldehyde and acetaldehyde) from canisters using an Entech proposed method.
- Performing a stability study for carbonyls that evaluates the effects of different canisters (using Entech, Restek and standard SUMMA canisters) and humidity (low and high

humidity) at two concentrations (low and high concentrations) for each canister. The selection of canister manufacturers was based on evaluating the typical canisters used in the NATTS monitoring network. The rational for performing the tests at low humidities is based on the variation of humidity between typical east to west coast sites and the variation between summer and winter samples. The rational for performing tests at low concentration is based on demonstrating the ruggedness of the method closer to the risk level and at high concentrations to determine the upper limits.

- Representing a real ambient sample matrix. A number of VOCs, including benzene, 1,3-butadiene, TCE, and PERC, were added to the same canister as the carbonyls during the study.
- Performing four replicate analysis of each canister manufacture to determine the stability by calculating acceptable limits of 25% Relative Percent Difference (RPD) and 15% Coefficient of Variation (CV).

The justification for the decisions used in this experimental design is presented below:

- Upper and lower concentrations – estimated upper level at 10 and lower level at 0.5 ppbv assumed in ambient air. Calibration standard range is from 0.25 to 15 ppbv, bracketing these two set points.
- Upper and lower humidity levels – estimated extremes in the humidity levels in the ambient air. Eighty percent humidity is an average ambient value representative across the United States. Ten percent is the extreme lower value.
- Because the canisters are prepared at subambient pressures, they can only be analyzed 5 times. Analyzing them more would bias the analytical results.
- Analysis was performed on four canisters from each supplier: Entech, Restek, AreoSphere, and SUMMA. The analysis that shows the lowest acceptable recovery levels was used to determine the method's accuracy and bias.

Table 1. presents the matrix used to obtain the precision and bias needed for each matrix condition.

Table 1. Stability Matrix

Canister	Humidity Level	Concentration Level
One canister from each of the following manufactures was prepared for each of these conditions: Entech, Restek, AreoSphere, SUMMA	High (80%)	High (10 ppbv)
	Low (10%)	Low (0.5 ppbv)
	High (80%)	High (10 ppbv)
	Low (10%)	Low (0.5 ppbv)

All standards were prepared and allowed to equilibrate for 24 hours before analysis. All standards were prepared at subambient pressure conditions due to the possibility of condensation on the sides of the canister when they were prepared under pressure and because the current UATMP and NATTS samplers collect subambient pressure canisters. The statistical results were determined using conditions for a 95 percent confidence level, 25 percent RPD and 15 percent CV. The sampling and analytical methodology derived from this task was completely described and documented as a SOP that follows National Laboratory Accreditation Counsel (NELAC) format.

4.0 PROCEDURE

Several techniques were examined and discussed in the previous report entitled *MDL Study for the Low-Volume PM10 Method – NATTS Development,* for EPA Contract No. 68-D-00-264, delivered on January 26, 2005. A summary of these findings is presented below:

- The current method uses a GC column temperatures starting at -30 °C based on a procedure from Entech Instrument's technical notes. Recovery for acetaldehyde, propionaldehyde and acrolein were low using this method.
- Different initial GC temperatures were tried (ranging between -10 to -30 °C) but the peak shapes and resolution decreased as the temperature was raised. The viable starting

temperature was determined to be at -30 °C.

- Increased carrier flow rates and differing ramping temperatures were assessed. Instrument calibration for acrolein with these modifications met MQOs, however, other TO-15 compounds failed MQOs under these new conditions.
- The ERG standard analytical method for determining TO-15 compounds was used. This method proved to be the most stable and produced acceptable recoveries.

Calibration by selected ion monitoring (SIM) was also performed. Acrolein measured by SIM demonstrated acceptable linear calibration for a calibration range of 0.25 to 15.0 ppbv. Continuing SIM calibration checks (at 5 ppbv) for acrolein showed acceptable precision (± 30 % RSD). Table 2. shows the stability of the calibration check standards for acrolein up to 5 days after calibration. All standards were prepared at 40-50% humidity. A summary of these conditions are presented in the final SOP.

Table 2. Calibration Check Standard Recoveries

Day after Calibration	Precision (% RSD)	Acceptable Recovery?
1	0%	Yes
2	0%	Yes
5	12.5%	Yes

During method development, it became evident that formaldehyde can not be measured from canister samples concurrently with ERG's routine TO-15 compounds. Calibration for acetaldehyde and propionaldehyde can be successfully performed from the canisters although the stability is lower than the acrolein.

In order to determine if acrolein is recoverable from field samples, a canister sample was collected with acrolein gas spiked through a NATTS TO-15 sampler. The inlet gas to the sampler was spiked with a known concentration of acrolein and 50% humidity using a mass flow controlled sampler certification system. Analysis of this single sample showed acceptable recovery for acrolein of ± 10 percent. While only a single datapoint, the results of this TO-15 spiked field sample indicate a high probability that acrolein can be measured from NATTs canister samples.

A stability study was performed using standards prepared in four types of canisters according to the work plan experimental matrix.

5.0 RESULTS

SIM GC/MS calibration was completed successfully under a new set of conditions described in the final SOP for this analysis. A correlation coefficient of 0.9976 (greater than 0.995 is determined acceptable) and a response factor of 9.47% linear (±30 % is acceptable) was achieved. Calibration from 0.25 to 15.0 ppbv was preformed using a full scan mode. This calibration used the current miroscale purge and trap technology already in place for the National Air Toxics program.

Table 3. presents the results for the acrolein recovery in the stability study. ERG's routine TO-15 compounds were also spiked into the canisters to simulate a "real world" sample and check for possible interferences. These compounds passed the method required bias and precision objectives. Representative recovery for selected TO-15 compounds are presented in Table 4. These compounds are representative of the other TO-15 compounds. Relative percent difference (RPD) was determined as the performance between the results of analysis at the time of preparation and the results of each consecutive week.

Table 3. Acrolein Recovery from Canisters

Canister ID	Relative Humidity (%)	Concentration Level (ppbv)	Week 1			Week 2			Week 3			Week 4		
			Results (ppbv)	RPD (%)	CV	Results (ppbv)	RPD (%)	CV	Results (ppbv)	RPD (%)	CV	Results (ppbv)	RPD (%)	CV
Entech	10	0.29	0.30	-3.39	2.40	0.27	7.14	5.05	ND	ND	ND	ND	ND	ND
	10	12.5	11.59	7.56	5.34	11.02	12.59	8.90	12.12	3.09	2.18	10.52	17.20	12.16
	80	0.25	0.29	-14.81	10.48	0.29	-14.81	10.48	ND	ND	ND	ND	ND	ND
	80	13.69	12.55	8.69	6.14	12.55	8.69	6.14	12.81	6.64	4.70	12.65	7.90	5.58
		AVERAGE		-0.49	6.09		3.40	7.64		4.86	3.44		12.55	8.87
Restek	10	0.30	0.37	-20.90	14.78	0.36	-18.18	12.86	0.38	-23.53	**16.64**	0.38	-23.53	**16.64**
	10	13.2	12.16	8.20	5.80	NA	NA	NA	11.14	16.93	11.97	10.49	22.88	**16.18**
	80	0.47	0.47	0.00	0.00	0.43	8.89	6.29	0.48	-2.11	1.49	0.62	**-27.52**	**19.46**
	80	14.56	13.59	6.89	4.87	13.55	7.19	5.08	13.68	6.23	4.41	11.83	20.69	14.63
		AVERAGE		-1.45	6.36		-0.70	8.07		-0.62	8.63		-1.87	**16.73**
SUMMA	10	0.33	0.34	-2.99	2.11	0.33	0.00	0.00	0.35	-5.88	4.16	0.40	-19.18	13.56
	10	12.25	9.96	20.62	14.58	9.24	**28.01**	**19.81**	8.47	**36.49**	**25.80**	7.58	**47.10**	**33.30**
	80	0.35	0.36	-2.82	1.99	0.39	-10.81	7.64	0.24	**37.29**	**26.37**	ND	ND	ND
	80	14.24	13.41	6.00	4.25	14.85	-4.19	2.97	15.85	-10.70	7.57	12.12	16.08	11.37
		AVERAGE		5.21	5.73		3.25	7.60		14.30	**15.97**		14.67	**19.41**
AeroSphere	10	0.33	0.53	**-46.51**	**32.89**	0.69	**-70.59**	**49.91**	0.77	**-80.00**	**56.57**	0.82	**-85.22**	**60.26**
	10	13.42	12.57	6.54	4.63	12.12	10.18	7.20	11.89	12.09	8.55	12.13	10.10	7.14
	80	0.45	0.44	2.25	1.59	0.41	9.30	6.58	0.47	-4.35	3.07	0.52	-14.43	10.21
	80	14.53	14.27	1.81	1.28	14.32	1.46	1.03	15.72	-7.87	5.56	12.59	14.31	10.12
		AVERAGE		-8.98	10.09		-12.41	**16.18**		-20.03	**18.44**		-18.81	**21.93**

NA = Bad analytical run – canister was not opened

ND = Not detected

Results listed in bold are outside the required relative percent difference (RPD) of 25% and the coefficient of variation (CV) of 15%.

Table 4. Selected TO-15 Compound Recoveries from Canisters

Compound	Canister Type							
	Entech		Restek TO		Summa		Aerosphere	
	RPD (%)	CV	RPD (%)	CV	RPD (%)	CV	RPD (%)	CV
Benzene	14.09 (7.59 – 24.80)	9.96 (5.37 - **17.53**)	14.13 (7.41 – 22.97)	9.99 (5.24 - **16.24**)	11.96 (4.15 – 21.05)	8.46 (2.93 - 14.89)	13.53 (4.88 - 21.62)	9.56 (3.45 - **15.29**)
Tetrachloroethylene	-7.46 (-17.22 –3.15)	5.55 (1.35 - 12.17)	-4.62 (-16.55 - 1.90)	3.65 (0.00 - 11.71)	-7.87 (-15.69 – 0)	5.56 (0.00 - 11.09)	-8.56 (-17.54 – 1.83)	6.21 (1.23 - 12.41)
1,3-Butadiene	-2.98 (-23.26 – **25.79**)	7.62 (0.12 - **18.23**)	-9.33 (**-42.86** – 3.83)	7.16 (0.00 - **30.30**)	-8.23 (**-36.19** – **25.55**)	9.10 (0.00 - **25.59**)	-8.86 (**-35.51** – **27.71**)	9.41 (0.00 - **25.11**)
Trichloroethylene	-0.09 (-8.17 – 5.65)	2.49 (0.00 - 5.78)	0.48 (-9.01 – 6.06)	2.58 (0.46 - 6.37)	-4.74 (-23.23 - 5.71)	4.40 (0.19 - **16.43**)	-2.00 (-11.99 – 4.00)	2.56 (0.00 - 8.48)

Note: Results listed in **bold** are outside the required relative percent difference (RPD) of 25% and the coefficient of variation (CV) of 15%

6.0 DATA INTERPRETATION AND CONCLUSIONS

Based on the analysis of acrolein during this study, there is no trend or general reduction in concentration for acrolein for any of the canister manufactures. However, at least one canister per manufacture showed significant reduction in acrolein recovery. The following observations are note worthy:

- The two Entech canisters prepared at the low concentration showed no acrolein recovery after week 3 regardless of the relative humidity added to the canister.
- One Restek TO canister at the low concentration, low humidity was above the required control limits of 15% CV after week 3 and one of the canisters at the low concentration, high humidity was above the required control limits of 25% RPD and 15% CV after 4 weeks.
- One SUMMA canister at high concentration, low humidity was above the required control limits starting on week 2, and one canister at low concentration, high humidity was above the control limits starting on week.
- One Aerosphere canister at low concentration, low humidity was above the required control limits throughout the study.
- The average RPD and CV without these anomalies are within the control limits required for air toxic programs (25% RPD, 15% CV).
- Based on the results presented in Table 3. there is a statistically significant decrease in measured acrolein throughout the study (from week 1 to week 4) showing the necessity to analyze the sample no later than 4 weeks after sampling.

Analysis of canisters containing known concentrations of acrolein demonstrated acceptable calibration using the GC/MS full SCAN and SIM methods. Daily continuing calibrations for acrolein at concentrations of 5.00 ppbv passed daily quality objectives during this study. TO-15 sampler certification recoveries for acrolein also passed quality objectives.

7.0 RECOMENDATIONS

ERG laboratory's detection limit for acrolein is 0.11 µg/m^3 which is higher than the 0.05 µg/m^3 noncancer health risk threshold concentration. On preliminary review, the majority of the samples received from sites across the country have concentrations above ERG's detection limit. Based on these results, ERG recommends modifying the VOC analytical procedures used to analyze canisters as described below:

- Acrolein should be measured by SIM GC/MS according to the procedures in Appendix A. This procedure should begin at ERG on samples taken after July 2005.
- Detection of acrolein below the detection limit will be reported qualitatively following the approved NATTS Quality Assurance Project Plan's mass spectrometric criteria.
- Results for acrolein measured by SIM GC/MS should be reported even through the method detection limit is higher than the health effect risk level.

Implementation of acrolein analysis from canisters should include the following requirements:

- Laboratories that generate acrolein data used to evaluate RfC must adjust analysis procedures to demonstrate detection limits near or below these risk thresholds.
- Laboratories using this method need to demonstrate that they can analyze acrolein with consistency and accuracy described in the Standard Operating Procedure (SOP). The SOP is attached as Appendix A.
- The EPA will need to create a method code in order for the acrolein data to be reported in the Air Quality System (AQS) database.

A copy of the Standard Operating Procedure for the Determination of Acrolein and Other

Volatile Organic Compounds (VOCs) In Air Collected In Canisters and Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS) Standard Operating Procedures is presented in Appendix A.

8.0 REFERENCES

1. *Compendium Method TO-15, Determination of Volatile Organic Compounds (VOCs) In AirCollected In Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS),* EPA-ORD, Cincinnati, Ohio; U.S. Environmental Protection Agency, 1999.

2. *Compendium Method TO-11A, Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC),* EPA-ORD, Cincinnati, Ohio; U.S. Environmental Protection Agency, 1999.

Appendix A

Procedure for the Determination of Acrolein and other Volatile Organic Compounds (VOCs) In Air Collected In Canisters and Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS)