



Project Summary

Stability of Parts-Per-Million Organic Cylinder Gases and Results of Source Test Analysis Audits: Status Report #8

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A repository of 45 gaseous compounds including hydrocarbons, halocarbons, oxygenated, and sulfurous species has been established under contract with the U.S. Environmental Protection Agency (EPA). 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 176 different audits. The results of these audits, a description of the experimental procedures used for analyses, and available stability data are presented in this status report. Generally the audit results are within 15 percent of the expected values.

Compound stabilities have been determined through multiple analyses of the cylinders containing them. Stability data for up to seven years is available for many compounds and over four 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 which 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 by developing an extensive repository of gaseous 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.

Table 1. Audit Materials Currently in the Repository

Compound	Low Concentration Range			High Concentration Range		
	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
Propylene	3	5 - 20	Al	6	3000 - 20,000	Al
Methane/Ethane	—	—	—	3	300 - 700	Al
Propane	3	5 - 20	Al	4	1000 - 9000(M), 200 - 800(E)	Al
Toluene	4	5 - 20	Al	3	300 - 700	Al
Hydrogen Sulfide	7	5 - 50	Al	4	1000 - 20,000	Al
Meta-Xylene	2	5 - 20	S	4	100 - 700	LS
Methyl Acetate	2	5 - 20	S	2	300 - 700	Al
Chloroform	4	5 - 20	S	2	300 - 700	S
Carbonyl Sulfide	1	5 - 20	Al	1	300 - 700	S
Methyl Mercaptan	3	3 - 10	Al	4	100 - 400	Al
Hexane	2	20 - 90	Al	—	—	—
1,2-Dichloroethane	4	5 - 20	Al	1	1000 - 3000	LS
Cyclohexane	—	—	—	4	100 - 600	Al
Methyl Ethyl Ketone	1	30 - 80	S	1	80 - 200	Al
Methanol	1	30 - 80	Al	—	—	—
1,2-Dichloropropane	2	3 - 20	Al	—	—	—
Trichloroethylene	2	5 - 20	Al	2	300 - 700	Al
1,1-Dichloroethylene	2	5 - 20	Al	2	100 - 600	Al
**1,2-Dibromoethylene	—	—	—	2	100 - 600	Al
Perchloroethylene	2	5 - 20	S	—	—	—
Vinyl Chloride	8	5 - 30	S	2	300 - 700	LS
1,3-Butadiene	3	5 - 60	Al	—	—	—
Acrylonitrile	3	5 - 20	Al	—	—	—
**Aniline	—	—	—	1	300 - 500	Al
Methyl Isobutyl Ketone	1	5 - 20	Al	—	—	—
**Para-dichlorobenzene	—	—	—	—	—	—
**Ethylamine	—	—	—	—	—	—
**Formaldehyde	—	—	—	—	—	—
Methylene Chloride	3	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	2	750 - 2000	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.

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 compounds in the cylinders are important. Along with acquisition of new compounds and verification of their concentrations, an extensive stability study

Table 2. Typical Audit Results

Industry	Audit Material	Cylinder Concentration (ppm)	Client Audit Bias (%)
Maleic anhydride production	Benzene in N ₂	138	-9.4
		300	+4.7
Vinyl chloride production	1,2-Dichloroethane in N ₂	93	+6.0
		462	+3.7
Vegetable oil plant	Hexane in N ₂	82	+5.6
		1982	+3.0
Degreasing Vent	Trichloroethylene in N ₂	14.9	-0.4
		566	-8.7

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. 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 is also included with the cylinders which provides general instructions for performance of the audit. 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, 176 individual audits have been initiated, and 166 are complete. The results obtained for a few typical performance audits are shown in Table 2 and the rest are given in the full status report. Generally, the results of the audits show close agreement ($\pm 15\%$) with the actual cylinder concentrations measured by RTI.

Most of the cylinders in the repository are analyzed at least four times to determine the stability of these compounds; some are analyzed as many as eight 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 eight analyses over two to six 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.

References

1. R. K. M. Jayanty, C. Parker, C. E. Decker, W. F. Gutknecht, J. E. Knoll and D. J. von Lehmden, "Quality Assurance for Emission Analysis Systems," *Environmental Science and Technology*, 17(6), 257-263A (1983).
2. G. B. Howe, R. K. M. Jayanty, A. V. Rao, W. F. Gutknecht, C. E. Decker, and D. J. von Lehmden, "Evaluation of Selected Gaseous Halocarbons for Use in Source Test Performance Audits," *J. of Air Pollution Control Association*, 33(9) 823-826 (1983).

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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 #8," (Order No. PB 87-141 461/AS; Cost: \$13.95, subject to change) will be available only from:

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