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Project Summary

Stability of Parts-per-Billion Hazardous Organic Cylinder Gases and Performance Audit Results of Source Test and Ambient Air Measurement Systems: Status Report #4

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An evaluation of 29 gaseous organic compounds at parts-per-billion (ppb) levels in compressed gas cylinders has been established under a contract with the United States Environmental Protection Agency (USEPA). The primary objectives of this on-going project are: (1) to evaluate the quality of measurements made by USEPA, state/local agencies, or their contractors by using ppb gas cylinders for performance audits to assess the relative accuracy of source measurement systems during hazardous waste trial burn tests and ambient air monitoring programs; (2) to verify the manufacturer's certified analysis of the multi-component gas mixtures; (3) to determine the stability of the gas mixtures with time; and (4) to develop new audit materials as requested by USEPA.

The cylinders consist of five mixtures of five, six, eight, nine, and eighteen organic compounds each. These mixtures were blended by a commercial gas supplier in aluminum cylinders in a balance gas of nitrogen. The five component mixture (Group I) contains carbon tetrachloride, chloroform, tetrachloroethylene (perchloroethylene), vinyl chloride and benzene. The nine component mixture (Group II) includes trichloroethylene, 1,2-dichloroethane (ethylene dichloride), 1,2-dibromoethane (ethylene dibromide), acetonitrile, trichlorofluoromethane (F-11), dichlorodifluoromethane (F-12) bromomethane (methyl bromide), methyl ethyl ketone and 1,1,1-trichloroethane. The eight component mixture (Group III) includes pyridine*, vinylidene chloride, 1,1,2-trichloro-1,2,2-trifluoroethane (F-113), 1,2-dichloro-1,1,2,2-tetrafluoroethane (F-114), acetone, 1,4-dioxane, toluene, and chlorobenzene. The six component mixture (Group IV) includes acrylonitrile, 1,3-butadiene, ethylene oxide, methylene chloride, propylene oxide and o-xylene. The eighteen component mixture (Group V) includes vinyl chloride, 1,3-butadiene, bromomethane, trichlorofluoromethane, (F-11), methylene chloride, chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane, benzene, carbon tetrachloride, 1,2-dichloropropane, trichloroethylene, toluene, 1,2-dibromoethane, tetrachloroethylene, chlorobenzene, ethylbenzene and o-xylene. To date, 198 performance audits have been initiated and 172

*Although Group III cylinders contain pyridine, the concentrations are not certified due to severe analytical difficulties

are complete. 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. Generally, the results of the audits show reasonable agreement (± 50 percent) with the audit material concentrations measured by Research Triangle Institute (RTI), considering the low concentrations of the organics and the anticipated uncertainty associated with independent analyses conducted by an audit laboratory.

Stability studies for all Group I, Group II, Group III (except pyridine), Group IV and Group V compounds have been performed. Results indicate that all the compounds tested are adequately stable for use as reliable audit materials with the exception of ethylene oxide and propylene oxide at low concentrations.

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

The application of Quality Assurance practices is important to the generation of high-quality environmental data. The Quality Assurance Division of USEPA's Environmental Monitoring Systems Laboratory has initiated a program to supply audit materials for use during hazardous waste trial burn tests and ambient air measurements. RTI under contract to the USEPA has responded to this need through development of gas cylinders containing 29 gaseous organic compounds at ppb levels in compressed gas cylinders. The gaseous compounds are to be used in performance audits as designated by the USEPA Project Officer. These performance audits are to assess the relative accuracy of source measurement systems during hazardous waste trial burn tests and ambient air monitoring programs.

The audit materials currently contain 29 compounds selected on the basis of anticipated needs of USEPA's Office of Solid Waste and Office of Air Quality Planning and Standards. Table 1 lists the five groups of compounds, the concentration ranges, and the number of cylinders in each group. The balance gas for all gas mixtures is nitrogen and the cylinder construction material is aluminum.

The gaseous compounds are acquired from commercial suppliers in compressed gas cylinders. These cylinders, in conjunction with an appropriate delivery system, are used directly as sources of the gaseous compounds during performance audits. The accuracy of the supplier-reported levels of these compounds is verified through measurement of specially prepared standards supplied by the National Bureau of Standards (NBS) as compressed gas mixtures in aluminum cylinders.

The accuracy of the cylinder concentrations and the verification of stability of the compounds in the cylinders are important. Along with

Table 1. *PPB Level Organic Gases Currently Available*

Group	No. of Cylinders	Concentration Range of Each Compound (ppb)
Group I*	29	7-90
	12	90-430
	12	430-10,000
Group II**	12	7-90
	6	90-430
Group III***	14	7-90
	3	90-200
Group IV****	12	7-90
	6	430-10,000
Group V*****	6	1-40

* *Group I Compounds: Carbon tetrachloride, chloroform, tetrachloroethylene, benzene, and vinyl chloride.*

** *Group II Compounds: Trichloroethylene, 1,2-dichloroethane, 1,2-dibromoethane, acetonitrile, trichlorofluoromethane (F-11), dichlorodifluoromethane (F-12), bromomethane, methyl ethyl ketone, and 1,1,1-trichloroethane.*

*** *Group III Compounds: Pyridine[1], Vinylidene Chloride, 1,1,2-trichloro-1,2,2-trifluoroethane (F-113), 1,2-dichloro-1,1,2,2-tetrafluoroethane (F-114), acetone, 1,4-dioxane, toluene, and chlorobenzene.*

[1]Pyridine concentrations are not certified due to analytical problems

**** *Group IV Compounds: Acrylonitrile, 1,3-butadiene, ethylene oxide, methylene chloride, propylene oxide, and o-xylene.*

***** *Group V Compounds: Vinyl chloride, 1,3-butadiene, bromomethane, trichlorofluoromethane (F-11), methylene chloride, chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane, benzene, carbon tetrachloride, 1,2-dichloropropane, trichloroethylene, toluene, 1,2-dibromoethane, tetrachloroethylene, chlorobenzene, ethylbenzene, and o-xylene.*

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 the cylinder gases that are currently available.

Procedure

Once a mixture of compounds is chosen, a commercial supplier is contacted to determine if a cylinder containing the compounds of interest can be prepared. If so, the manufacturer prepares the cylinder gases and determines the concentration of the analytes in the cylinder at least two times. The cylinder is sent to RTI where its contents are analyzed as soon as it arrives. The gas mixtures are again analyzed at 2 months, 6 months, 12 months and on a yearly basis following the initial analysis to determine the stability of the gas mixtures.

All recent analyses (1987) for Group I, II, III, IV and V mixtures are performed using a Nutech automated cryogenic preconcentration apparatus with cryofocusing in conjunction with a Hewlett-Packard 5880A gas chromatograph equipped with flame ionization detector. Previous analyses (prior to 1987) of all the mixtures are performed by direct injection instead of cryogenic preconcentration. The gas chromatographic parameters used in the measurement of individual compounds in Group I, Group II, Group III, Group IV and Group V are described in the status report.

Compressed gas cylinder standard mixtures obtained from NBS are used as calibration standards for Group I, Group II, Group III, Group IV and Group V A different NBS standard was analyzed as internal quality control on each day of RTI analysis.

RTI supplies cylinder gases for audits upon request from the USEPA, state or local agencies or their contractors. When a request is received, the cylinder is then shipped by a freight carrier to the laboratory being audited. A letter is also included with the cylinder 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. There is no charge for the audit except the cost of returning the audit cylinder.

Results and Discussion

To date, 198 performance audits have been initiated; 172 are complete. The results obtained are given in the status report. Generally, the audit results are within ± 50 percent of the audit concentrations measured by RTI

Relative accuracies of the cylinder gas analyses for Group I, Group II, Group III, Group IV and Group V have been determined using NBS primary standards. An examination of the data in the status report to assess long-term stability shows that values for the compounds in the Group I, Group II, Group III, Group IV and Group V cylinders vary by less than 10 percent for 3 to 5 analyses over a one to three year period. This variation indicates the im-precision of the measurement process. Precision of the measurement process will be greatly enhanced once the analytical system becomes fully automated

The procedure used for the determination of day-to-day measurement uncertainty (repeatability) for the five groups of compounds and estimates of uncertainty values are presented in the status report.

Conclusions

Compressed gas cylinders containing 29 gaseous organic compounds at parts-per-billion levels has been used successfully in audits to assess the relative accuracy and precision of analytical systems, especially those used during hazardous waste trial burn tests and ambient air monitoring. To date, 198 performance audits have been initiated and 172 are complete. Generally the audit results are within ± 50 percent of the audit concentrations measured by RTI

Stability studies for 29 gaseous organic compounds included in the cylinders have been performed to determine the feasibility of using them as audit materials. Results indicate that all of the organics tested are stable enough for use as reliable audit materials except ethylene oxide and propylene oxide at low concentrations.

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The complete Status Report #4, entitled "Stability of Parts-per-Billion Hazardous Organic Cylinder Gases and Performance Audit Results of Source Test and Ambient Air Measurement Systems," (Order No. PB 88-201 504/AS; Cost: $25.95, subject to change) will be available only from:
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