

**Thermodynamic ( $p, \rho, T$ ) characterization of a reference high-calorific natural gas mixture when hydrogen is added up to 20 % (mol/mol)**

**Supplementary File**

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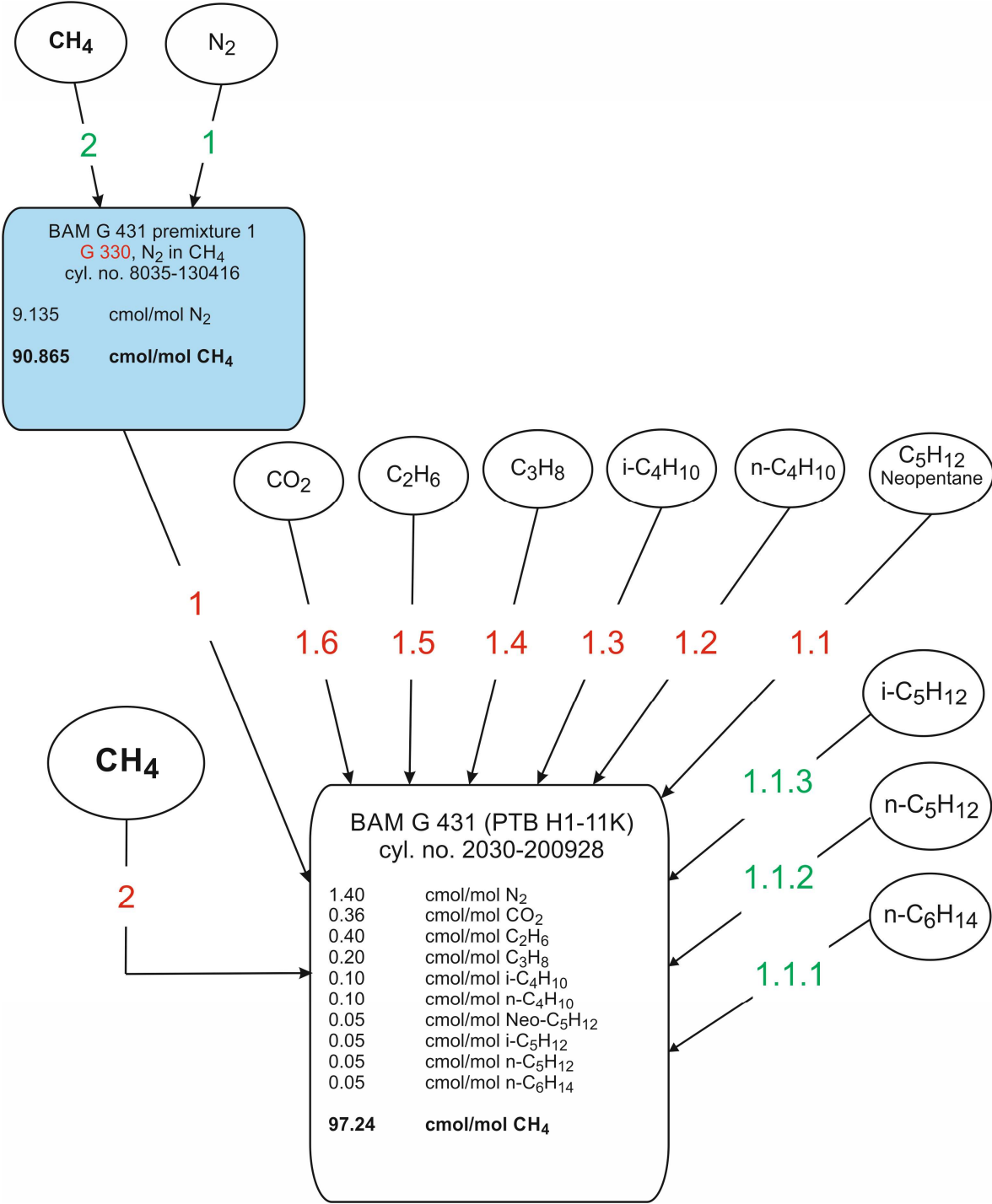
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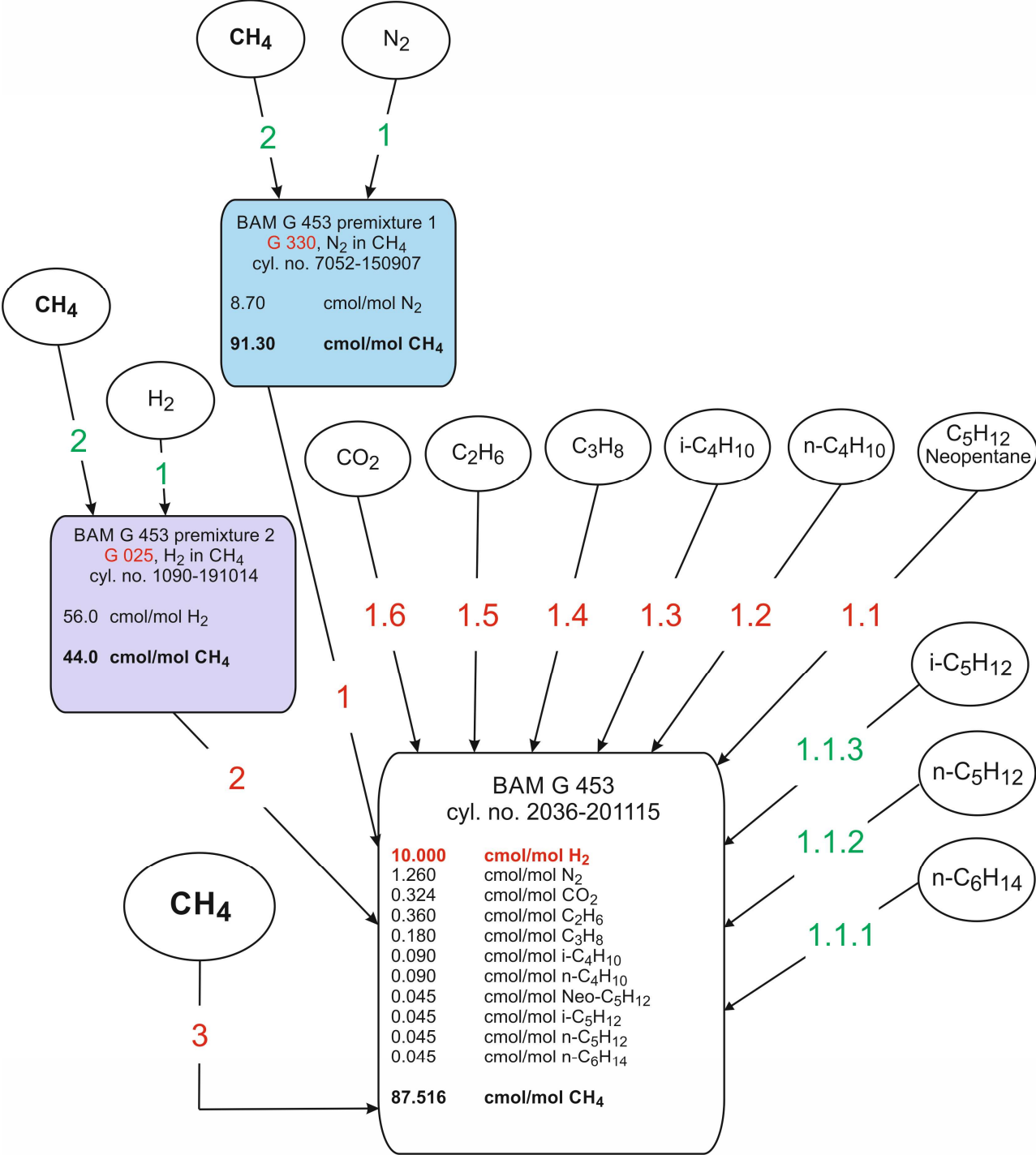
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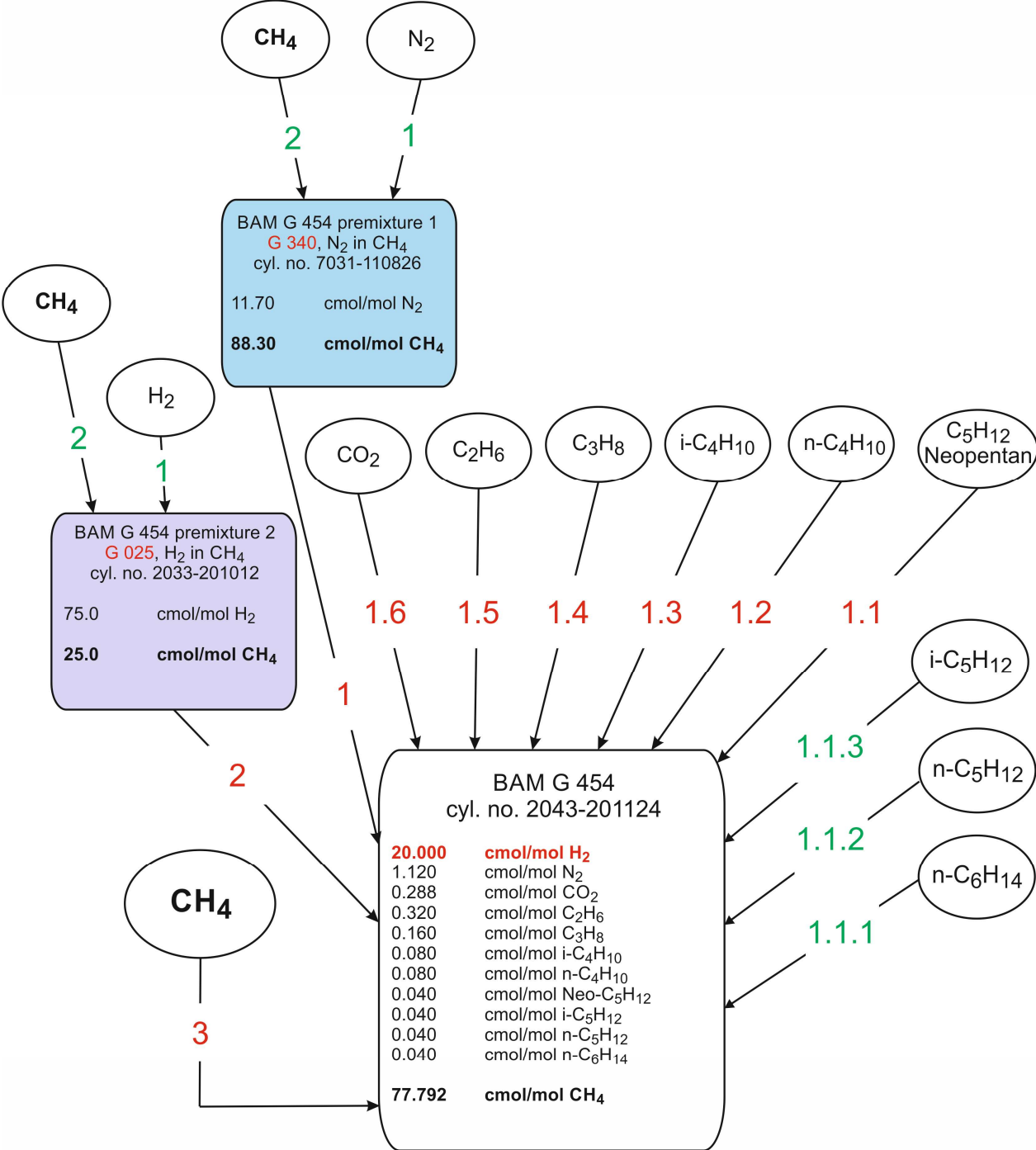
**Figure S1.** Preparation chart for the 11-component (H<sub>2</sub>-free) natural gas mixture G 431 showing the constituting pure compounds and premixtures as well as the ideal target concentrations.



**Figure S2.** Preparation chart for the 12-component H<sub>2</sub>-enriched (10 mol-%) natural gas mixture G 453 showing the constituting pure compounds and premixtures.



**Figure S3.** Preparation chart for the 12-component H<sub>2</sub>-enriched (20 mol-%) natural gas mixture G 454 showing the constituting pure compounds and premixtures.



The numbers on the chart indicate the individual filling steps during the preparation in ascending order.

1, 2, 3, ...: direct filling from a container into the recipient and subsequent weighing

1.1, 1.2, 1.3, ...: transfer from a minicylinder using a purge gas (indicated by 1)

1.1.1, 1.1.2, ...: transfer from a (gas-tight) syringe (can be followed by a transfer from a minicylinder) using a purge gas (either a pure gas or a mixture)

Gas portions as determined during the preparation of the G 431 mixture (Fig. S1):

Premixture 1, cylinder no.: 8035-130416, total pressure: 125 bar			
1	nitrogen	142.539 g	directly
2	methane	813.661 g	directly
Final mixture, cylinder no.: 2030-200928, total pressure: 143 bar			
1.1.1	<i>n</i> -hexane	2.762 g	syringe, $V = 10$ ml
1.1.2	<i>n</i> -pentane	2.315 g	syringe, $V = 10$ ml
1.1.3	isopentane	2.311 g	syringe, $V = 10$ ml
1.1	neopentane	2.368 g	minicylinder, $V = 25$ ml
1.2	<i>n</i> -butane	3.745 g	minicylinder, $V = 25$ ml
1.3	isobutane	3.743 g	minicylinder, $V = 25$ ml
1.4	propane	5.689 g	minicylinder, $V = 25$ ml
1.5	ethane	7.687 g	minicylinder, $V = 50$ ml
1.6	carbon dioxide	10.194 g	minicylinder, $V = 50$ ml
1	premixture 1	168.777 g	directly, purge gas for 1.1.1 to 1.6
2	methane	856.590 g	directly

Gas portions as determined during the preparation of the G 453 mixture (Fig. S2):

Premixture 1, cylinder no.: 7052-150907, total pressure: 125 bar			
1	nitrogen	136.537 g	directly
2	methane	819.992 g	directly
Premixture 2, cylinder no.: 1090-191014, total pressure: 110 bar			
1	hydrogen	55.586 g	directly
2	methane	347.289 g	directly
Final mixture, cylinder no.: 2036-201115, total pressure: 150 bar			
1.1.1	<i>n</i> -hexane	2.598 g	syringe, $V = 10$ ml
1.1.2	<i>n</i> -pentane	2.184 g	syringe, $V = 10$ ml
1.1.3	isopentane	2.179 g	syringe, $V = 10$ ml
1.1	neopentane	2.182 g	minicylinder, $V = 25$ ml
1.2	<i>n</i> -butane	3.519 g	minicylinder, $V = 25$ ml
1.3	isobutane	3.527 g	minicylinder, $V = 25$ ml
1.4	propane	5.330 g	minicylinder, $V = 25$ ml
1.5	ethane	7.273 g	minicylinder, $V = 50$ ml
1.6	carbon dioxide	9.580 g	minicylinder, $V = 50$ ml
1	premixture 1	165.506 g	directly, purge gas for 1.1.1 to 1.6
2	premixture 2	97.869 g	directly
3	methane	714.916 g	directly

Gas portions as determined during the preparation of the G 454 mixture (Fig. S3):

Premixture 1, cylinder no.: 7031-110826, total pressure: 100 bar			
1	nitrogen	140.192 g	directly
2	methane	638.391 g	directly
Premixture 2, cylinder no.: 2033-201012, total pressure: 130 bar			
1	hydrogen	87.857 g	directly
2	methane	233.613 g	directly
Final mixture, cylinder no.: 2043-201124, total pressure: 149 bar			
1.1.1	<i>n</i> -hexane	2.317 g	syringe, $V = 10$ ml
1.1.2	<i>n</i> -pentane	1.936 g	syringe, $V = 10$ ml
1.1.3	isopentane	1.933 g	syringe, $V = 10$ ml
1.1	neopentane	1.944 g	minicylinder, $V = 25$ ml
1.2	<i>n</i> -butane	3.106 g	minicylinder, $V = 25$ ml
1.3	isobutane	3.105 g	minicylinder, $V = 25$ ml
1.4	propane	4.730 g	minicylinder, $V = 25$ ml
1.5	ethane	6.445 g	minicylinder, $V = 50$ ml
1.6	carbon dioxide	8.493 g	minicylinder, $V = 50$ ml
1	premixture 1	116.425 g	directly, purge gas for 1.1.1 to 1.6
2	premixture 2	98.703 g	directly
3	methane	668.061 g	directly

**Table S1.** Gravimetric (real) composition of the natural gas mixtures studied and the premixtures used for the preparation. Information on impurities from the supplier are included; impurity compounds are marked in *italic* type.

Component	Mixture G 431 cylinder no.: 2030-200928		Mixture G 453 cylinder no.: 2036-201115	
	$x_i /$ ( $10^{-2} \text{ mol} \cdot \text{mol}^{-1}$ )	$U(x_i) (k = 2) /$ ( $10^{-2} \text{ mol} \cdot \text{mol}^{-1}$ )	$x_i /$ ( $10^{-2} \text{ mol} \cdot \text{mol}^{-1}$ )	$U(x_i) (k = 2) /$ ( $10^{-2} \text{ mol} \cdot \text{mol}^{-1}$ )
methane	97.2361	0.0020	87.5221	0.0023
hydrogen	–	–	9.9928	0.0031
nitrogen	1.40097	0.00028	1.25838	0.00024
carbon dioxide	0.361460	0.000113	0.324953	0.000092
ethane	0.398705	0.000033	0.360839	0.000031
propane	0.201221	0.000020	0.180328	0.000019
<i>n</i> -butane	0.100398	0.000052	0.090235	0.000047
isobutane	0.100431	0.000023	0.090531	0.000021
<i>n</i> -pentane	0.050072	0.000023	0.045181	0.000021
isopentane	0.049928	0.000023	0.045043	0.000021
neopentane	0.050781	0.000022	0.044754	0.000020
<i>n</i> -hexane	0.049883	0.000018	0.044883	0.000016
<i>oxygen</i>	<i>0.000012</i>	<i>0.000012</i>	<i>0.000014</i>	<i>0.000010</i>
<i>hydrogen</i>	<i>0.000003</i>	<i>0.000003</i>	–	–
<i>carbon monoxide</i>	<i>0.0000003</i>	<i>0.0000003</i>	<i>0.000001</i>	<i>0.000001</i>
<i>propene</i>	<i>0.0000002</i>	<i>0.0000002</i>	<i>0.0000002</i>	<i>0.0000002</i>
<i>ethene</i>	<i>0.00000004</i>	<i>0.00000005</i>	<i>0.00000004</i>	<i>0.00000004</i>
<i>nitric oxide</i>	<i>0.00000002</i>	<i>0.00000002</i>	<i>0.00000002</i>	<i>0.00000002</i>
	Mixture G 431 premixture 1 (G 330) cylinder no.: 8035-130416		Mixture G 453 premixture 1 (G 330) cylinder no.: 7052-150907	
methane	90.8816	0.0019	91.2937	0.0019
nitrogen	9.11813	0.00098	8.70608	0.00098
<i>carbon dioxide</i>	<i>0.000201</i>	<i>0.000120</i>	<i>0.000201</i>	<i>0.000121</i>
<i>oxygen</i>	<i>0.000011</i>	<i>0.000013</i>	<i>0.000013</i>	<i>0.000013</i>
<i>hydrogen</i>	<i>0.000005</i>	<i>0.000004</i>	<i>0.000003</i>	<i>0.000003</i>
<i>ethane</i>	<i>0.000003</i>	<i>0.000002</i>	<i>0.000003</i>	<i>0.000002</i>
<i>carbon monoxide</i>	<i>0.0000011</i>	<i>0.0000013</i>	<i>0.0000004</i>	<i>0.0000005</i>



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Mixture G 453 premixture 2 (G 025) cylinder no.: 1090-191004		
hydrogen	56.0186	0.0151
methane	43.9812	0.0019
<i>nitrogen</i>	<i>0.000116</i>	<i>0.000107</i>
<i>carbon dioxide</i>	<i>0.000102</i>	<i>0.000058</i>
<i>oxygen</i>	<i>0.000020</i>	<i>0.000017</i>
<i>carbon monoxide</i>	<i>0.000006</i>	<i>0.000006</i>
<i>ethane</i>	<i>0.000013</i>	<i>0.000008</i>

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Mixture G 454 cylinder no.: 2043-201124		
methane	77.7981	0.0023
hydrogen	19.9945	0.0046
nitrogen	1.11842	0.00027
carbon dioxide	0.288529	0.000084
ethane	0.320307	0.000031
propane	0.160279	0.000019
n-butane	0.079774	0.000042
isobutane	0.079823	0.000019
n-pentane	0.040107	0.000019
isopentane	0.040017	0.000019
neopentane	0.039945	0.000018
n-hexane	0.040092	0.000015
<i>oxygen</i>	<i>0.000014</i>	<i>0.000011</i>
<i>hydrogen</i>	–	–
<i>carbon monoxide</i>	<i>0.000002</i>	<i>0.000002</i>
<i>propene</i>	<i>0.0000002</i>	<i>0.0000002</i>
<i>ethene</i>	<i>0.00000003</i>	<i>0.00000004</i>
<i>nitric oxide</i>	<i>0.00000001</i>	<i>0.00000002</i>

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Mixture G 454 premixture 1 (G 340) cylinder no.: 7031-110826		
methane	88.8284	0.0091
nitrogen	11.17156	0.00164

<i>carbon dioxide</i>	<i>n. a.</i>	<i>n. a.</i>
<i>oxygen</i>	<i>n. a.</i>	<i>n. a.</i>
<i>hydrogen</i>	<i>n. a.</i>	<i>n. a.</i>
<i>ethane</i>	<i>n. a.</i>	<i>n. a.</i>
<i>carbon monoxide</i>	<i>n. a.</i>	<i>n. a.</i>
<hr/> Mixture G 454 premixture 2 (G 025) cylinder no.: 2033-201012		
hydrogen	74.9545	0.0128
methane	25.0453	0.0016
<i>nitrogen</i>	<i>0.000088</i>	<i>0.000072</i>
<i>carbon dioxide</i>	<i>0.000063</i>	<i>0.000034</i>
<i>oxygen</i>	<i>0.000022</i>	<i>0.000022</i>
<i>carbon monoxide</i>	<i>0.000007</i>	<i>0.000009</i>
<i>ethane</i>	<i>0.0000008</i>	<i>0.0000005</i>
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**Table S2.** Results of the gas chromatographic (GC) analysis and relative deviations between gravimetric preparation and GC analysis for the three reference natural gas mixtures studied in this work. The results are followed by the gravimetric composition of the employed validation mixtures (bracketing analysis according to ISO 12963).

Component	Relative deviation between gravimetric composition and GC analysis			Relative deviation between gravimetric composition and GC analysis			Relative deviation between gravimetric composition and GC analysis		
	Concentration	Concentration	Concentration	Concentration	Concentration	Concentration	Concentration	Concentration	Concentration
	$10^2 x_i / \text{mol/mol}$	$10^2 U(x_i) / \text{mol/mol}$	%	$10^2 x_i / \text{mol/mol}$	$10^2 U(x_i) / \text{mol/mol}$	%	$10^2 x_i / \text{mol/mol}$	$10^2 U(x_i) / \text{mol/mol}$	%
	G 431, BAM no.: 2030-200928			G 453, BAM no.: 2036-201115			G 454, BAM no.: 2043-201124		
Methane	97.2348	0.0045	-0.001	87.5242	0.0124	0.002	77.8023	0.0187	0.005
Hydrogen	-	-	-	9.9901	0.0111	-0.026	19.9902	0.0184	-0.022
Nitrogen	1.4006	0.0016	-0.023	1.2583	0.0012	-0.003	1.1178	0.0010	-0.055
Carbon dioxide	0.3628	0.0019	0.365	0.3252	0.0014	0.065	0.2885	0.0019	-0.018
Ethane	0.3989	0.0030	0.050	0.3611	0.0027	0.061	0.3207	0.0029	0.128
Propane	0.2013	0.0008	0.051	0.1804	0.0010	0.034	0.1604	0.0010	0.081
<i>n</i> -Butane	0.1004	0.0002	0.016	0.0903	0.0001	0.033	0.0799	0.0001	0.101
Isobutane	0.1004	0.0001	0.013	0.0905	0.0001	0.018	0.0799	0.0001	0.122
<i>n</i> -Pentane	0.0501	0.0002	0.087	0.0452	0.0002	-0.018	0.0401	0.0002	0.086
Isopentane	0.0499	0.0001	0.032	0.0451	0.0001	0.081	0.0400	0.0001	0.050

Neopentane	0.0508	0.0001	0.006	0.0447	0.0001	-0.026	0.0400	0.0001	0.122
<i>n</i> -Hexane	0.0499	0.0002	0.022	0.0449	0.0001	0.080	0.0401	0.0001	0.074
	Validation mixture BAM no: 1083-191203 (lower bracket)			Validation mixture BAM no.: 2035-201109 (lower bracket)			Validation mixture BAM no.: 2042-201122 (lower bracket)		
Methane	97.3920	0.0022		88.1236	0.0023		78.9676	0.0021	
Hydrogen	–	–		9.5147	0.0031		18.9337	0.0045	
Nitrogen	1.31651	0.00027		1.19824	0.00030		1.06501	0.00028	
Carbon dioxide	0.342872	0.000114		0.308391	0.000101		0.273484	0.000092	
Ethane	0.377777	0.000034		0.342841	0.000033		0.304656	0.000031	
Propane	0.191152	0.000022		0.170067	0.000021		0.151800	0.000020	
<i>n</i> -Butane	0.094863	0.000050		0.085324	0.000045		0.075723	0.000040	
Isobutane	0.094977	0.000022		0.085613	0.000021		0.075960	0.000019	
<i>n</i> -Pentane	0.047448	0.000023		0.042813	0.000021		0.038111	0.000019	
Isopentane	0.047614	0.000023		0.042761	0.000021		0.038033	0.000019	
Neopentane	0.047101	0.000021		0.042881	0.000020		0.037935	0.000018	
<i>n</i> -Hexane	0.047633	0.000016		0.042782	0.000016		0.038001	0.000015	
<i>Oxygen</i>	<i>0.000012</i>	<i>0.000012</i>		<i>0.000014</i>	<i>0.000011</i>		<i>0.000015</i>	<i>0.000011</i>	
<i>Hydrogen</i>	<i>0.000003</i>	<i>0.000003</i>		–	–		–	–	
<i>Carbon monoxide</i>	<i>0.0000003</i>	<i>0.0000002</i>		<i>0.000001</i>	<i>0.000001</i>		<i>0.000002</i>	<i>0.000002</i>	

<i>Propene</i>	0.0000002	0.0000002	0.0000002	0.0000002	0.0000002	0.0000002
<i>Ethene</i>	0.00000013	0.00000011	0.00000003	0.00000004	0.00000003	0.00000004
<i>Nitric oxide</i>	0.00000002	0.00000002	0.00000002	0.00000002	0.00000001	0.00000002
	Validation mixture BAM no: 6098-191209 (upper bracket)		Validation mixture BAM no.: 2037-201117 (upper bracket)		Validation mixture BAM no.: 2044-201130 (upper bracket)	
Methane	97.0985	0.0022	86.8725	0.0025	76.7016	0.0021
Hydrogen	–	–	10.5120	0.0033	20.9777	0.0047
Nitrogen	1.47274	0.00028	1.32675	0.00033	1.17730	0.00027
Carbon dioxide	0.379488	0.000111	0.342171	0.000097	0.302677	0.000087
Ethane	0.418538	0.000037	0.378328	0.000035	0.336258	0.000031
Propane	0.210275	0.000022	0.189702	0.000022	0.168337	0.000019
<i>n</i> -Butane	0.105241	0.000054	0.094599	0.000049	0.084057	0.000044
Isobutane	0.105051	0.000024	0.094881	0.000022	0.084098	0.000020
<i>n</i> -Pentane	0.052474	0.000025	0.047353	0.000022	0.042013	0.000020
Isopentane	0.052547	0.000025	0.047262	0.000022	0.041871	0.000020
Neopentane	0.052589	0.000023	0.047095	0.000021	0.041943	0.000019
<i>n</i> -Hexane	0.052533	0.000017	0.047399	0.000018	0.042069	0.000016
<i>Oxygen</i>	0.000012	0.000012	0.000013	0.000011	0.000015	0.000011
<i>Hydrogen</i>	0.000003	0.000002	–	–	–	–

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<i>Carbon monoxide</i>	0.0000002	0.0000002	0.0000001	0.0000001	0.0000002	0.0000002
<i>Propene</i>	0.0000002	0.0000002	0.0000002	0.0000002	0.0000002	0.0000002
<i>Ethene</i>	0.00000014	0.00000013	0.00000004	0.00000004	0.00000003	0.00000004
<i>Nitric oxide</i>	0.00000002	0.00000002	0.00000002	0.00000002	0.00000002	0.00000002

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