NPL
National Physical Laboratory

Report

NPL REPORT AS 029

EURO.QM-S3

EURAMET 886
Comparison of multi-component ambient VOC measurements

Final Report

Robin Grenfell, Chris Brookes, Gergely Vargha, Paul Quincey, Martin Milton, Peter Woods, Peter Harris, Pascual Ballesta, Hannele Hakola, Mariapaola Sassi, Rosalia Patier, Gwi Suk Heo, Yong-Doo Kim, Hyun-Gil Bae, Jerry Rhoderick, Rob Wessel, Marina Fröhlich and Rainer Steinbrecher

December 2008

National Physical Laboratory | Hampton Road | Teddington | Middlesex | United Kingdom | TW11 0LW

Switchboard 020 8977 3222 | **NPL Helpline** 020 8943 6880 | **Fax** 020 8943 6458 | **www.npl.co.uk**

EURAMET 886

Comparison of multi-component ambient VOC measurements

Final Report

Robin Grenfell[1], Chris Brookes[1], Gergely Vargha[1], Paul Quincey[1], Martin Milton[1], Peter Woods[1], Peter Harris[1], Pascual Ballesta[2], Hannele Hakola[3], Mariapaola Sassi[4], Rosalia Patier[5], Gwi Suk Heo[6], Yong-Doo Kim[6], Hyun-Gil Bae[6], Jerry Rhoderick[7], Rob Wessel[8], Marina Fröhlich[9] and Rainer Steinbrecher[10]

December 2008

[1]National Physical Laboratory, Teddington, United Kingdom
[2]European Commission – Joint Research Centre, Institute for Environment and Sustainability, Ispra, Italy
[3]Finnish Meteorological Institute, Helsinki, Finland
[4]Istituto Nazionale di Ricerca Metrologica, Torino, Italy
[5]Instituto de Salud Carlos III, Madrid, Spain
[6]Korea Research Institute of Standards and Science, Daejeon, Republic of Korea
[7]National Institute of Standards and Technology, Gaithersburg, United States of America
[8]NMi Van Swinden Laboratorium, Delft, the Netherlands
[9]Umweltbundesamt GmbH, Vienna, Austria
[10]World Calibration Centre for Volatile Organic Compounds, Forschungszentrum Karlsruhe, Institute for Meteorology and Climate Research, Garmisch-Partenkirchen, Germany

ISSN: 1754-2928

National Physical Laboratory
Queens Road, Teddington, Middlesex, TW11 0LW

Approved on behalf of Managing Director, NPL
By Alan Brewin, Business Leader, Analytical Science Team

Contents

Executive Summary

NPL prepared, analysed and circulated gas cylinders containing mixtures of Volatile Organic Compounds (VOCs) at amount fractions of a few nmol/mol (molar ppb). The set of VOCs was the set of ozone precursors listed in the Ambient Ozone Directive 2002/3/EC Annex VI. This Report describes all activities involved in delivering this comparison including measurement of cylinder stability.

The 10 participants* were:

Laboratory Name	
ERLAP (Joint Research Centre)	European Commission
FMI	Finland
INRiM	Italy
ISCIII	Spain
KRISS	South Korea
NIST	United States of America
NMi	Netherlands
NPL	United Kingdom
UBA(A)	Austria
WCC-VOC (FZK, IMK-IFU)	Global Atmosphere Watch (Garmisch Partenkirchen)

During this exercise the stability trial of 1-10 nmol/mol VOC mixtures showed less than 0.6% drift for most species over 1 year. Further work, providing increasing statistical weight, has shown less than 0.3% annual drift for all species over 2 years (see Annex G). The accuracy of these standards was further strengthened by the comparison results, which showed good agreement between participants preparing independent standards for the exercise (KRISS, NIST and NMi).

* CHMI (Czech Republic) agreed to participate but did not submit results before the closing date of the comparison.

Part 1: Preparation of synthetic VOC mixtures

The project began with the preparation of 22 mixtures in 10 litre cylinders containing the following VOCs at amount fractions between 1 and 10 nmol/mol, with a dilution gas of known purity.

Table 1. List of the 30 VOCs in the comparison mixtures

ethane	hexane (*n*-hexane)
ethene (ethylene)	2-methylpentane (*i*-hexane)
ethyne (acetylene)	heptane (*n*-heptane)
propane	octane (*n*-octane)
propene	2,2,4-trimethylpentane (*i*-octane)
butane (*n*-butane)	benzene
2-methylpropane (*i*-butane or iso-butane)	toluene
but-1-ene (1-butene)	ethylbenzene
trans-but-2-ene (*trans*-2-butene)	*m*+*p*-xylene
cis-but-2-ene (*cis*-2-butene)	*o*-xylene
1,3-butadiene	1,2,4-trimethylbenzene
pentane (*n*-pentane)	1,2,3-trimethylbenzene
2-methylbutane (*i*-pentane)	1,3,5-trimethylbenzene
pent-1-ene (1-pentene)	
trans-pent-2-ene (*trans*-2-pentene)	
2-methyl-1,3-butadiene (isoprene)	

All mixtures were prepared in Air Products 10.0 litre aluminium gas cylinders, treated internally with the proprietary *Quantum passivation* process to inhibit hydrocarbon adsorption on the walls. The source of the balance gas for all mixtures was Air Products *BIP plus* nitrogen. The nitrogen was flowed through in-line filters and cold traps to remove impurities while filling.

High concentration mixtures (μmol/mol range) were prepared directly using source components. All components were added gravimetrically as a gas, liquefied gas or liquid, using loop injections, which involves the individual weighing of each component and the diluent nitrogen gas. The concentrations of the individual hydrocarbons have been quantified from the gravimetric data with corrections made from the purity analysis, which was assessed by gas chromatographic analysis.

Participant mixtures and working standards were prepared gravimetrically using the high concentration mixtures and the high purity nitrogen balance gas. Two distinct parent mixtures with VOC amount fractions in the range 180 to 380 nmol/mol were used, named V3 and V4, so that there were two distinct mixtures with different component ratios. The two parent mixtures are compared in Table A1 (Annex A) by comparing the response factors obtained when analysing them on the same gas chromatograph.

The composition of each participant mixture was checked for stability by analysing them against a working standard soon after manufacture ("t = 0") and again with a new working standard after an interval of approximately 4 months ("t = 4 months"). Each mixture was checked for stability again against a new working standard when returned to NPL to make up the third round of the stability trial. The third round of

analysis was approximately 12 months after the first round ("t = 12 months"). The new working standards were freshly diluted from the higher concentration parent mixtures prior to each round of analysis. The working standards were verified using a suite of NPL in-house standards.

The parent mixtures of the two versions (V3 and V4) were used to make 4 working standards each (#1, #2, #13 and #15). See Table C2 for working standard gravimetric amount fractions and uncertainties. Working standards #1 and #2 were made and used in the stability trials at t = 0, working standards #13 were made and used at t = 4 months and working standards #15 were made and used at t = 12 months. Participant mixtures were analysed against working standards from the opposing version to minimise errors associated with correlation.

Different gas chromatographs with slightly different methods were used in the analysis at t = 0 and t = 4 months. The method used at t = 12 months is identical to the method used at t = 4 months. The two methods are summarised in the table below:

Table 2. Analytical methods used to measure the VOC mixtures

Apparatus	**t = 0**	**t = 4 months and t = 12 months**
Gas Chromatograph Model	Varian 3600	Varian 3600 CX
Inlet tubing	1/16" Silcosteel tubing	1/16" Silcosteel tubing
Sample preconcentration trap	Tenax TA	Glass Beads
Trapping temperature	-99°C	-165°C
Column	PLOT Al_2O_3/KCl, 50m 0.53mm ID	PLOT Al_2O_3/KCl, 50m 0.53mm ID
Carrier Gas	Helium	Helium
Detector	FID	FID

The results from the 3 rounds of the stability trial are presented in Table A2.

NPL have reviewed their uncertainty analysis for these gravimetric mixtures, a process that incorporates the results from the complete study (see Annex C). The uncertainties associated with the gravimetric preparation of these standards are significantly lower than the analytical precision to which we can measure them. The gravimetric amount fractions for each participant mixture are also given in Table A2.

Part 2: Cross-checking of assigned gravimetric values

The measurement of each mixture against reference standards allows the gravimetric concentrations assigned to each cylinder to be checked for mislabelling or calculation errors.

The criterion for a "significant" difference for component i in cylinder j at time t = 0 is:

$$\left| \frac{x_{ij}(t=0) - x_{ij}(grav)}{u_{ai}} \right| > 2$$

Where 2 gives a "2 sigma" test for the modulus of the left hand side.

$x_{ij}(t = 0)$ is the measured concentration of component i in cylinder j in the first round of analysis and $x_{ij}(grav)$ is the gravimetric concentration of component i in cylinder j. u_a is an estimate of the measurement uncertainty which has been evaluated over the 3 rounds of analysis using the standard deviation of the results. See Annex C for a full description of the uncertainty calculation ($u_a \equiv u_{prec}$). We would expect 5 % of the values to lie outside the range $-2 < y < 2$ (where y is the term inside the modulus brackets) using a confidence interval of 95% associated with this uncertainty.

The graph below shows the plot of this data for 638 data points comprised of 29 component results (in the 30 components m-xylene and p-xylene are reported as 1 result), 2 versions and 11 cylinders in each version measured at the start of the exercise.

This graph shows a 2σ test for calculation of measurement difference using the square root of the average variance of the results from the 3 rounds of analysis as u_a

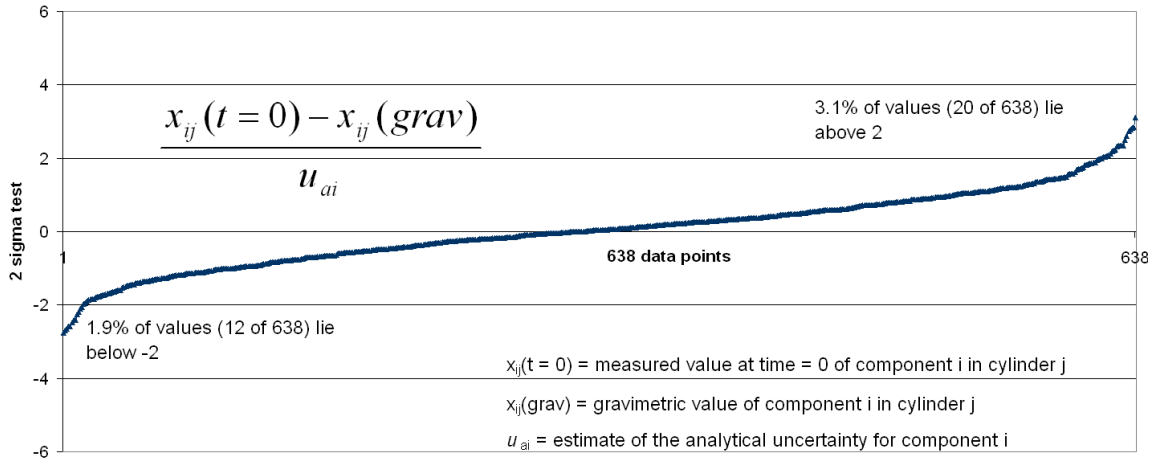


Figure 1. 2σ test as a cross-check of assigned gravimetric values

5% of the values lie outside of the range $-2 < y < 2$ so we can infer that there is no statistically significant variations in the consistencies of the gravimetric concentrations and the measured values at time $t = 0$.

Part 3: Evaluation of the stability in synthetic VOC mixtures

The data from the 3 rounds of stability trials were analysed to identify any statistically significant drift. Each round of analysis was performed against a new working standard that was prepared from a high concentration parent to eliminate errors associated with drift common to the reference and test mixtures. It can be assumed that the percentage drift in these high concentration mixtures is negligible compared with percentage drifts in the low concentration mixtures.

A statistical model was drawn up that treats all cylinders as identical to calculate an estimate for the parameter of drift for each species using the 3 rounds of data at $t = 0$, 4 months and 12 months.

The drift test is based on the hypotheses that

- There is negligible drift in the parent mixtures (at 200 nmol/mol) from which freshly diluted reference mixtures were made at each of the three rounds.

- There is no expectation that the drift of different species will be related, therefore the statistical modelling is done for each species individually. A single drift parameter has been estimated for each version (V3 or V4) of the mixture and for each species.

This last hypothesis effectively assumes that any drift is a property of the species rather than the cylinder. Any result that is an outlier from this model suggests that the cylinder may have "failed" in some way.

The drift tests are based on three sets of measurements, carried out at $t = 0$, 4 months and 12 months. The drift rates were estimated by fitting the model

$$\frac{y_{ij}(t = \Delta t)}{y_{iref}(t = \Delta t)} = c_{ij} + d_i^n * \Delta t + \varepsilon_{ij}^t$$

where the left hand side term represents the fractional deviation from the gravimetric reference value for species i in cylinder j measured at time Δt. $y_{ij}(t = \Delta t)$ is the measured response factor of component i in cylinder j and $y_{iref}(t = \Delta t)$ is the measured response factor of component i in the working standard both measured at time = Δt. d_i^n is the drift rate for species i in version n and c_{ij} is an offset for species i in cylinder j at time $t = 0$. This offset is, in effect, a check on the validity of the gravimetric values similar to that in Part 2, but using all three measurements of each cylinder rather than just the one at $t = 0$. The random error in the measurement of species i in cylinder j at time t is ε_{ij}^t. The measurement of 11 cylinders of 2 versions at three times (0, 4 months and 12 months) gave 65* data points for each species. The model described above has 22 offsets and 2 drift rates per species (one for each version).

* One cylinder was returned empty therefore the number of data points for each species reduced by one from that expected (66).

Hence the data have 65 - 24 = 41 degrees of freedom. The model above was fitted to the data.

The residual sum of squares for the fit for each species were normalised by u_a (for that species) and compared with the expectation value of the chi-squared distribution for 41 degrees of freedom. This tests whether the ε_{ij}^{t} are explained by the estimated uncertainty u_a for that species (Figure 4).

A graph showing drift estimates for all species from the two versions can be seen below:*

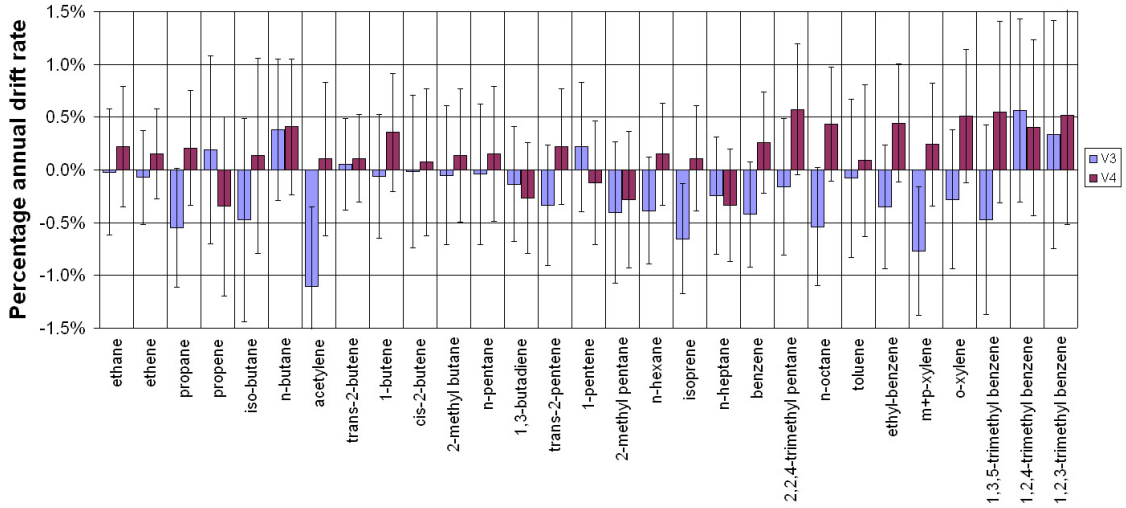


Figure 2. Estimate of the annual drift rate over 3 rounds of stability trials for two versions of 1-10 nmol/mol 30 component ozone precursor mixtures

NOTE: In this figure a value of 1% on the y-axis means that the annual drift rate *d* is 0.01 over the 12 month period of the stability trial.

This model is an indication of any preferential drift for any given species, assuming all species have the same behaviour in all cylinders.

* See Annex G for an updated graph of stability data over an extended (2-year) period.

The model value for the offset (c_{ij}) with respect to its estimated uncertainty was also tested.

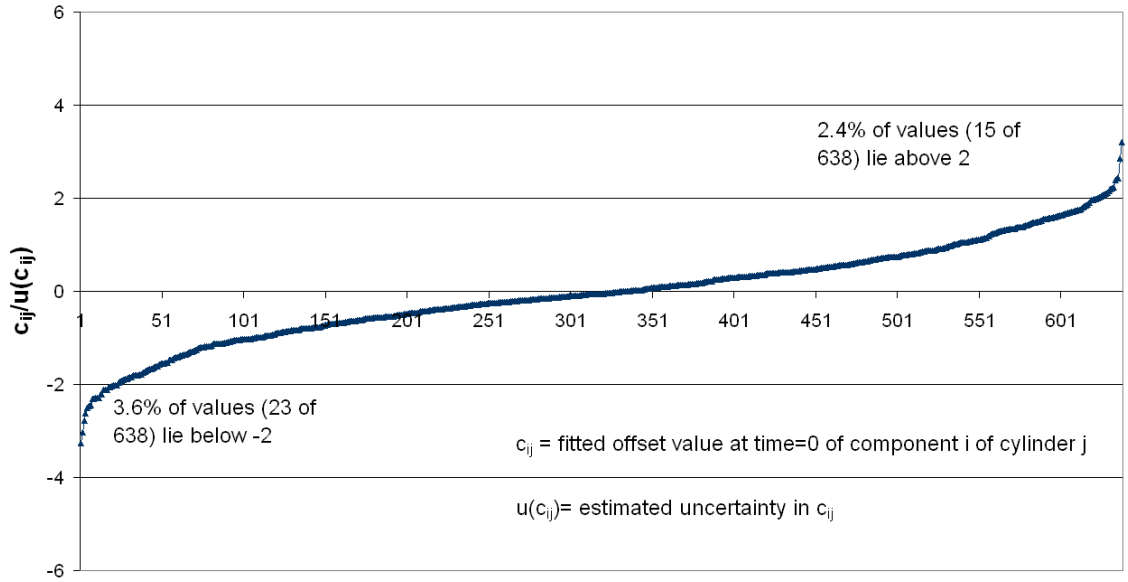


Figure 3. This chart shows the 2σ test for the fitted offset with respect to its estimated uncertainty

According to this plot there are no significant outliers exhibiting a significant offset from the gravimetric value.

Individual cylinders and individual results were examined for outliers by plotting the residual deviations normalised by the analytical uncertainty, u_a as described above, as in Figure 4. No significant outliers were found in each set of 65 data points for each species.

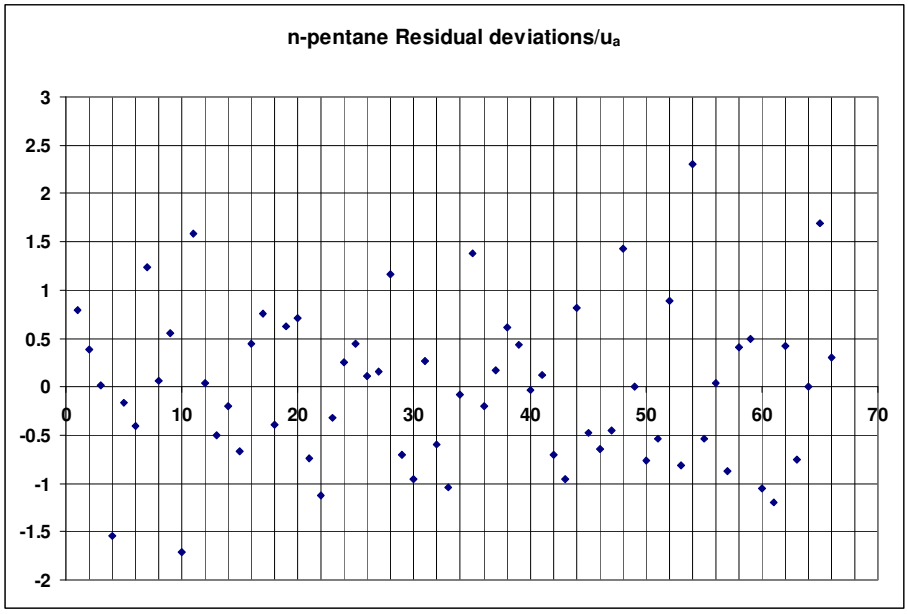


Figure 4. Plotting residual deviations divided by the analytical measurement uncertainty provides information on outliers

As a final test the data can be grouped per component and per cylinder to look for any major issues with stability or analytical error. The following graphs show examples of these tests. See Table A2 for the details of the individual analyses on each participant mixture and the corresponding cylinder reference (V3 #3 to V4 # 14).

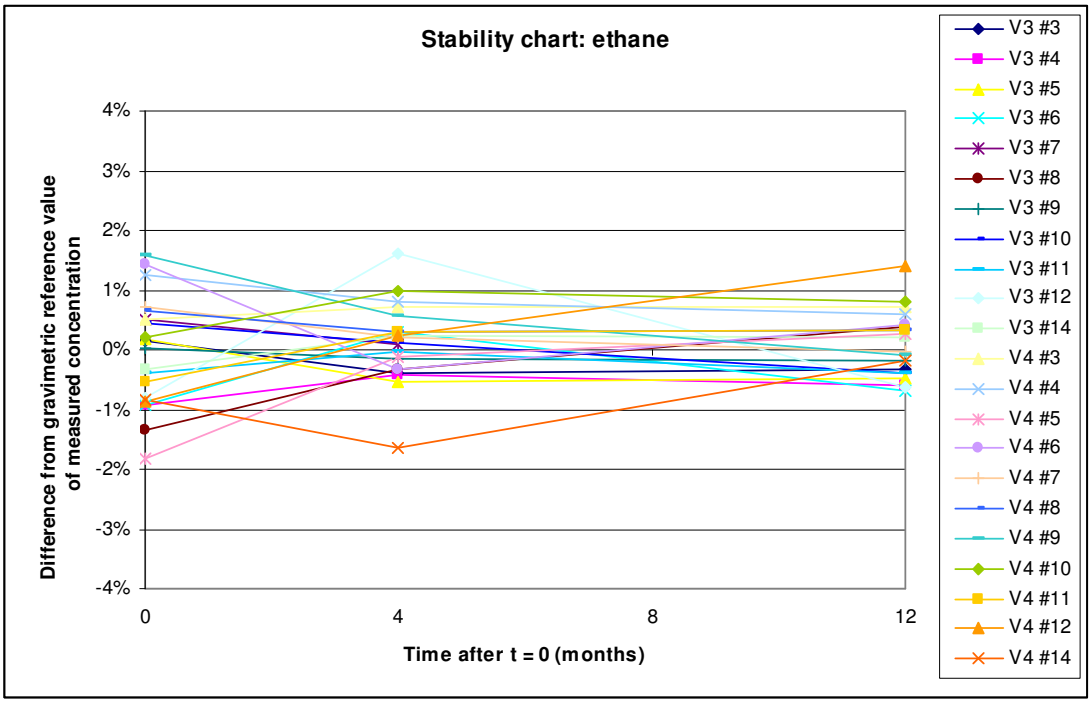


Figure 5. Ethane stability chart over 3 rounds of analysis

A small measurement uncertainty for ethane (u_{prec} = 0.68% - see Annex C) leads to a confident assessment of no drift in ethane in any of the cylinders.

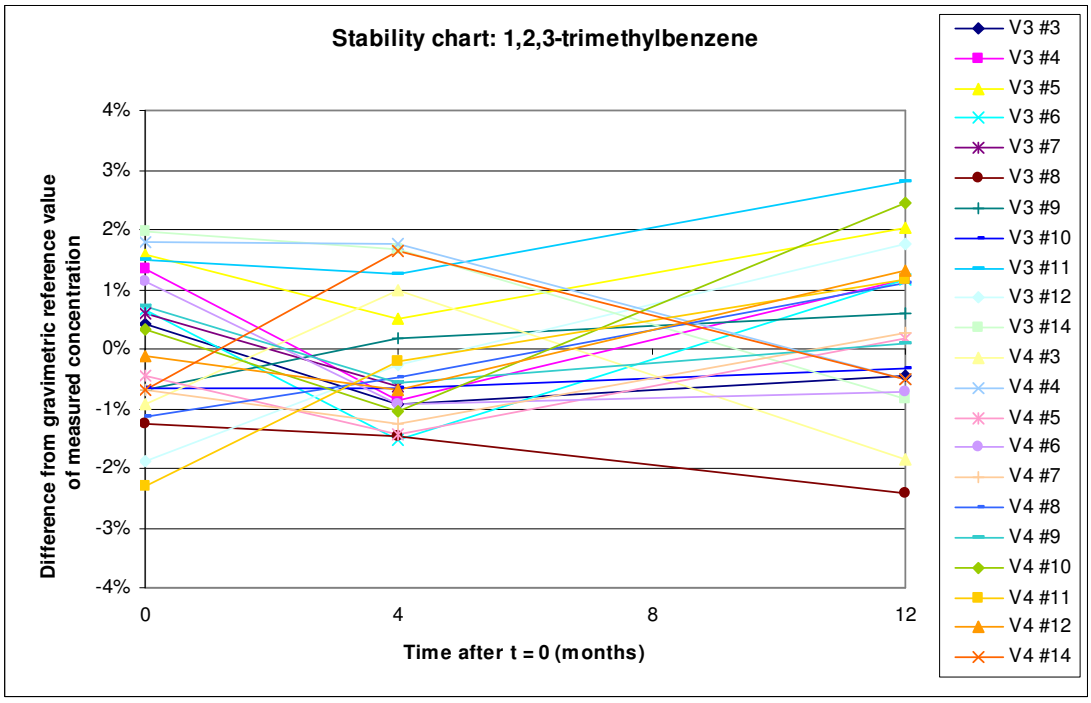


Figure 6. 1,2,3-trimethylbenzene stability chart over 3 rounds of analysis

The greater spread of data in Figure 6 is indicative of a more challenging component to measure (u_{prec} = 1.24% - see Annex C). There is still no obvious drift in any of the mixtures; this is backed up by the statistical drift estimate (Figure 2).

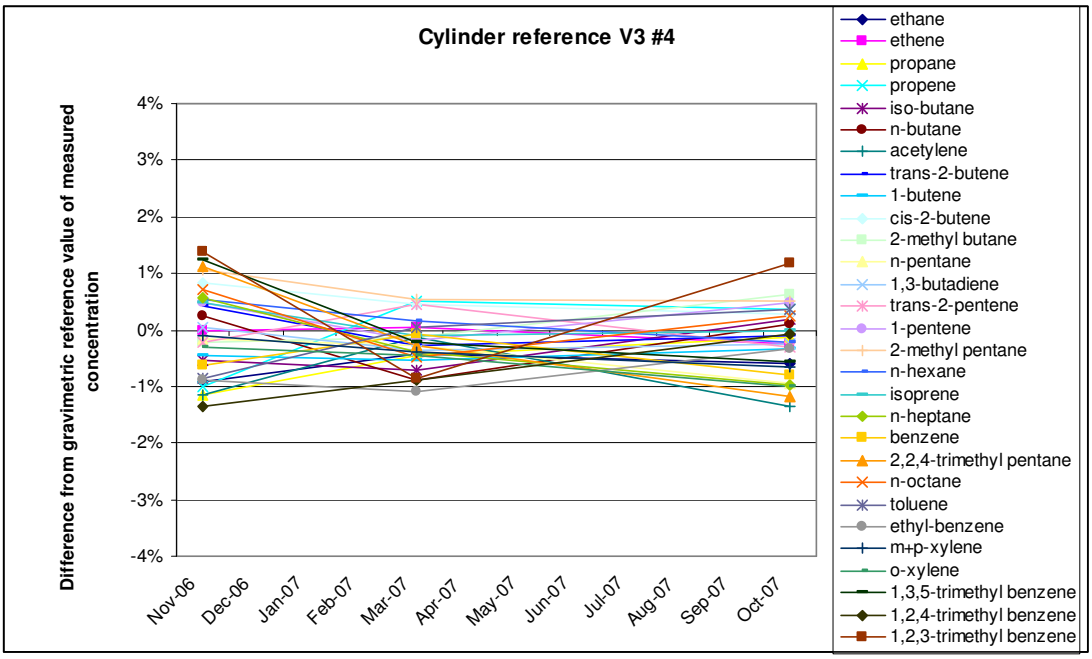


Figure 7. All stability data for cylinder number 4 from version 3 (Ref: V3 #4)

A complete set of these graphs for all the individual species can be found in Annex D.

Our conclusion is that there is no evidence of change in concentration in any of these synthetic VOC mixtures that can be attributed with confidence to the stability of the mixture rather than measurement uncertainty over the period of this study.

Part 4: Participant results

The 10 participants* were:

Laboratory Name	
ERLAP (Joint Research Centre)	European Commission
FMI	Finland
INRiM	Italy
ISCIII	Spain
KRISS	South Korea
NIST	United States of America
NMi	Netherlands
NPL	United Kingdom
UBA(A)	Austria
WCC-VOC (FZK, IMK-IFU)	Global Atmosphere Watch (Garmisch Partenkirchen)

Laboratory methods can be found in Annex F.

4.1 Data

This table shows the date the data was received by NPL for each participating laboratory and any amendments made after submission. See Table B2 for the project timeline.

Table 3. Dates of data submission and subsequent amendments

Participating laboratory	Date data received at NPL	Amendments made (date received)
ERLAP (JRC)	12-July-07	Uncertainty correction (05-October-07)
FMI	10-August-07	
INRiM	25-February-08	
ISCIII	10-August-07	
KRISS	27-August-07	
NIST	15-August-07	
NMi	20-August-07	
NPL	N/A	
UBA(A)	01-August-07	Misidentification (20-February-08)
WCC-VOC (FZK, IMK-IFU)	26-Feb-08	

For details of amendments made see Participant reports in Annex F.

* CHMI (Czech Republic) agreed to participate but did not submit results before the closing date of the comparison.

4.2 Calculation of degrees of equivalence

In this report the degrees of equivalence are reported relative to the Key Comparison Reference Value. The participant results in general agree well with the gravimetric data. This agreement supports, along with the findings from the stability trial, the assignment of the gravimetric value as the KCRV.

The degree of equivalence, D_i, for laboratory i with respect to the reference value is given by two terms: $D_i = (x_i - x_{i\text{kcrv}})$ and U_i, its expanded uncertainty ($k = 2$), both expressed as a percentage relative to the gravimetric KCRV.

Where,

$U_i = 2(u(x_i)^2 + u(x_{i\text{kcrv}})^2)^{1/2}$.

x_i = reported amount fraction by laboratory i;

$x_{i\text{kcrv}}$ = KCRV of participant mixture analysed by laboratory i;

$u(x_{i\text{kcrv}}) = u_{i\text{prec}} + u_{i\text{grav}}$ (see Annex C for detailed uncertainty estimates)

Table 4 shows the degrees of equivalence for the participating laboratories expressed as a percentage of the Key Comparison Reference Value (KCRV).

Table 4. Degrees of equivalence expressed relative to the KCRV for all participants (spaces indicate that no data was received)

Participant	ERLAP (JRC)			FMI			INRiM			ISCIII			KRISS		
Species	D_i		$U(D_i)$	D_i		$U(D_i)$	D_i		$U(D_i)$	D_i		$U(D_i)$	D_i		$U(D_i)$
ethane	0.6%	+/-	7.2%	-4.3%	+/-	4.1%	0.6%	+/-	4.3%	-64.1%	+/-	3.0%	-1.5%	+/-	2.4%
ethene	3.1%	+/-	9.3%	-2.5%	+/-	12.8%	-0.6%	+/-	4.4%	-58.2%	+/-	3.2%	-0.6%	+/-	2.1%
propane	0.0%	+/-	5.0%	-4.3%	+/-	5.0%	-0.2%	+/-	5.6%	-63.9%	+/-	2.7%	-1.4%	+/-	2.7%
propene	-11.7%	+/-	4.6%	-3.3%	+/-	17.6%	-0.5%	+/-	4.9%	-61.6%	+/-	3.4%	-0.4%	+/-	2.7%
iso-butane	0.2%	+/-	7.4%	-5.5%	+/-	11.5%	-0.1%	+/-	4.4%	-60.7%	+/-	3.6%	0.6%	+/-	3.6%
n-butane	0.0%	+/-	6.9%	-14.1%	+/-	12.1%	-0.2%	+/-	4.1%	-60.8%	+/-	3.2%	1.7%	+/-	2.9%
acetylene	9.0%	+/-	10.8%	11.5%	+/-	20.2%	0.3%	+/-	4.6%	-9.9%	+/-	12.4%	0.2%	+/-	2.5%
trans-2-butene	0.1%	+/-	7.1%	-6.0%	+/-	17.9%	-0.1%	+/-	3.9%	-61.0%	+/-	2.7%	-8.1%	+/-	2.1%
1-butene	0.2%	+/-	7.5%	1.4%	+/-	28.4%	0.2%	+/-	4.5%	-60.4%	+/-	3.0%	1.3%	+/-	2.6%
cis-2-butene	-0.1%	+/-	6.4%	-4.4%	+/-	18.2%	0.0%	+/-	4.2%	-75.0%	+/-	3.4%	9.5%	+/-	2.7%
2-methylbutane	0.3%	+/-	6.0%	-1.6%	+/-	14.8%	-0.2%	+/-	4.1%	-50.0%	+/-	3.8%	1.1%	+/-	3.0%
n-pentane	0.2%	+/-	6.5%	-2.2%	+/-	11.8%	0.0%	+/-	4.0%	-64.2%	+/-	2.9%	1.2%	+/-	2.9%
1,3-butadiene	0.4%	+/-	6.3%	1.6%	+/-	19.4%	-0.5%	+/-	4.2%	6.8%	+/-	7.7%	1.2%	+/-	2.5%
trans-2-pentene	0.5%	+/-	5.6%	-4.4%	+/-	18.2%	-0.3%	+/-	4.1%	-58.0%	+/-	3.5%	2.1%	+/-	2.8%
1-pentene	0.4%	+/-	5.8%				-0.5%	+/-	4.3%	-58.7%	+/-	2.9%	1.6%	+/-	3.5%
2-methyl pentane	0.6%	+/-	5.8%	-16.0%	+/-	22.0%	-0.1%	+/-	4.1%				3.4%	+/-	3.3%
n-hexane	0.1%	+/-	4.3%	-7.6%	+/-	21.3%	-0.5%	+/-	4.1%	-65.9%	+/-	4.1%	0.7%	+/-	3.0%
isoprene	0.8%	+/-	7.4%	2.9%	+/-	33.0%	-0.5%	+/-	4.0%	-18.4%	+/-	7.1%	3.6%	+/-	3.0%
n-heptane	-0.1%	+/-	4.1%	-30.5%	+/-	19.5%	-0.5%	+/-	3.9%				-0.5%	+/-	3.2%
benzene	-0.8%	+/-	5.0%	33.6%	+/-	26.7%	-0.5%	+/-	3.9%				1.8%	+/-	3.3%
2,2,4-trimethyl pentane	0.0%	+/-	4.4%				-0.5%	+/-	4.0%				1.4%	+/-	3.1%
n-octane	-0.5%	+/-	3.9%				-0.3%	+/-	4.9%				-1.9%	+/-	3.2%
toluene	0.9%	+/-	6.2%	15.7%	+/-	23.1%	-0.6%	+/-	4.9%				0.3%	+/-	3.3%
ethylbenzene	0.3%	+/-	5.0%	-1.1%	+/-	13.8%							-3.8%	+/-	3.5%
m+p-xylene	1.8%	+/-	6.9%	0.5%	+/-	26.6%							-4.3%	+/-	3.5%
o-xylene	-0.2%	+/-	13.9%	3.7%	+/-	27.1%							-3.6%	+/-	3.6%
1,3,5-trimethyl benzene	3.1%	+/-	10.5%	3.1%	+/-	20.6%							-3.5%	+/-	4.6%
1,2,4-trimethyl benzene	6.4%	+/-	17.1%	3.1%	+/-	18.8%							-6.4%	+/-	4.4%
1,2,3-trimethyl benzene	5.6%	+/-	12.3%	8.4%	+/-	19.6%							1.6%	+/-	5.3%

Table 4. Degrees of equivalence expressed relative to the KCRV for all participants (spaces indicate that no data was received)

Participant	NIST			NMi			NPL			UBA(A)			WCC-VOC		
Species	D_i		$U(D_i)$	D_i		$U(D_i)$	D_i		$U(D_i)$	D_i		$U(D_i)$	D_i		$U(D_i)$
ethane	-1.7%	+/-	2.3%	-0.5%	+/-	2.5%	-0.3%	+/-	1.8%	-19.9%	+/-	3.7%	1.0%	+/-	1.9%
ethene	-2.0%	+/-	1.9%	0.3%	+/-	2.3%	-0.3%	+/-	1.6%	4.5%	+/-	21.5%	0.4%	+/-	2.0%
propane	-1.0%	+/-	1.8%	-0.3%	+/-	2.4%	-0.2%	+/-	1.8%	0.5%	+/-	6.3%	0.6%	+/-	2.4%
propene	-0.5%	+/-	2.4%	0.5%	+/-	2.9%	-0.8%	+/-	2.4%	-0.2%	+/-	12.0%	0.1%	+/-	2.7%
iso-butane	-0.4%	+/-	2.9%	-0.3%	+/-	3.0%	-0.4%	+/-	3.8%	1.7%	+/-	3.9%	0.7%	+/-	2.6%
n-butane	0.8%	+/-	2.7%	1.3%	+/-	2.6%	0.0%	+/-	1.9%	0.7%	+/-	3.4%	1.0%	+/-	2.0%
acetylene	-6.7%	+/-	2.6%	-3.1%	+/-	2.6%	1.4%	+/-	2.4%	-1.2%	+/-	6.2%	0.4%	+/-	2.3%
trans-2-butene	-6.9%	+/-	2.2%	0.1%	+/-	2.2%	-0.1%	+/-	1.5%	0.2%	+/-	6.2%	0.8%	+/-	1.7%
1-butene	1.9%	+/-	2.4%	0.0%	+/-	2.4%	0.0%	+/-	2.0%	0.7%	+/-	4.3%	0.8%	+/-	2.0%
cis-2-butene	-4.0%	+/-	2.6%	-1.3%	+/-	2.6%	-0.2%	+/-	2.3%	-25.0%	+/-	12.6%	0.8%	+/-	2.1%
2-methylbutane	-0.6%	+/-	1.9%	0.9%	+/-	2.6%	0.2%	+/-	2.1%	37.0%	+/-	42.7%	0.5%	+/-	2.3%
n-pentane	-0.6%	+/-	2.0%	0.4%	+/-	2.6%	0.2%	+/-	2.1%	1.2%	+/-	3.1%	0.6%	+/-	2.3%
1,3-butadiene	-2.7%	+/-	2.9%	3.0%	+/-	2.4%	0.7%	+/-	2.1%	7.5%	+/-	8.1%	-0.2%	+/-	1.9%
trans-2-pentene	4.2%	+/-	3.0%	-0.1%	+/-	2.4%	-0.4%	+/-	2.0%	4.3%	+/-	8.8%	0.6%	+/-	2.2%
1-pentene	0.8%	+/-	3.0%	0.4%	+/-	2.4%	-0.2%	+/-	1.9%	2.8%	+/-	5.9%	0.0%	+/-	2.1%
2-methyl pentane	-2.0%	+/-	3.1%	-1.5%	+/-	2.4%	0.1%	+/-	2.1%	-0.6%	+/-	3.0%	0.8%	+/-	2.3%
n-hexane	-0.3%	+/-	2.9%	-0.8%	+/-	2.4%	0.5%	+/-	1.7%	-3.0%	+/-	8.1%	0.5%	+/-	2.1%
isoprene	9.5%	+/-	3.1%	-0.7%	+/-	2.4%	1.1%	+/-	2.0%		+/-		0.5%	+/-	2.1%
n-heptane	0.4%	+/-	2.3%	0.1%	+/-	2.3%	-0.2%	+/-	1.9%	0.2%	+/-	4.3%	0.6%	+/-	2.4%
benzene	0.8%	+/-	3.9%	-0.3%	+/-	3.1%	0.0%	+/-	1.8%	-0.2%	+/-	3.5%	1.1%	+/-	3.1%
2,2,4-trimethyl pentane	0.4%	+/-	2.5%	0.2%	+/-	3.3%	0.4%	+/-	1.8%	0.3%	+/-	4.5%	0.7%	+/-	2.4%
n-octane	1.8%	+/-	2.1%	-0.3%	+/-	3.3%	0.7%	+/-	2.0%	0.0%	+/-	4.0%	1.0%	+/-	3.7%
toluene	-0.6%	+/-	5.2%	1.2%	+/-	3.5%	0.5%	+/-	2.8%	-0.6%	+/-	7.9%	3.3%	+/-	8.5%
ethylbenzene	12.9%	+/-	4.8%	-0.2%	+/-	3.4%	0.9%	+/-	2.9%	0.2%	+/-	4.4%	12.1%	+/-	29.8%
m+p-xylene	8.7%	+/-	4.2%	1.3%	+/-	3.5%	0.4%	+/-	2.8%	0.1%	+/-	2.8%	7.9%	+/-	23.3%
o-xylene	9.7%	+/-	4.7%	2.9%	+/-	3.6%	0.1%	+/-	2.6%	-0.2%	+/-	5.5%	8.9%	+/-	30.3%
1,3,5-trimethyl benzene	23.7%	+/-	10.1%	2.6%	+/-	3.7%	0.3%	+/-	3.3%	-4.7%	+/-	4.4%			
1,2,4-trimethyl benzene	27.1%	+/-	9.7%	4.7%	+/-	3.7%	1.0%	+/-	4.0%	-6.5%	+/-	6.1%			
1,2,3-trimethyl benzene	30.4%	+/-	10.7%	0.4%	+/-	5.6%	0.4%	+/-	3.4%	-6.0%	+/-	5.0%			

4.3 Graphs of equivalence

The following charts display the degrees of equivalence for the participating laboratories and its associated expanded uncertainty with respect to the KCRV.

ERLAP:

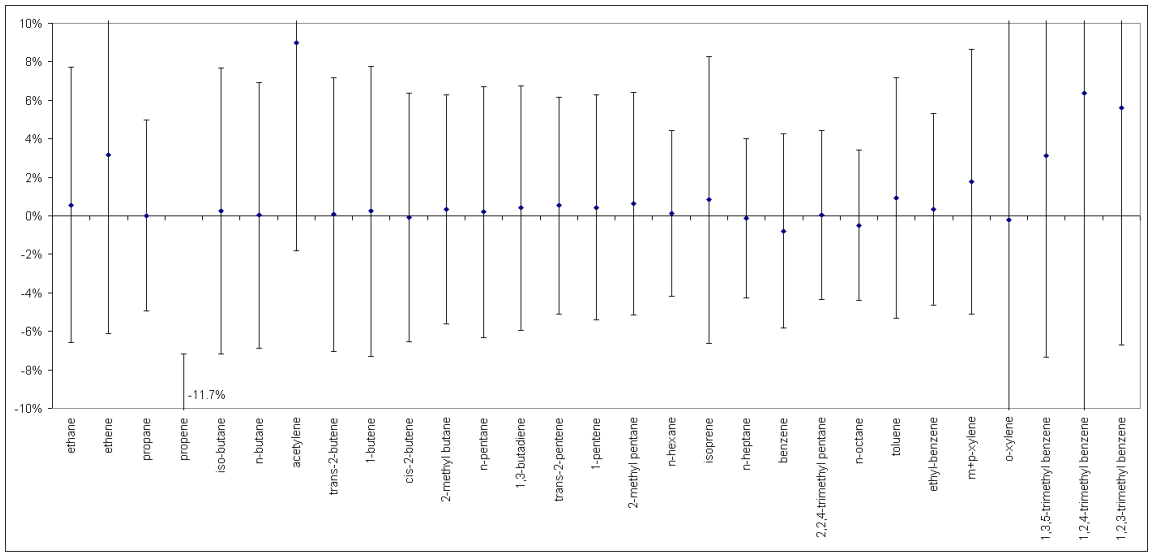


Figure 8. ERLAP degrees of equivalence and expanded uncertainty

FMI:

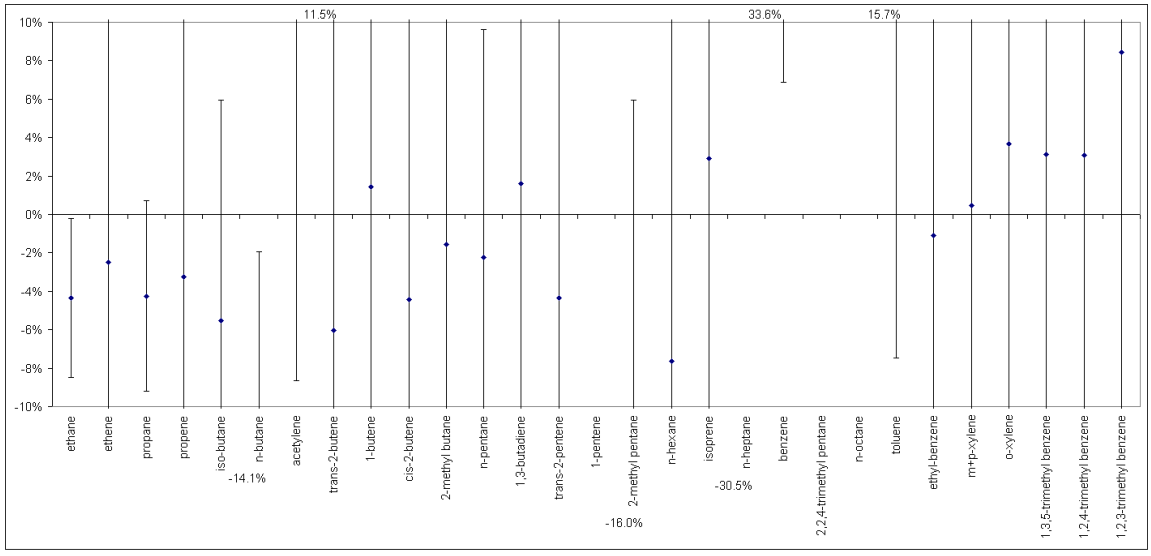


Figure 9. FMI degrees of equivalence and expanded uncertainty

INRiM:

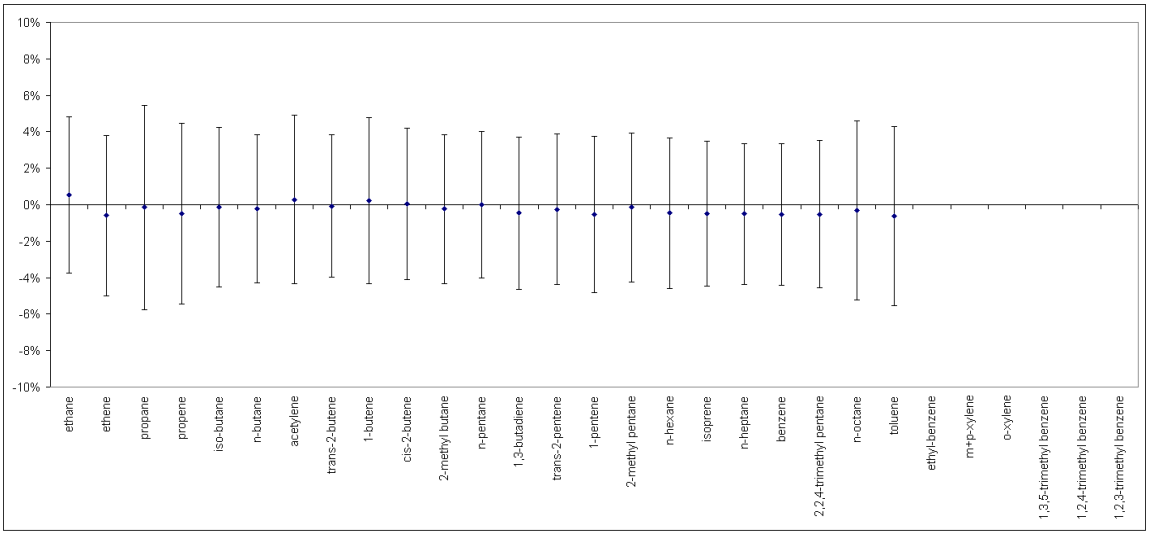


Figure 10. INRiM degrees of equivalence and expanded uncertainty

ISCIII:

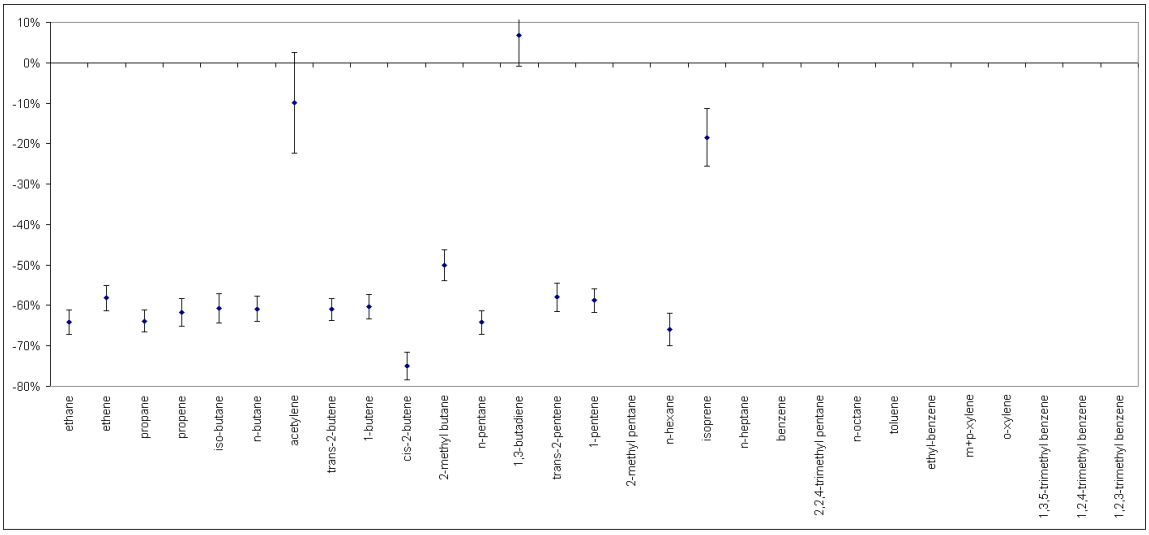


Figure 11. ISCIII degrees of equivalence and expanded uncertainty

KRISS:

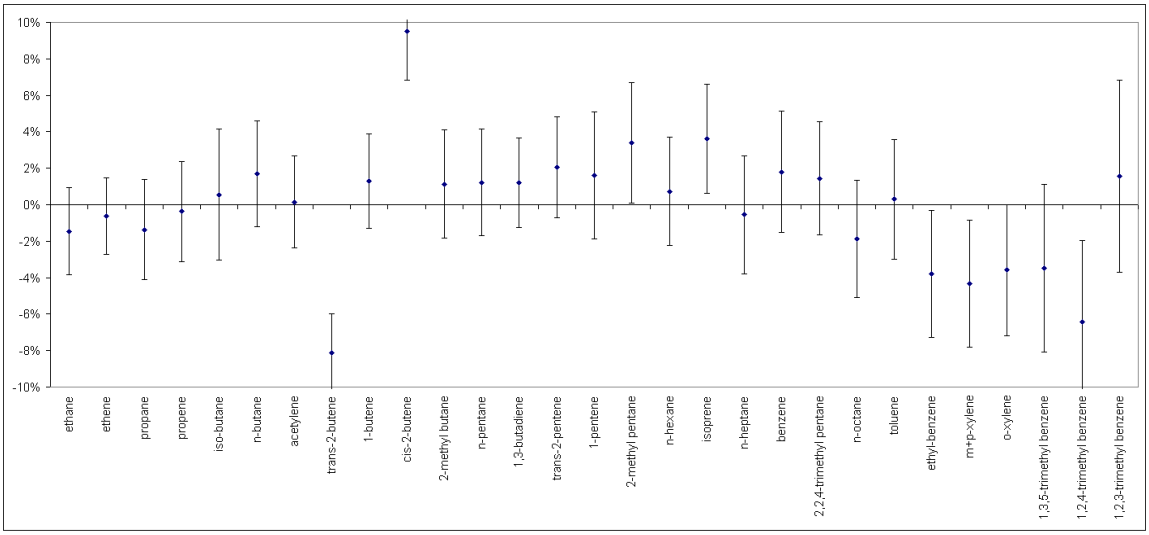


Figure 12. KRISS degrees of equivalence and expanded uncertainty

NIST:

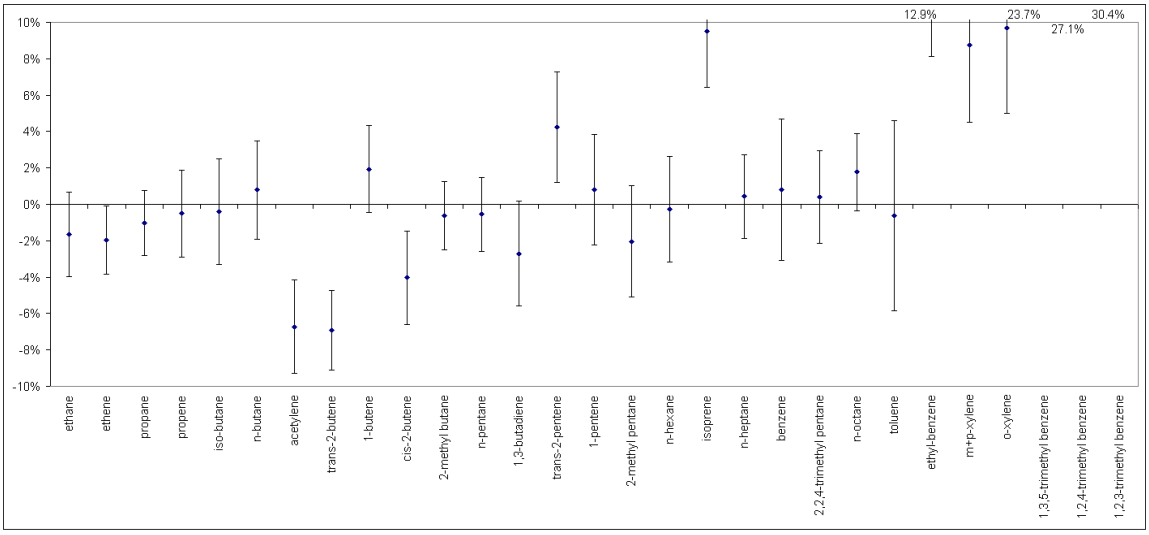


Figure 13. NIST degrees of equivalence and expanded uncertainty

NMi:

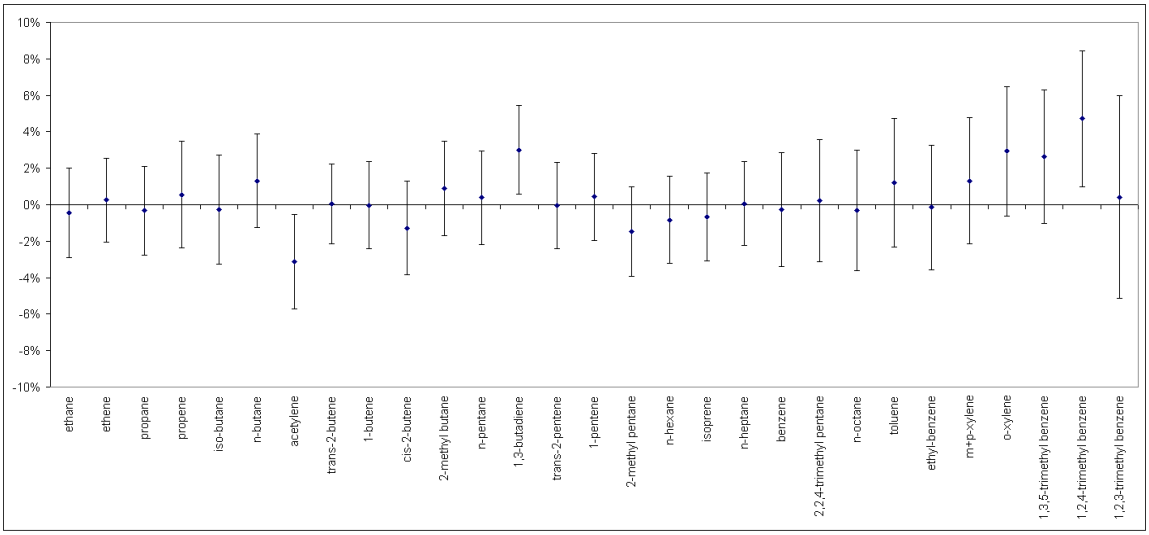


Figure 14. NMi degrees of equivalence and expanded uncertainty

NPL:

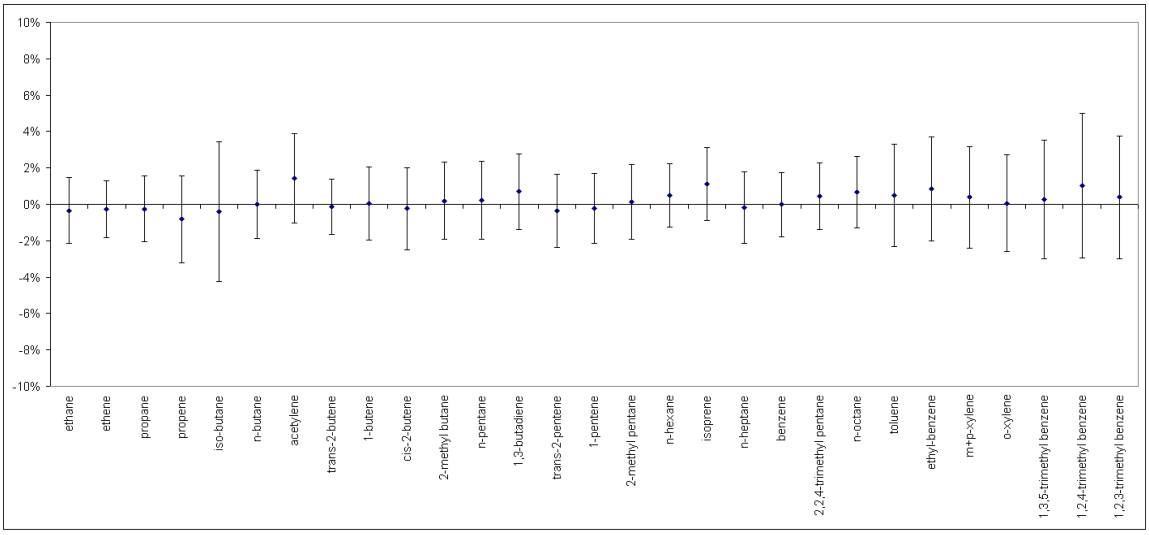


Figure 15. NPL degrees of equivalence and expanded uncertainty

UBA(A):

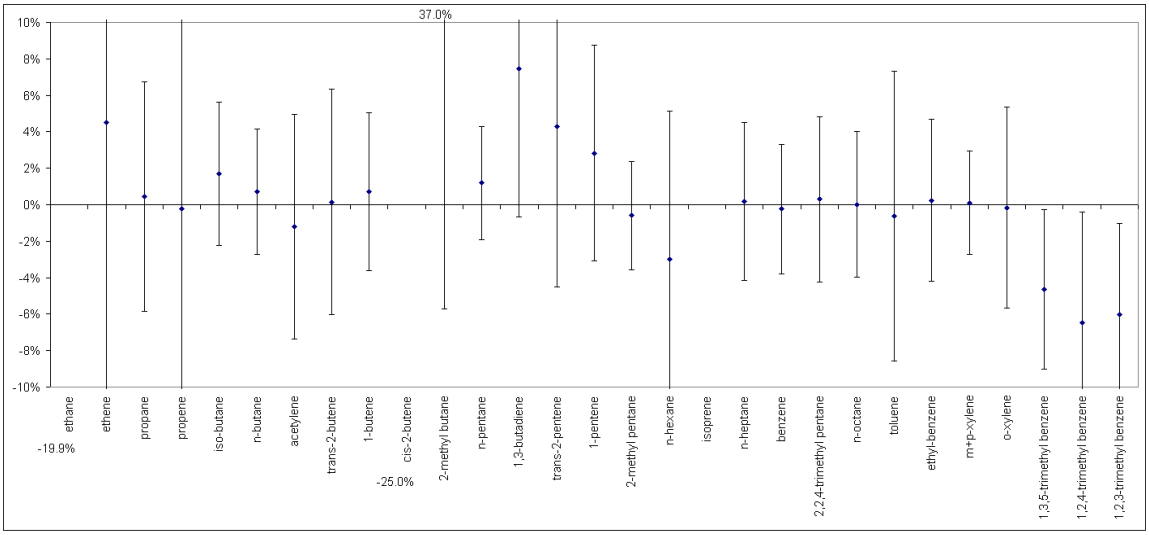


Figure 16. UBA(A) degrees of equivalence and expanded uncertainty

WCC-VOC (FZK, IMK-IFU):

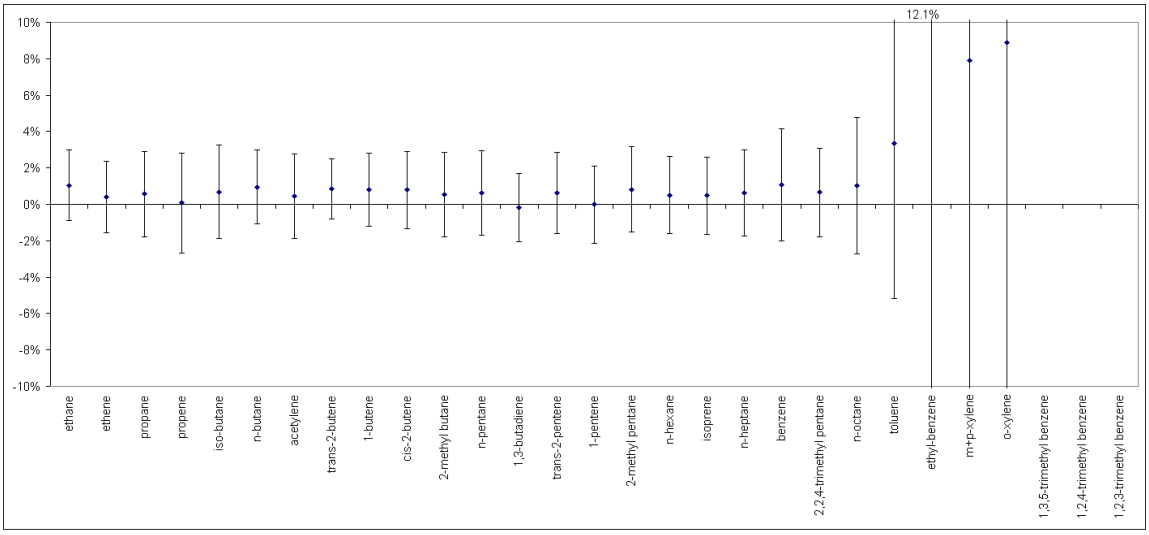


Figure 17. WCC-VOC degrees of equivalence and expanded uncertainty

4.4 Results charts – grouped by component

The following charts show the performance of the participants grouped by components. Components may be grouped into categories related to their nature or simply by sections of a chromatogram.

acetylene, 1,3-butadiene, isoprene:

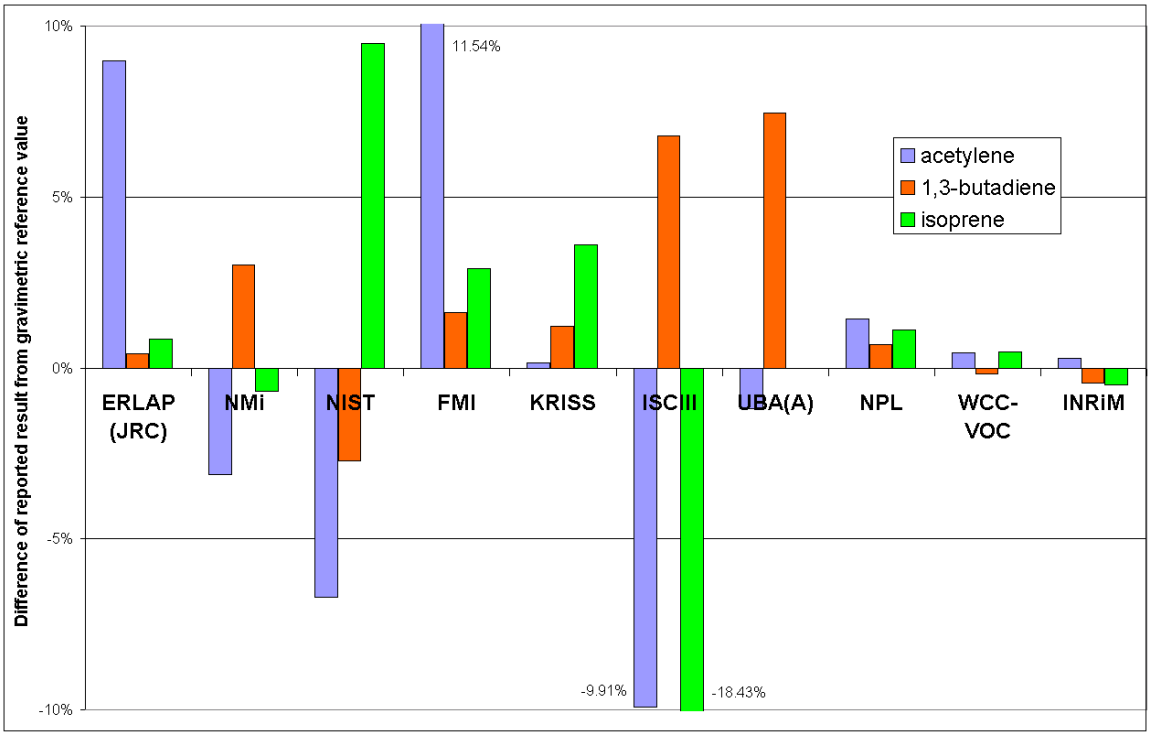


Figure 18. UBA(A) did not report a result for isoprene.

These are difficult components to measure due to their multiple double and triple bonds.

ethane, ethene, propane, propene, iso-butane, n-butane:

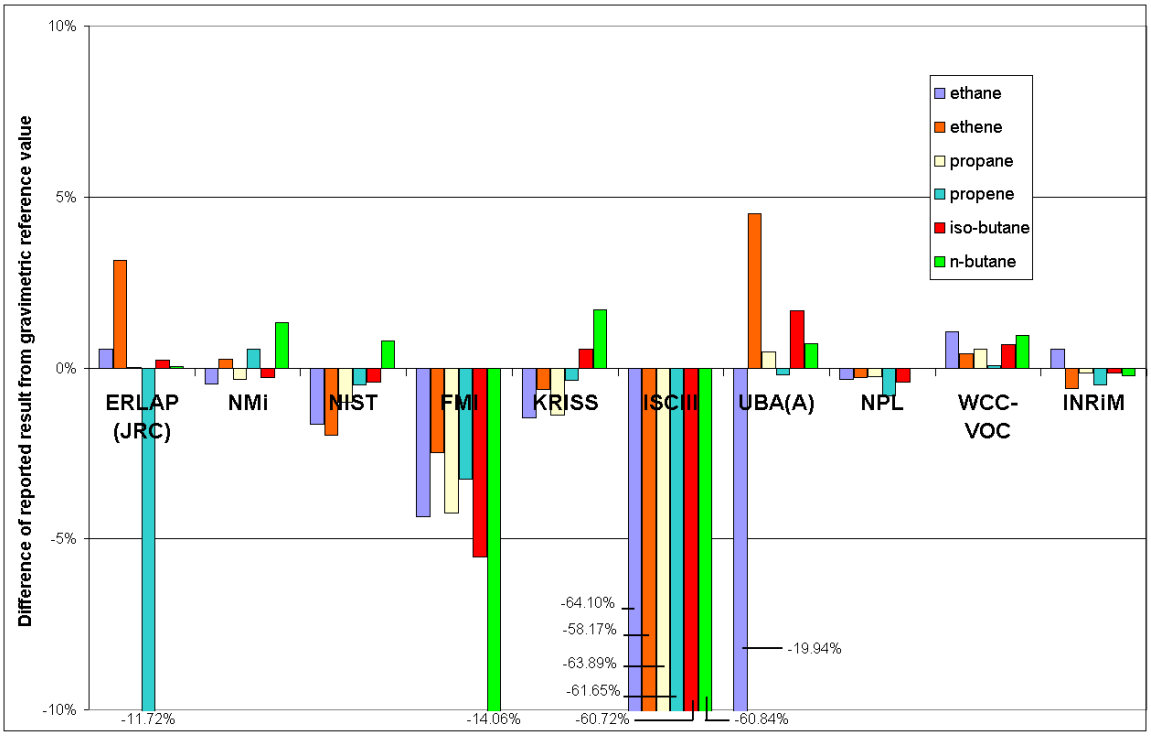


Figure 19.

These are some of the most volatile components in the mixture. Poor performance here might indicate problems with trapping the more volatile components.

trans-2-butene, 1-butene, cis-2-butene, 2-methylbutane, n-pentane, trans-2-pentene, 1-pentene, 2-methylpentane, n-hexane:

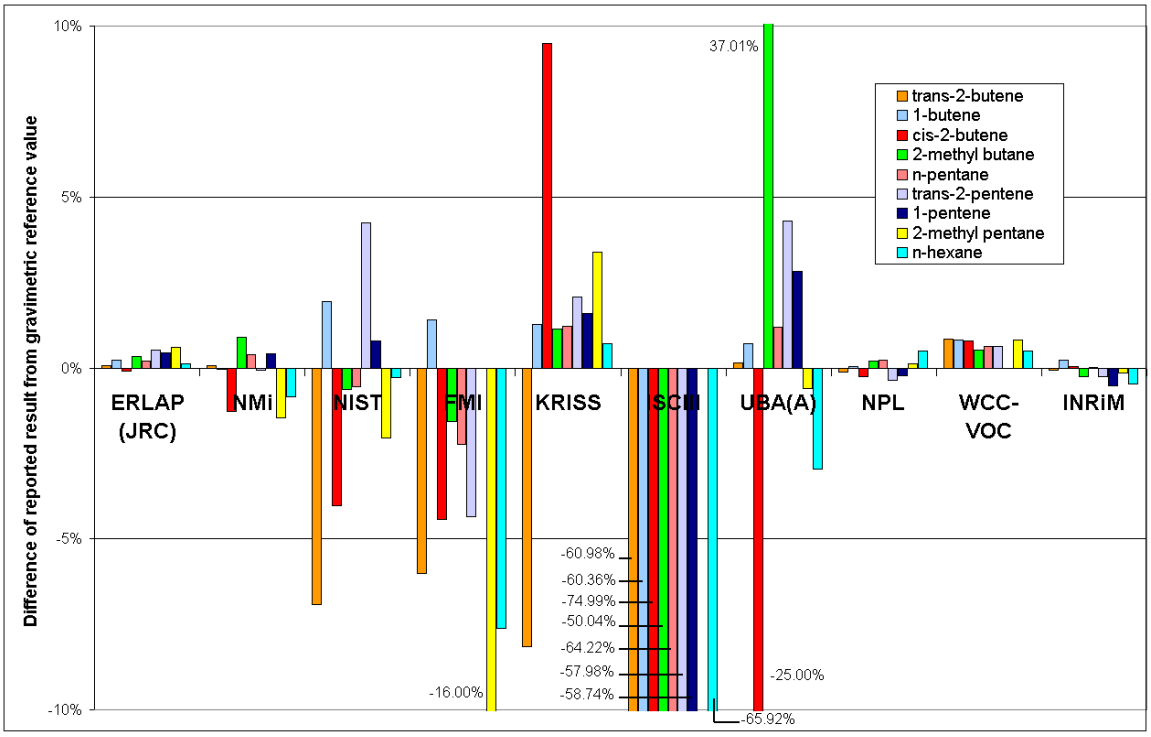


Figure 20. FMI did not report a result for 1-pentene. ISCIII did not report a result for 2-methylpentane.

These components should be some of the more straightforward to measure. Problems here might be due to incorrect identification due to the complex chromatograms generated.

n-heptane, benzene, 2,2,4-trimethylpentane, n-octane, toluene:

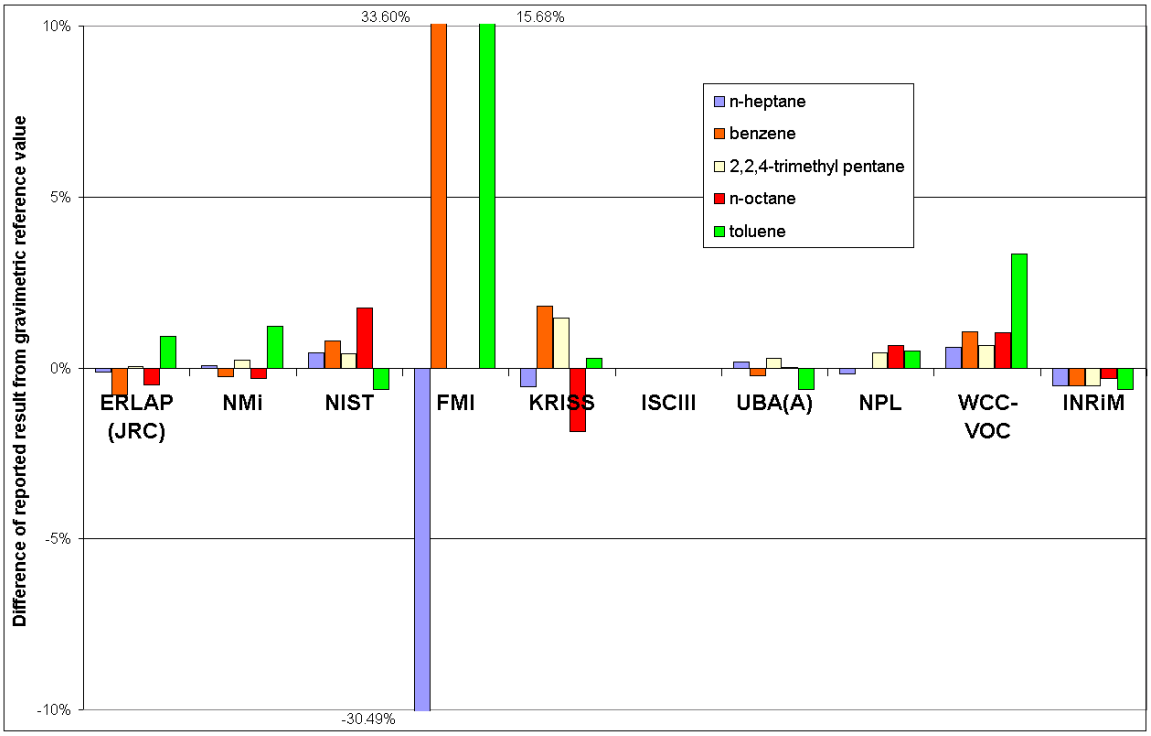


Figure 21. FMI did not report results for 2,2,4-trimethylpentane or n-octane. ISCIII did not report results for any of these components.

This should be a relatively straightforward group of components to measure. We have one case of probable incorrect identification but overall a good agreement amongst the participants.

ethylbenzene, m+p-xylene, o-xylene:

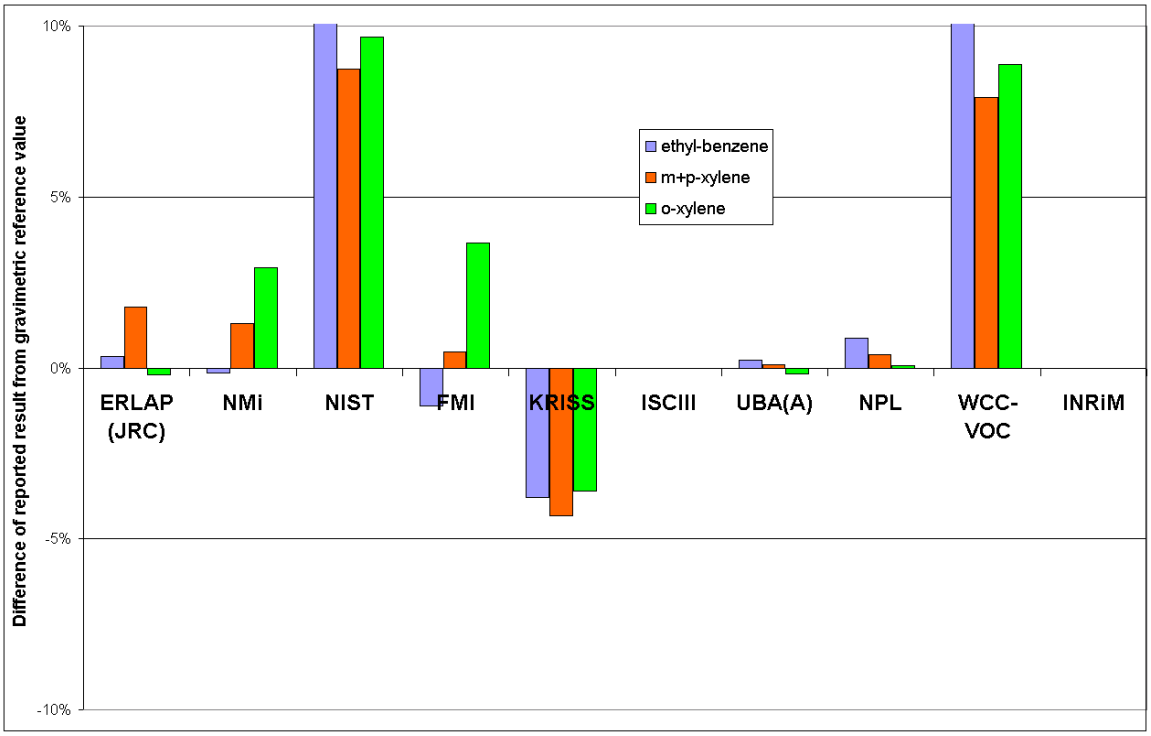


Figure 22. ISCIII & INRiM did not report results for any of these components.

Less volatile components are challenging to sample. Generally each participant performs to an equivalent degree for all components in this group.

1,3,5-, 1,2,4-, 1,2,3-trimethylbenzene:

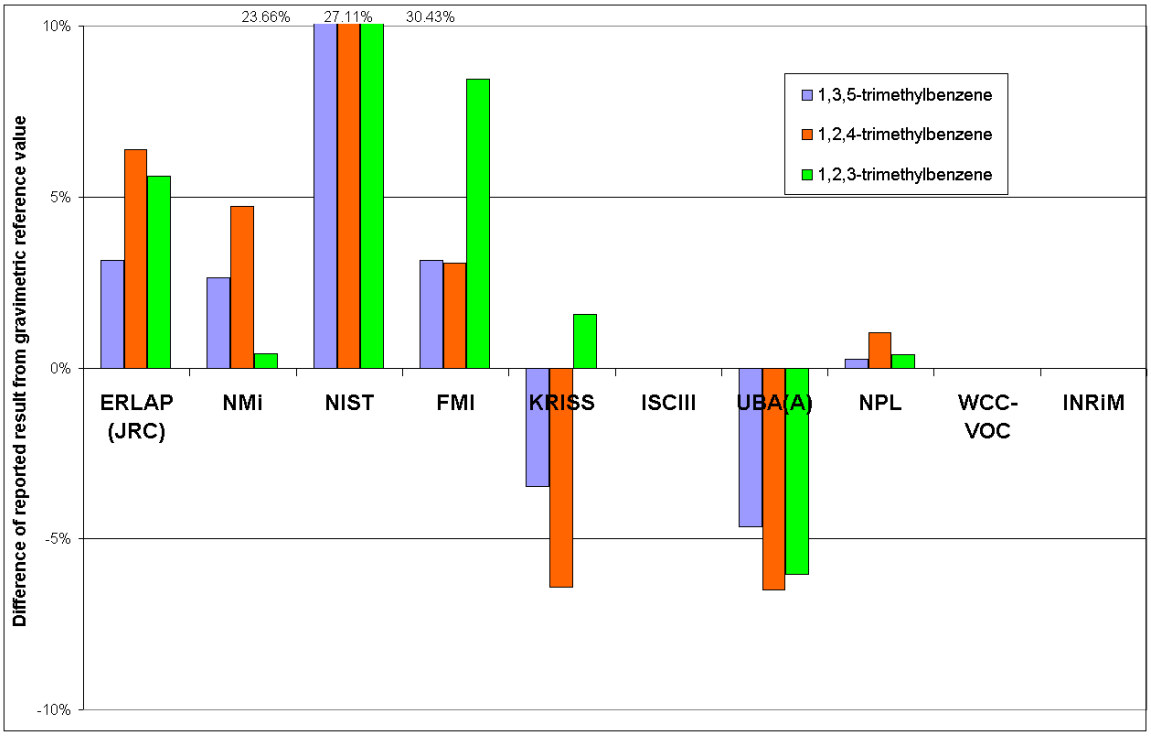
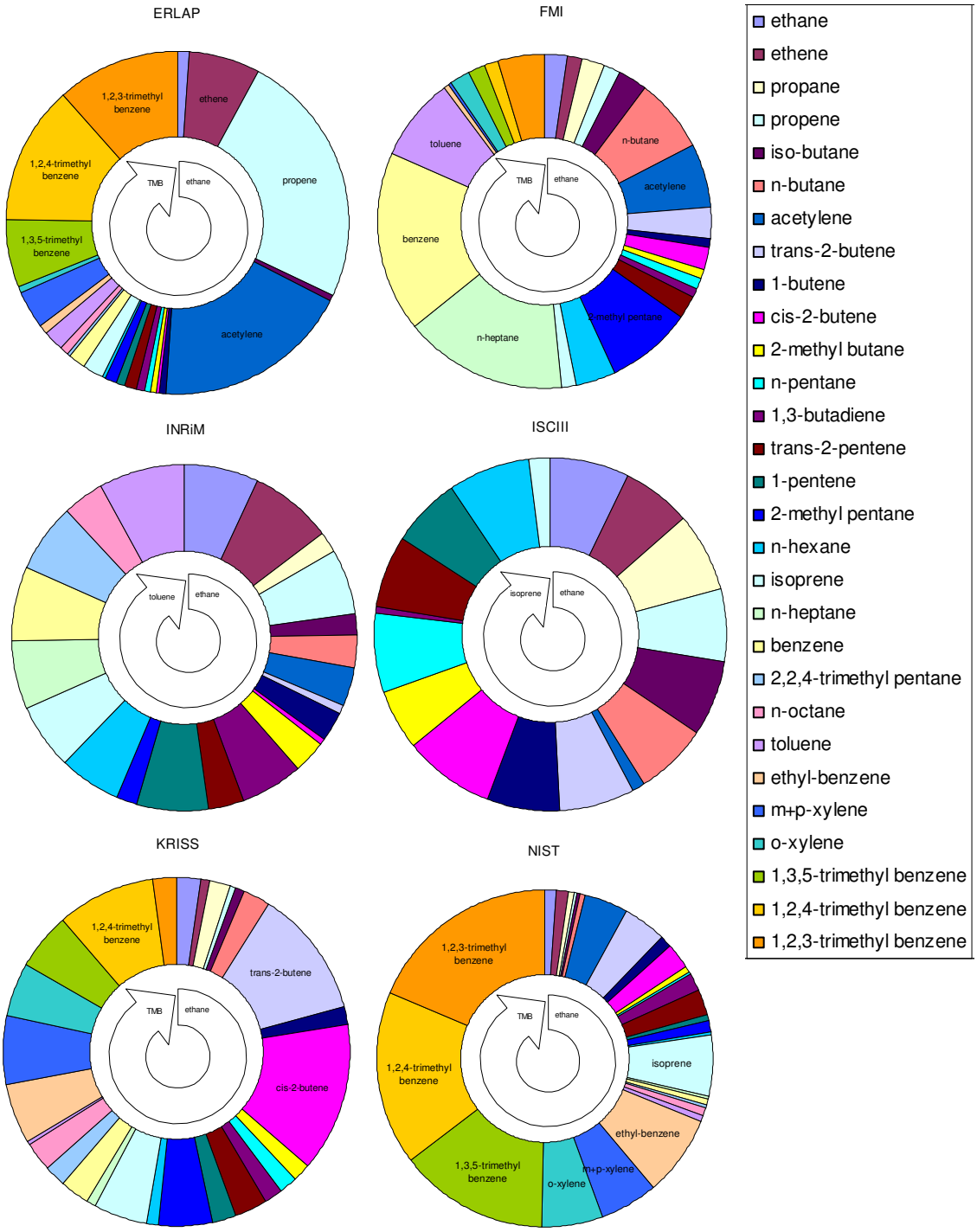


Figure 23. ISCIII, WCC-VOC & INRiM did not report results for any of these components.

As in the previous group participants will generally perform to an equivalent degree with these low volatility components.

4.4 Proportion of error

The following charts map the relative deviation from the KCRV for each component for each participant. The components represented by the largest segments of these plots exhibit the greatest deviation from the KCRV. This gives an indication of the most challenging species for each participant. These plots do not provide information on performance relative to other participants but show which components each participant reported furthest from the KCRV.



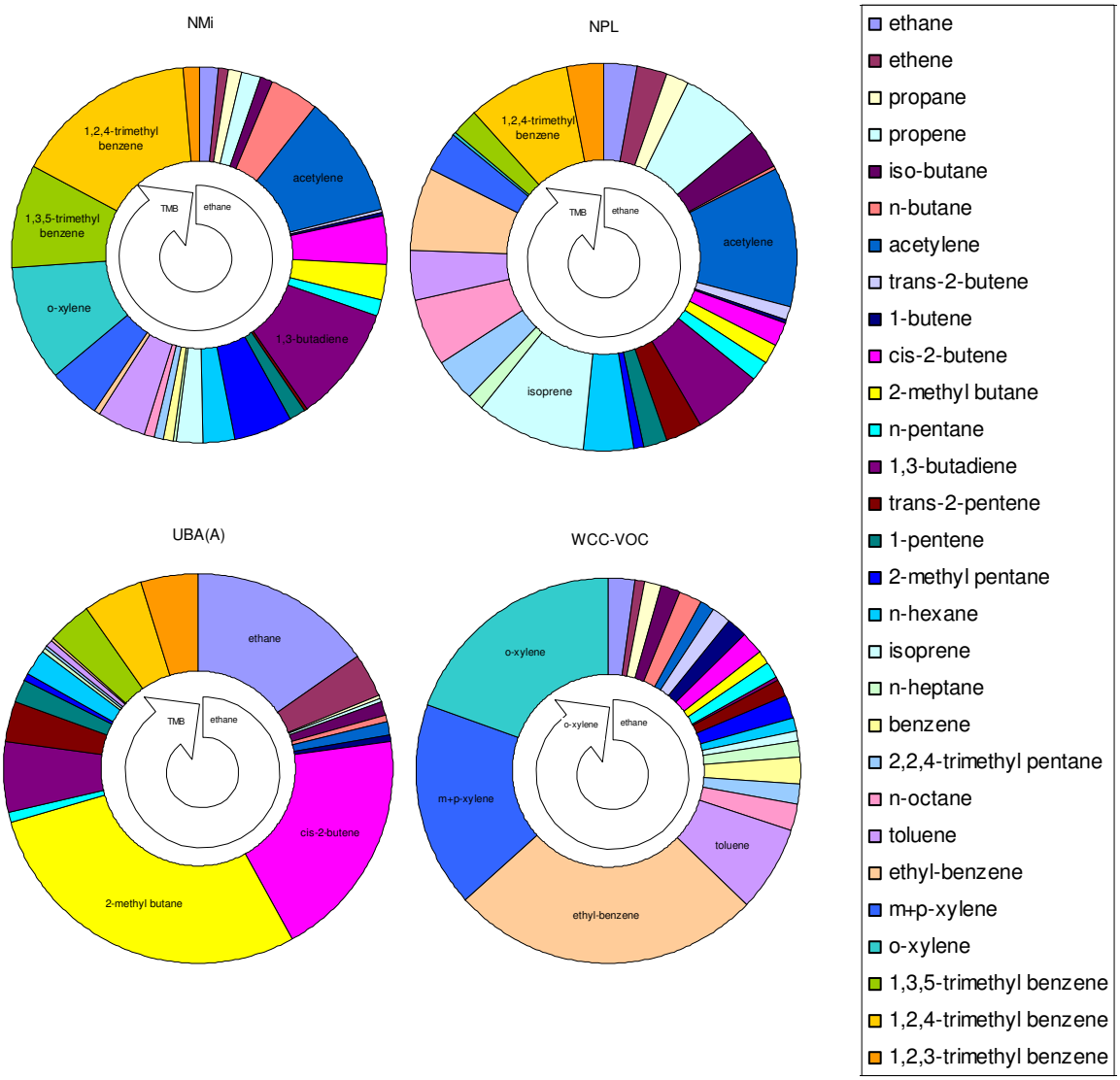


Figure 24. Relative deviation from the KCRV for each component for each participant. The internal arrow indicates the portion of the complete list (right) reported by the participants (TMB = trimethylbenzenes)

Annex A: Supporting data for the synthetic mixtures

Table A1: Gravimetric amount fractions (nmol/mol) of the two parent mixtures (V3 and V4) and the percentage difference between their measured response factors.

Component	Amount fraction (nmol/mol)		Difference in response factors (V3 versus V4)
	Parent V3 D95 4939	Parent V4 D95 4773	
ethane	329.3	288.5	**0.75%**
ethene	327.5	287.0	**0.79%**
propane	326.1	285.7	**0.74%**
propene	323.2	283.2	**0.86%**
iso-butane	348.1	390.0	**0.64%**
n-butane	337.9	378.6	**0.58%**
acetylene	327.4	286.9	**0.35%**
trans-2-butene	337.8	378.4	**0.64%**
1-butene	332.5	372.4	**0.78%**
cis-2-butene	333.1	373.2	**0.60%**
2-methylbutane	251.1	258.9	**0.86%**
n-pentane	254.7	262.7	**0.92%**
1,3-butadiene	323.1	283.1	**0.68%**
trans-2-pentene	242.5	250.1	**0.65%**
1-pentene	247.1	254.8	**0.90%**
2-methyl pentane	251.3	259.2	**0.66%**
n-hexane	251.6	259.5	**0.49%**
isoprene	251.7	259.6	**0.50%**
n-heptane	248.4	256.2	**0.31%**
benzene	204.6	184.9	**0.73%**
2,2,4-trimethyl pentane	253.2	261.2	**0.31%**
n-octane	250.8	258.6	**0.18%**
toluene	176.0	159.0	**1.05%**
ethylbenzene	188.0	206.3	**-0.07%**
m+p-xylene	372.0	408.1	**-0.23%**
o-xylene	184.6	202.5	**-0.09%**
1,3,5-trimethyl benzene	180.3	197.8	**-0.51%**
1,2,4-trimethyl benzene	189.1	207.4	**0.19%**
1,2,3-trimethyl benzene	172.3	189.0	**0.12%**

Table A2: Participant mixtures. For each cylinder, the gravimetric value and the analytical value at $t = 0$, $t = 4$ months and $t = 12$ months is presented.
NB: V3 #6 is the 6th cylinder from version 3.

	Amount fraction (nmol/mol)							
Cylinder ref:	V3 #3 D95 4825				V3 #4 D95 4945			
Component	$t = 0$	$t = 4$ months	$t = 12$ months	Grav. value	$t = 0$	$t = 4$ months	$t = 12$ months	Grav. value
ethane	6.75	6.71	6.72	**6.74**	6.68	6.71	6.70	**6.74**
ethene	6.66	6.69	6.71	**6.69**	6.69	6.70	6.68	**6.69**
propane	6.66	6.65	6.66	**6.67**	6.60	6.64	6.66	**6.67**
propene	6.66	6.51	6.65	**6.59**	6.53	6.63	6.62	**6.60**
iso-butane	7.17	7.06	6.91	**7.10**	7.07	7.05	7.12	**7.10**
n-butane	6.92	6.80	6.86	**6.89**	6.91	6.83	6.90	**6.90**
acetylene	6.74	6.60	6.51	**6.68**	6.61	6.67	6.59	**6.68**
trans-2-butene	6.90	6.87	6.87	**6.89**	6.92	6.87	6.89	**6.89**
1-butene	6.80	6.76	6.76	**6.78**	6.76	6.75	6.76	**6.79**
cis-2-butene	6.90	6.77	6.75	**6.80**	6.85	6.83	6.82	**6.80**
2-methyl butane	5.12	5.14	5.02	**5.12**	5.11	5.12	5.16	**5.12**
n-pentane	5.22	5.17	5.16	**5.20**	5.19	5.18	5.15	**5.20**
1,3-butadiene	6.65	6.56	6.53	**6.59**	6.60	6.57	6.58	**6.59**
trans-2-pentene	4.97	4.97	4.87	**4.95**	4.94	4.97	4.93	**4.95**
1-pentene	5.04	5.05	5.05	**5.04**	5.07	5.03	5.07	**5.04**
2-methyl pentane	5.14	5.14	5.09	**5.13**	5.18	5.16	5.16	**5.13**
n-hexane	5.13	5.15	5.08	**5.13**	5.16	5.14	5.12	**5.14**
isoprene	5.11	5.13	5.11	**5.13**	5.16	5.13	5.14	**5.14**
n-heptane	5.09	5.09	5.05	**5.07**	5.10	5.05	5.02	**5.07**
benzene	4.19	4.18	4.10	**4.17**	4.15	4.17	4.14	**4.18**
2,2,4-trimethyl pentane	5.19	5.17	5.13	**5.17**	5.22	5.15	5.11	**5.17**
n-octane	5.12	5.10	5.13	**5.12**	5.15	5.09	5.13	**5.12**
toluene	3.59	3.60	3.54	**3.59**	3.56	3.59	3.60	**3.59**
ethyl-benzene	3.85	3.82	3.83	**3.84**	3.80	3.80	3.82	**3.84**
m+p-xylene	7.65	7.59	7.61	**7.59**	7.58	7.56	7.54	**7.59**
o-xylene	3.74	3.74	3.75	**3.77**	3.76	3.75	3.73	**3.77**
1,3,5-trimethyl benzene	3.68	3.64	3.66	**3.68**	3.72	3.67	3.66	**3.68**
1,2,4-trimethyl benzene	3.84	3.84	3.85	**3.86**	3.81	3.82	3.86	**3.86**
1,2,3-trimethyl benzene	3.53	3.48	3.50	**3.51**	3.56	3.49	3.56	**3.52**

	Amount fraction (nmol/mol)							
Cylinder ref:	V3 #5 D83 8907				V3 #6 D95 4965			
Component	$t = 0$	$t = 4$ months	$t = 12$ months	Grav. value	$t = 0$	$t = 4$ months	$t = 12$ months	Grav. value
ethane	6.75	6.70	6.71	**6.74**	6.68	6.76	6.69	**6.74**
ethene	6.75	6.73	6.69	**6.69**	6.73	6.71	6.71	**6.69**
propane	6.65	6.62	6.69	**6.67**	6.66	6.69	6.64	**6.67**
propene	6.54	6.57	6.59	**6.60**	6.56	6.61	6.65	**6.60**
iso-butane	7.12	7.11	7.03	**7.10**	7.01	7.24	7.14	**7.10**
n-butane	6.90	6.93	6.97	**6.89**	6.90	6.95	6.91	**6.89**
acetylene	6.77	6.63	6.70	**6.68**	6.70	6.72	6.52	**6.68**
trans-2-butene	6.88	6.89	6.90	**6.89**	6.87	6.89	6.93	**6.89**
1-butene	6.81	6.79	6.79	**6.79**	6.76	6.80	6.84	**6.79**
cis-2-butene	6.74	6.79	6.89	**6.80**	6.75	6.80	6.80	**6.80**
2-methyl butane	5.10	5.12	5.08	**5.12**	5.13	5.13	5.21	**5.12**
n-pentane	5.19	5.21	5.17	**5.20**	5.15	5.22	5.27	**5.20**
1,3-butadiene	6.58	6.59	6.52	**6.59**	6.59	6.60	6.64	**6.59**
trans-2-pentene	4.96	4.93	4.98	**4.95**	4.90	4.98	4.98	**4.95**
1-pentene	5.01	5.05	5.16	**5.04**	4.95	5.05	5.02	**5.04**
2-methyl pentane	5.12	5.14	5.11	**5.13**	5.09	5.16	5.20	**5.13**
n-hexane	5.15	5.16	5.16	**5.13**	5.05	5.12	5.16	**5.13**
isoprene	5.15	5.16	5.15	**5.14**	5.11	5.17	5.10	**5.14**
n-heptane	5.01	5.08	5.09	**5.07**	5.02	5.05	5.11	**5.07**
benzene	4.18	4.17	4.16	**4.18**	4.14	4.17	4.18	**4.18**
2,2,4-trimethyl pentane	5.19	5.15	5.18	**5.17**	5.12	5.19	5.24	**5.17**
n-octane	5.15	5.14	5.09	**5.12**	5.11	5.17	5.14	**5.12**
toluene	3.58	3.56	3.61	**3.59**	3.56	3.59	3.67	**3.59**
ethyl-benzene	3.86	3.79	3.81	**3.84**	3.85	3.79	3.84	**3.84**
m+p-xylene	7.64	7.54	7.55	**7.59**	7.66	7.59	7.60	**7.59**
o-xylene	3.81	3.73	3.76	**3.77**	3.79	3.72	3.76	**3.77**
1,3,5-trimethyl benzene	3.79	3.66	3.69	**3.68**	3.70	3.71	3.66	**3.68**
1,2,4-trimethyl benzene	3.95	3.84	3.90	**3.86**	3.83	3.85	3.95	**3.86**
1,2,3-trimethyl benzene	3.57	3.53	3.59	**3.52**	3.54	3.46	3.56	**3.52**

	Amount fraction (nmol/mol)							
Cylinder ref:	V3 #7 D83 8784				V3 #8 D95 4778			
Component	$t = 0$	$t = 4$ months	$t = 12$ months	Grav. value	$t = 0$	$t = 4$ months	$t = 12$ months	Grav. value
ethane	6.77	6.75	X	**6.74**	6.65	6.72	6.76	**6.74**
ethene	6.71	6.67	X	**6.69**	6.63	6.67	6.71	**6.69**
propane	6.80	6.65	X	**6.67**	6.70	6.63	6.62	**6.67**
propene	6.56	6.65	X	**6.60**	6.54	6.58	6.62	**6.59**
iso-butane	7.12	7.18	X	**7.10**	6.98	6.94	7.14	**7.10**
n-butane	6.89	6.96	X	**6.89**	6.84	6.93	6.86	**6.89**
acetylene	6.62	6.73	X	**6.68**	6.62	6.67	6.59	**6.68**
trans-2-butene	6.94	6.92	X	**6.89**	6.88	6.88	6.87	**6.89**
1-butene	6.81	6.78	X	**6.78**	6.83	6.78	6.76	**6.78**
cis-2-butene	6.78	6.83	X	**6.80**	6.72	6.82	6.72	**6.80**
2-methyl butane	5.10	5.10	X	**5.12**	5.04	5.13	5.06	**5.12**
n-pentane	5.19	5.20	X	**5.20**	5.18	5.24	5.17	**5.20**
1,3-butadiene	6.61	6.55	X	**6.59**	6.53	6.55	6.54	**6.59**
trans-2-pentene	4.98	4.97	X	**4.95**	4.91	4.92	4.93	**4.95**
1-pentene	5.06	5.06	X	**5.04**	5.01	5.05	5.03	**5.04**
2-methyl pentane	5.16	5.15	X	**5.13**	5.11	5.08	5.12	**5.13**
n-hexane	5.13	5.08	X	**5.13**	5.14	5.12	5.10	**5.13**
isoprene	5.15	5.09	X	**5.14**	5.14	5.15	5.12	**5.14**
n-heptane	5.13	5.02	X	**5.07**	5.06	5.06	5.00	**5.07**
benzene	4.18	4.16	X	**4.18**	4.16	4.17	4.17	**4.18**
2,2,4-trimethyl pentane	5.23	5.19	X	**5.17**	5.14	5.20	5.21	**5.17**
n-octane	5.20	5.10	X	**5.12**	5.09	5.16	5.08	**5.12**
toluene	3.61	3.56	X	**3.59**	3.60	3.54	3.58	**3.59**
ethyl-benzene	3.88	3.80	X	**3.84**	3.82	3.79	3.83	**3.84**
m+p-xylene	7.64	7.57	X	**7.59**	7.55	7.59	7.56	**7.59**
o-xylene	3.83	3.75	X	**3.77**	3.70	3.70	3.72	**3.77**
1,3,5-trimethyl benzene	3.70	3.65	X	**3.68**	3.64	3.65	3.65	**3.68**
1,2,4-trimethyl benzene	3.86	3.80	X	**3.86**	3.79	3.77	3.91	**3.86**
1,2,3-trimethyl benzene	3.54	3.49	X	**3.52**	3.47	3.46	3.43	**3.52**

	Amount fraction (nmol/mol)							
Cylinder ref:	V3 #9 D95 4944				V3 #10 D95 4968			
Component	$t = 0$	$t = 4$ months	$t = 12$ months	Grav. value	$t = 0$	$t = 4$ months	$t = 12$ months	Grav. value
ethane	6.74	6.73	6.73	**6.74**	6.77	6.75	6.71	**6.74**
ethene	6.67	6.69	6.70	**6.69**	6.77	6.63	6.68	**6.69**
propane	6.77	6.72	6.62	**6.67**	6.63	6.66	6.59	**6.67**
propene	6.58	6.44	6.54	**6.60**	6.68	6.56	6.51	**6.60**
iso-butane	7.27	7.03	7.07	**7.10**	7.04	7.06	6.96	**7.10**
n-butane	6.88	6.93	7.06	**6.89**	6.98	6.98	6.81	**6.90**
acetylene	6.73	6.58	6.70	**6.68**	6.65	6.74	6.60	**6.68**
trans-2-butene	6.89	6.91	6.89	**6.89**	6.89	6.91	6.93	**6.89**
1-butene	6.79	6.87	6.82	**6.79**	6.79	6.78	6.69	**6.79**
cis-2-butene	6.71	6.78	6.79	**6.80**	6.89	6.81	6.70	**6.80**
2-methyl butane	5.14	5.11	5.11	**5.12**	5.09	5.12	5.09	**5.12**
n-pentane	5.23	5.15	5.16	**5.20**	5.21	5.17	5.24	**5.20**
1,3-butadiene	6.62	6.61	6.64	**6.59**	6.57	6.64	6.57	**6.59**
trans-2-pentene	4.99	4.98	4.92	**4.95**	4.98	4.96	4.88	**4.95**
1-pentene	5.11	5.05	4.98	**5.04**	5.08	5.06	5.06	**5.04**
2-methyl pentane	5.18	5.17	5.17	**5.13**	5.13	5.13	5.10	**5.13**
n-hexane	5.12	5.15	5.10	**5.13**	5.18	5.12	5.13	**5.13**
isoprene	5.18	5.12	5.07	**5.14**	5.16	5.14	5.10	**5.14**
n-heptane	5.09	5.11	5.09	**5.07**	5.06	5.06	5.07	**5.07**
benzene	4.16	4.14	4.21	**4.18**	4.20	4.20	4.13	**4.18**
2,2,4-trimethyl pentane	5.18	5.20	5.25	**5.17**	5.21	5.15	5.16	**5.17**
n-octane	5.10	5.15	5.07	**5.12**	5.16	5.14	5.03	**5.12**
toluene	3.65	3.59	3.59	**3.59**	3.61	3.62	3.55	**3.59**
ethyl-benzene	3.79	3.82	3.80	**3.84**	3.84	3.85	3.82	**3.84**
m+p-xylene	7.63	7.59	7.55	**7.59**	7.58	7.71	7.61	**7.59**
o-xylene	3.78	3.75	3.72	**3.77**	3.73	3.80	3.75	**3.77**
1,3,5-trimethyl benzene	3.76	3.66	3.73	**3.68**	3.67	3.71	3.70	**3.68**
1,2,4-trimethyl benzene	3.91	3.86	3.86	**3.86**	3.80	3.89	3.86	**3.86**
1,2,3-trimethyl benzene	3.49	3.52	3.54	**3.52**	3.49	3.49	3.50	**3.52**

	Amount fraction (nmol/mol)							
Cylinder ref:	V3 #11 D95 4937				V3 #12 D95 4804			
Component	$t = 0$	$t = 4$ months	$t = 12$ months	Grav. value	$t = 0$	$t = 4$ months	$t = 12$ months	Grav. value
ethane	6.72	6.74	6.72	**6.74**	6.69	6.85	6.70	**6.74**
ethene	6.78	6.69	6.70	**6.70**	6.68	6.68	6.71	**6.69**
propane	6.73	6.71	6.70	**6.67**	6.63	6.65	6.59	**6.67**
propene	6.51	6.64	6.66	**6.60**	6.62	6.62	6.56	**6.60**
iso-butane	6.98	7.04	7.01	**7.10**	7.10	7.12	6.94	**7.10**
n-butane	6.73	6.91	6.95	**6.90**	6.92	6.89	6.93	**6.89**
acetylene	6.70	6.65	6.62	**6.68**	6.62	6.67	6.63	**6.68**
trans-2-butene	6.83	6.86	6.87	**6.90**	6.91	6.88	6.88	**6.89**
1-butene	6.80	6.68	6.76	**6.79**	6.78	6.76	6.82	**6.79**
cis-2-butene	6.70	6.83	6.76	**6.80**	6.75	6.77	6.80	**6.80**
2-methyl butane	5.14	5.16	5.12	**5.12**	5.08	5.02	5.15	**5.12**
n-pentane	5.24	5.23	5.19	**5.20**	5.12	5.16	5.27	**5.20**
1,3-butadiene	6.60	6.58	6.57	**6.59**	6.58	6.60	6.67	**6.59**
trans-2-pentene	4.97	4.93	4.95	**4.95**	4.89	4.88	4.93	**4.95**
1-pentene	5.02	5.07	5.03	**5.04**	5.00	5.04	5.02	**5.04**
2-methyl pentane	5.14	5.16	5.08	**5.13**	5.07	5.09	5.04	**5.13**
n-hexane	5.14	5.14	5.11	**5.14**	5.10	5.11	5.05	**5.13**
isoprene	5.17	5.13	5.13	**5.14**	5.11	5.09	5.12	**5.14**
n-heptane	5.08	5.03	5.02	**5.07**	5.06	5.04	5.08	**5.07**
benzene	4.18	4.18	4.15	**4.18**	4.16	4.19	4.18	**4.18**
2,2,4-trimethyl pentane	5.20	5.20	5.10	**5.17**	5.13	5.16	5.16	**5.17**
n-octane	5.14	5.14	5.16	**5.12**	5.15	5.10	5.10	**5.12**
toluene	3.62	3.59	3.61	**3.59**	3.58	3.56	3.59	**3.59**
ethyl-benzene	3.87	3.85	3.83	**3.84**	3.82	3.82	3.83	**3.84**
m+p-xylene	7.66	7.64	7.59	**7.59**	7.59	7.57	7.48	**7.59**
o-xylene	3.83	3.75	3.80	**3.77**	3.78	3.75	3.78	**3.77**
1,3,5-trimethyl benzene	3.77	3.68	3.69	**3.68**	3.63	3.63	3.74	**3.68**
1,2,4-trimethyl benzene	3.90	3.90	3.92	**3.86**	3.83	3.84	3.84	**3.86**
1,2,3-trimethyl benzene	3.57	3.56	3.62	**3.52**	3.45	3.51	3.58	**3.52**

	Amount fraction (nmol/mol)			
Cylinder ref:	V3 #14 D29 2401			
Component	$t = 0$	$t = 4$ months	$t = 12$ months	Grav. value
ethane	6.72	6.75	6.75	6.74
ethene	6.64	6.69	6.67	6.69
propane	6.68	6.64	6.63	6.67
propene	6.60	6.46	6.48	6.60
iso-butane	7.10	7.03	7.14	7.10
n-butane	6.88	6.96	6.91	6.89
acetylene	6.77	6.62	6.66	6.68
trans-2-butene	6.93	6.90	6.90	6.89
1-butene	6.75	6.85	6.83	6.78
cis-2-butene	6.78	6.88	6.78	6.80
2-methyl butane	5.12	5.11	5.08	5.12
n-pentane	5.27	5.17	5.19	5.20
1,3-butadiene	6.60	6.55	6.58	6.59
trans-2-pentene	4.99	5.02	4.97	4.95
1-pentene	5.08	5.09	5.08	5.04
2-methyl pentane	5.21	5.17	5.12	5.13
n-hexane	5.18	5.11	5.15	5.13
isoprene	5.19	5.07	5.11	5.14
n-heptane	5.07	5.04	5.01	5.07
benzene	4.21	4.19	4.17	4.18
2,2,4-trimethyl pentane	5.22	5.11	5.19	5.17
n-octane	5.15	5.05	5.13	5.12
toluene	3.61	3.62	3.58	3.59
ethyl-benzene	3.88	3.79	3.81	3.84
m+p-xylene	7.76	7.49	7.58	7.59
o-xylene	3.77	3.73	3.78	3.77
1,3,5-trimethyl benzene	3.75	3.60	3.69	3.68
1,2,4-trimethyl benzene	3.92	3.85	3.83	3.86
1,2,3-trimethyl benzene	3.59	3.58	3.49	3.52

	Amount fraction (nmol/mol)							
Cylinder ref:	V4 #3 D95 4790				V4 #4 D95 4815			
Component	$t = 0$	$t = 4$ months	$t = 12$ months	Grav. value	$t = 0$	$t = 4$ months	$t = 12$ months	Grav. value
ethane	5.95	5.96	5.96	**5.92**	5.99	5.97	5.95	5.92
ethene	5.89	5.91	5.89	**5.88**	5.92	5.86	5.90	5.88
propane	5.89	5.85	5.90	**5.86**	5.88	5.88	5.92	5.86
propene	5.76	5.79	5.74	**5.79**	5.80	5.82	5.91	5.79
iso-butane	8.05	7.90	8.01	**7.97**	7.95	8.00	8.19	7.97
n-butane	7.79	7.69	7.78	**7.74**	7.75	7.79	7.69	7.74
acetylene	5.82	5.79	5.81	**5.86**	5.83	5.96	5.84	5.86
trans-2-butene	7.74	7.68	7.89	**7.73**	7.72	7.84	7.73	7.74
1-butene	7.66	7.65	7.64	**7.61**	7.60	7.63	7.70	7.61
cis-2-butene	7.65	7.68	7.61	**7.63**	7.63	7.67	7.56	7.63
2-methyl butane	5.31	5.30	5.29	**5.29**	5.32	5.40	5.33	5.29
n-pentane	5.39	5.39	5.40	**5.37**	5.39	5.47	5.38	5.37
1,3-butadiene	5.79	5.78	5.68	**5.79**	5.78	5.81	5.82	5.79
trans-2-pentene	5.11	5.14	5.14	**5.11**	5.14	5.14	5.16	5.11
1-pentene	5.20	5.24	5.14	**5.21**	5.25	5.24	5.26	5.21
2-methyl pentane	5.29	5.26	5.24	**5.30**	5.29	5.30	5.25	5.30
n-hexane	5.31	5.28	5.29	**5.30**	5.32	5.32	5.38	5.30
isoprene	5.25	5.31	5.24	**5.31**	5.27	5.36	5.34	5.31
n-heptane	5.21	5.22	5.20	**5.24**	5.25	5.23	5.20	5.24
benzene	3.76	3.80	3.81	**3.78**	3.78	3.77	3.76	3.78
2,2,4-trimethyl pentane	5.27	5.36	5.36	**5.34**	5.34	5.33	5.37	5.34
n-octane	5.24	5.25	5.29	**5.29**	5.25	5.25	5.24	5.29
toluene	3.23	3.25	3.22	**3.25**	3.26	3.26	3.22	3.25
ethyl-benzene	4.20	4.22	4.22	**4.22**	4.21	4.21	4.21	4.22
m+p-xylene	8.31	8.40	8.36	**8.34**	8.34	8.34	8.33	8.34
o-xylene	4.09	4.13	4.14	**4.14**	4.15	4.15	4.16	4.14
1,3,5-trimethyl benzene	4.04	4.07	4.01	**4.04**	4.09	4.07	4.12	4.04
1,2,4-trimethyl benzene	4.24	4.27	4.23	**4.24**	4.24	4.28	4.27	4.24
1,2,3-trimethyl benzene	3.83	3.90	3.79	**3.86**	3.93	3.93	3.84	3.86

	Amount fraction (nmol/mol)							
Cylinder ref:	V4 #5 D83 8896				V4 #6 D83 8930			
Component	$t = 0$	$t = 4$ months	$t = 12$ months	Grav. value	$t = 0$	$t = 4$ months	$t = 12$ months	Grav. value
ethane	5.81	5.91	5.93	5.92	6.01	5.90	5.94	**5.92**
ethene	5.83	5.89	5.82	5.88	5.93	5.91	5.91	**5.88**
propane	5.83	5.85	5.86	5.86	5.84	5.85	5.86	**5.86**
propene	5.78	5.71	5.75	5.79	5.86	5.81	5.80	**5.79**
iso-butane	7.96	7.98	7.92	7.97	8.01	7.96	7.92	**7.97**
n-butane	7.66	7.73	7.65	7.74	7.78	7.76	7.74	**7.74**
acetylene	5.84	5.81	5.91	5.86	5.89	5.85	5.94	**5.87**
trans-2-butene	7.69	7.72	7.71	7.74	7.76	7.75	7.75	**7.74**
1-butene	7.48	7.68	7.59	7.61	7.59	7.67	7.67	**7.62**
cis-2-butene	7.56	7.62	7.53	7.63	7.65	7.62	7.67	**7.63**
2-methyl butane	5.24	5.24	5.28	5.29	5.29	5.31	5.34	**5.29**
n-pentane	5.36	5.36	5.39	5.37	5.37	5.41	5.43	**5.37**
1,3-butadiene	5.79	5.77	5.75	5.79	5.82	5.84	5.81	**5.79**
trans-2-pentene	5.07	5.14	5.12	5.11	5.13	5.10	5.11	**5.11**
1-pentene	5.18	5.22	5.25	5.21	5.21	5.19	5.18	**5.21**
2-methyl pentane	5.25	5.30	5.30	5.30	5.29	5.20	5.31	**5.30**
n-hexane	5.28	5.33	5.29	5.30	5.28	5.28	5.28	**5.31**
isoprene	5.31	5.29	5.29	5.31	5.30	5.26	5.32	**5.31**
n-heptane	5.22	5.26	5.21	5.24	5.22	5.25	5.27	**5.24**
benzene	3.76	3.77	3.79	3.78	3.77	3.79	3.80	**3.78**
2,2,4-trimethyl pentane	5.31	5.28	5.34	5.34	5.35	5.31	5.38	**5.34**
n-octane	5.29	5.27	5.31	5.29	5.28	5.25	5.31	**5.29**
toluene	3.22	3.27	3.24	3.25	3.25	3.23	3.23	**3.25**
ethyl-benzene	4.19	4.18	4.21	4.22	4.21	4.23	4.23	**4.22**
m+p-xylene	8.27	8.32	8.26	8.34	8.31	8.39	8.34	**8.34**
o-xylene	4.11	4.09	4.14	4.14	4.11	4.16	4.14	**4.14**
1,3,5-trimethyl benzene	3.99	4.07	4.02	4.04	4.02	4.04	4.06	**4.04**
1,2,4-trimethyl benzene	4.27	4.18	4.31	4.24	4.27	4.22	4.25	**4.24**
1,2,3-trimethyl benzene	3.85	3.81	3.87	3.86	3.91	3.83	3.84	**3.87**

	Amount fraction (nmol/mol)							
Cylinder ref:	V4 #7 D95 4775				V4 #8 D95 4936			
Component	$t = 0$	$t = 4$ months	$t = 12$ months	Grav. value	$t = 0$	$t = 4$ months	$t = 12$ months	Grav. value
ethane	5.96	5.93	5.92	**5.92**	5.96	5.93	5.94	**5.92**
ethene	5.86	5.89	5.91	**5.88**	5.91	5.89	5.88	**5.88**
propane	5.86	5.89	5.85	**5.86**	5.89	5.88	5.85	**5.86**
propene	5.77	5.80	5.70	**5.79**	5.77	5.84	5.74	**5.79**
iso-butane	7.94	7.91	7.90	**7.97**	7.98	7.95	7.84	**7.97**
n-butane	7.71	7.76	7.73	**7.74**	7.76	7.77	7.80	**7.74**
acetylene	5.81	5.95	5.82	**5.86**	5.89	5.92	5.77	**5.86**
trans-2-butene	7.64	7.74	7.69	**7.74**	7.74	7.72	7.72	**7.74**
1-butene	7.62	7.62	7.56	**7.61**	7.62	7.57	7.61	**7.61**
cis-2-butene	7.54	7.66	7.56	**7.63**	7.64	7.60	7.53	**7.63**
2-methyl butane	5.24	5.31	5.23	**5.29**	5.30	5.32	5.30	**5.29**
n-pentane	5.37	5.38	5.31	**5.37**	5.40	5.39	5.33	**5.37**
1,3-butadiene	5.74	5.80	5.75	**5.79**	5.79	5.85	5.79	**5.79**
trans-2-pentene	5.08	5.15	5.07	**5.11**	5.11	5.15	5.10	**5.11**
1-pentene	5.18	5.18	5.15	**5.21**	5.21	5.21	5.22	**5.21**
2-methyl pentane	5.28	5.33	5.24	**5.30**	5.30	5.27	5.21	**5.30**
n-hexane	5.30	5.28	5.33	**5.30**	5.32	5.32	5.30	**5.30**
isoprene	5.32	5.32	5.28	**5.31**	5.31	5.28	5.34	**5.31**
n-heptane	5.21	5.23	5.15	**5.24**	5.22	5.25	5.20	**5.24**
benzene	3.76	3.73	3.74	**3.78**	3.74	3.77	3.77	**3.78**
2,2,4-trimethyl pentane	5.29	5.34	5.30	**5.34**	5.37	5.35	5.30	**5.34**
n-octane	5.26	5.31	5.26	**5.29**	5.28	5.30	5.30	**5.29**
toluene	3.22	3.21	3.23	**3.25**	3.25	3.25	3.31	**3.25**
ethyl-benzene	4.17	4.15	4.22	**4.22**	4.21	4.21	4.30	**4.22**
m+p-xylene	8.26	8.22	8.34	**8.34**	8.35	8.29	8.44	**8.34**
o-xylene	4.11	4.12	4.11	**4.14**	4.12	4.13	4.17	**4.14**
1,3,5-trimethyl benzene	4.05	3.98	4.01	**4.04**	4.07	3.99	4.07	**4.04**
1,2,4-trimethyl benzene	4.21	4.15	4.23	**4.24**	4.26	4.20	4.31	**4.24**
1,2,3-trimethyl benzene	3.84	3.82	3.87	**3.86**	3.82	3.85	3.91	**3.86**

	Amount fraction (nmol/mol)							
Cylinder ref:	V4 #9 D83 8781				V4 #10 D95 4947			
Component	$t = 0$	$t = 4$ months	$t = 12$ months	Grav. value	$t = 0$	$t = 4$ months	$t = 12$ months	Grav. value
ethane	6.01	5.95	5.91	**5.92**	5.93	5.98	5.96	**5.92**
ethene	5.92	5.87	5.87	**5.88**	5.86	5.89	5.88	**5.88**
propane	5.97	5.89	5.87	**5.86**	5.81	5.86	5.90	**5.86**
propene	5.83	5.80	5.74	**5.79**	5.79	5.70	5.85	**5.79**
iso-butane	8.06	7.94	8.02	**7.97**	7.99	7.96	7.96	**7.97**
n-butane	7.74	7.81	7.82	**7.74**	7.76	7.75	7.83	**7.74**
acetylene	5.86	5.80	5.88	**5.86**	5.86	5.85	5.88	**5.86**
trans-2-butene	7.74	7.72	7.80	**7.74**	7.77	7.73	7.71	**7.74**
1-butene	7.64	7.55	7.75	**7.61**	7.63	7.59	7.60	**7.61**
cis-2-butene	7.70	7.64	7.80	**7.63**	7.66	7.76	7.70	**7.63**
2-methyl butane	5.29	5.27	5.33	**5.29**	5.33	5.33	5.27	**5.29**
n-pentane	5.36	5.38	5.40	**5.37**	5.39	5.37	5.34	**5.37**
1,3-butadiene	5.82	5.78	5.82	**5.79**	5.84	5.83	5.86	**5.79**
trans-2-pentene	5.11	5.15	5.14	**5.11**	5.13	5.13	5.12	**5.11**
1-pentene	5.22	5.22	5.18	**5.21**	5.21	5.25	5.25	**5.21**
2-methyl pentane	5.30	5.31	5.25	**5.30**	5.30	5.33	5.33	**5.30**
n-hexane	5.30	5.34	5.37	**5.30**	5.32	5.30	5.29	**5.30**
isoprene	5.33	5.31	5.37	**5.31**	5.35	5.29	5.32	**5.31**
n-heptane	5.26	5.24	5.26	**5.24**	5.27	5.22	5.29	**5.24**
benzene	3.81	3.73	3.83	**3.78**	3.78	3.77	3.77	**3.78**
2,2,4-trimethyl pentane	5.34	5.31	5.43	**5.34**	5.35	5.36	5.32	**5.34**
n-octane	5.31	5.26	5.35	**5.29**	5.32	5.29	5.39	**5.29**
toluene	3.29	3.24	3.29	**3.25**	3.27	3.25	3.30	**3.25**
ethyl-benzene	4.30	4.22	4.24	**4.22**	4.25	4.19	4.24	**4.22**
m+p-xylene	8.46	8.27	8.42	**8.34**	8.36	8.32	8.40	**8.34**
o-xylene	4.15	4.10	4.18	**4.14**	4.16	4.12	4.20	**4.14**
1,3,5-trimethyl benzene	4.10	4.01	4.08	**4.04**	4.10	4.02	4.05	**4.04**
1,2,4-trimethyl benzene	4.35	4.20	4.30	**4.24**	4.28	4.21	4.27	**4.24**
1,2,3-trimethyl benzene	3.89	3.84	3.87	**3.86**	3.88	3.82	3.96	**3.86**

	Amount fraction (nmol/mol)							
Cylinder ref:	V4 #11 D95 4934				V4 #12 D95 4932			
Component	$t = 0$	$t = 4$ months	$t = 12$ months	Grav. value	$t = 0$	$t = 4$ months	$t = 12$ months	Grav. value
ethane	5.89	5.93	5.94	**5.92**	5.87	5.93	6.00	**5.92**
ethene	5.84	5.83	5.87	**5.88**	5.88	5.90	5.91	**5.88**
propane	5.80	5.83	5.91	**5.86**	5.82	5.86	5.83	**5.86**
propene	5.80	5.72	5.73	**5.79**	5.85	5.88	5.68	**5.79**
iso-butane	7.90	7.97	8.15	**7.97**	7.97	8.11	8.10	**7.97**
n-butane	7.81	7.73	7.75	**7.74**	7.67	7.76	7.77	**7.74**
acetylene	5.90	5.90	5.84	**5.86**	5.87	5.89	5.84	**5.86**
trans-2-butene	7.76	7.71	7.70	**7.73**	7.71	7.72	7.69	**7.74**
1-butene	7.60	7.61	7.50	**7.61**	7.62	7.64	7.69	**7.61**
cis-2-butene	7.62	7.64	7.61	**7.63**	7.60	7.68	7.69	**7.63**
2-methyl butane	5.28	5.25	5.27	**5.29**	5.28	5.30	5.33	**5.29**
n-pentane	5.36	5.30	5.34	**5.37**	5.33	5.33	5.44	**5.37**
1,3-butadiene	5.86	5.76	5.81	**5.79**	5.75	5.85	5.79	**5.79**
trans-2-pentene	5.10	5.09	5.08	**5.11**	5.10	5.12	5.18	**5.11**
1-pentene	5.19	5.17	5.15	**5.21**	5.23	5.20	5.25	**5.21**
2-methyl pentane	5.33	5.22	5.20	**5.30**	5.27	5.32	5.32	**5.30**
n-hexane	5.36	5.28	5.30	**5.30**	5.33	5.28	5.31	**5.30**
isoprene	5.39	5.25	5.32	**5.31**	5.32	5.31	5.33	**5.31**
n-heptane	5.30	5.21	5.17	**5.24**	5.23	5.22	5.22	**5.24**
benzene	3.80	3.76	3.78	**3.78**	3.78	3.80	3.78	**3.78**
2,2,4-trimethyl pentane	5.39	5.32	5.32	**5.34**	5.31	5.35	5.38	**5.34**
n-octane	5.32	5.26	5.28	**5.29**	5.30	5.30	5.29	**5.29**
toluene	3.25	3.20	3.19	**3.25**	3.25	3.25	3.23	**3.25**
ethyl-benzene	4.20	4.20	4.23	**4.22**	4.24	4.22	4.19	**4.22**
m+p-xylene	8.37	8.30	8.30	**8.34**	8.34	8.37	8.27	**8.34**
o-xylene	4.18	4.10	4.14	**4.14**	4.17	4.17	4.12	**4.14**
1,3,5-trimethyl benzene	3.96	4.03	4.07	**4.04**	4.05	3.99	4.12	**4.04**
1,2,4-trimethyl benzene	4.30	4.20	4.29	**4.24**	4.30	4.20	4.27	**4.24**
1,2,3-trimethyl benzene	3.78	3.86	3.91	**3.86**	3.86	3.84	3.92	**3.86**

	Amount fraction (nmol/mol)			
Cylinder ref:	V4 #14 D29 2405			
Component	$t = 0$	$t = 4$ months	$t = 12$ months	Grav. value
ethane	5.87	5.82	5.91	**5.92**
ethene	5.85	5.84	5.92	**5.87**
propane	5.90	5.82	5.83	**5.86**
propene	5.64	5.73	5.81	**5.79**
iso-butane	8.00	8.10	7.90	**7.97**
n-butane	7.62	7.74	7.85	**7.74**
acetylene	5.83	5.88	5.97	**5.86**
trans-2-butene	7.78	7.73	7.75	**7.73**
1-butene	7.58	7.66	7.68	**7.61**
cis-2-butene	7.61	7.53	7.70	**7.63**
2-methyl butane	5.28	5.25	5.32	**5.29**
n-pentane	5.28	5.36	5.34	**5.37**
1,3-butadiene	5.80	5.76	5.77	**5.79**
trans-2-pentene	5.11	5.08	5.14	**5.11**
1-pentene	5.19	5.21	5.20	**5.21**
2-methyl pentane	5.23	5.29	5.32	**5.30**
n-hexane	5.27	5.31	5.32	**5.30**
isoprene	5.30	5.33	5.33	**5.30**
n-heptane	5.24	5.24	5.26	**5.24**
benzene	3.78	3.78	3.79	**3.78**
2,2,4-trimethyl pentane	5.30	5.32	5.42	**5.34**
n-octane	5.24	5.29	5.32	**5.29**
toluene	3.22	3.25	3.26	**3.25**
ethyl-benzene	4.22	4.25	4.26	**4.22**
m+p-xylene	8.34	8.44	8.44	**8.34**
o-xylene	4.14	4.11	4.18	**4.14**
1,3,5-trimethyl benzene	4.01	4.05	4.09	**4.04**
1,2,4-trimethyl benzene	4.24	4.23	4.26	**4.24**
1,2,3-trimethyl benzene	3.84	3.93	3.84	**3.86**

Annex B: Cylinder allocation & project timeline

Table B1: Cylinder allocation and despatch

Laboratory	Cylinders		Despatch		Return	
	Number	Reference	Date	Pressure (bar)	Date	Pressure (bar)
ERLAP	D95 4790	V4 #3	09-May-07	99	23-Jul-07	44
FMI	D83 8781	V4 #9	11-Jun-07	102	20-Jul-07	87
INRiM	D83 8781	V4 #9	03-Sep-07	86	10-Mar-08	81
ISCIII	D95 4945	V3 #4	12-Jun-07	103	10-Oct-07	102
KRISS	D95 4825	V3 #3	17-May-07	102	10-Sep-07	81
NIST	D83 8896	V4 #5	17-May-07	100	28-Aug-07	94
NMi	D95 4815	V4 #4	17-May-07	102	15-Aug-07	81
NPL	D95 4804	V3 #12	25-Jul-07	100	23-Nov-07	90
UBA(A)	D95 4965	V3 #6	11-Jun-07	102	31-Jul-07	65
IMK (IFU-FZK)	D29 2401	V3 #14	10-Oct-07	102	10-Dec-07	102

Table B2: Project timeline

EVENT	**DATE**
First cylinder despatched	09-May-2007
First participant results sent to JRC	25-Jul-2007
Interim NPL report sent to JRC including all gravimetric and stability data	04-Sep-2007
Preliminary results sent to all EURAMET/CCQM participants who had reported their results	07-Feb-2008
Preliminary JRC report circulated	08-Feb-2008
NPL presentation of preliminary results to EURAMET and CCQM participants at METCHEM, Istanbul.	14-Feb-08
Final NPL report sent to JRC	09-May-2008
Final JRC report circulated	09-Oct-2008

Annex C: Uncertainty estimate

A measurement of a participant standard consisted of 2 analyses of the participant standard and 3 analyses of the working standard in the sequence A-B-A-B-A.

The uncertainty assigned to a result is calculated by evaluating the standard deviation of the sample across all 3 rounds of measurements. This was achieved by averaging the relative variances calculated from each round of each version and then taking the square root. This estimate for the measurement uncertainty was used in calculating the expanded uncertainty for the drift parameter.

Table C1: Variance of measured concentration difference from gravimetric value and the square root of the average variance expressed relative to the gravimetric value

	VARIANCE							SQRT(AVG VAR)
	Round 1		Round 2		Round 3			Relative to Grav
	v4	v3	v4	v3	v4	v3	AVG	
ethane	1.20E-04	3.81E-05	5.18E-05	3.51E-05	2.14E-05	1.27E-05	4.66E-05	**0.68%**
ethene	3.37E-05	5.62E-05	2.11E-05	1.59E-05	2.43E-05	4.04E-06	2.59E-05	**0.51%**
propane	7.55E-05	8.19E-05	1.37E-05	2.16E-05	2.87E-05	3.05E-05	4.20E-05	**0.65%**
propene	1.06E-04	6.46E-05	1.04E-04	1.20E-04	1.34E-04	9.12E-05	1.03E-04	**1.02%**
iso-butane	3.54E-05	1.44E-04	7.36E-05	1.28E-04	1.97E-04	1.55E-04	1.22E-04	**1.11%**
n-butane	5.71E-05	5.93E-05	1.67E-05	6.09E-05	6.22E-05	9.76E-05	5.90E-05	**0.77%**
acetylene	2.88E-05	9.10E-05	9.35E-05	6.13E-05	9.42E-05	8.28E-05	7.53E-05	**0.87%**
trans-2-butene	2.75E-05	2.01E-05	2.68E-05	7.42E-06	5.75E-05	9.29E-06	2.48E-05	**0.50%**
1-butene	3.84E-05	1.44E-05	2.97E-05	5.52E-05	8.61E-05	4.44E-05	4.47E-05	**0.67%**
cis-2-butene	3.62E-05	1.10E-04	5.58E-05	2.01E-05	1.27E-04	6.40E-05	6.90E-05	**0.83%**
2-methyl butane	2.93E-05	3.31E-05	7.69E-05	4.76E-05	3.71E-05	1.17E-04	5.69E-05	**0.75%**
n-pentane	4.21E-05	6.65E-05	6.40E-05	3.35E-05	6.10E-05	8.04E-05	5.79E-05	**0.76%**
1,3-butadiene	3.50E-05	2.25E-05	3.46E-05	1.83E-05	6.50E-05	5.87E-05	3.90E-05	**0.62%**
trans-2-pentene	1.65E-05	5.25E-05	2.60E-05	5.81E-05	4.43E-05	5.94E-05	4.28E-05	**0.65%**
1-pentene	1.56E-05	8.92E-05	2.28E-05	9.41E-06	7.63E-05	8.27E-05	4.93E-05	**0.70%**
2-methyl pentane	2.95E-05	6.48E-05	6.79E-05	3.34E-05	8.14E-05	7.86E-05	5.92E-05	**0.77%**
n-hexane	2.43E-05	5.08E-05	1.80E-05	2.00E-05	3.88E-05	4.98E-05	3.36E-05	**0.58%**
isoprene	4.84E-05	3.39E-05	3.48E-05	3.73E-05	4.09E-05	1.71E-05	3.54E-05	**0.59%**
n-heptane	3.24E-05	4.19E-05	7.15E-06	2.78E-05	7.26E-05	6.14E-05	4.05E-05	**0.64%**
benzene	2.35E-05	2.24E-05	3.70E-05	1.64E-05	4.55E-05	5.22E-05	3.28E-05	**0.57%**
2,2,4-trimethyl pentane	4.86E-05	5.77E-05	2.23E-05	3.09E-05	7.01E-05	1.00E-04	5.49E-05	**0.74%**
n-octane	3.39E-05	3.34E-05	1.85E-05	4.63E-05	5.57E-05	6.07E-05	4.14E-05	**0.64%**
toluene	4.64E-05	5.74E-05	4.42E-05	5.59E-05	1.29E-04	1.07E-04	7.34E-05	**0.86%**
ethyl-benzene	6.38E-05	6.13E-05	4.64E-05	3.83E-05	4.97E-05	9.75E-06	4.49E-05	**0.67%**
m+p-xylene	4.38E-05	5.17E-05	5.77E-05	5.15E-05	5.95E-05	2.75E-05	4.86E-05	**0.70%**
o-xylene	5.66E-05	1.10E-04	3.71E-05	4.47E-05	4.42E-05	4.97E-05	5.70E-05	**0.76%**
1,3,5-trimethyl benzene	1.24E-04	2.01E-04	6.56E-05	8.40E-05	9.45E-05	6.56E-05	1.06E-04	**1.03%**
1,2,4-trimethyl benzene	7.93E-05	2.03E-04	7.45E-05	9.27E-05	5.02E-05	9.62E-05	9.93E-05	**1.00%**
1,2,3-trimethyl benzene	1.32E-04	1.63E-04	1.30E-04	1.10E-04	1.41E-04	2.45E-04	1.53E-04	**1.24%**

Table C2: Working standard amount fractions and associated gravimetric uncertainties.

	Amount fraction (nmol/mol)									
	Version 3					Version 4				
Number:	#1	#2	#13	#15	U_{grav}	#1	#2	#13	#15	U_{grav}
ethane	6.74	6.74	6.74	6.74	0.02	5.91	5.92	5.92	5.92	0.02
ethene	6.70	6.69	6.69	6.69	0.02	5.87	5.87	5.88	5.88	0.02
propane	6.68	6.67	6.67	6.67	0.02	5.86	5.86	5.86	5.86	0.02
propene	6.60	6.59	6.60	6.59	0.02	5.78	5.79	5.79	5.79	0.02
iso-butane	7.11	7.10	7.10	7.10	0.01	7.97	7.97	7.97	7.97	0.01
n-butane	6.90	6.89	6.90	6.89	0.01	7.73	7.74	7.74	7.74	0.01
acetylene	6.68	6.68	6.68	6.68	0.02	5.86	5.86	5.86	5.86	0.02
trans-2-butene	6.90	6.89	6.89	6.89	0.01	7.73	7.73	7.74	7.73	0.01
1-butene	6.79	6.78	6.79	6.78	0.01	7.61	7.61	7.61	7.61	0.01
cis-2-butene	6.80	6.79	6.80	6.80	0.01	7.62	7.63	7.63	7.63	0.01
2-methyl butane	5.13	5.12	5.12	5.12	0.01	5.29	5.29	5.29	5.29	0.01
n-pentane	5.20	5.20	5.20	5.20	0.01	5.37	5.37	5.37	5.37	0.01
1,3-butadiene	6.60	6.59	6.59	6.59	0.02	5.78	5.78	5.79	5.79	0.01
trans-2-pentene	4.95	4.95	4.95	4.95	0.01	5.11	5.11	5.11	5.11	0.01
1-pentene	5.04	5.04	5.04	5.04	0.01	5.20	5.21	5.21	5.21	0.01
2-methyl pentane	5.13	5.13	5.13	5.13	0.01	5.29	5.30	5.30	5.30	0.01
n-hexane	5.14	5.13	5.14	5.13	0.01	5.30	5.30	5.30	5.30	0.01
isoprene	5.14	5.13	5.14	5.14	0.01	5.30	5.30	5.31	5.31	0.01
n-heptane	5.07	5.07	5.07	5.07	0.01	5.23	5.24	5.24	5.24	0.01
benzene	4.18	4.17	4.18	4.18	0.01	3.78	3.78	3.78	3.78	0.01
2,2,4-trimethyl pentane	5.17	5.16	5.17	5.17	0.01	5.33	5.34	5.34	5.34	0.01
n-octane	5.12	5.11	5.12	5.12	0.01	5.28	5.28	5.29	5.29	0.01
toluene	3.59	3.59	3.59	3.59	0.01	3.25	3.25	3.25	3.25	0.01
ethyl-benzene	3.84	3.84	3.84	3.84	0.03	4.21	4.22	4.22	4.22	0.03
m+p-xylene	7.59	7.59	7.59	7.59	0.08	8.34	8.34	8.34	8.34	0.08
o-xylene	3.77	3.76	3.77	3.77	0.03	4.14	4.14	4.14	4.14	0.03
1,3,5-trimethyl benzene	3.68	3.68	3.68	3.68	0.02	4.04	4.04	4.04	4.04	0.03
1,2,4-trimethyl benzene	3.86	3.86	3.86	3.86	0.03	4.24	4.24	4.24	4.24	0.03
1,2,3-trimethyl benzene	3.52	3.51	3.52	3.52	0.03	3.86	3.86	3.86	3.86	0.03

U_{grav} – expanded uncertainty (k=2) associated with gravimetric amount fraction

All working standards were verified using NPL primary standards to within the analytical uncertainty for each species.

Working standards were prepared directly from high concentration parent mixtures to eliminate errors associated with drifts common to the reference and test cylinders.

The parent mixtures of the two versions (V3 and V4) were used to make 4 working standards each (#1, #2, #13 and #15). Working standards #1 & #2 were made and used in the stability trials at $t = 0$, working standards #13 were made and used at $t = 4$ months and working standards #15 were made and used at $t = 12$ months. Test cylinders were analysed against working standards from the opposing version to minimise errors associated with correlation.

Table C3: Synthetic standard parent mixture amount fractions and associated gravimetric uncertainties (nmol/mol).

Component	Parent V3 D95 4939	U_{grav}	Parent V4 D95 4773	U_{grav}
ethane	329.3	0.8	288.5	0.7
ethene	327.5	0.8	287.0	0.8
propane	326.1	0.8	285.7	0.7
propene	323.2	0.8	283.2	0.7
iso-butane	348.1	0.4	390.0	0.5
n-butane	337.9	0.5	378.6	0.5
acetylene	327.4	0.8	286.9	0.8
trans-2-butene	337.8	0.5	378.4	0.6
1-butene	332.5	0.5	372.4	0.5
cis-2-butene	333.1	0.5	373.2	0.6
2-methyl butane	251.1	0.4	258.9	0.4
n-pentane	254.7	0.4	262.7	0.5
1,3-butadiene	323.1	0.7	283.1	0.6
trans-2-pentene	242.5	0.5	250.2	0.5
1-pentene	247.0	0.3	254.8	0.3
2-methyl pentane	251.3	0.3	259.2	0.3
n-hexane	251.6	0.4	259.5	0.4
isoprene	251.7	0.5	259.6	0.5
n-heptane	248.4	0.3	256.2	0.4
benzene	204.6	0.3	184.9	0.3
2,2,4-trimethyl pentane	253.2	0.3	261.1	0.3
n-octane	250.8	0.3	258.6	0.4
toluene	176.0	0.2	159.0	0.2
ethyl-benzene	188.0	1.3	206.3	1.4
m+p-xylene	371.9	1.9	408.1	2.0
o-xylene	184.6	1.3	202.5	1.4
1,3,5-trimethyl benzene	180.3	1.2	197.8	1.3
1,2,4-trimethyl benzene	189.1	1.2	207.4	1.3
1,2,3-trimethyl benzene	172.3	1.4	189.0	1.6

U_{grav} – expanded uncertainty (k=2) associated with gravimetric amount fraction

The parent mixtures were verified against each other at the start of the exercise ($t = 0$). Sensitive but indirect stability checks were made on the parent mixtures as they were diluted to produce low concentration working standards for the stability tests at $t = 4$ & 12 months. From these and NPL's experience with similar mixtures, the best estimates for concentration and uncertainty at $t = 4$ and $t = 12$ months are the same as at $t = 0$.

Table C4: Relative uncertainties associated with the reported amount fractions of synthetic test cylinders.

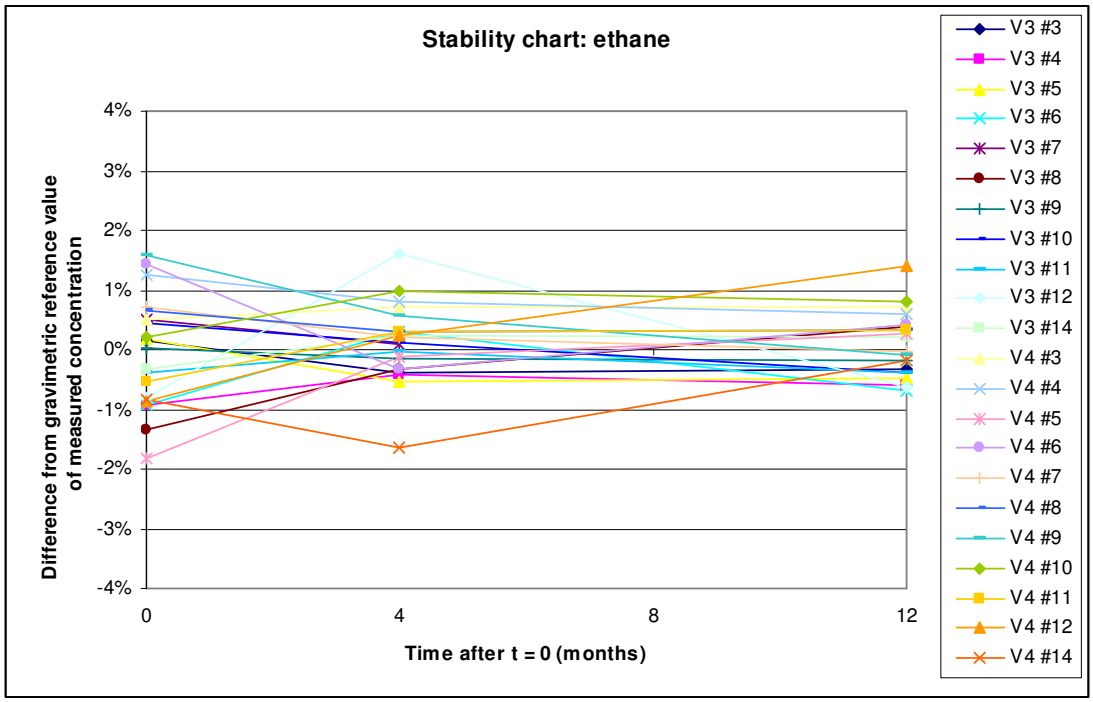
	SQRT(AVG VAR) u_{prec}	u_{grav}	Combined uncertainty (k=1)	Expanded uncertainty (k=2) of the KCRV
ethane	0.68%	0.16%	0.70%	**1.40%**
ethene	0.51%	0.15%	0.53%	**1.06%**
propane	0.65%	0.15%	0.67%	**1.33%**
propene	1.02%	0.13%	1.03%	**2.06%**
iso-butane	1.11%	0.09%	1.11%	**2.23%**
n-butane	0.77%	0.09%	0.78%	**1.55%**
acetylene	0.87%	0.14%	0.88%	**1.76%**
trans-2-butene	0.50%	0.10%	0.51%	**1.02%**
1-butene	0.67%	0.09%	0.68%	**1.35%**
cis-2-butene	0.83%	0.10%	0.84%	**1.67%**
2-methyl butane	0.75%	0.11%	0.76%	**1.51%**
n-pentane	0.76%	0.10%	0.77%	**1.53%**
1,3-butadiene	0.62%	0.12%	0.63%	**1.26%**
trans-2-pentene	0.65%	0.13%	0.66%	**1.32%**
1-pentene	0.70%	0.09%	0.71%	**1.41%**
2-methyl pentane	0.77%	0.09%	0.78%	**1.55%**
n-hexane	0.58%	0.10%	0.59%	**1.18%**
isoprene	0.59%	0.11%	0.60%	**1.20%**
n-heptane	0.64%	0.09%	0.65%	**1.29%**
benzene	0.57%	0.09%	0.58%	**1.15%**
2,2,4-trimethyl pentane	0.74%	0.09%	0.75%	**1.49%**
n-octane	0.64%	0.09%	0.65%	**1.29%**
toluene	0.86%	0.09%	0.86%	**1.73%**
ethyl-benzene	0.67%	0.36%	0.76%	**1.52%**
m+p-xylene	0.70%	0.51%	0.87%	**1.73%**
o-xylene	0.76%	0.36%	0.84%	**1.68%**
1,3,5-trimethyl benzene	1.03%	0.33%	1.08%	**2.16%**
1,2,4-trimethyl benzene	1.00%	0.33%	1.05%	**2.11%**
1,2,3-trimethyl benzene	1.24%	0.42%	1.31%	**2.62%**

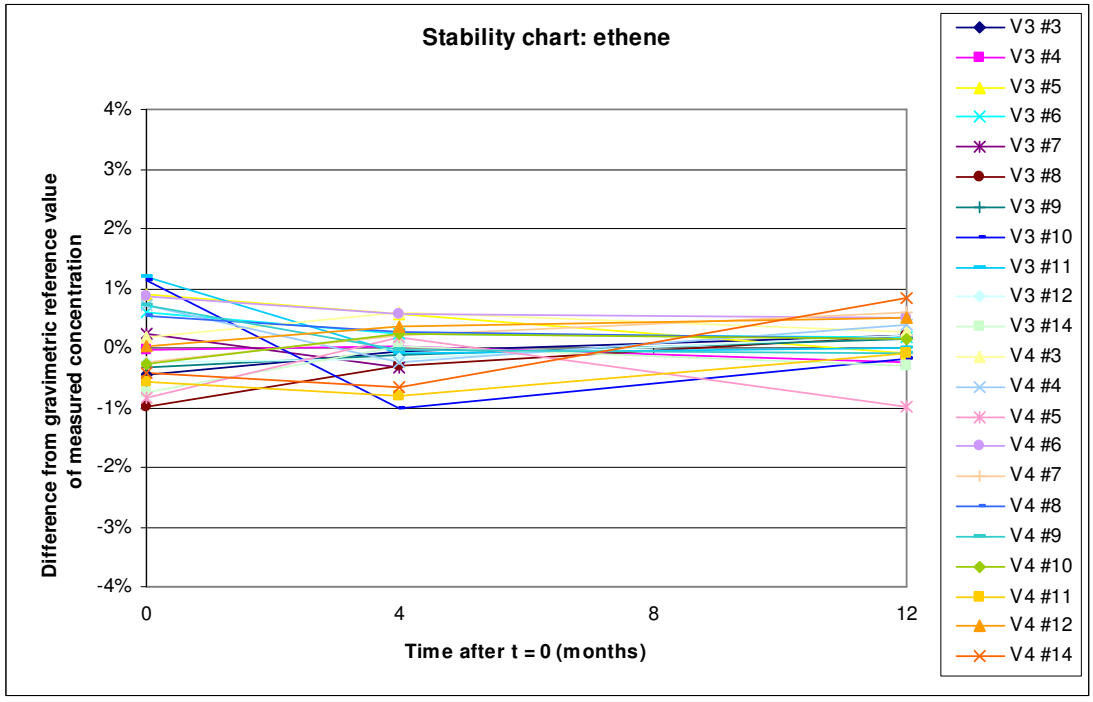
u_{grav} – gravimetric uncertainty of the working standard
KCRV – Key Comparison Reference Value

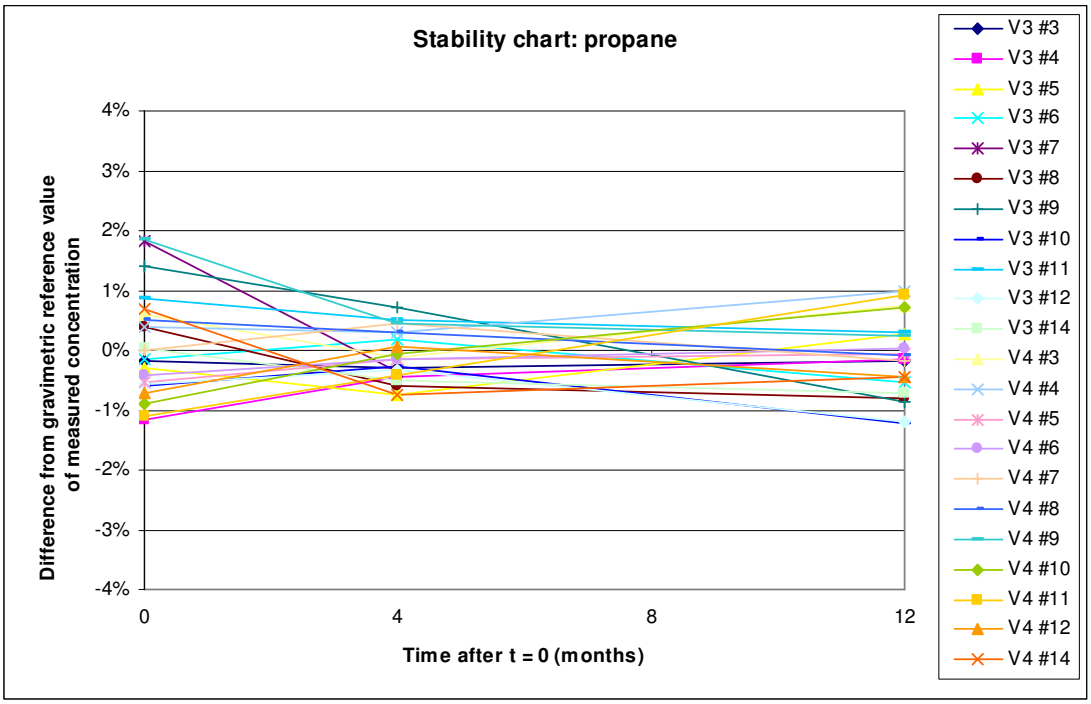
The associated uncertainty in the Key Comparison Reference Value (KCRV) was calculated by combining in quadrature (as k=1) the analytical uncertainty given by the precision of measurements over the 3 rounds of analysis ($u_{prec} \equiv$ SQRT(AVG VAR) from Table C1) and the gravimetric uncertainty associated with the reference cylinder (u_{grav}). The uncertainties apply to the measurements at t = 0, 4 and 12 months.

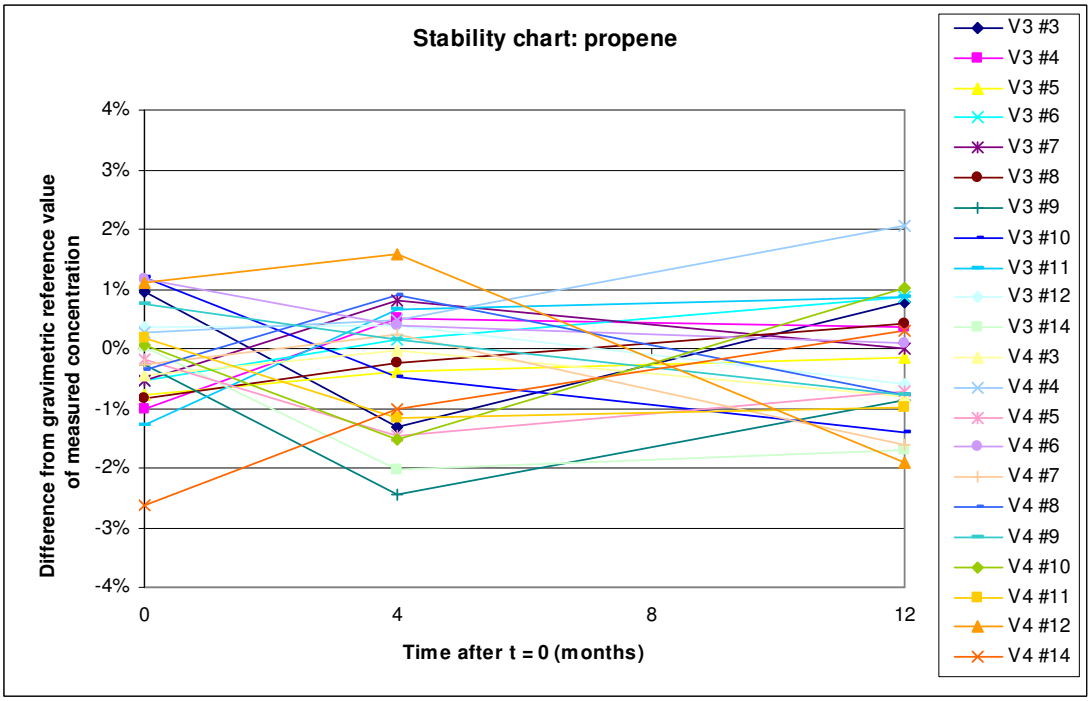
Annex D: Individual component stability charts

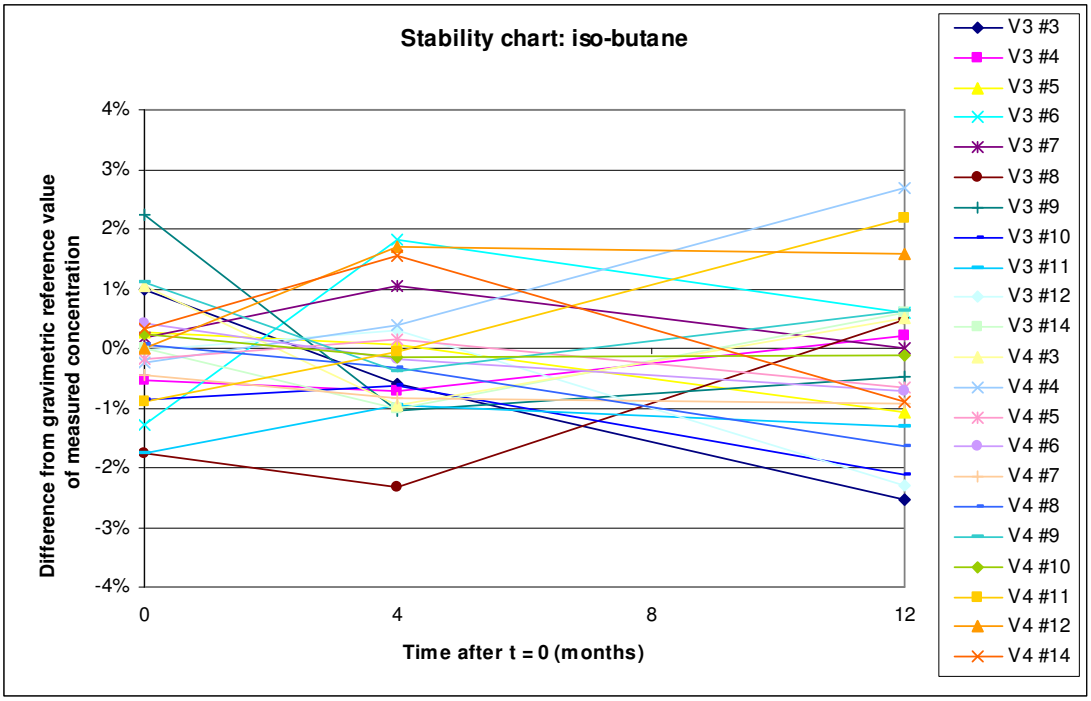
The following charts show the complete results for each component in all cylinders (V3/4 #3-#12 & #14) measured over 3 rounds of stability trials.

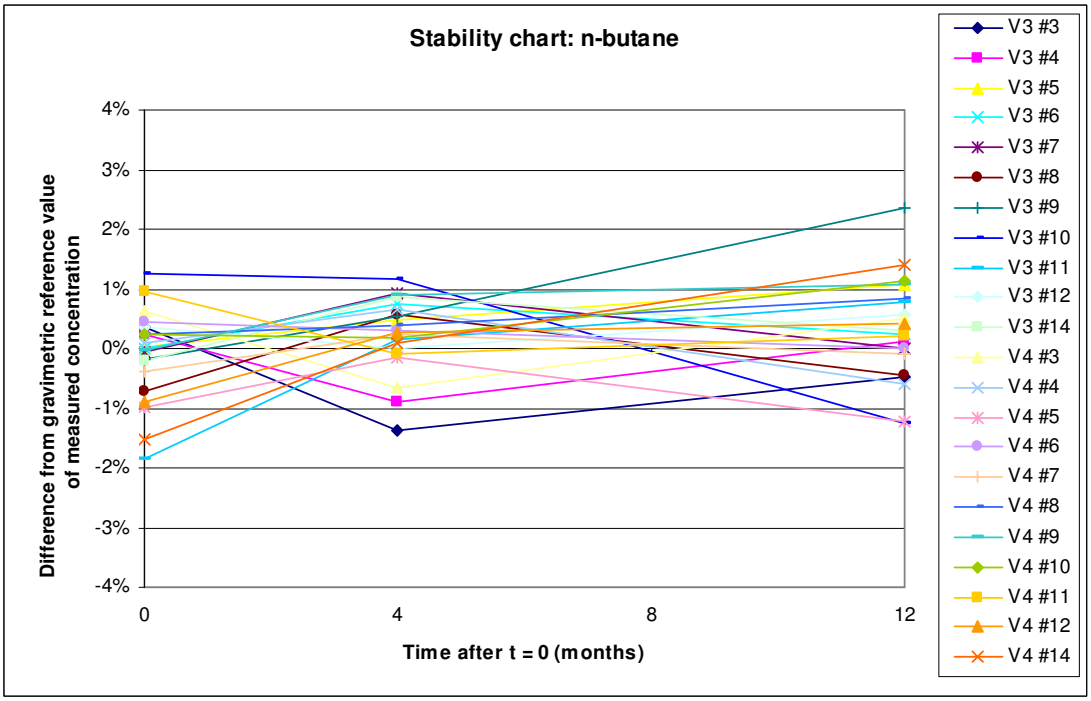


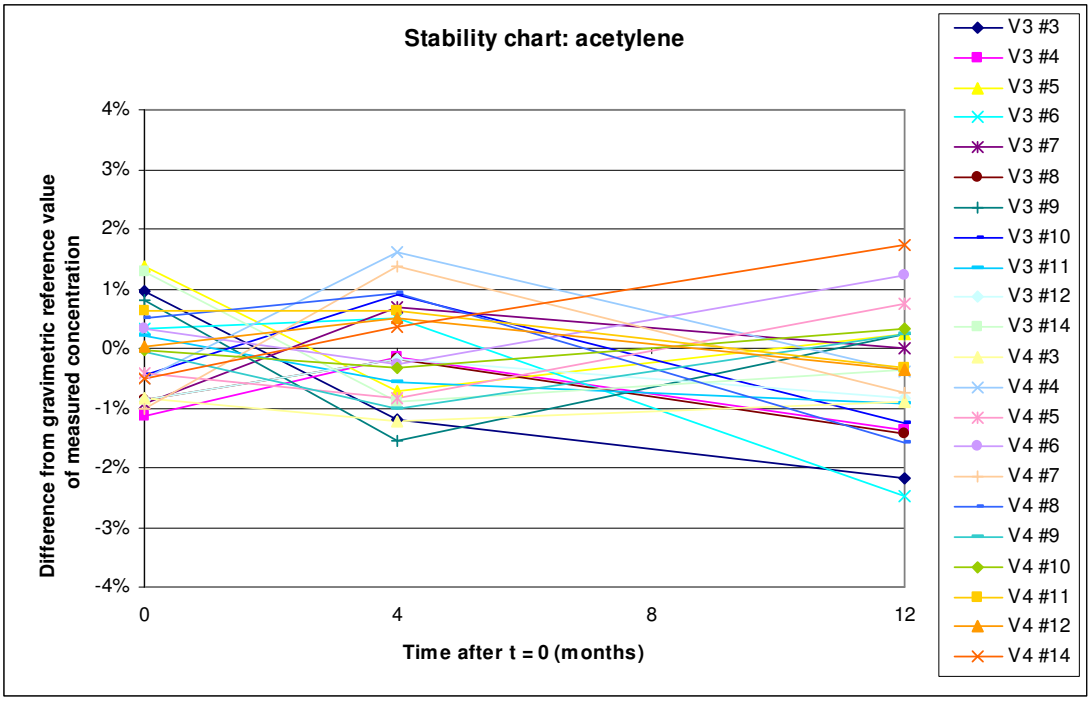


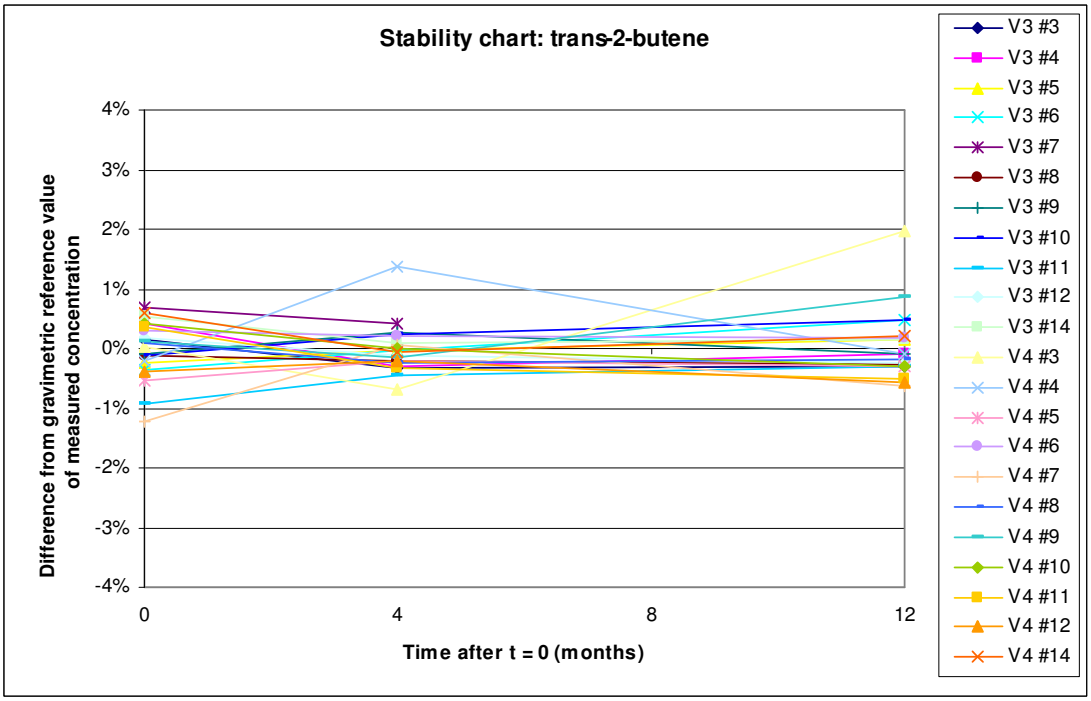

Stability chart: propane
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

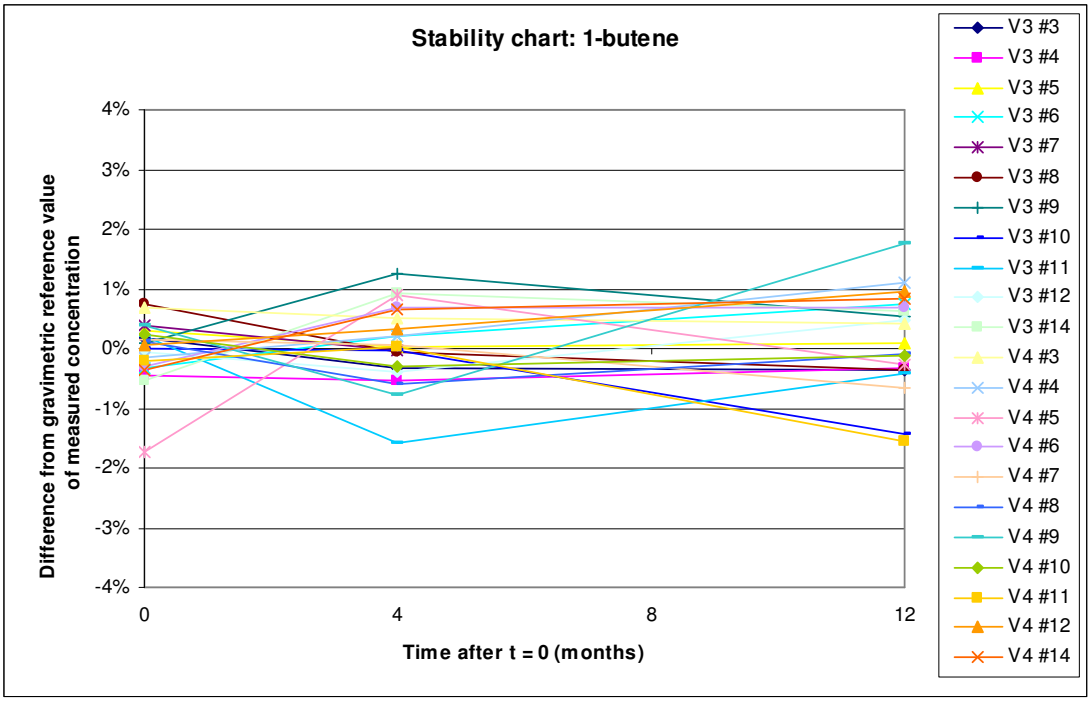

Stability chart: propene
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

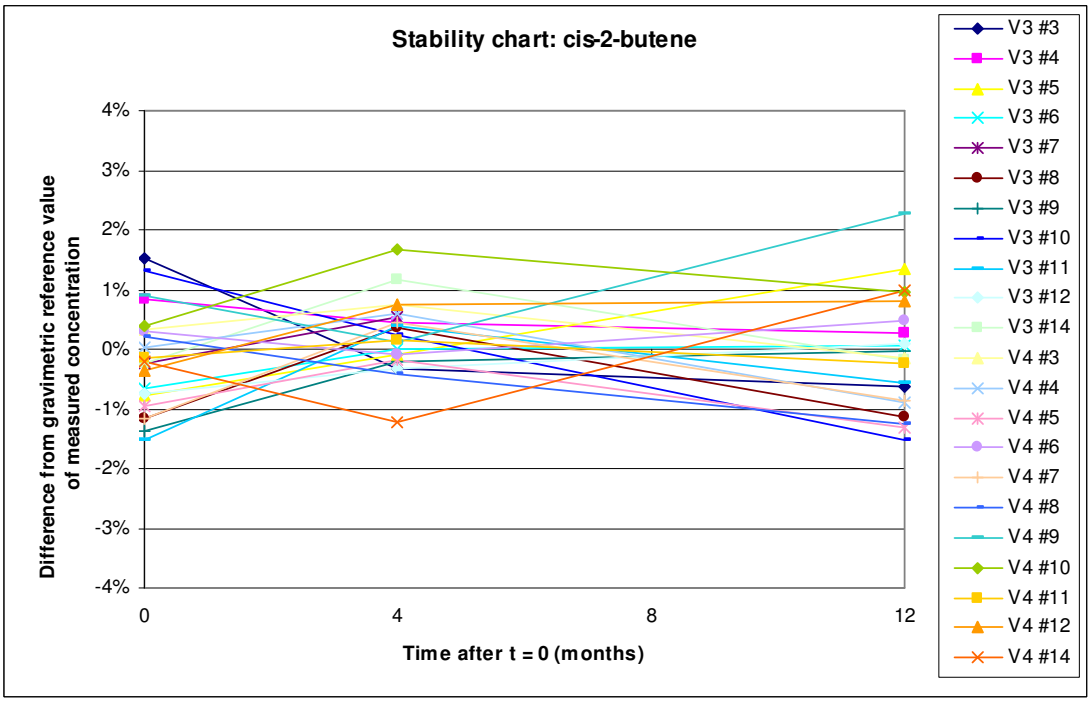

Stability chart: iso-butane
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

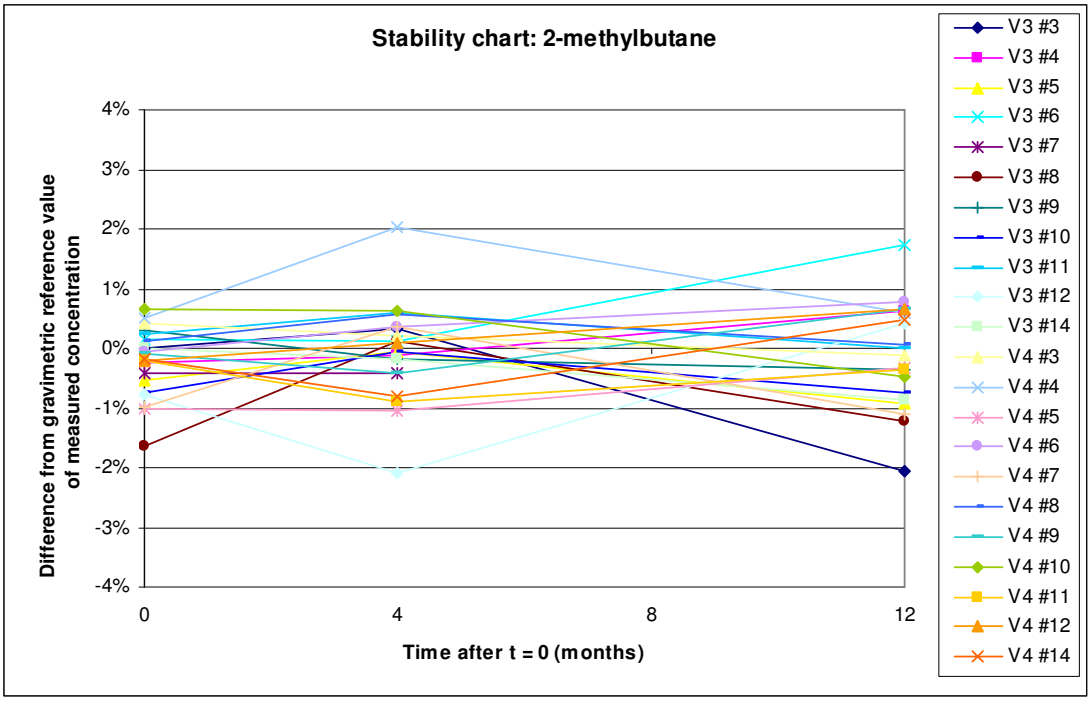

Stability chart: n-butane
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

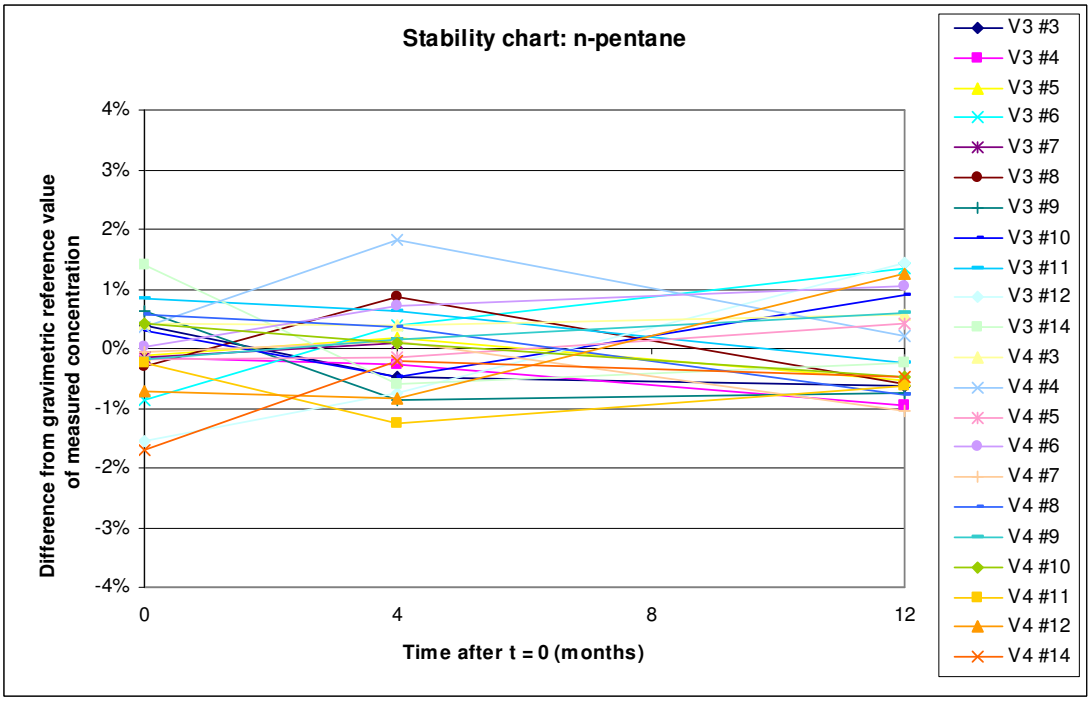

Stability chart: acetylene
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

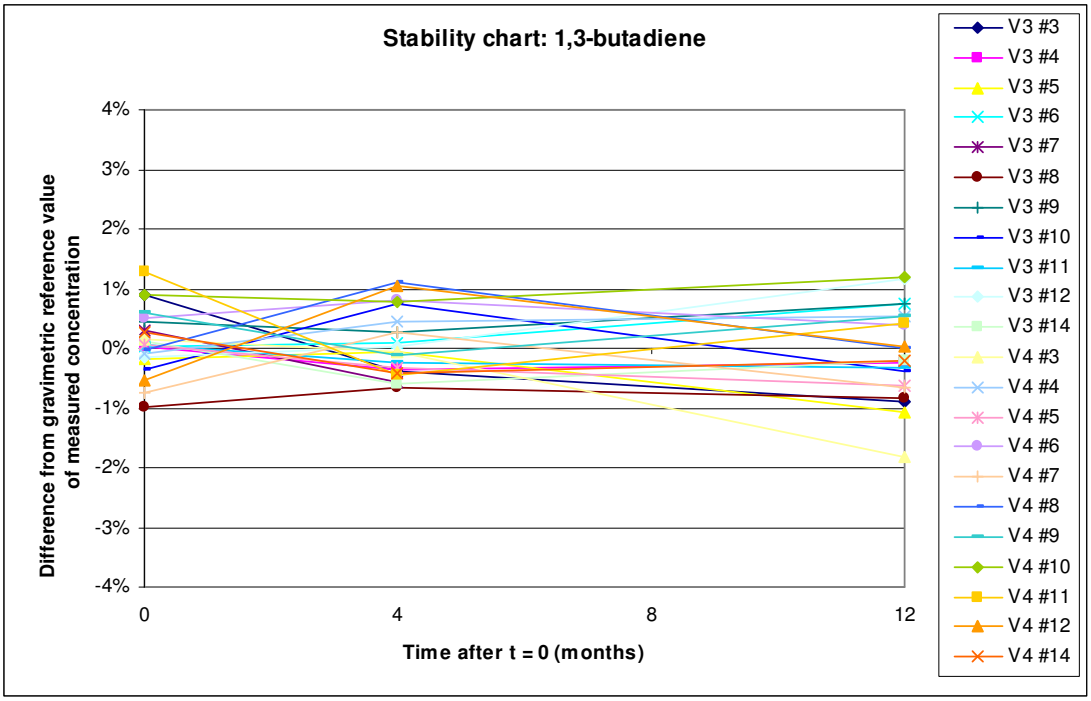

Stability chart: trans-2-butene
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

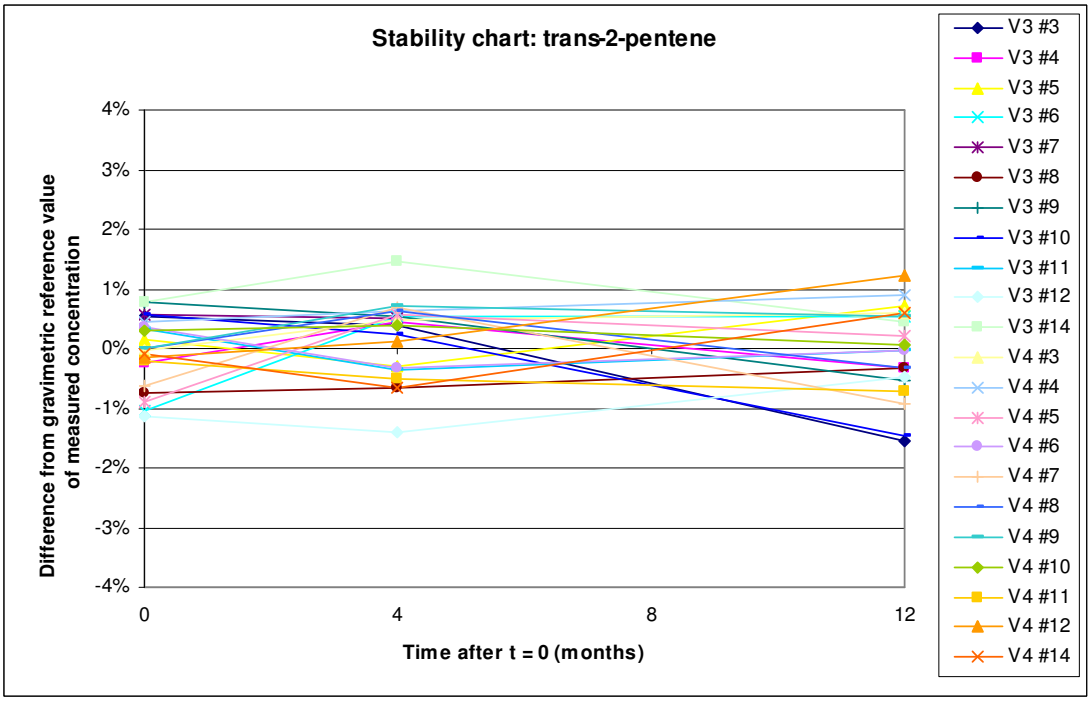

Stability chart: 1-butene
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

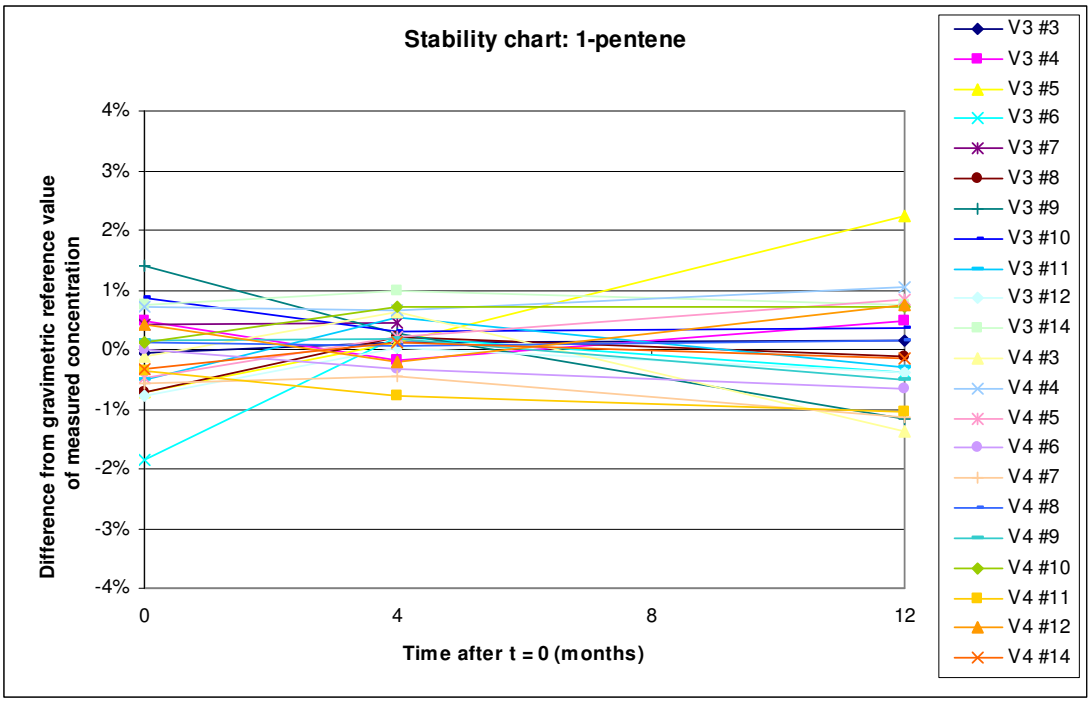

Stability chart: cis-2-butene
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

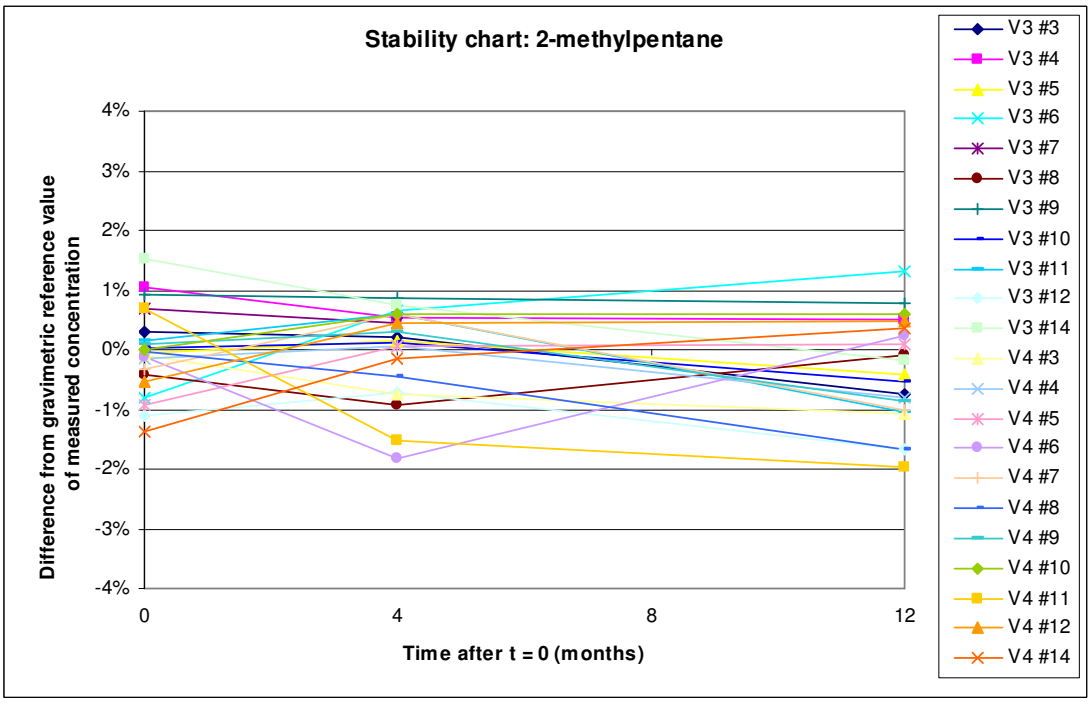

Stability chart: 2-methylbutane
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

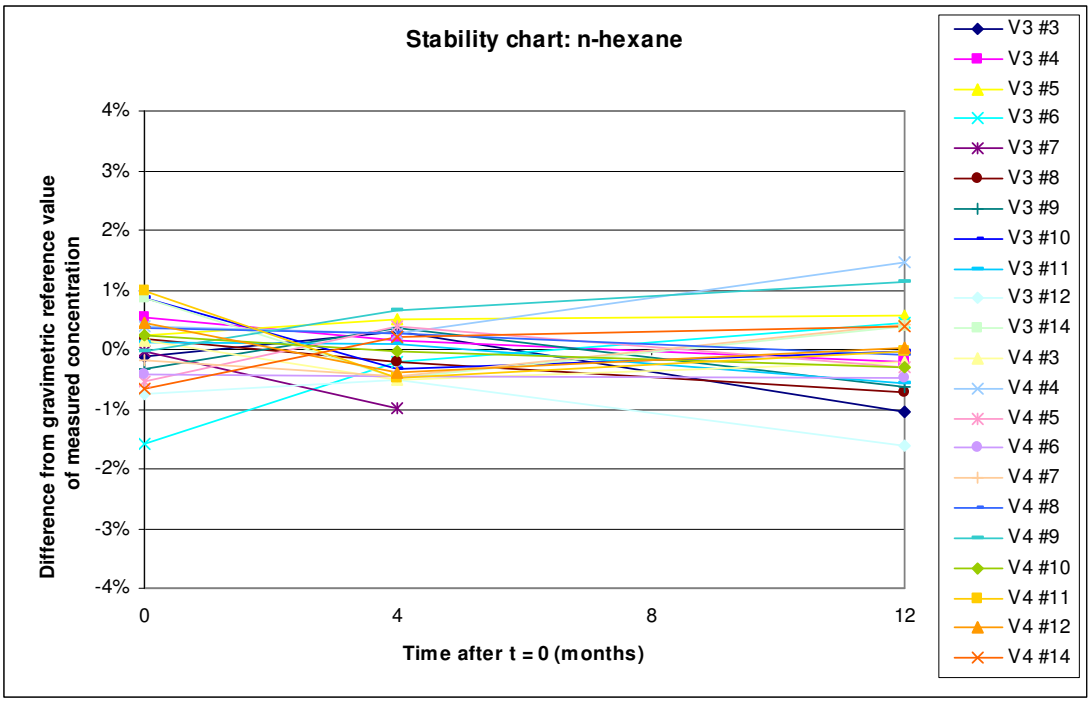

Stability chart: n-pentane
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

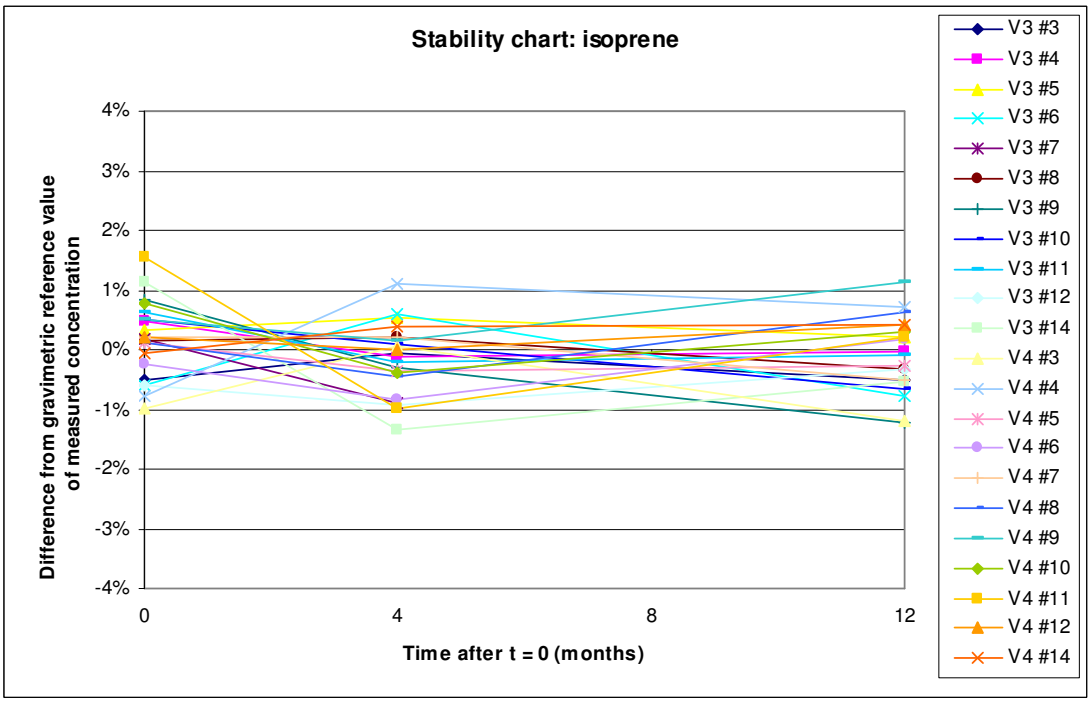

Stability chart: 1,3-butadiene
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

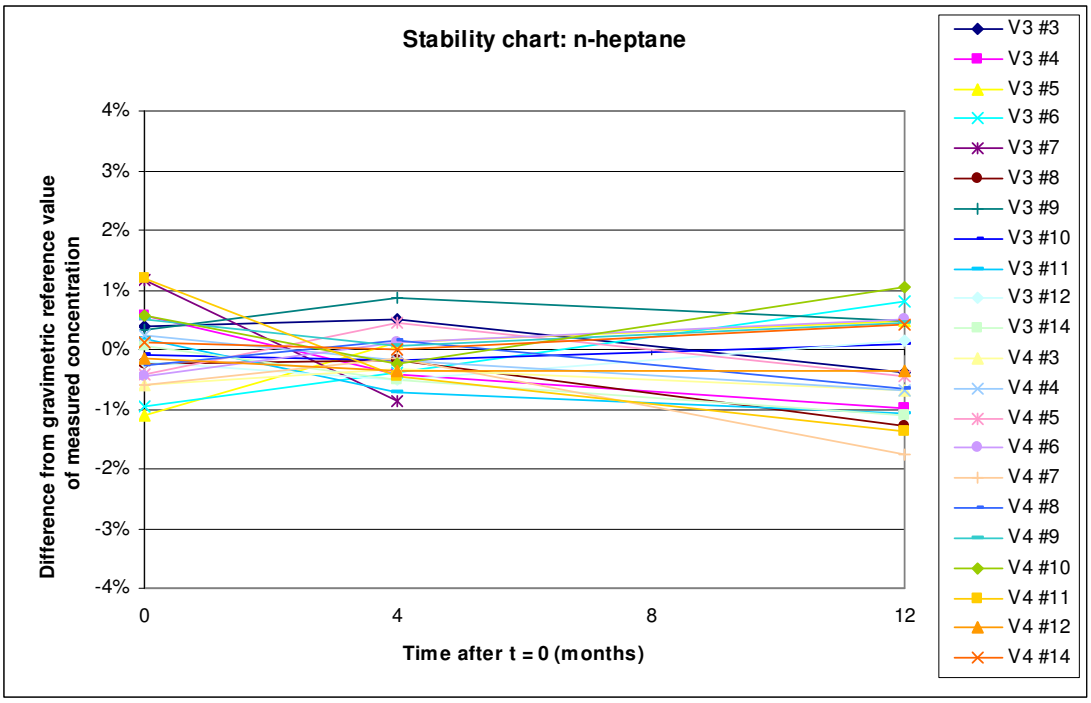

Stability chart: trans-2-pentene
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

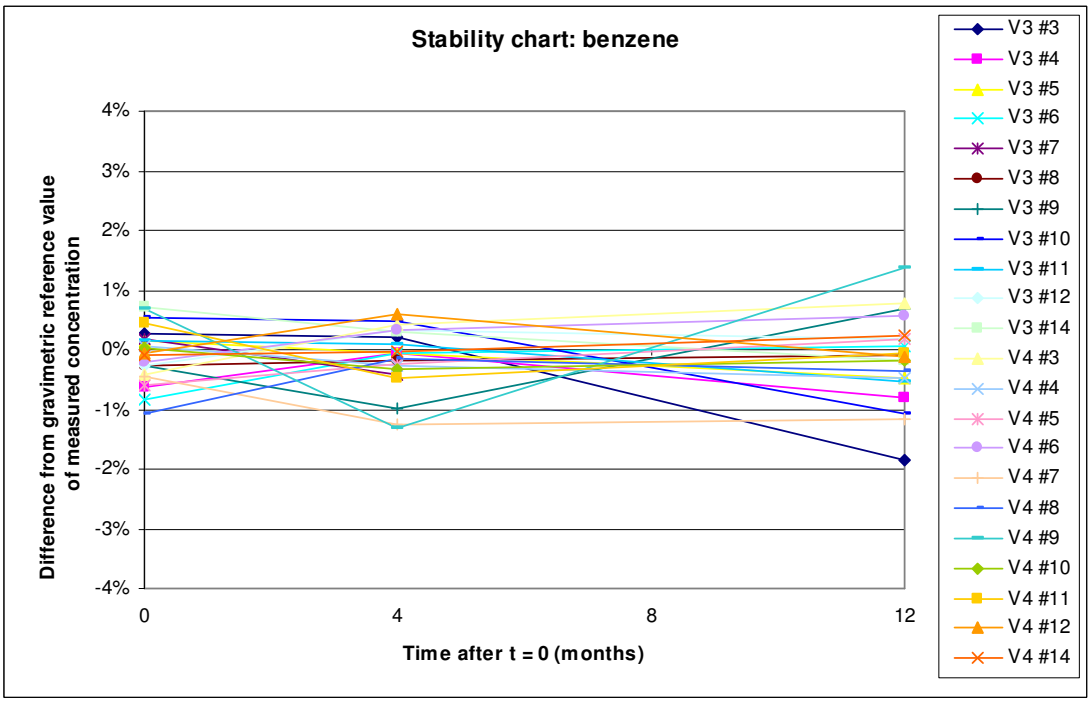

Stability chart: 1-pentene
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

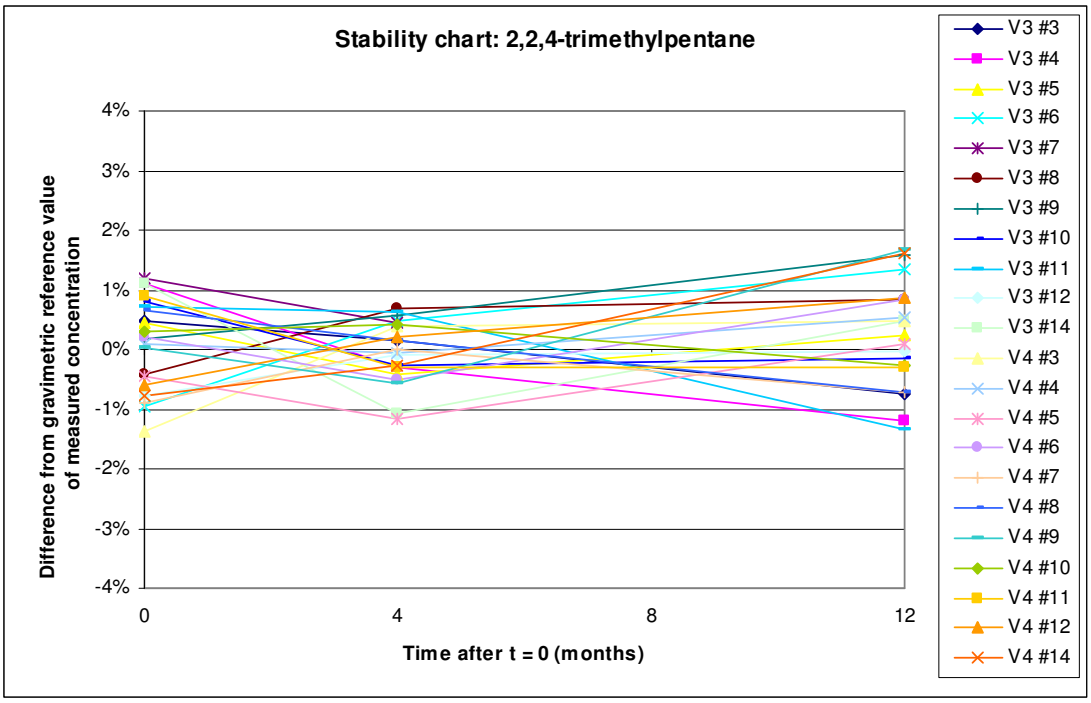

Stability chart: 2-methylpentane
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

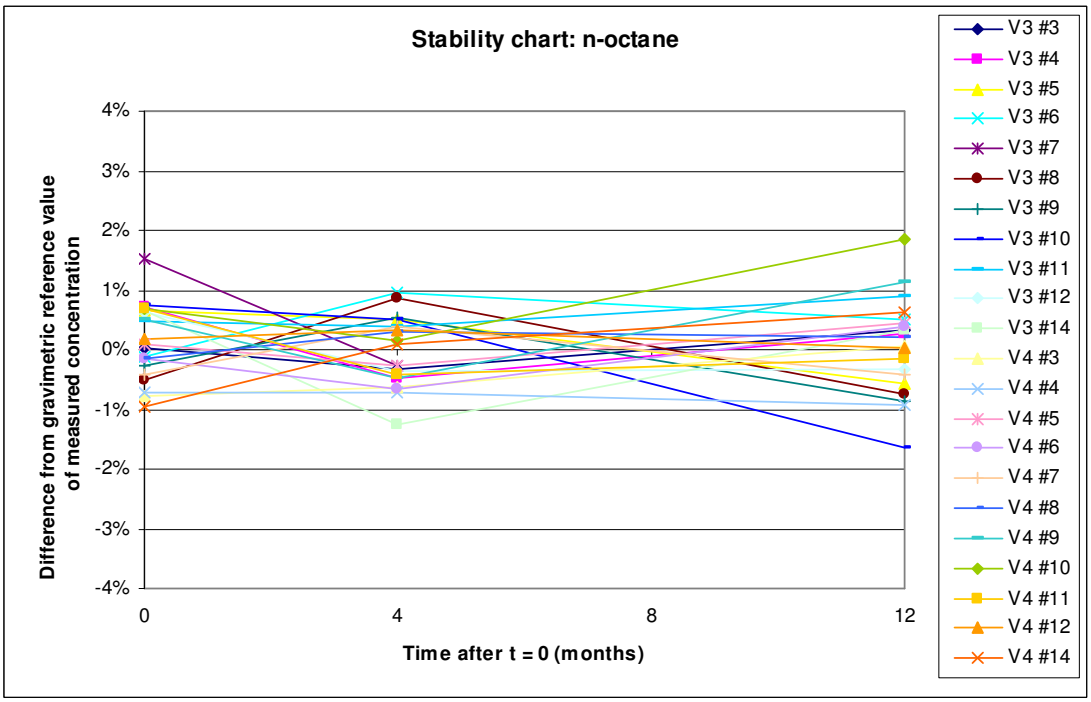

Stability chart: n-hexane
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

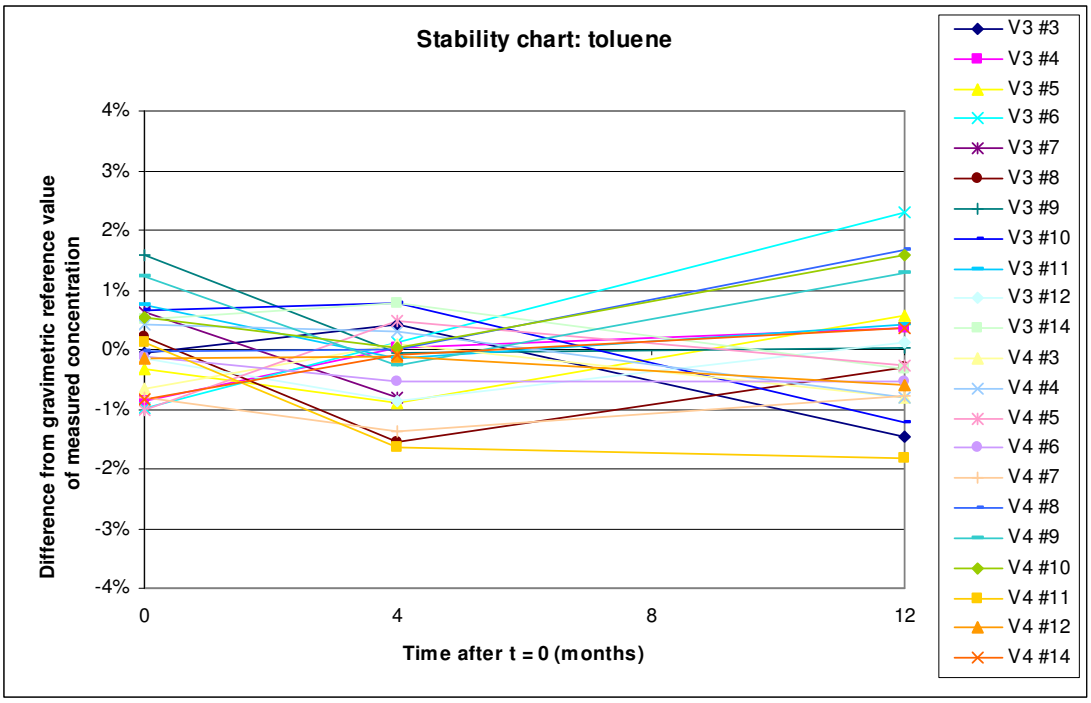

Stability chart: isoprene
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

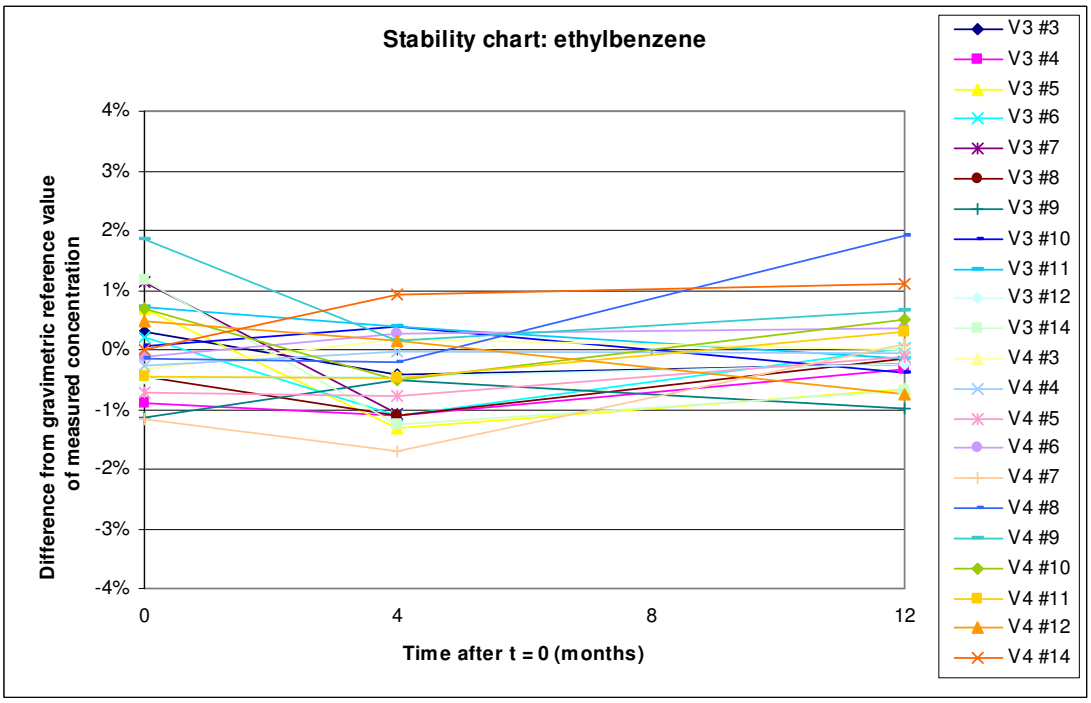

Stability chart: n-heptane
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

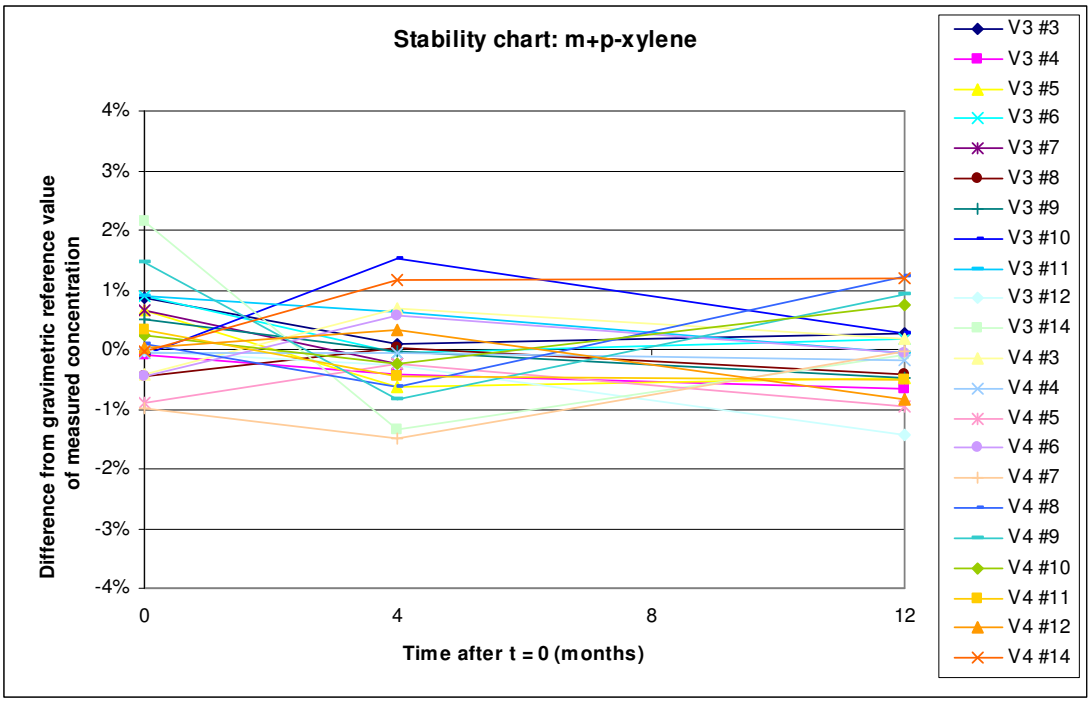

Stability chart: benzene
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

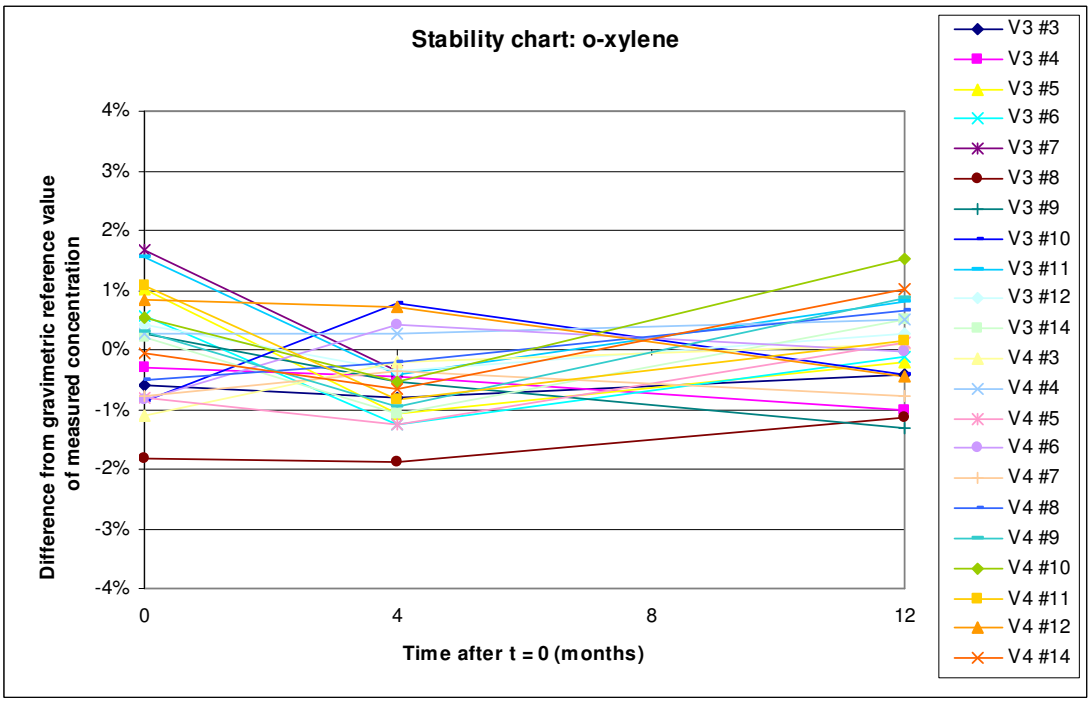

Stability chart: 2,2,4-trimethylpentane
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

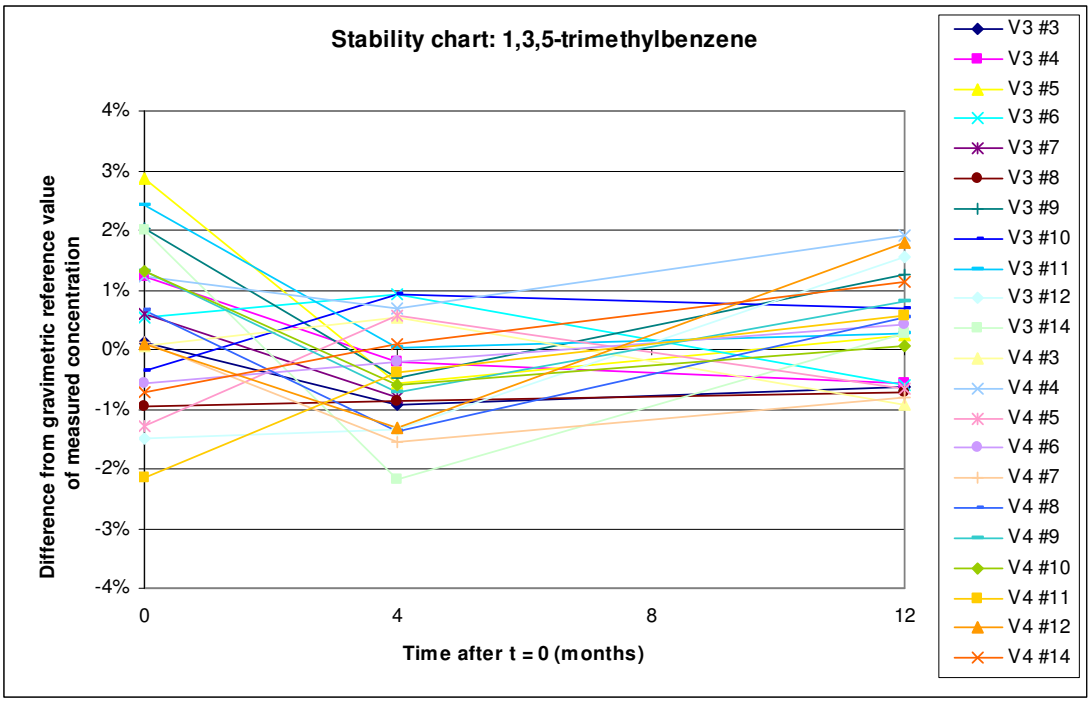

Stability chart: n-octane
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

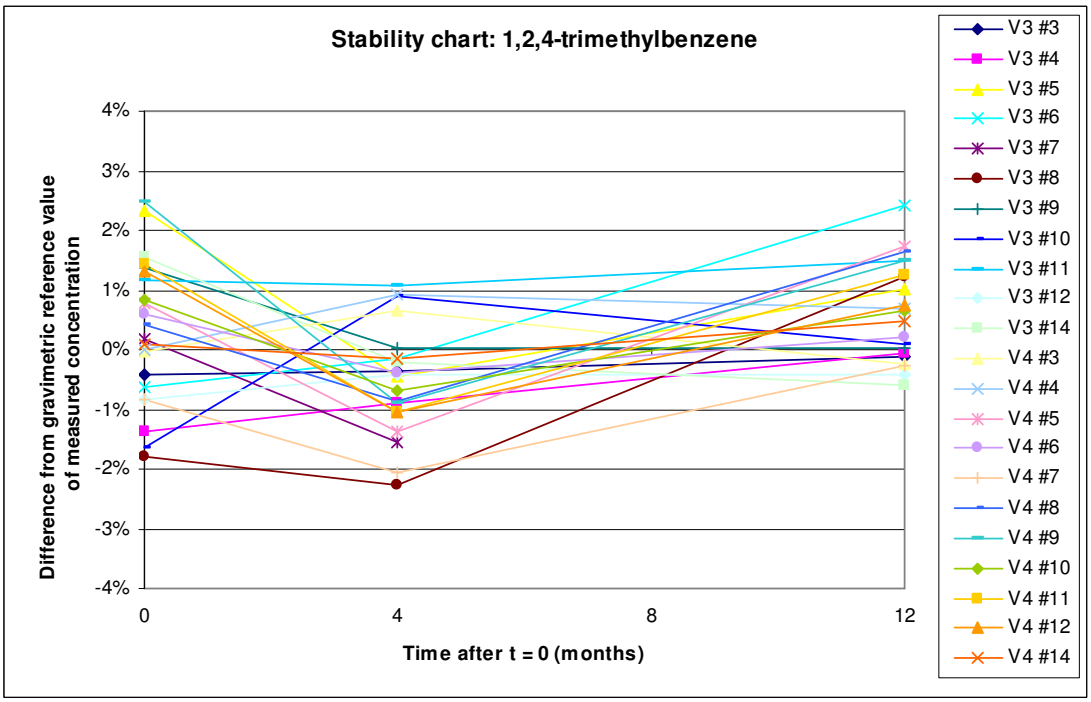

Stability chart: toluene
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

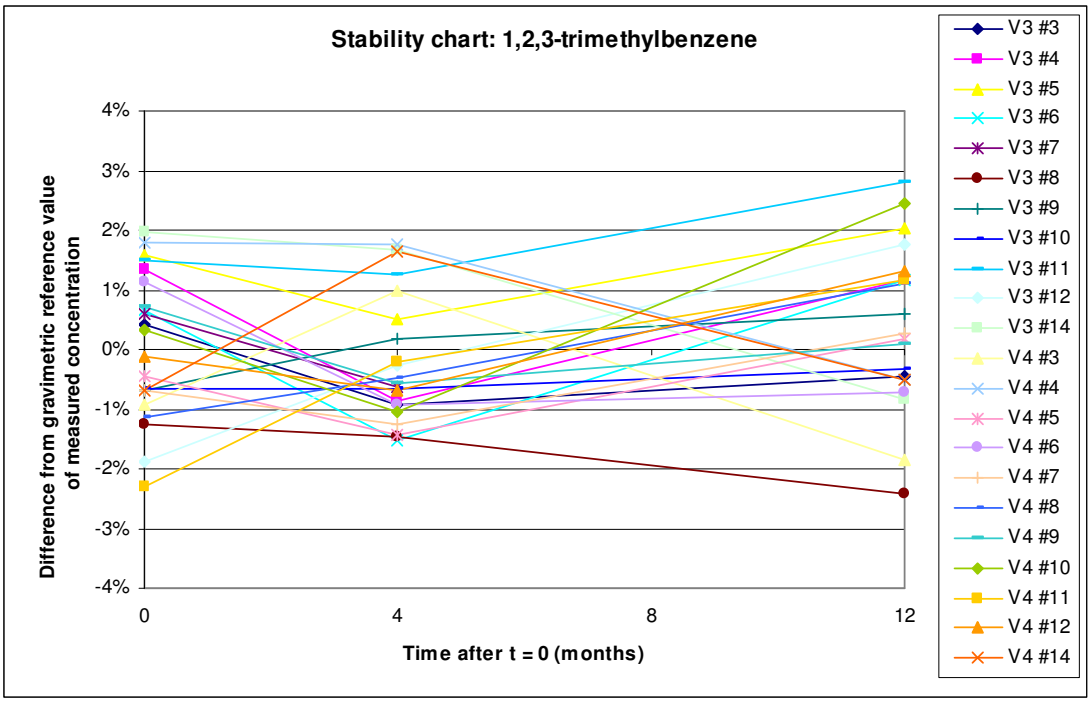

Stability chart: ethylbenzene
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14


Stability chart: m+p-xylene
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14


Stability chart: o-xylene
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14


Stability chart: 1,3,5-trimethylbenzene
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14


Stability chart: 1,2,4-trimethylbenzene
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14


Stability chart: 1,2,3-trimethylbenzene
Difference from gravimetric reference value of measured concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t = 0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

Annex F: Participant reports

Laboratory : European Reference Laboratory for Air Pollution ERLAP
Joint Research Centre. European Commission
Cylinder number : D95 4790 Gravimetric mixture

NOMINAL COMPOSITION
- 30 species of hydrocarbon : 1 to 10.10^{-9} mol/mol
- nitrogen : balance

Date cylinder received: 21/05/2007

Cylinder pressure on arrival: 80 bars

Dates of measurements: from 25/06/2007 to 30/06/2007

Measurement method used: Gas Chromatography + FID
Turbomatrix Perkin Elmer on-line sampling +GC 6890 Agilent with Dean Switch double column (BP1 and Alumina)

Instrument calibration:

By primary reference gas mixture 30 hydrocarbons species (ozone precursors in N2), certified by NPL 14/09/2006, cylinder n D95 4835. Approx. concentration 4 ppb (m/m) for each species. The calibration line was obtained by changing the sampling volume.

Sample handling:

Cylinders were kept in the laboratory for at least 2 weeks before the analysis was carried out to reach stable conditions. Cylinders were connected to the instrument for sampling through a 1/8" Teflon tube of about 1 m length. A pressure reducer with a needle valve was used to regulate the inlet flow pressure to about 2 bars. A sampling flow was automatically regulated by the mass flow of the instrument, which was operating at a fixed flow of about 25 ml/min.

Components used in the uncertainty calculation:
Uncertainty of the reference material,
Uncertainty of the sampling procedure (sampling volume, adsorption in the pipe),
Uncertainty of the calibration procedure (ISO 6143), multi-point calibration
Reproducibility uncertainty based on 5 analyses during 5 different days with 5 different calibrations.
Approximate volume of cylinder gas used during analysis:
The sampling time was fixed to guarantee a total sampling volume of 400 ml per analysis.

Cylinder pressure at dispatch back to NPL: 45 bars
Date of dispatch back to NPL: 6/07/2007

Laboratory : European Reference Laboratory for Air Pollution. ERLAP
Cylinder number : D95 4790

Results:

Analyte	Result (mol/mol)	Measurement uncertainty (95% confidence) (mol/mol)	
ethane	5.95	5.54	6.37
ethylene (ethene)	6.06	5.52	6.60
Propane	5.86	5.58	6.14
Propene	5.11	4.87	5.34
i-butane (2-methylpropane)	7.99	7.42	8.55
Butane	7.74	7.22	8.26
acetylene (ethyne)	6.39	5.77	7.02
trans-2-butene	7.74	7.19	8.28
1-butene	7.63	7.07	8.20
cis-2-butene	7.62	7.14	8.09
i-pentane (2-methylbutane)	5.31	5.00	5.61
Pentane	5.38	5.04	5.72
1,3-butadiene	5.81	5.45	6.17
trans-2-pentene	5.14	4.86	5.42
1-pentene	5.23	4.93	5.52
i-hexane (2-methylpentane)	5.33	5.03	5.62
Hexane	5.31	5.09	5.53
isoprene (2-methyl-1,3-butadiene)	5.35	4.96	5.74
Heptane	5.23	5.02	5.43
Benzene	3.75	3.56	3.93
2,2,4-trimethylpentane (i-octane)	5.34	5.12	5.56
Octane	5.26	5.07	5.46
Toluene	3.28	3.09	3.48
Ethylbenzene	4.23	4.03	4.43
m+p-xylene	8.49	7.93	9.04
o-xylene	4.13	3.56	4.70
1,3,5-trimethylbenzene	4.17	3.75	4.58
1,2,4-trimethylbenzene	4.51	3.79	5.23
1,2,3-trimethylbenzene	4.08	3.62	4.55

ERLAP (JRC) reported an error in their reported uncertainties to NPL on 05/10/2008 after they had received gravimetric data as AQUILLA coordinating laboratory (see Annex B for comparison timeline). The error was reported as follows “In the original submission there was an error in the excel sheet for the final uncertainty combination of the individual analysis, which they were not divided by 5 and the standard deviation of 5 analysis was missing”. The results sheet was re-submitted as follows with the revised uncertainties.

Laboratory : European Reference Laboratory for Air Pollution. ERLAP
Cylinder number : D95 4790 Gravimetric mixture

Results*:

Analyte	Result (mol/mol)	Measurement uncertainty (95% confidence) (mol/mol)	
ethane	5.95	5.72	6.18
ethylene (ethene)	6.06	5.76	6.36
Propane	5.86	5.72	6.01
Propene	5.11	4.99	5.23
i-butane (2-methylpropane)	7.97	7.71	8.22
Butane	7.74	7.49	8.00
acetylene (ethyne)	6.39	6.09	6.70
trans-2-butene	7.74	7.47	8.00
1-butene	7.63	7.33	7.93
cis-2-butene	7.62	7.39	7.84
i-pentane (2-methylbutane)	5.31	5.15	5.46
Pentane	5.38	5.23	5.54
1,3-butadiene	5.81	5.61	6.01
trans-2-pentene	5.14	5.02	5.28
1-pentene	5.23	5.07	5.40
i-hexane (2-methylpentane)	5.33	5.19	5.48
Hexane	5.31	5.21	5.41
isoprene (2-methyl-1,3-butadiene)	5.35	5.16	5.54
Heptane	5.23	5.09	5.36
Benzene	3.75	3.65	3.85
2,2,4-trimethylpentane (i-octane)	5.34	5.23	5.45
Octane	5.26	5.15	5.38
Toluene	3.28	3.17	3.40
Ethylbenzene	4.23	4.08	4.37
m+p-xylene	8.49	8.12	8.85
o-xylene	4.13	3.76	4.49
1,3,5-trimethylbenzene	4.17	3.89	4.44
1,2,4-trimethylbenzene	4.51	3.92	5.10
1,2,3-trimethylbenzene	4.07	3.76	4.38

The cylinder for ERLAP had a pressure of 44 Bar when returned to NPL. The effect of 50% loss of contents from one of these 30 component VOC mixtures, in a short timeframe (< 2 months), has not been investigated.

* Revised uncertainties

Laboratory : Finnish Meteorological Institute
Cylinder number : D838781

NOMINAL COMPOSITION
- 30 species of hydrocarbon : 1 to 10.10^{-9} mol/mol
- nitrogen : balance

Date cylinder received: 20.6 2007

Cylinder pressure on arrival:
85 bar

Dates of measurements:
27.6 2007 and 4.7 2007

Measurement method used:
C2-C5 compounds are collected into stainless steel canisters and analyzed with GC/FID. and an Al_2O_3/KCl PLOT column (50 m, i.d. 0.32 mm). Prior to analysis, samples are passed through a stainless steel tube (10cm* 1/4'') filled with K_2CO_3 and NaOH in order to dry them. Air samples are concentrated in two liquid nitrogen traps. The first trap is a stainless steel loop (1/8''*125cm) filled with glass beads, while the other one is a capillary trap.

Aromatic hydrocarbons are analyzed from adsorbent tubes (Tenax-TA- Carbopack-B) using Perkin-Elmer thermodesorption system (Perkin-Elmer Turbo Matrix 650) together with HP GC/MS.

Instrument calibration:
Light hydrocarbons were calibrated using NPL standard (cylinder no: APE 409196) received in November 2005.

Aromatic hydrocarbons were calibrated using liquid standards prepared from pure standards diluted to methanol (5 point calibration, concentrations from 0.2 to 40 ng/tube). Methanol was flushed of prior to the analysis with pure N2.

Sample handling:
Light hydrocarbons were taken into 0.85 l stainless steel canisters and analyzed from there. Aromatic hydrocarbons were collected onto Tenax-TA-Carbopack-B tubes using a pump with about 100 ml/min flow rate.

Components used in the uncertainty calculation:
The uncertainty of the canister analysis was evaluated by sampling two canisters each time for a year, analyzing both of them and calculating the standard deviation of the two analyses.

The uncertainty of the aromatic hydrocarbons has been evaluated using partial uncertainties of following partial uncertainties: sampling and analysis (from RSD of triplicate samples), standard preparation, injection of standards, blank levels, desorption efficiency, sampling flow.

Approximate volume of cylinder gas used during analysis:
5 liters

Cylinder pressure at dispatch back to NPL:
86 bars

Date of dispatch back to NPL:
5.7 2007

Laboratory : Finnish Meteorological Institute
Cylinder number : D838781

Results:

Analyte	Result (mol/mol)	Measurement uncertainty (95% confidence) (mol/mol)
ethane	5.66	0.23
ethylene (ethene)	5.73	0.75
propane	5.61	0.28
propene	5.60	1.01
i-butane (2-methylpropane)	7.53	0.90
butane	6.65	0.93
acetylene (ethyne)	6.54	1.18
trans-2-butene	7.27	1.38
1-butene	7.72	2.16
cis-2-butene	7.29	1.38
i-pentane (2-methylbutane)	5.21	0.78
pentane	5.25	0.63
1,3-butadiene	5.88	1.12
trans-2-pentene	4.89	0.93
1-pentene		
i-hexane (2-methylpentane)	4.45	1.16
hexane	4.90	1.13
isoprene (2-methyl-1,3-butadiene)	5.46	1.75
heptane	3.64	1.02
benzene	5.05	1.01
2,2,4-trimethylpentane (i-octane)		
octane		
toluene	3.76	0.75
ethylbenzene	4.17	0.58
m+p-xylene	8.38	2.21
o-xylene	4.29	1.12
1,3,5-trimethylbenzene	4.17	0.83
1,2,4-trimethylbenzene	4.37	0.79
1,2,3-trimethylbenzene	4.19	0.75

Laboratory : Istituto Nazionale di Ricerca Metrologica*
Cylinder number : D83 8781

Introduction
The standard provided by NPL (D838781) contained a mixture of 30 volatile organic compounds within a nominal range between 1 nmol/mol and 10 nmol/mol :
ethane, ethene, ethyne, propane, propene, n-butane, i-butane, 1-butene, trans-2-butene, cis-2-butene, 1,3-butadiene, n-pentane, i-pentane, 1-pentene, 2-pentene, isoprene, n-hexane, i-hexane, n-heptane, n-octane, i-octane, benzene, toluene, ethyl benzene, m-xylene, p-xylene, o-xylene, 1,2,4-trimethyl benzene, 1,2,3- trimethyl benzene, 1,3,5- trimethyl benzene.
This report describes the analysis of this unknown by gas chromatography against a NPL gas standard containing the same compounds at a nominal value of 4 nmol/mol.

Reference method
A VARIAN- CP3800 Gas Chromatograph equipped with a flame ionization detector (FID) and a 30 m x 0,32 mm plot fused silica capillary column (coated plot silica) was used to determine the following compounds: ethane, ethane, ethyne, propane and propene.
A second fused silica capillary column 60 m x 0,25 mm and a second FID detector was used to determine the following compounds: n-butane, i-butane, 1-butene, trans-2-butene, cis-2-butene, 1,3-butadiene, n-pentane, i-pentane, 1-pentene, 2-pentene, isoprene, n-hexane, i-hexane, n-heptane, n-octane, i-octane, benzene, toluene, ethyl benzene, m-xylene, p-xylene, o-xylene, 1,2,4-trimethyl benzene, 1,2,3- trimethyl benzene, 1,3,5- trimethyl benzene.
With this equipment was not possible to determine: 1,2,4-trimethyl benzene, 1,2,3-trimethyl benzene, 1,3,5- trimethyl benzene.
A cryogenic pre-concentrator was used to collect 400 ml samples and inject them onto the capillary columns. A Shott low-volume regulator set at a pressure of 2,5 bar was used for the sampling. A same injection line was used to inject the gas from the standard and from the unknown. The use in the system of a mass-flow controller prevent from measurement fluctuation due to ambient pressure instability.

Setup parameters:
- Detector temperature: 250 °C
- Injection temperature: 60 °C
- Pre-concentration trap temperature at -120 °C and desorption at 200 °C
- Temperature program of the columns: -30 °C, hold 8,55 min, temp. rate 40 °C/min to 20 °C and 5 °C/min to 120 °C, 20 °C/min to 220 °C, hold 16 min, 43 °C/min to -30
- Carrier gas: Helium high purity

Software
VARIAN GALAXIE.

Calibration standards
Two NPL gas standards containing the 30 compounds at a nominal value of 4 nmol/mol and expanded uncertainty of 0,08 nmol/mol (2% relative).

* INRiM submitted results after the deadline and after an interim report was distributed by the JRC with participant lab and co-ordinating lab data.

Instrument calibration
The calibration of the instrument was made at the nominal value 4 nmol/mol for each compound with two different standards.
It was assumed that the FID detectors were linear in the interval 1 nmol/mol – 10 nmol/mol and no correction for non-linearity was made.

Sample handling
The cylinders were kept many days in the laboratory where the analysis was done at a temperature 20 ± 2 °C.

Analytical procedure
16 cleaning cycles of the GC system was done with high pure Nitrogen and analyzed in order to monitor the line stability and the presence of contaminants.
The analysis was performed for 4 consecutive days with the following sequence:

- 1 blank run (carrier gas)
- 5 NPL standard run
- 1 blank run
- 5 unknown run
- 1 blank run
- 1 cleaning run (nitrogen)

That correspond to 4 measurements obtained by 5 sub-measurements.

Uncertainty estimate
The uncertainty of each measurement was estimated combining the standard deviation of the 5 sub-measurements (repeatability of the sample) with the uncertainty of the reference values and with the calibration uncertainty (evaluated from the measurement of the two certified gas standards and obtained from the combination of the standard deviation of the measured values with the uncertainty of the two reference values).
The uncertainty of the final results was estimated combining the mean of the 4 measurement uncertainties with the standard deviation of the mean values (reproducibility of the measurements).

Results
The results obtained for ethylbenzene, m-xylene, p-xylene and o-xylene show uncertainties too high for the practical applications (10% to 18% relative uncertainty). The measurement system was not than considered appropriate for the determination of this compounds, that will not be reported in the result tables.

Laboratory : Istituto Nazionale di Ricerca Metrologica
Cylinder number : D83 8781

Final results

Species	Mole fraction (nmol/mol)	Coverage factor	Expanded uncertainty (nmol/mol)	Expanded uncertainty (% relative)
ethane	5,95	2	0,24	4,1%
ethene	5,84	2	0,25	4,2%
ethyne	5,88	2	0,25	4,3%
propane	5,85	2	0,32	5,5%
propene	5,76	2	0,26	4,6%
i-butane	7,96	2	0,30	3,7%
1-butene	7,63	2	0,33	4,3%
1,3-butadiene	5,76	2	0,23	4,0%
butane	7,72	2	0,29	3,7%
trans-2-butene	7,73	2	0,29	3,7%
cis-2-butene	7,63	2	0,29	3,8%
i-pentane	5,28	2	0,20	3,7%
1-pentene	5,18	2	0,21	4,1%
pentane	5,37	2	0,20	3,7%
isoprene	5,28	2	0,20	3,8%
trans-2-pentene	5,10	2	0,20	4,0%
2-methylpentane	5,29	2	0,20	3,8%
hexane	5,28	2	0,21	4,1%
benzene	3,76	2	0,14	3,7%
2,2,4-trimethylpentane	5,31	2	0,20	3,8%
heptane	5,21	2	0,19	3,7%
toluene	3,23	2	0,15	4,5%
octane	5,27	2	0,25	4,7%

Laboratory : Instituto de Salud Carlos III
Cylinder number : D 954945

NOMINAL COMPOSITION
- 30 species of hydrocarbon : 1 to 10.10^{-9} mol/mol
- nitrogen : balance

Date cylinder received: 21.06.2007

Cylinder pressure on arrival: 100 bar

Dates of measurements: 26.07.2007; 30.07.2007; 02.08.2007

Measurement method used: The analysis was realized by thermal desorption using a Perkin Elmer ATD desorption unit. First the compounds were freezed cryogenically on a liner maintained at – 30 ºC and then transferred to the GC column by heating the liner to 200 ºC. The separation was accomplished on a 50 m capillary column (0,534 mm I.D). The column was maintained at 65 ºC for 2 min and then at 200 ºC at 5 ºC/min. A Finnigan Trace GC ultra gas chromatograph with a flame ionization detector was used for the analysis. The detector temperature was maintained at 280 ºC

Instrument calibration: Two calibration lines with five points between 0 nmol/mol and 50 nmol/mol. Reference material was Praxair (no ISO 17025 accredited) with concentrations of measurand about 50 nmol/mol, except isoprene, acetylene and 1,3 butadiene with about 10 nmol/mol. The expanded uncertainties were 6 %.

Sample handling: The gas in cylinder by means of one pressure reductor passed to thermal desorption unit and gas chromatograph.

Components used in the uncertainty calculation:
Uncertainty of reference material
Uncertainty of repeatibility

Approximate volume of cylinder gas used during analysis: 0,100 l

Cylinder pressure at dispatch back to NPL: ~ 90 bar

Date of dispatch back to NPL: 14.08.2007

Laboratory : Instituto de Salud Carlos III (Spain)
Cylinder number : D95 4945

Results:

Analyte	Result (mol/mol)	Measurement uncertainty (95% confidence) (mol/mol)
ethane	$2{,}42 \cdot 10^{-9}$	$0{,}18 \cdot 10^{-9}$
ethylene (ethene)	$2{,}80 \cdot 10^{-9}$	$0{,}20 \cdot 10^{-9}$
propane	$2{,}41 \cdot 10^{-9}$	$0{,}16 \cdot 10^{-9}$
propene	$2{,}53 \cdot 10^{-9}$	$0{,}18 \cdot 10^{-9}$
i-butane (2-methylpropane)	$2{,}79 \cdot 10^{-9}$	$0{,}20 \cdot 10^{-9}$
butane	$2{,}70 \cdot 10^{-9}$	$0{,}19 \cdot 10^{-9}$
acetylene (ethyne)	$6{,}02 \cdot 10^{-9}$	$0{,}82 \cdot 10^{-9}$
trans-2-butene	$2{,}69 \cdot 10^{-9}$	$0{,}17 \cdot 10^{-9}$
1-butene	$2{,}69 \cdot 10^{-9}$	$0{,}18 \cdot 10^{-9}$
cis-2-butene	$1{,}70 \cdot 10^{-9}$	$0{,}20 \cdot 10^{-9}$
i-pentane (2-methylbutane)	$2{,}56 \cdot 10^{-9}$	$0{,}18 \cdot 10^{-9}$
pentane	$1{,}86 \cdot 10^{-9}$	$0{,}13 \cdot 10^{-9}$
1,3-butadiene	$7{,}04 \cdot 10^{-9}$	$0{,}50 \cdot 10^{-9}$
trans-2-pentene	$2{,}08 \cdot 10^{-9}$	$0{,}16 \cdot 10^{-9}$
1-pentene	$2{,}08 \cdot 10^{-9}$	$0{,}13 \cdot 10^{-9}$
i-hexane (2-methylpentane)		
hexane	$1{,}75 \cdot 10^{-9}$	$0{,}20 \cdot 10^{-9}$
isoprene (2-methyl-1,3-butadiene)	$4{,}19 \cdot 10^{-9}$	$0{,}36 \cdot 10^{-9}$
heptane	-	-
benzene	-	-
2,2,4-trimethylpentane (i-octane)	-	-
octane	-	-
toluene	-	-
ethylbenzene	-	-
m+p-xylene	-	-
o-xylene	-	-
1,3,5-trimethylbenzene	-	-
1,2,4-trimethylbenzene	-	-
1,2,3-trimethylbenzene	-	-

Laboratory : KRISS (Report written by Gwi Suk Heo)
Cylinder number : D954825

NOMINAL COMPOSITION
- 30 species of hydrocarbon : 1 to 10.10^{-9} mol/mol
- nitrogen : balance

Date cylinder received: June 1, 2007

Cylinder pressure on arrival: 1500 psig

Dates of measurements: from August 18 to August 25 of 2007

Measurement method used: Cryoconcentration-GC-FID methods were used.
Sample was concentrated at glass bead (or Tenax) trap at -175 oC (or -150 oC), after that refocused at -180 oC before transferring to GC column (DB-1, 60 m x 0.32 mm x 1 um, column flow 2 mL/min). 200 mL of sample gas was used for each analysis. GC oven temp was set as; minus 50 oC → 7 oC/min → 160 oC → 20 oC/min → 220 oC. Entech 7100 concentrator was used with Agilent 6890 GC. FID temp 250 oC. Euromat 886 cylinder and KRISS CRM were analyzed five times (this counted by one set). Three or four set of measurement were repeated.

Instrument calibration: KRISS CRM was used for calibration. KRISS CRM was prepared by gravimerty. Two CRMs (D518923, C2382) were used for calibration.

KRISS CRM Analyte	Certified value (nmol/mol)	Uuncertainty (95% confidence) (nmol/mol)	KRISS CRM used for calibration
ethane	5.21	0.10	D518923
ethylene (ethene)	5.12	0.08	D518923
propane	5.12	0.12	D518923
propene	5.24	0.09	D518923
i-butane (2-methylpropane)	5.30	0.09	D518923
butane	5.44	0.10	D518923
acetylene (ethyne)	5.16	0.08	D518923
trans-2-butene	5.06	0.09	D518923
1-butene	5.17	0.09	D518923
cis-2-butene	5.43	0.09	D518923
i-pentane (2-methylbutane)	5.47	0.13	D518923
pentane	5.60	0.13	D518923
1,3-butadiene	5.23	0.09	D518923
trans-2-pentene	5.52	0.12	D518923
1-pentene	5.50	0.16	D518923
i-hexane (2-methylpentane)	5.15	0.12	D518923
hexane	5.19	0.11	D518923
isoprene (2-methyl-1,3-butadiene)	5.51	0.13	D518923
heptane	5.12	0.14	C2382

benzene	5.16	0.14	D518923
2,2,4-trimethylpentane (i-octane)	5.22	0.13	D518923
octane	5.24	0.16	C2382
toluene	5.04	0.13	C2382
ethylbenzene	5.02	0.15	C2382
m+p-xylene	5.04	0.16	C2382
o-xylene	5.10	0.16	C2382
1,3,5-trimethylbenzene	5.02	0.20	C2382
1,2,4-trimethylbenzene	4.97	0.21	C2382
1,2,3-trimethylbenzene	5.00	0.21	C2382

Sample handling: Sample was kept in room temp (at 25 oC) before use. Gas pressure regulator was attached to Euromet cylinder. 10 psig outlet pressure released to concentration system for analysis.

Components used in the uncertainty calculation: for details, confer attachment at end of result's report.

Major uncertainty factors related to intercomparsion analysis and CRM prepapration (example: benzene)

Quantity	Value	Standard uncertainty	Degrees of freedom	Sensitivity coefficient	Uncertainty contribution	Corr.-coeff.	Index
Ratio	0.82455	$4.71 \cdot 10^{-3}$	3	5.16	0.0243 ppb	0.37	0.139
f_{press}	1.00000	$2.50 \cdot 10^{-3}$	50	4.25	0.0106 ppb	0.16	0.027
f_{ads}	1.00000	$5.00 \cdot 10^{-3}$	50	4.25	0.0213 ppb	0.33	0.107
f_{homo}	1.00000	$9.50 \cdot 10^{-3}$	50	4.25	0.0404 ppb	0.62	0.385
x_{22ppm}	1.02500 ppm	$9.17 \cdot 10^{-3}$ ppm	156	4.15	0.0380 ppb	0.58	0.342
C_{22}	4.2514 ppb	0.0651 ppb	95				

Quantity	Unit	Definition
C_{22}	ppb	conc of benzene from analysis
Ratio		GC peak area ratio (Asample/Astandard) - Each reading value is average of 3 analysis
fpress		factor for pressure difference in sample introduction
fads		factor for adsorption loss of gas compositon in 5 ppb std cylinder
fhomo		uncertainty related to homogeneity in 5 ppb std gas
x22ppm	ppm	concentration of benzene in 1 ppm std gas (MD2607)

Approximate volume of cylinder gas used during analysis: About 200 L(300 psi pressure decrease) of gas sample was used for intercomparison analysis.
Cylinder pressure at dispatch back to NPL: 1200 psig(82 bar)

Date of dispatch back to NPL: August 28, 2007

Laboratory : KRISS
Cylinder number : D954825

Results:

Analyte	Result (nmol/mol)	Measurement uncertainty (95% confidence) (mol/mol)
ethane	6.64	0.13
ethylene (ethene)	6.65	0.12
propane	6.58	0.16
propene	6.57	0.12
i-butane (2-methylpropane)	7.14	0.20
butane	7.01	0.17
acetylene (ethyne)	6.69	0.12
trans-2-butene	6.33	0.13
1-butene	6.87	0.15
cis-2-butene	7.44	0.14
i-pentane (2-methylbutane)	5.18	0.13
pentane	5.26	0.13
1,3-butadiene	6.67	0.14
trans-2-pentene	5.05	0.12
1-pentene	5.12	0.16
i-hexane (2-methylpentane)	5.30	0.15
hexane	5.17	0.14
isoprene (2-methyl-1,3-butadiene)	5.32	0.14
heptane	5.04	0.15
benzene	4.25	0.13
2,2,4-trimethylpentane (i-octane)	5.24	0.14
octane	5.02	0.15
toluene	3.60	0.10
ethylbenzene	3.69	0.12
m+p-xylene	7.26	0.23
o-xylene	3.63	0.12
1,3,5-trimethylbenzene	3.55	0.15
1,2,4-trimethylbenzene	3.61	0.15
1,2,3-trimethylbenzene	3.57	0.16

Laboratory : NIST (USA)
Cylinder number : D83 8896

NOMINAL COMPOSITION
- 30 species of hydrocarbon : 1 to 10.10^{-9} mol/mol
- nitrogen : balance

Date cylinder received: June 2007

Cylinder pressure on arrival: 105 bar

Dates of measurements: July 16 into July 18, 2007 continuous; July 18 into July 20, 2007 continuous; July 23 into July 25, 2007 continuous; August 6 into August 9, 2007 continuous; August 9 into August 11, 2007 continuous; August 13 into August 14, 2007 continuous; August 16, 200;

Measurement method used:

Gas Chromatography with flame ionization detection coupled with an Entech 7100 preconcentrator; 30 m x 0.32 cm capillary column GASPRO temperature programmed and a 25 m x 0.32 cm capillary PLOT (Al_2O_3/KCl) temperature programmed;

Instrument calibration:

11 Primary Mixture Standards (PSMs); 1 to 8 PSMs used for each compound;

Sample handling:

Cryogenic preconcentration; 500 mL of sample or PSM with cryogenic trapping on the head of the column before injection;

Components used in the uncertainty calculation:

1-uncertainty in the PSMs; 2-standard devitaion in the RATIOs of the PSMs to EUROMET sample D83 8896; 3- uncertainty in calibration

Approximate volume of cylinder gas used during analysis: 10 bar

Cylinder pressure at dispatch back to NPL: 95 bar

Date of dispatch back to NPL: August 16,2007

Laboratory : NIST (USA)
Cylinder number : D83 8896

Results:

Analyte	Result (nmol/mol) (ppb)	Measurement uncertainty (95% confidence) (nmol/mol) (ppb)
ethane	5.82	± 0.11
ethylene (ethene)	5.76	± 0.09
propane	5.80	± 0.07
propene	5.76	± 0.07
i-butane (2-methylpropane)	7.94	± 0.15
butane	7.80	± 0.17
acetylene (ethyne)	5.47	± 0.11
trans-2-butene	7.20	± 0.15
1-butene	7.76	± 0.15
cis-2-butene	7.32	± 0.15
i-pentane (2-methylbutane)	5.26	± 0.06
pentane	5.34	± 0.07
1,3-butadiene	5.63	± 0.15
trans-2-pentene	5.33	± 0.14
1-pentene	5.25	± 0.14
i-hexane (2-methylpentane)	5.19	± 0.14
hexane	5.29	± 0.14
isoprene (2-methyl-1,3-butadiene)	5.81	± 0.15
heptane	5.26	± 0.10
benzene	3.81	± 0.14
2,2,4-trimethylpentane (i-octane)	5.36	± 0.11
octane	5.38	± 0.09
toluene	3.23	± 0.16
ethylbenzene	4.76	± 0.19
m+p-xylene	9.07	± 0.32
o-xylene	4.54	± 0.18
1,3,5-trimethylbenzene	5.00	± 0.40
1,2,4-trimethylbenzene	5.39	± 0.40
1,2,3-trimethylbenzene	5.04	± 0.40

Laboratory : NMi VSL
Cylinder number : D954815

NOMINAL COMPOSITION
- 30 species of hydrocarbon : 1 to 10.10^{-9} mol/mol
- nitrogen : balance

Date cylinder received: 22 May 2007

Cylinder pressure on arrival: 98 bar

Dates of measurements:
Measurement 1 was performed in the period 9 – 13 July 2007
Measurement 2 was performed in the period 16 – 20 July 2007
Measurement 3 was performed in the period 23 – 26 July 2007
A test measurement has also been carried out but the results have not been used in this report.

Measurement method used:
Cold trap (thermal desorption –15/300 ºC) - Gas Chromatography – FID

The measurement system consists of :
- cold trap system: Unity + Air Server, Markes International
- gas chromatograph: Thermo Finnegan GC Trace
- detector: FID
- column: capillary column, Plot fused silica, coating Al2O3/KCl, 50 m x 0.32 mm ID
- carrier gas: Helium

Analytical conditions:
- sample volume: 300 mL gas mixture
- cold trap: multi-layer adsorbent material,
  adsorption at -15ºC for 15 min
  desorption at 300 ºC for 5 min
- temperature program:
  40 ºC hold 2 min
  7ºC/min to 150 ºC
  10 ºC/min to 205, hold 10 min

The Euromet cylinder and the standard cylinders were connected to the cold trap through 1/16” silica steel tubing.

Instrument calibration:

The calibration standards for the measurement of Euromet 886 are Primary Standard Materials (PSM) prepared at NMi by gravimetric method (according to ISO 6142).
A set of 4 gas standard mixtures (1- 10 nmol/mol) including acetylene, 2-pentene and i-octane has been prepared ex-novo in 2007 for the Euromet 886 comparison.

In addition to this set, other 5 PSMs prepared in the period 2003- 2006 and with proved stability were used. This group did not include acetylene, 2-pentene and i-octane.

Due to the poor purity of 1,2,3-trimethylbenzene (<95 %mass fraction) no gas standard mixtures were prepared for the analysis of this component. The measured value of 1,2,3-trimethylbenzene in the Euromet gas mixture has been extrapolated by use of 1,2,4-trimethylbenzene calibration standards. The uncertainty source due to extrapolation is taken into account while estimating the uncertainty of the measurement result.

The purity of gas and liquid standards was measured in the laboratory by GC (and Karl Fischer coulometer).
The purity of the nitrogen (with a Built in Purifier), used as balance gas, was specified by the manufacturer as > 99.9999%(mol/mol) and it was confirmed by gas chromatography.
The estimated uncertainty of the standards is calculated from the uncertainty in the preparation, which include uncertainty of the weighing, uncertainty of the molar masses and from the uncertainty in the purity of the components. The major factor affecting the estimated uncertainty is the component purity.

Measurement procedure:
Three series of measurements (calibrants + sample cylinder measurement).

Each series of measurements was performed in 4 consecutive days. Every day the Euromet cylinder was analysed in combination with two or three standard gas mixtures in the concentration range between 1 and 10 nmol/mol (see example: Scheme_1).
Each gas mixture has been analysed 5 times consecutively (sub-measurements). The first measurement, considered as an equilibration step, has not been included in the data processing.

Scheme_1

Day 1	**Day 2**	**Day 3**	**Day 4**
Euromet gas mix	Euromet gas mix	Euromet gas mix	Euromet gas mix
Gas mix A 1 nmol/mol	Gas mix C 5 nmol/mol	Gas mix F 5 nmol/mol	Gas mix J 10 nmol/mol
Gas mix B 2 nmol/mol	Gas mix D 5 nmol/mol	Gas mix I 10 nmol/mol	Gas mix K 10 nmol/mol
	Gas mix E 5 nmol/mol		

The components in the mixture were measured together, but each of them was treated separately.

The mathematical model adopted for each component and for each series of measurements was a weighed line of regression of y on x, where y represents the mean response (peak area) of the group of sub-measurements of the calibrants and x its concentration (nmol/mol). The additional weight given to the points of the curve is inversely proportional to their corresponding variance.

There was no correction for pressure and for temperature. The laboratory temperature was kept constant at 20.5 ± 0.5 °C.

The mean response (peak area) of the group of sub-measurements of the sample was used to calculate the corresponding concentration (nmol/mol). The results for each of the three series of measurements are the average values coming from the results of each group. The final reported result is the mean of the series results.

An extra check of the reliability of the measurement results has been carried out by analysing the Euromet gas mixtures against dynamic prepared standard gas mixtures (C6-C9 components). The measurement results are in line with those obtained by analysis with gravimetric standards (see table _1 Euromet 886 results dynamic versus gravimetric standards).

Table_1 Euromet 886 results dynamic versus gravimetric standards

	gravimetric	**dynamic**	
	Concentration	**Concentration**	**delta**
	nmol/mol	**nmol/mol**	**(%)**
benzene	3.77	3.79	0.6
n-octane	5.27	5.40	2.4
toluene	3.29	3.24	-1.4
ethylbenzene	4.21	4.27	1.4
m-p-Xylene	8.45	8.47	0.3
o-Xylene	4.26	4.31	1.1
1,3,5-TMB	4.15	4.13	-0.5
1,2,4-TMB	4.44	4.32	-2.6

Sample handling:
The Euromet cylinder was connected to a pressure reducer before being connected to the measuring instrument. The outlet pressure was set to 2 bar.
During the different measuring periods, the gas mixture has been kept together with the calibration standards in the laboratory room at a temperature of 20.5 ± 0.5 ºC.

Components used in the uncertainty calculation:
The contribution to uncertainty of the assigned values derives from the uncertainty of the calibration standards and from the measurement itself.
The standard uncertainty of the calibration standards, u(std), is described in the "Instrument Calibration" paragraph.
The uncertainty due to measurement is expressed as uncertainty in the sample concentration result, u(x;exp), and it takes into account the lack-of-fit and the regression coefficients uncertainties . The uncertainty in the sample response of one series of measurements, expressed as u(ÿ,exp) is calculated using the one-way ANOVA and it is the square root of the sum of the within group of sub-measurements variance, s2(r), divided by the total number of sub-measurements and the between group of sub-measurements variance, s2(A), divided by the number of groups .
The combined uncertainty in a series of measurements, u(series), is calculated from u(x;exp), u(ÿ;exp) divided by the slope coefficient and from the uncertainty of the

calibration standards, u(std). The u(std) value used is the uncertainty in the standard closest in concentration to the sample value.
The uncertainty in the final result is then the pooled estimate of uncertainty of the series added of the standard deviation of the three series results and the sum is divided by square root of 3. The expanded uncertainty (see the table_2) is expressed in nmol/mol and has a coverage factor k=2.
Finally, after grouping the components of the mixtures in two (respectively C2-C7 aliphatics and C8 aliphatics + aromatics), the "reported uncertainty" of measurement is calculated by rounding each component expanded uncertainty to the largest expanded uncertainty of the group (respectively two and three percent). For 1,2,3-trimethylbenzene the reported uncertainty is five percent due to the contribution of extrapolation of the measurement result.

Table_2 data results expressed in nmol/mol

	Ethane	**Ethene**	**propane**	**propene**	**isobutane**	**butane**	**acetylene**	**trans-2-butene**	**1-butene**	**cis-2-butene**
Series I	5.86	5.85	5.87	5.81	7.96	7.84	5.62	7.76	7.63	7.56
Series II	5.90	5.90	5.83	5.82	7.92	7.81	5.70	7.72	7.58	7.49
Series III	5.92	5.91	5.83	5.83	7.97	7.85	5.72	7.74	7.62	7.55
Average	**5.89**	**5.89**	**5.84**	**5.82**	**7.95**	**7.84**	**5.68**	**7.74**	**7.61**	**7.53**
s	0.03	0.03	0.02	0.01	0.03	0.02	0.05	0.02	0.03	0.04
u(series,pooled)	0.06	0.06	0.06	0.05	0.08	0.08	0.07	0.07	0.09	0.07
u(combined)	0.04	0.04	0.04	0.03	0.05	0.05	0.05	0.04	0.06	0.05
U (k=2)	0.08	0.08	0.08	0.06	0.10	0.10	0.11	0.08	0.11	0.09
U reported	**0.12**	**0.12**	**0.12**	**0.12**	**0.16**	**0.16**	**0.11**	**0.15**	**0.15**	**0.15**

	i-pentane	**pentane**	**1,3-butadiene**	**trans-2-pentene**	**1-pentene**	**2-methyl pentane**	**n-hexane**	**isoprene**	**n-heptane**
Series I	5.36	5.40	6.00	5.14	5.23	5.21	5.25	5.29	5.22
Series II	5.34	5.39	5.97	5.10	5.24	5.22	5.26	5.26	5.25
Series III	5.32	5.36	5.91	5.10	5.22	5.23	5.27	5.26	5.25
Average	**5.34**	**5.39**	**5.96**	**5.11**	**5.23**	**5.22**	**5.26**	**5.27**	**5.24**
s	0.02	0.02	0.04	0.02	0.01	0.01	0.01	0.02	0.02
u(series,pooled)	0.06	0.06	0.07	0.06	0.09	0.07	0.05	0.06	0.05
u(combined)	0.04	0.03	0.05	0.04	0.05	0.04	0.03	0.03	0.03
U (k=2)	0.07	0.07	0.10	0.08	0.10	0.08	0.06	0.07	0.06
U reported	**0.11**	**0.11**	**0.12**	**0.10**	**0.10**	**0.10**	**0.11**	**0.11**	**0.10**

	benzene	**i-octane**	**n-octane**	**toluene**	**Ethyl benzene**	**m/p-xylene**	**o-xylene**	**1,3,5-TMB**	**1,2,4-TMB**	**1,2,3-TMB**
Series I	3.78	5.33	5.29	3.33	4.21	8.46	4.30	4.12	4.41	3.85
Series II	3.76	5.37	5.27	3.29	4.22	8.44	4.22	4.13	4.42	3.88
Series III	3.76	5.34	5.24	3.25	4.20	8.44	4.26	4.20	4.48	3.92
Average	**3.77**	**5.35**	**5.27**	**3.29**	**4.21**	**8.45**	**4.26**	**4.15**	**4.44**	**3.88**
s	0.01	0.02	0.03	0.04	0.01	0.01	0.04	0.04	0.04	0.03
u(series,pooled)	0.05	0.05	0.08	0.06	0.06	0.13	0.07	0.08	0.06	0.06
u(combined)	0.03	0.03	0.05	0.04	0.04	0.08	0.04	0.05	0.04	0.04
U (k=2)	0.06	0.06	0.10	0.08	0.07	0.16	0.09	0.10	0.09	0.08
U reported	**0.11**	**0.16**	**0.16**	**0.10**	**0.13**	**0.25**	**0.13**	**0.12**	**0.13**	**0.19**

Approximate volume of cylinder gas used during analysis:

10-12 L per series of analysis

Cylinder pressure at dispatch back to NPL: 78 bar

Date of dispatch back to NPL: 10 August 2007

Laboratory : NMi VSL
Cylinder number : D954815

Results:

Analyte	Result (mol/mol)	Measurement uncertainty (95% confidence) (mol/mol)
ethane	5.89×10^{-9}	0.12×10^{-9}
ethylene (ethene)	5.89×10^{-9}	0.12×10^{-9}
propane	5.84×10^{-9}	0.12×10^{-9}
propene	5.82×10^{-9}	0.12×10^{-9}
i-butane (2-methylpropane)	7.95×10^{-9}	0.16×10^{-9}
butane	7.84×10^{-9}	0.16×10^{-9}
acetylene (ethyne)	5.68×10^{-9}	0.11×10^{-9}
trans-2-butene	7.74×10^{-9}	0.15×10^{-9}
1-butene	7.61×10^{-9}	0.15×10^{-9}
cis-2-butene	7.53×10^{-9}	0.15×10^{-9}
i-pentane (2-methylbutane)	5.34×10^{-9}	0.11×10^{-9}
pentane	5.39×10^{-9}	0.11×10^{-9}
1,3-butadiene	5.96×10^{-9}	0.12×10^{-9}
trans-2-pentene	5.11×10^{-9}	0.10×10^{-9}
1-pentene	5.23×10^{-9}	0.10×10^{-9}
i-hexane (2-methylpentane)	5.22×10^{-9}	0.10×10^{-9}
hexane	5.26×10^{-9}	0.11×10^{-9}
isoprene (2-methyl-1,3-butadiene)	5.27×10^{-9}	0.11×10^{-9}
heptane	5.24×10^{-9}	0.10×10^{-9}
benzene	3.77×10^{-9}	0.11×10^{-9}
2,2,4-trimethylpentane (i-octane)	5.35×10^{-9}	0.16×10^{-9}
octane	5.27×10^{-9}	0.16×10^{-9}
toluene	3.29×10^{-9}	0.10×10^{-9}
ethylbenzene	4.21×10^{-9}	0.13×10^{-9}
m+p-xylene	8.45×10^{-9}	0.25×10^{-9}
o-xylene	4.26×10^{-9}	0.13×10^{-9}
1,3,5-trimethylbenzene	4.15×10^{-9}	0.12×10^{-9}
1,2,4-trimethylbenzene	4.44×10^{-9}	0.13×10^{-9}
1,2,3-trimethylbenzene	3.88×10^{-9}	0.19×10^{-9}

Laboratory : National Physical Laboratory
Cylinder number : D95 4804

NOMINAL COMPOSITION
- 30 species of hydrocarbon : 1 to 10.10^{-9} mol/mol
- nitrogen : balance

Date cylinder received: July 2007

Cylinder pressure on arrival: 100 bar

Dates of measurements:
25th July, 22nd August, 13th September, 22nd & 23rd November 2007

Measurement method used:
Gas Chromatograph: Varian 3600 CX with Flame Ionisation Detector
Column: PLOT Al_2O_3/KCl ; length: 50m; inner diameter: 0.53mm
Sample preconcentration trap (glass beads: trap at -165°C – desorb at 190°C)
Sample volume: 100ml
Column oven profile: 30°C hold 13mins – 3°C/min to 200°C
Column flow 6ml/min

Instrument calibration:
NPL 30 component ozone precursor primary standard
Approximate amount fraction 4 nmol/mol for each species.

Sample handling:

The sample line from cylinder to GC was set up using connectors and flow controllers designed at NPL to reduce dead volume to a minimum. Tubing was 1/16" silcosteel® tubing from Restek©. Flow of all samples taken was fixed at nominally $50ccmin^{-1}$ and matched from sample to standard. All samples flowed for at least 5 minutes prior to sampling. 100ml sample used per analysis and a sequence A-B-A-B-A was adopted for the Standard (A) and "Unknown" (B).

Components used in the uncertainty calculation:
Standard deviation of the measured values, gravimetric and stability uncertainty of the primary reference standard.

Approximate volume of cylinder gas used during analysis:
5L

Cylinder pressure at dispatch back to NPL: 95 bar

Date of dispatch back to NPL: November 2007

Laboratory : National Physical Laboratory
Cylinder number : D95 4804

Results:

Analyte	Result (nmol/mol)	Measurement uncertainty (95% confidence) (nmol/mol)
ethane	**6.72**	**0.08**
ethylene (ethene)	**6.67**	**0.08**
propane	**6.66**	**0.08**
propene	**6.54**	**0.08**
i-butane (2-methylpropane)	**7.07**	**0.22**
butane	**6.89**	**0.07**
acetylene (ethyne)	**6.78**	**0.11**
trans-2-butene	**6.88**	**0.08**
1-butene	**6.79**	**0.10**
cis-2-butene	**6.78**	**0.10**
i-pentane (2-methylbutane)	**5.13**	**0.08**
pentane	**5.21**	**0.08**
1,3-butadiene	**6.64**	**0.11**
trans-2-pentene	**4.93**	**0.07**
1-pentene	**5.03**	**0.06**
i-hexane (2-methylpentane)	**5.13**	**0.07**
hexane	**5.16**	**0.07**
isoprene (2-methyl-1,3-butadiene)	**5.19**	**0.08**
heptane	**5.06**	**0.07**
benzene	**4.18**	**0.06**
2,2,4-trimethylpentane (i-octane)	**5.19**	**0.05**
octane	**5.15**	**0.08**
toluene	**3.61**	**0.08**
ethylbenzene	**3.87**	**0.09**
m+p-xylene	**7.62**	**0.17**
o-xylene	**3.77**	**0.08**
1,3,5-trimethylbenzene	**3.69**	**0.09**
1,2,4-trimethylbenzene	**3.90**	**0.13**
1,2,3-trimethylbenzene	**3.53**	**0.07**

Laboratory : Umweltbundesamt GmbH
Cylinder number : D95 4965

NOMINAL COMPOSITION
- 30 species of hydrocarbon : 1 to 10.10^{-9} mol/mol
- nitrogen : balance

Date cylinder received: 13/06/2007

Cylinder pressure on arrival: ~ 110 bar

Dates of measurements: 25.06.2007, 2.07.2007

Measurement method used:
C2-C6:
AIRMOVOC C2-C6 # 5821204
PoraplotQ 30m x 0.53mm
13ml/min sampling for 10mins
C6-C12:
AIRMOVOC C6-C12 # 2811204
WCOT Fused Silica DB-1 30m x 0.18mm
16ml/min sampling for 10mins

Instrument calibration:

Manufacturer	National Physical Laboratory NPL
certification date	Aug-05
Expired date	Aug-06
Pressure of the cylinder	80 bar

additional reference material 1:
manufacturer: National Physical Laboratory NPL
certification date: Aug. 05
expired date: Aug.06
APE 313679
concentrations of the mixture of 30 hydrocarbons:
1,4 - 10,2 ppb
additional reference material 2:
manufacturer: Nederlands Meetinstituut NMI
certification date: 09.02.2006
expired date: 09.02.2009
Number: 3220237-01
concentrations of the mixture of 29 hydrocarbons:
9,4 - 10,8 ppb

Sample handling:
Sample gas tube:
External: PFA: 4mm id., length 2m (1m drier typ Nafion), synth. air for drying.
Internal: PFA: 2 mm id., length 50cm, stainless steel capillary: 1 mm id., length 30cm.
Cooling system C2 - C6: compressed air (Vortex-effect)
Detection: FID (C2 - C6, C6 - C12)
Flow control: critical orifice

Components used in the uncertainty calculation:
Uncertainty of the reference material
Uncertainty caused by varying response factors (standard deviation of the response factors)
Uncertainty caused by varying concentrations of the 5 measurements (standard deviation of the concentrations of the 5 measurements)
Calibration standard (reference material) and sample were applied under repeatability conditions; as reference material and sample showed comparable concentrations, we used one-point calibration for our measurements)

Approximate volume of cylinder gas used during analysis:

Cylinder pressure at dispatch back to NPL: ~70 bar

Date of dispatch back to NPL: 27/06/2007

Laboratory : Umweltbundesamt GmbH (Austria)
Cylinder number : D95 4965

Results:

Analyte	Result (mol/mol)	Measurement uncertainty (95% confidence) (mol/mol)
ethane	5.4	+/- 0,22
ethylene (ethene)	7.0	+/- 1,44
propane	6.7	+/- 0,41
propene	6.6	+/- 0,77
i-butane (2-methylpropane)	7.2	+/- 0,23
butane	6.9	+/- 0,21
acetylene (ethyne)	6.6	+/- 0,40
trans-2-butene	6.9	+/- 0,42
1-butene	6.8	+/- 0,28
cis-2-butene	5.1	+/- 0,85
i-pentane (2-methylbutane)	7.0	+/- 2,18
pentane	5.3	+/- 0,14
1,3-butadiene	7.1	+/- 0,53
trans-2-pentene	5.2	+/- 0,43
1-pentene	5.2	+/- 0,29
i-hexane (2-methylpentane)	5.1	+/- 0,13
hexane	5.0	+/- 0,42
isoprene (2-methyl-1,3-butadiene)		
heptane	5.1	+/- 0,21
benzene	4.2	+/- 0,14
2,2,4-trimethylpentane (i-octane)	5.2	+/- 0,22
octane	5.1	+/- 0,19
toluene	3.6	+/- 0,28
ethylbenzene	3.8	+/- 0,16
m+p-xylene	7.6	+/- 0,17
o-xylene	3.8	+/- 0,19
1,3,5-trimethylbenzene	3.5	+/- 0,14
1,2,4-trimethylbenzene	3.6	+/- 0,22
1,2,3-trimethylbenzene	3.3	+/- 0,15

Umweltbundesamt GmbH (Austria) notified NPL of a reporting error on 20/02/2008 after submission of their results (see Annex B for comparison timeline). The error applied to *i*-pentane (2-methylbutane) and *cis*-2-butene. The correction is as follows:

cis-2-butene	6.9	+/- 1,85
i-pentane (2-methylbutane)	5.2	+/- 0,85

Laboratory : WCC-VOC, FZK, IMK-IFU
Cylinder number : D29 2401

NOMINAL COMPOSITION
- 30 species of hydrocarbon : 1 to 10.10^{-9} mol/mol
- nitrogen : balance

Date cylinder received:
13.11.07

Cylinder pressure on arrival:
1500 PSI

Dates of measurements:
21.11.; 22.11.; 27.11.; 28.11.

Measurement method used:
two-dimensional GC-FID analysis

Instrument calibration:
Daily with NPL D83 8784R

Sample handling:
Automatic pre-concentration

Components used in the uncertainty calculation:
Reported standard uncertainty of the calibration standard and standard uncertainty of the sample analysis (n=4)

$$u_{meas} = 2\sqrt{u^2_{standard} + u^2_{sample}}$$

Approximate volume of cylinder gas used during analysis:
400 ml

Cylinder pressure at dispatch back to NPL:
1400 psi

Date of dispatch back to NPL:
05.12.2007

Laboratory : WCC-VOC, FZK IMK-IFU
Cylinder number : D29 24016

Results:

Analyte	Result (nmol/mol)	Measurement uncertainty (95% confidence)(nmol/mol)
ethane	6,81	0,09
ethylene (ethene)	6,72	0,11
propane	6,71	0,13
propene	6,60	0,12
i-butane (2-methylpropane)	7,15	0,09
butane	6,96	0,09
acetylene (ethyne)	6,71	0,10
trans-2-butene	6,95	0,09
1-butene	6,84	0,10
cis-2-butene	6,85	0,09
i-pentane (2-methylbutane)	5,15	0,09
pentane	5,23	0,09
1,3-butadiene	6,58	0,09
trans-2-pentene	4,98	0,09
1-pentene	5,04	0,08
i-hexane (2-methylpentane)	5,17	0,09
hexane	5,16	0,09
isoprene (2-methyl-1,3-butadiene)	5,16	0,09
heptane	5,10	0,10
benzene	4,22	0,12
2,2,4-trimethylpentane (i-octane)	5,20	0,10
octane	5,17	0,18
toluene	3,71	0,30
ethylbenzene	4,30	1,14
m+p-xylene	8,19	1,76
o-xylene	4,1	1,14
1,3,5-trimethylbenzene	-	-
1,2,4-trimethylbenzene	-	-
1,2,3-trimethylbenzene	-	-

Annex G: Extended stability trial

Since the conclusion of the EURAMET 886 study a 4th round of stability analysis, approximately 24 months after t = 0, was completed on the 21 remaining cylinders from the exercise. As in previous rounds new working standards were diluted from the 200 nmol/mol parents and the measured values at t = 24 months were input into the statistical model. This latest data has further confirmed the excellent stability of these species in these cylinders with less than 0.3% annual drift in all species over the 2 year stability trial.

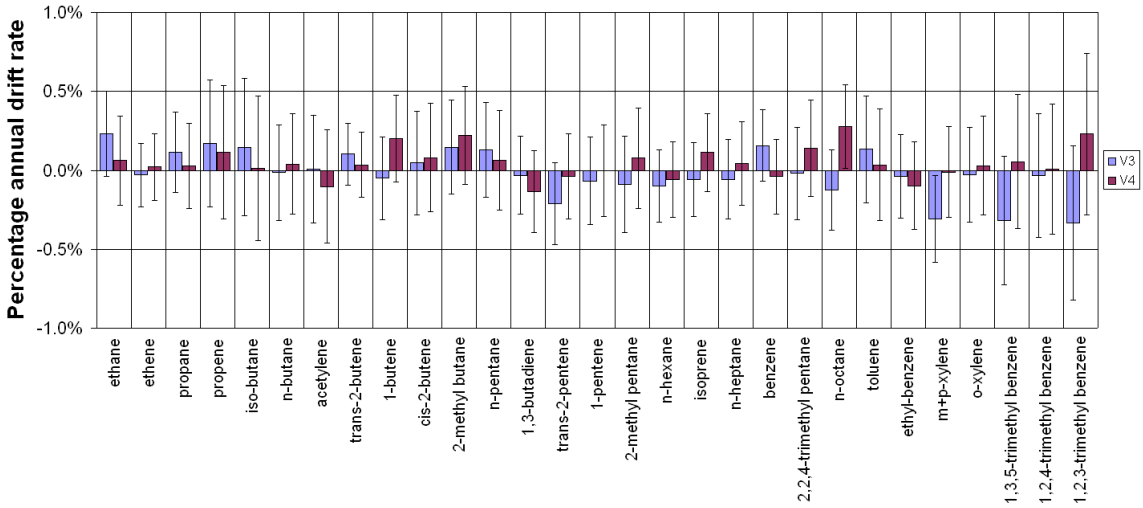


Figure 25. Estimate of the annual drift rate over 2 years and 4 rounds of stability trials for 22 cylinders of 1-10 nmol/mol 30 component ozone precursors.

NOTE: In this figure a value of 1% on the y-axis means that the annual drift rate *d* is 0.01 over the 24 month period of the stability trial.