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Stability of Air Toxic Gases Listed in Title III Clean Air Act Amendments

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INTRODUCTION

Under Title III of the 1990 Clean Air Act Amendments, the U.S. Environmental Protection Agency (EPA) has recently proposed Test Method 301 entitled "Field Validation of Emission Concentrations from Stationary Sources."[1] This method, as specified in the applicable subpart of the Amendments, is to be used whenever a source owner or operator proposes a test method to meet an EPA requirement for which a validated method is not available. This method includes procedures for determining and documenting the quality, i.e., systematic error (bias) and random error (precision), of the measured concentrations of the source emissions. In proposed Test Method 301, the requirement was added that a performance audit material must be analyzed if it is available. The method also stated that the analyst shall sample and analyze the performance audit sample three times according to the instructions provided with the audit sample. Therefore, EPA's Atmospheric Research and Exposure Assessment Laboratory has initiated a program to develop stable and accurate organic standards (listed in Title III, 1990 Clean Air Act Amendments) for use in performance audits. The Research Triangle Institute (RTI), under contract to EPA, has responded to this need by developing a repository of 59 gaseous organic compounds in compressed gas cylinders and recyclable aluminum containers (Scotty IV). Three concentration ranges were selected: low (20 to 200 ppb), mid-level (0.5 to 5 ppm), and high (5 to 50 ppm). The recyclable aluminum containers were obtained only in the low concentration range with pressures generally below 400 psig. The compressed gas cylinders contain pressures up to 2000 psig.

In order to ensure that the concentration of each gas standard had not changed, each standard was analyzed periodically for stability. The gas mixtures were analyzed initially by the manufacturer before shipment to RTI. Upon receipt from the gas manufacturer, RTI analyzed the gas mixtures to verify the manufacturer's certified analysis. Subsequently, the gas mixtures were analyzed periodically (analyzed at 2 to 4 months, 12 months, and thereafter yearly) to determine any change in concentration of the organic compounds.

Compressed gas cylinders containing toxic organics at ppm and ppb levels that have been used successfully for performance audits during environmental measurements are described extensively in the literature.[2-6] A list of organic standards that are currently available for Test Method 301, the procedures used to determine the stability of the gas mixtures, and examples of stability data are given in this paper. In addition, the usefulness and the stability of organic compounds in Scotty IV containers are described.

AUDIT MATERIALS CURRENTLY AVAILABLE

In 1990, Title III of the Clean Air Act Amendments listed 189 air toxics for which EPA must develop Maximum Achievable Control Technology (MACT) regulations. Fifty-nine gaseous organic compounds out of 189 compounds were selected. The selected compounds were used to perform the stability study and as audit materials to conduct performance audits during field validation of emission concentrations from stationary sources. Table I lists these compounds, which are currently available in

TABLE I. Organic cylinder gases currently available for clean air act aegulations.

Available Gases	
Acetaldehyde	Hexachloroethane
Acetonitrile	Hexachloro 1,3-butadiene
Acrolein	Isooctane
Allyl chloride	Methanol
Benzene	Methyl bromide
Bromoform	Methyl chloride
Bromomethane	Methylene chloride
Bis (2-chloromethyl) ether	Methyl ethyl ketone
Carbon disulfide	Methyl isobutyl ketone
Carbon tetrachloride	Methyl iodide
Carbonyl sulfide	Methyl methacrylate
Chlorobenzene	Methyl-t-butyl ether
2 Chloro-1,3-butadiene	2-Nitropropane
Chloroform	Perchloroethylene
Chloromethyl benzene	Perchloroethane
Chloroprene	Propylene oxide
Cumene	Propanol
1,2-Dibromoethane	Propionaldehyde
1,2-Dichloroethane	Styrene
1,1-Dichloroethane	1,1,2,2-Tetrachloroethane
1,1-Dichloroethylene	Toluene
Dichloroethyl ether	Trichloroethylene
1,2-Dichloropropane	1,2,4-Trichlorobenzene
1,3-Dichloropropane	1,1,2-Trichloroethane
1,4-Dioxane	2,2,4-Trimethylpentane
Ethylene oxide	Vinyl acetate
Ethyl benzene	Vinyl bromide
Ethyl chloride	Vinyl chloride
Ethyl acrylate	p-Xylene
Hexane	

the audit repository. Each compound was prepared in compressed gas cylinders in a balance gas of nitrogen. The Scotty IV's contained only the low concentration range.

EXPERIMENTAL PROCEDURES

The principal objective of this study was to determine the stability of gas mixtures in compressed gas cylinders and recyclable containers (Scotty IV) over time. All measurements were made by gas chromatography (GC) using flame ionization (FID) and flame photometric (FPD) detectors.

INSTRUMENTATION

Analyses of gas mixtures above the 1-ppm level were performed with a Hewlett-Packard 5880 GC with a FID and a FPD. The FPD was used principally for measurement of sulfur-containing species. Gaseous samples were injected onto the appropriate column using a six-port Valco gas sampling valve constructed of Hastalloy C (high nickel content and low absorptive properties) mounted near the injection port. The valve was equipped with interchangeable sample loops to allow the injection of a fixed volume of gas. After separation of the compound from nitrogen, the detector response was integrated electronically. GC conditions for analysis have been described in a separate report.[4]

Analyses of gas mixtures below the 1-ppm level (e.g., ~100 ppb mixtures in compressed gas cylinders and recyclable containers) were performed using a Nutech automated cryotrapping apparatus configured to a Hewlett-Packard 5880A GC equipped with a subambient oven controller and flame ionization and electron capture detectors (FID/ECD). The carrier gas outlet flow from the column was split approximately 10:1 between the FID and ECD using a vitreous silica outlet splitter. Both the FID and the ECD signals were processed with the HP-5880A Level 4 processors.

STANDARDIZATION AND MEASUREMENT

The GC for the gas mixtures was calibrated using appropriate calibration standards comprised of known concentrations of gases in nitrogen. The preparation method for or source of calibration standards varied depending on the compound involved. National Institute of Standards and Technology-Standard Reference Materials (NIST-SRMs) of benzene and perchloroethylene were used to calibrate the GC for those two compounds.

When NIST-SRMs were not available, known concentrations of analytes were generated from permeation tubes or from pure compounds. The calibration gases for hydrogen sulfide, vinyl chloride, and ethylene oxide were generated using a permeation tube/dilution system. For all other compounds, the calibration standard preparation technique consisted of syringe injection of known quantities of pure (<99.95%) organic compound into an evacuated blank checked stainless steel canister of known volume. The canister was then filled with pure nitrogen, and its final pressure was measured with a Heise-gauge. The concentration of the gas mixture was calculated using the Ideal Gas Law. The

sample was diluted further by depressurization and repressurization with pure nitrogen to achieve its desired concentration. A standard was prepared fresh for each time period. For each of these approaches, multipoint calibration curves were prepared each time a cylinder gas was analyzed.

ANALYTICAL QUALITY CONTROL

As a quality control check on the accuracy of calibration mixtures prepared by the pressure-dilution technique, NIST-SRMs of benzene or propane in nitrogen were analyzed by GC-FID against selected compound calibration standards. The prepared calibration mixture was used to establish the detector response on a ppm-carbon basis.

During both the ppm- and ppb-level cylinder gas analyses, replicate injections of both the audit cylinder gases and the calibration standards were performed until the relative standard deviation of replicate injections was less than 1 percent.

RESULTS AND DISCUSSION

Stability Studies - Cylinder Gases

The data collected over time from the measurement of cylinder concentrations were used to estimate the stabilities of the organic gases. Cylinder gas stability data are important for several reasons. First, audit materials used by Federal, State, and local governmental agencies must be stable to be considered reliable standards for auditing measurement methods during regulatory compliance emission tests. Second, if organic gases in cylinders are stable, other investigators may more readily use cylinder gases as calibration standards and/or quality control check samples. Finally, if cylinder contents are stable, government agencies may conduct performance audits to assess the accuracy of the measurement methods being developed during tests for operating permits under Title III of the 1990 Clean Air Act Amendments.

The term "stability," as it pertains to the study of gaseous compounds, is defined as the change in concentration with time for a given cylinder at a specified concentration range. To ensure that the concentration of each gas standard had not changed, each standard was analyzed periodically for stability. A two-tiered stability assessment was conducted. In the first tier, on each standard, the commercial gas manufacturer conducted one or two analyses prior to shipment. Once a gas standard was received from the gas manufacturer, it was analyzed as soon as within one month, then reanalyzed periodically to determine any change in concentration.

The stability data obtained to date for 30 of the organics (listed in the Clean Air Act Regulations) in the ppm-level gas cylinders have been published in a status report. An example of

stability data for selected organic cylinder gases is shown in Table II. (The stability studies for the remaining 29 compounds are in progress.) An examination of the stability data for many of the organics in the ppm-level cylinder gases shows that the

TABLE II. Example of stability data for selected ppm-level gases in compressed gas cylinders.

Day	Benzene	Toluene	Chloroform	Perchloro-ethylene	Vinyl Chloride
Conc.	9.14[a]	9.0[a]	9.81[a]	7.98[a]	8.52[a]
Date[b]	5/4/78	3/29/83	1/10/86	7/6/79	10/1/79
Conc.	9.10	8.51	8.92	8.40	7.85
Day[c]	132	744	534	52	700
Conc.	7.80	8.04	9.45	7.92	8.41
Day	302	1063	756	376	1812
Conc.	8.50	9.07	9.74	7.94	8.15
Day	1005	1548	1077	1818	2524
Conc.	8.17	9.37	9.54	6.88	8.13
Day	1209	1766	1201	2440	2914
Conc.	8.42	9.12	9.91	7.83	7.60
Day	2162	2092	2020	2901	3088
Conc.	8.40	8.79	9.44	7.68	7.79
Day	2784	2597	----	3118	3404
Conc.	8.72	9.44	----	7.39	7.66
Day	3326	2915	----	3580	3844
Conc.	8.88	9.07	----	7.69	7.49
Day	3549	----	----	3834	4265
Conc.	9.17	----	----	7.37	7.67
Day	3887	----	----	4323	----
Conc.	8.89	----	----	7.38	----
Day	4778	----	----	----	----
Conc.	8.80	----	----	----	----

a = Manufacturer's analysis
b = Date of RTI first analysis.
c = Number of days since RTI's first analysis.

results varied by less than 10 percent over a period of up to ten years. This variation results primarily from random error during the stability analytical measurements. The possible sources of experimental errors in the measurement process that contribute to this variability include: (1) the variability of the instrumentation used for analysis (2) the stability of the calibration standards and (3) the accuracy of independently-produced calibration standards where NIST-SRMs do not exist.

Estimates of day-to-day measurement uncertainty (repeatability) for all components have not been performed. However, the measurement uncertainties for the halocarbons and eight other organics have been published in the open literature.[2,3] The measurement uncertainty varied from less than 1 percent to 10 percent depending on the compound, and a major portion of the uncertainty was attributed to the method of preparation of the calibration standard. The uncertainty of the GC analysis was determined to be less than 2 percent by multiple injections of the gas during same-day analyses.

Stability Studies - Cylinder Gases vs. Scotty IV Containers

As noted, RTI has obtained organic gases at 20- to 200-ppb ranges in both compressed gas cylinders and recyclable containers (Scotty IV) to determine their stabilities. Recyclable containers (Scotty IV) are especially suitable for holding audit materials for a number of reasons including simplicity, portability, and low cost. However, the stability of organic compounds in these containers is not well established. Hence, stability studies of the 59 organic compounds in both compressed gas cylinders and Scotty IV containers have been initiated. Table III summarizes the results of the stability studies of organic gases in compressed gas cylinders and Scotty IV containers. An examination of the data indicates that the stability in Scotty IV containers depends on the type of compound held; in general, many compounds (23 out of 59) were found to be unstable relative to those in compressed gas cylinders. Ten of the 59 organic compounds (Acetaldehyde, 1,3-dichloropropane, ethylene oxide (below 100 ppb), propylene oxide (below 100 ppb), ethyl acrylate, hexachloro-1,3-butadiene, methanol, propanol, propionaldehyde, and 1,2,4-trichlorobenzene) were found to be unstable in cylinders as well as in Scotty IV containers; thus they are not suitable as audit materials.

SUMMARY AND CONCLUSIONS

Compressed gas cylinders containing 59 gaseous organic compounds at three concentration levels have been evaluated for use in calibration and performance audits during source emissions measurements. Stability studies indicate that many of these organic compounds have been found to be stable in compressed gas cylinders but unstable for certain compounds in recyclable containers. A compound was rated stable if the concentration did

Table III. Summary of stability of organic cylinder gases 3-Ft.^{3} Scotty IV containers vs. 150-FT.^{3} compressed gas cylinders at ppb levels.[a,b]

Compound	3-ft.^{3} Scotty IV	150-ft.^{3} Cylinders
Acetaldehyde	Unstable	Unstable
Acetonitrile	Unstable	X
Acrolein	Unstable	X
Allyl chloride	X	X
Benzene	X	X
Bromoform	X	X
Bromomethane	N/A	X
Bis (2-Chloromethyl)ether	Unstable	X
Carbon disulfide	X	X
Carbon tetrachloride	X	X
Carbonyl sulfide	X	X
Chlorobenzene	X	X
2-Chloro-1,3-butadiene[b]	N/A	N/A
Chloroform	X	X
Chloromethyl benzene	Unstable	X
Chloroprene	N/A	N/A
Cumene	X	X
1,2-Dibromoethane	Unstable	X
1,2-Dichloroethane	X	X
1,1-Dichloro-ethylane	X	X
1,1-Dichloro-ethylene	X	X
1,1-Dichloroethyl ether	Unstable	X
1,2-Dichloro-propane	X	X
1,3-Dichloro-propane	Unstable	Unstable
1,4-Dioxane	Unstable	X
Ethylene oxide	Unstable	Unstable
Ethyl benzene	X	X
Ethyl chloride	X	X
Ethyl acrylate	Unstable	Unstable
Hexane	X	X
Hexachloro-ethane[c]	N/A	N/A
Hexachloro 1,3-Butadiene	Unstable	Unstable
Isooctane	X	X
Methanol	Unstable	Unstable
Methyl bromide	X	X
Methyl chloride	X	X
Methylene chloride	X	X
Methyl ethyl ketone	Unstable	X
Methyl isobutyl ketone	Unstable	X
Methyl iodide	X	X
Methyl methacrylate	X	X
Methyl-t-butylether	X	X

Table III (Continued)

Compound	3-ft.^{3} Scotty IV	150-ft.^{3} Cylinders
2-Nitropropane	Unstable	X
Perchloro-ethylene	X	X
Perchloro-ethane	N/A	N/A
Propylene oxide	Unstable	Unstable
Propanol	Unstable	Unstable
Propionaldehyde	Unstable	Unstable
Styrene	X	X
1,1,2,2-Tetrachloroethane	Unstable	X
Toluene	X	X
Trichloro-ethylene	X	X
1,2,4-Tri-chlorobenzene	Unstable	Unstable
1,1,2-Tri-chloroethane	X	X
2,2,4-Tri-methylpentane	N/A	N/A
Vinyl acetate	Unstable	X
Vinyl bromide	X	X
Vinyl chloride	X	X
Xylene	Unstable	X

X = stable; N/A = not analyzed
a = nominal concentration 20-200 ppb
b = Reactive
c = Encountered analytical problems

not change by 10 percent over its period of testing (up to ten years). Ten compounds (acetaldehyde, 1,3-dichloropropane, ethylene oxide, propylene oxide, ethyl acrylate, hexachloro-1,3-butadiene, methanol, propanol, propionaldehyde, and 1,2,4-trichlorobenzene) were found to be unstable in cylinders as well as in Scotty IV containers and are therefore not recommended for use as audit materials.

DISCLAIMER

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16. ABSTRACT

A repository of 59 organic compounds has been established by the U.S. Environmental Protection Agency (EPA) for use as gas standards in performance audits during field validation of emission concentrations from stationary sources. These compounds are listed in Title III of the 1990 Clean Air Act Amendment. The compounds are prepared in compressed gas cylinders and recyclable aluminum containers. Three concentration ranges were selected: low (20 to 200 ppb), mid-level (0.5 to 5 ppm), and high (5 to 50 ppm). The recyclable aluminum containers were only prepared in the low range, and pressures were generally below 400 psig. The compressed gas cylinders contained pressures up to 2000 psig. In this program to ensure that the concentration of each gas standard had not changed, each standard was analyzed periodically for stability. The gas mixtures were analyzed by the manufacturer before shipment. They were then analyzed upon receipt, and reanalyzed periodically to determine any change in concentration. The stability data obtained to date indicates that many compounds are stable in the compressed gas cylinders; however, some of the compounds in the recyclable containers are not stable.

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