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Development of gas standards from solid 1,4-dichlorobenzene

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Abstract

For over fifteen years the National Institute of Standards and Technology (NIST) has been preparing gas standards containing volatile organic compounds at sub μmol/mol (ppm) concentrations. These standards have been prepared using organic compounds that are either gases or liquids at room temperature. A microgravimetric technique was developed previously to prepare standards containing these compounds in treated aluminum gas cylinders using a one step dilution. Requests were received to prepare gas standards containing the compound 1,4-dichlorobenzene. These requests posed a major problem in that 1,4-dichlorobenzene is a solid at room temperature. Research was undertaken, using the microgravimetric procedure, to determine if it was feasible to prepare gas standards from solid phase compounds. In the first stage of research the liquid phase compound 1,2-dichlorobenzene, previously studied at NIST in gas mixtures, was used as an internal standard. Results from analyses of a prepared gas standard showed that the response factor on a gas chromatograph flame-ionization detector for 1,3-dichlorobenzene was 3% less than that for 1,2-dichlorobenzene. Additional analyses using liquid solution standards also showed a lower response factor for 1,3-dichlorobenzene of 2.9% on average. It was assumed that 1,4-dichlorobenzene would have a similar response and that the 1,2-dichlorobenzene response could be used to determine the concentration of 1,4-dichlorobenzene. Analyses of a liquid solution standard confirmed that the response factor for 1,4-dichlorobenzene was on average 3.2% less than that of 1,2-dichlorobenzene. A gas standard was prepared containing 1,2- and 1,4-dichlorobenzene at nominal concentrations of 250 nmol/mol (ppb). Analytical results showed that the concentration of 1,4-dichlorobenzene determined from 1,2-dichlorobenzene was within 3% of the gravimetric value. Further research using two standards containing 1,4-dichlorobenzene revealed that they agreed exactly with the gravimetric concentrations. These results verified the ability to prepare accurate gas standards of 1,4-dichlorobenzene in gas cylinders.

1. Introduction

The compound 1,4-dichlorobenzene is of interest to such agencies as the United States Environmental Protection Agency (US-EPA) and the California Air Resources Board (CARB) in their toxic organic air monitoring programs. The US-EPA has listed 1,4-dichlorobenzene as a priority pollutant. It is of interest due to its human health effects. Prolonged and repeated exposure to 1,4-dichlorobenzene may result in permanent damage to the liver, lungs, and kidneys. The compound is a suspected carcinogen and is also thought to cause leukemia. This compound is used commercially as an insecticide for control of ants and fruit borers, especially in peach trees. It may be applied to tobacco seed beds for blue mold control and to leather and fabrics to control mildew and mold. In domestic use it is a combatant against clothes moths. Sometimes 1,4-dichlorobenzene is used as a fumigant for garbage and restrooms. It is used as

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a chemical intermediate for the production of engineering plastics used for surface coatings and model resins [3].

In order to determine the amount of 1,4-dichlorobenzene in ambient air, gas standards are needed to calibrate the analytical instruments used to make those determinations. 1,4-Dichlorobenzene is a solid in the form of crystals at room temperature, with a melting point of 53°C. Therefore it was thought to be extremely difficult, if not impossible, to quantitatively transfer a solid organic compound into an aluminum gas cylinder and have it remain completely in the gas phase. A micrograviметric technique previously developed to prepare gas standards from liquid organic compound was considered as a possible method [1,2]. Research was undertaken to determine if this micrograviметric technique could be employed to accurately prepare gas standards containing 1,4-dichlorobenzene in nitrogen.

2. Experimental

2.1. Chemicals

The reagents 1,2-dichlorobenzene and 1,4-dichlorobenzene were purchased from commercial suppliers. These compounds were analyzed for impurities by gas chromatography–mass spectrometry (GC–MS) and gas chromatography–flame ionization detection (GC–FID) at NIST. High purity nitrogen (99.9995%) diluent gas was obtained from a commercial gas supplier. The nitrogen was analyzed by NIST and was found to be free of the compounds of interest.

2.2. Gas cylinders

New 30 liter volume aluminum gas cylinders with CGA-350 brass valves were used to prepare the gravimetric standards. The cylinders were cleaned by the manufacturer using a caustic etch process followed by an acid wash. These cylinders were then treated by Scott Specialty Gases using a proprietary chemical vapor deposition process, ACULIFE®[1], to passivate the interior wall surface.

2.3. Weighing apparatus

The solid and liquid organics were sealed into glass capillary tubes and weighed before and after filling on a microbalance. The balance used has a mechanical tare capacity of up to 2.99 g, an electrical weighing range of 15 mg, and a readability of 0.1 μg. The 30 liter aluminum gas cylinders were weighed on a floor balance with a capacity of 54 kg and a readability of 1 g.

2.4. Gravimetric procedure for preparing gas standards

A micrograviметric procedure was used to prepare the gas standards containing 1,2-dichlorobenzene and the solid 1,4-dichlorobenzene. A thin-walled glass capillary tube of 1.6 mm O.D. by approximately 2.0 cm long was prepared from a 10 cm tube by heating a section in a flame and pulling it into a fine point. The tube was broken in the thin drawn area, leaving a very small opening. The other end of the tube was drawn out to a fine point and then sealed. Several tubes were prepared in this manner and then weighed several times against a control tube sealed at both ends. This control tube was weighed first and last, being used to correct for balance drift. A small amount of 1,4-dichlorobenzene crystals was placed in a glass vial. This vial was heated using a heat gun until the crystals melted. The open end of a capillary tube was placed into the liquid 1,4-dichlorobenzene in the vial. A plastic syringe was adapted onto the vial. While still heating the vial with the now liquid 1,4-dichlorobenzene, the syringe plunger

[1] *Disclaimer.* Certain commercial equipment, instruments or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards an Technology, nor does it imply that the materials or equipment are necessarily the best available for the purpose.

was pulled out, drawing air from the vial and enclosed capillary tube. When the syringe plunger was subsequently released, liquid 1,4-dichlorobenzene moved into the capillary tube. The capillary tube was removed and centrifuged such that the liquid was forced to the sealed end. Some of the 1,4-dichlorobenzene crystallized on the capillary walls before it was forced to the sealed end of the tube. The open capillary end was then flame sealed. The 1,4-dichlorobenzene quickly recrystallized in the capillary tube. Acetone, in which 1,4-dichlorobenzene is very soluble, was used to carefully wipe the capillary tube to remove any 1,4-dichlorobenzene which may have crystallized on the outside surface. The capillary tube was reweighed three times to determine the amount of organic compound. A capillary tube containing 1,2-dichlorobenzene was prepared in the same manner, except that heating the vial was not necessary since the compound is already a liquid at room temperature.

An evacuated, preweighed cylinder was fitted with the appropriate CGA-350 fitting to which a piece of tubing, made from fluorinated ethylene-propylene copolymer, was attached. The capillary tube containing the 1,4-dichlorobenzene was inserted into the tubing. The diameter of the tubing was such that the capillary fit tightly and created a seal. Since 1,4-dichlorobenzene boils at 174°C, the potential for recrystallization of the compound in the valve fitting before it actually reached the interior of the cylinder was a major concern. The stainless steel fitting on the cylinder valve was therefore heated (the temperature inside the fitting was measured at 200°C) during transfer. After opening the cylinder valve, the capillary tube was broken at the end closest to the valve. Heating the capillary tube with a heat gun first liquified the crystalline 1,4-dichlorobenzene and eventually vaporized the compound, at which point it was pulled into the cylinder by the vacuum. After it appeared that all the 1,4-dichlorobenzene had been vaporized, the other end of the capillary tube was broken. The area was purged with pure nitrogen, with continued heating, to flush residual 1,4-dichlorobenzene into the cylinder. The 1,2-dichlorobenzene was then added into the cylinder in the same manner except that only some heat was needed. High-purity nitrogen was then added to a pressure of 12.4 MPa and the cylinder weighed to determine the amount added. The concentrations of the two organic compounds were calculated on a nmol/mol basis using the weight data.

Caution. Since the compounds employed are toxic, all procedures involving the use of the pure reagents were performed in a exhaust hood. Before the cylinders were pressurized with high-purity nitrogen, all manifold fittings were checked for leaks. Safety glasses were worn at all times. Extreme care must also be taken not to overheat the cylinder valve to prevent melting of the material in the safety relief valve.

2.5. Analytical conditions

Analysis of the gas standards was conducted using a gas chromatograph equipped with a flame-ionization detector (GC–FID) operated at 250°C. A 60 m × 0.75 mm I.D. open tubular capillary column coated with a 1 μm thick film of polyethylene glycol was use. The initial temperature was held at 50°C for 4 min then temperature programmed to 240°C at 10°C/min. The column carrier flow-rate was 10 ml/min of nitrogen with a detector make-up flow of 30 ml/min. Each sample was cryogenically trapped at −100°C for 5 min at a sample flow-rate of 50 ml/min. Flow was controlled by a mass flow controller. After the trapping sequence was finished, the sample valve was actuated to the inject position. The sample trap was electrically heated to 200°C to desorb the analytes into the GC column.

3. Results and discussion

It is ideal to prepare a standard containing organic species using the simplest technique possible so as to reduce errors and sources for compound loss. Since 1,4-dichlorobenzene is a solid at room temperature there was a major

concern as to whether it could be quantitatively transferred to a gas cylinder without losing some, if not all, by crystallization on the surface of the transfer area. One possible method would be to place some 1,4-dichlorobenzene in a small stainless steel container fitted with a valve, warm it slightly, and transfer that headspace into an evacuated cylinder. However, this method would be limited to preparing high concentration mixtures. Successive dilutions of this high concentration standard would be required to reach a low nmol/mol concentration mixture, due to weighing limitations. This method would greatly increase the possibility of losing 1,4-dichlorobenzene in the transfer process. The amount of 1,4-dichlorobenzene needed to prepare a 250 nmol/mol gas standard in one step using a 30 l aluminum gas cylinder is approximately 6.5 mg. Use of the headspace method to prepare the standard would result in weighing errors of approximately 10%; therefore, a microgravimetric technique previously used to prepared organic gas standards for liquids [1,2] was modified for use with low melting point solids. The cylinder valve fitting in which the transfer of the 1,4-dichlorobenzene to the cylinder would take place would be heated to 200°C.

Instead of preparing, at a minimum, two gas standards containing 1,4-dichlorobenzene to determine the ability to prepare a mixture, one was prepared which also contained 1,2-dichlorobenzene as an internal standard. Previous work at NIST with the compound 1,2-dichlorobenzene has shown that gas standards containing this compound are both accurate and stable. The standards were compared to each other by GC–FID using the previously described analytical conditions. Regression analysis was used to plot gravimetric concentration versus GC peak area response. The resulting line was then used to determine the concentration of the standards using the peak area response. The average absolute residual was 0.02% indicating good agreement between standards. The expanded relative uncertainty in the gravimetric concentration is 1.0%. This uncertainty is determined from the equation $U = ku_c$. The coverage factor k equals 2 (a confidence interval of approximately 95%) and u_c is the root sum of squares of the uncertainties arising from weighing the 1,2-dichlorobenzene and nitrogen and their purities. These results demonstrate the ability to prepare accurate 1,4-dichlorobenzene standards.

Theoretically, 1,2-dichlorobenzene and 1,4-dichlorobenzene should have the same molar response to the FID. The compounds have the same number of carbon atoms, and differ only by the placement of the chlorine atoms. Consequently, the 1,2-dichlorobenzene could potentially be used as an internal standard and the 1,4-dichlorobenzene concentration could be determined by comparison. Previous work at NIST involving the comparison of 1,3-dichlorobenzene to 1,2-dichlorobenzene, both liquids at room temperature, has shown that these two compounds have the same FID response factor to within 3%. Table 1 shows data for three gas standards, each containing 1,3- and 1,2-di-

Table 1
Response ratios for 1,2-dichlorobenzene and 1,3-dichlorobenzene in several gas standards

Standard	1,2-Dichlorobenzene			1,3-Dichlorobenzene			Percent diff.
	Avg. peak response	Grav. conc.[a]	Response factor	Avg. peak response	Grav. conc.[a]	Response factor	
009020	46980	460.2	102.1	48793	491.7	99.2	2.9
033788	13066	127.7	102.3	25317	251.7	100.6	1.7
033820	6619	64.4	102.7	10612	106.3	99.8	2.8
							average = 2.5

[a] Gravimetric concentration is in nanomole/mole, with a preparation uncertainty of ±1% at the 95% confidence level.

chlorobenzene. The peak response given is an average of three injections made for each cylinder, which resulted in a maximum standard deviation of 0.4% for the same mixture. A response factor was determined for each compound by dividing the average GC peak area response by the appropriate gravimetric concentration. The response factor for 1,3-dichlorobenzene was 2.5% less than that for 1,2-dichlorobenzene. A solution standard of 1,2- and 1,3-dichlorobenzene in acetone was prepared. Five injections of 0.1 μl of the standard resulted in an average response factor for 1,3-dichlorobenzene that was 2.9% less than that of 1,2-dichlorobenzene, confirming the gas standards results. An assumption was therefore made that a difference in response factors for 1,2- and 1,4-dichlorobenzene of the same magnitude might occur under the same analytical conditions. A solution standard of 1,2- and 1,4-dichlorobenzene at nominal 5000 μmol/mol each in acetone was prepared. Five injections of 0.1 μl were made, resulting in an average response factor for 1,4-dichlorobenzene that was 3.2% less than that for 1,2-dichlorobenzene. This difference was considered acceptable and it was concluded that 1,2-dichlorobenzene could be used as an internal standard to determine the 1,4-dichlorobenzene concentration. It should be noted that this difference in response factors may change or be nonexistent using a different type of column material and GC conditions; therefore, when using such a method, the analytical conditions must be well qualified for the compounds being studied.

The gravimetric standard prepared was analyzed using the conditions described earlier. A ratio was calculated for each analysis by dividing the 1,4-dichlorobenzene GC peak area response by that for the 1,2-dichlorobenzene. This ratio was then multiplied by the gravimetric concentration of the 1,2-dichlorobenzene. Table 2 shows the results of several analyses of the standard. The average concentration determined for 1,4-dichlorobenzene was 288.9 ± 9.2 nmol/mol (the uncertainty of 9.2 representing the

Table 2
Results of October 1993 and February 1994 analysis of standard ALM-033823

October 1993		February 1994	
Ratio of 1,4-dichlorobenzene[a] to 1,2-dichlorobenzene[b]	Concentration[c] of 1,4-dichlorobenzene from 1,2-dichlorobenzene	Ratio of 1,4-dichlorobenzene to 1,2-dichlorobenzene	Concentration[a] of 1,4-dichlorobenzene from 1,2-dichlorobenzene
1.190	290.9	1.163	284.2
1.168	285.4	1.164	284.4
1.191	291.0	1.164	284.4
1.187	290.0	1.166	284.9
1.178	287.8	1.167	285.2
1.197	292.4	1.167	285.2
1.166	284.9	1.167	285.2
		1.168	285.5
		1.169	285.7
		1.169	285.7
Avg. = 1.182	288.9	1.166	285.0
S.D. = 0.012	2.9	0.002	0.5
R.S.D. = 1.0%	1.0%	0.2%	0.2%

[a] Gravimetric concentration is 290.4 nmol/mol.
[b] Gravimetric concentration is 238.6 nmol/mol.
[c] Concentration is in nmol/mol.

variance in response factors). The standard deviation of the average concentration was 3 nmol/mol, which is 1.0% relative. This value is in excellent agreement with the calculated gravimetric concentration of 290.2 nmol/mol.

After this gas standard was shelved for four months, it was again analyzed. Table 2 shows the data for this analysis. The average concentration of the 1,4-dichlorobenzene determined by ratioing to the 1,2-dichlorobenzene was 285.0 ± 9.1 nmol/mol with a standard deviation of 1 nmol/mol, or 0.4% relative. The analytical precision was much better for this analysis; however, the average concentration determined for this analysis was 3.9 nmol/mol less (1.4%) than that for the first analysis. It might appear from this data that the 1,4-dichlorobenzene concentration is decreasing in the cylinder. Taking into account the uncertainty in the concentrations, the determinations of 1,4-dichlorobenzene are within the error bars; therefore, it can be stated that the compound is not degrading in the cylinder. Long term stability of 1,4-dichlorobenzene in a gas mixture is unknown beyond four months. Data from as many as eight gas standards containing 1,2- and 1,3-dichlorobenzene show that these two compounds are stable in a gas mixture for at least 2.5 years at concentrations as low as 5 nmol/mol. Table 3 shows stability data for one of those mixtures. It is highly likely that 1,4-dichlorobenzene would behave in a similar manner and be stable over years.

From the data in Table 2 it appeared that it was feasible to prepare a gas standard for a solid organic compound at room temperature. Because one standard is not conclusive, a second standard was prepared containing both compounds. The standard was analyzed using the exact same conditions. Table 4 shows the results of that analysis. The concentration of the 1,4-dichlorobenzene was calculated from the ratio to 1,2-dichlorobenzene. The value for 1,4-dichlorobenzene of 284.5 nmol/mol calculated from this ratio is low by 5.9 nmol/mol (2.0%) when compared to the gravimetric concentration of 290.4 ± 2.9 nmol/mol. This value still lies within the ±3.2% range of 281–290 nmol/mol.

The data in Table 4 supplied further evidence that the preparation procedure was feasible for this particular solid organic compound. Comparison of the 1,4-dichlorobenzene concentrations in each cylinder could have a greater impact on the accuracy of the procedure. The

Table 4
Results of analysis of second standard ALM-040272

Ratio of 1,4-dichlorobenzene[a] to 1,2-dichlorobenzene[b]	Concentration[c] of 1,4-dichlorobenzene from 1,2-dichlorobenzene
1.198	285.8
1.191	284.2
1.192	284.4
1.190	283.9
1.192	284.4
1.191	284.2
1.192	284.4
1.194	284.9
Avg. = 1.192	284.5
S.D. = 0.003	0.6
R.S.D. = 0.2%	0.2%

[a] Gravimetric concentration is 290.4 nmol/mol.
[b] Gravimetric concentration is 238.6 nmol/mol.
[c] Concentration is in nmol/mol.

Table 3
Stability of 1,2- and 1,3-dichlorobenzene gas standards (ALM-008399)

Compound	Gravimetric concentration[a]	Concentration, nmol/mol February 1990	July 1992
1,2-Dichlorobenzene	5.01 ± 0.05	5.2 ± 0.3	5.0 ± 0.3
1,3-Dichlorobenzene	4.99 ± 0.05	5.2 ± 0.3	5.0 ± 0.3

[a] Concentration is in nmol/mol (ppb). The uncertainty is derived from the equation $U = ku_c$ where u_c represents the preparation errors and the coverage factor k equals 2.

Table 5
Comparison of two 1,4-dichlorobenzene standards

Standard	Average GC response	Gravimetric concentration[a]	Concentration[a] vs. ALM-040272
ALM-033823	148954	290.2 ± 2.9	290.2
ALM-040272	149072	290.4 ± 2.9	-

[a] Concentration in nmol/mol. The uncertainty is at the 95% confidence level determined from the equation $U = ku_c$.

two standards were analyzed together using the exact same conditions. Table 5 shows the data for this comparison. The GC peak area response for 1,4-dichlorobenzene in the first standard (ALM-033823) was divided by the peak area for the second standard (ALM-040272). This ratio was then multiplied by the gravimetric concentration for 1,4-dichlorobenzene in the first standard. The resulting concentration of 290.2 nmol/mol was exactly the same as the calculated gravimetric concentration of 290.2 nmol/mol. These results add more support to the ability to accurately prepare gas standards from solid 1,4-dichlorobenzene at low concentration levels.

4. Conclusions

Results of this research exhibit strong support that gas standards containing 1,4-dichlorobenzene can be prepared without losses. The possibility exists, but is not likely, that the same amount of 1,4-dichlorobenzene is lost each time a gas standard is prepared. It is more likely to have random losses from mixture to mixture, which the data do not support. The data provide strong evidence that accurate gas standards can be prepared from crystalline 1,4-dichlorobenzene when care is taken using this procedure. It is likely that other organic compounds that are solids at room temperature can be quantitatively transferred into a gas cylinder, resulting in the preparation of accurate gas standards. It is ideal to include a compound of similar structure in the mixture as an internal standard. The compound should be a liquid at room temperature, be well characterized in a gas mixture, and theoretically have the same FID response. This research has shown the ability to quantitatively and accurately prepare gas standards with a relative uncertainty of 1.0% at the 95% confidence level using a compound that is crystralline at room temperature.

References

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