Development of hydrocarbon gas standards

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ABSTRACT

Methodology is described for the gravimetric preparation and analytical evaluation of accurate, stable, multicomponent gas standards in compressed gas cylinders containing C_2–C_{10} alkane, alkene and aromatic hydrocarbons in pure nitrogen or air. Standards have been prepared containing up to fourteen hydrocarbons in a single mixture at concentrations ranging from 5–2000 nmol/mol (ppb). Analysis of hydrocarbons at the low ppb level requires cyrogenic preconcentration. Depending on the combination of hydrocarbons in any one gas mixture, several analytical gas chromatographic columns may be required to achieve baseline separations of all the compounds. The sum of preparative and analytical error components of the uncertainty associated with the concentrations of the hydrocarbons at the 95% confidence level typically ranges from 0.5–5.0%. This total uncertainty depends on the concentration level and the hydrocarbon. Intercomparative analyses of new and previously prepared standards have verified that such mixtures are stable for at least nine months, with the exception of ethyne (acetylene) which has a stability of less than nine months.

INTRODUCTION

Interest in the measurement and determination of ambient non-methane hydrocarbons has increased over the past decade. This increased interest is due to the fact that these non-methane hydrocarbons, along with nitrogen oxides, are primary precursors of ozone (O_3) and other oxidants which are major constituents of photochemical smog [1]. Regulators, such as the Environmental Protection Agency (EPA) and state governments, require data from baseline measurements of ambient hydrocarbon concentrations to help determine the level of reduction in ambient hydrocarbon concentrations required to achieve the national ambient air quality standards for ozone [2,3]. The photochemical reactivity of hydrocarbons differs between the different compounds, thus making it desirable to know the ambient concentrations of individual hydrocarbons. This aids regulators in developing control measures and can also be used as input to urban atmosphere models [4,5]. These models are then used to estimate increases in pollution based on growth of industry and in the numbers of automobiles as well as decreases resulting from anti-pollution measures.

Many studies have been conducted over the years to measure the concentrations of various hydrocarbons in the atmosphere. One example is given by McAllister *et al.* [6] who conducted a study from 1984–1988 where they measured the concentrations of hydrocarbons in 69 cities representing 27 states and the District of Columbia. Their data showed that over that time period average site non-methane organic compounds (NMOC) concentrations decreased in 39 cases while increasing in 19 and remained constant in 11. The total NMOC concentration for any one city was typically less than 1 μmol/mol (ppm). The concentrations of individual hydrocarbons in these studies vary depending on the sampling site. For instance, Lonneman *et al.* [7] report

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concentrations of individual hydrocarbons in the Lincoln Tunnel in New Jersey that ranged from 10 to 400 nmol/mol (ppb) in 1982. The concentrations in an outside air tunnel ventilation sample ranged from 1 to 50 nmol/mol.

In order to determine the concentration of hydrocarbons at these levels, and to follow long term trends, it is essential to have accurate and stable gas standards. Researchers have used several different sources of standards to calibrate instruments. Greenberg and Zimmerman [8] have used their own laboratory standard of 2,2-dimethylbutane (neohexane) in air for their remote continental studies. Nelson and Quigley [9] calculated hydrocarbon concentrations in their Sydney, Australia study using National Institute of Standards and Technology (NIST) methane and propane in air Standard Reference Materials (SRMs). Stump and Dropkin [10] used a vaporization system into which a pure hydrocarbon was injected and mixed with a controlled flow of air. A sample was withdrawn with a gas tight syringe and injected into a Tedlar bag containing a known volume of zero air for dilution to the desired concentration.

A considerable technical effort has been undertaken over the past 10 years at the NIST to develop stable trace level standards of volatile organic compounds in a pure matrix gas. These mixtures have been prepared in compressed aluminum gas cylinders using a microgravimetric technique developed at NIST [11–13]. This paper describes the research and development leading to the preparation of hydrocarbon gas standards in treated aluminum gas cylinders using the microgravimetric technique and other methods. The analytical methods as well as sample preparation for analysis will be discussed.

EXPERIMENTAL

Chemicals

The hydrocarbon compounds were purchased from commercial suppliers. The hydrocarbons were analyzed for impurities by gas chromatography–mass spectrometry (GC–MS) and gas chromatography–flame ionization detection (GC–FID) at NIST. The ultrahigh purity nitrogen (99.9995%) and ultra pure air used as diluent gases, were obtained from commercial sources. These gases were analyzed by NIST for any of the hydrocarbons of interest.

Gas cylinders

New aluminum gas cylinders with CGA-350 stainless steel valves were used to prepare the hydrocarbon standards. Cylinder sizes of 3.4, 5.8 and 30 l were used. The cylinders were pre-cleaned by a commercial supplier in a manner that excluded contamination with trace hydrocarbons and halocarbons, and then treated to deactivate the internal walls.

Weighing apparatus

The gaseous hydrocarbon compounds (C_2–C_4) were weighed into a size 3.4-l cylinder using a two-pan balance with a sensitivity of 0.001 g. The cylinder to which these hydrocarbons were added was weighed against a tare cylinder. The liquid hydrocarbon compounds (C_5–C_{10}) were sealed into glass capillary tubes and weighed on an ultra microbalance, then introduced into a 3.4-l cylinder. 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. When using the 5.8-l cylinders, an electrical top-loading balance having a capacity of 15 kg and a 0.1 g sensitivity was used for weight determinations. A floor balance with a 54 kg capacity and a 1 g sensitivity was used to weigh the 30-l cylinders. The sensitivity of this balance was improved to 0.5 g using NIST calibrated weights to minimize "round up" errors.

Gravimetric procedure for preparing gas standards

The gas standards to be developed were to contain hydrocarbons of which some are gases (C_2–C_4) and the others liquids (C_5–C_{10}) at room temperature. We started with those compounds which are gases at room temperature. A new 3.4-l aluminum gas cylinder was evacuated and weighed. Each gaseous hydrocarbon was added through a manifold system in an amount yielding 0.5% in 12.4 MPa of air or nitrogen, starting with the lowest vapor pressure compound. The cylinder was weighed on the two-pan balance after each individual addition. After all

gaseous hydrocarbons of interest were added to the cylinder, diluent gas was added to the appropriate pressure (12.4 MPa) and the cylinder reweighed on the two-pan balance. Gravimetric concentrations of the hydrocarbons in the mixture were then calculated on a mol/mol basis using the data from the weighings. The cylinder was then heated (less than 70°C) to create temperature gradients within the cylinder to thoroughly mix all the constituents.

The next step in the preparation sequence included the use of a microgravimetric technique developed at NIST [11–13] followed by a dilution step. The goal was to prepare a standard at the 2 µmol/mol (ppm) level that contained the gaseous and liquid compounds. Calculations were made to determine the amount of each liquid hydrocarbon needed to prepare a mixture in 13.8 MPa (2000 p.s.i.) of nitrogen or air resulting in 2 µmol/mol of each compound. The high purity hydrocarbons, which are liquid at room temperature, were weighed into thin-walled borosilicate glass capillary tubes. The appropriate nut and nipple, usually CGA-350, was attached to an evacuated preweighed aluminum gas cylinder. A short piece of PTFE tubing was attached to the nut and nipple using the appropriate fittings. The capillary tube containing the liquid hydrocarbon was inserted into the PTFE tubing. The cylinder valve was opened and the end of the capillary tube closest to the cylinder valve was broken. The cylinder vacuum pulls in the liquid as heat is applied to the capillary if necessary to facilitate vaporization. After addition of all the liquids, the cylinder was weighed. A precalculated amount of the 0.5% C$_2$–C$_4$ standard was then added to the cylinder. The cylinder was again weighed to determine the amount of the 0.5% standard transferred. The cylinder was then pressurized to 13.8 MPa of nitrogen and the cylinder reweighed. The concentrations were calculated on a µmol/mol basis using the weight data.

The last step to achieve a gravimetric standard at the 5–50 nmol/mol (ppb) level was accomplished by dilution. A new aluminum gas cylinder was evacuated and weighed. A precalculated amount of the 2 µmol/mol hydrocarbon standard needed to result in a 5–50 nmol/mol

standard was added to the evacuated cylinder followed by a weight measurement. The cylinder was then pressurized to 13.8 MPa with nitrogen or air and the cylinder reweighed. The concentrations of the hydrocarbons were calculated on a nmol/mol basis.

Several standards were prepared at the 0.5% and 2 µmol/mol levels followed by preparation of the ppb level standards from the 2 µmol/mol standards. This procedure was used so as to eliminate any bias that might occur from using just one initial standard from which all other standards would be blended.

Four different groups of hydrocarbon standards were developed, each group containing a different combination of compounds. Table I lists the compounds in each group of standards and gives the nominal concentrations. The preparation procedure previously described was used to prepare groups 1 and 2. Since the compounds

TABLE I

GROUPS OF HYDROCARBON MIXTURES STUDIED

Compound	Nominal concentration in nmol/mol (ppb)			
	Group 1	Group 2	Group 3	Group 4
Ethane	20	50		
Ethene		50		
Ethyne (acetylene)		50		
Propane	20	50		
Propene		50		
n-Butane	20	50		
Isobutane	20	50		
1-Butene		50		
Isobutene		50		
n-Pentane	20	50		
Isopentane	20	50		5.0
1-Pentene		50		
n-Hexane	20	50	100	
3-Methylpentane	20			5.0
2-Methyl-2-butene		50		
n-Heptane	20			
n-Octane	20		50	
n-Decane			25	
Benzene	20		100	5.0
Toluene	20		100	5.0
meta-Xylene			50	5.0
para-Xylene				5.0
ortho-Xylene	20			5.0

in the third and fourth groups are all liquids at room temperature, the first step in the preparation procedure, blending of a 0.5% standard, was eliminated. Several 2 μmol/mol standards were prepared and then the ppb level standards were prepared from the 2 μmol/mol standards.

Measurement apparatus

Analysis of the hydrocarbon gas standards were conducted using a gas chromatograph equipped with a flame ionization detector. Several different columns and conditions were used to obtain optimum baseline separation for each hydrocarbon in the gravimetric standards.

Method 1. A 25 m × 0.53 mm I.D. open tubular capillary column coated with a 10 μm thick film of aluminum oxide/potassium chloride (Al_2O_3/KCl) was used. The initial temperature was held at 35°C for 12 min then programmed to 45°C at 2°C/min, then to 180°C at 10°C/min and held at this final temperature for 30 min. The column carrier flow-rate was 2.8 ml/min and the detector make-up flow-rate was 28 ml/min (both nitrogen). An example of a chromatogram generated by this method is shown in Fig. 1a.

Method 2. A 1.8 m × 3.2 mm I.D. stainless-steel column packed with phenylisocyanate on 80/100 mesh Porasil C was used. The initial temperature was held at 30°C for 7 min then programmed to 60°C (the maximum allowable) at 10°C/min and held at this final temperature for 40 min. The column carrier flow-rate was 25 ml/min of nitrogen. An example of a chromatogram generated by this method is shown in Fig. 1b.

Method 3. A 30 m × 0.53 mm I.D. open wide bore capillary column containing GS-Q (a porous polymer) was used. The initial temperature was held at 60°C for 7 min then programmed to 240°C at 5°C/min. The column carrier flow-rate was 10 ml/min and the detector make-up flow-rate was 25 ml/min (both nitrogen). An example of a chromatogram generated by this method is shown in Fig. 1c.

Method 4. A 60 m × 0.75 mm I.D. open tubular capillary column coated with a 1 μm thick film of polyethylene glycol was used. The initial temperature was held at 50°C for 10 min

then programmed to 185°C at 6°C/min. The column carrier flow-rate was 5 ml/min and the detector make-up flow-rate was 30 ml/min (both nitrogen). An example of a chromatogram generated by this method is shown in Fig. 1d.

Method 5. A 60 m × 0.75 mm I.D. open tubular capillary column coated with a 1 μm thick film of dimethylpolysiloxane phase was used. The initial temperature was held at 30°C isothermal for 8 min then programmed to 200°C at 10°C/min. The column carrier flow-rate was 5 ml/min and the detector make-up flow-rate was 25 ml/min (both nitrogen). An example of a chromatogram generated by this method is shown in Fig. 1e.

The flame ionization detector was operated at 250°C for all the above methods. Due to the low analyte concentrations, it was necessary to concentrate the sample before injection onto the GC column. Several methods of concentrating have been reported, including "on-column enrichment" at cryogenic temperatures [14]. Other techniques include collecting the sample on cartridges packed with charcoal [15], graphitized carbon black [16] and Tenax [17], followed by desorption techniques. The use of an automatic cryogenic trapping unit set at −170°C and equipped with a trap packed with glass wool [10] has been used. Another method has been the use of traps packed with small diameter glass beads using liquid argon or oxygen as the cryogen [9,18]. The authors used techniques similar to those others have reported [8,13,19,20]. The hydrocarbon gas sample was cryogenically trapped either manually using liquid argon or with an automated system using liquid nitrogen programmed at a cryogenic temperature of −180°C. The sample flow-rate was controlled at 50 ml/min using a mass flow controller. The sample was cryogenically trapped in a 0.1-ml sample loop on a six-port gas sampling valve for 5 min. When manually trapping, hot water (90°C) was used to vaporize the sample. Two 0.1-ml stainless-steel sample loops were employed for the study: one was used empty and the other one was packed with 100–120 mesh dimethylchlorosilane treated glass beads. In the automatic trapping system the sample was vaporized by programming to a 150°C purge tempera-
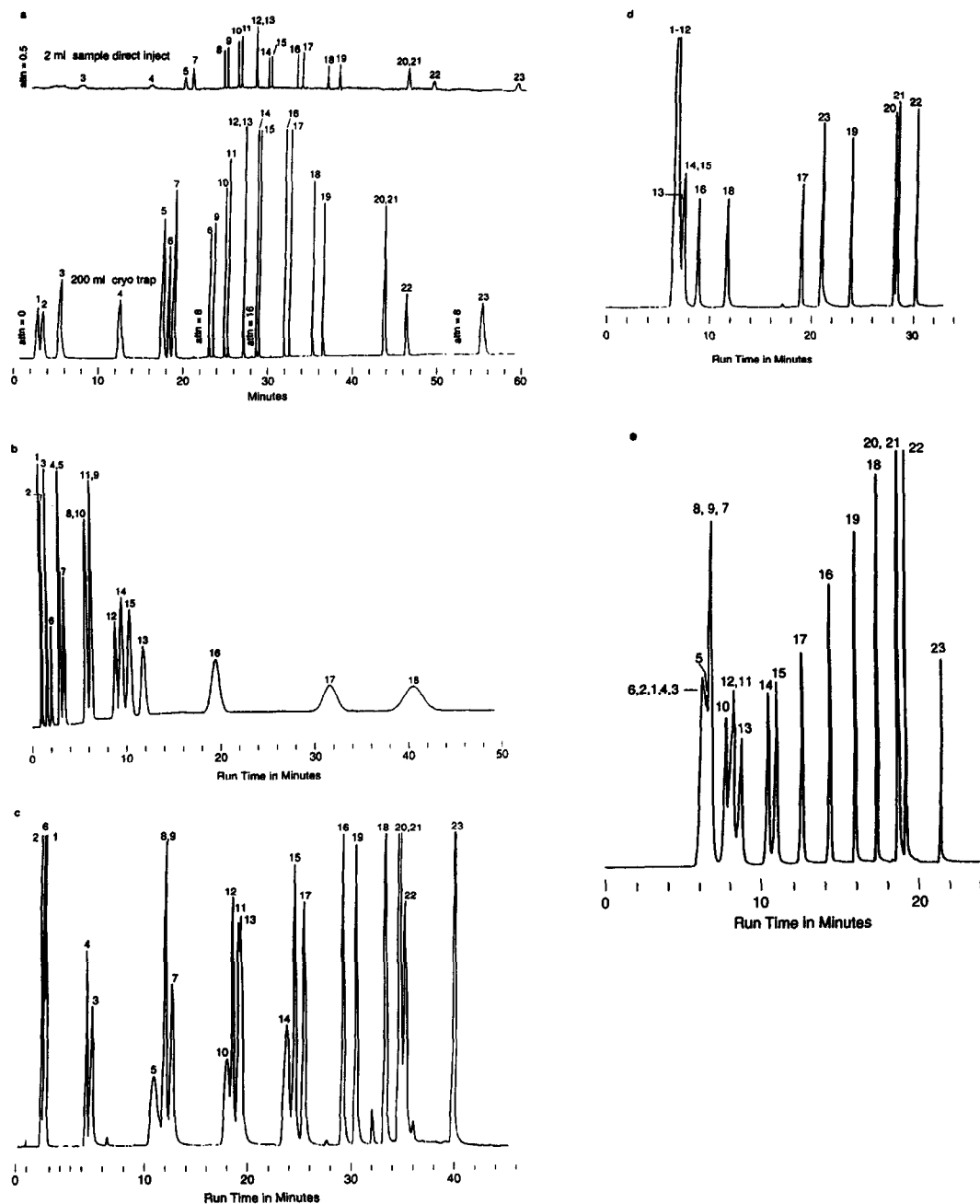
Fig. 1. (a) 25 m × 0.53 mm I.D. capillary column coated with 10 μm thick film Al₂O₃/KCl, 35°C for 12 min to 200°C at 2°C/min and hold. (b) 1.8 m × 3.2 mm I.D. stainless-steel column packed with phenylisocyanate on 80–100 mesh Porasil C, 30°C for 7 min to 60°C at 10°C/min and hold. (c) 30 m × 0.53 mm I.D. porous polymer capillary column, 60°C for 7 min to 240°C at 5°C/min and hold. (d) 60 m × 0.75 mm I.D. capillary column coated with 1 μm thick film polyethylene glycol, 30°C for 10 min to 180°C at 4°C/min. (e) 60 m × 0.75 mm I.D. capillary column coated with 1 μm thick film dimethylpolysiloxane phase, 30°C for 8 min to 200°C at 10°C/min and hold. Peaks: 1 = ethane; 2 = ethene; 3 = propane; 4 = propene; 5 = isobutane; 6 = ethyne (acetylene); 7 = n-butane; 8 = 1-butene; 9 = isobutene; 10 = isopentane; 11 = n-pentane; 12 = 1-pentene; 13 = 2-methyl-2-butene; 14 = 3-methylpentane; 15 = n-hexane; 16 = n-heptane; 17 = benzene; 18 = n-octane; 19 = toluene; 20 = para-xylene; 21 = meta-xylene; 22 = ortho-xylene; 23 = n-decane.

ture. The sampling procedure was computer controlled so as to maximize reproducability.

RESULTS AND DISCUSSION

The objective of this research was to determine if accurate and stable gas standards containing alkane, alkene, alkyne and aromatic hydrocarbons in a nitrogen or air matrix could be developed. The study involved a total of 23 hydrocarbons of interest to the US Environmental Protection Agency (EPA) and the State of California Air Resources Board (CARB), at concentrations ranging from 5–2000 nmol/mol (ppb). The standards were to be used to certify mixtures of hydrocarbons for use in EPA's and CARB's programs for studying ozone precursors in automobile exhaust.

Uncertainty in standards preparation

Taking the weighing imprecisions and the determination of impurities in the pure hydrocarbons and matrix gases into account, the uncertainty in the gravimetric concentrations of each compound ranged from 0.2–0.5% (1 standard deviation) at the 10 nmol/mol level. This uncertainty includes the standard deviations in the mean weight measurements and the uncertainty in the impurities in the pure hydrocarbon compounds and the diluent gas.

Analysis of standards

Analyzing hydrocarbons at the 5–100 ppb range using GC–FID is difficult. When using a capillary column of 0.53 mm I.D. or larger, 2 ml is the maximum amount of gaseous sample that can be directly injected onto the column without having problems with peak distortion. The amount of each compound injected under these conditions is low, resulting in poor precision from replicate analyses ranging from 2–10% depending on the hydrocarbon. However, when using cryogenic preconcentration, trapping of 250 ml of sample can be easily obtained resulting in a 100-fold increase in the amount of each compound injected, which improved the imprecisions to 0.1–1.5%. Fig. 1a illustrates the increase in signal when using cryogenic preconcentration *versus* direct injection of 2 ml of sample.

Differences in the results of using the two different stainless steel sample loops, unpacked *vs.* packed with dimethylchlorosilane treated glass beads, was most noticeable for the C_2 hydrocarbons. Table II lists the GC responses for the C_2 compounds using the different sample loops. In each case, the response is greater using the packed trap. However, the ethyne (acetylene) response does not increase proportionally to the ethane and ethene. Given that ethane, ethene and acetylene all have equal FID response [21], the lower relative response of acetylene must be a result of poor trapping efficiency, probably due to its possible reactivity and volatility.

For the analysis of the first group of compounds, the capillary column coated with $Al_2O_3/$ KCl separated all the compounds within 48 min except for the *meta-* and *para*-xylenes (see Fig. 1a). The packed column containing phenyliso-

TABLE II

GC–FID RESPONSES FOR C_2 COMPOUNDS USING PACKED AND UNPACKED TRAPS

Compound	GC response	
	Stainless-steel empty 15 cm × 1.6 mm I.D.	Stainless-steel packed with glass beads 15 cm × 1.6 mm I.D.
Ethane	4593	11 152
Ethene	3560	11 603
Ethyne (acetylene)	1535	2363

cyanate on Porasil C separated all the compounds up to n-octane in less tan 45 min (see Fig. 1b). However, due to its low maximum temperature of 60°C, the toluene and xylenes take over 50 min to elute. The later eluting peaks are also very broad on this column resulting in poor precision in the peak integration. The porous polymer capillary column separated all the compounds, except for the xylenes, in less than 40 min (see Fig. 1c). However, the isobutane and isopentane tend to have broad peaks which tail into the n-butane and n-pentane, respectively. Overall, the best separations and peak shapes were obtained on the Al_2O_3/KCl capillary column. The xylenes could be made to elute earlier by ramping the temperature at a high rate after the elution of toluene. This resulted in a reasonable GC run time. Of all the columns studied, the xylenes are best separated and analyzed using method 4 which employed the polyethylene glycol capillary column (see Fig. 1d).

The second group of compounds has fewer higher boiling hydrocarbons but has more of the volatile compounds, which complicates the analysis. The packed column has a run time of less than 15 min, but was incapable of separating six compounds contained within three peaks (see Fig. 1b). Lower starting temperatures and ramping rates could not resolve these compounds. The capillary column coated with Al_2O_3/KCl separated most of the compounds and resulted in all around good peak symmetry (see Fig. 1a). One precaution to be noted is that the authors found that with increased column use, the retention times of most of the compounds increased, most notably acetylene. Over a period of hours of use the acetylene peak eventually merged with the n-butane peak. Lowering the starting temperature again resulted in the acetylene eluting after the n-butane. The reason for this is not known. Though the 1-pentene and 2-methyl-2-butene were not separated using this column, they were separable by the packed column. Therefore, both methods 1 and 2 were utilized for analyzing the second group of compounds.

Measurements of the third and fourth groups of compounds were relatively simple. Four of the

five methods described earlier will accomplish the analysis of the third group. Method 5 using the capillary column coated with dimethylpolysiloxane was the technique used to analyze this group of standards (see Fig. 1e). The run time was shortened to less than 18 min by using different conditions stated below since only six compounds were present in this group. The initial temperature was held at 45°C for 8 min then programmed to 145°C at 10°C/min. Method 4 was used to separate the compounds in the fourth group (see Fig. 1d). The meta- and para-xylenes were not completely separated under these conditions. The separation of these compounds can be improved using a longer hold time at the initial oven temperature and a slower ramping rate, but this results in a longer analysis time. Despite some drawbacks method 4 was employed for the measurement of the xylenes.

Intercomparison of standards

The agreement between the 0.5% hydrocarbon standards was excellent. These standards were then used to prepare the 2 μmol/mol mixtures. These 2 μmol/mol standards were compared with each other along with other primary standards in the NIST inventory. The data were plotted with gravimetric concentration on the x-axis and GC response on the y-axis and analyzed by linear regression. Table III shows the results of the linear regression analysis of the propane data. The agreement between the new 2 μmol/mol standards and the older standards was excellent. The average residual was 0.20%, and the correlation coefficient (r^2) was 0.9999. This suggests that the preparation method was accurate and that there was no known bias. Table IV shows the linear regression for the 2 μmol/mol n-pentane standards. There were no NIST primary standards available for n-pentane at this level with which to compare. This set of standards compared very well with $r^2 = 0.9998$. Similar results were obtained for the other hydrocarbons studied.

After determining that there was good agreement between the 2 μmol/mol standards, the nmol/mol level standards were prepared for the respective groups. The standards from all the

TABLE III

LINEAR REGRESSION OF 2 μmol/mol (ppm) PROPANE STANDARDS

Sample number	GC response	Gravimetric concentration	Predicted concentration	Percent difference
x207013	102 660	9.502	9.501	−0.01
x207064	30 807	2.839	2.838	−0.05
000611	27 946	2.571	2.572	+0.05
ALM-009011	25 376	2.326	2.334	+0.35
ALM-008390	24 276	2.236	2.232	−0.18
CAL-8711	23 140	2.123	2.127	+0.17
000690	12 179	1.117	1.110	−0.61
			average absolute difference =	0.20

Correlation coefficient = 0.9999
y-Intercept = 207
Standard error of estimate of y = 58

TABLE IV

LINEAR REGRESSION FOR 2 μmol/mol (ppm) n-PENTANE STANDARDS

Sample number	GC response	Gravimetric concentration	Predicted concentration	Percent difference
ALM-009011	46 488	2.385	2.386	+0.03
CAL-8711	40 532	2.083	2.080	−0.16
ALM-008390	38 818	1.989	1.992	+0.13
			average absolute difference =	0.11

Correlation coefficient = 0.9998
y-Intercept = 72
Standard error of estimate for y = 83

groups were compared and the data pooled where there were common hydrocarbons between sets of standards. Linear regression was then applied to the data for each hydrocarbon. Table V shows the results for the standards containing n-hexane. The agreement between standards is good with a r^2 of 0.9997 and an average residual of 1.4%. These results show very good agreement when considering the uncertainty in the preparation of the standards is 0.2–0.5% (1 S.D.) and the imprecision of replicate analyses is at least 1.4%. Similar results were obtained for the other 23 compounds studied, which validated the accuracy in the preparation procedure. Table VI gives the gravimetric and analytical concentrations for each hydrocarbon in each standard prepared. In each case, the analytical concentrations, as determined from linear regression of the complete set of standards, agrees very well with the gravimetric concentrations.

Stability of hydrocarbon standards

The stability of a gas mixture is determined by periodic intercomparison to a set of standards. A new standard is prepared to compare with the "aged" set to assure that the standards are not decaying in concentration. Table VII shows stability data for a hydrocarbon standard from

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TABLE V

LINEAR REGRESSION FOR nmol/mol (ppb) n-HEXANE STANDARDS

Sample number	GC response	Gravimetric concentration	Predicted concentration	Percent difference
ALM-008392	859.99	123.5	124.3	+0.6
ALM-009003	682.78	99.86	98.57	−1.3
ALM-009012	548.80	79.45	79.12	−0.4
ALM-009016	338.51	48.75	48.60	−0.3
ALM-009006	337.20	47.74	48.41	+1.4
ALM-009026	327.06	46.46	46.93	+0.8
ALM-009010	273.86	38.61	39.21	+1.6
X138312	152.57	21.75	21.61	−0.7
FF9755	68.22	9.66	9.36	−3.1
X138362	37.85	5.17	4.96	−4.2
			average absolute difference =	1.4

Correlation coefficient = 0.9997
y-Intercept = 3.71
Standard error of estimate of y = 4.58

TABLE VI

GRAVIMETRIC CONCENTRATION *VERSUS* PREDICTED CONCENTRATION FROM LINEAR REGRESSION OF DATA FOR EACH HYDROCARBON IN A GROUP II STANDARD

Compound	Gravimetric concentration[a]	Predicted concentration[a]
Ethane	50.64 ± 0.41	51.2 ± 2.0
Ethene	53.25 ± 0.43	53.6 ± 1.0
Ethyne (acetylene)	53.99 ± 0.43	54.1 ± 1.0
Propane	55.99 ± 0.45	56.1 ± 1.0
Propene	49.08 ± 0.39	49.2 ± 1.0
n-Butane	50.89 ± 0.41	51.0 ± 0.9
Isobutane	60.64 ± 0.49	60.8 ± 1.1
1-Butene	51.89 ± 0.42	52.0 ± 0.9
Isobutene	52.78 ± 0.42	52.9 ± 0.9
n-Pentane	49.81 ± 0.40	49.6 ± 0.9
Isopentane	47.45 ± 0.38	47.4 ± 0.8
1-Pentene	48.77 ± 0.39	48.9 ± 1.1
n-Hexane	47.74 ± 0.38	48.0 ± 1.0
2-Methyl-2-butene	51.32 ± 0.41	51.5 ± 1.1

[a] Concentrations are in nmol/mol (ppb). The uncertainty is at the 95% confidence interval.

the first group of compounds and one from the second. The uncertainties following the concentrations are at the 95% confidence interval. The data show that the hydrocarbons have remained stable for 10 months with the exception of ethyne. The ethyne has decreased by 20% in the standard. Decreases in ethyne concentration have been noticed in other NIST gravimetric standards at the ppb levels. However, the ethyne has remained stable in the higher concentration 2 ppm standards. Further stability checks of these NMOC standards are planned in the future.

CONCLUSIONS

The results of this study show that primary NMOC gravimetric standards can be accurately and precisely prepared at the 5–100 ppb range with uncertainties in the preparation of ±1% (95% confidence interval). These standards have been found to be stable for a period of at least 10 months. These standards will be used to certify gas mixtures containing hydrocarbons which can then be used in various research and environmental programs, such as ozone precursor studies and automobile exhaust. This research has provided background work for the future development of a light hydrocarbon SRM.

TABLE VII

STABILITY DATA FOR HYDROCARBON STANDARDS FROM THE FIRST AND SECOND GROUPS OF COMPOUNDS

Compound	Concentrations in nmol/mol (pbb)[a]			
	Group 1		Group 2	
	June 1990	January 1991	July 1990	May 1991
Ethane	18.9 ± 0.9	20.1 ± 1.0	51.2 + 2.0	50.7 ± 2.0
Ethene			53.6 ± 1.0	53.2 ± 1.0
Ethyne (acetylene)			54.1 ± 1.0	43.4 ± 1.0
Propane	20.5 ± 1.4	21.5 ± 1.0	56.1 ± 1.0	55.8 ± 1.0
Propene			49.2 ± 1.0	49.3 ± 1.0
n-Butane	20.9 ± 1.0	20.9 ± 1.0	51.0 ± 0.9	50.7 ± 0.9
Isobutane	20.4 ± 1.0	21.2 ± 1.3	60.8 ± 1.1	60.6 ± 1.1
1-Butene			52.0 ± 0.9	51.7 ± 0.9
Isobutene			52.9 ± 0.9	52.6 ± 0.9
n-Pentane	20.4 ± 1.0	20.9 ± 1.0	49.6 ± 0.9	49.7 ± 0.9
Isopentane	20.3 ± 1.0	20.7 ± 1.0	47.4 ± 0.8	47.4 ± 0.9
1-Pentene			48.9 ± 1.1	49.1 ± 1.1
n-Hexane	20.0 ± 1.0	20.3 ± 1.0	48.0 ± 1.0	47.8 ± 1.0
3-Methylpentane	20.0 ± 1.0	20.3 ± 1.0		
2-Methyl-2-butene			51.5 ± 1.1	51.5 ± 1.1
n-Heptane	20.0 ± 1.0	20.2 ± 0.9		
n-Octane	19.8 ± 1.0	19.9 ± 1.0		
Benzene	20.7 ± 1.4	20.2 ± 1.0		
Toluene	19.9 ± 1.0	20.1 ± 1.0		
ortho-Xylene	19.3 ± 1.4	19.1 ± 1.0		

[a] The total uncertainties are the estimated upper limit error of the respective concentrations and are at the 95% confidence interval.

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