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Project Summary

Stability of Parts-Per-Million Organic Cylinder Gases and Results of Source Test Analysis Audits—Status Report #9

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The U.S. Environmental Protection Agency (EPA) has evaluated the suitability of 45 gaseous compounds including hydrocarbons, halocarbons, oxygenated, and sulfurous species for use as standards for measuring stationary source emissions. The main objectives of this on-going project are (1) to provide gas mixtures to EPA, state/local agencies, or their contractors, as performance audit standards to assess the accuracy of measuring source emissions from certain organic chemical manufacturing industries, (2) to corroborate the vendor's certified analysis of the gas mixtures by in-house analysis, (3) to determine the stability of the gas mixtures with time by in-house analysis, and (4) to explore the feasibility of new audit materials as requested by EPA.

Thus far, 31 mixtures have been used to conduct 214 different audits. The results of these audits, a description of the experimental procedures used for analyses, and available stability data are presented in the full status report.

Compound stabilities have been determined through multiple analyses of the cylinders containing them. Stability data for up to 8 years is available for many compounds and over 5 years for most compounds. Compounds that are unstable and not suitable for use as an audit material are identified.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, 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

Accurate measurement of hydrocarbons, halocarbons, and sulfur-containing compounds in ambient and source samples is essential to any environmental monitoring program. The potential for achieving acceptable accuracy is enhanced by the availability of reliable standards that can be used to check or validate the measurement process. The Research Triangle Institute (RTI) under contract to the Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency (EPA), has responded to this need through the development of cylinder gases for 39 compounds. These gaseous compounds are to be used in performance audits as designated by the EPA Project Officer. These performance audits are to assess the accuracy of source emission measurements in certain organic manufacturing industries.

Currently 45 different compounds have been investigated as audit materials. Six of these gaseous compounds have been found to be unstable in cylinders and not suitable as audit materials. The other 39 gaseous compounds in the repository are suitable for conducting performance audits during

source testing. Table 1 lists the 45 compounds, the concentration ranges for each compound, the number of cylinders of each compound, and the cylinder construction material. Additional compounds are procured, as needed.

The gaseous compounds are acquired from commercial suppliers in compressed gas cylinders; these same cylinders, along with an appropriate delivery system, are used directly as sources of the gaseous compounds during performance audits. The compressed gas cylinder is especially suitable as an audit device because of its simplicity, portability, low cost, flexibility in analyte delivery over a broad concentration range, reliability, and ruggedness for interstate shipping. The accuracy of the supplier-reported levels of these compounds are verified through measurement using National Bureau of Standards - Standard Reference Materials (NBS-SRMs), commercial permeation tubes, and/or reagent grade pure liquids as standards. The permeation rates of the commercially available tubes are verified by RTI before use.

The accuracy of the "known" cylinder concentrations and the stability of the

Table 1. *Audit Materials Currently in the Repository*

	Low Concentration Range			High Concentration Range		
Compound	No. of Cylinders	Concentration Range (ppm)	Cylinder Construction*	No. of Cylinders	Concentration Range (ppm)	Cylinder Construction*
Benzene	7	5 - 20	S	10	60 - 400	S
Ethylene	3	5 - 20	Al	4	300 - 700	Al
				6	3,000 - 20,000	Al
Propylene	3	5 - 20	Al	3	300 - 700	Al
Methane/Ethane	--	--	--	4	1,000 - 9,000(M), 200 - 800(E)	Al
Propane	3	5 - 20	Al	3	300 - 700	Al
				4	1,000-20,000	Al
Toluene	4	5 - 20	Al	4	100 - 700	LS
Hydrogen Sulfide	6	5 - 50	Al	7	100 - 700	Al
Meta-Xylene	2	5 - 20	S	2	300 - 700	LS
Methyl Acetate	2	5 - 20	S	2	300 - 700	S
Chloroform	4	5 - 20	S	1	300 - 700	S
Carbonyl Sulfide	1	5 - 20	Al	4	100 - 400	Al
Methyl Mercaptan	3	3 - 10	Al	--	--	--
Hexane	2	20 - 90	Al	--	--	--
1,2-Dichloroethane	4	5 - 20	Al	4	100 - 600	Al
Cyclohexane	--	--	--	1	80 - 200	Al
Methyl Ethyl Ketone	4	5 - 50	S	--	--	--
Methanol	1	30 - 80	Al	--	--	--
1,2-Dichloropropane	2	3 - 20	Al	2	300 - 700	Al
Trichloroethylene	2	5 - 20	Al	2	100 - 600	Al
1,1-Dichloroethylene	2	5 - 20	Al	2	100 - 600	Al
1,2-Dibromoethylene**	--	--	--	--	--	--
Perchloroethylene	2	5 - 20	S	2	300 - 700	LS
Vinyl Chloride	8	5 - 30	S	--	--	--
1,3-Butadiene	3	5 - 60	Al	--	--	--
Acrylonitrile	3	5 - 20	Al	1	300 - 500	Al
Aniline**	--	--	--	--	--	--
Methyl Isobutyl Ketone	1	5 - 20	Al	--	--	--
Paradichlorobenzene**	--	--	--	--	--	--
Ethylamine**	--	--	--	--	--	--
Formaldehyde**	--	--	--	--	--	--
Methyl Chloride	4	1 - 20	Al	--	--	--
Carbon Tetrachloride	4	5 - 20	Al	--	--	--
Freon 113	1	5 - 20	Al	--	--	--
Methyl Chloroform	1	5 - 20	Al	--	--	--
Ethylene Oxide	5	5 - 20	Al	--	--	----
Propylene Oxide	1	5 - 20	Al	1	75 - 200	Al
Allyl Chloride	1	5 - 20	S	1	75 - 200	S
Acrolein	1	5 - 20	Al	1	100 - 300	Al
Chlorobenzene	3	5 - 20	Al	--	--	--
Carbon Disulfide	--	--	--	1	75 - 200	Al
Cyclohexanone**	--	--	--	--	--	----
EPA Method 25 Mixture***	6	100 - 200	Al	4	750 - 2,000	Al
Ethylene Dibromide	2	5 - 20	S	2	50 - 300	S
Tetrachloroethane	1	5 - 20	S	--	--	--

*Al = Aluminum; S = Steel; LS = Low Pressure Steel.

**Cylinders are no longer available; the compounds were found to be unstable in the cylinders.

***The gas mixture contains an aliphatic hydrocarbon, an aromatic hydrocarbon, and carbon dioxide in nitrogen. Concentrations shown are in ppmC.

compounds in the cylinders are important. Along with acquisition of new compounds and verification of their concentrations, an extensive stability study is being performed. This study involves periodic analyses of the contents of each of the cylinders in the repository.

Procedure

Once a compound is chosen, a commercial supplier is contacted to determine if a cylinder containing that compound can be prepared. If so, the manufacturer prepares the cylinder gases and determines the concentration of the analyte in the cylinder. The cylinder is sent to RTI where its contents are analyzed usually within seven days of its arrival. If the RTI value varies from the manufacturer's value by more than 10 percent, an analysis is performed by a third party (EPA or NBS). The cylinder contents are then analyzed one month after acquisition, two months after acquisition, and one year after acquisition.

All analyses are carried out using gas chromatography (GC). The column and detector are chosen so as to be optimum for the compound being measured. Three types of standards are used to generate gas concentrations for calibration of the GC for the measurement of audit materials. National Bureau of Standards - Standard Reference Materials (NBS-SRMs) of methane and propane are used as standards for the measurement of methane and propane audit materials. Propane is used to calibrate the chromatographic system for measurement of ethane, ethylene and propylene, assuming the FID response per carbon is constant from compound to compound. In a few others (e.g., vinyl chloride, ethylene oxide) gaseous standards are generated using permeation tubes. The standards for most of the other audit materials are prepared using pure liquids which are volatilized in a clean glass bulb or stainless steel sphere.

Audit requests are directed to RTI through the EPA Project Officer. The cylinder is then shipped by a freight carrier to the laboratory being audited. A letter that provides general instructions for performing the audit is included with the cylinders. The audit concentrations are provided to the requesting agency audit coordinator. After the laboratory being audited has analyzed the contents of the cylinder, the audit coordinator reports the value(s) to RTI, which in turn reports both the measured and accepted values to the Project Officer. The laboratory being audited then is responsible for shipping the cylinder back to RTI.

Results and Discussion

To date, 214 individual audits have been initiated and 194 are complete. The results obtained for a few typical performance audits are shown in Table 2 and the rest are given in the fall status report. Generally, the results of the audits show close agreement (± 15%) with the actual cylinder concentrations measured by RTI.

Most of the cylinder gases are analyzed at least four times to determine the stability of these compounds; some are analyzed as many as nine times. Absolute accuracies for the cylinder analyses have not been determined due to lack of NBS standards for most of the organic gas mixtures above one ppm. An examination of the analysis data shows values for individual cylinder analyses usually vary by less than ten percent for four to nine analyses over two to seven years. As the number of analyses per cylinder increases, detailed statistical analyses will be performed. Statistical analyses for ten halocarbons and eight other organics are presented in two journal publications[1,2] and the statistical analyses for the remaining compounds will be presented in a future report.

Conclusions

Cylinder gases of hydrocarbons, halocarbons, and sulfur species have been used successfully to assess the accuracy of gas chromatographic systems used to measure organic compounds in source emissions. Absolute accuracy has not been determined because of lack of standard reference materials; instead interlaboratory bias has been reported for the performance audits conducted during source testing. The interlaboratory bias determined has been generally within 15 percent for both low and high concentration gases.

Thirty-nine out of 45 gaseous compounds have demonstrated sufficient stability in cylinders for use as audit materials. Six compounds (ethylamine, paradichlorobenzene, cyclohexanone, formaldehyde, 1,2-dibromoethylene and aniline) are not recommended as audit materials for various reasons as discussed in the full status report. Detailed statistical analyses which would separate statistical deviations from true concentration changes with time for 18 gaseous compounds have been published in a journal publication and statistical analyses for the remaining compounds will be presented in a future report.

Table 2. Typical Audit Results

Industry	Audit Material	Cylinder Concentration (ppm)	Client Audit Bias (%)
Maleic anhydride production	Benzene in N_2	138 300	-9.4 +4.7
Vinyl chloride production	1,2-Dichloroethane in N_2	9.3 462	+6.0 +3.7
Vegetable oil plant	Hexane in N_2	82.2 1982	+5.6 +3.0
Degreasing Vent	Trichloroethylene in N_2	14.9 566	-0.4 -8.7

References

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The complete report, entitled "Stability of Parts-Per-Million Organic Cylinder Gases and Results of Source Test Analysis Audits—Status Report #9," (Order No. PB 88-158 761/AS; Cost: $14.95, subject to change) will be available only from:
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