United States
Environmental Protection
Agency

Research and Development

Environmental Monitoring Systems
Laboratory
Research Triangle Park NC 27711

EPA/600/S4-85/032 June 1985

EPA

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 #1

R. K. M. Jayanty, S. W. Cooper, J. Sokash, C. E. Decker, and D. J. von Lehmden

A repository of 14 gaseous organic compounds at parts-per-billion (ppb) levels in compressed gas cylinders has been established under the contract with the Environmental Protection Agency (EPA). the primary objectives of this on-going project are: (1) to provide accurate gas mixtures to EPA, state/local agencies, or their contractors 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 with time; (3) to determine the stability of the gas mixtures with time; and (4) to develop new audit materials as requested by EPA.

The repository consists of two mixtures of five and nine organic compounds each. These mixtures were blended in aluminum cylinders in a balance gas of nitrogen. The five component mixture (Group I) contains carbon tetrachloride, chloroform, perchloroethylene, vinyl chloride, and benzene. The nine component mixture (Group II) includes trichloroethylene, 1,2-dichloroethane, 1,2-dibromethane, acetonitrile, trichlorofluoromethane, dichlorodifluoromethane, bromomethane, methyl ethyl ketone, and 1,1,1-trichloroethane. To date, 20 performance audits have been initiated and 12 are complete. The results of these audits and a description of the experimental procedures used for analyses and available stability data are presented in this status report. Generally, the results of the audits show close agreement (plus or minus 50 percent) with the audit material concentrations measured by Research Triangle Institute.

Limited stability studies of all 14 gaseous organic compounds have been performed. Results indicate that all the compounds tested are adequately stable for use as reliable audit materials. Detailed statistical analyses which would separate statistical deviations from true concentration changes with time are in progress and will be presented in a future report.

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 EPA'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. The Research Triangle Institute (RTI), under contract to the U.S. Environmental Protection Agency (USEPA), has responded to this need through development of a repository of 14 gaseous organic compounds at parts-per-billion (ppb) levels in compressed gas cylinders. The gaseous compounds are to be used in performance audits as designated by the EPA 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 repository currently contains 14 compounds selected on the basis of anticipated needs of EPA's Office of Solid Waste. Table 1 lists the 14 compounds, the concentration ranges, and the number of cylinders for each group in the repository. 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 same cylinders, along 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 are verified through measurement using commercial permeation tubes. The permeation rates of the commercially available tubes are verified gravimetrically 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 being performed. This study involves periodic analyses of the contents of each of the cylinders in the repository.

Procedure

Once a mixture of compounds is chosen, a commercial supplier is contacted to determine if a cylinder containing those compounds can be prepared. If so, the manufacturer prepares the cylinder gases and determines the concentration of the analytes in the cylinder by at least two times. The cylinder is sent to RTI where its contents are analyzed usually within ten days of its arrival. If the RTI value varies from the manufacturer's value by more than 25 percent, an analysis is usually performed by a third party (EPA or NBS). The gas mixtures are again analyzed at 2 months, 6 months, and at one year following the initial analysis to determine the stability of the gas mixtures.

Table 1. PPB Level Organic Gases in Repository

Group	No. of Cylinders	Concentration Range of Each Compound (ppb)
Group I*	20	7-90
	12	90-430
Group II**	13	7-90
	3	90-430

*Group I Compounds—carbon tetrachloride, chloroform, perchloroethylene, vinyl chloride, and benzene.

**Group II Compounds—trichloroethylene, 1,2,-dichloroethane, 1,2-dibromoethane, acetonitrile, trichlorofluoromethane (Freon-11), dichlorodifluoromethane (Freon-12), bromoethane, methylethylketone, and 1,1,1-trichloroethane.

All analyses are performend using a Hewlett-Packard 5880A gas chromatograph equipped with flame ionization and electron capture detectors. The electron capture detector (ECD) has been used principally for measurement of all the chlorinated hydrocarbons except vinyl chloride. Vinyl chloride, benzene, methyl ethyl ketone, and acetonitrile are analyzed with flame ionization detector (FID). The gaseous samples are injected onto the columns by means of a six-port gas sampling valve constructed of Hastalloy C (high nickel content and low adsorption properties) mounted near the injection port. The valve is equipped with interchangeable sampling loops (1 cc and 10 cc) to allow the injection of variable but known volumes of gas. The gas chromatographic parameters used in the measurement of individual compounds are described in the status report.

Permeation tubes purchased from Metronics are generally used as calibration standards for all 14 organic compounds unless otherwise specified. The permeation rate of each permeation tube is determined every 15 to 30 days by weight-loss determination of each tube.

The RTI supplies repository cylinders for audits upon request from the EPA, 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 audi concentrations are provided to the requesting agency Audit Coordinator. Afte the laboratory being audited has analyzec the contents of the cylinder, the Audi Coordinator reports the value(s) to RTI which in turn reports both the measurec 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, 20 performance audits have been initiated; 15 are complete. All audits initiated have been for Group I compounds, since Group II compounds have only recently been verified and approved for performance audits. The results obtained for a few typical performance audits are shown in Table 1 and the rest are given in the status report. Generally, the audit results are within ± 50 percent of the audit concentrations measured by RTI.

Most of the cylinders in the repository are analyzed two to three times to determine the stability of the compounds.

Relative accuracies of the cylinder gas analyses for Group I compounds have been determined using the NBS primary standards. However, relative accuracies of cylinder gas analyses for Group II compounds will not be established until NBS primary standards are analyzed in conjunction with these gas cylinders. This will be done during the third RTI analyses of group II cylinder gases. An examination of stability data in the status report shows values for Group I individual cylinder gas analyses usually vary by less than 10 percent for 3 analyses over an 8-month period. Since only 3 months of stability analyses are currently available in Group II cylinders, a statement of the variability will be made in a future report. This variation indicates changes in cylinder contents (i.e., instability) and the imprecision of the measurement process. The possible sources of experimental error that could result in apparent changes in concentrations include: (1) the variability of the analytical technique used for analyses; (2) stability of and/or accuracy of calibration standards; and (3) the accuracy of reproducing standards. Each of these sources of variability contributes to the net uncertainty of the resulting stability data. Estimates of day-to-day measurement uncertainty (repeatability) for Group I and Group II compounds have not been performed at the present time. However, the repeatability measurements to determine the total uncertainty

will be performed in the near future. The repeatability measurement results will be included in a future report. The uncertainty for the gas chromatographic measurement has been determined to be less than 3 percent by multiple injections of the gas during same-day analysis.

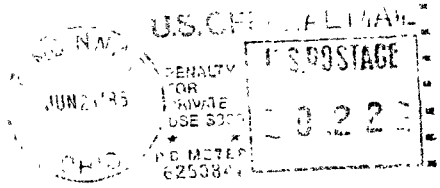
Conclusions

A repository of 14 gaseous organic compounds at parts-per-billion levels in compressed gas cylinders 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, 20 performance audits have been initiated and 15 are complete. Generally the audit results are within ± 50 percent of the audit concentrations measured by RTI.

Limited stability studies of all 14 gaseous organic compounds have been performed to determine the feasibility of using them as audit materials. Results indicate that all of the organics tested are adequately stable to be used as reliable audit materials. Detailed statistical analyses which would separate statistical deviations from true concentration changes with time are in progress and will be presented in a future report.

R. K. M. Jayanty, S. W. Cooper, J. Sokash, and C. E. Decker are with Research Triangle Institute, Research Triangle Park, NC 27709.
***Darryl J. von Lehmden** is the EPA Project Officer (see below).*
The complete report, entitled "Stability of Parts-Per-Billion Hazardous Organic Cylinder Gases and Performance Audit Results of Source Test and Ambient Air Measurment Systems," (Order No. PB 85-188 860/AS; 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
The EPA Project Officer can be contacted at:
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

☆ U.S. GOVERNMENT PRINTING OFFICE: 1985—559-016/27080



OCOC329 PS

U S ENVIR PROTECTION AGENCY
REGION 5 LIBRARY
230 S DEARBORN STREET
CHICAGO IL 60604