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Project Summary

Stability of Organic Audit Materials and Results of Source Test Analysis Audits

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A repository of 40 gaseous compounds including hydrocarbon, halocarbon, and sulfur species has been established under contract with the U.S. Environmental Protection Agency (USEPA). The main objectives of this on-going project are (1) to provide gas mixtures to EPA, state/local agencies, or their contractors, as performance audits to assess the accuracy of source emission measurements in 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, 18 compounds have been used to conduct 86 different audits. The results of these audits and a description of the experimental procedures used for analyses and available stability data are presented in the status report. Seventy percent of the audit results are within 10 percent of the expected values.

Compound stabilities have been determine through multiple analyses of the cylinders containing them. Stability values for all compounds are expressed as percent change per month. Calculated changes are typically found to be a few tenths of one percent per month, though many of these changes may not be significantly different from zero.

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 (USEPA), has responded to this need by developing an extensive repository of standard gaseous compounds. These standards 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.

The RTI repository currently contains 40 different compounds based on anticipated needs of EPA. Table 1 lists the compounds, the concentration ranges of each compound, and the

Table 1. Audit Materials Currently Held in the Repository

Compound	Low Concentration Range		High Concentration Range	
	No. of Cylinders	Concentration Range (ppm)	No. of Cylinders	Concentration Range (ppm)
Benzene	14	8 - 13	17	60 - 400
Ethylene	4	5 - 20	4	300 - 700
			6	3000 - 20,000
Propylene	4	5 - 20	4	300 - 700
Methane/Ethane	-	------	4	1000 - 6000(M), 200 - 700(E)
Propane	4	5 - 20	4	300 - 700
Toluene	2	5 - 20	2	300 - 700
Hydrogen Sulfide	4	5 - 20	2	300 - 700
Meta-Xylene	2	5 - 20	2	300 - 700
Methyl Acetate	2	5 - 20	2	300 - 700
Chloroform	2	5 - 20	2	300 - 700
Carbonyl Sulfide	2	5 - 20	2	100 - 300
Methyl Mercaptan	4	3 - 10	-	------
Hexane	2	20 - 80	2	1000 - 3000
1,2-Dichloroethane	4	5 - 20	4	100 - 600
Cyclohexane	-	------	1	100
Methyl Ethyl Ketone	1	50	-	------
Methanol	1	50	-	------
1,2-Dichloropropane	2	5 - 20	2	300 - 700
Trichloroethylene	2	5 - 20	2	100 - 600
1,1-Dichloroethylene	2	5 - 20	2	100 - 600
1,2-Dibromoethylene	2	5 - 20	2	100 - 600
Perchloroethylene	2	5 - 20	2	300 - 700
Vinyl Chloride	9	5 - 30	-	------
1,3-Butadiene	1	25	-	------
Acrylonitrile	2	5 - 20	2	300 - 700
Aniline	1	10	-	------
Methyl Isobutyl Ketone	1	10	1	50 - 100
Cyclohexanone	2	5 - 20	-	------
Para-dichlorobenzene	2	10 - 40	-	------
Ethylamine	2	10 - 60	-	------
Formaldehyde	-	----	-	------
Methylene Chloride	1	10	-	------
Carbon Tetrachloride	1	10	-	------
Freon 113	1	10	-	------
Methyl Chloroform	1	10	-	------
Ethylene Oxide	1	10	-	------
Propylene Oxide	1	5 - 20	1	75 - 200
Allyl Chloride	1	5 - 20	1	75 - 200
Acrolein	1	5 - 20	1	75 - 200
Chlorobenzene	1	5 - 20	-	------
Carbondisulfide	1	5 - 20	1	75 - 200

number of cylinders of each compound. Additional compounds are obtained 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 standard gas during performance audits. The compressed gas cylinder is especially suitable as an audit material 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-SRM's), commercial permeation tubes, and/or reagent grade pure liquids as standards. The permeation rate 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 is 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 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. The cylinder contents are then analyzed one month after acquisition, two months after acquisition, and one year after acquisition. The cylinder contents are also analyzed before a cylinder is sent out for an audit. This preaudit analysis may substitute for the annual analysis if it occurs within a month of the normal analysis due date.

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-SRM) methane and propane are used as standards for the measurement of methane and propane audit materials. These same gases are used to calibrate the chromatographic system for measurement of ethylene and propylene, assuming the FID response per carbon is constant for 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 volatized in a clean glass bulb.

Audit requests are directed to RTI through the EPA Project Officer. The cylinder and a regulator are 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 and regulator back to RTI.

Results and Discussion

To date, 86 individual audits have been initiated, and 83 are complete. The results obtained for a few typical performance audits are shown in Table 2 and the rest are given in the full report. Generally, the results of the audits show close agreement (±10%) with the actual cylinder concentrations measured prior to shipment.

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. An estimate of stability has been made for each cylinder that has been analyzed at least three times. This estimate is a calculation of percent change in concentration per month over the period that RTI has performed analyses of the cylinder contents. The calculation involves a linear regression analysis of the concentration of the analyte versus time in days. The slope and intercept determined by this regression analysis are then used to calculate percent change per month by the relationship:

$$\%\ Change/Month = \frac{slope}{y\ intercept} \times \frac{}{100 \times 30}$$

Examples of stability data are shown in Table 3. Changes are noted for each compound, although these changes may not be significantly different from zero. As the number of analyses per cylinder increases, additional statistical analyses will be performed.

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 10 percent for both low and high concentration gases.

Twenty-six out of 40 gaseous compounds have demonstrated sufficient stability in cylinders for use as audit materials. Four compounds (ethylamine, paradichlorobenzene, cyclohexanone, and aniline) are not recommended as audit materials for various reasons as discussed in the full report. Another 10 compounds (carbon tetrachloride, methylene chloride, methyl chloroform, Freon 113, ethylene oxide, propylene oxide, alkyl chloride, acrolein, chlorobenzene and carbondisulfide) have recently been added to the repository; the stability of these compounds remains to be studied. The estimates of stability are reported in terms of percent change per month. Detailed statistical analyses which would separate statistical deviations from true concentration change with time are in progress and will be presented in a journal publication.

Table 2. Typical Audit Results

Industry	Audit Material	Cylinder Concentration (ppm)	Client Audit Accuracy
Maleic anhydride production	Benzene in N	138	-9.4
		300	+4.7
Ester production	Propane in Air	10.1	+8.6
		710	+8.6
Vegetable oil plant	Hexane in N	82.2	+5.6
		1982	+3.0
Coke oven by-product	Benzene in N	88.4	-8.7
		8.2	+2.6

Table 3. Typical Stability Results

Compound	Concentration (ppm)	Period of Cylinder Analyses (months)	% Change/Month
Benzene	12.2	25	-0.15
Benzene	296	27	0.01
Hydrogen sulfide	9.15	37	-0.05
1,2 Dichloroethane	439	28	-0.10
Perchloroethylene	13.0	13	-0.23
Acrylonitrile	20.1	28	-1.07
Chloroform	348	33	-0.20
Propylene	14.8	25	0.06

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The complete report, entitled "Stability of Organic Audit Materials and Results of Source Test Analysis Audits," (Order No. PB 83-107 490; Cost: $11.50, subject to change) will be available only from:

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

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