Hydrocarbon Gas Standards at the pmol/mol Level to Support Ambient Atmospheric Measurements

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Studies of climate change increasingly recognize the diverse influences exerted by hydrocarbons in the atmosphere, including roles in particulates and ozone formation. Measurements of key non-methane hydrocarbons (NMHCs) suggest atmospheric concentrations ranging from low pmol/mol to nmol/mol, depending on location and compound. To accurately establish concentration trends and to relate measurement records from many laboratories and researchers, it is essential to have good calibration standards. Several of the world's National Metrology Institutes (NMIs) are developing primary and secondary reference gas standards at the nmol/mol level. While the U.S. NMI, the National Institute of Standards and Technology (NIST), has developed pmol/mol standards for halocarbons and some volatile organics, the feasibility of preparing well-characterized, stable standards for NMHCs at the pmol/mol level is not yet established. NIST recently developed a suite of primary standards by gravimetric dilution that contains 18 NM-HCs covering the concentration range of 60 pmol/mol to 230 pmol/mol. Taking into account the small but chemically significant contribution of NMHCs in the high-purity diluent nitrogen used in their preparation, the relative concentrations and short-term stability (2 to 3 months) of these NMHCs in the primary standards have been confirmed by chromatographic analysis. The gravimetric values assigned from the methods used to prepare the materials and the analytical concentrations determined from chromatographic analysis generally agree to within ± 2 pmol/mol. However, anomalous results for several of the compounds reflect the difficulties inherent in avoiding contamination and making accurate measurements at these very low levels.

Non-methane hydrocarbons (NMHCs) are emitted into the atmosphere by many anthropogenic sources including automobiles and other transportation vehicles, power stack emissions, and biomass burning, as well as from terrestrial and oceanic biogenic processes. Particularly in urban environments, NMHCs are important as precursors and contributors to atmospheric photochemical processes leading to the formation of particulates and secondary photo-oxidants, such as ozone that lead to photochemical smog.^{1,2} Some NMHCs (such as benzene and 1,3butadiene) are directly toxic to plants and/or animals, including humans. For these and other considerations, there is considerable interest in measuring the levels of NMHCs at ground level and in the upper atmosphere. Nelson and Quigley report a 1982 hydrocarbon study in Sydney, Australia.³ McAllister et al. describe measurements made from 1984 to 1988 in 69 cities in the United States.⁴ Apel et al. report the 1992 Southern Oxidants Study conducted in Atlanta, Georgia.⁵ Plassdulmer et al. describe the measurement of light NMHCs emitted from the mid-Atlantic ocean region.⁶ These and other studies find that typical NMHCs concentration levels range from tens of parts-per-10⁹ (nmol/mol) in urban atmospheres to well below 10 parts-per-10¹² (pmol/ mol) in remote environments.²

Gas standards containing NMHCs have been key components of these measurement studies. The 1992 Southern Oxidants Study (SOS) used a mixture of NMHCs in the range of 5 nmol/mol to 125 nmol/mol per component purposeproduced and value-assigned by the National Institute of Standards and Technology (NIST).^{5,7} In 2003, the World Calibration Centre for Volatile Organic Compounds (WCC-VOC), a part of the World Meteorological Organizations (WMO) Global Atmosphere Watch (GAW) program, coordinated the first comprehensive intercomparison among the GAW-VOC community.⁸ The main focus of the study was documenting the analytical capabilities of laboratories making measurements of NMHCs. The National Center for Atmospheric Research (NCAR) in Boulder, Colorado, prepared gas standards in canisters and sent them to participating labora-

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tories in Brazil, Canada, Czech Republic, Finland, Germany, Ireland, and Slovakia. NCAR established the traceability of their results for 21 NMHCs through the evaluation of reference materials purpose-produced by NIST, with agreement to within $\pm 5\%$. The participating laboratories determined concentrations for as many as 73 NMHCs in the NCAR canisters using their own calibration technology or other available standards. The relative differences between the reported results and the reference values ranged from 0.1% to more than 1000%. Excluding one participant who reported consistently discordant results, the average relative deviation of the results was 9.5% for the 21 NMHCs with traceable reference values and 20% for all of the NMHCs reported by at least two of the participants. Culminating in 2006, the multiyear Accurate Measurements of Hydrocarbons in the Atmosphere (AMOHA) study evaluated gas chromatographic methods used across Europe to determine NMHC concentrations, finding good agreement for some NMHCs and significant differences for others.^{9,10}

The AMOHA study used low nmol/mol calibration standards supplied by the National Physical Laboratory of the United Kingdom. Participants needed to dilute these standards to pmol/mol concentrations. While dilution is an established technique for creating a calibration curve in gas analysis, there are potential complications including establishing the purity of the diluent gas and the extent of adsorption/desorption of the NMHCs throughout the dilution system. Good metrological practice would be to confirm the low concentration region of the calibration curve using an appropriately certified reference gas mixture. There are several "metrological levels" of such standards. Primary standard gas mixtures (PSMs) are standards prepared using procedures (most often gravimetry) that enable establishing the traceability of measurement results to the International System of units (SI) with minimum uncertainty. PSMs are generally not available for purchase but are used within National Metrology Institutes (NMIs) and other CRM producers; however, as in the SOS and WCC-VOC studies, specialized PSMs are at time produced to support particular research programs. In general, the Certified Reference Materials (CRMs) that are available to the public are analyzed and value-assigned against one or more PSMs. The results of measurements made on CRMs are traceable to the SI but have somewhat greater assigned uncertainty than is possible with PSMs. CRMs value-assigned by NIST are termed Standard Reference Materials (SRMs).

Only a limited number of producers have developed NMHC gas CRMs at the nmol/mol level; fewer have done research and development in the pmol/mol region for NMHCs. NIST has experience delivering key halocarbons^{11–13} and some VOCs such as benzene at the pmol/mol level in aluminum cylinders. Pollman et al. have reported the preparation of C_2-C_7 hydrocarbons in stainless steel canisters prepared by the U.S. National Oceanic

and Atmospheric Administration (NOAA). Measurements made on NMHCs in these vessels were found to agree within 5% with those provided by several other laboratories in the U.S., Canada, and Europe.¹⁴ These researchers also reported mixed results for the stability of samples in NOAA network borosilicate glass flasks after one year of storage.

Given the demonstrated need for pmol/mol NMHC CRMs and the relative lack of data on methods and materials for their production, in 2007 NIST initiated a research program to determine the feasibility of producing NMHC CRMs at the pmol/mol level. This program has three phases: (1) development of a suite of five primary standard mixtures (PSMs) at pmol/mol concentrations containing a selected suite of NMHCs, (2) comparison of these standards with other NMIs, and (3) a 10-year stability check program. We here report the successful preparation of the five standards.

EXPERIMENTAL SECTION

NIST has developed a series of certified gas standards with NMHCs at ~5 nmol/mol concentrations for federal and state governments and academia.¹⁵ Procedures for preparing PSMs and CRMs have been documented and demonstrated with Standard Reference Material (SRM) 1800—Non-Methane Hydrocarbon Compounds in Nitrogen, which contains 15 NMHCs.^{16,17} The wellcharacterized pure hydrocarbons and PSMs used to prepare SRM 1800b—Eighteen Non-Methane Hydrocarbon Compounds in Nitrogen¹⁸ were used to prepare five PSMs having NMHCs at 60–230 pmol/mol levels. While recognizing that preparation of more PSMs would facilitate evaluating some issues, given the available resources five PSMs were judged to likely provide a sufficient first assessment of the CRM feasibility.

Cylinders. New aluminum gas cylinders, 29.5 and 5.9 L internal volume, were obtained commercially and used in the preparation of the pmol/mol PSMs. The cylinder manufacturer cleaned the interior of the cylinders with a caustic etch followed by an acid wash procedure. The cylinders were conditioned with the proprietary ACULIFE IV (Scott Specialty Gases, Plumstead-ville, PA) chemical vapor deposition process to render the inner walls chemically inert. The concentration levels of 15 NMHCs in the original SRM 1800, prepared in similarly treated aluminum cylinders, have remained stable since the initial certification in 1993 within their stated $\pm 2.0\%$ to $\pm 3.5\%$ relative uncertainty at 95% level of confidence.¹⁹

Regulators and Tubing. New two-stage, high-purity, low dead volume regulators were purchased for this project. It was specified that these regulators be processed and cleaned without using products that would contribute NMHC contamination. Silonite coated stainless steel tubing and traps are used in the cryogenic preconcentration unit and from the regulators on the cylinders

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Figure 1. Preparation scheme for the pmol/mol Primary Standard Mixture (PSM) suite. Uncertainties are standard deviations $(1 - \sigma)$ in the mass determinations.

to the sampling manifold to minimize absorption/desorption of NMHCs.

Diluent Nitrogen. Four cylinders of high-purity diluent nitrogen (N_2) gas obtained from a commercial supplier were used to prepare the pmol/mol PSMs. All materials were stated by their manufacturer to have a minimum purity of 99.9995% (excluding argon).

"Parent" nmol/mol Primary Standard Mixtures. Three of the mixtures used in the certification of SRM 1800b were selected as "parent" ≈ 5 nmol/mol materials for creating the desired pmol/mol PSMs. These parent mixtures were prepared from a "grand-parent" containing the NMHCs at ~250 nmol/mol that was developed from pure hydrocarbon reagents and diluent N₂.¹⁸

Weighing Apparatus. The 5.9 L cylinder was weighed on a Mettler XP10002S top-loading balance having a capacity of 10 kg and 0.01 g sensitivity. The 29.5 L cylinders were weighed on a Mettler SR64001 top-loading floor balance with a 64 kg capacity and 0.1 g sensitivity. A minimum of five independent weighings (tare, cylinder placement, stabilization, mass recording) were made after evacuation, after addition of the NMHC mixture from the parent PSM, and after completion of diluent addition.

Preparation of pmol/mol Primary Standard Mixtures. The five "child" PSMs were prepared as shown in Figure 1. Each cylinder was purged twice with diluent N_2 (~1.4 MPa). The second purge was analyzed chromatographically to confirm the absence of NMHC contamination. The cylinders were then evacuated, charged with an aliquot of the selected parent mixture, and brought to the desired nominal concentration by addition of diluent from one or two N_2 source cylinders as needed to achieve the required pressure. The PSM cylinders were weighed after evacuation, after the addition of the parent standard, and after each addition of N_2 diluent. When more than one diluent source was used, the mass of diluent from each source was determined from single weighings rather than as the average of multiple independent weighings.

Chromatographic Analysis. An Agilent 6890 gas chromatograph with a flame-ionization detector (GC/FID) was used for all analyses. A 30 m \times 0.32 mm J&W GASPRO capillary column was used to achieve baseline separation of the compounds. The column was temperature programmed from 70 to 220 °C at 5 °C/min and held 3 min with a helium column flow of 2 mL/ min for 2 min then to 4 mL/min. The FID was operated at 250 °C with a makeup flow of 30 mL/min helium. The standards were prepared for injection onto the column using an Entech 7100 preconcentrator, collecting 1000 mL of sample at a flow of 200 mL/min. The Agilent 6890 Chemstation software was used to integrate the peak areas. Integration in all cases was baseline to baseline with the exception of a few cases that required subtraction of an impurity on the shoulder of a main peak. The Chemstation software was used to collect the data and a macro program was used to transfer it to an Excel spreadsheet for further analysis. Sample blanks, that is the various high-purity diluent N2 sources used to prepare the standards, were periodically analyzed to both characterize the diluents and to ensure that results for target NMHCs in the PSMs were not degraded by memory effects. Within the target-specific measurement imprecision, no carry-over was observed for any analyte. See Estimation of NMHC in Diluent below for further information.

RESULTS AND DISCUSSION

In addition to the use of well-characterized, relatively highconcentration "parent" materials and careful weighing, successful preparation of PSMs at pmol/mol levels requires that great attention be given to all possible sources of NMHCs. These include impurities in the diluent N₂, absorption onto the cylinder walls, and contamination of the regulators and/or tubing used to connect the source gases to the pmol/mol PSM cylinders.

Preparation-Method Assignment of NMHC Concentrations. *Source Gases.* Since all parent and child PSMs are very dilute mixtures of NMHCs in N₂ diluent, in the absence of contamination, the mole-fraction concentration of the *i*th NMHC in the *j*th child, x_{ij} can be approximated as:

$$x_{ij} = \frac{x_{i,\text{parent}} m_{\text{parent}} + x_{i,\text{dil}} m_{\text{dil}}}{m_{\text{N}_2}} \tag{1}$$

where $x_{i,\text{parent}}$ is the mole-fraction concentration of the *i*th NMHC in the parent, m_{parent} is the mass of the parent added (calculated from the mass of the evacuated cylinder and the mass after

adding parent), $x_{i,\text{dil}}$ is the mole-fraction concentration of the NMHC in the diluent, m_{dil} is the mass of the diluent transferred (calculated from the mass after adding parent and after adding diluent), and m_{N_2} is the total mass of N_2 (parent and diluent, calculated from the mass of the evacuated cylinder and the mass after adding diluent). The combined uncertainty of the concentration, $u(x_{ij})$, is estimated from the standard uncertainties of these input quantities via propagation of uncertainties.²⁰ The uncertainties in the masses include weighing imprecision, the sensitivity of the balances, and an allowance for metal loss from the regulator during transfer manipulations. The uncertainty in the mole-fraction concentration in the diluent includes the uncertainty in the estimated trace NMHC concentrations in the N_2 cylinders and in the determination of the mass of diluent added from each N_2 cylinder used.

NMHC in Parent PSMs. Supporting Information Table S-1 lists the $x_{i,parent}$ mole-fraction NMHC concentrations for each parent. Previous chromatograms of the parent PSMs indicated extremely low levels of only a few impurities and none that interfered with the 18 NMHCs. PSM comparison programs undertaken by the Gas Analysis Working Group of the Consultative Committee on the Quantity of Matter—Chemistry, the "tip" of the international metrological committee's hierarchy, consistently demonstrate that the values assigned to NIST-produced PSM agree well with standards prepared by other NMIs.^{21–23}

Estimation of NMHC in Diluent. In contrast to the $x_{i,\text{parent}}$, the $x_{i,\text{dil}}$ of NMHC impurities in the diluent N₂ must be estimated from direct measurement. Note that "99.9995 % purity" allows for up to 5000 nmol/mol total nonargon impurities. Each cylinder of N₂ used to prepare the primary standards was analyzed by trapping 1000 mL of sample, the effective volume limit of the cryogenic preconcentrator. Detectable amounts (in the range of tens of pmol/mol, suggesting that the manufacturer's purity assessment was quite conservative) of several of the target NMHCs were found to be present in one or more of the cylinders. Supporting Information Figure S1-A–D display exemplar GC/ FID chromatograms for the four diluent sources.

Prior to preparing the child PSMs, no calibration standard existed suitable for the analysis of NMHCs at low pmol/mol levels. Therefore the \sim 60 pmol/mol PSM (cylinder CAL9493, hereafter termed PSM₆₀) was used as a reference standard for the analysis of the NMHC components detected in the diluent. Samples of 1000 mL trapped volume were injected a minimum of 5 times

where A_i is the average peak area for the *i*th NMHC in a non-LC PSM, $A_{i,\text{PSM}_{190:\text{before}}}$ is the corresponding average peak area for the immediately preceding PSM_{190} replicates, and $A_{i,\text{PSM}_{190:\text{after}}}$ is the average peak area for the immediately following PSM_{190} replicates. Six independent sets of ratios were obtained over a period of 10 days. Standard uncertainties for the non-LC ratios, $u(R_i)$, were estimated from the withinreplicate peak area standard deviation and the among-ratio standard deviations of the independent determinations.²⁴ The ratio for PSM_{190} , $R_{i,\text{PSM}_{190}}$, is defined as one (1.0000). The standard uncertainty for $R_{i,\text{PSM}_{190}}$, $u(R_{i,\text{PSM}_{190}})$, is estimated by linear regression of $u(R_i)$ as a function of R_i , approximating the estimate expected if PSM_{190} had also been analyzed as a non-LC PSM. Supporting Information Table S-4 lists the estimated relative ratios for all five of the pmol/mol PSMs.

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for each N₂ cylinder and for PSM₆₀. For each cylinder, the $x_{i,dil}$ were assessed as

$$x_{i,\text{dil}} = \frac{A_{i,\text{dil}}}{A_{i,\text{PSM}_{60}}} x_{i,\text{PSM}_{60}}$$
(2)

where $A_{i,dil}$ is the average GC/FID peak area for the *i*th NMHC component in the diluent, $A_{i,PSM_{60}}$ is the area in PSM₆₀, and $x_{i,PSM_{60}}$ is the mole-fraction concentration of the NMHC in PSM₆₀. Iterative assignment was required for the diluent (cylinder K025953) used to prepare PSM₆₀. Using an initial estimate of $x_{i,dil} = 0$, the estimated value from eq 2 was serially substituted into eq 1 until there was no appreciable change in the estimated value. The uncertainties in the assigned diluent concentrations, $u(x_{i,dil})$, were estimated from the standard deviations of the diluent and PSM₆₀ peak area determinations and the uncertainty in the (final) estimate of mole-fraction concentration in PSM₆₀, $u(x_{i,PSM_{60}})$.

For NMHCs that were not detected in the diluent, approximate detection limits were estimated as twice the baseline variability at the expected chromatographic retention-time. Both the $x_{i,dil}$ and $u(x_{i,dil})$ for these "non-detected" components were assigned values of one-half the detection limits. Supporting Information Table S-2 lists the assigned values for the 18 target NMHC components in the four N₂ sources. Supporting Information Table S-3 lists the assigned values in the five pmol/mol PSMs.

Validation of Assigned Preparative Values. Chromatographic Peak Area Ratio. The relative concentrations of each NMHC component in the five PSMs were determined from peak area ratios. The ~190 pmol/mol PSM (cylinder AAL072286, hereafter termed PSM₁₉₀) was designated as the lot control (LC). PSM₁₉₀ was analyzed before and immediately after analysis of each pmol/mol PSM. At least four replicate chromatograms were obtained for each PSM analysis. The peak area ratio (R_i) for each of the four non-LC PSMs relative to PSM₁₉₀ was estimated as

 $R_i = \frac{A_i}{(A_{i.\text{PSM}_{100}:\text{before}} + A_{i,\text{PSM}_{100}:\text{after}})/2}$

(3)

⁽²⁰⁾ Joint Committee for Guides in Metrology. Guide to the expression of uncertainty in measurement (GUM). JCGM 201, Sèvres, France, 2008. http://www.bipm.org/en/publications/guides/gum.html.

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⁽²⁴⁾ Accuracy (Trueness and Precision) of Measurement Methods and Results. Part 2: Basic Method for the Determination of Repeatability and Reproducibility of a Standard Measurement Method; ISO 5725-2; International Standards Organization: Geneva, Switzerland, 1994.

Regression Analysis. Assuming that the calculated mole-fraction concentrations in the pmol/mol PSMs and the GC/FID peak-area ratios are linearly related, $x_{ii} = \alpha_i + \beta_i \cdot R_{ii} + \varepsilon_i$ where *i* indexes the NMHC components and *j* the five pmol/mol PSMs, then linear regression can be used to estimate the model parameters. Since there are significant uncertainties associated with both x_{ii} and R_{ii} , an "errors in variables" (EiV) regression model that appropriately takes all of the known uncertainties into account must be used. Ripley and Thomson's functional linear estimation by maximum likelihood model (FREML)²⁵ and Milton and co-worker's generalized regression (GENLINE)²⁶ approaches, which provide identical results for first-order models, are in accord with the methods of analysis advocated in the ISO 6143 international standard for gas analysis.²⁷ In essence, this EiV model estimates α_i and β_i to minimize the root-mean square of the sum of the uncertainty-normalized residuals

$$\varepsilon_{\text{total}} = \sqrt{\sum_{j=1}^{N} \left(\left(\frac{\hat{x}_{ij} - x_{ij}}{u(x_{ij})} \right)^2 + \left(\frac{\hat{R}_{ij} - R_{ij}}{u(R_{ij})} \right)^2 \right) / (N - 2)} \quad (4)$$

where *N* is the number of data, N - 2 is the number of degrees of freedom, and \hat{x}_{ij} and \hat{R}_{ij} are the predicted values for x_{ij} and R_{ij} using the equation $\hat{x}_{ij} = \alpha_i + \beta_i \cdot \hat{R}_{ij}$. While requiring an iterative solution, this model produces identical estimates for \hat{x}_{ij} and \hat{R}_{ij} regardless of which is considered the "dependent" variable.

The linear-model parameter values provide insight into the success of the preparation procedure. If the x_{ij} are accurately determined and were either stable over the time period from preparation to GC/FID analysis or changed in proportion to the initial level in all five PSMs, then the intercepts, α_i , should be about zero and the slopes, β_i , should be about equal to the mole-fraction concentration of the component in PSM₁₉₀, $x_{i,PSM_{190}}$. Since the $x_{i,PSM_{190}}$ differ among the target NMHCs, it is more convenient to evaluate the slope normalized to its expected value, $\beta_i / x_{i, \text{PSM}_{100}}$, which should all be about unity. The uncertainties estimated for the intercept, $u(\alpha_i)$, and the normalized slope, $u(\beta_i/x_{i,\text{PSM}_{190}})$, help quantify what is meant by "about". Figure 2 displays the PSM₁₉₀normalized slopes as a function of intercept for all 18 components, along with their approximate 95% coverage intervals. Only for propane do either the intercept or normalized slope significantly (at the approximate 95% level of confidence) differ from the expected values.

The differences between the concentrations predicted by the model and those assigned by the preparative procedure enable evaluation of model linearity, the adequacy of the input uncertainty estimates, or both. The relative mole-fraction residual,

$$\varepsilon_{\text{MF},i} = \sqrt{\sum_{j=1}^{N} \left(\frac{D_{ij}}{x_{ij}}\right)^2 / (N-2)}; D_{ij} = \hat{x}_{ij} - x_{ij}$$
(5)

- (25) Ripley, B. D.; Thompson, M. Analyst 1987, 112 (4), 337–383. Linear Functional Relationship Estimation by Maximum Likelihood (FREML) freeware is available from http://www.rsc.org/Membership/Networking/ InterestGroups/Analytical/AMC/Software/FREML.asp.
- (26) Milton, M. J. T.; Harris, P. M.; Smith, I. M.; Brown, A. S.; Goody, B. A. *Metrologia* 2006, 43, S291–S298. XLGENLINE freeware is available through http://www.eurometros.org.
- (27) Gas Analysis—Comparison Methods for Determining and Checking the Composition of Calibration Gas Mixtures; ISO 6143; International Standards Organization: Geneva, Switzerland, 2001.



Figure 2. Normalized slope as a function of intercept. Each symbol represents the {intercept,slope} estimates for one of the 18 target NMHCs. The bars represent approximate 95% confidence intervals on the estimates. The dotted horizontal and vertical lines represent the expected zero-intercept and unit normalized slope expected for completely concordant assigned and measured values. Only for propane, represented by a solid square, does either the observed intercept or the slope differ significantly from the expected.

provides perhaps the most "chemically meaningful" summary statistic for each model. However, evaluating whether the uncertainties were appropriately estimated is facilitated by evaluating the uncertainty of the residuals:²⁸

$$u(D_{ij}) = \sqrt{u^{2}(\hat{x}_{ij}) + u^{2}(x_{ij})} \\ \approx \sqrt{u^{2}(\alpha_{j}) + (\beta_{j}\hat{R}_{ij})^{2} \left(\left(\frac{u(\beta_{j})}{\beta_{j}} \right)^{2} + \left(\frac{u(\hat{R}_{ij})}{\hat{R}_{ij}} \right)^{2} \right) + 2 \times \operatorname{cov}(\alpha_{j}, \beta_{j}) + u^{2}(x_{ij})}$$
(6)

where $cov(\alpha_{j},\beta_{j})$ is the covariance between the slope and intercept parameters. This covariance can be expressed as the product of the parameter uncertainties and the correlation between the parameters: $cov(\alpha_{j},\beta_{j}) = u(\alpha_{j}) \times u(\beta_{j}) \times \rho(\alpha_{j},\beta_{j})$. For all of the NMHCs studied here, ρ is about -0.90. Given this strong negative relationship, the usual practice of ignoring covariance between parameters overestimates the uncertainties on the residuals. GENLINE output includes an estimate for the covariance; it is not currently provided by FREML.

Anomalies. Table 1 lists the EiV regression parameter values for the 18 target NMHCs, with the few anomalous values listed in bold font. In addition to the exceptional intercept and slopes for propane, the $\varepsilon_{\text{total}}$ for *i*-butene and 1-pentene are large, $\varepsilon_{\text{%MF}}$ for *n*-nonane is somewhat large, and only four of the PSMs were usable for the determination of toluene and *o*-xylene. While the intercept for *o*-xylene is high, the uncertainty on the intercept is also large and therefore a difference from zero cannot be inferred. Figure 3 displays the data, regression model, and mole-fraction residuals for these six analytes; Supporting Information Figure S-3A–C displays this information for all of the target NMHCs.

⁽²⁸⁾ Bevington, P. R.; Robinson D. K. Data Reduction and Error Analysis for the Physical Sciences, 2nd ed.; WCB/McGraw-Hill: Boston, MA, 1992.

Table 1. Parameter Values for the Regression of pmol/mol Preparation Values onto GC/FID Measurements^a

analyte	N^b	residuals		intercept ^e		slope ^f		$\beta/x_{\text{PSM}_{190}}^{g}$		
		$\varepsilon_{\text{total}}^{c}$	$\varepsilon_{\rm \%MF}{}^d$	α	$u(\alpha)$	β	<i>u</i> (β)	value	u	$ ho^h$
ethane	5	0.56	0.8	-4.16	2.04	208.0	2.9	1.023	0.015	-0.91
propane	5	1.66	0.7	4.09	0.57	202.4	0.9	0.978	0.005	-0.90
propene	5	1.76	0.9	-2.65	1.03	197.7	1.3	1.009	0.007	-0.93
<i>n</i> -butane	5	0.58	0.3	-0.46	0.80	198.3	1.2	1.004	0.007	-0.91
<i>i</i> -butane	5	0.42	0.3	-0.71	1.00	202.9	1.4	1.001	0.008	-0.91
<i>i</i> -butene	5	3.17	2.4	0.08	0.97	181.6	1.4	0.987	0.008	-0.90
<i>n</i> -pentane	5	0.66	0.7	-1.85	1.08	195.1	1.8	1.010	0.010	-0.89
<i>i</i> -pentane	5	0.24	0.2	1.13	0.98	187.0	1.5	0.994	0.008	-0.90
1-pentene	5	3.46	3.1	-3.01	1.14	190.8	1.8	1.003	0.010	-0.90
<i>n</i> -hexane	5	0.91	1.0	-2.83	1.26	192.3	2.1	1.018	0.012	-0.90
<i>n</i> -heptane	5	1.35	2.2	-2.16	1.63	191.2	3.1	1.009	0.017	-0.90
<i>n</i> -octane	5	1.20	1.9	-1.93	1.56	192.2	3.2	1.001	0.017	-0.90
<i>i</i> -octane	5	1.40	1.1	-1.51	1.06	194.9	1.6	1.010	0.009	-0.91
<i>n</i> -nonane	5	1.73	3.7	-2.08	1.99	196.5	3.6	1.019	0.019	-0.89
<i>n</i> -decane	5	1.08	1.4	-1.43	1.73	186.8	2.6	0.996	0.014	-0.90
benzene	5	1.06	3.0	1.04	2.93	184.0	4.8	0.972	0.026	-0.89
toluene	4	1.43	3.4	0.46	2.91	190.1	5.6	1.000	0.030	-0.91
o-xylene	4	1.01	2.2	6.21	2.13	183.5	4.3	0.946	0.022	-0.91

^{*a*} Values suggesting anomalous results listed in bold font; see text for further information. ^{*b*} Number of PSMs used in the regression. ^{*c*} From eq 4; a residual estimate that considers uncertainties on both the mole-fraction preparation values and the GC/FID measurements. These estimates can be interpreted as Student's *t* values. The critical one-tailed 95% Student's *t* value for N = 5 is 3.18, for N = 4 is 4.3. ^{*d*} From eq 6; a residual estimate that addresses only the relative difference between the measured and the predicted mole-fraction preparation values. ^{*e*} Intercept and its associated uncertainty estimate, having units of pmol/mol; values significantly differing from zero indicate constant bias. ^{*f*} Slope and its associated uncertainty estimate, having units of pmol/mol relative to the preparation-assigned mole-fraction in PSM₁₉₀. ^{*g*} Ratio of the slope and the PSM₁₉₀ mole-fraction; values significantly differing from unity indicate proportional bias. ^{*h*} Correlation between the estimated intercept and slope parameters.

Toluene and o-Xylene. An anticipated hurdle in the preparation of accurate pmol/mol NMHC gas standards is the cleanliness of the starting gas cylinder and its valve. No measurable impurities were apparent in the high-purity N2 purge gas analyzed just prior to final evacuation prior to preparing the PSMs. However, one week after the PSMs were prepared, contamination peaks representing high molecular weight compounds were observed in PSM₁₆₀ (Figure 3 and Supporting Information Figure S-2C). As can be seen in Figure 4, this contamination severely impacts the toluene and o-xylene concentrations in PSM_{160} ; regression models for these two NMHCs are therefore based on the four uncontaminated PSMs. We speculate that the contamination is from solvents used to clean the cylinder valve of the oils used in the thread cutting process. Previous experience with known trichloroethylene contamination established that heating of the cylinder valve increases the amount of trichloroethylene seen in the GC/FID chromatogram. However, since only one standard was prepared from parent ALM024292, the issue of whether the contamination is related to the parent or the cylinder valve can not be resolved. Future preparative studies will be designed to protect against such confounding.

i-Butene and 1-Pentene. While contamination could also be the source of the small discrepancies in the PSM_{160} values for *i*-butene and 1-pentene visible in Figure 4, it is unlikely that these relatively volatile NMHCs would be present in a commercial solvent. Since PSM_{160} is the only child PSM prepared from parent ALM024292, such contamination cannot be ruled out. However, scrutiny of recent analytical data on all three of the parent PSMs used to prepare the child PSMs suggests rather that *i*-butene and 1-pentene levels in parents AAL067784 and AAL07124 have declined by several percent from the values assigned in 2004. While previous studies have revealed stability problems with the alkyne acetylene in cylinder gas mixtures but not for alkenes,¹⁵ it is plausible that alkenes may slowly react with the walls of at least some cylinders. If so, we anticipate that degradation may be more apparent at the pmol/mol levels of the child PSMs than at the nmol/mol levels of their parents. Such changes will be carefully evaluated as part of NIST's stability studies on this suite of PSMs.

n-Nonane. In contrast to the positive mole-fraction PSM₁₆₀ residual of the alkenes, degradation is not a plausible cause for the negative residual for *n*-nonane. The data suggest that the assigned *n*-nonane concentration in parent PSM ALM024292 is too large by about 5% or that the relative area of *n*-nonane in child PSM₁₆₀ is too small by about 5%. Review of the analytical history for the parent PSMs excludes such a large missassignment of a single parent. However, review of the original chromatograms for the child PSMs suggests that high-boiler contamination of PSM₁₆₀ (see Supporting Information Figure S-2C) more severely influences assessment of chromatographic baseline than was initially appreciated, leading to systematic underestimation as well as increased variability. (Unlike the processed chromatograms displayed in the Figures, the baselines of the original chromatograms are significantly curved but only in the *n*-nonane retention time region.) While less objective than the areas estimated using routine software settings, manual reintegration of the n-nonane peaks nearly eliminated the discrepancy.

Propane. Propane should be the "best behaved" of the 18 target NMHCs: NIST has long experience with propane in several matrices spanning a concentrations range of 10^9 and there has been excellent agreement among NMIs in several international comparisons.^{22,23} However, the data suggest that the assigned propane concentrations in all five child PSMs are *over*estimated by ~4 pmol/mol. Given the excellent linearity of the data, it is extremely unlikely that such a relatively constant bias could result from variably miss-assigned propane





Figure 3. Data and regression models for the anomalous NMHC components. The open symbols in each panel display the preparationassigned pmol/mol concentrations as a function of the measured relative peak areas for one NMHC. Open (black) circles denote data that was used in the estimation of the regression parameters; open (red) diamonds denote data that was not used. The small crosses centered in the open symbols represent approximate 95% confidence intervals on the values. The diagonal (black) line represents the errors-in-variables regression line. The solid (blue) squares display the difference between the regression-predicted and the assigned pmol/mol concentrations; the vertical (blue) bar about each square represents the approximate 95% confidence interval on the difference. The horizontal (blue) line denotes zero difference.

concentrations in the parent PSMs. It is more likely that the concentration of propane in all of the diluent N_2 sources is somehow overestimated and that the "propane" contaminate in the diluent N_2 cylinders is a composite of propane and an unknown compound. There are a number of "unknown" compounds present in all diluent sources (see Supporting Information Figure S-1A–D) and prior investigations at NIST using similar GC/FID techniques found that monofluoropro-

pane can interfere with propane determination. While chromatographic analysis using electron capture detection (ECD) did not indentify any halogenated species in the propane retention time region, ECD may not be sufficiently sensitive to monofluorinated species for detection at these low levels. We will continue to explore this peculiar result.

NMHCs as a Group. Taken individually, none of the intercepts for any NMHC other than propane can be confidently identified



Figure 4. Exemplar chromatograms of pmol/mol child PSMs. The same FID response scale is used for all five PSMs. These chromatograms have been processed to minimize baseline curvature. See the Supporting Information Figure S-2A-C for higher resolution displays.

as differing from zero. However, the large majority of the estimated intercepts are in the range of -1 pmol/mol to -2 pmol/mol (see Figure 2). With prefect data, this would suggest a few pmol/mol of most NMHCs are as yet unaccounted for somewhere within the preparation method or analytical system. While this bias is gratifyingly small, future work will attempt to identify its sources.

CONCLUSIONS

The $\pm 2 \text{ pmo/mol}$ agreement between the assigned concentrations and the relative analytical measurements for the majority of the NMHC targets demonstrates that the methods used to prepare the current suite of PSMs can produce self-consistent pmol/mol NMHC standards. However, great care must be taken to limit contamination in the cylinders, the cylinder valves, and the sampling system including the cryogenic preconcentration unit. The few observed discordances between the expected and observed measurements suggest that even more stringent precautions should be taken in the future. New cylinders should be charged with the intended diluent, analyzed with GC/FID or other similarly sensitive technique, set aside for many months, and reanalyzed before use. Any cylinders found to have impurity levels above those present in the original diluent should not be used. When checking these cylinders for cleanliness, the cylinder valves should be slightly warmed to enable GC/FID detection of any less-volatile contaminants.

Great care must also be taken to minimize the level of contamination in the diluent used to prepare the PSMs. The level of contamination in even the cleanest of commercial gases could be reduced by passing the diluent through a large trap designed to take out hydrocarbons. While it is difficult to characterize contamination at low pmol/mol levels, accurate characterization of the diluent becomes of ever greater importance the lower the desired levels of the target analytes. A certified NMHC standard having mole-fraction concentrations of ~100 pmol/mol or less could benefit research using dilution techniques to obtain lower concentrations from higher level standards by simplifying the assessment of diluent purity and the performance characteristics of the dilution system.

To facilitate evaluation of discrepancies between the preparative and measured values, future PSM suites should consist of at least two child PSMs for every parent PSM used. The evaluation of the various problems eventually traced to cylinder contamination would have been much simplified had PSM_{160} not been the only child of its parent.

Having demonstrated that self-consistent pmol/mol NMHC standards can be produced, investigations are now in progress addressing the long-term stability of all components and the metrological trueness (i.e., absence of bias) of the value-assignments. Stability studies under expected use conditions intrinsically take considerable time: the WMO/GAW desires at least 10 years of data. NIST will prepare new pmol/mol PSMs at 1 to 2 year intervals to validate the proposed modifications to the preparation procedure and to help monitor the stability of the current PSM suite. To explore the possible degradation of the alkenes, PSMs will be prepared in containers made of other materials or with different internal treatments. Given that there are no established reference materials suitable for evaluating the assigned values, comparison of results provided from completely independent assessments made by expert analysts at several institutions is the best available mechanism for revealing unrecognized biases, a key step in establishing the degree of metrological trueness. Such a collaborative study of PSM_{190} is in progress involving the National Physical Laboratory of the United Kingdom, the Korea Research Institute of Standards and Science of the Republic of Korea, and the Van Swinden Laboratorium of The Netherlands. We anticipate that at least one WMO/GAW-VOC laboratory will also participate.

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Disclaimer: Certain commercial equipment, instruments and materials are identified to specify experimental procedures as completely as possible. In no case does such identification imply a recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that any of the materials, instruments, or equipment identified are necessarily the best available for the purpose.

SUPPORTING INFORMATION AVAILABLE

Tables showing NMHC concentrations in parent PSMs, NMHC concentrations in N2 diluent, preparative NMHC concentrations in child PSMs, and relative GC/FID peak areas in child PSMs and Figures showing exemplar GC/FID chromatograms of diluents: segment 1, exemplar GC/FID chromatograms of diluents: segment 2, exemplar GC/FID chromatograms of diluents: segment 2, exemplar GC/FID chromatograms of diluents: segment 3, exemplar GC/FID chromatograms of PSMs: segment 1, exemplar GC/FID chromatograms of PSMs: segment 1, exemplar GC/FID chromatograms of PSMs: segment 2, exemplar GC/FID chromatograms of PSMs: segment 3, data and regression models—ethane to *i*-butene, data and regression models—*n*-pentane to *n*-octane, and data and regression models—*i*-octane to *o*-xylene. This material is available free of charge via the Internet at http://pubs.acs.org.

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