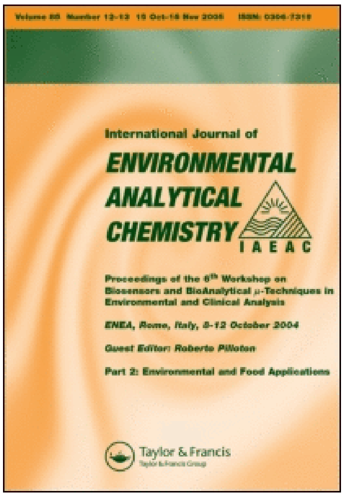

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The Preparation of a Standard Gas Mixture of C_5 and C_6 Hydrocarbons at a Concentration of 0.05 PPM

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A method for the preparation of a standard hydrocarbon gas mixture in a stainless steel cylinder is described. The mixture was made with twelve C_5 and C_6 hydrocarbons, liquid at room temperature, in synthetic air at a concentration of 0.05 ppm for each compound. Cylinder wall losses were satisfied by conditioning the wall with all of the compounds. Standard volumes of the equilibrium hydrocarbon vapor-air mixtures were calculated with a formula based on Dalton's Law of Partial Pressure and Amagat's Law of Partial Volume. Standard volumes were withdrawn from special flasks and transferred into the cylinder. Gas chromatographic analyses of the hydrocarbons were statistically examined. The standard volume technique, cylinder wall conditioning and analytical results are discussed.

INTRODUCTION

To date, there does not appear to be an experimental method in the literature for the preparation of a low concentration standard gas mixture of hydrocarbons normally liquid at room temperature.[1] Satisfactory standard mixtures of hydrocarbons normally gaseous at room temperatures and low concentrations have been prepared by volumetric, gravimetric, manometric and dynamic methods. For static gas mixtures, as the vapor pressure of the hydrocarbon decreases below one atmosphere and the concentration decreases, wall losses in a container occur, and in some cases the losses are considerable.

This laboratory had need of a mixture of C_5 and C_6 hydrocarbons to calibrate a gas chromatograph used to quantitate atmospheric C_5 and C_6 hydrocarbons in the 0.1 to 1 part per billion concentration range. Experiences with commercial preparations were unsatisfactory at this low concentration. The usual procedure of transferring aliquots of the liquid compounds was not feasible because of the inaccuracies in measuring the minute liquid volumes involved. By using aliquots of head space vapor-air mixtures of compounds at known temperature and vapor pressure, errors due to the measurement of compound volumes were minimized.

Observations made in this laboratory indicated serious losses of hydrocarbons at such low concentrations; therefore, it was necessary to condition a container wall before preparing a standard gas mixture in that container.

This paper describes a method whereby a satisfactorily accurate standard gas mixture of C_5 and C_6 hydrocarbons at a concentration of 0.05 ppm was prepared. A stainless steel cylinder was conditioned to the twelve gaseous C_5 and C_6 hydrocarbons by a stepwise and repeated process of: evacuation, injection of the gaseous hydrocarbons, pressurization and analysis. Standard volumes of the gaseous hydrocarbons, in a mixture of its vapor with air, were calculated using vapor pressure data, Dalton's Law, Amagat's Law, the ideal gas law, and a formula for gas concentrations expressed in parts per million. Each standard volume of each gaseous hydrocarbon was withdrawn from a special flask which contained only that hydrocarbon liquid in equilibrium with its vapor in the presence of air at one atmosphere. The volumes of standard gaseous hydrocarbons were injected into the conditioned, slightly-evacuated stainless steel cylinder and the cylinder was pressurized to twenty atmospheres with synthetic air. The cylinder contents were analyzed gas chromatographically and the gas chromatographic responses were taken as the standard responses for the prepared concentrations of hydrocarbons.

EXPERIMENTAL

Reagents

Wherever possible 99.5% to 99.9% pure grade; isopentane, *n*-pentane, 1-pentene, trans-2-pentene, cis-2-pentene, 2,2-dimethylbutane, 2-methylpentane, 3-methylpentane, *n*-hexane, 1-hexene, trans-2-hexene, and cis-2-hexene were used, and hydrocarbon-free synthetic air.

Apparatus

A stainless steel manifold equipped with valves, a stainless steel cylinder with regulator, 12–100 ml distillation flask with sidearm adapter, 50 μl, 100 μl, 250 μl gas tight syringes with valve and size 30 syringe needles, a pressurizing manifold, a manometer, a thermometer, assorted tube fittings and septa were used.

Instrumentation

FID gas chromotograph, sensitive to 10^{-14} amp., was used with a stainless steel column ⅛″ × 8′ packed with 20% β, β′ oxydiproprionitrile on activated alumina.

Procedure

The distillation flask (Figure 1) was used to provide the hydrocarbon vapor-air equilibrium mixture. Approximately ten milliliters of isopentane, *n*-pentane, 1-pentene, trans-2-pentene, cis-2-pentene, 2,2-dimethylbutane, 2-methylpentane, 3-methylpentane, *n*-hexane, 1-hexene, trans-2-hexene, cis-2-hexene were each placed in separate flasks. All apparatus was maintained at 21°C.

Technical grade reagents of a compound contained quantities of other compounds; namely, cis-2-pentene contained 4.9 mol per cent trans-2-pentene, 2-methylpentane was 95.1 mol per cent pure, 95.5 mol percent 3-methylpentane contained 3.5 mol percent 2-methylpentane, and the mixed 2-hexenes contained 63.6 mol percent cis-2-hexene and 35.6 mol percent trans-2-hexene.[2] In these instances, the standard volumes were calculated with the application of Raoult's, Dalton's and Amagat's Laws.

Conditioning of cylinder An all stainless steel manifold system (Figure 2) was attached to the stainless steel cylinder. Toggle valves V_1 and V_2 were opened. Impurities were removed from the cylinder at one torr pressure, or less, overnight. V_2 was closed and synthetic air was connected to the cylinder at A. Cylinder pressure was increased to about 500 torr with synthetic air and V_2 closed again. Twice the standard volume of each compound, Table I, was slowly withdrawn from the flask with a gas tight syringe equipped with a valve, injected at C and swept into the cylinder with three quick bursts of synthetic air through V_2. The septum at C was replaced with a plug and the cylinder pressurized to 20 atmospheres with synthetic air. V_3 was closed and the plug at C was replaced with a flow control valve and tube fitting for analysis. After two hours, the mixture was analyzed gas chromatographically, using the method and the concentration procedure as described in ASTM[3], except that the column was maintained at room temperature. The cylinder was exhausted to about 650 torr and additional quantities of those compounds giving no GC response were injected, by increments, into the cylinder. The cylinder was pressurized to 770 torr after each increment of compounds

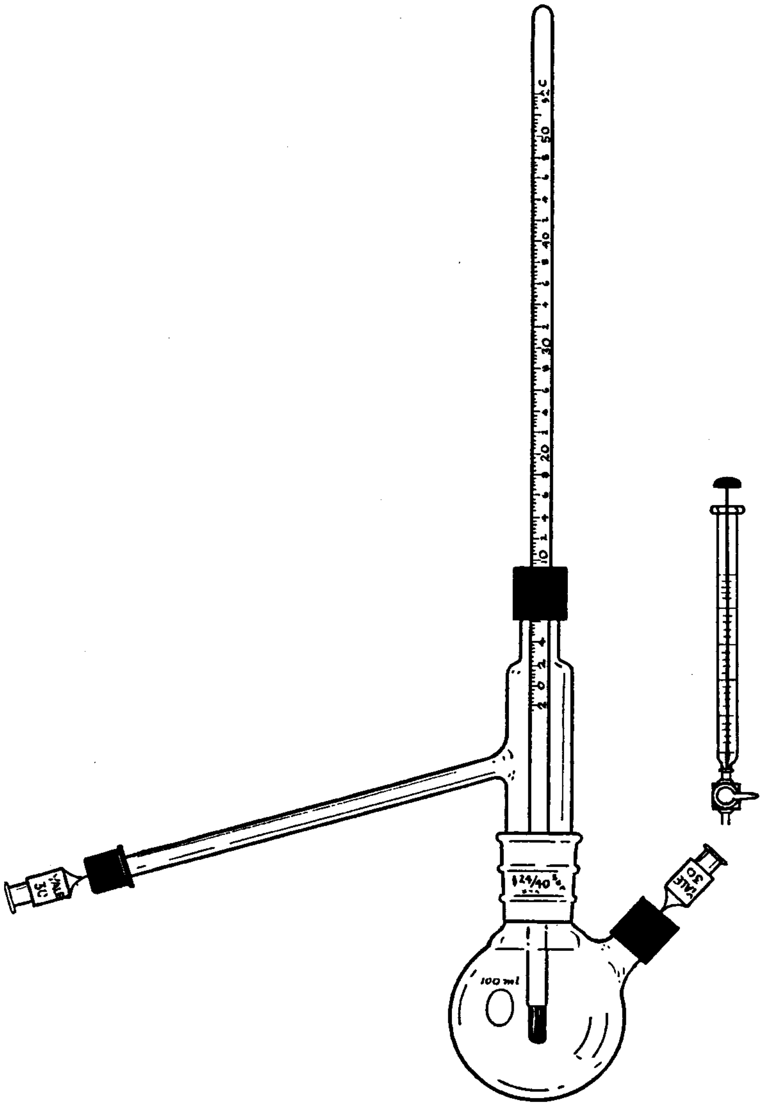

FIGURE 1 Apparatus for compound vapor-air mixtures.

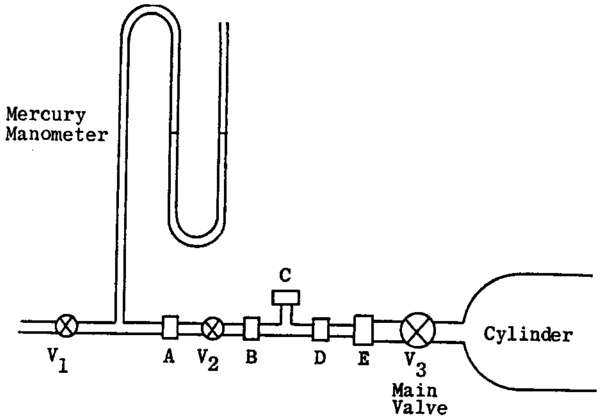

FIGURE 2 Gas dilution manifold used to inject compound vapors and pressurize with synthetic air.

and the mixture was analyzed. The above process of exhaustion, injection, pressurization, and analysis was repeated, until all compounds responded about equally. The cylinder was then pressurized to about 1000 torr, and exhausted. The mixture was checked gas chromatographically after every second and then after each single such flushing until the responses for all compounds were ten times the minimum detectable responses.

Standard volumes Dalton's and Amagat's Laws of Partial Pressure and Partial Volume, respectively, were applied to calculate the standard volumes (Table I) using the following formula:

$$v_1 = \frac{C \times H \times P \times p_r}{n_i \times 14.7} \tag{1}$$

which is a rearrangement of the formula used to calculate the concentration of a gaseous compound in a known volume and at a known pressure.

v_1 = standard volume of vapor-air mixture in μl
C = concentration in ppm
H = cylinder volume in liters
P = cylinder pressure in lbs/in^2
p_r = atmospheric pressure correction
n_i = mol fraction
14.7 = one atmosphere pressure in lbs/in^2

The factor, p_r, was applied to equalize the effect of changing atmospheric pressure on the standard volume of each compound.

Formula derivation The gas law at constant temperature is:

$$p_1 v_1 = p_2 v_2 \tag{2}$$

Let,

p_1 = standard atmospheric pressure in torr
p_2 = measured barometric pressure in torr
v_2 = volume of vapor-air mixture in μl
v_1 = corrected volume of vapor-air mixture in μl

The mol fraction of a compound vapor present in a mixture of air and compound is equal to the ratio of the vapor pressure to the total pressure:

$$n_1 = \frac{\text{vapor pressure of compound}}{\text{one atmosphere pressure}} \tag{3}$$

Combining (2) and (3), with v_1 and v_2 now being the volume of compound vapor only:

$$\frac{p_1}{p_2} \times v_1 \times n_i = v_2 \tag{4}$$

the formula for the calculation of the concentration of a compound in a mixture under pressure in a cylinder is:

$$C = \frac{v_2 \times 14.7}{H \times P} \tag{5}$$

Substituting for v_2 from Eq. (4):

$$C = \frac{(p_1/p_2) \times v_1 \times n_1 \times 14.7}{H \times P} \tag{6}$$

and rearranging,

$$v_1 = \frac{C \times H \times P \times (p_2/p_1)}{n_i \times 14.7} \tag{7}$$

Vapor pressures at 21°C were obtained from published data[2] or calculated from vapor pressure data[4] at 37.8°C using the Clausius–Clapeyron equation.[5] These vapor pressures were used to calculate the mol fractions for each compound as defined in Eq. (3).

Standard mixture The cylinder was taken to about 600 torr and the hydrocarbon standard volumes to give concentrations of 0.05 ppm for each compound at 20 atmospheres were slowly withdrawn from the flasks and introduced into the cylinder. The cylinder was pressurized to 20 atmospheres with synthetic air and an appropriate regulator affixed to the cylinder. Hydrocarbon responses were checked periodically with the gas chromatograph, for hydrocarbon stability.

TABLE I

Conditioning and standard volumes

Compound	Conditioning volumes	Standard volumes, μl
isopentane	3 ml	23.2
n-pentane	2 ml	30.7
1-pentene	3 ml	26.1
trans 2-pentene	100 μl	31.0[a]
cis 2-pentene	1.1 ml	33.0
2,2-dimethyl butane	300 μl	50.2
2-methylpentane	150 μl	77.1[b]
3-methylpentane	200 μl	90.2
n-hexane	200 μl	107.2
1-hexene	7 ml	78.0
trans 2-hexene	4 ml	91.0[c]
cis 2-hexene		165.7[d]

Cylinder volume: 18.32 liters.
Cylinder pressure: 20 atmospheres.

[a] Contribution from cis 2-pentene.
[b] Contribution from 3-methylpentane.
[c] Contribution from mixed 2-hexenes.
[d] Contribution from mixed 2-hexenes.

RESULTS AND DISCUSSION

The standard gas mixture was prepared by this method assuming that the losses in the transfer apparatus were negligible, compound vapors behaved as ideal gases, and there were no interactions between compounds.

Sources of error inherent in techniques usually employed in preparing standard gas mixtures were considered prior to developing the techniques used in this method. When prepared from aliquots of the liquid hydrocarbon, the uncertainty in reading the small liquid volume is an obvious source of error. Partial condensation on surfaces would be a source of error when a liquid compound is vaporized at an elevated temperature and the standard volume subsequently withdrawn with a colder device. Another source of error when one withdraws pure compound vapor from a closed system would be mixing, or dilution, of compound vapor with air. This source of error would be appreciable with pure compound vapors; and, more so with a temperature differential between the vapor and external air. All of these probable sources of error would be minimized using the technique developed in this method. There was close agreement of gas chromatographic responses between a 50 ppm *n*-hexane gas mixture prepared by direct vaporization of liquid volumes and one prepared with the technique used in this method.

Six mixtures were made successively over a period of time in a stainless steel cylinder. Gas chromatographic analyses of the cylinder contents for the initial preparation indicated there were losses, presumably wall losses. Most noticeable losses were sustained for isopentane, *n*-pentane, 1-pentene, cis-2-pentene, 2,2-dimethylbutane, 1-hexene, trans-2-hexene, and cis-2-hexene. Quantitites required to satisfy the cylinder "demand" ranged from about one standard volume to two to three orders of magnitude more than the standard volume (Table I). Losses did not appear to be a function of compound structure and also appeared to involve more than a uni-molecular surface layer.

The first three mixtures were prepared with the cylinder flushed to where the gas chromatographic responses to isopentane and *n*-pentane only were barely detectable. Those three mixtures were then prepared assuming that the cylinder wall was conditioned to the compounds such that there would be no further loss of standard amounts. The analyses for mixture 2 are presented in Table II (analyses for the first and third mixtures were essentially the same). When cylinder flushings for the fourth mixture were carried to the point when responses were definitely detectable for all compounds (except cis-2-pentene) and the standard mixture prepared, analytical responses were higher than for the previous three mixtures indicating an error in the previous flushing technique. Corroboration for this technique change on the fourth preparation was verified by preparing a fifth mixture and analyzing it. Gas chromatographic responses were essentially the same between the fourth and fifth mixtures. Finally, the cylinder was exhausted of the fifth mixture and flushed until the responses from each compound was definite and reduced to approximately ten times the minimum detectable response, to insure wall loss satisfaction, for all compounds. These background responses were essentially negligible when the standard volumes were introduced and the cylinder was pressurized to 20 atmospheres.

As detailed in Table II, the coefficients of variation of the second and fourth mixtures indicated large variations in compound responses within each mixture, probably pointing to unequal wall loss compensation. Apparently, the technique wherein a response of ten times the minimum detectable concentration for each compound was used as the criterion for the extent of flushing was most closely followed for the sixth preparation, as indicated by comparing the coefficients of variation. The mean responses of the C_5's and C_6's in preparations 4 and 6 were in good agreement. Statistical analysis of these data indicated no significant difference in the responses between C_5 and C_6 hydrocarbons in these mixtures, as shown in the last two lines of Table II.

The sixth mixture was taken to be the standard, in that the wall loss effect had been reduced to a minimum and the criteria for standard mixtures had been met. Concentrations of the compounds in the sixth mixture remained constant over a year's time.

TABLE II

Gas chromatographic responses to hydrocarbons in three preparations

Compounds	Preparation		
$5C_5$'s	2nd (11 assays)	4th (5 assays)	6th (8 assays)
isopentane	3754	9243	6200
n-pentane	2946	9200	8051
1-pentene	2397	9746	7209
trans 2-pentene	2329	5612	6615
cis 2-pentene	826	2048	6632
mean response	2450.4	7169.8	6941.4
coeff. of var.	43.8%	46.1%	10.3%
$7C_6$'s			
2,2-dimethylbutane	3383	9206	8185
2-methylpentane	1895	6370	7876
3-methylpentane	2178	7894	7243
n-hexane	2712	6230	5482
1-hexene	4063	5280	5511
trans 2-hexene	2567	4806	5880
cis 2-hexene	2205	3748	6526
mean response	2714.7	6219.1	6671.9
coeff. of var.	28.2%	29.9%	16.7%
significance of difference in response	NS($p = 0.50$)	NS($p = 0.17$)	NS($p = 0.26$)

NS—C_6 not significantly greater than C_5 at 95% level by the Wilcoxon–Mann–Whitney Two Sample test.

Comparable results, insofar as conditioning effects are concerned, for any other container with the same or other compounds used to prepare a standard gas mixture would probably not be the same. Each system needs to be investigated independently for losses.

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