Analytical Methods

RSCPublishing

ELECTRONIC SUPLEMENTARY INFORMATION

Petroleum hydrocarbons fractions in soils: development of analytical method and uncertainty associated.

Cite this: DOI: 10.1039/xoxxoooooox

Oscar Pindado Jiménez, Rosa M. Pérez Pastor and Olga Escolano Segovia

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

www.rsc.org/

This Electronic Supplementary Information summarises the uncertainty assessment of each hydrocarbon fraction and all the comments that could not be included into the text. This document is divided in 6 sections, including 13 figures and 24 tables.

Section 1: Definition of ranges of hydrocarbons and calibrate.

Table I: Equivalent number of carbons.
Table II: Definition of the ranges of aliphatic and aromatic hydrocarbons.
Table III: Total concentration injected in each calibration solution.
Figure I: Graphical representation of the instrumental response versus concentration of the calibration standards.

Section 2: Uncertainty of area.

Table IV: Uncertainty of chromatography area.

Section 3: Uncertainty of volume.

Table V: Uncertainty of volume: influence of temperature.
Table VI: Uncertainty of volume: influence of tolerance of volumetric material (syringe 1 mL).
Table VII: Uncertainty of volume: influence of repeatability (1 mL hexane).
Table VIII: Repeatability of a weighing of 1 mL hexane.

Section 4: Uncertainty of mass.

Table IX: Uncertainty of mass.
Table X: Repeatability of a weighing of 1 g of soil.

ELECTRONIC SUPLEMENTARY INFORMATION

Section 5: Uncertainty of calibration factor.

Section 6: Uncertainty of recovery.

Section 7: Uncertainty of inhomogeneity.

Section 8: Combined uncertainty: Kragten method.

Table I: Equivalent number of carbon atoms

Compound	Carbons	EC	Compounds	Carbons	EC	Compounds	Carbons	EC
Nonane	9	9	Pentacosano	25	25	Naphthalene	10	11.69
Decane	10	10	Hexacosano	26	26	Acenaphthylene	12	15.06
Undecane	11	11	Heptacosano	27	27	Acenaphthene	12	15.50
Dodecane	12	12	Octacosano	28	28	Fluorene	13	16.55
Tridecane	13	13	Nonacosano	29	29	Phenanthrene	14	19.36
Tetradecane	14	14	Triacontane	30	30	Anthracene	14	19.43
Pentadecane	15	15	Hentriacontane	31	31	Fluoranthene	16	21.85
Hexadecane	16	16	Dotriacontane	32	32	Pyrene	16	20.80
Heptadecane	17	17	Tritriacontane	33	33	Benzo(a)anthracene	18	26.37
Octadecane	18	18	Tetratriacontane	34	34	Chrysene	18	27.41
Nonadecane	19	19	Pentatriacontane	35	35	Benzo(b)fluoranthene	20	30.14
Eicosano	20	20	Hexatriacontane	36	36	Benzo(k)fluoranthene	20	30.14
Heneicosano	21	21	Heptatriacontane	37	37	Benzo(a)pyrene	20	31.34
Docosano	22	22	Octatriacontane	38	38	Indeno(123cd)pyrene	22	35.01
Tricosano	23	23	Nonatriacontane	39	39	Dibenzo(ah)anthracene	22	33.92
Tetracosano	24	24	Tetracontane	40	40	Benzo(ghi)perylene	22	34.01

Table II: Definition of the ranges of aliphatic and aromatic hydrocarbons

Ranges of Aliphatic hydrocarbons	Ranges of Aromatic hydrocarbons
$>C_{10}$ - C_{12}	$>EC_{10}$ - EC_{12}
$>C_{12}$ - C_{16}	$>EC_{12}$ - EC_{16}
$>C_{16}$ - C_{21}	$>EC_{16}$ - EC_{21}
$>C_{21}$ - C_{35}	$>EC_{21}$ - EC_{35}
$>C_{35}$	$>EC_{35}$

$>C_{10}$- C_{12} is defined as all aliphatic hydrocarbons compounds which contain between 11 and 12 carbon atoms. This range begins 0.1 minutes after the retention time of decane and finishes 0.1 minutes before the retention time of tridecane

$>C_{12}$- C_{16} is defined as all aliphatic hydrocarbons compounds which contain between 13 and 16 carbon atoms. This range begins 0.1 minutes before the retention time of tridecane and finishes 0.1 minutes before the retention time of heptadecane.

$>C_{16}$- C_{21} is defined as all aliphatic hydrocarbons compounds which contain between 17 and 21 carbon atoms. This range begins 0.1 minutes before the retention time of heptadecane and finishes 0.1 minutes before the retention time of docosane.

$>C_{21}$- C_{35} is defined as all aliphatic hydrocarbons compounds which contain between 22 and 35 carbon atoms. This range begins 0.1 minutes before the retention time of docosane and finishes 0.1 minutes before the retention time of hexatricontane.

$>C_{35}$ is defined as all aliphatic hydrocarbons compounds which contain more than 36 carbon atoms. This range begins 0.1 minutes before the retention time of hexatricontane and finishes 0.1 minutes after the retention time of tretracontane.

$>EC_{10}$- EC_{12} is defined as all aromatic hydrocarbons compounds which contain between 11 and 12 equivalent number of carbon atoms. This range begins 0.1 minutes before the retention time of naphthalene and finishes 0.1 minutes before the retention time of acenaphthylene.

$>EC_{12}$- EC_{16} is defined as all aromatic hydrocarbons compounds which contain between 13 and 16 equivalent number of carbon atoms. This range begins 0.1 minutes before the retention time of acenaphthylene and finishes 0.1 minutes before the retention time of fluorene.

$>EC_{16}$- EC_{21} is defined as all aromatic hydrocarbons compounds which contain between 17 and 21 equivalent number of carbon atoms. This range begins 0.1 minutes before the retention time of fluorene and finishes 0.1 minutes before the retention time of benzo(a)anthracene.

$>EC_{21}$- EC_{35} is defined as all aromatic hydrocarbons compounds which contain between 22 and 35 equivalent number of carbon atoms. This range begins 0.1 minutes before the retention time of benzo(a)anthracene and finishes 0.1 minutes before the retention time of indeno(123-cd)pyrene.

$>EC_{35}$ is defined as all aromatic hydrocarbons compounds which contain more than 36 equivalent number of carbon atoms. This range begins 0.1 minutes before the retention time of indeno(123-cd)pyrene and finishes 0.1 minutes after the retention time of benzo(ghi)perilene.

Table III: Total concentration injected in each calibration solution.

	Solution 1 (mg L^{-1})	Solution 2 (mg L^{-1})	Solution 3 (mg L^{-1})	Solution 4 (mg L^{-1})	Solution 5 (mg L^{-1})	Solution 6 (mg L^{-1})
TPH	80	200	400	800	1200	1600
Aliphatic						
$>C_{10} - C_{12}$	20	50	100	200	300	400
$>C_{12} - C_{16}$	40	100	200	400	600	800
$>C_{16} - C_{21}$	70	175	350	700	1050	1400
$>C_{21} - C_{35}$	140	350	700	1400	2100	2800
$>C_{35}$	50	125	250	500	750	1000
Aromatic						
$>EC_{10} - EC_{12}$	10	20	40	60	80	100
$>EC_{12} - EC_{16}$	10	20	40	60	80	100
$>EC_{16} - EC_{21}$	40	80	160	240	320	400
$>EC_{21} - EC_{35}$	50	100	200	300	400	500
$>EC_{35}$	30	60	120	180	240	300

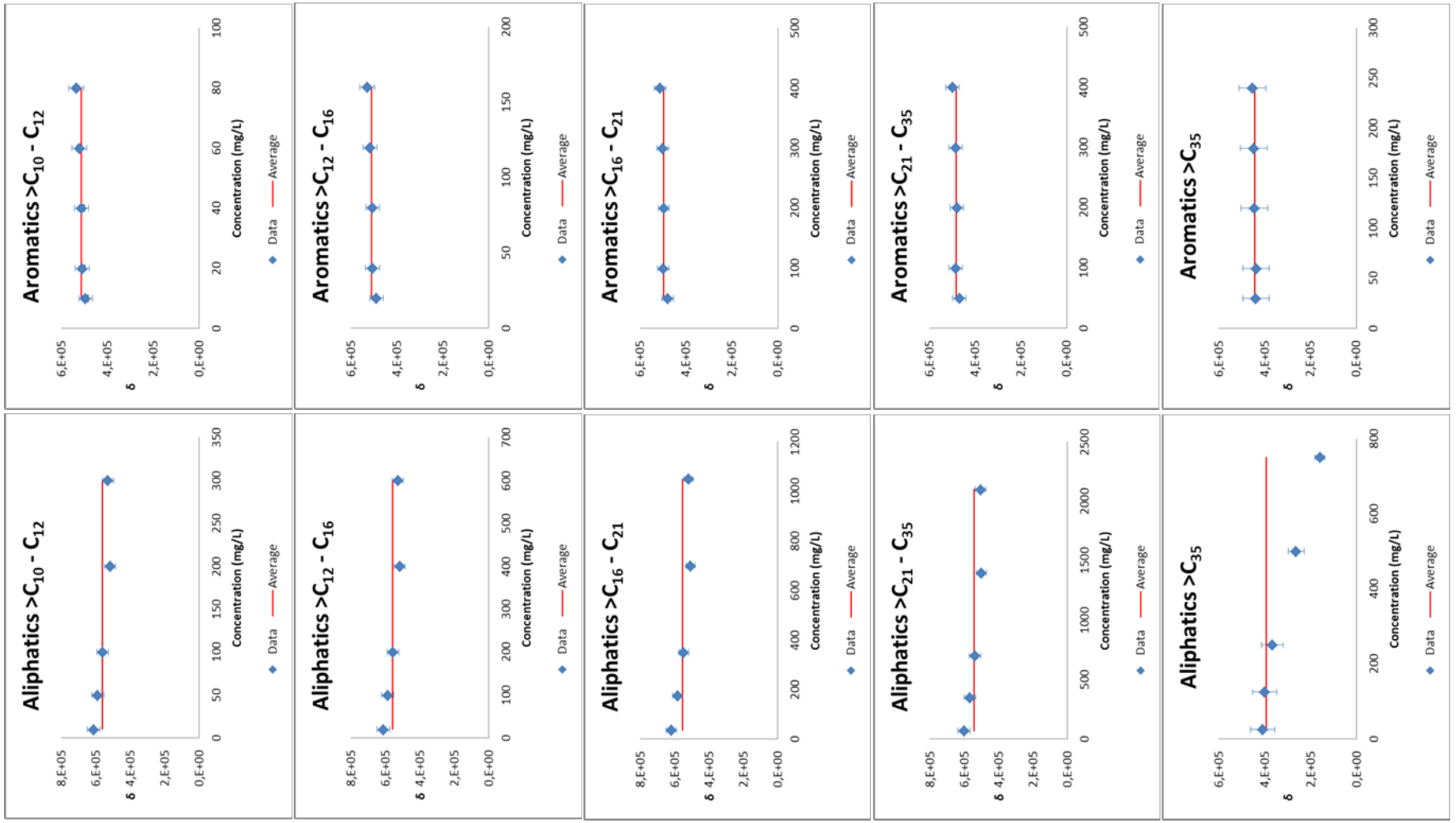

Figure 1: Graphical representation of the instrumental response versus concentration of the calibration standards.

Table IV: Uncertainty of chromatography area.

	Resolution (pA s)	u(resolution)	A x 10^6 (pA s)	$u(resolution)_r$ x 10^{-8}
TPH	1	0.577	78.7	0.7335
Aliphatic				
$>C_{10}$ - C_{12}	1	0.577	5.7	10.04
$>C_{12}$ - C_{16}	1	0.577	10.5	5.497
$>C_{16}$ - C_{21}	1	0.577	16.3	3.538
$>C_{21}$ - C_{35}	1	0.577	31.2	1.850
$>C_{35}$	1	0.577	14.9	3.867
Aromatic				
$>EC_{10}$ - EC_{12}	1	0.577	11.5	5.004
$>EC_{12}$ - EC_{16}	1	0.577	21.8	2.649
$>EC_{16}$ - EC_{21}	1	0.577	52.3	1.103
$>EC_{21}$ - EC_{35}	1	0.577	51.6	1.118
$>EC_{35}$	1	0.577	29.6	1.953

$$u(resolution)_r = \left(\frac{a/\sqrt{3}}{A} \right)$$

Table V: Uncertainty of volume: influence of temperature.

	Influence of temperature					
	Volume (mL)	ΔT (ºK)	α (ºK^{-1})	u(T) (mL)	$u(T)_r$	$(u(T)_r)^2$ x 10^{-5}
TPH	1	5	0.00135	0.00675	0.00390	1.519
Aliphatic						
>C_{10} - C_{12}	1	5	0.00135	0.00675	0.00390	1.519
>C_{12} - C_{16}	1	5	0.00135	0.00675	0.00390	1.519
>C_{16} - C_{21}	1	5	0.00135	0.00675	0.00390	1.519
>C_{21} - C_{35}	1	5	0.00135	0.00675	0.00390	1.519
>C_{35}	1	5	0.00135	0.00675	0.00390	1.519
Aromatic						
>EC_{10} - EC_{12}	1	5	0.00135	0.00675	0.00390	1.519
>EC_{12} - EC_{16}	1	5	0.00135	0.00675	0.00390	1.519
>EC_{16} - EC_{21}	1	5	0.00135	0.00675	0.00390	1.519
>EC_{21} - EC_{35}	1	5	0.00135	0.00675	0.00390	1.519
>EC_{35}	1	5	0.00135	0.00675	0.00390	1.519

$$u(T)_r = \left(\frac{V \times \Delta T \times \alpha}{\sqrt{3}} \right)$$

Table VI: Uncertainty of volume: influence of tolerance of volumetric material (syringe 1 mL)

		Influence of tolerance of syringe			
	Volume (mL)	Division (mL)	u(Tol) (mL)	$u(Tol)_r$	$(u(Tol)_r)^2$ x 10^{-5}
TPH	1	0.01	0.00408	0.00408	1.667
Aliphatic					
$>C_{10}$ - C_{12}	1	0.01	0.00408	0.00408	1.667
$>C_{12}$ - C_{16}	1	0.01	0.00408	0.00408	1.667
$>C_{16}$ - C_{21}	1	0.01	0.00408	0.00408	1.667
$>C_{21}$ - C_{35}	1	0.01	0.00408	0.00408	1.667
$>C_{35}$	1	0.01	0.00408	0.00408	1.667
Aromatic					
$>EC_{10}$ - EC_{12}	1	0.01	0.00408	0.00408	1.667
$>EC_{12}$ - EC_{16}	1	0.01	0.00408	0.00408	1.667
$>EC_{16}$ - EC_{21}	1	0.01	0.00408	0.00408	1.667
$>EC_{21}$ - EC_{35}	1	0.01	0.00408	0.00408	1.667
$>EC_{35}$	1	0.01	0.00408	0.0408	1.667

$$u(Tol)_r = \left(\frac{v/\sqrt{6}}{V} \right)$$

Table VII: Uncertainty of volume: influence of repeatability (1 mL hexane)

	Influence of repeatability			
	mass (g)	s (g)	$u(rep)_r$	$(u(rep)_r)^2$ x 10^{-7}
TPH	0.65813	0.00023	0.000344	1.183
Aliphatic				
$>C_{10}$ - C_{12}	0.65813	0.00023	0.000344	1.183
$>C_{12}$ - C_{16}	0.65813	0.00023	0.000344	1.183
$>C_{16}$ - C_{21}	0.65813	0.00023	0.000344	1.183
$>C_{21}$ - C_{35}	0.65813	0.00023	0.000344	1.183
$>C_{35}$	0.65813	0.00023	0.000344	1.183
Aromatic				
$>EC_{10}$ - EC_{12}	0.65813	0.00023	0.000344	1.183
$>EC_{12}$ - EC_{16}	0.65813	0.00023	0.000344	1.183
$>EC_{16}$ - EC_{21}	0.65813	0.00023	0.000344	1.183
$>EC_{21}$ - EC_{35}	0.65813	0.00023	0.000344	1.183
$>EC_{35}$	0.65813	0.00023	0.000344	1.183

$$u(rep)_r = \left(\frac{s}{m}\right)$$

Table VIII: Repeatability of a weighing of 1 mL hexane

	Weight (g)									
	1	2	3	4	5	6	7	8	Mean	s
Syringe	26.467	26.467	26.467	26.467	26.467	26.467	26.467	26.467		
Syringe + hexane	27.1249	27.1247	27.1248	27.1247	27.1247	27.1250	27.1246	27.1253		
Hexane	0.6582	0.6580	0.6581	0.6580	0.6580	0.6583	0.06579	0.06586	0.65813	0.00023

Table IX: Uncertainty of mass

	Influence of balance				Influence of repeatability				
	u(m)	mass	$u(m)_r$	$(u(m)_r)^2$	mass	s	u(rep)	$u(rep)_r$	$(u(rep)_r)^2$
	x 10^{-5}(g)	(g)	x 10^{-5}(g)	X 10^{-10}	(g)	x 10^{-4}(g)	x 10^{-4}(g)	x 10^{-4}	x 10^{-7}
TPH	3.1	1.0006	1.03	1.06	1.0006	6.966	4.021	4.018	1.615
Aliphatic									
$>C_{10}$ - C_{12}	3.1	1.0006	1.03	1.06	1.0006	6.966	4.021	4.018	1.615
$>C_{12}$ - C_{16}	3.1	1.0006	1.03	1.06	1.0006	6.966	4.021	4.018	1.615
$>C_{16}$ - C_{21}	3.1	1.0006	1.03	1.06	1.0006	6.966	4.021	4.018	1.615
$>C_{21}$ - C_{35}	3.1	1.0006	1.03	1.06	1.0006	6.966	4.021	4.018	1.615
$>C_{35}$	3.1	1.0006	1.03	1.06	1.0006	6.966	4.021	4.018	1.615
Aromatic									
$>EC_{10}$ - EC_{12}	3.1	1.0006	1.03	1.06	1.0006	6.966	4.021	4.018	1.615
$>EC_{12}$ - EC_{16}	3.1	1.0006	1.03	1.06	1.0006	6.966	4.021	4.018	1.615
$>EC_{16}$ - EC_{21}	3.1	1.0006	1.03	1.06	1.0006	6.966	4.021	4.018	1.615
$>EC_{21}$ - EC_{35}	3.1	1.0006	1.03	1.06	1.0006	6.966	4.021	4.018	1.615
$>EC_{35}$	3.1	1.0006	1.03	1.06	1.0006	6.966	4.021	4.018	1.615

$$u(m)_r = \left(\frac{u(m)}{m}\right) \quad ; \quad u(rep)_r \left(\frac{s/\sqrt{3}}{m}\right)$$

Table X: Repeatability of a weighing of 1 g of soil

	Weight (g)									
	1	2	3	4	5	6	7	8	Mean	s
Soil	1.00163	1.00148	1.00097	1.00049	1.00036	1.0002	0.99998	0.9997	1.0006	0.000696

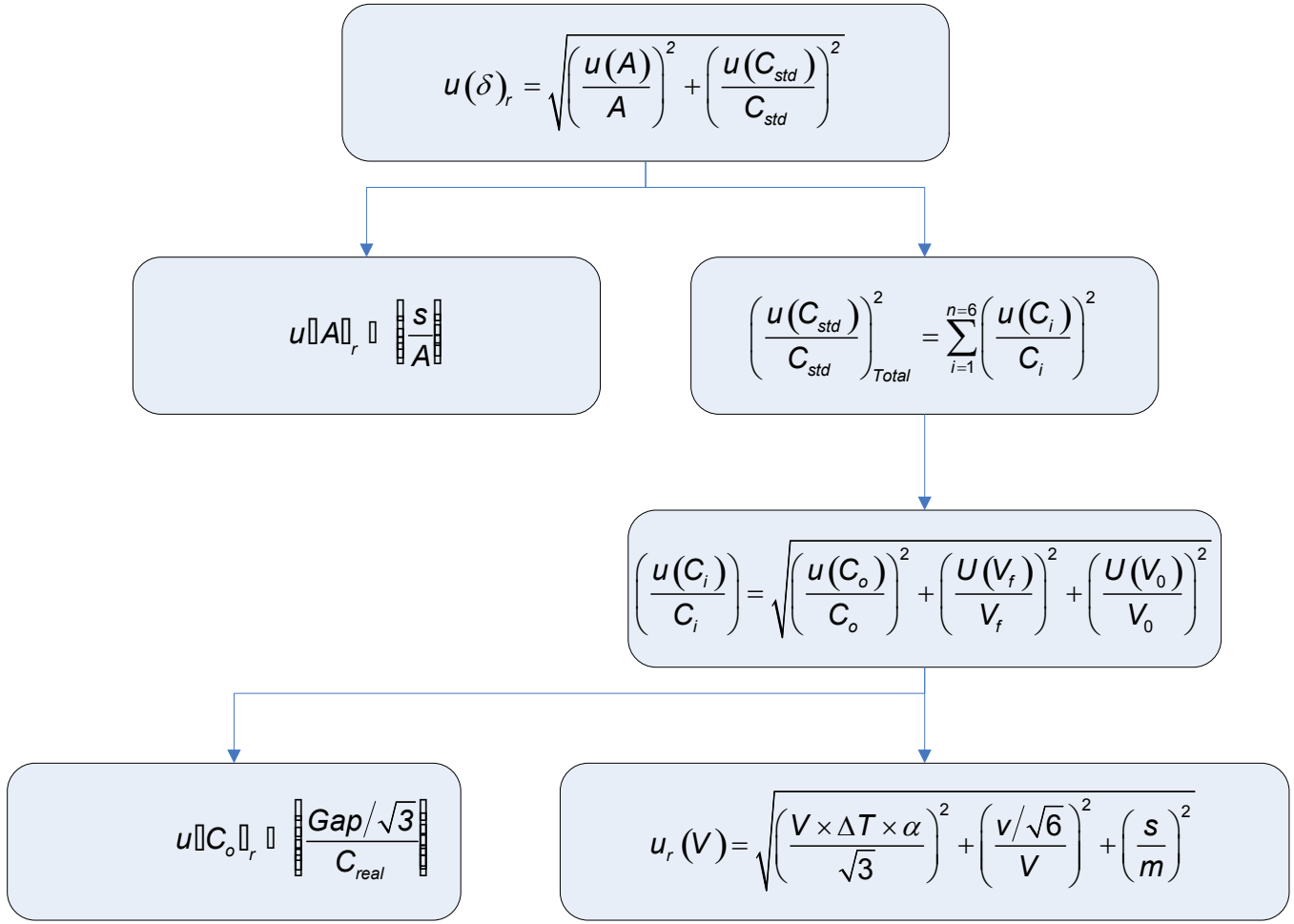

Figure II: Equations to calculate uncertainty of CF

Table XI: Uncertainty of δ: Influence of area.

	Influence of area			
	A	s (n=8)	$u(A)_r$	$(u(A)_r)^2$
	x 10^6 (pA s)	x 10^6 (pA s)	x 10^{-2}	x 10^{-4}
TPH	855	15.2	1.77	3.133
Aliphatic				
$>C_{10} - C_{12}$	45	0.6	1.25	1.562
$>C_{12} - C_{16}$	165	2.2	1.35	1.183
$>C_{16} - C_{21}$	104	0.9	0.83	0.0689
$>C_{21} - C_{35}$	324	4.3	1.34	1.796
$>C_{35}$	26	0.7	2.62	6.864
Aromatic				
$>EC_{10} - EC_{12}$	17	0.4	2.54	6.452
$>EC_{12} - EC_{16}$	62	2.7	4.43	19.62
$>EC_{16} - EC_{21}$	56	2.4	4.28	18.32
$>EC_{21} - EC_{35}$	29	1.3	4.46	19.89
$>EC_{35}$	27	0.8	2.80	7.840

$$u(A)_r = \text{[illegible]}$$

Table XII: Intermediate precision of area of the CRM-372

	Intermediate precision: Area x 10^6 (pA s)									
	1	2	3	4	5	6	7	8	Mean	s
TPH	837	846	841	839	866	871	865	873	855	15.2
Aliphatic										
$>C_{10}$ - C_{12}	44.2	44.4	44.2	43.9	45.1	45.2	44.9	45.4	44.7	0.6
$>C_{12}$ - C_{16}	162	163	163	162	166	167	166	167	165	2.2
$>C_{16}$ - C_{21}	103	104	104	103	105	104	104	105	104	0.9
$>C_{21}$ - C_{35}	318	321	322	320	328	329	326	330	324	4.3
$>C_{35}$	25.2	25.7	26.2	25.2	26.5	26.9	26.8	26.7	26	0.7
Aromatic										
$>EC_{10}$ - EC_{12}	16.0	16.8	17.0	17.0	16.0	16.9	16.3	16.4	17	0.4
$>EC_{12}$ - EC_{16}	58.9	61.0	58.8	60.0	63.9	64.5	64.9	65.0	62	2.7
$>EC_{16}$ - EC_{21}	53.0	54.5	52.9	54.1	57.0	58.1	58.3	58.3	56	2.4
$>EC_{21}$ - EC_{35}	28.2	28.5	27.8	28.1	30.1	30.7	30.4	30.7	29	1.3
$>EC_{35}$	27.5	27.2	26.3	26.3	28.3	28.3	27.6	27.7	27	0.8

Table XIII: Uncertainty of δ: Influence of stock solution

	Influence of stock solution					
	$C_{theorist}$ (mg mL^{-1})	C_{real} (mg mL^{-1})	Gap (mg mL^{-1})	$u(C_0)$ (mg mL^{-1})	$u(C_0)_r$ x 10^{-3}	$(u(C_0)_r)^2$ x 10^{-6}
TPH	1600	15937.8	62.2	35.9	2.25	5.06
Aliphatic						
$>C_{10}$ - C_{12}	1000	994.8	5.2	3.0	3.02	9.12
$>C_{12}$ - C_{16}	2000	1982.4	17.6	10.2	5.13	26.3
$>C_{16}$ - C_{21}	3500	3487.4	12.6	7.3	2.09	4.37
$>C_{21}$ - C_{35}	7000	6979.5	20.5	11.8	1.70	2.89
$>C_{35}$	2500	2493.7	6.3	3.6	1.46	2.13
Aromatic						
$>EC_{10}$ - EC_{12}	100	99.8	0.2	0.1	1.16	1.35
$>EC_{12}$ - EC_{16}	200	197.5	2.5	1.4	7.31	53.4
$>EC_{16}$ - EC_{21}	500	496.5	3.5	2.0	4.07	16.6
$>EC_{21}$ - EC_{35}	500	495	5	2.9	5.83	34.0
$>EC_{35}$	300	297.5	2.5	1.4	4.85	23.5

$$u(C_o)_r = \frac{Gap/\sqrt{3}}{C_{real}}$$

Table XIV: Uncertainty of δ: Influence of volume (contribution of temperature)

Influence of temperature					
Volume (mL)	ΔT (ºK)	α (ºK^{-1})	u(T) (mL)	$u(T)_r$	$(u(T)_r)^2$ Xx 10^{-8}
0.1	5	0.00135	0.0068	0.00 390	15.19
0.05	5	0.00135	0.00034	0.000198	3.796

Table XV: Uncertainty of δ: Influence of volume (contribution of tolerance of syringe)

Influence of tolerance of syringe				
Volume (mL)	Division (mL)	u(Tol) (mL)	$u(Tol)_r$	$(u(Tol)_r)_2$ x 10^{-5}
0.1	0.001	0.00041	0.00408	1.667
0.05	0.0005	0.00020	0.00408	1.667

Table XVI: Uncertainty of δ: Influence of volume (contribution of repeatability)

Influence of repeatability				
Volume (mL)	mass (g)	s (g)	$u(rep)_r$	$(u(rep)_r)^2$ x 10^{-5}
0.1	0.06593	0.000295	0.004476	2.004
0.05	0.03396	0.000125	0.003717	1.381

Table XVII: Repeatability of a weighing of 0.1 mL hexane

	Weight (g)									
	1	2	3	4	5	6	7	8	Mean	s
Syringe	15.5085	15.5085	15.5085	15.5085	15.5085	15.5085	15.5085	15.5085		
Syringe + hexane	15.5757	15.5748	15.5747	15.5742	15.5741	15.5742	15.5745	15.5743		
Hexane	0.06613	0.06628	0.06617	0.06563	0.06559	0.06567	0.06622	0.06575	0.06593	0.000295

Table XVIII: Repeatability of a weighing of 0.05 mL hexane

	Weight (g)									
	1	2	3	4	5	6	7	8	Mean	s
Syringe	12.8827	12.8827	12.8827	12.8827	12.8827	12.8827	12.8827	12.8827		
Syringe + hexane	12.9196	12.9168	12.9165	12.9165	12.9168	12.9166	12.9167	12.9165		
Hexane	0.03402	0.03413	0.03378	0.03385	0.03412	0.03395	0.03399	0.03387	0.03396	0.000125

Table XIX: Uncertainty of δ: Influence of volume (syringe 0.1 mL and 0.05 mL)

	V=0.1 mL				V=0.05 mL			
	$(u(T)_r)^2$ x 10^{-7}	$(u(Tol)_r)^2$ x 10^{-5}	$(u(rep)_r)^2$ x 10^{-5}	$(u(V)_r)^2$ x 10^{-5}	$(u(T)_r)^2$ x 10^{-8}	$(u(Tol)_r)^2$ x 10^{-5}	$(u(rep)_r)^2$ x 10^{-5}	$(u(V)_r)^2$ x 10^{-5}
TPH	1.519	1.667	2.004	3.6862	3.796	1.667	1.381	3.0518
Aliphatic								
$>C_{10}$ - C_{12}	1.519	1.667	2.004	3.6862	3.796	1.667	1.381	3.0518
$>C_{12}$ - C_{16}	1.519	1.667	2.004	3.6862	3.796	1.667	1.381	3.0518
$>C_{16}$ - C_{21}	1.519	1.667	2.004	3.6862	3.796	1.667	1.381	3.0518
$>C_{21}$ - C_{35}	1.519	1.667	2.004	3.6862	3.796	1.667	1.381	3.0518
$>C_{35}$	1.519	1.667	2.004	3.6862	3.796	1.667	1.381	3.0518
Aromatic								
$>EC_{10}$ - EC_{12}	1.159	1.667	2.004	3.6862	3.796	1.667	1.381	3.0518
$>EC_{12}$ - EC_{16}	1.159	1.667	2.004	3.6862	3.796	1.667	1.381	3.0518
$>EC_{16}$ - EC_{21}	1.159	1.667	2.004	3.6862	3.796	1.667	1.381	3.0518
$>EC_{21}$ - EC_{35}	1.159	1.667	2.004	3.6862	3.796	1.667	1.381	3.0518
$>EC_{35}$	1.159	1.667	2.004	3.6862	3.796	1.667	1.381	3.0518

Table XX: Uncertainty of δ: Components of uncertainty for each calibrate solution.

Calibrate solution	$u(C_0)_r$	$u(V_f)_r$	$u(V_0)_r$
1	$u(C_{std})$	$u(V_{100})_r$	-
2	$u(C_{std})$	$u(V_{100})_r$	$u(V_{100})_r$
3	$u(C_{std})$	$u(V_{100})_r$	$u(V_{100})_r$
4	$u(C_{std})$	$u(V_{100})_r$	$u(V_{50})_r$
5	$u(C_{std})$	$u(V_{100})_r$	$u(V_{50})_r$
6	$u(C_{std})$	$u(V_{100})_r$	$u(V_{50})_r$

Table XXI: Uncertainty of δ: Influence of standards of calibrate

	$u(C_1)_r$ x 10^{-3}	$u(C_2)_r$ x 10^{-3}	$u(C_3)_r$ x 10^{-3}	$u(C_4)_r$ x 10^{-3}	$u(C_5)_r$ x 10^{-3}	$u(C_6)_r$ x 10^{-3}	$u(C_{std})_r$ x 10^{-2}
TPH	6.476	8.877	8.877	8.512	8.512	8.512	2.042
Aliphatic							
$>C_{10}$ - C_{12}	6.780	9.101	9.101	8.746	8.746	8.746	2.100
$>C_{12}$ - C_{16}	7.946	10.00	10.00	9.678	9.678	9.678	2.333
$>C_{16}$ - C_{21}	6.420	8.836	8.836	8.470	8.470	8.470	2.031
$>C_{21}$ - C_{35}	6.304	8.752	8.752	8.382	8.382	8.382	2.009
$>C_{35}$	6.244	8.709	8.709	8.337	8.337	8.337	1.998
Aromatic							
$>EC_{10}$ - EC_{12}	6.180	8.864	8.864	8.290	8.290	8.290	1.986
$>EC_{12}$ - EC_{16}	9.501	11.27	11.27	10.99	10.99	10.99	2.659
$>EC_{16}$ - EC_{21}	7.309	9.502	9.502	9.162	9.162	9.162	2.204
$>EC_{21}$ - EC_{35}	8.418	10.38	10.38	10.07	10.07	10.07	2.430
$>EC_{35}$	7.772	9.862	9.862	9.535	9.535	9.535	2.297

$$u\left(C_{std}\right)_r = \sqrt{\sum_{i=1}^{n=6}\left(\frac{u\left(C_i\right)}{C_i}\right)^2}$$

Table XXII: Uncertainty of δ.

	$u(A)_r$ x 10^{-2}	$u(C_{std})_r$ x 10^{-2}	$u(\delta)_r$ x 10^{-2}
TPH	1.773	2.042	2.705
Aliphatic			
$>C_{10}$ - C_{12}	1.250	2.100	2.444
$>C_{12}$ - C_{16}	1.354	2.333	2.695
$>C_{16}$ - C_{21}	0.825	2.031	2.191
$>C_{21}$ - C_{35}	1.340	2.009	2.416
$>C_{35}$	2.616	1.998	2.878
Aromatic			
$>EC_{10}$ - EC_{12}	2.540	1.986	3.227
$>EC_{12}$ - EC_{16}	4.428	2.659	5.166
$>EC_{16}$ - EC_{21}	4.279	2.204	4.811
$>EC_{21}$ - EC_{35}	4.455	2.430	5.074
$>EC_{35}$	2.803	2.297	3.626

$$u(\delta)_r = \sqrt{\left(\frac{u(A)}{A}\right)^2 + \left(\frac{u(C_{std})}{C_{std}}\right)^2}$$

Table XXIII: Uncertainty of recovery.

	Recovery (%)										
	1	2	3	4	5	6	7	8	Mean	s	$u(R)_r$
TPH	120		91	91	87	138	103	78	101	21	0.0738
Aliphatic											
$>C_{10} - C_{12}$	96	113	106	97	109	105	88	106	102	8	0.0279
$>C_{12} - C_{16}$	106	92	87	77	89	88	95	102	92	9	0.0348
$>C_{16} - C_{21}$	102	89	94	87	90	88	91	93	92	5	0.0179
$>C_{21} - C_{35}$	124	113	127	125	120	114	122	124	121	5	0.0148
$>C_{35}$											
Aromatic											
$>EC_{10} - EC_{12}$	148	151	116	174	179	109	154	223	157	36	0.0817
$>EC_{12} - EC_{16}$	109	97	155	69	98	102	87	90	101	25	0.0872
$>EC_{16} - EC_{21}$	108	100	122	80	98	103	92	96	100	12	0.0431
$>EC_{21} - EC_{35}$	123	66	106	53	99	127	121	126	103	29	0.0989
$>EC_{35}$											

$$u(R)_r = \left(\frac{s/\sqrt{n}}{R} \right)$$

Table XXIV: Uncertainty of inhomogeneity.

	mass of hydrocarbons (mg kg^{-1})					
	1	2	3	Mean	s	$u(I)_r$
TPH	824	856	801	827.0	27.62	0.019
Aliphatic						
>C10-C12	6	6	5	5.7	0.58	0.059
>C12-C16	27	29	31	29.0	2.00	0.040
>C16-C21	112	124	115	117.0	6.24	0.031
>C21-C35	316	301	309	308.7	7.51	0.014
>C35	110	100	107	105.7	5.13	0.028
Aromatic						
>EC10-EC12	23	21	24	22.7	1.53	0.039
>EC12-EC16	24	24	22	23.3	1.15	0.029
>EC16-EC21	46	51	41	46.0	5.00	0.063
>EC21-EC35	106	127	121	118.0	10.82	0.053
>EC35	28	25	20	24.3	4.04	0.096

$$u_r(I) = \left(\frac{s/\sqrt{n}}{C_s} \right)$$

		(Area)	(Volume)	(δ)	(m)	(Rec)
	Value	855013091	1	365901	1	101
	Uncertainty	6,27	0,005654	9898	0,0004032	7
Area	855013091	855013097,3	855013091	855013097,3	855013091	855013097,3
Volume	1	1	1,005654	1	1,005654	1
δ	365901	365901	365901	375799	365901	375799
m	1	1	1	1	1,0004032	1
Recovery	101	101	101	101	101	108
Conc. (TPH)	23136	23136	23267	22527	23257	21067
		1,70E-04	1,31E+02	-6,09E+02	1,21E+02	-2,07E+03
U (TPH)$_{comb}$	2165	2,88E-08	1,71E+04	3,71E+05	1,47E+04	4,28E+06

Uncertainty	Value	
u(A)	7,33E-09	
u(V)	5,65E-03	
u(δ)	2,71E-02	
u(m)	4,03E-04	
u(R)	6,93E-02	
u(I)	1,93E-02	
u_c	9,55E-02	10%
Expanded (k=2)		19%

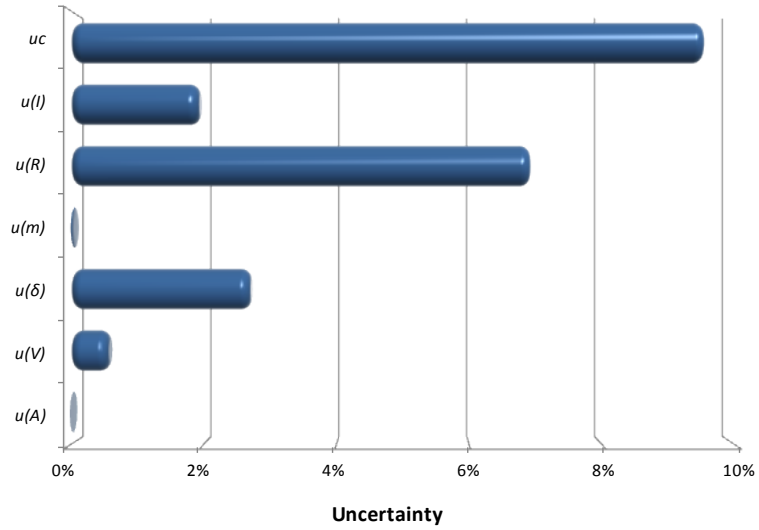

Figure III: Uncertainty combined of TPH.

		(Area)	(Volume)	(δ)	(m)	(Rec)
	Value	44692803	1	537812	1	102
	Uncertainty	4,48	0,005654	13144	0,0004032	5,2
Area	44692803	44692807,48	44692803	44692807,48	44692803	44692807,48
Volume	1	1	1,005654	1	1,005654	1
δ	537812	537812	537812	550956	537812	550956
m	1	1	1	1	1,0004032	1
Recovery	102	102	102	102	102	107,2
Conc. (TPH)	815	815	819	795	819	757
		8,17E-05	4,61E+00	-1,94E+01	4,28E+00	-5,80E+01
U (TPH)$_{comb}$	62	6,67E-09	2,12E+01	3,78E+02	1,83E+01	3,37E+03

Uncertainty	Value	
u(A)	1,0024E-07	
u(V)	5,6540E-03	
u(δ)	2,4440E-02	
u(m)	4,0320E-04	
u(R)	5,0980E-02	
u(I)	5,8820E-02	
u_c	9,5702E-02	10%
Expanded (k=2)		19%

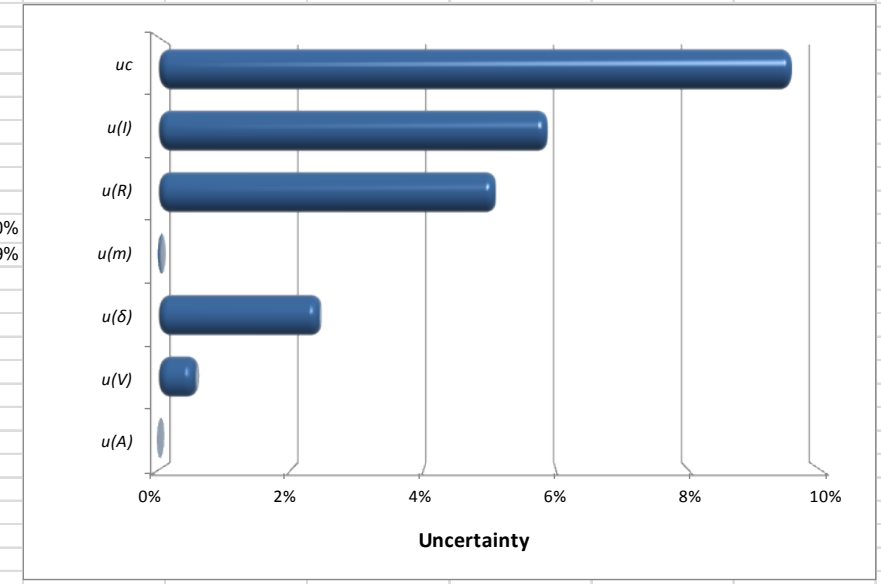

Figure IV: Uncertainty combined of >C_{10} – C_{12} (Aliphatic).

		(Area)	(Volume)	(δ)	(m)	(Rec)
	Value	164792217	1	522472	1	92
	Uncertainty	9,06	0,005654	14081	0,0004032	3,2
Area	164792217	164792226,1	164792217	164792226,1	164792217	164792226,1
Volume	1	1	1,005654	1	1,005654	1
δ	522472	522472	522472	536553	522472	536553
m	1	1	1	1	1,0004032	1
Recovery	92	92	92	92	92	95,2
Conc. (TPH)	3428	3428	3448	3338	3446	3226
		1,88E-04	1,94E+01	-9,00E+01	1,80E+01	-2,02E+02
U (TPH)$_{comb}$	223	3,55E-08	3,76E+02	8,09E+03	3,24E+02	4,09E+04

Uncertainty	Value	
u(A)	5,4978E-08	
u(V)	5,6540E-03	
u(δ)	2,6951E-02	
u(m)	4,0320E-04	
u(R)	3,4783E-02	
u(I)	3,9820E-02	
u_c	7,6236E-02	8%
Expanded (k=2)		15%

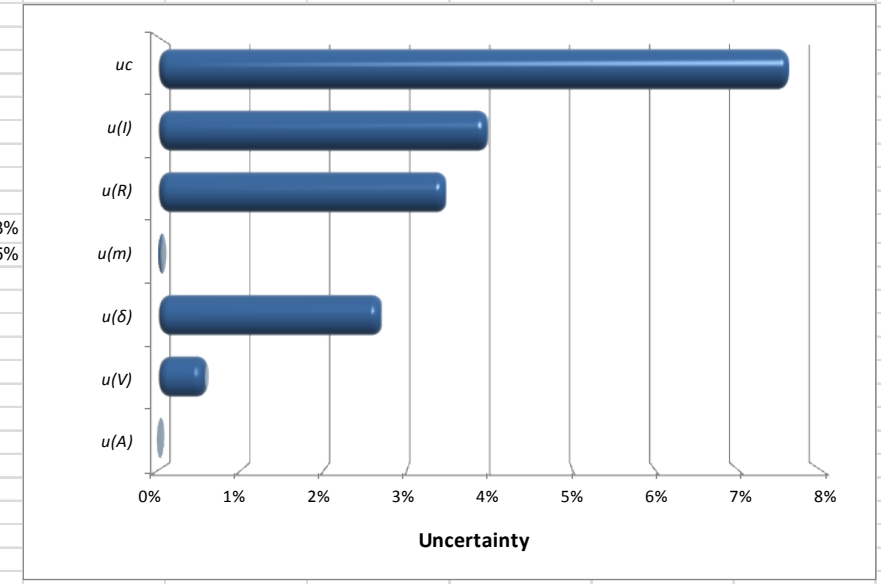

Figure V: Uncertainty combined of >C_{12} – C_{16} (Aliphatic).

		(Area)	(Volume)	(δ)	(m)	(Rec)
	Value	103929069	1	502038	1	92
	Uncertainty	3,68	0,005654	10999	0,0004032	1,8
Area	103929069	103929072,7	103929069	103929072,7	103929069	103929072,7
Volume	1	1	1,005654	1	1,005654	1
δ	502038	502038	502038	513037	502038	513037
m	1	1	1	1	1,0004032	1
Recovery	92	92	92	92	92	93,8
Conc. (TPH)	2250	2250	2263	2202	2262	2160
		7,97E-05	1,27E+01	-4,82E+01	1,18E+01	-9,05E+01
U (TPH)$_{comb}$	104	6,35E-09	1,62E+02	2,33E+03	1,39E+02	8,19E+03

Uncertainty	Value	
u(A)	3,5409E-08	
u(V)	5,6540E-03	
u(δ)	2,1909E-02	
u(m)	4,0320E-04	
u(R)	1,9565E-02	
u(I)	3,0820E-02	
u_c	5,5556E-02	6%
Expanded (k=2)		11%

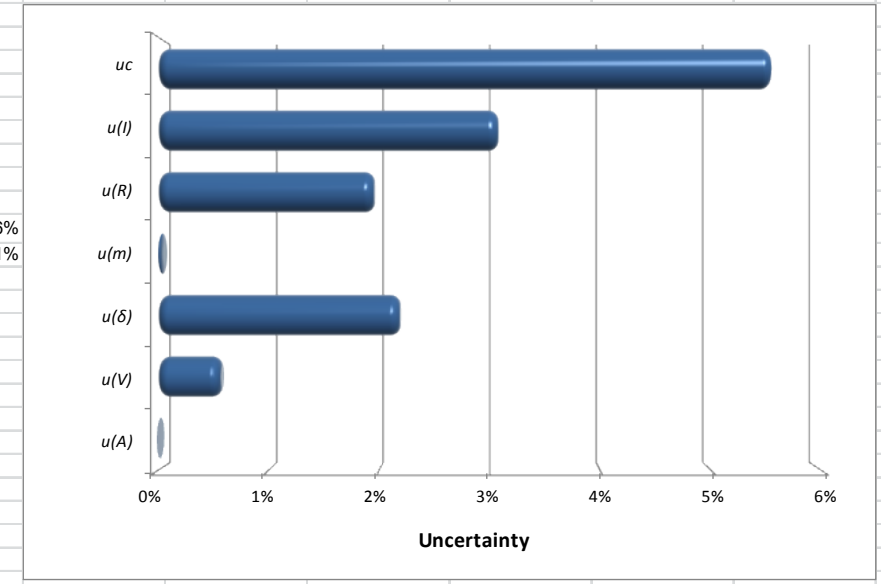

Figure VI: Uncertainty combined of >C_{16} – C_{21} (Aliphatic).

		(Area)	(Volume)	(δ)	(m)	(Rec)
	Value	324312745	1	536472	1	121
	Uncertainty	6	0,005654	12961	0,0004032	1,6
Area	324312745	324312751	324312745	324312751	324312745	324312751
Volume	1	1	1,005654	1	1,005654	1
δ	536472	536472	536472	549433	536472	549433
m	1	1	1	1	1,0004032	1
Recovery	121	121	121	121	121	122,6
Conc. (TPH)	4996	4996	5024	4878	5022	4815
		9,24E-05	2,82E+01	-1,18E+02	2,62E+01	-1,82E+02
U (TPH)$_{comb}$	220	8,54E-09	7,98E+02	1,39E+04	6,88E+02	3,29E+04

Uncertainty	Value	
u(A)	1,8501E-08	
u(V)	5,6540E-03	
u(δ)	2,4160E-02	
u(m)	4,0320E-04	
u(R)	1,3223E-02	
u(I)	1,4040E-02	
u_c	4,6186E-02	5%
Expanded (k=2)		9%

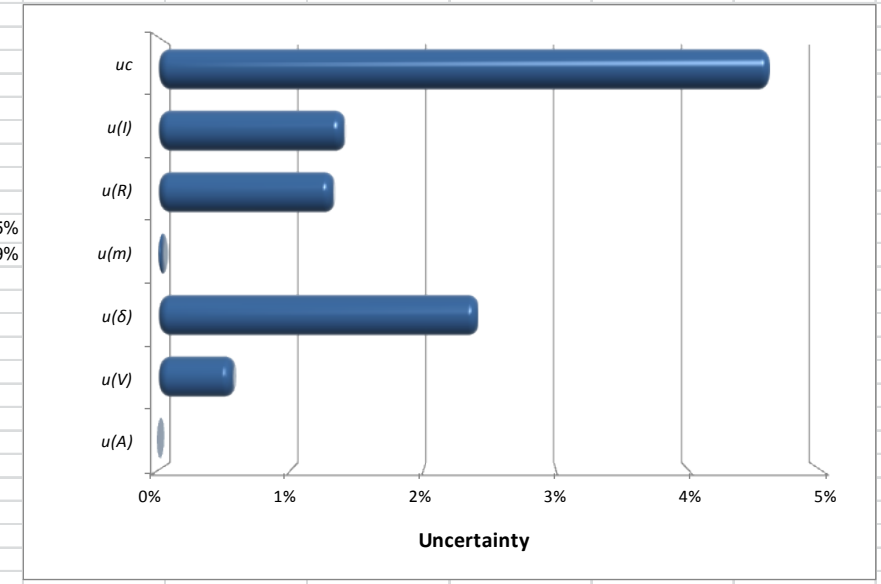

Figure VII: Uncertainty combined of >C_{21} – C_{35} (Aliphatic).

		(Area)	(Volume)	(δ)	(m)	(Rec)
	Value	26132055	1	494263	1	100
	Uncertainty	1,01	0,005654	14225	0,0004032	1,3
Area	26132055	26132056,01	26132055	26132056,01	26132055	26132056,01
Volume	1	1	1,005654	1	1,005654	1
δ	494263	494263	494263	508488	494263	508488
m	1	1	1	1	1,0004032	1
Recovery	100	100	100	100	100	101,3
Conc. (TPH)	529	529	532	514	531	507
		2,04E-05	2,99E+00	-1,48E+01	2,78E+00	-2,14E+01
U (TPH)$_{comb}$	26	4,18E-10	8,94E+00	2,19E+02	7,70E+00	4,57E+02

Uncertainty	Value	
u(A)	3,8650E-08	
u(V)	5,6540E-03	
u(δ)	2,8780E-02	
u(m)	4,0320E-04	
u(R)	1,3000E-02	
u(I)	2,8040E-02	
u_c	5,7136E-02	6%
Expanded (k=2)		11%

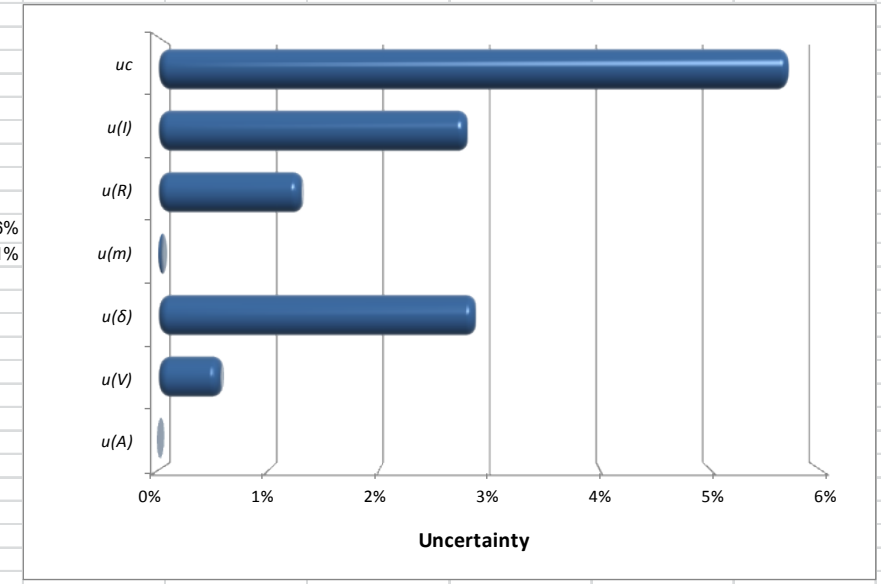

Figure VIII: Uncertainty combined of >C_{35} (Aliphatic).

		(Area)	(Volume)	(δ)	(m)	(Rec)
	Value	16537144	1	586361	1	157
	Uncertainty	0,08	0,005654	18922	0,0004032	12,8
Area	16537144	16537144,08	16537144	16537144,08	16537144	16537144,08
Volume	1	1	1,005654	1	1,005654	1
δ	586361	586361	586361	605283	586361	605283
m	1	1	1	1	1,0004032	1
Recovery	157	157	157	157	157	169,8
Conc. (TPH)	180	180	181	174	181	161
		8,69E-07	1,02E+00	-5,62E+00	9,43E-01	-1,87E+01
U (TPH)$_{comb}$	20	7,55E-13	1,03E+00	3,15E+01	8,89E-01	3,51E+02

Uncertainty	Value	
u(A)	4,8376E-09	
u(V)	5,6540E-03	
u(δ)	3,2270E-02	
u(m)	4,0320E-04	
u(R)	8,1529E-02	
u(I)	3,8100E-02	
u_c	1,1560E-01	12%
Expanded (k=2)		23%

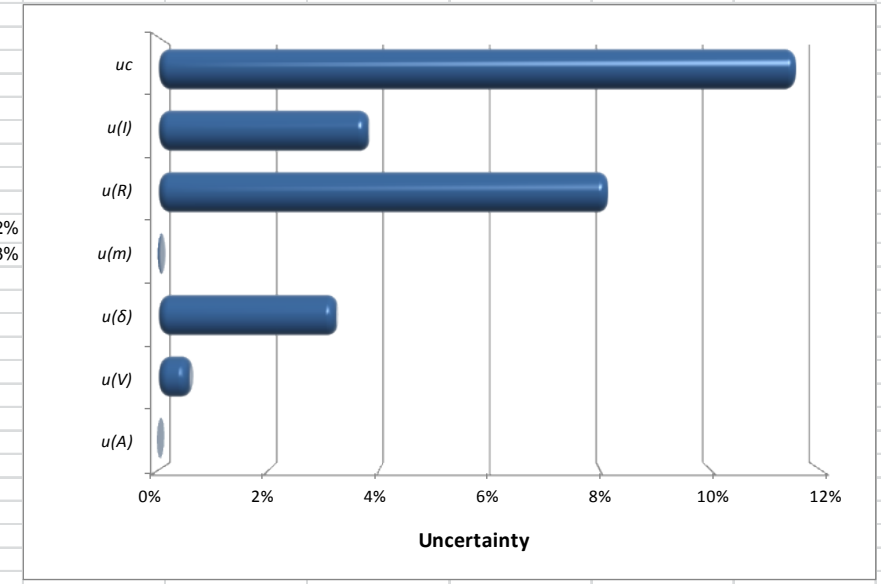

Figure IX: Uncertainty combined of >C_{10} – C_{12} (Aromatic).

		(Area)	(Volume)	(δ)	(m)	(Rec)
	Value	62076714	1	580012	1	101
	Uncertainty	1,64	0,005654	29673	0,0004032	8,8
Area	62076714	62076715,64	62076714	62076715,64	62076714	62076715,64
Volume	1	1	1,005654	1	1,005654	1
δ	580012	580012	580012	609685	580012	609685
m	1	1	1	1	1,0004032	1
Recovery	101	101	101	101	101	109,8
Conc. (TPH)	1060	1060	1066	1008	1065	927
		2,80E-05	5,99E+00	-5,16E+01	5,56E+00	-1,32E+02
U (TPH)$_{comb}$	142	7,84E-10	3,59E+01	2,66E+03	3,09E+01	1,75E+04

Uncertainty	Value	
u(A)	2,6419E-08	
u(V)	5,6540E-03	
u(δ)	5,1159E-02	
u(m)	4,0320E-04	
u(R)	8,7129E-02	
u(I)	2,8570E-02	
u_c	1,3729E-01	14%
Expanded (k=2)		27%

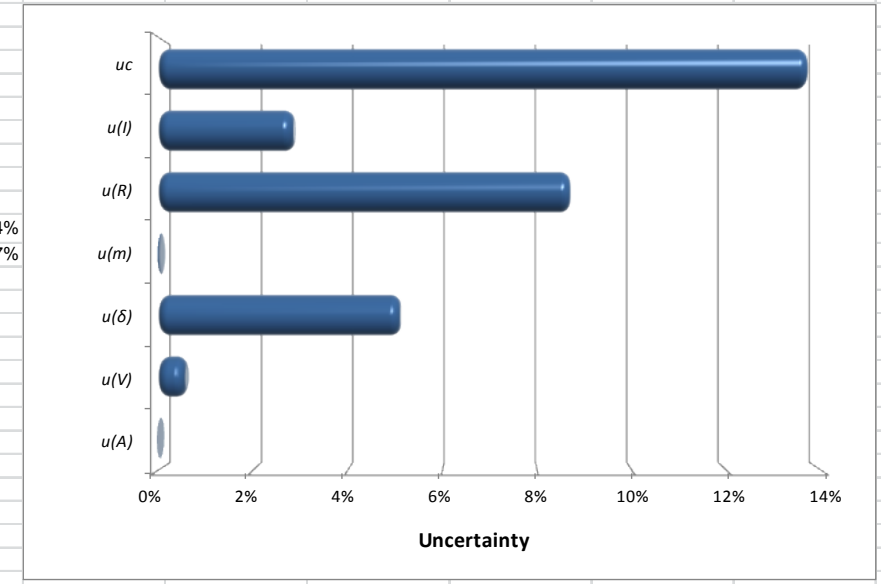

Figure X: Uncertainty combined of >C_{12} – C_{16} (Aromatic).

		(Area)	(Volume)	(δ)	(m)	(Rec)
	Value	55802955	1	559915	1	100
	Uncertainty	0,62	0,005654	26937	0,0004032	4,3
Area	55802955	55802955,62	55802955	55802955,62	55802955	55802955,62
Volume	1	1	1,005654	1	1,005654	1
δ	559915	559915	559915	586852	559915	586852
m	1	1	1	1	1,0004032	1
Recovery	100	100	100	100	100	104,3
Conc. (TPH)	997	997	1002	951	1002	912
		1,11E-05	5,63E+00	-4,57E+01	5,23E+00	-8,49E+01
U (TPH)$_{comb}$	97	1,23E-10	3,18E+01	2,09E+03	2,74E+01	7,22E+03

Uncertainty	Value	
u(A)	1,1111E-08	
u(V)	5,6540E-03	
u(δ)	4,8109E-02	
u(m)	4,0320E-04	
u(R)	4,3000E-02	
u(I)	6,2760E-02	
u_c	1,1563E-01	12%
Expanded (k=2)		23%

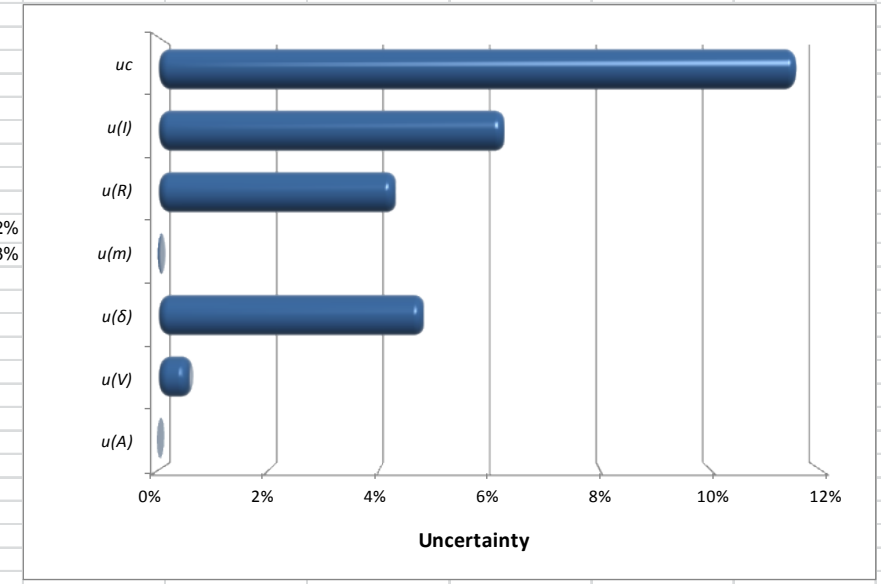

Figure XI: Uncertainty combined of >C_{16} – C_{21} (Aromatic).

		(Area)	(Volume)	(δ)	(m)	(Rec)
	Value	29314817	1	547233	1	103
	Uncertainty	0,33	0,005654	31411	0,0004032	10,1
Area	29314817	29314817,33	29314817	29314817,33	29314817	29314817,33
Volume	1	1	1,005654	1	1,005654	1
δ	547233	547233	547233	578644	547233	578644
m	1	1	1	1	1,0004032	1
Recovery	103	103	103	103	103	113,1
Conc. (TPH)	520	520	523	492	523	448
		5,85E-06	2,94E+00	-2,82E+01	2,73E+00	-7,22E+01
U (TPH)$_{comb}$	78	3,43E-11	8,65E+00	7,97E+02	7,45E+00	5,21E+03

Uncertainty	Value	
u(A)	1,1257E-08	
u(V)	5,6540E-03	
u(δ)	5,7400E-02	
u(m)	4,0320E-04	
u(R)	9,8058E-02	
u(I)	5,2920E-02	
u_c	1,5829E-01	16%
Expanded (k=2)		32%

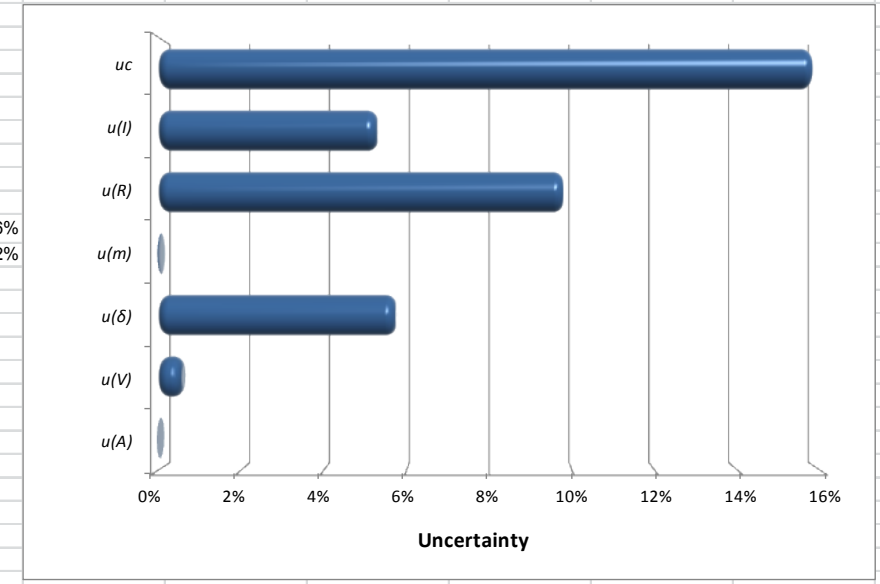

Figure XII: Uncertainty combined of >C_{21} – C_{35} (Aromatic).

		(Area)	(Volume)	(δ)	(m)	(Rec)
	Value	27422572	1	372386	1	100
	Uncertainty	0,53	0,005654	13502	0,0004032	9,9
Area	27422572	27422572,53	27422572	27422572,53	27422572	27422572,53
Volume	1	1	1,005654	1	1,005654	1
δ	372386	372386	372386	385888	372386	385888
m	1	1	1	1	1,0004032	1
Recovery	100	100	100	100	100	109,9
Conc. (TPH)	736	736	741	711	740	647
		1,42E-05	4,16E+00	-2,58E+01	3,87E+00	-8,98E+01
U (TPH)$_{comb}$	94	2,03E-10	1,73E+01	6,64E+02	1,49E+01	8,06E+03

Uncertainty	Value	
u(A)	1,9327E-08	
u(V)	5,6540E-03	
u(δ)	3,6258E-02	
u(m)	4,0320E-04	
u(R)	9,9000E-02	
u(I)	9,5890E-02	
u_c	1,5919E-01	16%
Expanded (k=2)		32%

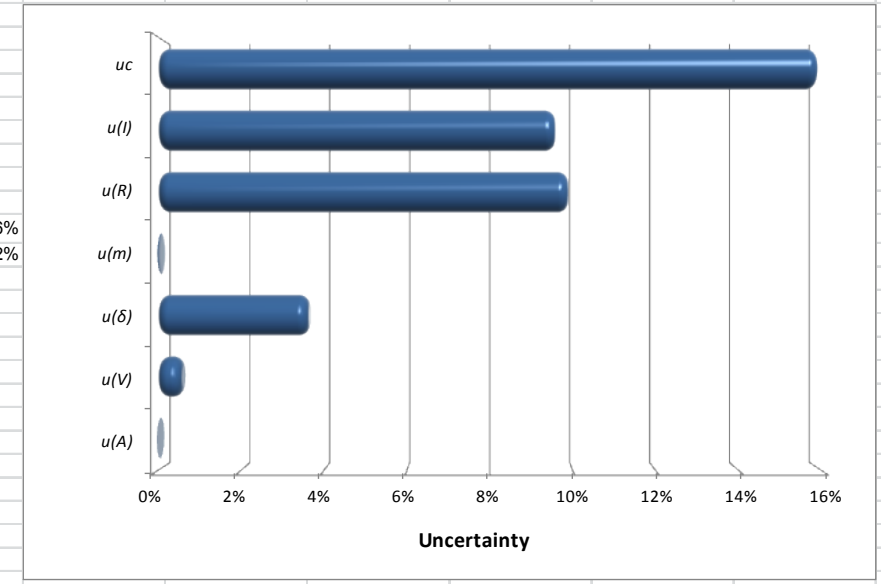

Figure XIII: Uncertainty combined of >C_{35} (Aromatic).