A N N E X E S

A N N E X A

Procedure ISO 16703$_{mod}$ distributed to participants

Udkast til analyseforskrift

Bestemmelse af olieindhold i jord ved gaskromatografi
Modificeret ISO/DIS 16703

Indhold i analyseforskrift

1 ISO/DIS 16703-Mod.

1.1 Titel

Modificeret ISO/DIS 16703 – bestemmelse af olieindhold i jord ved gaskromatografi.

1.2 Jordanalyse

Metoden kan benyttes til bestemmelse af indholdet af total kulbrinter (olieforbindelser), BTEX´er og PAH´er i jordprøver ved anvendelse af gaskromatografi med flammeionisations detektion (GC-FID) og med massespektrometrisk detektion (GC-MS) efter ekstraktion med acetone/pentan.

1.3 Adskillelse af naturlige og petrogene kulbrinter

Metoden kan anvendes til en standardiseret kvantificering af markører for kulbrinter af naturlig og petrogen oprindelse, herunder indhold af kendte naturlige kulbrinter ved GC-FID og GC-MS analyse.

1.4 Anvendelsesområde

Måleområdet fra detektionsgrænse til valideret koncentration:

C6 – C10:	<2,5 - 5000 mg/kg TS
C10 – C25:	<5 - 5000 mg/kg TS
C25 – C 35:	<10 - 5000 mg/kg TS
C35 – C40:	<15 - 5000 mg/kg TS
Samlet:	<20 – 5000 mg/kg TS
BTEX:	<0,01 – 3,33 mg/kg TS
PAH:	<0,005 – 3,33 mg/kg TS

2 Reference

”ISO/DIS 16703 Soil Quality – Determination of Mineral Oil Content by Gas Chromatography – 2001 February”, Draft International Standard. /1/

3 Anvendelsesområde

Metoden kan benyttes til at bestemme indholdet af totalkulbrinter, BTEX og PAH-forbindelser i jord samt petrogene kulbrinter og naturlige kulbrinter.

3.1 Totalkulbrinter

Metoden kan anvendes i forbindelse med kvantificering af olieforurening i jordprøver. Olieforurening omfatter produkter som benzin, gasolie, motorolie og lignende. Olieprodukter består af organiske kulbrinter.

Totalkulbrinter defineres som summen af organiske stoffer, der ekstrahereres fra en given jordprøve ved ekstraktion med acetone/pentan (1:1), samt detekteres med GC-FID. Totalkulbrinterne fra benzen til og med C40 har kogepunkt imellem 80 – 525 °C.

Meget flygtige forbindelser med kogepunkt under 80 °C medregnes således ikke, da de vil skjules under solventtoppen.

Totalkulbrinter beregnes i fire fraktioner som dog opgives i tre fraktioner samt en sum af totalkulbrinter. Fraktionerne opdeles udfra visse n-alkaners kogepunkt.

Resultaterne angives i analyserapporten som følgende fraktioner, jf. tabel 3-1.

Fraktion	Indhold	Detektionsgrænse [mg/kg TS]
1. fraktion	Benzen – C10	<2,5
2. fraktion	> C10 – C25	<5,0
3. fraktion	>C25–C35 + >C35–C40 = > C25-C40	<25
Totalkulbrinter	Benzen–C10 + >C10–C25 + >C25–C40 = Benzen – C40	

Tabel 3-1. Kulbrinte fraktioner.

Metodens lineære måleområde er dokumenteret op til 5000 mg/kg TS. Ved prøver med indhold højere end dette skal ekstraktet fortyndes til en koncentration indenfor måleområdet. Detektionsgrænsen for metoden er bestemt i de enkelte fraktioner, se tabel 3-1.

3.2 BTEX

Enkeltkomponenterne benzen, toluen, ethylbenzen og meta- para- og ortoxylen omtales samlet som BTEX.

BTEX i jord stammer hovedsagelig fra benzinforurening. TEX forekommer i op til 18% pr. enkeltkomponent i benzin /2/. Desuden forefindes BTEX i lavere koncentration i andre olieprodukter og kan f.eks. frigives fra tjære.
BTEX er organiske opløsningsmidler og kan forekomme som enkeltstoffer.
BTEX angives i analyserapporten som enkeltstoffer jf. tabel 3-2.

BTEX	Detektionsgrænse MS [mg/kg TS]
Benzen	<0,01
Toluen	<0,01
Ethylbenzen	<0,01
m- p-xylen	<0,01
o-xylen	<0,01

Tabel 3-2. BTEX.

Metodens lineære måleområde er dokumenteret op til 3,33 mg/kg TS for hver enkeltkomponent. Metodens detektionsgrænse er bestemt på GC- MS og ses i tabel 3-2.

3.3 PAH

Metoden kan benyttes til bestemmelse af Poly Aromatiske Hydrocarboner (PAH). PAH-forbindelser er komponenter i tjære og i mindre mængder i de tungere olieprodukter.

Metoden kan benyttes til bestemmelse af alle 16 US-EPA PAH´er.
De 7 forbindelser som kontrolleres i forbindelse med de danske jordkvalitetskrav der er fastlagt i Vejledning fra Miljøstyrelsen /3/ er et udsnit af disse EPA PAH´er.

16 US-EPA PAH	7 MST PAH
Naphthalen	
Acenaphthylen	
Acenaphthen	
Flouren	
Phenanthren	
Anthracen	
Fluoranthen	Fluoranthen
Pyren	
Benz(a)anthracen	
Chrysen/triphenylen	
Benzo(b+j+k)fluoranthener	Benzo(b+j+k)fluoranthener
Benzo(a)pyren	Benzo(a)pyren
Indeno(1,2,3-cd)pyren	Indeno(1,2,3-cd)pyren
Dibenz(a,h)anthracen	Dibenz(a,h)anthracen
Benzo(ghi)perylen	

Tabel 3-3. PAH-forbindelser.

Reelt er det 18 PAH-forbindelser, da benzo(j)fluoranthen ikke hører til EPA-PAH forbindelserne, men kun meget vanskeligt kan adskilles fra henholdsvis benzo(b)fluoranthen og benzo(k)fluoranthen. Desuden kan chrysen ikke under normale omstændigheder adskilles fra triphenylen, se kapitel 4.

Metodens lineære måleområde er dokumenteret op til 3,33 mg/kg TS for hver PAH-komponent. Metodens detektionsgrænse er bestemt på GC- MS til <0,005 mg/kg TS for hver af de enkelte PAH-forbindelser.

3.4 Kvantificering af petrogene kulbrinter

Metoden kan benyttes til bestemmelse af udvalgte petrogene kulbrinter /7/

Petrogene kulbrinter er komponenter, der indgår i mineralolie, og som er karakteristiske for mineralolie. Følgende petrogene kulbrinter er omfattet af denne analyseforskrift.

Komponent
Sum af naphthalener:
Naphthalen
Methylnaphthalener[1]
Dimethylnaphthalener[2]
Trimethylnaphthalener[3]
Sum af phenanthrener:
Phenanthren
Methylphenanthrener[4]
Dimethylphenanthrener[5]
Hopan(30ab)
Som led i den kvalitative vurdering af prøven kan yderligere bestemmes:
n-Alkaner[6]
Acykliske isoprenoider[7]
Øvrige hopaner[8]

Tabel 3-4. Petrogene kulbrinter.

3.5 Kvantificering af naturlige kulbrinter

Metoden kan benyttes til kvantificering af bidrag af naturlige kulbrinter til totalkulbrinteindholdet jf. /7/.

Metoden omfatter phytosteroler og ulige n-alkaner, der skønnes at stamme fra naturligt forekommende kulbrinter, og som interfererer med totalkulbrinteindholdet (beregnes på baggrund af bestemmelse af n-alkaner C24 - C33).

[1] 2-mehylnaphthalen og 1-methylnaphthalen
[2] 2,6-; 2,7-; 1,3-; 1,7-; 1,6-; 2,3-; 1,4-; 1,5- og 1,2-Dimethylnaphthalen
[3] 1,3,7-; 1,3,6-; 1,3,5-; 1,4,6-; 2,3,6-; 1,6,7- (=2,3,8-); 1,2,7-; 1,2,6-; 1,2,4- og 1,2,5-trimethylnaphthalen
[4] 3-; 2-; 9- og 1-Methylphenanthren
[5] 3,6-; 2,6-; 2,7-; 3,5-; 1,3-; 2,10-; 3,9-; 3,10-; 1,6-; 2,5-; 2,9-; 1,7-; 2,3-; 1,9-; 4,9-; 4,10- og 1,8-Dimethylphenanthren
[6] n-Alkanerne C14; C15; C16; C17; C18; C19; C20; C21; C22; C24; C25; C26; C27; C28; C29; C30; C31; C32; C33 og C34.
[7] Farnesan, nor-pristan, pristan og phytan
[8] Ts, Tm, 29ab, 31abS og 31abR

4 Interferenser

4.1 Totalkulbrinter

Apolære og svagt polære forbindelser f.eks. stammende fra plantemateriale, mosejord eller gammel havbund vil give bidrag til indholdet af totalkulbrinter, og vil interferere på identifikationen af olieproduktet /4/.
Polære fedtstoffer, vegetabilske- og animalske olier der medekstaheres fra en given jordprøve kan give interferens ved kromatografering, men vil være let genkendelig for en erfaren kemiker.
En del af denne interferens kan identificeres og fratrækkes efter analyse ved GC-MS scan /7/.

Chlorerede opløsningsmidler samt andre forbindelse, der ikke er rene kulbrinter, vil blive medbestemt i totalkulbrinteindholdet, men detekteres med lavere respons pga. FI-detektoren svagere respons overfor chlor, ilt mm.

4.2 PAH

Mange PAH-forbindelser har identisk molekylvægt samt en struktur og fysisk-kemiske egenskaber, der ligner hinanden meget. Derfor er det vanskeligt fuldstændigt at undgå interferens i bestemmelsen af PAH. Det er derfor af stor vigtighed, at laboratoriet ved GC-MS-bestemmelsen benytter optimale kromatografiske betingelser for at opnå størst mulig separation mellem muligt interfererende forbindelser /5/.

Da forskellige kromatografiske kolonner har forskellig separation af individuelle PAH-forbindelser, og da separationen desuden er stærkt afhængig af det brugte ovntemperaturprogram, er det op til det enkelte laboratorium at sikre mindst mulig interferens i bestemmelserne. I de tilfælde, hvor interferens ikke kan undgås, bør der angives en sum af de individuelle forbindelser samt klart angives, hvilke forbindelser det drejer sig om. De bedst kendte interferenser på normal GC-kolonner er chrysen og triphenylen samt benzo(b)fluoranthen, benzo(j)fluoranthen og benzo(k)fluoranthen /5/. Disse forbindelser angives normalt som en sum af benzo(b+j+k)fluoranthen og chrysen/triphenylen.

4.3 BTEX

4.3.1 FID

Andre enkeltkomponenter med samme retentionstid kan fejlagtigt identificeres som en af BTEX'erne. F.eks. har cyclohexan og benzen stort set samme retentionstid ved den her anvendte kolonne.

4.3.2 MS

Der er ikke konstateret problemer med interferens på BTEX ved GC-MS.

5 Princip

En prøve af ca. 60 gram jord ekstraheres ved mekanisk rystning med acetone og pentan i 12 – 16 timer. Herefter tilsættes vand og det organiske lag separeres. En passende mængde af dette ekstrakt analyseres til bestemmelse af totalkulbrinter ved anvendelse af kapillar gaskromatografi med flammeionisationsdetektion. En anden del af ekstraktet kan analyseres for BTEX eller PAH ved kapillar gaskromatografi med massespektrometrisk detektion i SIM-mode. Ekstraktet kan yderligere analyseres for petrogene og naturlige kulbrinter ved kapillar gaskromatografi med massespektrometrisk detektion i Scan-mode.

6 Apparatur

6.1 Prøveglas

Der skal anvendes membranglas[9]. Et glas volumen på 100 mL er passende til både jord, opløsningsmidler samt plads til omrystning. Det anbefales at anvende 100 mL Duranglas.

Glasudstyr rengøres[10] ved normal opvask efterfulgt af varmebehandling ved 400-500 °C i min. 2 timer. Renheden af glasvarerne skal være dokumenteret. Der skal en ny membran i glassene imellem hver anvendelse. Membranen skal være teflonbelagt på indersiden.

Det er en fordel at kende glassets vægt, før disse sendes ud til kunden. Således kan denne glasvægt subtraheres fra vægten af det fyldte glas.

6.2 Rysteapparat

Et apparat der anvendes til at ryste prøverne i membranglassene. Det anbefales, at placere glassene i vandret liggende position, mens de rystes, således at de rystes i samme retning som centeraksen af glassene, altså på langs. Det er vigtigt, at anvende kraftig rystning for at opnå ligevægt inden for den angivne ekstraktionstid. Der anbefales en amplitude på 7 cm og en rystefrekvens på 200 slag pr. minut. Andre specifikationer kan være tilfredsstillende, men dette skal valideres af det enkelte laboratorium inden brug.

6.3 Centrifuge

En centrifuge til separation af faserne efter ekstraktion. Det er hensigtsmæssigt, hvis centrifugen har mulighed for at centrifugere membranglassene for at undgå overførsel af prøverne til nyt glasudstyr.

6.4 GC-kolonne

Følgende kolonnedimensioner anbefales: 30 m, 0,25 mm ID og 0,25 µm filmtykkelse, 5 % phenylmethylsiloxan. Kolonner med lav blødning og mulighed for høje temperaturer anbefales.
Under metodeudviklingen er anvendt HP-5MS 19091S-433. Andre kolonner kan benyttes, hvis de lever op til kravene om kromatografisk ydeevne.

[9] Forsynet med et låg, hvori der sidder et septum, som tillader at opløsningsmidler injiceres igennem membranen.
[10] Med mindre der anvendes engangsglasvarer.

6.5.1 GC-FID

Gaskromatografisk system med kapillarkolonne og flammeionisationsdetektor (FID). FID er karakteristisk ved, at alle kulbrinter stort set giver samme respons, hvilket er essentielt for metodens anvendelighed. GC-system med temperatur- og trykstyring, kapillarkolonne og splitless injektion anbefales. Et datasystem til beregning af kromatografiske arealer ved brug af tvungen basislinieprojektion, og som er i stand til at gemme og reintegrere kromatografiske data bør benyttes.

Instrument	GC	Program
GC-FID	HP6890 SERIE PLUS	Chemstation A.07.01 (682)

Tabel 6-1. Det anvendte apparatur under metodeudvikling.

6.5.2 GC-MS

Et gaskromatografisk system med kapillarkolonne og massespektrometrisk detektion (MS). MS er karakteristisk ved at detektere ioner i forhold til deres masse/ladningsforhold (m/z), hvilket gør detektionen mere specifik i forhold til enkeltstoffer.

GC-system bør have temperaturstyring, splitless injektion og anvende kapillarkolonne. Trykstyring af bæregassen anbefales for bedre reproducerbarhed. Massespektrometret skal have mulighed for anvendelse af SIM (single ion monitoring) og Scan (scaning over alle ioner) samt være tilkoblet et datasystem, der tillader dataopsamling og lagring af alle data, der optages i det kromatografiske forløb. Datasystemet skal kunne søge datafilerne for ioner med specifikke masser og skal kunne udskrive ionresponset i forhold til tiden eller scan-nummer. Datasystemet skal kunne integrere såvel som reintegrere signalet for ethvert udtrukket ionspor.

Instrument	GC	MS	Program
GC-MS	HP 6890 N	MS Detektor 5973 Network	MSD software C.00.01

Tabel 6-2. Det anvendte apparatur under metodeudvikling.

7 Standarder og kontrol

7.1 Kemikalier

De anvendte kemikalier skal være af analytisk renhedsgrad og velegnede til formålet.

- Acetone
- n-Pentan
- Vand
- Monobrombenzen
- O-terphenyl
- Squalan

Såfremt der foretages bestemmelse ved GC-MS anvendes yderligere:

- Phenanthren-d10
- Fluoranthen-d10
- Benzo(a)pyren-d12

Der anbefales brug af færdigkøbte ampuller[11] som kalibreringsstandarder og kontrolopløsninger. De nævnte ampuller har været anvendt under metodeudviklingen, men tilsvarende ampuller kan sandsynligvis anvendes uden yderligere afprøvning.

- Florida TRPH standard, Restek Cat.#31266
- BTEX/Naphthalen Standard, Restek Cat.#58361
- Mineral oil Standard, BAM KS 5004
- Custom BTEX/Naphtalene standard, Restek Cat.#57366
- SV Calibration Mix, Restek Cat.#31011
- PAH mixture, Agilent Technologies Cat.: 8500-6035

7.2 Ekstraktionsopløsninger

7.2.1 Afprøvning af opløsningsmidler

Der anvendes pentan og acetone af analysekvalitet. Når pentanen og acetonen modtages på laboratoriet afprøves deres renhed med hensyn til BTEX og PAH. Vandet, der anvendes, afprøves sammen med acetonen.

7.2.1.1 Pentan

Der fyldes en vial med pentan, som analyseres på GC-FID og GC-MS efter metoderne beskrevet i afsnit 8 og 10. Pentanen kan godkendes til analyse, når den ikke indeholder BTEX eller PAH i koncentrationer over detektionsgrænsen for hver enkelt komponent.

[11] Med certifikater.

7.2.1.2 Acetone og vand
20 mL acetone håndrystes med 20 mL afprøvet pentan i ca. 1 min. Der tilsættes 30 mL vand, og der rystes 1 min. Der tappes en vial fra pentanfasen, som analyseres på GC-FID og GC-MS efter metoderne beskrevet i afsnit 8 og 10. Acetonen og vandet kan godkendes til analyse, når den pentan, det er rystet med, ikke indeholder BTEX eller PAH i koncentrationer over detektionsgrænsen for hver enkelt komponent. Hvis der opstår problemer i forhold til dette, afprøves acetonen og vandet hver for sig.

7.2.2 Stamopløsning af intern standard

De interne standarder, der anvendes til bestemmelse på GC-FID er monobrombenzen, o-terphenyl og squalan.
De interne standarder der anvendes til bestemmelse af PAH på GC-MS er phenanthren-d10, fluoranthen-d10 og benzo(a)pyren-d12.

7.2.2.1 IS Stamopløsning GC-FID (IS Stam 1, 2 og 3)
Der afvejes 1 gram af henholdsvis monobrombenzen, o-terphenyl og squalan til hver sin 100 mL målekolbe. De nøjagtige afvejede mængder noteres. Målekolberne fyldes til mærket med afprøvet pentan (7.2.1.1). De tre stamopløsninger kaldes henholdsvis *IS Stam 1, 2 og 3*.
Koncentrationen i hver opløsning er 10000 mg/L.

7.2.2.2 IS Stamopløsning GC-MS (IS-MS)
Der afvejes 0,1 gram af henholdvis phenanthren-d10, fluoranthen-d10 og benzo(a)pyren-d12 i samme 100 mL målekolbe. Den nøjagtige afvejede mængde noteres. Målekolben fyldes til mærket med afprøvet pentan (7.2.1.1). Koncentrationen i opløsningen *IS-MS* er 1000 mg/L.

7.2.2.3 Intern standard opløsning (IS-opl.)
En 100 mL målekolbe fyldes halvt med afprøvet pentan (7.2.1.1). Der udtages med fuldpipette 1 mL af hver af *IS Stam 1, 2 og 3* (7.2.2.1) samt 1 mL af *IS-MS* (7.2.2.2) som tilsættes ned i pentanen i en100 mL målekolbe. Målekolben fyldes op til mærket med afprøvet pentan og mærkes *IS-opl*.
Koncentrationen i opløsningen er 100 mg/L.

7.2.3 Pentan med intern standard (Pentan IS)

En 2000 mL målekolbe fyldes halvt op med afprøvet pentan (7.2.1.1). Der tilsættes 1 mL af hver af *IS Stam 1, 2 og 3* (7.2.2.1) samt 1 mL af *IS-MS* (7.2.2.2) ned i pentanen i 2000 mL målekolbe. Målekolben fyldes op til mærket med afprøvet pentan.

Koncentration i opløsningen er 5 mg/L for de interne standarder til FID og 0,5 mg/L for de interne standarder til MS[12].

Det er vigtigt at Pentan IS (7.2.3) og IS opl. (7.2.2.3) er fremstillet ud fra samme Stam (7.2.2.1) og IS-MS (7.2.2.2).

7.2.4 Blindprøver

7.2.4.1 Sekvensblind
Der fyldes en række vials af den til prøverne anvendte pentan IS (7.2.3). Disse opbevares på køl indtil analysetidspunktet.

[12] Dette gør sig også gældende for alle standarder og kontroller.

7.2.4.2 Metodeblind
Der udrystes mindst et prøveglas om dagen, præcis som om det var en prøve (8.2). Pentanen aftappes og analyseres som en prøve. Denne må ikke give indhold over detektionsgrænsen for de enkelte parametre.

7.3 Totalkulbrinter og BTEX

7.3.1 Standard totalkulbrinter og BTEX (STD-opl.)

En ampul af Florida TRPH standard, Restek Cat.#31266 konc. 500 mg/L og en ampul BTEX/Naphthalene Standard, Restek Cat.#58361 konc. 2000 mg/L tempereres til stuetemperatur.

7.3.1.1 STD-opl.
En 100 mL målekolbe fyldes halvt med afprøvet pentan (7.2.1.1). Der afpipetteres med fuldpipette 1 mL af Florida-ampullen og 250 µL af BTEX-ampullen over i 100 mL målekolbe. Der afpipetteres 5 mL af *IS-opl.* (7.2.2.3) over i 100 mL målekolben. Der fyldes op med afprøvet pentan til mærket. Koncentration af *STD-opl.* er 5 mg/L. Denne hældes på vials uden headspace over væsken. Opbevares på køl indtil analyse.

7.3.2 Kontrol totalkulbrinter (KNT-opl.)

7.3.2.1 Stamopløsning knt.:
En ampul af Mineral oil Standard, BAM KS 5004 tempereres til stuetemperatur. Der afvejes ca. 0,8 g Mineral oil Standard i en 100 mL målekolbe. Den nøjagtige vægt noteres. Målekolben fyldes til mærket med afprøvet pentan (7.2.1.1). Kolben rystes omhyggeligt. Koncentrationen af olien i *Stamopløsning knt.* er ca. 8000 mg/L.

7.3.2.2 KNT-opl:
En 100 mL målekolbe fyldes halvt med afprøvet pentan (7.2.1.1). Der udtages med fuldpipette 10 mL af tempereret *stamopløsning knt.* til 100 mL målekolben. Der afpipetteres 5 mL af *IS-opl.* (7.2.2.3) over i 100 mL målekolben. Der fyldes op med afprøvet pentan til mærket. Koncentrationen af *KNT-opl* er ca. 800 mg/L, koncentrationen skal beregnes nøjagtigt, før indsættelse i kontrolkort. *KNT-opl.* hældes på vials uden headspace over væsken. Opbevares på køl indtil analyse.

7.3.3 Kontrol BTEX (BTEX-knt.)

En ampul af Custom BTEX/Naphthalen standard, Restek Cat.#57366 konc. 200 mg/L tempereres til stuetemperatur.

7.3.3.1 BTEX-knt.
En 100 mL målekolbe fyldes halvt op med afprøvet pentan (7.2.1.1). Der udtages 500 µL af BTEX ampullen til 100 mL målekolbe. Der afpipetteres 5 mL af *IS-opl.* (7.2.2.3) over i 100 mL målekolben. Der fyldes op med afprøvet pentan til mærket. Koncentrationen af *BTEX-knt* er 1,0 mg/L pr. enkeltkomponent. *BTEX-knt.* hældes på vials uden headspace over væsken. Opbevares på køl indtil analyse.

7.4 PAH på GC-MS

7.4.1 Standard og kontrol PAH-forbindelser (PAH-STD)

En ampul af (PAH'er) SV Calibration Mix, Restek Cat.#31011 med konc. 2000 mg/L tempereres til stuetemperatur.

7.4.1.1 PAH-std.
En 200 mL målekolbe fyldes halvt op med afprøvet pentan (7.2.1.1). Der udtages 500 µL af PAH ampullen til 200 mL målekolbe. Der tilsættes 1 mL af *IS-MS* (7.2.2.2) over i 200 mL målekolben. Der fyldes op med afprøvet pentan til mærket. Koncentrationen af *PAH-std* er 5,0 mg/L pr. enkeltkomponent. *PAH-std*. hældes på vials uden headspace over væsken. Opbevares på køl indtil analyse.

7.4.1.2 PAH-knt.
En ampul af PAH mixture, Agilent Technologies Cat.: 8500-6035 med konc. 501 mg/L tempereres til stuetemperatur.

En 100 mL målekolbe fyldes halvt op med afprøvet pentan (7.2.1.1). Der udtages 200 µL af PAH mixture til 100 mL målekolbe. Der tilsættes 500 µL af *IS-MS* (7.2.2.2) over i 100 mL målekolben. Der fyldes op med afprøvet pentan til mærket. Koncentrationen af *PAH-knt* er 1,0 mg/L pr. enkeltkomponent. *PAH-knt*. hældes på vials uden headspace over væsken. Opbevares på køl indtil analyse.

7.5 Petrogene kulbrinter

7.5.1 Standarder

Ampuller kan erhverves ved. f. eks. Chiron, Restek eller tilsvarende.

Komponent	Ampul
Naphthalen	Se PAH standard 7.4.1.1
Methylnaphthalener (MN)	1- og 2-Methylnaphthalen. Ampuller af 1,0 mg/ml fra Chiron i isooctan (0811,15 og 0812,15)
Dimethylnaphthalener (DMN)	2,6-Dimethylnaphthalen. Ampul 1,0 mg/ml fra Chiron i isooctan (0729,12)
Trimethylnaphthalener (TMN)	2,3,5-Trimethylnaphthalen. Ampul 1,0 mg/ml fra Chiron i isooctan (0706,13)
Phenanthren	Se PAH standard 7.4.1.1
Methylphenanthrener (MP)	2-Methylphenanthren. Ampul 1,0 mg/ml fra Chiron i isooctan (0812,15)
Dimethylphenanthrener (DMP)	3,6-Dimethylphenanthren. Ampul 0,5 mg/ml fra Chiron i isooctan (0768,16)
n-Alkaner	S-4066 Hydrocarbon mixture C14-C32 fra Chiron 1,00 mg af hver i 1 ml isooctan og Florida TRPH standard, Restek Cat.#31266 konc. 500 mg/L
Acykliske isoprenoider	indgår i S-4066 Hydrocarbon mixture
Hopaner	17α(H),21β(H)-Hopan (30ab) ampul fra Chiron 1 ml i isooctan, 0,1 mg/ml

Tabel 7-1. Petrogene kulbrinter.

7.5.1.1 Petrogen kulbrintestandard
En 50 mL målekolbe fyldes halvt op med pentan IS (7.2.3). Der udtages 500 µL af MN, DMN, TMN, MP og DMP-ampullerne samt S-4066 (tabel 7-1) i 50 mL målekolbe. Der fyldes op med afprøvet pentan til mærket. Koncentrationen af *Petrogen kulbrintestandard* fremgår af tabel 7-2.

Komponent	Koncentration i Petrogen kulbrintestandard
1- og 2-Methylnaphthalen	10 mg/L
2,6-Dimethylnaphthalen	10 mg/L
2,3,5-Trimethylnaphthalen	10 mg/L
2-Methylphenanthren	10 mg/L
3,6-Dimethylphenanthren	5 mg/L
n-Alkaner	10 mg/L, Florida TRHP standard se 7.3.1.1 (5 mg/L)
Acykliske isoprenoider	10 mg/L
17α(H),21β(H)-Hopan (30ab)	1,0 mg/L

Tabel 7-2. Koncentration af petrogene kulbrinter.

7.5.2 Kontroller

7.5.2.1 Fuelolieopløsning

Fremstil opløsning med fuelolie til kontrol af retentionstider. Denne opløsning kan også anvendes til kontrol ved gentagne målinger.

Afvej 100 mg fuelolie i en 100 ml målekolbe. Fyld op til mærket med pentan IS. Koncentration 1000 mg/L.

8 Ekstraktionsprocedure

8.1 Prøven

8.1.1 Prøveudtagning

Der henvises til Miljøstyrelsen: Vejledning om prøveudtagning og analyse af jord /3/.

Efter udtagning af en jordprøve overføres den hurtigt til en membranglas, der lukkes umiddelbart herefter. Det er vigtigt at sikre, at glaskanten og gevindet er fri for jordpartikler, for at sikre en tæt lukning af membranglasset. Prøveudtagningskeen skal have en diameter, som er mindre end åbningen af membranglasset for at forhindre partikler på glaskant og gevind.

Det anbefales at anvende 100 mL membranglas f.eks. af typen redcap-glas. Der tilsættes jord så glasset omtrent halvfuldt, hvilket svarer til en prøvemængde på ca. 60 g. Tørstofindholdet heri vil ca. svare til 50 g.

Membranglasset må maksimalt fyldes halvt op for at tillade tilsætning af opløsningsmiddel og vand, og for at sikre tilfredsstillende bevægelser i forbindelse med ekstraktionen.

Der skal udtages en parallel prøve til bestemmelse af tørstof. Hertil kan enhver tætsluttende emballage benyttes. Tørstof bestemmes i henhold til DS 204, idet der tages en større mængde jord i anvendelse 10-20 g.

Endvidere kan det anbefales at udtage en eller flere parallelle prøver til yderligere undersøgelser eller som ekstra prøve i tilfælde af uforudsete problemer.

8.1.2 Forholdsregler

Jordprøven skal ankomme til laboratoriet i 100 mL membranglas f.eks. af typen redcap-glas. Kunden skal have fyldt glasset omtrent halvfuldt, svarende til en prøvemængde på ca. 60 g. Tørstofindholdet heri vil ca. svare til 50 g.

Der skal desuden medfølge en delprøve til tørstofbestemmelse.

Hvis prøver modtages i anden emballage end membranglas, skal dette opgives på analysecertifikatet, idet tab af flygtige forbindelser kan forventes i forbindelse med prøvehåndteringen.

Hvis mængden af jordprøve er for lille, under 30 g, skal det kommenteres på analysecertifikatet. Eventuelt skal detektionsgrænsen hæves.

Hvis prøven er på mere end 100 g, skal beholderen åbnes og overskydende jord fjernes, således at der gøres plads til opløsningsmidler samt sikres plads til optimal omrystning. Dette skal rapporteres sammen med resultaterne.

8.1.3 Opbevaring

Prøven skal opbevares ved ca. 4 °C i mørke. Prøven skal transporteres til laboratoriet så hurtigt som muligt og inden for 1 døgn efter udtagning.

8.2 Ekstraktionsproceduren

Ekstraktion af prøverne skal påbegyndes indenfor et døgn efter modtagelse på laboratoriet.

8.2.1 Afvejning

Jordprøverne foreligger i 100 mL membranglas f.eks. af typen Duranglas, hvor kunden har fyldt glasset omtrent halvfuldt, hvilket svarer til en prøvemængde på ca. 60 g.

Det halvt fyldte membranglas vejes og mængden af jord bestemmes ved at subtrahere glasvægten. Hvis glasvægten ikke kendes, vejes den tomme flaske efter ekstraktion, rengøring og tørring. Det er en fordel, at kunden anvender forvejede glas.

Hvis prøver modtages i en anden type beholder, afvejes der 60 g prøve i et 100 mL membranglas. Det skal sikres ved homogenisering at prøven repræsenterer den samlede prøve, og der udtages delprøver jævnt fordelt over den totale prøve.

8.2.2 Tilsætning af acetone/pentan

Der injiceres 20 mL af den afprøvede acetone (7.2.1.2) til prøven gennem membranen i låget. Ryst glasset kort i hånden. Injicer 20 mL pentan med intern standard (7.2.3) til prøven gennem membranen[13]. Skru låget af og skift membranen. Dette sikrer, at glasset er helt tæt under udrystning. Ryst glasset kraftigt i hånden, indtil en ensartet suspension er nået[14].

8.2.3 Rystning

Glassene lægges ned på langs på rysteapparatet og spændes fast. Rysteapparatet indstilles på en rystefrekvens 200 slag pr. min. med en amplitude på 7 cm. Prøverne rystes i 12 til 16 timer. Derefter tages de af rysteapparatet og tappes umiddelbart herefter.

8.2.4 Aftapning

Når prøverne er taget af rysteapparatet tilsættes 30 mL vand (7.2.1.2). Prøverne rystes 1 min. og henstilles et kort øjeblik. Ved mange prøver dannes en fri klar pentanfase øverst i glasset, denne kan umiddelbart tappes i vials. I andre tilfælde kan det være nødvendigt at centrifugere glasset for at få faserne til at adskille.

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[13] Det er muligt, at låget kan tages af et kort øjeblik, når pentanen tilsættes. Dette er ikke afprøvet under metodeudviklingen.

[14] For visse jordtyper samt referencematerialer kan det være nødvendigt at tilsætte ekstra acetone eller vand for at opnå suspension.

Der aftappes det antal vials, der skal benyttes til analysen[15] samt en ekstra til opbevaring. Vials opbevares på køl indtil analysetidspunktet.

[15] Afhængigt af antal analyseparametre.

9 Fremgangsmåde for totalkulbrinter og BTEX ved GC-FID

9.1 Klargøring og kalibrering af GC-FID

9.1.1 Klargøring/opstart af GC

Gaskromatografen skal være klargjort og vedligeholdt før opstart af prøvesekvens. Injektionsnålen skal være ren og skylleskålene fyldt op. Det anbefales at skifte liner dagligt samt skære 1-2 cm af kolonnen dagligt. Guldpladen skal være ren og uden ridser. Kolonnen skal opretholde tilfredsstillende adskillelse af enkeltkomponenter[16], samt have minimal kolonne blødning.

9.1.2 Metode/betingelser

Der skal vælges betingelser, så der opnås en tilfredsstillende kromatografering af hele området fra benzen til n-alkan C_{40}.

Kravene til ydeevne er:

- Der skal kunne opnås ensartet respons for de enkelte n-alkaner i hele det kromatografiske område. Enkelttoppene skal have en pæn kromatografisk form. Bedømmes visuelt.
- 2. fraktion kvantificeres overfor summen af C12, C16, C20 og C24.
  3. fraktion kvantificeres overfor C28, C30, C32 og C34.
  4. fraktion kvantificeres overfor C36 og C38. Det stillede krav er, at det laveste respons indenfor et interval skal udgøre mindst 2/3 af det største.
- Der må ikke være uhensigtsmæssig diskriminering af tungere forbindelser. Arealet af C40 skal udgøre mindst 60% af arealet for C20.

I tabel 9-1 ses GC-programmet, anvendt under metodeudviklingen.

Betingelser	GC-FID
Injektionsbetingelser	350 °C Tryk 11,7 psi. Splitless-tid 1,0 min. Helium som bæregas.
Ovnprogram	Starttemp 35 °C. Starttemp holdes 3 min, herefter 15 °C/min til 315 °C. Sluttemp holdes 18 min.
Kolonne	HP5 MS 30.0 meter 250 µm ID 0,25 µm filmtykkelse. Flow 1,0 ml/min
Detektor	Temperatur 315 °C Hydrogen 30 ml/min. Luft 400 ml/min. Makeup 30 ml/min.

Tabel 9- 1. GC-metoden, der anbefales.

[16] Kontrolleres let ved adskillelse af C17-pristan og C18-phytan.

9.1.3 Sekvens/prøveserie

Det anbefales at analysere en *sekvensblind (7.2.4.1),* en *STD-opl.* (7.3.1.1), en *KNT-opl.* (7.3.2.2) og en *BTEX-knt*[17]. (7.3.3.1) først og sidst i hver prøveserie. Desuden en sekvensblind efter 10 prøver. Der er erfaring for, at en sekvens ikke bør være længere end 20 prøver af hensyn til GC'ens performance. Der skal for hver serie ekstraktioner analyseres en *metodeblind (7.2.4.2).*

9.1.4 Kalibrering og kontrol

9.1.4.1 Totalkulbrinter
Det kontrolleres, at:

- der ikke er megen kolonneblødning eller overslæb på blindprøverne.
- forholdet af C40/C20 i standarden (*STD-opl.* (7.3.1.1)) er mindst 60%.
- indholdet i kontrolprøven (*KNT-opl.* (7.3.2.2)) giver 80-120% af nominel værdi[18].

9.1.4.2 BTEX på GC-FID
Det kontrolleres, at:

- der ikke er indhold af BTEX i blindprøverne højere end detektionsgrænsen.
- arealet af de enkelte BTEX'er i standarden (*STD-opl.* (7.3.1)) er fornuftige i forhold til hinanden. Arealet af toluen ≅ ethylbenzen ≅ ½*m-p-xylen ≅ o-xylen, benzen ned til 80% af de andre.
- indholdet i kontrolprøven *BTEX-knt.*(7.3.3.1) giver 80-120% af nominel værdi.

9.2 Resultater

9.2.1 Beregning

9.2.1.1 Total kulbrinter
Retentionstiden for benzen, C10, C25, C35 og C40 i standarden *(STD-opl.* (7.3.1)) findes. Disse tider plus 0,2 min[19] benyttes til at opdele kromatogrammet af prøver og blindprøver i fraktioner.
Responset af en given prøve fratrækkes metodeblind (7.2.4.2) og arealerne af de interne standarder inden koncentrationen beregnes. Dette gøres for de enkelte fraktioner.

Indholdet i prøverne beregnes efter følgende formel.

$$\text{Indhold}\,[\text{mg/kg TS}] = \frac{(A_{frak.} / A_{ISfrak.}) * C_{std} * V_{ext} * 100}{(A_{std.} / A_{ISstd.}) * m * TS\%}$$

Hvor,

$A_{frak.}$	:	Arealet for den pågældende fraktion.
$A_{IS\ frak.}$	:	Arealet for den interne standard i pågældende fraktion.
$A_{std.}$	:	Summen af arealet for de n-alkaner, der hører til pågældende fraktion, se tabel 9-2.

[17] Kun nødvendigt hvis der skal kvantificeres BTEX på prøverne.
[18] Beregnet udfra den nøjagtige afvejede mængde.
[19] Benzen minus 0,2 min.

$A_{IS\ std.}$: Arealet for den tilsvarende interne standard i standarden.
$C_{std.}$: Koncentrationen af standarden i mg/L
V_{ext} : Volumen af ekstraktionsmiddel i mL
m : Prøvens vægt i gram
TS % : Procent tørstof

Beregning af fraktioner				
Beregnes som totalarealet	Beregnes overfor sumarealet af	Beregnes i forhold til intern standard	Opgives som	Totalindholdet [mg/kg TS]:
Benzen – C10	Toluen	monobrombenzen	**1. fraktion** benzen – C10	fra benzen til og med C10
> C10 – C25	C12 + C16 +C20 +C24	o-terphenyl	**2. fraktion** > C10 – C25	fra C10 til og med C25
> C25–C35	C28 + C30 + C32 +C34	o-terphenyl	**3. fraktion** >C25–C35 + >C35–C40	fra C25 til og med C35 summeret med fra C35 til og med C40
> C35–C40	C36 + C38	o-terphenyl		
			Totalkulbrinter benzen–C10 + >C10–C25 + >C25–C40	Fra og med benzen til og med C10 summeret med fra C10 til og med C25 summeret med fra C25 til og med C40

Tabel 9-2. Beregning af de enkelte fraktioner.

Hvis der forekommer interferens på o-terphenyl, således at dens areal afviger mere end 20% i forhold til det gennemsnitlige areal for o-terphenyl i sekvensblinderne beregnes i forhold til squalan.

9.2.1.2 BTEX på GC-FID

BTEX'ernes retentionstider identificeres i standardkromatogrammet (*STD-opl.* (7.3.1)). BTEX i prøverne integreres udfra retentionstiden af standarden +/- 0,2 min. Arealet for den enkelte BTEX fratrækkes eventuelt blindindhold (7.2.4.2).
Indholdet af enkeltkomponenter beregnes efter følgende formel:

$$\text{Indhold}\,[\text{mg/kg TS}] = \frac{(A_{komp.} / A_{ISpr.}) * C_{std} * V_{ext} * 100}{(A_{std.} / A_{ISstd.}) * m * TS\%}$$

Hvor,
$A_{komp.}$: arealet for den enkelte komponent.
$A_{IS\ pr.}$: arealet for interne standard (monobrombenzen) i prøven.
$A_{std.}$: arealet for samme komponent i standarden.
$A_{IS\ std.}$: arealet for intern standard (monobrombenzen) i standarden.
$C_{std.}$: koncentrationen af standarden i mg/L
V_{ext} : volumen af ekstraktionsmiddel i mL
m : prøvens vægt i gram
TS % : procent tørstof

Resultater opgives med to betydende cifre.

10 Fremgangsmåde for PAH og BTEX-MS

10.1 Klargøring og kalibrering af GC-MS

10.1.1 Klargøring/opstart af GC

GC vedligeholdes og klargøres som i afsnit 9.1.1. Kolonnen skal opretholde tilfredsstillende adskillelse af enkeltkomponenter[20]. MS skal være kontrolleret for utætheder samt tunet.

10.1.2 Metode/betingelser

I tabel 10-1 ses GC-MS metoden som anbefales til bestemmelse af PAH og BTEX ved MS.

Betingelser	GC-MS
Injektionsbetingelser	300 °C Tryk 6,77 psi. Splitless-tid 0,30 min. Helium som bæregas.
Ovnprogram	Starttemp 35 °C. Starttemp holdes 3 min, herefter 15 °C/min til 315 °C. Sluttemp holdes 8 min
Kolonne	HP5 MS 30.0 meter 250 µm ID 0,25 µm filmtykkelse. Flow 1,0 ml/min
Detektor	HP standard

Tabel 10-1. GC-MS metoden, der har været anvendt under validering.

10.1.3 Sekvensopbygning

10.1.3.1 BTEX på MS
Det anbefales at analysere en blindprøve(7.2.4.2), en *STD-opl.* (7.3.1) og en *BTEX-knt.* (7.3.2.2) først og sidst i hver prøveserie. Desuden en blindprøve (7.2.4.1) og en *BTEX-knt.* (7.3.2.2) efter hver 10 prøve.

10.1.3.2 PAH på MS
Det anbefales at analysere en blindprøve (7.2.4.2), en *PAH-std.* (7.4.1.1) og en *PAH-knt.* (7.4.1.2) først og sidst i hver prøveserie. Desuden en blindprøve (7.2.4.1) og en *PAH-knt.* (7.4.1.2) efter hver 10 prøver.

10.1.4 Kalibrering og kontrol

Kvantificeringsdelen i MS skal opdateres i forhold til standard (*std-opl.7.3.1.1 /PAH-std. 7.4.1.1),* således at retentionstider og forholdet mellem target og qualifierion passer i forhold til den aktuelle standard.

[20] Kontrolleres let ved adskillelse af indeno(1,2,3-cd)pyren og dibenz(ah)anthracen

Det kontrolleres, at:

- der ikke er indhold af BTEX/PAH i blindprøven højere end detektionsgrænsen (sekvensblind 7.2.4.1).
- arealet af enkeltkomponenterne i standarden (*std-opl. (7.3.1.1)/PAH-std.(7.4.1.1))* er fornuftige i forhold til hinanden.
- indholdet i kontrolprøven (*BTEX-knt.*(7.3.3.1)/*PAH-knt.* (7.4.1.2) giver 80-120% af nominel værdi.

10.2 Resultater

10.2.1 Beregning

PAH/BTEX i prøverne integreres udfra retentionstiden af standarden. Det kontrolleres at target/qualifierion forholdet er tilsvarende forholdet i standarden, normalt 80-120%. Dette kan dog fraviges specielt i nærheden af detektionsgrænsen, hvor en visuel vurdering kan godtages.

Arealet for den enkelte PAH/BTEX fratrækkes eventuelt blindindhold (7.2.4.1).

Indholdet af enkeltkomponenter beregnes efter følgende formel:

$$\text{Indhold}\,[\text{mg/kg TS}] = \frac{(A_{\text{komp.}} / A_{\text{ISpr.}}) * C_{\text{std}} * V_{\text{ext}} * 100}{(A_{\text{std.}} / A_{\text{ISstd.}}) * m * TS\%}$$

Hvor;

$A_{\text{komp.}}$	:	arealet for den enkelte komponent.
$A_{\text{IS pr}}$	:	arealet forden interne standard i prøven.
$A_{\text{std.}}$	:	arealet for samme komponent i standarden.
$A_{\text{IS std.}}$	:	arealet for den interne standard i standarden.
$C_{\text{std.}}$	:	koncentrationen af standarden i mg/L
V_{ext}	:	volumen af ekstraktionsmiddel i mL
m	:	prøvens vægt i gram
TS %	:	procent tørstof

Alle BTEX beregnes overfor monobrombenzen som intern standard. I tabel 10-2 kan det ses hvilken intern standard de enkelte PAH'er beregnes overfor.

Intern standard	phenanthren-d10	flouranthen-d10	benzo(a)pyren-d12
PAH-forbindelser	Naphtalen	Anthracen	Benzo(bjk)fluoranthen
	Acenaptylen	Fluoranthen	Benzo(a)pyren
	Acenaphten	Pyren	Indeno(1,2,3-cd)pyren
	Fluoren	Benz(a)anthracen	Dibenz(ah)anthracen
	Phenanthren	Chrysen	Benzo(ghi)perylen

Tabel 10-2. Interne standarder til PAH-MS.

Resultater opgives med to betydende cifre.

11 Fremgangsmåde GC-MS-Scan

11.1 Klargøring og kalibrering af GC-MS

11.1.1 Klargøring/opstart af GC

GC vedligeholdes og klargøres som i afsnit 9.1.1. Kolonnen skal opretholde tilfredsstillende adskillelse af enkeltkomponenter[21]. MS skal være kontrolleret for utætheder samt tunet.

11.1.2 Metode/betingelser

I tabel 11-1 ses GC-MS metoden som anbefales til bestemmelse af petrogene kulbrinter.

Betingelser	GC-MS
Injektionsbetingelser	300 °C Tryk 6,77 psi. Splitless-tid 0,30 min. Helium som bæregas.
Ovnprogram	Starttemp 35 °C. Starttemp holdes 3 min, herefter 15 °C/min til 315 °C. Sluttemp holdes 8 min
Kolonne	HP5 MS 30.0 meter 250 µm ID 0,25 µm filmtykkelse. Flow 1,0 ml/min
Detektor	HP standard, scan ion 35 m/z – 500 m/z

Tabel 11-1. GC-MS metoden, der har været anvendt under validering.

11.1.3 Sekvensopbygning

11.1.3.1 Petrogen kulbrintestandard
Det anbefales at analysere en blindprøve (7.2.4.2), en *std. opl.* (7.3.1.1.) en *petrogen kulbrintestandard* (7.5.1.1) og fuelolieopløsning (7.5.2.1) først og sidst i hver prøveserie. Desuden en blindprøve (7.2.4.1) og en *fuelolieopløsning* (7.5.2.1) efter hver 10 prøver.

11.1.4 Kalibrering og kontrol

Kvantificeringsdelen i MS skal opdateres i forhold til standard (*std-opl.7.3.1.1 /Petrogen kulbrintestandard. 7.5.1.1)*, således at retentionstider passer i forhold til den aktuelle standard.

Der foretages kontrol jf. afsnit 10.1.4.

[21] Kontrolleres let ved adskillelse af indeno(1,2,3-cd)pyren og dibenz(ah)anthracen

11.2.1 Petrogene kulbrinter. Beregning

Kulbrinterne i prøverne integreres udfra retentionstiden af standarden og de homologe rækker af naphthalener og phenanthrener integreres udfra retentionstider fundet i fuelolien. Tilsvarende integreres hopaner udfra retentionstider opnået fra fuelolien.

Følgende ionspor anbefales:

Komponent		MS ion (m/z)
Naphthalen	Naphthalen	128
1- og 2-Methylnaphthalen	1- og 2-Methylnaphthalen	142
Dimethylnaphthalener	2,6-Dimethylnaphthalen	156
Trimethylnaphthalener	2,3,5-Trimethylnaphthalen	170
Phenanthren	Phenanthren	178
Methylphenanthrener	2-Methylphenanthren	192
Dimethylphenanthrener	3,6-Dimethylphenanthren	206
Trimethylphenanthrener	3,6-Dimethylphenanthren (indholdet overestimeres evt. *0,01)	220
Hopanerne	17α(H),21β(H)-Hopan (30ab) evt. n-alkan C30, areal std*0,23	191
n-alkaner	Lige; overfor n-alkaner Ulige; overfor nærmeste foregående lige n-alkan	113
Pristan	Pristan	113
Phytan	Phytan	113

Tabel 11-2. Valg af kalibrant og ionspor

Indholdet af enkeltkomponenter beregnes efter følgende formel:

$$\text{Indhold}\,[\text{mg/kg TS}] = \frac{(A_{komp.} / A_{ISpr.}) * C_{std} * V_{ext} * 100}{(A_{std.} / A_{ISstd.}) * m * TS\%}$$

Hvor;

$A_{komp.}$: arealet for den enkelte komponent.
$A_{IS\ pr}$: arealet forden interne standard i prøven.
$A_{std.}$: arealet for samme komponent i standarden.
$A_{IS\ std.}$: arealet for den interne standard i standarden.
$C_{std.}$: koncentrationen af standarden i mg/L
V_{ext} : volumen af ekstraktionsmiddel i mL
m : prøvens vægt i gram
TS % : procent tørstof

Alle kulbrinter kan beregnes overfor o-terphenyl som intern standard.

Resultater opgives med to betydende cifre.
Følgende forhold og koncentrationer i tabel 11-3 beregnes jf /7/.

Parameter
Til rapportering beregnes følgende:
Sum af naphthalener
Sum af phenanthrener
Hopan(30ab)
Desuden kan som led i den kvalitative vurdering af prøven beregnes
Isoprenoidforhold:
n-alkan C17/pristan
n-alkan C18/phytan
pristan/phytan
CPI-indeks:
CPI(15 - 21)
CPI(25 - 33)
Øvrige hopaner

Tabel 11-3: Kvalitativ og kvantitativ bestemmelse af petrogene kulbrinter

Hvor CPI[22] beregnes som følger;

$$CPI(15-21) = \frac{2*(C15+C17+C19+C21)}{(C14+C16+C18+C20)+(C16+C18+C20+C22)}$$

$$CPI(25-33) = \frac{2*(C25+C27+C29+C31+C33)}{(C24+C26+C28+C30+C32)+(C26+C28+C30+C32+C34)}$$

11.2.2 Naturlige kulbrinter. Beregning

Sitosterol lokaliseres udfra ionspor af ion 93 m/z, samt udfra massespektrum. Phytosterolerne lokaliseres ved ionspor 93 m/z, og integreres og beregnes ved GC-FID. Integrering foretages ved at trække basislinie umiddelbart under phytosteroltoppene (ikke til basisliniebund). Phytosterolerne kvantificeres over for de standarder, der anvendes for kulbrintefraktioner i det pågældende kogepunktsinterval. Summen af phytosteroler kan trækkes fra totalkulbrinteindholdet fundet ved GC-FID for at korrigere for indhold af naturlige kulbrinter.

Indholdet af phytosterol i prøverne beregnes efter følgende formel.

$$\text{Indhold}\,[\text{mg/kg TS}] = \frac{(A_{phytosterol.} / A_{ISfrak.}) * C_{std} * V_{ext} * 100}{(A_{std.} / A_{ISstd.}) * m * TS\%}$$

Hvor,

$A_{phytosterol}$: Arealet af phytosteroler ved GC-FID.
$A_{IS\ frak.}$: Arealet for den interne standard i pågældende fraktion.
$A_{std.}$: Summen af arealet for de n-alkaner, der hører til pågældende fraktion, se tabel 9-2.

Fordelingen af ulige hhv. lige n-alkaner samt summen af de ulige n-alkaner fremgår af beregningen af enkeltkomponenterne jf. 11.2.1.

De ulige n-alkaner, der kan trækkes fra totalkulbrinteindholdet fundet ved GC-FID, beregnes som differencen mellem den ulige n-alkan fratrukket indholdet af den lige n-alkan umiddelbart før.

[22] "Carbon preference indeks", giver som navnet antyder et udtryk for foretrukne kulstofforbindelser. Jf. afsnit 12.8 i hovedrapporten for yderligere forklaring.

Ulige n-alkaner fra naturlige kulbrinter =
$(C25-C24)+(C27-C26)+(C29-C28)+(C31-C30)+(C33-C32)$

11.3 Vejledning

11.3.1 Petrogene kulbrinter

De fundne indhold anvendes til vurdering af, hvorvidt der er indhold af petrogene kulbrinter i jordprøven /7 /.

11.3.2 Naturlige kulbrinter

Indhold fundet ved GC-MS/GC-FID trækkes fra totalkulbrinteindholdet fundet ved GC-FID. Herved fås korrigeret totalkulbrinteindhold.

12 Metodeoplysninger

12.1.1 Detektionsgrænse, præcision og nøjagtighed

Der er under metodeudviklingen valideret detektionsgrænser svarende til dem angivet i tabel 12-1. Præcision og nøjagtighed er også opgivet i tabel 12-1 som middelværdier for BTEX og PAH. Værdierne fundet for de enkelte stoffer kan forefindes i valideringsrapporten for analysemetoden /8/. Disse emner bør eftervises regelmæssigt på det enkelte laboratorium samt når metoden tages i brug.

Prøve	DL [mg/kg TS]	Præcision					
		S_b %		S_w %		RSD %	
		Lav	høj	Lav	høj	Lav	høj
Kulbrinter:							
Benzen - C10	<2,5						
C10 - C25	<5						
C25 – C40	<25						
Totalkulbrinter sum	<32,5	15	10	12	8	19	12
BTEX – FID:	<0,1						
BTEX – MS:	<0,01	14	8	5	5	14	9
PAH – MS:	<0,005	15	13	12	10	19	17

Tabel 12-1. Detektionsgrænse, Præcision og nøjagtighed.

12.1.2 Linearitet

Der er under valideringen vist koncentrationsområder, hvori der er en lineær sammenhæng mellem respons og koncentration. I disse områder kan metoden anvendes med enkeltpunktskalibrering (som i denne forskrift). Linearitet skal eftervises regelmæssigt af de enkelte laboratorier, der anvender denne metode.

13 Analyserapport

Analyserapporten skal som minimum indeholde følgende:

- Henvisning til denne metode.
- Nøjagtig identifikation og prøvemærkning af den enkelte prøve.
- Angivelse af tidspunktet for prøvernes modtagelse på laboratoriet, og hvornår ekstraktionen er indledt.
- Koncentrationen i mg/kg TS for hver komponent, der er bestemt. Samt evt. sum af totalkulbrinter/PAH eller BTEX, der er bestemt.
- Afvigelser fra analyseforskriften skal angives.
- Hvis BTEX er bestemt ved GC-FID skal det anføres at identificationen alene er udført udfra retentionstid.
- Detektionsgrænse og usikkerhed for den enkelte analyseparameter.
- Kvalitativ information udfra GC-FID kromatogrammet som angivelse af olietype, nedbrydningsgrad, tegn på PAH eller chlorerede opløsningsmidler.
- Udspecificering ved hjælp af vejledning /7/ af indhold af kulbrinter, der ikke umiddelbart kan henføres til mineralolieprodukter.

14 Litteratur

/1/ ”ISO/DIS 16703 Soil Quality – Determination of Mineral Oil Content by Gas Chromatography – 2001 February”, Draft International Standard.

/2/ Kemiske stoffers opførsel i jord og grundvand: Bind 2, Projekt om jord og grundvand fra Miljøstyrelsen nr. 20 1996.

/3/ Vejledning fra miljøstyrelsen: Prøveudtagning og analyse af jord, nr. 13. 1998.

/4/ Bestemmelse af olie i jord. Gaskromatografisk metode, november 1998, Miljøstyrelsens Referencelaboratorium. VKI

/5/ Bestemmelse af PAH i jord, Februar 2000, Miljøstyrelsens Jordforureningskontor, VKI.

/6/ DS 204:1980. Vandundersøgelser. Tørstof og glødetest.

/7/ Videreudvikling af metoder til analyse af olie i jord. Miljørapport nr. xxx 2003.

A N N E X B

List of participants

PARTICIPANT		
AnalyCen A/S	Fredericia	Denmark
AnalyCen Laboratoriet Oy	Tampare	Finland
Analytica AB	Malmø	Sweden
Eurofins Danmark A/S	Viborg	Denmark
Eurofins Norge A/S	Oslo	Norway
Højvang Miljølaboratorium	Dianalund	Denmark
MILANA - Miljølaboratoriet	Helsingør	Denmark
Miljøcenter Vestjylland I/S	Holstebro	Denmark
Miljølaboratoriet Storkøbenhavn I/S	Glostrup	Denmark
Steins Laboratorium A/S, Miljø og Agro	Brørup	Denmark

A N N E X C

Information to participants

INSTRUCTION

1. The samples are to be analysed on **22 April 2004**. This is understood as follows: we request that samples be extracted the 22nd or if necessary the 23rd of April, and that the GC analysis be performed as soon as possible thereafter.

2. The samples must be stored in the dark at room temperature.

3. The samples are eight different samples consisting of soil. Sample amounts as well as parameters and approximate range of concentrations are shown in the attached plan. The number of parameters to be analysed by the participants differ, depending on whether the laboratory has registered to analyse only parameters covered by GC/FID or to analyse the full programme of parameters. The plan shows the full programme.

4. The soil was passed through a mesh and homogenised before filling into sample glasses.

5. Please perform two determinations of each parameter per sample. Two sample glasses for each sample is provided for the purpose. The determinations must be true duplicate determinations, i.e. each sub-sample must pass through all steps in the method. It is important to the statistical data analysis that two results for each sample be reported.

6. All samples are to be analysed according to the draft method previously distributed: "Bestemmelse af olieindhold i jord ved gaschromatografi. Modificeret ISO/DIS 16703". ***It is very important for data interpretation that the draft method be followed to the letter.***

7. Two samples, sample E and sample G, are also analysed using the method normally applied in the laboratory. Four sample glasses are therefore supplied for these two samples.

8. Do not determine total solids for the samples. Results are to be reported in mg/kg of the sample as it is supplied.

9. A list showing the empty weight ("tom vægt") for all sample glasses for samples C – H is supplied. The sample weight is found by weighing of the sample glass with the content and subtraction of the glass weight found in the tables, using the number of the glass shown on the label. ***It is therefore important to weigh the sample glass before adding extractant.*** The results for sample A and B are calculated based on a sample weight of 60,0 g.

10. Results for the method evaluation study are entered into the result form. Some parameters may be analysed by either GC/FID or GC/MS. The chosen method is indicated in the column "Analysemetode". Result forms (in Danish) are attached. Laboratories choosing to perform analyses by both GC/FID and GC/MS are kindly requested to copy the result form.

11. For the analyses performed using the laboratory's own method (sample E and G), a separate result form is attached. The form includes all parameters of the method evaluation study. However, laboratories are requested only to report results for parameters normally included in the laboratory's own method. The method is specified using the method identification numbers shown in the method form (in Danish with a few English hints), which is also attached.

12. Results should be posted or sent by fax in due time for arrival at KPMG **no later than 10 May 2004**.

KPMG
Att.: Gitte Goldschmidt (fax no.: (+45) 38 18 38 82)
Box 250
DK-2000 Frederiksberg
Denmark

13. The results of the proficiency test will be sent from KPMG to the participants **no later than 21 May 2004**. Each laboratory's results will be presented using a laboratory code, known only to the laboratory itself and the Danish Environmental Protection Agency. A report for the method performance study including an evaluation of the method and recommendations will be submitted to the Environmental Protection Agency before the end of June 2004. Following approval the report will be distributed to the participants.

INFORMATION ON THE SAMPLES

Number of samples	Sample identification	Sample amount	Parameters	Expected concentration range
2	A1	60 g wet weight	$>C_{10} – C_{25}$ $>C_{25} – C_{40}$ total hydrocarbons	total hydrocarbons: 25 – 100 mg/kg
			fluoranthene benzo(b+j+k)fluoranthene benzo(a)pyrene indeno(1,2,3-cd)pyrene dibenz(a,h)anthracene	≤ 0,2 mg/kg for each parameter
			sum of naphthalenes sum of phenanthrenes	0,1 – 2 mg/kg for each parameter
			17α(H),21β(H)-hopane	≤ 0,2 mg/kg
			pristane n-C_{18}/phytane pristane/phytane	-
			CPI(25-33)	-
2	A2	60 g wet weight	benzene toluene ethylbenzene m+p-xylene o-xylene	0,01 – 0,2 mg/kg for each parameter*

Number of samples	Sample identification	Sample amount	Parameters	Expected concentration range
2	B	60 g wet weight	benzene toluene ethylbenzene m+p-xylene o-xylene	total hydrocarbons: ca. 200 mg/kg
			$C_6H_6 – C_{10}$ $>C_{10} – C_{25}$ $>C_{25} – C_{40}$ total hydrocarbons	
			sum of naphthalenes sum of phenanthrenes	
			17α(H),21β(H)-hopane	
			n-C_{17}/pristane n-C_{18}/phytane pristanephytane	
			CPI(15-21) CPI(25-33)	
			Qualitative evaluation**	
2	C	60 g wet weight	$C_6H_6 – C_{10}$ $>C_{10} – C_{25}$ $>C_{25} – C_{40}$ total hydrocarbons	total hydrocarbons: ca. 200 mg/kg
			sum of naphthalenes sum of phenanthrenes	
			17α(H),21β(H)-hopane	
			n-C_{17}/pristane n-C_{18}/phytane pristane/phytane	
			CPI(15-21) CPI(25-33)	
			Qualitative evaluation**	

Number of samples	Sample identification	Sample amount	Parameters	Expected concentration range
2	D	60 g wet weight	benzene toluene ethylbenzene m+p-xylene o-xylene	total hydrocarbons: ca. 300 mg/kg
			$C_6H_6 – C_{10}$ $>C_{10} – C_{25}$ $>C_{25} – C_{40}$ total hydrocarbons	
			fluoranthene benzo(b+j+k)fluoranthene benzo(a)pyrene indeno(1,2,3-cd)pyrene dibenz(a,h)anthracene	
			sum of naphthalenes sum of phenanthrenes	
			17α(H),21β(H)-hopane	
			$n\text{-}C_{17}$/pristane $n\text{-}C_{18}$/phytane pristane/phytane	
			CPI(15-21) CPI(25-33)	
			Qualitative evaluation**	
4	E	60 g wet weight	$C_6H_6 – C_{10}$ $>C_{10} – C_{25}$ $>C_{25} – C_{40}$ total hydrocarbons	total hydrocarbons: ca. 800 mg/kg
			sum of naphthalenes sum of phenanthrenes	
			17α(H),21β(H)-hopane	
			$n\text{-}C_{17}$/pristane $n\text{-}C_{18}$/phytane pristane/phytane	
			CPI(15-21) CPI(25-33)	
			Qualitative evaluation**	

Number of samples	Sample identification	Sample amount	Parameters	Expected concentration range
2	F	60 g wet weight	$C_6H_6 – C_{10}$ $>C_{10} – C_{25}$ $>C_{25} – C_{40}$ total hydrocarbons	total hydrocarbons: ca. 500 mg/kg
			fluoranthene benzo(b+j+k)fluoranthene benzo(a)pyrene indeno(1,2,3-cd)pyrene dibenz(a,h)anthracene	
			sum of naphthalenes sum of phenanthrenes	
			17α(H),21β(H)-hopane	
			$n\text{-}C_{17}$/pristane $n\text{-}C_{18}$/phytane pristane/phytane	
			CPI(15-21) CPI(25-33)	
			Qualitative evaluation**	
4	G	60 g wet weight	$C_6H_6 – C_{10}$ $>C_{10} – C_{25}$ $>C_{25} – C_{40}$ total hydrocarbons	total hydrocarbons: ca. 500 mg/kg
			fluoranthene benzo(b+j+k)fluoranthene benzo(a)pyrene indeno(1,2,3-cd)pyrene dibenz(a,h)anthracene	
			sum of naphthalenes sum of phenanthrenes	
			17α(H),21β(H)-hopane	
			$n\text{-}C_{17}$/pristane $n\text{-}C_{18}$/phytane pristane/phytane	
			CPI(15-21) CPI(25-33)	
			Qualitative evaluation**	

Number of samples	Sample identification	Sample amount	Parameters	Expected concentration range
2	H	60 g wet weight	benzene toluene ethylbenzene m+p-xylene o-xylene	total hydrocarbons: ca. 5000 mg/kg
			$C_6H_6 – C_{10}$ $>C_{10} – C_{25}$ $>C_{25} – C_{40}$ total hydrocarbons	
			fluoranthene benzo(b+j+k)fluoranthene benzo(a)pyrene indeno(1,2,3-cd)pyrene dibenz(a,h)anthracene	
			sum of naphthalenes sum of phenanthrenes	
			17α(H),21β(H)-hopane	
			$n\text{-}C_{17}$/pristane $n\text{-}C_{18}$/phytane pristane/phytane	
			CPI(15-21) CPI(25-33)	
			Qualitative evaluation**	

* Concentrations are close to or under the limit of detection for GC/FID.

** Qualitative evaluation according to the method, section 13, eighth bullet point

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A N N E X D

Results of preparatory investigations

Test of sample preparation procedure: naturally contaminated sample.

	Concentration mg/kg ww			
Sample no.	C_6H_6 - C_{10}	>C_{10} - C_{25}	>C_{25} - C_{35}	C_6H_6 - C_{35}
G 1	4,0	446	64	514
G 3	2,6	468	64	535
G 5	< 2,5	430	60	493
G 7	< 2,5	409	52	463
G 9	2,9	428	66	496
G 11	< 2,5	428	58	488
G 13	< 2,5	401	59	460
G 15	< 2,5	409	55	465
G 17	< 2,5	403	50	455
G 19	< 2,5	430	54	485
G 21	< 2,5	430	50	481
G 23	< 2,5	459	64	524
Average	**< 2,5**	**428**	**58**	**488**
CV		**5%**	**10%**	**5%**

Test of sample preparation procedure: spiking of mineral oil

	Concentration mg/kg ww			
Sample no.	C_6H_6 - C_{10}	>C_{10} - C_{25}	>C_{25} - C_{35}	C_6H_6 - C_{35}
B14	4,0	95	78	177
B15	< 2,5	106	136	243
B16	6,4	97	82	186
B17	< 2,5	94	75	172
B18	6,4	92	74	173
B19	4,1	89	68	161
B20	3,5	89	71	164
B21	4,6	103	75	183
B22	9,2	99	75	183
B23	6,2	94	76	176
Average	**6**	**96**	**81**	**181**
CV	**34%**	**6%**	**24%**	**13%**
Results after exclusion of sample B 15				
Average	**6**	**95**	**75**	**175**
CV	**34%**	**5%**	**5%**	**5%**

Test of sample preparation procedure: spiking with volatile components

Samples prepared by spiking into the vessel and immediately closing the lid

	Concentration mg/kg ww				
Sample no.	Benzene	Toluene	Ethylben-zene	m+p-Xylene	o-Xylene
17 March 2004					
A2	0,16	0,18	0,19	0,19	0,21
A11	0,17	0,19	0,18	0,19	0,20
A15	0,17	0,18	0,19	0,19	0,20
Average	**0,16**	**0,18**	**0,19**	**0,19**	**0,20**
CV	**3,3%**	**0,7%**	**0,6%**	**0,6%**	**1,3%**
23 March 2004					
A1	0,14	0,16	0,17	0,17	0,18
A6	0,19	0,21	0,23	0,23	0,23
A18	0,10	0,11	0,13	0,14	0,16
A22	0,17	0,19	0,20	0,20	0,21
Average	**0,15**	**0,17**	**0,18**	**0,18**	**0,20**
CV	**30,6%**	**28,6%**	**26,8%**	**24,0%**	**18,0%**
26 March 2003					
A5	0,15	0,17	0,18	0,18	0,20
A8	0,11	0,14	0,14	0,15	0,17
A17	0,13	0,16	0,17	0,17	0,18
A20	0,12	0,14	0,15	0,15	0,17
Average	**0,12**	**0,15**	**0,16**	**0,16**	**0,18**
CV	**16,2%**	**12,3%**	**11,6%**	**10,5%**	**9,2%**

Samples prepared by spiking through the closure of the sample container, leaving the sample to stabilise overnight and changing the membrane in a quick operation.

	Concentration mg/kg ww				
Sample no.	Benzene	Toluene	Ethylben-zene	m+p-Xylene	o-Xylene
26 March 2004					
A25	0,16	0,20	0,20	0,20	0,21
A26	0,19	0,22	0,22	0,22	0,24
A27	0,20	0,22	0,22	0,22	0,24
A28	0,24	0,26	0,26	0,25	0,26
Average	**0,20**	**0,22**	**0,22**	**0,22**	**0,24**
CV	**9,4%**	**6,1%**	**5,4%**	**5,3%**	**6,1%**

A N N E X E

Sample preparation

Stock solutions	Prepared from	Concentration
PAH intermed.	2,00 mL SV calibration mix, Restec #31011 (2 mg/mL) Pentane to 50,00 mL	0,080 mg/L Naphthalene 0,080 mg/L Phenanthrene 0,080 mg/L Fluoranthene 0,160 mg/L Benzo(g+j+k)fluoranthene 0,080 mg/L Benzo(a)pyrene 0,080 mg/L Indeno(1,2,3-cd)pyrene 0,080 mg/L Dibenz(a,h)anthracene
Spike A1	1,00 mL PAH intermed. 1,25 mL Alkanes C14 - C32, Chiron S-4066 (1 mg/mL) 1,25 mL Pristane, Chiron #0635.19 (1 mg/mL) 1,25 mL Phytane, Chiron #0629.20 (1 mg/mL) 1,00 mL CPI control standard 1, Chiron S-4025 (0,2 - 1 mg/mL) 1,00 mL CPI control standard 2, Chiron S-4026 (0,2 - 1 mg/mL) 1,00 mL CPI control standard 3, Chrion S-4027 (0,2 - 1 mg/mL) 0,75 mL 1-Methylnaphthalene, Chiron #0712.11 (1 mg/ml) 0,75 mL 2-Methylnaphthalene, Chiron #0713,11 (1 mg/mL) 0,75 mL 2,6-Dimethylnaphthalene, Chiron #0729.12 (1 mg/mL) 1,00 mL 2,3,5-Trimethylnaphthalene, Chiron #0706.13 (0,5 mg/mL) 0,75 mL 2-Methylphenanthrene, Chiron #0812.15 (1 mg/mL) 1,00 mL 3,6-Dimethylphenanthrene, Chiron #0768.16 (0,5 mg/mL) 2,00 mL 17α(H),21β(H)-Hopane, Chiron #0132.30 (1 mg/mL) Pentane to 50,00 mL	0,0016 mg/mL Naphthalene 0,0016 mg/mL Phenanthrene 0,0016 mg/mL Fluoranthene 0,0032 mg/mL Benzo(b+k)fluoranthene 0,0016 mg/mL Benzo(a)pyrene 0,0016 mg/mL Indeno (1,2,3-cd)pyrene 0,0016 mg/mL Dibenz(a,h)anthracene 0,025 mg/mL C14 0,025 mg/mL C16 0,025 mg/mL C18 0,025 mg/mL C20 0,085 mg/mL C22 0,060 mg/mL C23 0,073 mg/mL C24 0,048 mg/mL C25 0,061 mg/mL C26 0,036 mg/mL C27 0,049 mg/mL C28 0,024 mg/mL C29 0,037 mg/mL C30 0,025 mg/mL C32 0,050 mg/mL pristane 0,050 mg/mL phytane 0,015 mg/mL 1-Methylnaphthalene 0,015 mg/mL 2-Methylnaphthalene 0,015 mg/mL 2,6-Dimethylnaphthalene 0,010 mg/mL 2,3,5-Trimethylnaphthalene 0,015 mg/mL 2-Methylphenanthrene 0,010 mg/mL 3,6-Dimethylphenanthrene 0,004 mg/mL 17α(H),21β(H)-Hopane
Florida TRPH std.	Restec #31266	0,5 mg/mL C8 0,5 mg/mL C10 0,5 mg/mL C12 0,5 mg/mL C14 0,5 mg/mL C16 0,5 mg/mL C18 0,5 mg/mL C20 0,5 mg/mL C22 0,5 mg/mL C24 0,5 mg/mL C26 0,5 mg/mL C28 0,5 mg/mL C30 0,5 mg/mL C32 0,5 mg/mL C34 0,5 mg/mL C36 0,5 mg/mL C38 0,5 mg/mL C40

Stock solutions	Prepared from	Concentration
Spike BTEX	0,75 mL Supelco aromats (2 mg/mL) Methanol to 100 mL	15 mg/L Benzene 15 mg/L Toluene 15 mg/L Ethylbenzene 30 mg/L m+p-Xylene 15 mg/L o-Xylene
Spike B1	0,709 g Fuel oil Dichlormethane to 100 mL	7,09 g/L Total hydrocarbons
Spike B2	0,503 g Diesel Methanol to 100 mL	5,03 g/L Total hydrocarbons
Spike E	6,533 g Fuel oil Dichlormethane to 100 mL	65,33 g/L Total hydrocarbons
Spike H	17,47 g Diesel Dichlormethane to 150 mL	116,48 g/L Total hydrocarbons

Preparation of soil samples

Approx. 5 kg soil is passed quickly through a 10 mm mesh sieve. The soil is transferred to a Ril-san bag. The bag is closed to leave plenty of space round the soil. The soil is mixed in the Ril-san bag by thorough kneading. The soil is now ready for weighing into glass extraction vessels.

Weigh 60 g of soil into each extraction vessel. Samples to be spiked are weighed accurately, that is 60 g $\pm$ 0,5 g. During the weighing operation the bulk soil is mixed at regular intervals to avoid fractionation.

Spiking of soil samples

Spiking is done directly into each weighed subsample in the glass extraction vessel. Samples containing volatile components (sample A2, B, D and H): Add the spike solution through the membrane in the lid of the extraction vessel. Shake the vessel thoroughly. Leave the glasses overnight for stabilisation and then change the membrane quickly.

Samples without volatile components: Add the spike solution before closing the lid.

Sample	Sample preparation	Concentration
A 1	60 g Sandy clay soil from a cliff on the shore of Lillebælt, Denmark 1000 µL Spike A1 250 µL Florida TRPH std.	0,027 mg/kg Naphthalene 0,027 mg/kg Phenanthrene 0,027 mg/kg Fluoranthene 0,053 mg/kg Benzo(b+k)fluoranthene 0,027 mg/kg Benzo(a)pyrene 0,027 mg/kg Indeno (1,2,3-cd)pyrene 0,027 mg/kg Dibenz(a,h)anthracene 2,08 mg/kg C12 2,50 mg/kg C14 2,50 mg/kg C16 2,50 mg/kg C18 2,50 mg/kg C20 3,50 mg/kg C22 1,00 mg/kg C23 3,30 mg/kg C24 0,800 mg/kg C25 3,10 mg/kg C26 0,600 mg/kg C27 2,90 mg/kg C28 0,400 mg/kg C29 2,70 mg/kg C30 2,50 mg/kg C32 2,08 mg/kg C34 2,08 mg/kg C36 2,08 mg/kg C38 2,08 mg/kg C40 0,833 mg/kg Pristane 0,833 mg/kg Phytane 0,250 mg/kg 1-Methylnaphthalene 0,250 mg/kg 2-Methylnaphthalene 0,250 mg/kg 2,6-Dimethylnaphthalene 0,167 mg/kg 2,3,5-Trimethylnaphthalene 0,250 mg/kg 2-Methylphenanthrene 0,167 mg/kg 3,6-Dimethylphenanthrene 0,067 mg/kg 17α(H),21β(H)-Hopane
	Concentrations recalculated into the parameters of the method evaluation study	23,7 mg/kg >C_{10} - C_{25} 20,7 mg/kg >C_{25} - C_{40} 44,4 mg/kg Total hydrocarbons
		0,027 mg/kg Fluoranthene 0,053 mg/kg Benzo(b+k)fluoranthene 0,027 mg/kg Benzo(a)pyrene 0,027 mg/kg Indeno (1,2,3-cd)pyrene 0,027 mg/kg Dibenz(a,h)anthracene
		0,94 mg/kg Sum af naphthalenes 0,44 mg/kg Sum af phenanthrenes
		0,067 mg/kg 17α(H),21β(H)-Hopane
		0,833 mg/kg Pristane 3,0 n-C18/Phytane 1,0 Pristane/phytane
		0,13 CPI(25-33)
A2	60 g Sandy clay soil from a cliff on the shore of Lillebælt, Denmark 300 µL Spike BTEX	0,075 mg/kg Benzene 0,075 mg/kg Toluene 0,075 mg/kg Ethylbenzene 0,15 mg/kg m+p-Xylene 0,075 mg/kg o-Xylene

Sample	Sample preparation	Concentration
B	60 g Sandy clay soil from a cliff on the shore of Lillebælt, Denmark 1500 µL Spike B1 750 µL Spike B2	b_1 mg/kg Benzene b_2 mg/kg Toluene b_3 mg/kg Ethylbenzene b_4 mg/kg m+p-Xylene b_5 mg/kg o-Xylene
		b_6 mg/kg C_6H_6 - C_{10} b_7 mg/kg >C_{10} - C_{25} b_8 mg/kg >C_{25} - C_{40} b_9 + 240 mg/kg Total hydrocarbons
		b_{10} mg/kg Sum af naphthalenes b_{11} mg/kg Sum af phenanthrenes
		b_{12} mg/kg 17α(H),21β(H)-Hopane
		b_{13} n-C17/Pristane b_{14} n-C18/Phytane b_{15} Pristane/phytane
		b_{16} CPI(15-21) b_{17} CPI(25-33)
C	60 g Sandy clay soil from a cliff on the shore of Lillebælt, Denmark + Compost (1+3)	c_1 mg/kg C_6H_6 - C_{10} c_2 mg/kg >C_{10} - C_{25} c_3 mg/kg >C_{25} - C_{40} c_4 mg/kg Total hydrocarbons
		c_5 mg/kg Sum af naphthalenes c_6 mg/kg Sum af phenanthrenes
		c_7 mg/kg 17α(H),21β(H)-Hopane
		c_8 n-C17/Pristane c_9 n-C18/Phytane c_{10} Pristane/phytane
		c_{11} CPI(15-21) c_{12} CPI(25-33)
D	60 g Soil (no. 130,01) from RGS 90, Grøften (a soil remediation company). Equal to sample B from Eurofins proficiency test SOLID-9 (2003-5) 1000 µL Spike BTEX	0,25 mg/kg Benzene 0,25 mg/kg Toluene 0,25 mg/kg Ethylbenzene 0,50 mg/kg m+p-Xylene 0,25 mg/kg o-Xylene
		<DL mg/kg C_6H_6 - C_{10} 250 mg/kg >C_{10} - C_{25} d_1 + 72 mg/kg >C_{25} - C_{40} d_2 + 320 mg/kg Total kulbrinter
		d_3 mg/kg Fluoranthene d_4 mg/kg Benzo(b+k)fluoranthene d_5 mg/kg Benzo(a)pyrene d_6 mg/kg Indeno (1,2,3-cd)pyrene d_7 mg/kg Dibenz(a,h)anthracene
		d_8 mg/kg Sum af naphthalenes d_9 mg/kg Sum af phenanthrenes
		d_{10} mg/kg 17α(H),21β(H)-Hopane
		d_{11} n-C17/Pristane d_{12} n-C18/Phytane d_{13} Pristane/phytane
		d_{14} CPI(15-21) d_{15} CPI(25-33)

Sample	Sample preparation	Concentration
E	60 g Sandy clay soil from a cliff on the shore of Lillebælt, Denmark + Compost (1+3) 750 µL Spike E	e_1 mg/kg C_6H_6 - C_{10} e_2 mg/kg >C_{10} - C_{25} e_3 mg/kg >C_{25} - C_{40} c_4 + 820 mg/kg Total hydrocarbons
		e_5 mg/kg Sum af naphthalenes e_6 mg/kg Sum af phenanthrenes
		e_7 mg/kg 17α(H),21β(H)-Hopane
		e_8 n-C17/Pristane e_9 n-C18/Phytane e_{10} Pristane/phytane
		e_{11} CPI(15-21) e_{12} CPI(25-33)
F	Soil from road sweeping	f_1 mg/kg C_6H_6 - C_{10} f_2 mg/kg >C_{10} - C_{25} f_3 mg/kg >C_{25} - C_{40} f_4 mg/kg Total hydrocarbons
		f_5 mg/kg Fluoranthene f_6 mg/kg Benzo(b+k)fluoranthene f_7 mg/kg Benzo(a)pyrene f_8 mg/kg Indeno (1,2,3-cd)pyrene f_9 mg/kg Dibenz(a,h)anthracene
		f_{10} mg/kg Sum af naphthalenes f_{11} mg/kg Sum af phenanthrenes
		f_{12} mg/kg 17α(H),21β(H)-Hopane
		f_{13} n-C17/Pristane f_{14} n-C18/Phytane f_{15} Pristane/phytane
		f_{16} CPI(15-21) f_{17} CPI(25-33)
G	60 g Soil (no. 4084) from RGS 90, Grøften (a soil remediation company).	g_1 mg/kg C_6H_6 - C_{10} g_2 mg/kg >C_{10} - C_{25} g_3 mg/kg >C_{25} - C_{40} g_4 mg/kg Total hydrocarbons
		g_5 mg/kg Fluoranthene g_6 mg/kg Benzo(b+k)fluoranthene g_7 mg/kg Benzo(a)pyrene g_8 mg/kg Indeno (1,2,3-cd)pyrene g_9 mg/kg Dibenz(a,h)anthracene
		g_{10} mg/kg Sum af naphthalenes g_{11} mg/kg Sum af phenanthrenes
		g_{12} mg/kg 17α(H),21β(H)-Hopane
		g_{13} n-C17/Pristane g_{14} n-C18/Phytane g_{15} Pristane/phytane
		g_{16} CPI(15-21) g_{17} CPI(25-33)

Sample	Sample preparation	Concentration
H	60 g Sandy clay soil from a cliff on the shore of Lillebælt, Denmark + Compost (1+3) 2500 µL Spike H	h_1 mg/kg Benzene h_2 mg/kg Toluene h_3 mg/kg Ethylbenzene h_4 mg/kg m+p-Xylene h_5 mg/kg o-Xylene
		h_6 mg/kg C_6H_6 - C_{10} h_7 mg/kg >C_{10} - C_{25} h_8 mg/kg >C_{25} - C_{40} c_4 + 4850 mg/kg Total hydrocarbons
		h_{10} mg/kg Fluoranthene h_{11} mg/kg Benzo(b+k)fluoranthene h_{12} mg/kg Benzo(a)pyrene h_{13} mg/kg Indeno (1,2,3-cd)pyrene h_{14} mg/kg Dibenz(a,h)anthracene
		h_{15} mg/kg Sum af naphthalenes h_{16} mg/kg Sum af phenanthrenes
		h_{17} mg/kg 17α(H),21β(H)-Hopane
		h_{18} n-C17/Pristane h_{19} n-C18/Phytane h_{20} Pristane/phytane
		h_{21} CPI(15-21) h_{22} CPI(25-33)

A N N E X F

Homogeneity and stability

Homogeneity test **Method evaluation study - oil in soil**

Sample **A1**
Parameter **Total hydrocarnons, mg/kg**

Date	Ssample	I	II	M. bottle	Var.replicate	Day mean	Day var.
20-04-04	A1 6	77,2		77,2			
	A1 7	89,9		89,9			
	A1 11	90,2		90,2			
	A1 12	71,3		71,3			
	A1 14	65,4		65,4			
	A1 15	74,1		74,1			
	A1 16	74,6		74,6			
	A1 22	82,6		82,6			
	A1 27	75,9		75,9			
	A1 31	78,2		78,2			
	A1 33	80,3		80,3			
	A1 37	84,8		84,8		78,7	54,06

Homogentet

F test value = var.bottle/var.rep.	3,490
F critical value = inv. 95%(f bottle,f rep)	4,027
F critical value = inv.99%(f bottle,f rep)	7,790

	s	var.	f
Replicate	3,936	15,49	6
Bottle	7,353	54,06	11

s(w) standard deviation within a laboratory in the method evaluation study = 2,24

s(L) standard deviation between laboratories in the method evaluation study = 10,39

Eurofins' standard deviation from internal quality control s(w) = 9,23

s = standard deviation
M. = mean
Var. = variance
Rep. = Replicate = within the bottle
Bottle = between bottles
f = number of degrees of freedom

Conclusion

Homogeneity: Standard deviation between bottles is tested against expected relative standard deviation for replicates of 5%. The F-test value is less than the critical value F(95%) in the homogeneity test and the samples are therefore considered homogeneous.

Test of stability and homogeneity **Method evaluation study - oil in soil**

Sample **B**
Parameter **Total Hydrocarbons mg/kg**

Date	Sample	I	II	M. bottle	Var. replicate	Day mean	Day var.
20-04-04	B12	161,1		161,1			
	B29	183,6		183,6			
	B46	175,0		175,0		173,3	128,95
22-04-04	B7	187,9		187,9			
	B24	182,4		182,4			
	B36	185,5		185,5		185,2	7,60
26-04-04	B18	191,9		191,9			
	B43	190,9		190,9			
	B45	192,6		192,6		191,8	0,72
28-04-04	B11	196,5		196,5			
	B28	185,9		185,9			
	B47	192,4		192,4		191,6	28,52

Homogeneity

F test value = var.bottle./var.rep.	0,613
F criatical value = inv. 95%(f bottle,f rep)	4,284
F critical value = inv.99%(f bottle,f rep)	8,466

	s	var.	f	Stab mean
Replicate	9,274	86,00	6	
Bottle	7,262	52,73	6	
Stability	8,696	75,61	3	185,5

Stability tested against var. replicate

F test value = var.stab./var.rep.	0,879
F critical value = inv. 95%(f stab,f rep)	4,757
F criatical value = inv.99%(f stab,f rep)	9,780

s(w) standard deviation within a laboratory in the method evaluation study'	27,80
s(L) standard deviation between laboratories in the method evaluation stuc	45,13
Eurofins' standard deviation from intern quality control s(w) =	21,75
Eurofins' standard deviation from internal quality control s(b) =	-

s = standard deviation
Var. = variance
Rep = replicate
Bottle = between bottles
Stab = stability = between days
f = number of degrees of freedom

Conclusion

Homogeneity: Standard deviation between bottles is tested against expected relative standard deviation for replicates of 5%. The F-test value is less than 1 in the homogeneity test and the samples are therefore considered homogeneous.

Stability: Standard deviation between days is tested against expected relative standard deviation for replicates of 5%. The F-test value is less than 1 stability test and the samples are therefore considered stable.

Homogeneity test **Method evaluation study - oil in soil**

Sample **C**
Parameter **Total hydrocarbons, mg/kg**

Date	Sample	I	II	M. bottle	Var.replicate	Day mean	Day var.
22-04-04	C1	69,7		69,7			
	C3	72,4		72,4			
	C5	65,3		65,3			
	C6	62,0		62,0			
	C13	52,1		52,1			
	C17	61,7		61,7			
	C19	66,8		66,8			
	C20	65,7		65,7			
	C25	69,8		69,8			
	C28	59,0		59,0			
	C36	67,5		67,5			
	C38	67,0		67,0		64,9	30,51

Homogeneity

F test value = var.bottle/var.rep.	2,897
F critical value = inv. 95%(f bottle,f rep)	4,027
F critical value = inv.99%(f bottle,f rep)	7,790

	s	var.	f
Replicate	3,246	10,53	6
Bottle	5,524	30,51	11

s(w) standard deviation within a laboratory in the method evaluation study = 8,41

s(L) standard deviation between laboratories in the method evaluation stuc 39,32

Eurofins' standard deviation from internal quality control s(w) = 7,61

s = standard deviation
M. = mean
Var. = variance
Rep. = Replicate = within the bottle
Bottle = between bottles
f = number of degrees of freedom

Conclusion

Homogeneity: The standard deviation between bottles is tested against an expected relative deviation of replicates of 5%. The F-test value is less than the critical value F(95%) in the homogeneity test and the samples are therefore considered homogeneous.

Stability and homogeneity test **Method evaluation stu**

Sample **D**
Parameter **Total hydrocarabons**

Date	Sample	I	II	M. bottle	Var. replicate	Day mean	Day var.
20-04-04	D 8	406,0		406,0			
	D 29	442,9		442,9			
	D 46	427,8		427,8		425,6	343,22
26-04-04	D 1	462,8		462,8			
	D 10	461,9		461,9			
	D 35	475,2		475,2		466,6	54,88
28-04-04	D 4	452,1		452,1			
	D 18	456,0		456,0			
	D 41	439,3		439,3		449,1	76,61

Homogeneity

F test value = var.bottle/(0,3*S(L))^2	0,533
F critical value = inv. 95%(f bottle,f rep)	3,374
F critical value = inv.99%(f bottle,f rep)	5,802

	s	var.	f	Stab mean
Replicate	22,405	501,99	9	
Bottle	12,579	158,24	6	
Stability	20,604	424,52	2	447,1

Stability tested by var. replicate

F test value = var.stab./(0,3*S(L))^2	0,846
F critical value = inv. 95%(f stab,f rep)	4,256
F critical value = inv.99%(f stab,f rep)	8,022

s(w) standard deviation within a laboratories in the proficiency test =	6,04
s(L) standard deviation between laboratories in the proficiency test =	57,46
Eurofins' standard deviation from internal quality control s(w) =	52,55
Eurofins' standard deviation from internal quality control s(b) =	-

s = standard deviation
Var. = variance
Rep = replicate = within the bottle
Bottle = between bottles
Stab = stability = between days
f = number of degrees of freedom

Conclusion

Homogeneity: The repeatability standard deviation in this test is larger than 0.3 * s(L) in the method evaluation study. The standard deviation between bottles is therefore tested against 0.3 * s(L). As the F-test value is less than 1 in the homogeneity test, the samples are considered homogeneous.

Stability: The standard deviation between days was tested against 0.3 * s(L). The F-test value is smaller than 1 in the stability test and therefore the samples are considered stable.

Homogeneity test **Method evaluation study - oil in soil**

Sample **E**
Parameter **Total hydrocarbons, mg/kg**

Date	Sample	I	II	M. bottle	Var.replicate	Day mean	Day var.
26-04-04	E6	442,5		442,5			
	E7	436,2		436,2			
	E8	409,6		409,6			
	E10	444,3		444,3			
	E25	427,7		427,7			
	E30	403,8		403,8			
	E31	461,8		461,8			
	E32	472,4		472,4			
	E36	420,3		420,3			
	E61	442,1		442,1			
	E64	402,2		402,2			
	E66	449,5		449,5		434,4	498,06

Homogeneity

F test value = var.bottle/var.rep.	1,056
F critical value = inv. 95%(f bottle,f rep)	4,027
F critical value = inv.99%(f bottle,f rep)	7,790

	s	var.	f
Replicate	21,718	471,68	6
Bottle	22,317	498,06	11

s(w) standard deivation within a laboraotory in the method evaluation study 37,14

s(L) standard deviation between laboratories in the method evaluation stuc 110,20

Eurofins' standard deviation from internal quality control s(w) = 50,94

s = standard deviation
M. = mean
Var. = variance
Rep. = Replicate = within the bottle
Bottle = between bottles
f = number of degrees of freedom

Conclusion

Homogenitet: The standard deviation between bottles is tested agains an expected relative standard deviation for replicates of 5%. The F-test value is less than the critical value F(95%) in the homogeneity test and the samples are considered homogeneous.

Homogeneity test **Method evaluation study - oil in soil**

Sample **F**
Parameter **Total hydrocarbons, mg/kg**

Date	Sample	I	II	M. bottle	Var.replicate	Day mean	Day var.
20-04-04	F1	588,7		588,7			
	F5	446,3		446,3			
	F9	463,7		463,7			
	F12	455,7		455,7			
	F20	563,2		563,2			
	F23	491,4		491,4			
	F26	481,5		481,5			
	F28	485,9		485,9			
	F30	464,8		464,8			
	F33	467,5		467,5			
	F39	384,4		384,4			
	F41	398,2		398,2		474,3	3337,75

Homogeneity

F test value = var.bottle/var.rep.	5,935
F critical value = inv. 95%(f bottle,f rep)	4,027
F critical value = inv.99%(f bottle,f rep)	7,790

	s	var.	f
Replicate	23,714	562,34	6
Bottle	57,773	3337,75	11

s(w) standard deviation within a laboratory in the method evaluation study = 68,57

s(L) standard deviation between laboratories in the method evaluation stuc 105,3

Eurofins' standard deviation from internal quality control s(w) = 55,62

s = standard deviation
M. = mean
Var. = variance
Rep. = Replicate = within the bottle
Bottle = between bottles
f = number of degrees of freedom

Conclusion

Homogeneity: The standard deviation between bottles is tested against an expected relative standard deviation for replicates of 5%. The F-test value is less than the critical value F(99%) but is higher than F(95%) in the homogeneity test. The samples are considered homogeneous.

Test of stability and homogeneity **Method evaluation study - oil in soil**

Sample **H**
Parameter **Total hydrocarbons mg/kg**

Date	Sample	I	II	M. bottle	Var. replicate	Day mean	Day var.
20-04-04	H 11	4323,1		4323,1			
	H 25	3998,2		3998,2			
	H 46	4298,2		4298,2		4206,5	32699,3
22-04-04	H 1	4210,2		4210,2			
	H 14	4130,5		4130,5			
	H 20	4181,7		4181,7		4174,1	1632,6
26-04-04	H 15	4113,5		4113,5			
	H 21	4102,6		4102,6			
	H 31	3724,8		3724,8		3980,3	48971,2
28-04-04	H 2	4262,3		4262,3			
	H 18	4211,5		4211,5			
	H 34	4319,2		4319,2		4264,3	2906,47

Homogeneity

F test value = var.bottle./var.rep.	0,653
F critical value = inv. 95%(f bottle,f rep)	4,284
F critical value = inv.99%(f bottle,f rep)	8,466

	s	var.	f	Stab mean
Replicate	207,8	43187,3	6	
Bottle	167,9	28192,3	6	
Stability	123,1	15161,7	3	4156,3

Stability tested against var. replicate

F test value = var.stab./var.rep.	0,351
F critical value = inv. 95%(f stab,f rep)	4,757
F critical value = inv.99%(f stab,f rep)	9,780

s(w) standard deviation within a laboratory in the method evaluation study	64,20
s(L) standard deviation between laboratories in the method evaluation stuc	1205
Eurofins' standard deviation from internal quality control s(w) =	487,41
Eurofins' standard deviation from internal quality control s(b) =	-

s = standard deviation
Var. = variance
Rep = replicate
Bottle = between bottles
Stab = stability = between days
f = number of degrees of freedom

Conclusion

Homogeneity: Standard deviation between bottles is tested against the expected relative standard deviation for replicates of 5%. The F-test value is less than 1 in the homogeneity test and the samples are therefore considered homogeneous.

Stabilitet: Standard deviation between days is tested against the expected relative standard deviation for replicates of 5%. The F-test value is less than 1 in the homogeneity test and the samples are therefore considered stable.

Test of stability and homogeneity **Method evaluation study - olie i jord**

Sample **A2**
Parameter **Benzene, mg/kg**

Date	Sample	I	II	M. bottle	Var. replicate	Day mean	Day var.
20-04-04	A2 3	0,055		0,055			
	A2 30	0,066		0,066			
	A2 45	0,064		0,064		0,062	0,000
22-04-04	A2 2	0,031		0,031			
	A2 8	0,051		0,051			
	A2 32	0,079		0,079		0,054	0,001
26-04-04	A2 1	0,054		0,054			
	A2 7	0,056		0,056			
	A2 38	0,078		0,078		0,063	0,000
28-04-04	A2 14	0,075		0,075			
	A2 28	0,071		0,071			
	A2 44	0,052		0,052		0,066	0,000

Homogeneity

F test value = var.bottle./var.rep.	3,220
F critical value = inv. 95%(f bottle,f rep)	4,284
F critical value = inv.99%(f bottle,f rep)	8,466

	s	var.	f	Stab mean
Replicate	0,006	0,00	6	
Bottle	0,011	0,00	6	
Stability	0,005	0,00	3	0,061

Stabilitet tested overfor var. replicate

F test value = var.stab./var.rep.	0,762
F critical value = inv. 95%(f stab,f rep)	4,757
F critical value = inv.99%(f stab,f rep)	9,780

s(w) standard deviation withn a laboratory in the method evaluation study = 0,015

s(L) standard deviation between laboratories in the method evaluation stuc 0,044

Eurofins' standard deviation from internal quality control s(w) =

Eurofins' standard deviation from internal quality control s(b) =

s = standard deviation
Var. = variance
Rep = replicate
Bottle = between bottles
Stab = stability = between days
f = number of degrees of freedom

Conclusion

Homogenitet: The standard deviation between bottles is tested against an expected relative standard deviation for replicates of 10%. The F-test value is less than the critical value F(95%) in the homogeneity test and the samples are therefore considered homogeneous.

Stability: The standard deviation between days is tested against an expected relative standard deviation for replicates of 10%. The F-test value is less than 1 in the stability test and the samples are therefore considered stable.

Test of stability and homogeneity **Method evaluation study - oil in soil**

Sample **D**
Parameter **Benzene, mg/kg**

Date	Sample	I	II	M. bottle	Var. replicate	Day mean	Day var.
20-04-04	D 8	0,153		0,153			
	D 29	0,118		0,118			
	D 46	0,087		0,087		0,119	0,001
22-04-04	D 6	0,162		0,162			
	D 31	0,104		0,104			
	D 40	0,293		0,293		0,186	0,009
26-04-04	D 1	0,137		0,137			
	D 10	0,143		0,143			
	D 35	0,081		0,081		0,120	0,001
28-04-04	D 4	0,103		0,103			
	D 18	0,139		0,139			
	D 41	0,092		0,092		0,111	0,001

Homogeneiy

F test value = var.bottle./var.rep.	5,346
F critical value = inv. 95%(f bottle,f rep)	4,284
F critical value = inv.99%(f bottle,f rep)	8,466

	s	var.	f	Stab mean	
Replicate	0,013	0,00	6		
Bottle	0,031	0,00	6		0,23122
Stability	0,035	0,00	3	0,134	0,26022

Stability tested against var. replicate

F test value = var.stab./var.rep.	6,772
F critical value = inv. 95%(f stab,f rep)	4,757
F critical value = inv.99%(f stab,f rep)	9,780

s(w) standard deviation within a laboratory in the method evaluation study 0,030

s(L) standard deviation between laboratories in the method evaluation stuc 0,045

Eurofins' standard deviation from internal quality control s(w) =

Eurofins' standard deviation from internal quality control s(b) =

s = standard deviation
Var. = variance
Rep = replicate
Bottle = between bottles
Stab = stability = between days
f = number of degrees of freedom

Conclusion

Homogenitet: The standard deviation between bottles is tested against an expected relative standard deviation for replicates of 10%. The F-test value is less than the critical value, F(99%), but higher than F(95%) in the homogeneity test. The samples are considered homogeneous.

Stability: The standard deviation between days is tested against an expected relative standard deviation for replicates of 10%. The F-test value is less than the critical value, F(99%), but higher than F(95%) in the stability test. The samples are considered stable.

Stability and homogeneity test **Method evaluation study - oil in soil**

Sample **H**
Parameter **Benzene, mg/kg**

Date	Sample	I	II	M. bottle	Var. replicate	Day mean	Day var.
20-04-04	H 11	1,46		1,46			
	H 25	1,51		1,51			
	H 46	1,29		1,29		1,42	0,013
22-04-04	H 1	0,99		0,99			
	H 14	1,55		1,55			
	H 20	1,59		1,59		1,38	0,116
26-04-04	H 15	0,90		0,90			
	H 21	1,63		1,63			
	H 31	0,80		0,80		1,11	0,203
28-04-04	H 2	1,04		1,04			
	H 18	1,18		1,18			
	H 34	0,88		0,88		1,03	0,022

Homogeneity

F test value = var.bottle/(0,3*S(L))^2	29,574
F critical value = inv. 95%(f bottle,f rep)	4,284
F critical value = inv.99%(f bottle,f rep)	8,466

	s	var.	f	Stab mean
Replicate	0,124	0,015	6	
Bottle	0,282	0,080	6	
Stability	0,193	0,037	3	1,24

Stability tested by var. replicate

F test value = var.stab./(0,3*S(L))^2	13,868
F critical value = inv. 95%(f stab,f rep)	4,757
F critical value = inv.99%(f stab,f rep)	9,780

s(w) standard deviation within a laboratories in the proficiency test = 0,030

s(L) standard deviation between laboratories in the proficiency test = 0,173

Eurofins' standard deviation from internal quality control s(w) =

Eurofins' standard deviation from internal quality control s(b) =

s = standard deviation
Var. = variance
Rep = replicate = within the bottle
Bottle = between bottles
Stab = stability = between days
f = number of degrees of freedom

Conclusion

Homogeneity: The repeatability standard deviation in this test is larger than 0.3 * s(L) in the proficiency test. The standard deviation between bottles is therefore tested against 0.3 * s(L). The F-test value is higher than the critical value. The samples are therefore inhomogeneous. See further in the Quality Documentation report.

Stability: The standard deviation between days was tested against 0.3 * s(L). The F-test value is higher than the critical value. The samples are therefore unstable. See further in the Quality Documentation report.

Test of stability and homogeneity **Method evaluation study - olie i jord**

Sample **A2**
Parameter **Benzene, mg/kg**

Date	Sample	I	II	M. bottle	Var. replicate	Day mean	Day var.
20-04-04	A2 3	0,055		0,055			
	A2 30	0,066		0,066			
	A2 45	0,064		0,064		0,062	0,000
22-04-04	A2 2	0,031		0,031			
	A2 8	0,051		0,051			
	A2 32	0,079		0,079		0,054	0,001
26-04-04	A2 1	0,054		0,054			
	A2 7	0,056		0,056			
	A2 38	0,078		0,078		0,063	0,000
28-04-04	A2 14	0,075		0,075			
	A2 28	0,071		0,071			
	A2 44	0,052		0,052		0,066	0,000

Homogeneity

F test value = var.bottle./var.rep.	3,220
F critical value = inv. 95%(f bottle,f rep)	4,284
F critical value = inv.99%(f bottle,f rep)	8,466

	s	var.	f	Stab mean
Replicate	0,006	0,00	6	
Bottle	0,011	0,00	6	
Stability	0,005	0,00	3	0,061

Stabilitet tested overfor var. replicate

F test value = var.stab./var.rep.	0,762
F critical value = inv. 95%(f stab,f rep)	4,757
F critical value = inv.99%(f stab,f rep)	9,780

s(w) standard deviation withn a laboratory in the method evaluation study = 0,015

s(L) standard deviation between laboratories in the method evaluation stuc 0,044

Eurofins' standard deviation from internal quality control s(w) =

Eurofins' standard deviation from internal quality control s(b) =

s = standard deviation
Var. = variance
Rep = replicate
Bottle = between bottles
Stab = stability = between days
f = number of degrees of freedom

Conclusion

Homogenitet: The standard deviation between bottles is tested against an expected relative standard deviation for replicates of 10%. The F-test value is less than the critical value F(95%) in the homogeneity test and the samples are therefore considered homogeneous.

Stability: The standard deviation between days is tested against an expected relative standard deviation for replicates of 10%. The F-test value is less than 1 in the stability test and the samples are therefore considered stable.

Test of stability and homogeneity **Method evaluation study - oil in soil**

Sample **B**
Parameter **o-Xylene, mg/kg**

Date	Sample	I	II	M. bottle	Var. replicate	Day mean	Day var.
20-04-04	B12	0,039		0,039			
	B29	0,040		0,040			
	B46	0,038		0,038		0,039	0,000
22-04-04	B7	0,040		0,040			
	B24	0,048		0,048			
	B36	0,034		0,034		0,041	0,000
26-04-04	B18	0,040		0,040			
	B43	0,024		0,024			
	B45	0,007		0,007		0,024	0,000
28-04-04	B11	0,046		0,046			
	B28	0,007		0,007			
	B47	0,045		0,045		0,033	0,000

Homogenitet

F test value = var.bottle./var.rep.	22,136
F critical valuei = inv. 95%(f bottle,f rep)	4,284
F critical value = inv.99%(f bottle,f rep)	8,466

	s	var.	f	Stab mean
Replicate	0,003	0,00	6	
Bottle	0,016	0,00	6	
Stability	0,008	0,00	3	0,034

Stability tested against var. replicate

F test value = var.stab./var.rep.	5,133
F critical value = inv. 95%(f stab,f rep)	4,757
F critical value = inv.99%(f stab,f rep)	9,780

s(w) standard deviation within a laboratory in the method evaluation study 0,013

s(L) standard deivation between laboratories in the method evaluation stuc 0,005

Eurofins' standard deviation from internal quality controll s(w) =

Eurofins' standard deviation from internal quality control s(b) =

s = standard deviation
Var. = variance
Rep = replicate
Bottle = between bottles
Stab = stability = between days
f = number of degrees of freedom

Conclusion

Homogenitet: The standard deviation between bottles is tested against an expected relative standard deviation for replicates of 10%. The F-test value is higher than the critical value F(95%) in the homogeneity test and the samples are considered inhomogeneous.

Stability: The standard deviation between days is tested against an expected relative standard deviation for replicates of 10%. The F-test values is higher than the critical value F(95%) in the stability test and the samples are considered instable.

Stability and homogeneity test **Method evaluation study - oil in soil**

Sample **D**
Parameter **o-Xylene, mg/kg**

Date	Sample	I	II	M. bottle	Var. replicate	Day mean	Day var.
20-04-04	D 8	0,252		0,252			
	D 29	0,254		0,254			
	D 46	0,244		0,244		0,250	2,80E-05
22-04-04	D 6	0,271		0,271			
	D 31	0,248		0,248			
	D 40	0,207		0,207		0,242	1,05E-03
26-04-04	D 1	0,280		0,280			
	D 10	0,252		0,252			
	D 35	0,243		0,243		0,258	3,72E-04
28-04-04	D 4	0,245		0,245			
	D 18	0,236		0,236			
	D 41	0,246		0,246		0,242	3,03E-05

Homogeneity

F test value = var.bottle/(0,3*S(L))^2	2,989
F critical value = inv. 95%(f bottle,f rep)	4,284
F critical value = inv.99%(f bottle,f rep)	8,466

	s	var.	f	Stab mean
Replicate	0,025	6,16E-04	6	
Bottle	0,012	1,44E-04	6	
Stability	0,008	5,96E-05	3	0,248

Stability tested by var. replicate

F test value = var.stab./(0,3*S(L))^2	1,241
F critical value = inv. 95%(f stab,f rep)	4,757
F critical value = inv.99%(f stab,f rep)	9,780

s(w) standard deviation within a laboratories in the proficiency test = 0,016

s(L) standard deviation between laboratories in the proficiency test = 0,023

Eurofins' standard deviation from internal quality control s(w) =

Eurofins' standard deviation from internal quality control s(b) =

s = standard deviation
Var. = variance
Rep = replicate = within the bottle
Bottle = between bottles
Stab = stability = between days
f = number of degrees of freedom

Conclusion

Homogeneity: The repeatability standard deviation in this test is larger than 0.3 * s(L) in the proficiency test. The standard deviation between bottles is therefore tested against 0.3 * s(L). As the F-test value is less than the critical value (F95%) in the homogeneity test, the samples are considered homogeneous.

Stability: The standard deviation between days was tested against 0.3 * s(L). The F-test value is smaller than the critical value (F95%) in the stability test and therefore the samples are considered stable.

Stability and homogeneity test **Method evaluation study - oil in soil**

Sample **H**
Parameter **o-Xylene, mg/kg**

Date	Sample	I	II	M. bottle	Var. replicate	Day mean	Day var.
20-04-04	H 11	5,99		5,99			
	H 25	5,97		5,97			
	H 46	5,44		5,44		5,80	0,098
22-04-04	H 1	6,26		6,26			
	H 14	6,02		6,02			
	H 20	6,13		6,13		6,14	0,014
26-04-04	H 15	6,15		6,15			
	H 21	6,02		6,02			
	H 31	6,13		6,13		6,10	0,005
28-04-04	H 2	6,24		6,24			
	H 18	6,19		6,19			
	H 34	5,70		5,70		6,04	0,090

Homogeneity

F test value = var.bottle/(0,3*S(L))^2	2,035
F critical value = inv. 95%(f bottle,f rep)	4,284
F critical value = inv.99%(f bottle,f rep)	8,466

	s	var.	f	Stab mean
Replicate	0,602	0,362	6	
Bottle	0,254	0,064	6	
Stability	0,153	0,023	3	6,02

Stability tested by var. replicate

F test value = var.stab./(0,3*S(L))^2	0,737
F critical value = inv. 95%(f stab,f rep)	4,757
F critical value = inv.99%(f stab,f rep)	9,780

s(w) standard deviation within a laboratories in the proficiency test =	0,03
s(L) standard deviation between laboratories in the proficiency test =	0,59
Eurofins' standard deviation from internal quality control s(w) =	0,00
Eurofins' standard deviation from internal quality control s(b) =	0,00

s = standard deviation
Var. = variance
Rep = replicate = within the bottle
Bottle = between bottles
Stab = stability = between days
f = number of degrees of freedom

Conclusion

Homogeneity: The repeatability standard deviation in this test is larger than 0.3 * s(L) in the proficiency test. The standard deviation between bottles is therefore tested against 0.3 * s(L). As the F-test value is less than the critical value (F95%) in the homogeneity test, the samples are considered homogeneous.

Stability: The standard deviation between days was tested against 0.3 * s(L). The F-test value is smaller than 1 in the stability test and therefore the samples are considered stable.

A N N E X G

Symbols and abbreviations

Tables

<	"Less than" - results are not included in calculations
U, UL, **	Results excluded manually
UC, C**	Cochran outlier. Results are not included in statistical data analysis
UG, G**	Grubbs outlier. Results are not included in statistical data analysis

Plots

<	"Less than" - results are not included in plots
U, UL, **	Results excluded manually, not included in plots
•	Assigned value (= ”true” value)

Statistical symbols

μ	Assigned value
p	Number of laboratories included in calculations. This is equal to number of laboratories reporting results minus any laboratories excluded on the basis of a professional estimation (**) minus Cochran outliers (UC) and minus Grubbs outliers (UG)
n	Number of results included in calculations
m	Average of all non-excluded results
M	Median
d	Average difference between results from a pair of samples, corrected for split
t	Test size at Student's t-test
p	A probability level for statistical test
s	Standard deviation
F	Test size for F-test
s_i	The standard deviation of one participant, equal to the variation of repeated determinations of one sample
s_r	Standard deviation within a laboratory
s_r^2	Repeatability
s_L	Standard deviation between laboratories

s_L^2	Laboratory variance
s_R	Reproducibility standard deviation
s_R^2	Reproducibility
CV_r	Coefficient of variation within a laboratory $(s_r \cdot 100)/\mu$
CV_R	Total coefficient of variation $(s_R \cdot 100)/\mu$

A N N E X H

Control of recovery

Benzene, mg/kg
Control of recovery, average of results

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H
1	0.1700	0.4800	-	0.5350 UG	-	-	-	0.2450
2	-	-	-	-	-	-	-	0.0550
3	0.0440	0.0305	-	-	-	-	-	0.4615
4	0.0515	-	-	0.1090	-	-	-	0.1240
5	0.0500	-	-	-	-	-	-	0.1450
6	0.0590	0.0170	-	0.1585	-	-	-	0.1580
7	-	-	-	-	-	-	-	-
8A	0.1360	-	-	0.1405	-	-	-	0.0544
8B	0.0618	-	-	0.1390	-	-	-	0.1795
9	-	-	-	-	-	-	-	-
10A	0.0970	-	-	0.2445	-	-	-	0.5890
10B	0.0639	-	-	0.1131	-	-	-	0.1665
No of labs., p	9	3	0	6	0	0	0	10
No of repl., n	2	2	2	2	2	2	2	2
m	0.0815	0.1758	-	0.1508	-	-	-	0.2178
s^2	0.0019	0.0694	-	0.0025	-	-	-	0.0303
s	0.0441	0.2635	-	0.0495	-	-	-	0.1741
Assigned value, μ	0.06	0.01	-	0.15	-	-	-	0.17
Recovery, %	135.8	1758.3	-	100.5	-	-	-	128.1
$t = \sqrt{p} \cdot (m-\mu)/s$	1.4600	1.0901	-	0.0375	-	-	-	0.8678
Sign. level, p(t)	0.1824	0.3895	-	0.9715	-	-	-	0.4081

No test statistics were found to be significant
UG denotes a Grubbs outlier

Toluene, mg/kg
Control of recovery, average of results

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H
1	0.0200	0.0230	-	0.2000	-	-	-	1.850
2	0.0500	0.0250	-	0.1400	-	-	-	0.280
3	0.0315	0.0265	-	0.1815	-	-	-	1.962
4	0.0455	0.0280	-	0.1835	-	-	-	2.635
5	0.0300	0.0300	-	0.1500	-	-	-	3.440
6	0.0550	0.0410 UG	-	0.2020	-	-	-	2.650
7	0.0110	0.0310	-	0.1250	-	-	-	1.580
8A	0.1330	0.0516 UG	-	0.2235	-	-	-	2.734
8B	0.0768	0.0246	-	0.2060	-	-	-	3.061
9	-	-	-	-	-	-	-	0.590
10A	0.0630	-	-	0.1910	-	-	-	3.335
10B	0.0604	0.0270	-	0.1765	-	-	-	2.945
No of labs., p	11	8	0	11	0	0	0	12
No of repl., n	2	2	2	2	2	2	2	2
m	0.0524	0.0269	-	0.1799	-	-	-	2.255
s^2	0.0011	0.0000	-	0.0009	-	-	-	1.055
s	0.0332	0.0027	-	0.0302	-	-	-	1.027
Assigned value, μ	0.06	0.03	-	0.2	-	-	-	2.6
Recovery, %	87.3	89.6	-	90.0	-	-	-	86.7
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.7618	-3.2321	-	-2.2059	-	-	-	-1.1633
Sign. level, p(t)	0.4638	0.0144 *	-	0.0519	-	-	-	0.2693

* denotes that there is a significant difference (t-test, 5%-level)
** denotes that there is a significant difference (t-test, 1%-level)
*** denotes that there is a significant difference (t-test, 0.1%-level)
UG denotes a Grubbs outlier

Ethylbenzene, mg/kg
Control of recovery, average of results

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H
1	0.0465	0.0230	-	0.2150	-	-	-	1.750
2	0.0350	0.0250	-	0.1700	-	-	-	0.455
3	0.0340	0.0150	-	0.1950	-	-	-	1.103
4	0.0455	0.0195	-	0.2045	-	-	-	1.777
5	0.0450	0.0350	-	0.2250	-	-	-	1.765
6	0.0555	0.0295	-	0.2010	-	-	-	1.770
7	0.0060	0.0160	-	0.1850	-	-	-	1.230
8A	0.0740	0.0280	-	0.2205	-	-	-	1.901
8B	0.0556	0.0169	-	0.2110	-	-	-	1.998
9	- U	-	-	- U	-	-	-	0.995
10A	0.0490	-	-	0.2205	-	-	-	1.820
10B	0.0407	0.0165	-	0.2065	-	-	-	1.965
No of labs., p	11	10	0	11	0	0	0	12
No of repl., n	2	2	2	2	2	2	2	2
m	0.0442	0.0224	-	0.2049	-	-	-	1.544
s^2	0.0003	0.0000	-	0.0003	-	-	-	0.233
s	0.0168	0.0068	-	0.0166	-	-	-	0.483
Assigned value, μ	0.05	0.02	-	0.2	-	-	-	1.8
Recovery, %	88.5	112.2	-	102.5	-	-	-	85.8
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.1334	1.1307	-	0.9801	-	-	-	-1.8355
Sign. level, p(t)	0.2835	0.2874	-	0.3502	-	-	-	0.0936

No test statistics were found to be significant
U denotes data excluded from the data file

m+p-Xylene, mg/kg
Control of recovery, average of results

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H
1	0.0985	0.1000	-	0.4850	-	-	-	8.050
2	0.0700	0.0750	-	0.3550	-	-	-	2.690
				UG				UG
3	0.0675	0.1145	-	0.4755	-	-	-	7.913
4	0.0920	0.0905	-	0.4640	-	-	-	8.393
5	0.0850	0.1350	-	0.5100	-	-	-	7.185 UC
6	0.1085	0.1370	-	0.4720	-	-	-	7.875
7	0.0100	0.0980	-	0.4050 UG	-	-	-	5.305 UG
8A	0.1380	0.1220	-	0.5025	-	-	-	8.637
8B	0.1015	0.0770	-	0.4680	-	-	-	8.954
9	- U	- U	- U	- U	- U	- U	- U	- U
10A	0.0940	0.1035	-	0.4850	-	-	-	7.020
10B	0.0995	0.1026	-	0.5050	-	-	-	8.350
No of labs., p	11	11	0	9	0	0	0	8
No of repl., n	2	2	2	2	2	2	2	2
m	0.0877	0.1050	-	0.4852	-	-	-	8.149
s^2	0.0010	0.0004	-	0.0003	-	-	-	0.343
s	0.0320	0.0207	-	0.0170	-	-	-	0.586
Assigned value, μ	0.1	0.1	-	0.50	-	-	-	8.0
Recovery, %	87.7	105.0	-	97.0	-	-	-	101.9
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.2777	0.8031	-	-2.6033	-	-	-	0.7196
Sign. level, p(t)	0.2302	0.4406	-	0.0315 *	-	-	-	0.4951

* denotes that there is a significant difference (t-test, 5%-level)
** denotes that there is a significant difference (t-test, 1%-level)
*** denotes that there is a significant difference (t-test, 0.1%-level)
UC denotes a Cochran outlier
UG denotes a Grubbs outlier
U denotes data excluded from the data file

o-Xylene, mg/kg
Control of recovery, average of results

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H
1	0.0620	0.0500	-	0.2400	-	-	-	3.800
2	0.0500	0.0450	-	0.1700	-	-	-	2.490
3	0.0410	0.0480	-	0.2300	-	-	-	3.308
4	0.0610	0.0455	-	0.2230	-	-	-	3.705
5	0.0500	0.0600	-	0.2300	-	-	-	3.265 UC
6	0.0665	0.0700	-	0.2360	-	-	-	3.905
7	0.0120	0.0370	-	0.2000	-	-	-	2.645
8A	0.0804	0.0528	-	0.2320	-	-	-	3.872
8B	0.0588	0.0370	-	0.2260	-	-	-	4.025
9	-	0.1700 UG	-	0.3900 UG	-	-	-	1.865 UC
10A	0.0680	0.0570	-	0.2625	-	-	-	3.830 UC
10B	0.0713	0.0514	-	0.2465	-	-	-	4.075
No of labs., p	11	11	0	11	0	0	0	9
No of repl., n	2	2	2	2	2	2	2	2
m	0.0564	0.0503	-	0.2269	-	-	-	3.536
s^2	0.0003	0.0001	-	0.0006	-	-	-	0.352
s	0.0184	0.0097	-	0.0243	-	-	-	0.593
Assigned value, μ	0.07	0.05	-	0.25	-	-	-	3.7
Recovery, %	80.6	100.7	-	90.8	-	-	-	95.6
$t = \sqrt{p} \cdot (m-\mu)/s$	-2.4447	0.1116	-	-3.1453	-	-	-	-0.8289
Sign. level, p(t)	0.0346 *	0.9134	-	0.0104 *	-	-	-	0.4312

* denotes that there is a significant difference (t-test, 5%-level)
** denotes that there is a significant difference (t-test, 1%-level)
*** denotes that there is a significant difference (t-test, 0.1%-level)
UC denotes a Cochran outlier
UG denotes a Grubbs outlier

C_6H_6 - C_{10}, mg/kg
Control of recovery, average of results

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H
1	-	7.075	5.550	8.950	5.950	7.850	4.400	216.00
2	-	2.405	-	3.170	-	-	-	177.50
3	-	2.655	2.010	6.401	1.292	2.741	0.948 UC	155.91
4	-	2.740	-	2.225	-	-	-	186.35
5	-	-	-	-	-	-	-	230.00
6	-	6.390	-	10.595 UC	-	14.700	3.530 UC	276.00
7	-	4.000	-	10.000	-	-	-	82.50
8A	-	6.090	3.085	10.035	3.310	10.330	-	224.00
8B	-	5.160	3.050	11.130	3.305	9.975	-	216.50
9	-	17.650 UC	17.650 UC	97.000 UG	18.850 UC	22.550 UC	11.100	44.20
10A	-	-	-	3.750	-	2.795	-	258.50
10B	-	-	-	-	-	-	-	-
No of labs., p	0	8	4	8	4	6	2	11
No of repl., n	2	2	2	2	2	2	2	2
m	-	4.564	3.424	6.958	3.464	8.065	7.750	187.95
s^2	-	3.468	2.258	12.492	3.649	21.793	22.445	5032.16
s	-	1.862	1.503	3.534	1.910	4.668	4.738	70.94
Assigned value, μ	-	-	2.5	-	2.5	-	2.5	190
Recovery, %	-	-	136.9	-	138.6	-	310.0	98.9
$t = \sqrt{p} \cdot (m-\mu)/s$	-	-	1.2295	-	1.0096	-	1.5672	-0.0958
Sign. level, p(t)	-	-	0.3065	-	0.3871	-	0.3616	0.9256

No test statistics were found to be significant
UC denotes a Cochran outlier
UG denotes a Grubbs outlier

>C_{10} - C_{25}, mg/kg
Control of recovery, average of results

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H
1	23.74	80.95	23.00	273.00	120.00	108.00	289.00	3680.0
2	18.90	66.95	13.50	210.40	133.35	99.10	330.20	3290.0
3	20.93	78.47	12.93	327.07	119.38	105.09	255.73	3679.6
4	20.11	75.65	17.32	275.70	114.45	101.25	291.65	3747.6
5	21.50	94.00 UC	27.50	265.00	145.00	135.00	265.00	4200.0
6	26.80	114.70 UC	29.75	273.00	151.00	134.00	378.00	4075.0
7	23.50	62.00	31.00	308.00	96.50	122.50	177.00	1375.0
8A	28.27	88.23	23.49	287.23	137.13	123.19	289.49	4145.5 UC
8B	27.44	84.69	29.23	308.76	120.89	121.24	301.31	3840.0
9	7.20	6.90 UG	31.60 UC	107.20 UG	75.15	169.00 UC	85.00	1446.5
10A	24.50	86.25	12.20	290.50	146.00	111.00	358.00	4950.0
10B	-	-	-	-	-	-	-	-
No of labs., p	11	8	10	10	11	10	11	10
No of repl., n	2	2	2	2	2	2	2	2
m	22.08	77.90	21.99	281.87	123.53	116.04	274.58	3428.4
s^2	33.71	87.14	55.46	1015.56	519.22	168.62	6809.41	21102.6
s	5.81	9.34	7.45	31.87	22.79	12.99	82.52	1149.4
Assigned value, μ	24	79	25	280	130	110	290	3700
Recovery, %	92.0	98.6	88.0	100.7	95.0	105.5	94.7	92.7
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.0962	-0.3335	-1.2773	0.1852	-0.9415	1.4702	-0.6197	-0.7473
Sign. level, p(t)	0.2987	0.7485	0.2335	0.8572	0.3687	0.1756	0.5493	0.4739

No test statistics were found to be significant
UC denotes a Cochran outlier
UG denotes a Grubbs outlier

>C_{25} - C_{40}, mg/kg
Control of recovery, average of results

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H
1	21.70	70.80	124.00	136.00	400.00	719.00	190.00	193.5
2	16.85	45.15	81.30	92.75	412.95	818.85	322.55	295.1
3	9.76	43.05	59.91	163.45	258.32	506.04	37.05	110.2
4	-	62.50	104.80	137.25	354.45	629.35	103.10	141.3
5	-	130.00 UC	140.00	180.00	650.00	1400.00 UG	275.00	340.0
6	17.60	77.75	138.00	139.00	475.00	859.50	61.65	304.0
7	18.50	39.00	76.50	185.00	297.00	673.50	40.00	109.0
8A	17.02	66.45	105.75	153.79	403.89	725.67	114.12	153.5
8B	17.27	50.80	126.97	202.78	376.46	788.51	83.64	148.5
9	33.55	22.70	22.70	155.20	465.35	1460.50 UC	17.40	441.0
10A	-	79.00	117.50	146.00	455.00	711.50	91.50	178.0
10B	-	-	-	-	-	-	-	-
No of labs., p	8	10	11	11	11	9	11	11
No of repl., n	2	2	2	2	2	2	2	2
m	19.03	55.72	99.77	153.75	413.49	714.66	121.45	219.5
s^2	45.45	342.48	1319.42	875.18	10691.05	11241.81	9959.58	11852.2
s	6.74	18.51	36.32	29.58	103.40	106.03	99.80	108.9
Assigned value, μ	21	63	110	140	410	760	90	170
Recovery, %	90.6	88.4	90.7	109.8	100.9	94.0	134.9	129.1
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.8263	-1.2442	-0.9344	1.5412	0.1120	-1.2829	1.0453	1.5069
Sign. level, p(t)	0.4359	0.2449	0.3721	0.1543	0.9130	0.2354	0.3205	0.1628

No test statistics were found to be significant
UC denotes a Cochran outlier
UG denotes a Grubbs outlier

Total hydrocarbons, mg/kg
Control of recovery, average of results

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H
1	45.45	159.00	152.50	418.00	526.50	834.50	484.00	4090.0
2	38.60	114.50	94.90	306.30	546.70	918.50	653.00	3762.5
3	20.93	121.52	72.83	496.92	377.71	611.13	292.77	3945.7
4	20.11	140.90	122.10	415.20	468.95	730.60	444.75	4075.1
5	-	225.00	170.00	445.00	790.00	1500.00 UG	530.00	4800.0
6	44.40	199.50	168.00	423.00	625.50	1008.50	443.50	4660.0
7	42.00	105.00	107.50	502.00	393.50	796.00	216.00	1565.0
8A	45.30	160.76	132.32	451.05 UC	517.68	859.19	403.61	4523.0 UC
8B	44.70	140.65	159.25	522.67	500.66	919.72	384.96	4205.0
9	40.70	47.35	47.35	359.00	540.50	1629.00 UC	103.05	1931.5
10A	24.50	165.00	129.50	440.00	601.00	825.50	449.50	5390.0
10B	-	-	-	-	-	-	-	-
No of labs., p	10	11	11	10	11	9	11	10
No of repl., n	2	2	2	2	2	2	2	2
m	36.67	143.56	123.30	432.81	535.34	833.74	400.47	3842.5
s^2	110.49	2284.49	1581.71	4361.28	12841.57	13431.85	22807.95	53623.3
s	10.51	47.80	39.77	66.04	113.32	115.90	151.02	1205.7
Assigned value, μ	44	140	120	430	520	880	430	4100
Recovery, %	83.3	102.5	102.7	100.7	102.9	94.7	93.1	93.7
$t = \sqrt{p} \cdot (m-\mu)/s$	-2.2056	0.2471	0.2748	0.1345	0.4488	-1.1975	-0.6486	-0.6754
Sign. level, p(t)	0.0548	0.8098	0.7890	0.8959	0.6631	0.2654	0.5312	0.5164

No test statistics were found to be significant
UC denotes a Cochran outlier
UG denotes a Grubbs outlier

Fluoranthene, mg/kg
Control of recovery, average of results

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H
1	0.0300	-	-	0.3650	-	0.3100	0.0200	0.0450
2	0.0280	-	-	-	-	0.3425	0.0220	0.0530
3	-	-	-	-	-	-	-	-
4	0.0240	-	-	0.2920	-	0.7370 UC	0.0340 UC	0.0245
5	- U	- U	- U	- U	- U	- U	- U	- U
6	0.0245	-	-	0.3375	-	0.2305	0.0185	0.0420
7	0.0245	-	-	0.3100	-	0.2500	0.0320	0.0490
8A	0.0278	-	-	0.3400	-	0.2775	0.0200	0.0668
8B	0.0268	-	-	0.3470	-	0.2800	0.0197	0.0617
9	0.0109 UG	-	-	0.1450 UG	-	0.3135 UC	0.0107	-
10A	-	-	-	-	-	-	-	-
10B	0.0233	-	-	0.3370	-	0.2440	0.0230	0.0374
No of labs., p	8	0	0	7	0	7	8	8
No of repl., n	2	2	2	2	2	2	2	2
m	0.0261	-	-	0.3326	-	0.2764	0.0207	0.0474
s^2	0.0000	-	-	0.0006	-	0.0016	0.0000	0.0002
s	0.0024	-	-	0.0242	-	0.0395	0.0059	0.0135
Assigned value, μ	0.027	-	-	0.34	-	0.26	0.02	0.05
Recovery, %	96.6	-	-	97.8	-	106.3	103.6	94.8
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.0775	-	-	-0.8043	-	1.0954	0.3453	-0.5427
Sign. level, p(t)	0.3170	-	-	0.4519	-	0.3154	0.7400	0.6042

No test statistics were found to be significant
UC denotes a Cochran outlier
UG denotes a Grubbs outlier
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Benzo(b+j+k)fluoranthene, mg/kg
Control of recovery, average of results

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H
1	0.0600	-	-	0.4050	-	0.6500	0.0200	0.0750
2	0.0640	-	-	-	-	0.6985	0.0445	0.0625
3	-	-	-	-	-	-	-	-
4	0.0505	-	-	0.3390	-	0.8355	0.0850 UC	0.0565
5	- U	- U	- U	- U	- U	- U	- U	- U
6	0.0490	-	-	0.3650	-	0.4975	0.0250	0.0590
7	0.0490	-	-	0.3800	-	0.5500	0.0190	0.0620
8A	0.0521	-	-	0.3855	-	0.6070	0.0250	0.0570
8B	0.0525	-	-	0.3590	-	0.5715	0.0260	0.0568
9	0.0175 UG	-	-	0.1350 UG	-	0.4640	0.0147	-
10A	-	-	-	-	-	-	-	-
10B	0.0481	-	-	0.3415	-	0.5330	0.0347	0.0498
No of labs., p	8	0	0	7	0	9	8	8
No of repl., n	2	2	2	2	2	2	2	2
m	0.0531	-	-	0.3679	-	0.6008	0.0261	0.0598
s^2	0.0000	-	-	0.0006	-	0.0131	0.0001	0.0001
s	0.0058	-	-	0.0240	-	0.1143	0.0095	0.0073
Assigned value, μ	0.053	-	-	0.37	-	0.58	0.026	0.059
Recovery, %	100.2	-	-	99.4	-	103.6	100.4	101.4
$t = \sqrt{p} \cdot (m-\mu)/s$	0.0642	-	-	-0.2364	-	0.5454	0.0279	0.3203
Sign. level, p(t)	0.9506	-	-	0.8210	-	0.6004	0.9785	0.7581

No test statistics were found to be significant
UC denotes a Cochran outlier
UG denotes a Grubbs outlier
U denotes data excluded from the data file

Benzo(a)pyrene, mg/kg
Control of recovery, average of results

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H
1	0.0300	-	-	0.2100	-	0.3150	0.0200	0.0250
2	0.0260	-	-	-	-	0.3125	0.0240	0.0195
3	-	-	-	-	-	-	-	-
4	0.0250	-	-	0.1740	-	0.4245 UC	0.0515 UC	0.0200
5	- U	-	-	-	-	0.2920	- U	- U
6	0.0240	-	-	0.1900	-	0.2520	0.0155	0.0220
7	0.0225	-	-	0.1800	-	0.2500	0.0110	0.0185
8A	0.0277	-	-	0.1875	-	0.2850	0.0147	0.0201
8B	0.0264	-	-	0.1890	-	0.2725	0.0155	0.0204
9	0.0083	-	-	0.0673 UG	-	0.2215	0.0082	-
10A	-	-	-	-	-	-	-	-
10B	0.0146	-	-	0.1590	-	0.2135	0.0177	0.0161
No of labs., p	9	0	0	7	0	9	8	8
No of repl., n	2	2	2	2	2	2	2	2
m	0.0227	-	-	0.1842	-	0.2682	0.0158	0.0202
s^2	0.0000	-	-	0.0002	-	0.0013	0.0000	0.0000
s	0.0069	-	-	0.0158	-	0.0367	0.0049	0.0026
Assigned value, μ	0.027	-	-	0.18	-	0.27	0.016	0.020
Recovery, %	84.1	-	-	102.3	-	99.3	98.9	100.9
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.8624	-	-	0.7076	-	-0.1452	-0.1038	0.2047
Sign. level, p(t)	0.0996	-	-	0.5058	-	0.8881	0.9202	0.8436

No test statistics were found to be significant
UC denotes a Cochran outlier
UG denotes a Grubbs outlier
U denotes data excluded from the data file

Indeno(1,2,3-cd)pyrene, mg/kg
Control of recovery, average of results

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H
1	0.0300	-	-	0.1950	-	0.2550	-	0.0200
2	0.0235	-	-	-	-	0.3200	0.0160	0.0230
3	-	-	-	-	-	-	-	-
4	0.0255	-	-	0.1920	-	0.3810	0.0380 UC	0.0240
5	- U	- U	- U	- U	- U	- U	- U	- U
6	0.0255	-	-	0.1835	-	0.2615	0.0110	0.0245
7	0.0240	-	-	0.1600	-	0.2350	0.0050	0.0215
8A	0.0341 UC	-	-	0.2175	-	0.3055	0.0128	0.0227
8B	0.0329	-	-	0.2410	-	0.2885	0.0118	0.0226
9	0.0092	-	-	0.0723	-	0.1785	0.0049	-
10A	-	-	-	-	-	-	-	-
10B	0.0195	-	-	0.1420	-	0.1760	0.0111	0.0085 UG
No of labs., p	8	0	0	8	0	9	7	7
No of repl., n	2	2	2	2	2	2	2	2
m	0.0238	-	-	0.1754	-	0.2668	0.0104	0.0226
s^2	0.0001	-	-	0.0027	-	0.0044	0.0000	0.0000
s	0.0072	-	-	0.0518	-	0.0662	0.0041	0.0015
Assigned value, μ	0.027	-	-	0.19	-	0.26	0.012	0.022
Recovery, %	88.0	-	-	92.3	-	102.6	86.3	102.8
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.2789	-	-	-0.7965	-	0.3071	-1.0699	1.0630
Sign. level, p(t)	0.2417	-	-	0.4519	-	0.7666	0.3258	0.3287

No test statistics were found to be significant
UC denotes a Cochran outlier
UG denotes a Grubbs outlier
U denotes data excluded from the data file

Dibenz(a,h)anthracene, mg/kg
Control of recovery, average of results

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H
1	0.0300	-	-	0.0500	-	0.0750	-	-
2	0.0225	-	-	-	-	0.0675	-	0.0050
3	-	-	-	-	-	-	-	-
4	0.0265	-	-	0.0420	-	0.0935 UC	0.0140 UG	0.0050
5	- U	- U	- U	- U	- U	- U	- U	- U
6	0.0250	-	-	0.0355	-	0.0600	-	0.0055
7	0.0240	-	-	0.0450	-	0.0630	-	0.0060
8A	0.0308 UC	-	-	0.0429	-	0.0780	0.0028	0.0050
8B	0.0314 UC	-	-	0.0448	-	0.0811	0.0024	0.0049
9	0.0083	-	-	0.0164	-	0.0430	0.0008	-
10A	-	-	-	-	-	-	-	-
10B	0.0212	-	-	0.0370	-	0.0525	0.0030	-
No of labs., p	7	0	0	8	0	8	4	6
No of repl., n	2	2	2	2	2	2	2	2
m	0.0225	-	-	0.0392	-	0.0650	0.0022	0.0052
s^2	0.0000	-	-	0.0001	-	0.0002	0.0000	0.0000
s	0.0069	-	-	0.0103	-	0.0131	0.0010	0.0004
Assigned value, μ	0.027	-	-	0.042	-	0.065	0.005	0.005
Recovery, %	83.3	-	-	93.3	-	100.0	44.8	104.5
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.7326	-	-	-0.7711	-	0.0013	-5.5841	1.2586
Sign. level, p(t)	0.1339	-	-	0.4659	-	0.9990	0.0113 *	0.2637

* denotes that there is a significant difference (t-test, 5%-level)
** denotes that there is a significant difference (t-test, 1%-level)
*** denotes that there is a significant difference (t-test, 0.1%-level)
UC denotes a Cochran outlier
UG denotes a Grubbs outlier
U denotes data excluded from the data file

Sum of naphthalenes, mg/kg
Control of recovery, average of results

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H
1	1.0500	0.6600	- U	0.3650	0.1200	- U	- U	44.000
2	1.6495	2.6120	-	-	1.1280	0.2110	0.2345	131.050
3	-	-	-	-	-	-	-	-
4	1.0500	1.1190	-	0.5480	0.5215	0.3115	0.1775	87.050
5	1.4800	2.8100 UC	0.300	3.2100 UC	1.0950	0.3050	0.8950 UG	160.000
6	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-
8A	0.8210	1.3680	0.013	1.2165	0.6700	0.1180	0.1755	105.226
8B	0.8725	1.3825	0.024	0.1910	0.5335	0.1475	0.1765	81.535
9	-	-	-	-	-	-	-	-
10A	-	-	-	-	-	-	-	-
10B	0.8490	1.0100	- U	0.5130	0.5220	0.0608	0.1090	42.200
No of labs., p	7	6	3	5	7	6	5	7
No of repl., n	2	2	2	2	2	2	2	2
m	1.1103	1.3586	0.112	0.5667	0.6557	0.1923	0.1746	93.009
s^2	0.1072	0.4477	0.026	0.1518	0.1257	0.0104	0.0020	1872.457
s	0.3274	0.6691	0.163	0.3896	0.3545	0.1021	0.0445	43.272
Assigned value, μ	0.94	1	0.02	0.5	0.5	0.1	0.2	90
Recovery, %	118.1	135.9	560.8	113.3	131.1	192.3	87.3	103.3
$t = \sqrt{p} \cdot (m-\mu)/s$	1.3760	1.3127	0.9808	0.3828	1.1621	2.2148	-1.2777	0.1840
Sign. level, p(t)	0.2180	0.2463	0.4301	0.7214	0.2893	0.0776	0.2705	0.8601

No test statistics were found to be significant
UC denotes a Cochran outlier
UG denotes a Grubbs outlier
U denotes data excluded from the data file

Sum of phenanthrenes, mg/kg
Control of recovery, average of results

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H
1	0.3900	0.1400	- U	0.2450	0.2400	0.1600	0.0200	3.185
2	0.3940	0.4770	-	-	1.0875	0.2955	0.1300	7.633
3	-	-	-	-	-	-	-	-
4	0.4495	0.6000	0.0175	0.5545	1.4955	1.7220 UC	0.2500	11.200
5	0.4300	0.7650 UC	0.0250	0.4600	1.2050	0.4050	0.2000	9.650
6	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-
8A	0.3400	0.7770	0.0190	0.6405	2.6385 UC	0.6595	0.2525	8.320
8B	0.3630	0.7550	0.0315	0.6050	2.1455	0.4810	0.2490	6.341
9	-	-	-	-	-	-	-	-
10A	-	-	-	-	-	-	-	-
10B	0.2920	0.4490	0.0028	0.3475	1.0300	0.2180	0.3817 UC	8.935
No of labs., p	7	6	5	6	6	6	6	7
No of repl., n	2	2	2	2	2	2	2	2
m	0.3798	0.5330	0.0192	0.4754	1.2006	0.3698	0.1836	7.895
s^2	0.0029	0.0556	0.0001	0.0240	0.3889	0.0340	0.0087	6.656
s	0.0536	0.2358	0.0107	0.1549	0.6236	0.1845	0.0931	2.580
Assigned value, μ	0.4	0.6	0.02	0.5	1	0.3	0.2	8
Recovery, %	94.9	88.8	95.8	95.1	120.1	123.3	91.8	98.7
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.9972	-0.6961	-0.1758	-0.3887	0.7879	0.9274	-0.4319	-0.1078
Sign. level, p(t)	0.3572	0.5174	0.8690	0.7135	0.4665	0.3963	0.6838	0.9177

No test statistics were found to be significant
UC denotes a Cochran outlier
U denotes data excluded from the data file

17alfa(H),21beta(H)-Hopane, mg/kg
Control of recovery, average of results

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H
1	0.125 UC	0.110	0.165 UC	0.360	0.640	2.400	0.210	0.060
2	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-
4	0.050	-	-	0.131	0.207	0.690	0.106	-
5	-	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-
8A	0.077	0.070	0.040	0.194	0.393	1.216	0.144	0.115
8B	0.064	0.063 UC	0.058	0.204	0.338	1.226	0.131	0.097
9	-	-	-	-	-	-	-	-
10A	-	-	-	-	-	-	-	-
10B	- U	- U	- U	- U	- U	- U	- U	- U
No of labs., p	3	2	2	4	4	4	4	3
No of repl., n	2	2	2	2	2	2	2	2
m	0.064	0.090	0.049	0.222	0.394	1.383	0.148	0.091
s^2	0.000	0.001	0.000	0.010	0.033	0.523	0.002	0.001
s	0.014	0.028	0.013	0.098	0.181	0.723	0.044	0.028
Assigned value, μ	0.07	0.07	0.06	0.20	0.34	1.2	0.14	0.09
Recovery, %	90.7	128.6	80.8	111.1	116.0	115.2	105.5	100.7
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.8340	1.0000	-1.2778	0.4538	0.5982	0.5052	0.3487	0.0409
Sign. level, p(t)	0.4920	0.5000	0.4227	0.6808	0.5918	0.6482	0.7503	0.9711

No test statistics were found to be significant
UC denotes a Cochran outlier
U denotes data excluded from the data file

Pristane, mg/kg
Control of recovery, average of results

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H
1	0.890	-	-	-	-	-	-	-
2	0.340	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-
4	0.401	-	-	-	-	-	-	-
5	0.840	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-
8A	1.025	-	-	-	-	-	-	-
8B	0.872	-	-	-	-	-	-	-
9	-	-	-	-	-	-	-	-
10A	-	-	-	-	-	-	-	-
10B	0.993	-	-	-	-	-	-	-
No of labs., p	7	0	0	0	0	0	0	0
No of repl., n	2	2	2	2	2	2	2	2
m	0.766	-	-	-	-	-	-	-
s^2	0.078	-	-	-	-	-	-	-
s	0.278	-	-	-	-	-	-	-
Assigned value, μ	0.83	-	-	-	-	-	-	-
Recovery, %	92.3	-	-	-	-	-	-	-
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.6089	-	-	-	-	-	-	-
Sign. level, p(t)	0.5649	-	-	-	-	-	-	-

No test statistics were found to be significant

n-C17/pristane
Control of recovery, average of results

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H
1	-	1.357	- U	0.2930	1.850	- U	0.079	1.223
2	-	1.165	-	0.2300	3.610	1.515	0.135	1.075
3	-	-	-	-	-	-	-	-
4	-	1.350	5.20	0.1700	3.950	2.050	0.085	1.110
5	-	1.805	- U	0.4150 UC	5.135	1.905	0.645 UC	2.815
6	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-
8A	-	1.864	-	0.1370	5.173	1.352	- U	1.100
8B	-	1.828	-	0.1240	2.034	2.448	- U	0.865
9	-	-	-	-	-	-	-	-
10A	-	-	-	-	-	-	-	-
10B	-	1.120	2.37	0.2705	3.255	2.310	0.168	1.845
No of labs., p	0	7	2	6	7	6	4	7
No of repl., n	2	2	2	2	2	2	2	2
m	-	1.498	3.78	0.2041	3.573	1.930	0.117	1.433
s^2	-	0.105	4.00	0.0050	1.764	0.187	0.002	0.465
s	-	0.325	2.00	0.0708	1.328	0.432	0.043	0.682
Assigned value, μ	-	1.4	-	0.2	3.3	2	0.1	1.2
Recovery, %	-	107.0	-	102.0	108.3	96.5	116.9	119.4
$t = \sqrt{p} \cdot (m-\mu)/s$	-	0.8016	-	0.1413	0.5430	-0.3971	0.7923	0.9049
Sign. level, p(t)	-	0.4534	-	0.8932	0.6067	0.7077	0.4861	0.4004

No test statistics were found to be significant
UC denotes a Cochran outlier
U denotes data excluded from the data file

n-C18/phytane
Control of recovery, average of results

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H
1	3.149	1.903	- U	0.1570	- U	- U	- U	1.635
2	3.180	1.805	2.20	0.4250	2.650	0.845	0.310 UG	1.690
3	-	-	-	-	-	-	-	-
4	3.000	1.550	5.25 UC	0.2250	3.700	1.620	0.025	1.455
5	3.150 UC	2.595	- U	0.3400	4.755	1.415	0.055	1.520
6	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-
8A	3.583	1.820	-	0.2230	4.651	1.281	0.047	1.243
8B	3.706	1.936	-	0.2550	2.276	1.236	- U	1.264
9	-	-	-	-	-	-	-	-
10A	-	-	-	-	-	-	-	-
10B	2.510	1.460	7.31	0.2255	2.800	0.596	0.045	1.260
No of labs., p	6	7	2	7	6	6	4	7
No of repl., n	2	2	2	2	2	2	2	2
m	3.188	1.867	4.75	0.2644	3.472	1.165	0.043	1.438
s^2	0.184	0.135	13.08	0.0080	1.129	0.143	0.000	0.035
s	0.429	0.367	3.62	0.0894	1.063	0.378	0.013	0.187
Assigned value, μ	3.0	1.8	-	0.24	-	1.1	0.05	1.5
Recovery, %	106.3	103.7	-	110.1	-	105.9	86.0	95.9
$t = \sqrt{p} \cdot (m-\mu)/s$	1.0732	0.4822	-	0.7212	-	0.4238	-1.0999	-0.8777
Sign. level, p(t)	0.3322	0.6467	-	0.4979	-	0.6893	0.3517	0.4139

No test statistics were found to be significant
UC denotes a Cochran outlier
UG denotes a Grubbs outlier
U denotes data excluded from the data file

Pristane/phytane
Control of recovery, average of results

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H
1	0.984	1.627	- U	1.202	- U	- U	1.308	1.558
2	1.000	1.720	-	1.305	0.400 UG	0.665	1.315	1.860
3	-	-	-	-	-	-	-	-
4	0.970	1.500	1.00	1.150	0.815	1.050	1.500	1.600
5	0.980	1.620	- U	1.160	0.795	0.720	1.335	0.650
6	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-
8A	0.962	1.756	-	1.328	0.857 UC	0.998	1.577	1.780
8B	0.926	1.816	-	1.390	0.764	1.090	1.594	1.586
9	-	-	-	-	-	-	-	-
10A	-	-	-	-	-	-	-	-
10B	0.932	1.625	1.67	1.140	0.847	1.005	1.320	1.160
No of labs., p	7	7	2	7	4	6	7	7
No of repl., n	2	2	2	2	2	2	2	2
m	0.965	1.666	1.34	1.239	0.805	0.921	1.421	1.456
s^2	0.001	0.011	0.22	0.010	0.001	0.033	0.017	0.176
s	0.027	0.105	0.47	0.100	0.035	0.181	0.130	0.419
Assigned value, μ	1.0	1.7	-	1.2	0.8	0.9	1.4	1.6
Recovery, %	96.5	98.0	-	103.3	100.6	102.4	101.5	91.0
$t = \sqrt{p} \cdot (m-\mu)/s$	-3.4180	-0.8464	-	1.0359	0.2924	0.2874	0.4306	-0.9078
Sign. level, p(t)	0.0142 *	0.4298	-	0.3402	0.7890	0.7854	0.6818	0.3990

* denotes that there is a significant difference (t-test, 5%-level)
** denotes that there is a significant difference (t-test, 1%-level)
*** denotes that there is a significant difference (t-test, 0.1%-level)
UC denotes a Cochran outlier
UG denotes a Grubbs outlier
U denotes data excluded from the data file

CPI(15-21)
Control of recovery, average of results

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H
1	-	0.665	- U	1.800	0.560 UC	- U	- U	0.690
2	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-
4	-	1.140	0.450	3.500	0.990	1.150	5.050	1.000
5	-	1.095	-	1.785	1.050	1.050	1.995	0.950
6	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-
8A	-	1.288	1.070	0.877	0.993	1.191	0.352	1.215
8B	-	1.268	0.929	0.736	0.916	1.281	0.368	1.113
9	-	-	-	-	-	-	-	-
10A	-	-	-	-	-	-	-	-
10B	-	1.145	1.510	3.545	1.065	1.325	3.505	1.205
No of labs., p	0	6	4	6	5	5	5	6
No of repl., n	2	2	2	2	2	2	2	2
m	-	1.100	0.990	2.040	1.003	1.199	2.254	1.029
s^2	-	0.051	0.191	1.515	0.003	0.012	4.156	0.039
s	-	0.226	0.437	1.231	0.059	0.109	2.039	0.197
Assigned value, μ	-	1.2	-	-	1.0	1.2	-	1.0
Recovery, %	-	91.7	-	-	100.3	99.9	-	102.9
$t = \sqrt{p} \cdot (m-\mu)/s$	-	-1.0798	-	-	0.1062	-0.0144	-	0.3581
Sign. level, p(t)	-	0.3295	-	-	0.9205	0.9892	-	0.7349

No test statistics were found to be significant
UC denotes a Cochran outlier
U denotes data excluded from the data file

CPI(25-33)
Control of recovery, average of results

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H
1	0.090	0.380 UG	- U	- U	0.905	- U	- U	- U
2	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-
4	0.190 UC	0.990	0.780	3.750	0.960	3.800	1.800	1.050
5	0.120	1.010	-	3.425	1.105	4.940	2.210	0.935
6	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-
8A	0.143	1.098	5.825 UC	4.147	1.082	7.235	3.381	0.972
8B	0.139	1.066	2.036	3.083	1.082	6.752	3.870	0.972
9	-	-	-	-	-	-	-	-
10A	-	-	-	-	-	-	-	-
10B	0.121	1.002	1.810	3.130	0.955	5.005	1.880	0.977
No of labs., p	5	5	3	5	6	5	5	5
No of repl., n	2	2	2	2	2	2	2	2
m	0.123	1.033	1.542	3.507	1.015	5.546	2.628	0.981
s^2	0.000	0.002	0.448	0.199	0.007	2.004	0.883	0.002
s	0.021	0.047	0.670	0.447	0.085	1.416	0.940	0.042
Assigned value, μ	0.13	1.0	-	3.5	1.0	-	-	1.0
Recovery, %	94.3	103.3	-	100.2	101.5	-	-	98.1
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.7885	1.5885	-	0.0355	0.4274	-	-	-0.9963
Sign. level, p(t)	0.4745	0.1874	-	0.9733	0.6869	-	-	0.3755

No test statistics were found to be significant
UC denotes a Cochran outlier
UG denotes a Grubbs outlier
U denotes data excluded from the data file

C_6H_6 - C_{10}, mg/kg
Control of recovery, average of results

Laboratory	Level E	Level G
1	-	-
2A	-	-
2B	-	-
3	-	-
4	-	-
5	-	-
6	-	-
7	-	-
8A	-	-
8B	-	-
9	2.70	2.40
10	-	-
No of labs., p	1	1
No of repl., n	2	2
m	2.70	2.40
s^2	-	-
s	-	-
Assigned value, μ	2.5	2.5
Recovery, %	108.0	96.0
$t = \sqrt{p} \cdot (m-\mu)/s$	-	-
Sign. level, p(t)	-	-

No test statistics were found to be significant

>C_{10} - C_{25}, mg/kg
Control of recovery, average of results

Laboratory	Level E	Level G
1	111.00	372.00
2A	-	-
2B	120.10	346.75
3	98.57	380.69
4	143.10	352.20
5	-	-
6	-	-
7	-	-
8A	89.89	457.37
8B	117.92	407.36
9	12.80	151.00
10	-	-
No of labs., p	7	7
No of repl., n	2	2
m	99.05	352.48
s^2	1734.28	9302.82
s	41.64	96.45
Assigned value, μ	110	370
Recovery, %	90.0	95.3
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.6954	-0.4806
Sign. level, p(t)	0.5128	0.6479

No test statistics were found to be significant

>C_{25} - C_{40}, mg/kg
Control of recovery, average of results

Laboratory	Level E	Level G
1	207.00	54.00
2A	-	-
2B	201.40	39.00
3	268.16	55.17
4	328.95	42.60
5	-	-
6	-	-
7	-	-
8A	230.78	74.54
8B	271.50	64.06
9	89.00	39.90
10	-	-
No of labs., p	7	7
No of repl., n	2	2
m	228.11	52.75
s^2	5695.61	177.91
s	75.47	13.34
Assigned value, μ	230	54
Recovery, %	99.2	97.7
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.0661	-0.2472
Sign. level, p(t)	0.9494	0.8130

No test statistics were found to be significant

Total hydrocarbons, mg/kg
Control of recovery, average of results

Laboratory	Level E	Level G
1	318.00	426.00
2A	-	-
2B	321.85	386.35
3	366.74	435.87
4	472.05	394.80
5	-	-
6	-	-
7	-	-
8A	320.67	531.90
8B	389.43	471.43
9	105.00	193.00
10	-	-
No of labs., p	7	7
No of repl., n	2	2
m	327.68	405.62
s^2	12657.38	11217.12
s	112.51	105.91
Assigned value, μ	330	430
Recovery, %	99.3	94.3
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.0546	-0.6090
Sign. level, p(t)	0.9582	0.5648

No test statistics were found to be significant

Fluoranthene, mg/kg
Control of recovery, average of results

Laboratory	Level E	Level G	
1	-	0.0200	
2A	-	0.0260	
2B	-	-	
3	-	-	
4	-	0.0155	
5	-	0.0700	UC
6	-	-	
7	-	-	
8A	-	0.0278	
8B	-	0.0192	
9	-	-	
10	-	-	
No of labs., p	0	5	
No of repl., n	2	2	
m	-	0.0217	
s^2	-	0.0000	
s	-	0.0051	
Assigned value, μ	-	0.02	
Recovery, %	-	108.4	
$t = \sqrt{p} \cdot (m-\mu)/s$	-	0.7459	
Sign. level, p(t)	-	0.4972	

No test statistics were found to be significant
UC denotes a Cochran outlier

Benzo(b+j+k)fluoranthene, mg/kg
Control of recovery, average of results

Laboratory	Level E	Level G
1	-	-
2A	-	0.0350
2B	-	-
3	-	-
4	-	0.0240
5	-	0.0550
6	-	-
7	-	-
8A	-	0.0346
8B	-	0.0264
9	-	-
10	-	-
No of labs., p	0	5
No of repl., n	2	2
m	-	0.0350
s^2	-	0.0001
s	-	0.0122
Assigned value, μ	-	0.026
Recovery, %	-	134.6
$t = \sqrt{p} \cdot (m-\mu)/s$	-	1.6469
Sign. level, p(t)	-	0.1749

No test statistics were found to be significant

Benzo(a)pyrene, mg/kg
Control of recovery, average of results

Laboratory	Level E	Level G	
1	-	0.0200	
2A	-	0.0175	
2B	-	-	
3	-	-	
4	-	0.0130	
5	-	0.0400	UC
6	-	-	
7	-	-	
8A	-	0.0212	
8B	-	0.0195	UC
9	-	0.0100	
10	-	-	
No of labs., p	0	5	
No of repl., n	2	2	
m	-	0.0163	
s^2	-	0.0000	
s	-	0.0047	
Assigned value, μ	-	0.016	
Recovery, %	-	102.1	
$t = \sqrt{p} \cdot (m-\mu)/s$	-	0.1562	
Sign. level, p(t)	-	0.8834	

No test statistics were found to be significant
UC denotes a Cochran outlier

Indeno(1,2,3-cd)pyrene, mg/kg
Control of recovery, average of results

Laboratory	Level E	Level G	
1	-	-	
2A	-	0.0155	
2B	-	-	
3	-	-	
4	-	0.0130	
5	-	0.0400	UC
6	-	-	
7	-	-	
8A	-	0.0175	
8B	-	0.0173	
9	-	-	
10	-	-	
No of labs., p	0	4	
No of repl., n	2	2	
m	-	0.0158	
s^2	-	0.0000	
s	-	0.0021	
Assigned value, μ	-	0.012	
Recovery, %	-	131.7	
$t = \sqrt{p} \cdot (m-\mu)/s$	-	3.6858	
Sign. level, p(t)	-	0.0346	*

* denotes that there is a significant difference (t-test, 5%-level)
** denotes that there is a significant difference (t-test, 1%-level)
*** denotes that there is a significant difference (t-test, 0.1%-level)
UC denotes a Cochran outlier

Dibenz(a,h)anthracene, mg/kg
Control of recovery, average of results

Laboratory	Level E	Level G
1	-	-
2A	-	-
2B	-	-
3	-	-
4	-	-
5	-	-
6	-	-
7	-	-
8A	-	0.00475
8B	-	0.00500
9	-	-
10	-	-
No of labs., p	0	2
No of repl., n	2	2
m	-	0.00488
s^2	-	0.00000
s	-	0.00018
Assigned value, μ	-	0.003
Recovery, %	-	162.5
$t = \sqrt{p} \cdot (m-\mu)/s$	-	15.0000
Sign. level, p(t)	-	0.0424 *

* denotes that there is a significant difference (t-test, 5%-level)
** denotes that there is a significant difference (t-test, 1%-level)
*** denotes that there is a significant difference (t-test, 0.1%-level)

Sum of naphthalenes, mg/kg
Control of recovery, average of results

Laboratory	Level E	Level G
1	-	-
2A	-	-
2B	-	-
3	-	-
4	0.4685	0.1245
5	-	-
6	-	-
7	-	-
8A	-	-
8B	-	-
9	-	-
10	-	-
No of labs., p	1	1
No of repl., n	2	2
m	0.4685	0.1245
s^2	-	-
s	-	-
Assigned value, μ	0.5	0.2
Recovery, %	93.7	62.2
$t = \sqrt{p} \cdot (m-\mu)/s$	-	-
Sign. level, p(t)	-	-

No test statistics were found to be significant

Sum of phenanthrenes, mg/kg
Control of recovery, average of results

Laboratory	Level E	Level G
1	-	-
2A	-	-
2B	-	-
3	-	-
4	1.150	0.1395
5	-	-
6	-	-
7	-	-
8A	-	-
8B	-	-
9	-	-
10	-	-
No of labs., p	1	1
No of repl., n	2	2
m	1.150	0.1395
s^2	-	-
s	-	-
Assigned value, μ	1	0.2
Recovery, %	115.0	69.8
$t = \sqrt{p} \cdot (m-\mu)/s$	-	-
Sign. level, p(t)	-	-

No test statistics were found to be significant

17alfa(H),21beta(H)-Hopane, mg/kg
Control of recovery, average of results

Laboratory	Level E	Level G
1	-	-
2A	-	-
2B	-	-
3	-	-
4	0.1870	0.1015
5	-	-
6	-	-
7	-	-
8A	-	-
8B	-	-
9	-	-
10	-	-
No of labs., p	1	1
No of repl., n	2	2
m	0.1870	0.1015
s^2	-	-
s	-	-
Assigned value, μ	-	0.14
Recovery, %	-	72.5
$t = \sqrt{p} \cdot (m-\mu)/s$	-	-
Sign. level, p(t)	-	-

No test statistics were found to be significant

n-C17/pristane,
Control of recovery, average of results

Laboratory	Level E	Level G
1	-	-
2A	-	-
2B	-	-
3	-	-
4	3.65	0.0965
5	-	-
6	-	-
7	-	-
8A	-	-
8B	-	-
9	-	-
10	-	-
No of labs., p	1	1
No of repl., n	2	2
m	3.65	0.0965
s^2	-	-
s	-	-
Assigned value, μ	3.3	0.1
Recovery, %	110.6	96.5
$t = \sqrt{p} \cdot (m-\mu)/s$	-	-
Sign. level, p(t)	-	-

No test statistics were found to be significant

n-C18/phytane,
Control of recovery, average of results

Laboratory	Level E	Level G
1	-	-
2A	-	-
2B	-	-
3	-	-
4	4.05	0.086
5	-	-
6	-	-
7	-	-
8A	-	-
8B	-	-
9	-	-
10	-	-
No of labs., p	1	1
No of repl., n	2	2
m	4.05	0.086
s^2	-	-
s	-	-
Assigned value, μ	-	0.05
Recovery, %	-	172.0
$t = \sqrt{p} \cdot (m-\mu)/s$	-	-
Sign. level, p(t)	-	-

No test statistics were found to be significant

Pristane/phytane,
Control of recovery, average of results

Laboratory	Level E	Level G
1	-	-
2A	-	-
2B	-	-
3	-	-
4	0.960	1.25
5	-	-
6	-	-
7	-	-
8A	-	-
8B	-	-
9	-	-
10	-	-
No of labs., p	1	1
No of repl., n	2	2
m	0.960	1.25
s^2	-	-
s	-	-
Assigned value, μ	0.8	1.3
Recovery, %	120.0	96.2
$t = \sqrt{p} \cdot (m-\mu)/s$	-	-
Sign. level, p(t)	-	-

No test statistics were found to be significant

CPI(15-21)
Control of recovery, average of results

Laboratory	Level E	Level G
1	-	-
2A	-	-
2B	-	-
3	-	-
4	1.010	3.70
5	-	-
6	-	-
7	-	-
8A	-	-
8B	-	-
9	-	-
10	-	-
No of labs., p	1	1
No of repl., n	2	2
m	1.010	3.70
s^2	-	-
s	-	-
Assigned value, μ	1.0	-
Recovery, %	101.0	-
$t = \sqrt{p} \cdot (m-\mu)/s$	-	-
Sign. level, p(t)	-	-

No test statistics were found to be significant

CPI(25-33)
Control of recovery, average of results

Laboratory	Level E	Level G
1	-	-
2A	-	-
2B	-	-
3	-	-
4	0.910	0.935
5	-	-
6	-	-
7	-	-
8A	-	-
8B	-	-
9	-	-
10	-	-
No of labs., p	1	1
No of repl., n	2	2
m	0.910	0.935
s^2	-	-
s	-	-
Assigned value, μ	1.0	-
Recovery, %	91.0	-
$t = \sqrt{p} \cdot (m-\mu)/s$	-	-
Sign. level, p(t)	-	-

No test statistics were found to be significant

A N N E X I

Results from participants

Benzene mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H	Method
	Assigned value mg/kg 0.06	Assigned value mg/kg 0.01	Assigned value mg/kg -	Assigned value mg/kg 0.15	Assigned value mg/kg -	Assigned value mg/kg -	Assigned value mg/kg -	Assigned value mg/kg 0.17	
1	0.170 0.170	0.480 0.480	- -	0.590 0.480	- -	- -	- -	0.210 0.280	2
2	- -	- -	- -	- -	- -	- -	- -	0.05 0.06	
3	0.039 0.049	0.033 0.028	- -	- -	- -	- -	- -	0.448 0.475	1
4	0.049 0.054	<0.01 <0.01	- -	0.126 0.092	- -	- -	- -	0.128 0.120	2
5	<0.01 0.05	<0.01 <0.01	- -	<0.01 <0.01	- -	- -	- -	0.18 0.11	2
6	0.062 0.056	0.018 0.016	- -	0.154 0.163	- -	- -	- -	0.161 0.155	2
7	- -	- -	- -	<0.1 -	- -	- -	- -	- -	
8A	- 0.136	- <0.01	- -	0.162 0.119	- -	- -	- -	0.0944 0.0143	
8B	0.0842 0.0393	<0.01 <0.01	- -	0.139 -	- -	- -	- -	0.182 0.177	
9	- -	- -	- -	- -	- -	- -	- -	- -	
10A	0.109 0.085	<0.04 <0.04	- -	0.246 0.243	- -	- -	- -	0.578 0.60	1
10B	0.0598 0.0679	- -	- -	0.151 0.0751	- -	- -	- -	0.165 0.168	2

Toluene mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H	Method
	Assigned value mg/kg 0.06	Assigned value mg/kg 0.03	Assigned value mg/kg -	Assigned value mg/kg 0.2	Assigned value mg/kg -	Assigned value mg/kg -	Assigned value mg/kg -	Assigned value mg/kg 2.6	
1	0.010 0.030	0.023 0.023	- -	0.230 0.170	- -	- -	- -	1.90 1.80	2
2	0.05 0.05	0.02 0.03	- -	0.15 0.13	- -	- -	- -	0.27 0.29	1
3	0.033 0.030	0.023 0.030	- -	0.188 0.175	- -	- -	- -	1.975 1.948	1
4	0.053 0.038	0.025 0.031	- -	0.198 0.169	- -	- -	- -	2.687 2.582	2
5	0.02 0.04	0.04 0.02	- -	0.15 0.15	- -	- -	- -	3.59 3.29	2
6	0.057 0.053	0.050 0.032	- -	0.199 0.205	- -	- -	- -	2.69 2.61	2
7	0.011 -	0.031 -	- -	0.1 0.15	- -	- -	- -	1.63 1.53	2
8A	- 0.133	- 0.0516	- -	0.229 0.218	- -	- -	- -	2.600 2.867	
8B	0.0927 0.0608	0.0182 0.0309	- -	0.206 -	- -	- -	- -	3.042 3.081	
9	- -	- -	- -	- -	- -	- -	- -	0.57 0.61	9
10A	0.060 0.066	<0.04 <0.04	- -	0.228 0.154	- -	- -	- -	3.61 3.06	1
10B	0.0570 0.0637	0.0256 0.0284	- -	0.217 0.136	- -	- -	- -	2.96 2.93	2

Ethylbenzene mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H	Method
	Assigned value mg/kg 0.05	Assigned value mg/kg 0.02	Assigned value mg/kg -	Assigned value mg/kg 0.2	Assigned value mg/kg -	Assigned value mg/kg -	Assigned value mg/kg -	Assigned value mg/kg 1.8	
1	0.043 0.050	0.023 0.023	- -	0.230 0.200	- -	- -	- -	1.80 1.70	2
2	0.03 0.04	0.02 0.03	- -	0.17 0.17	- -	- -	- -	0.46 0.45	1
3	0.036 0.032	0.013 0.017	- -	0.189 0.201	- -	- -	- -	1.110 1.095	1
4	0.043 0.048	0.018 0.021	- -	0.211 0.198	- -	- -	- -	1.789 1.765	2
5	0.04 0.05	0.04 0.03	- -	0.21 0.24	- -	- -	- -	1.82 1.71	2
6	0.057 0.054	0.038 0.021	- -	0.202 0.200	- -	- -	- -	1.85 1.69	2
7	0.006 -	0.016 -	- -	0.2 0.17	- -	- -	- -	1.24 1.22	2
8A	- 0.0740	- 0.0280	- -	0.227 0.214	- -	- -	- -	1.885 1.918	
8B	0.0683 0.0428	0.0126 0.0211	- -	0.211 -	- -	- -	- -	2.017 1.980	
9	0.36 U 0.98 U	- -	- -	0.75 U - U	- -	- -	- -	1.00 0.99	9
10A	0.048 0.050	<0.04 <0.04	- -	0.248 0.193	- -	- -	- -	1.78 1.86	1
10B	0.0404 0.0409	0.0153 0.0177	- -	0.233 0.180	- -	- -	- -	1.97 1.96	2

U: The result has been excluded by flagging in the data file

m+p-Xylene mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H	Method
	Assigned value mg/kg 0.1	Assigned value mg/kg 0.1	Assigned value mg/kg -	Assigned value mg/kg 0.50	Assigned value mg/kg -	Assigned value mg/kg -	Assigned value mg/kg -	Assigned value mg/kg 8.0	
1	0.087 0.110	0.100 0.100	- -	0.510 0.460	- -	- -	- -	8.10 8.0	2
2	0.07 0.07	0.06 0.09	- -	0.35 0.36	- -	- -	- -	2.74 2.64	1
3	0.069 0.066	0.099 0.130	- -	0.459 0.492	- -	- -	- -	7.959 7.867	1
4	0.088 0.096	0.084 0.097	- -	0.462 0.466	- -	- -	- -	8.426 8.361	2
5	0.07 0.10	0.15 0.12	- -	0.48 0.54	- -	- -	- -	7.55 6.82	2
6	0.114 0.103	0.175 0.099	- -	0.470 0.474	- -	- -	- -	7.97 7.78	2
7	0.010 -	0.098 -	- -	0.4 0.41	- -	- -	- -	5.35 5.26	2
8A	- 0.138	- 0.122	- -	0.509 0.496	- -	- -	- -	8.563 8.710	
8B	0.123 0.0800	0.060 0.0940	- -	0.468 -	- -	- -	- -	8.990 8.918	
9	1.18 U 2.77 U	0.28 U - U	- U - U	2.25 U - U	- U - U	- U - U	- U - U	1.24 U 2.49 U	9
10A	0.096 0.092	0.095 0.112	- -	0.536 0.434	- -	- -	- -	6.87 7.17	1
10B	0.102 0.0969	0.0962 0.109	- -	0.557 0.453	- -	- -	- -	8.40 8.30	2

U: The result has been excluded by flagging in the data file

o-Xylene mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H	Method
	Assigned value mg/kg 0.07	Assigned value mg/kg 0.05	Assigned value mg/kg -	Assigned value mg/kg 0.25	Assigned value mg/kg -	Assigned value mg/kg -	Assigned value mg/kg -	Assigned value mg/kg 3.7	
1	0.057 0.067	0.047 0.053	- -	0.250 0.230	- -	- -	- -	3.80 3.80	2
2	0.05 0.05	0.04 0.05	- -	0.17 0.17	- -	- -	- -	2.49 2.49	1
3	0.041 0.041	0.042 0.054	- -	0.230 0.230	- -	- -	- -	3.336 3.280	1
4	0.059 0.063	0.043 0.048	- -	0.225 0.221	- -	- -	- -	3.699 3.711	2
5	0.04 0.06	0.07 0.05	- -	0.23 0.23	- -	- -	- -	3.46 3.07	2
6	0.068 0.065	0.090 0.050	- -	0.239 0.233	- -	- -	- -	3.94 3.87	2
7	0.012 -	0.037 -	- -	0.2 0.20	- -	- -	- -	2.65 2.64	2
8A	- 0.0804	- 0.0528	- -	0.237 0.227	- -	- -	- -	3.843 3.900	
8B	0.0684 0.0491	0.0303 0.0436	- -	0.226 -	- -	- -	- -	4.035 4.015	
9	- -	0.17 -	- -	0.39 -	- -	- -	- -	1.24 2.49	9
10A	0.066 0.070	0.051 0.063	- -	0.284 0.241	- -	- -	- -	3.74 3.92	1
10B	0.0703 0.0722	0.0485 0.0542	- -	0.269 0.224	- -	- -	- -	4.08 4.07	2

C6H6 - C10 mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H	Method
	Assigned value mg/kg	Assigned value mg/kg	Assigned value mg/kg	Assigned value mg/kg	Assigned value mg/kg	Assigned value mg/kg	Assigned value mg/kg	Assigned value mg/kg	
	-	-	2.5	-	2.5	-	2.5	190	
1	-	6.97	5.8	9.9	6.4	8.0	4.4	224	1
	-	7.18	5.3	8.0	5.5	7.7	-	208	
2	-	2.23	<2.5	3.10	<2.5	<2.5	<2.5	180.6	1
	-	2.58	<2.5	3.24	<2.5	<2.5	<2.5	174.4	
3	-	2.45	2.15	7.032	1.421	2.793	1.162	157.128	
	-	2.86	1.87	5.770	1.163	2.689	0.734	154.700	
4	-	2.32	<2	2.39	<2	<2	<2	192.5	1
	-	3.16	<2	2.06	<2	<2	<2	180.2	
5	-	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	230	1
	-	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	230	
6	-	6.68	<2.5	13.7	<2.5	14.4	3.52	271	1
	-	6.10	<2.5	7.49	<2.5	15.0	3.54	281	
7	-	4	<1	10	<1	<1	<1	83	9
	-	-	<1	-	<1	<1	-	82	
8A	-	-	3.12	10.35	<2.5	10.95	<2.5	234	
	-	6.09	3.05	9.72	3.31	9.71	<2.5	214	
8B	-	5.12	2.62	11.13	3.42	10.89	<2.5	209	
	-	5.20	3.48	-	3.19	9.06	<2.5	224	
9	-	19.7	19.7	97.0	22.9	26.4	11.1	44.2	9
	-	15.6	15.6	-	14.8	18.7	-	44.2	
10A	-	<2.5	<2.5	4.3	<2.5	2.95	<2.5	262	1
	-	<2.5	<2.5	3.2	<2.5	2.64	<2.5	255	
10B	-	-	-	-	-	-	-	-	
	-	-	-	-	-	-	-	-	

>C10 - C25 mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H	Method
	Assigned value mg/kg 24	Assigned value mg/kg 79	Assigned value mg/kg 25	Assigned value mg/kg 280	Assigned value mg/kg 130	Assigned value mg/kg 110	Assigned value mg/kg 290	Assigned value mg/kg 3.700	
1	24.1 23.38	78.1 83.8	23.9 22.1	276 270	114 126	104 112	289 -	3680 3680	1
2	17.2 20.6	70.2 63.7	13.2 13.8	209.6 211.2	132.4 134.3	103.6 94.6	328.1 332.3	3322 3258	1
3	21.748 20.113	79.15 77.79	12.92 12.94	329.37 324.77	115.04 123.72	107.31 102.87	247.29 264.17	3660.46 3698.70	1
4	20.39 19.82	75.1 76.2	16.88 17.77	278.7 272.7	116.3 112.6	105.2 97.3	252.5 330.8	3749.8 3745.3	1
5	22 21	110 78	26 29	260 270	140 150	130 140	270 260	4300 4100	1
6	26.9 26.7	144 85.4	29.6 29.9	261 285	147 155	131 137	307 449	4110 4040	1
7	24 23	62 -	30 32	308 -	104 89	133 112	177 -	1370 1380	9
8A	28.15 28.40	- 88.23	21.71 25.27	271.82 302.64	135.28 138.98	111.95 134.43	245.58 333.40	4545 3746	
8B	27.33 27.55	84.17 85.22	31.00 27.45	308.76 -	116.28 125.50	127.21 115.27	317.21 285.42	3795 3885	
9	8.3 6.1	6.0 7.8	26.5 36.7	107.2 -	72.3 78.0	138 200	76.3 93.7	1466 1427	9
10A	25.5 23.5	87.0 85.5	12.3 12.1	294 287	146 146	116 106	355 361	4930 4970	1
10B	- -	- -	- -	- -	- -	- -	- -	- -	

>C25 - C40 mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H	Method
	Assigned value mg/kg 21	Assigned value mg/kg 63	Assigned value mg/kg 110	Assigned value mg/kg 140	Assigned value mg/kg 410	Assigned value mg/kg 760	Assigned value mg/kg 90	Assigned value mg/kg 170	
1	21.6 21.8	65.6 76.0	138 110	140 132	370 430	685 753	190 -	204 183	1
2	15.6 18.1	47.0 43.3	79.5 83.1	93.8 91.7	399.0 426.9	781.4 856.3	365.9 279.2	318.7 271.6	1
3	9.525 9.995	42.22 43.87	58.38 61.43	161.50 165.41	238.52 278.13	504.41 507.66	34.62 39.47	107.00 113.391	1
4	<32.5 <32.5	61.0 64.0	107.9 101.7	132.8 141.7	343.3 365.6	633.9 624.8	112.1 94.1	150.2 132.3	1
5	<25 <25	160 100	140 140	180 180	620 680	1300 1500	310 240	320 360	1
6	17.5 17.7	84.4 71.1	136 140	142 136	449 501	810 909	52.2 71.1	323 285	1
7	18 19	39 -	78 75	185 -	275 319	706 641	40 -	124 94	9
8A	16.29 17.75	- 66.45	97.81 113.68	144.58 162.99	368.13 439.65	621.83 829.52	121.75 106.48	161 146	
8B	17.51 17.02	51.60 49.99	123.06 130.89	202.78 -	364.28 388.64	809.56 767.46	81.04 86.24	162 135	
9	36.0 31.1	21.0 24.4	21.0 24.4	155.2 -	417.4 513.3	1209 1712	10.4 24.4	451 431	9
10A	<25 <25	83.2 74.8	112 123	142 150	436 474	716 707	98.2 84.8	164 192	1
10B	- -	- -	- -	- -	- -	- -	- -	- -	

Total hydrocarbons mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H	Method
	Assigned value mg/kg 44	Assigned value mg/kg 140	Assigned value mg/kg 120	Assigned value mg/kg 430	Assigned value mg/kg 520	Assigned value mg/kg 880	Assigned value mg/kg 430	Assigned value mg/kg 4.100	
1	45.7 45.2	151 167	168 137	426 410	491 562	797 872	484 -	4110 4070	1
2	35.4 41.8	119.5 109.5	92.8 97.0	306.5 306.1	531.8 561.6	885.3 951.7	694.2 611.8	3821 3704	1
3	21.75 20.11	121.37 121.66	71.30 74.36	497.90 495.95	353.56 401.85	611.72 610.53	281.91 303.64	3924.59 3966.79	1
4	20.39 19.82	138.4 143.4	124.8 119.4	413.9 416.5	459.6 478.3	739.1 722.1	464.6 424.9	4092.5 4057.7	1
5	<32.5 <32.5	270 180	170 170	440 450	760 820	1400 1600	570 490	4900 4700	1
6	44.4 44.4	236 163	166 170	417 429	595 656	956 1061	363 524	4710 4610	1
7	42 42	105 -	108 107	502 -	379 408	839 753	216 -	1580 1550	9
8A	44.44 46.15	- 160.76	122.64 142.00	426.75 475.35	503.41 531.94	744.73 973.66	367.33 439.88	4940 4106	
8B	44.84 44.57	140.88 140.42	156.68 161.82	522.67 -	483.98 517.33	947.66 891.79	398.25 371.66	4166 4244	
9	44.2 37.2	46.8 47.9	46.8 47.9	359 -	490 591	1347 1911	97.8 108.3	1961 1902	9
10A	25.5 23.5	170 160	124 135	440 440	582 620	835 816	453 446	5360 5420	1
10B	- -	- -	- -	- -	- -	- -	- -	- -	

Fluoranthene mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H	Method
	Assigned value mg/kg 0.027	Assigned value mg/kg -	Assigned value mg/kg -	Assigned value mg/kg 0.34	Assigned value mg/kg -	Assigned value mg/kg 0.26	Assigned value mg/kg 0.02	Assigned value mg/kg 0.05	
1	0.03 0.03	- -	- -	0.380 0.350	- -	0.29 0.33	0.02 -	0.04 0.05	2
2	0.028 0.028	- -	- -	<0.005 <0.005	- -	0.364 0.321	0.020 0.024	0.045 0.061	2
3	- -	- -	- -	- -	- -	- -	- -	- -	
4	0.024 0.024	- -	- -	0.247 0.337	- -	1.25 0.224	0.044 0.024	0.026 0.023	2
5	0.484 U 0.677 U	- U - U	- U - U	1.534 U 1.700 U	- U - U	2.588 U 2.257 U	0.478 U 0.827 U	0.382 U 0.027 U	2
6	0.025 0.024	- -	- -	0.315 0.360	- -	0.239 0.222	0.021 0.016	0.045 0.039	2
7	0.024 0.025	- -	- -	- 0.31	- -	0.23 0.27	0.032 -	0.043 0.055	2
8A	0.0274 0.0281	- -	- -	0.363 0.317	- -	0.321 0.234	0.0204 0.0195	0.0728 0.0607	
8B	0.0262 0.0273	- -	- -	0.347 -	- -	0.306 0.254	0.0195 0.0198	0.0653 0.0581	
9	0.0100 0.0117	- -	- -	0.145 -	- -	0.158 0.469	0.0066 0.0147	- -	9
10A	- -	- -	- -	- -	- -	- -	- -	- -	
10B	0.0231 0.0234	- -	- -	0.422 0.252	- -	0.238 0.250	0.0245 0.0215	0.0391 0.0356	2

U: The result has been excluded by flagging in the data file

Benzo(b+j+k)fluoranthene mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H	Method
	Assigned value mg/kg 0.053	Assigned value mg/kg -	Assigned value mg/kg -	Assigned value mg/kg 0.37	Assigned value mg/kg -	Assigned value mg/kg 0.58	Assigned value mg/kg 0.026	Assigned value mg/kg 0.059	
1	0.06 0.06	- -	- -	0.420 0.39	- -	0.60 0.70	0.02 -	0.08 0.07	2
2	0.062 0.066	- -	- -	<0.005 <0.005	- -	0.750 0.647	0.036 0.053	0.067 0.058	2
3	- -	- -	- -	- -	- -	- -	- -	- -	
4	0.050 0.051	- -	- -	0.304 0.374	- -	1.16 0.511	0.136 0.034	0.063 0.050	2
5	0.738 U 0.951 U	- U - U	- U - U	0.723 U 1.018 U	- U - U	3.796 U 4.931 U	1.626 U 2.072 U	0.684 U <0.005 U	2
6	0.049 0.049	- -	- -	0.334 0.396	- -	0.509 0.486	0.025 0.025	0.062 0.056	2
7	0.048 0.050	- -	- -	- 0.38	- -	0.50 0.60	0.019 -	0.059 0.065	2
8A	0.0529 0.0512	- -	- -	0.411 0.360	- -	0.646 0.568	0.0240 0.0259	0.0561 0.0579	
8B	0.0516 0.0533	- -	- -	0.359 -	- -	0.592 0.551	0.0259 0.0260	0.0616 0.0520	
9	0.0166 0.0183	- -	- -	0.135 -	- -	0.288 0.640	0.0083 0.0211	- -	9
10A	- -	- -	- -	- -	- -	- -	- -	- -	
10B	0.0460 0.0501	- -	- -	0.381 0.302	- -	0.539 0.527	0.0330 0.0363	0.0494 0.0502	2

U: The result has been excluded by flagging in the data file

Benzo(a)pyrene mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H	Method
	Assigned value mg/kg 0.027	Assigned value mg/kg -	Assigned value mg/kg -	Assigned value mg/kg 0.18	Assigned value mg/kg -	Assigned value mg/kg 0.27	Assigned value mg/kg 0.016	Assigned value mg/kg 0.020	
1	0.03 0.03	- -	- -	0.22 0.20	- -	0.30 0.33	0.02 -	0.03 0.02	2
2	0.025 0.027	- -	- -	<0.005 <0.005	- -	0.337 0.288	0.019 0.029	0.021 0.018	2
3	- -	- -	- -	- -	- -	- -	- -	- -	
4	0.025 0.025	- -	- -	0.153 0.195	- -	0.609 0.240	0.084 0.019	0.024 0.016	2
5	0.066 U 0.068 U	- -	- -	<0.005 <0.005	- -	0.264 0.320	0.106 U <0.005 U	0.041 U <0.005 U	2
6	0.024 0.024	- -	- -	0.172 0.208	- -	0.258 0.246	0.016 0.015	0.023 0.021	2
7	0.022 0.023	- -	- -	- 0.18	- -	0.23 0.27	0.011 -	0.017 0.020	2
8A	0.0272 0.0281	- -	- -	0.197 0.178	- -	0.311 0.259	0.0134 0.0160	0.0185 0.0216	
8B	0.0257 0.0270	- -	- -	0.189 -	- -	0.290 0.255	0.0160 0.0149	0.0234 0.0174	
9	0.0083 0.0083	- -	- -	0.0673 -	- -	0.170 0.273	0.0050 0.0114	- -	9
10A	- -	- -	- -	- -	- -	- -	- -	- -	
10B	0.0140 0.0151	- -	- -	0.178 0.140	- -	0.219 0.208	0.0170 0.0184	0.0165 0.0156	2

U: The result has been excluded by flagging in the data file

Indeno(1,2,3-cd)pyrene mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H	Method
	Assigned value mg/kg 0.027	Assigned value mg/kg -	Assigned value mg/kg -	Assigned value mg/kg 0.19	Assigned value mg/kg -	Assigned value mg/kg 0.26	Assigned value mg/kg 0.012	Assigned value mg/kg 0.022	
1	0.03 0.03	- -	- -	0.20 0.19	- -	0.25 0.26	<0.02 -	0.02 0.02	2
2	0.023 0.024	- -	- -	<0.005 <0.005	- -	0.363 0.277	0.014 0.018	0.024 0.022	2
3	- -	- -	- -	- -	- -	- -	- -	- -	
4	0.025 0.026	- -	- -	0.183 0.201	- -	0.495 0.267	0.059 0.017	0.028 0.020	2
5	0.558 U 1.143 U	- U - U	- U - U	<0.005 U <0.005 U	- U - U	0.722 U 2.106 U	1.208 U 3.401 U	0.376 U <0.005 U	2
6	0.026 0.025	- -	- -	0.174 0.193	- -	0.260 0.263	0.011 0.011	0.025 0.024	2
7	0.024 0.024	- -	- -	- 0.16	- -	0.21 0.26	0.005 -	0.021 0.022	2
8A	0.0376 0.0306	- -	- -	0.224 0.211	- -	0.329 0.282	0.0121 0.0134	0.0205 0.0248	
8B	0.0334 0.0324	- -	- -	0.241 -	- -	0.328 0.249	0.0134 0.0102	0.0248 0.0204	
9	0.0083 0.0100	- -	- -	0.0723 -	- -	0.138 0.219	0.0033 0.0065	- -	9
10A	- -	- -	- -	- -	- -	- -	- -	- -	
10B	0.0196 0.0194	- -	- -	0.163 0.121	- -	0.182 0.170	0.0105 0.0116	0.0087 0.0082	2

U: The result has been excluded by flagging in the data file

Dibenz(a,h)anthracene mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H	Method
	Assigned value mg/kg 0.027	Assigned value mg/kg -	Assigned value mg/kg -	Assigned value mg/kg 0.042	Assigned value mg/kg -	Assigned value mg/kg 0.065	Assigned value mg/kg 0.005	Assigned value mg/kg 0.005	
1	0.03 0.03	- -	- -	0.05 0.05	- -	0.07 0.08	<0.02 -	<0.02 <0.02	2
2	0.022 0.023	- -	- -	<0.005 <0.005	- -	0.074 0.061	<0.005 <0.005	0.005 0.005	2
3	- -	- -	- -	- -	- -	- -	- -	- -	
4	0.026 0.027	- -	- -	0.035 0.049	- -	0.125 0.062	0.014 <0.005	0.005 <0.005	2
5	0.597 U 0.790 U	- U - U	- U - U	<0.005 U <0.005 U	- U - U	<0.005 U 2.642 U	1.310 U 2.419 U	0.167 U <0.005 U	2
6	0.025 0.025	- -	- -	0.032 0.039	- -	0.059 0.061	<0.005 <0.005	0.005 0.006	2
7	0.024 0.024	- -	- -	- 0.045	- -	0.058 0.068	<0.005 -	0.006 0.006	2
8A	0.0350 0.0265	- -	- -	0.0440 0.0418	- -	0.0846 0.0715	0.0027 0.0028	0.0044 0.0055	
8B	0.0334 0.0294	- -	- -	0.0448 -	- -	0.0914 0.0707	0.0028 0.0020	0.0049 0.0049	
9	0.0083 0.0083	- -	- -	0.0164 -	- -	0.0362 0.0498	0 0.0016	- -	9
10A	- -	- -	- -	- -	- -	- -	- -	- -	
10B	0.0214 0.0209	- -	- -	0.0400 0.0339	- -	0.0523 0.0526	0.0029 0.0031	- -	2

U: The result has been excluded by flagging in the data file

Sum of naphthalenes mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H	Method
	Assigned value mg/kg 0.94	Assigned value mg/kg 1	Assigned value mg/kg 0.02	Assigned value mg/kg 0.5	Assigned value mg/kg 0.5	Assigned value mg/kg 0.1	Assigned value mg/kg 0.2	Assigned value mg/kg 90	
1	1.05 1.05	0.65 0.67	0.0 U 0.0 U	0.37 0.36	0.12 0.12	0.0 U 0.0 U	0.0 U - U	43.40 44.60	3
2	1.572 1.727	2.618 2.606	<0.05 <0.05	<0.05 <0.05	1.145 1.111	0.183 0.239	0.207 0.262	136.59 125.51	3
3	- -	- -	- -	- -	- -	- -	- -	- -	
4	1.04 1.06	1.107 1.131	<0.010 <0.01	0.540 0.556	0.498 0.545	0.532 0.091	0.156 0.199	84.9 89.2	3
5	1.52 1.44	3.01 2.61	0.41 0.19	3.00 3.42	1.23 0.96	0.45 0.16	0.80 0.99	160 160	3
6	- -	- -	- -	- -	- -	- -	- -	- -	
7	- -	- -	- -	- -	- -	- -	- -	- -	
8A	0.816 0.826	- 1.368	0.013 0.012	1.231 1.202	0.794 0.546	0.128 0.108	0.172 0.179	115.191 95.260	
8B	0.882 0.863	1.374 1.391	0.035 0.013	0.191 -	0.534 0.533	0.146 0.149	0.156 0.197	85.905 77.166	
9	- -	- -	- -	- -	- -	- -	- -	- -	
10A	- -	- -	- -	- -	- -	- -	- -	- -	
10B	0.836 0.862	1.01 1.01	0.000 U 0.000 U	0.513 0.513	0.507 0.537	0.0570 0.0645	0.147 0.0710	41.2 43.2	3

U: The result has been excluded by flagging in the data file

Sum of phenanthrenes mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H	Method
	Assigned value mg/kg 0.4	Assigned value mg/kg 0.6	Assigned value mg/kg 0.02	Assigned value mg/kg 0.5	Assigned value mg/kg 1	Assigned value mg/kg 0.3	Assigned value mg/kg 0.2	Assigned value mg/kg 8	
1	0.40 0.38	0.14 0.14	0.0 U 0.10 U	0.26 0.23	0.24 0.24	0.15 0.17	0.02 -	3.22 3.15	3
2	0.370 0.418	0.463 0.491	<0.05 <0.05	<0.05 <0.05	1.115 1.060	0.277 0.314	0.110 0.150	7.636 7.630	3
3	- -	- -	- -	- -	- -	- -	- -	- -	
4	0.466 0.433	0.59 0.61	0.023 0.012	0.493 0.616	1.532 1.459	3.111 0.333	0.301 0.199	11.1 11.3	3
5	0.43 0.43	0.98 0.55	0.02 0.03	0.46 0.46	1.21 1.20	0.47 0.34	0.14 0.26	9.8 9.5	3
6	- -	- -	- -	- -	- -	- -	- -	- -	
7	- -	- -	- -	- -	- -	- -	- -	- -	
8A	0.335 0.345	- 0.777	0.016 0.022	0.666 0.615	3.208 2.069	0.846 0.473	0.237 0.268	8.934 7.707	
8B	0.358 0.368	0.804 0.706	0.041 0.022	0.605 -	2.103 2.188	0.492 0.470	0.215 0.283	6.661 6.021	
9	- -	- -	- -	- -	- -	- -	- -	- -	
10A	- -	- -	- -	- -	- -	- -	- -	- -	
10B	0.301 0.283	0.435 0.463	0.0022 0.0034	0.417 0.278	1.02 1.04	0.199 0.237	0.6953 0.0681	8.52 9.35	3

U: The result has been excluded by flagging in the data file

17alfa(H),21beta(H)-Hopane mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H	Method
	Assigned value mg/kg 0.07	Assigned value mg/kg 0.07	Assigned value mg/kg 0.06	Assigned value mg/kg 0.20	Assigned value mg/kg 0.34	Assigned value mg/kg 1.2	Assigned value mg/kg 0.14	Assigned value mg/kg 0.09	
1	0.14 0.11	0.11 0.11	0.26 0.07	0.35 0.37	0.62 0.66	2.40 2.40	0.21 -	0.07 0.05	3
2	- -	- -	- -	- -	- -	- -	- -	- -	
3	- -	- -	- -	- -	- -	- -	- -	- -	
4	<0.05 0.05	<0.05 <0.05	- -	0.114 0.147	0.187 0.227	0.693 0.686	0.112 0.100	<0.1 <0.1	3
5	- -	- -	- -	- -	- -	- -	- -	- -	
6	- -	- -	- -	- -	- -	- -	- -	- -	
7	- -	- -	- -	- -	- -	- -	- -	- -	
8A	0.076 0.078	- 0.070	0.039 0.040	0.196 0.192	0.467 0.318	1.185 1.246	0.141 0.148	0.123 0.108	
8B	0.063 0.064	0.067 0.059	0.051 0.064	0.204 -	0.328 0.347	1.197 1.254	0.138 0.123	0.126 0.067	
9	- -	- -	- -	- -	- -	- -	- -	- -	
10A	- -	- -	- -	- -	- -	- -	- -	- -	
10B	2.70 U 2.90 U	4.73 U 4.84 U	9.01 U 8.98 U	20.4 U 22.9 U	35.1 U 32.9 U	97.4 U 96.3 U	13.6 U 13.4 U	7.36 U 9.48 U	3

U: The result has been excluded by flagging in the data file

Pristane mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H	Method
	Assigned value mg/kg 0.83	Assigned value mg/kg -	Assigned value mg/kg -	Assigned value mg/kg -	Assigned value mg/kg -	Assigned value mg/kg -	Assigned value mg/kg -	Assigned value mg/kg -	
1	0.88 0.90	- -	- -	- -	- -	- -	- -	- -	3
2	0.30 0.38	- -	- -	- -	- -	- -	- -	- -	9
3	- -	- -	- -	- -	- -	- -	- -	- -	
4	0.388 0.415	- -	- -	- -	- -	- -	- -	- -	3
5	0.85 0.83	- -	- -	- -	- -	- -	- -	- -	3
6	- -	- -	- -	- -	- -	- -	- -	- -	
7	- -	- -	- -	- -	- -	- -	- -	- -	
8A	1.078 0.972	- -	- -	- -	- -	- -	- -	- -	
8B	0.781 0.963	- -	- -	- -	- -	- -	- -	- -	
9	- -	- -	- -	- -	- -	- -	- -	- -	
10A	- -	- -	- -	- -	- -	- -	- -	- -	
10B	0.986 1.00	- -	- -	- -	- -	- -	- -	- -	3

n-C17/pristane
ISO5725, table A: Results from participating laboratories:

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H	Method
	Assigned value	Assigned value	Assigned value	Assigned value	Assigned value	Assigned value	Assigned value	Assigned value	
	-	1.4	-	0.2	3.3	2	0.1	1.2	
1	-	1.306	0 U	0.313	1.00	0 U	0.079	1.25	
	-	1.408	0 U	0.273	2.70	0 U	-	1.195	
2	-	1.15	-	0.22	3.83	1.45	0.15	1.04	
	-	1.18	-	0.24	3.39	1.58	0.12	1.11	
3	-	-	-	-	-	-	-	-	
	-	-	-	-	-	-	-	-	
4	-	1.3	4.8	0.18	4.1	1.4	0.10	1.11	
	-	1.4	5.6	0.16	3.8	2.7	0.07	1.11	
5	-	1.69	0 U	0.34	5.47	1.99	1.16	2.79	
	-	1.92	0 U	0.49	4.80	1.82	0.13	2.84	
6	-	-	-	-	-	-	-	-	
	-	-	-	-	-	-	-	-	
7	-	-	-	-	-	-	-	-	
	-	-	-	-	-	-	-	-	
8A	-	-	-	0.129	3.175	0.774	0 U	0.986	
	-	1.864	-	0.145	7.172	1.929	0 U	1.214	
8B	-	1.809	-	0.124	0.919	1.150	0 U	1.226	
	-	1.846	-	-	3.150	3.746	0 U	0.504	
9	-	-	-	-	-	-	-	-	
	-	-	-	-	-	-	-	-	
10A	-	-	-	-	-	-	-	-	
	-	-	-	-	-	-	-	-	
10B	-	1.08	2.37	0.291	3.14	2.36	0.178	1.47	
	-	1.16	-	0.250	3.37	2.26	0.159	2.22	

U: The result has been excluded by flagging in the data file

n-C18/phytane
ISO5725, table A: Results from participating laboratories:

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H	Method
	Assigned value	Assigned value	Assigned value	Assigned value	Assigned value	Assigned value	Assigned value	Assigned value	
	3.0	1.8	-	0.24	-	1.1	0.05	1.5	
1	3.152	2.0435	0 U	0.131	0 U	0 U	0 U	1.654	
	3.146	1.762	0 U	0.183	1.786 U	0 U	- U	1.615	
2	3.30	1.78	2.17	0.44	2.42	0.85	0.28	1.63	
	3.06	1.83	2.22	0.41	2.88	0.84	0.34	1.75	
3	-	-	-	-	-	-	-	-	
	-	-	-	-	-	-	-	-	
4	3.0	1.6	6.8	0.19	3.5	2.3	0.03	1.41	
	3.0	1.5	3.7	0.26	3.9	0.94	0.02	1.50	
5	1.64	2.46	0 U	0.31	5.16	1.50	0.05	1.54	
	4.66	2.73	0 U	0.37	4.35	1.33	0.06	1.50	
6	-	-	-	-	-	-	-	-	
	-	-	-	-	-	-	-	-	
7	-	-	-	-	-	-	-	-	
	-	-	-	-	-	-	-	-	
8A	3.519	-	-	0.222	4.676	1.230	0.037	1.173	
	3.648	1.820	-	0.224	4.626	1.332	0.057	1.313	
8B	3.762	1.995	-	0.255	1.665	1.419	0 U	1.258	
	3.650	1.876	-	-	2.887	1.053	0.046 U	1.270	
9	-	-	-	-	-	-	-	-	
	-	-	-	-	-	-	-	-	
10A	-	-	-	-	-	-	-	-	
	-	-	-	-	-	-	-	-	
10B	2.54	1.43	7.31	0.209	2.53	0.958	0.0696	1.28	
	2.48	1.49	-	0.242	3.07	0.233	0.0203	1.24	

U: The result has been excluded by flagging in the data file

Pristane/phytane
ISO5725, table A: Results from participating laboratories:

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H	Method
	Assigned value	Assigned value	Assigned value	Assigned value	Assigned value	Assigned value	Assigned value	Assigned value	
	1.0	1.7	-	1.2	0.8	0.9	1.4	1.6	
1	0.957	1.565	0 U	1.154	0 U	0 U	1.308	1.538	
	1.011	1.690	0 U	1.250	0.714 U	0 U	-	1.577	
2	0.98	1.73	-	1.24	0.47	0.52	1.31	1.79	
	1.02	1.71	-	1.37	0.33	0.81	1.32	1.93	
3	-	-	-	-	-	-	-	-	
	-	-	-	-	-	-	-	-	
4	0.94	1.7	1.3	1.1	0.79	1.4	1.6	1.5	
	1.0	1.3	0.71	1.2	0.84	0.7	1.4	1.7	
5	1.00	1.57	0 U	1.17	0.83	0.70	1.37	0.66	
	0.96	1.67	0 U	1.15	0.76	0.74	1.30	0.64	
6	-	-	-	-	-	-	-	-	
	-	-	-	-	-	-	-	-	
7	-	-	-	-	-	-	-	-	
	-	-	-	-	-	-	-	-	
8A	1.002	-	-	1.289	1.163	1.080	1.589	1.816	
	0.921	1.756	-	1.367	0.550	0.915	1.564	1.745	
8B	0.835	1.865	-	1.390	0.771	1.663	1.447	1.625	
	1.017	1.767	-	-	0.756	0.517	1.741	1.546	
9	-	-	-	-	-	-	-	-	
	-	-	-	-	-	-	-	-	
10A	-	-	-	-	-	-	-	-	
	-	-	-	-	-	-	-	-	
10B	0.927	1.65	1.67	1.12	0.813	1.04	1.34	1.32	
	0.937	1.60	-	1.16	0.881	0.970	1.30	1.00	

U: The result has been excluded by flagging in the data file

CPI(15-21)
ISO5725, table A: Results from participating laboratories:

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H	Method
	Assigned value	Assigned value	Assigned value	Assigned value	Assigned value	Assigned value	Assigned value	Assigned value	
	-	1.2	-	-	1.0	1.2	-	1.0	
1	-	0.64	0 U	1.94	0.36	0 U	0 U	0.69	
	-	0.69	0 U	1.66	0.76	0 U	- U	0.69	
2	-	-	-	-	-	-	-	-	
	-	-	-	-	-	-	-	-	
3	-	-	-	-	-	-	-	-	
	-	-	-	-	-	-	-	-	
4	-	1.16	0.45	3.1	1.0	1.0	4.6	1.0	
	-	1.12	0.45	3.9	0.98	1.3	5.5	1.0	
5	-	1.19	-	1.67	1.07	1.06	2.14	1.03	
	-	1.00	-	1.90	1.03	1.04	1.85	0.87	
6	-	-	-	-	-	-	-	-	
	-	-	-	-	-	-	-	-	
7	-	-	-	-	-	-	-	-	
	-	-	-	-	-	-	-	-	
8A	-	-	1.273	0.853	0.991	1.077	0.352	1.194	
	-	1.288	0.867	0.900	0.995	1.304	0.353	1.235	
8B	-	1.251	0.951	0.736	0.906	1.262	0.358	1.255	
	-	1.285	0.908	-	0.926	1.300	0.378	0.972	
9	-	-	-	-	-	-	-	-	
	-	-	-	-	-	-	-	-	
10A	-	-	-	-	-	-	-	-	
	-	-	-	-	-	-	-	-	
10B	-	1.12	1.36	3.43	1.07	1.06	2.77	1.15	
	-	1.17	1.66	3.66	1.06	1.59	4.24	1.26	

U: The result has been excluded by flagging in the data file

CPI(25-33)
ISO5725, table A: Results from participating laboratories:

Laboratory	Level A	Level B	Level C	Level D	Level E	Level F	Level G	Level H	Method
	Assigned value 0.13	Assigned value 1.0	Assigned value -	Assigned value 3.5	Assigned value 1.0	Assigned value -	Assigned value -	Assigned value 1.0	
1	0.09 0.09	0.35 0.41	0 U 0 U	0 U 0 U	0.82 0.99	0 U 0 U	0 U - U	0 U 0 U	
2	- -	- -	- -	- -	- -	- -	- -	- -	
3	- -	- -	- -	- -	- -	- -	- -	- -	
4	0.11 0.27	0.99 0.99	0.79 0.77	4.0 3.5	0.96 0.96	3.7 3.9	1.7 1.9	1.2 0.9	
5	0.12 0.12	0.98 1.04	- -	3.37 3.48	1.05 1.16	5.40 4.48	2.29 2.13	0.83 1.04	
6	- -	- -	- -	- -	- -	- -	- -	- -	
7	- -	- -	- -	- -	- -	- -	- -	- -	
8A	0.142 0.145	- 1.098	7.912 3.739	3.666 4.629	1.117 1.047	6.860 7.610	4.095 2.668	1.055 0.889	
8B	0.135 0.142	1.077 1.055	2.048 2.024	3.083 -	1.044 1.119	6.772 6.732	4.324 3.417	0.983 0.962	
9	- -	- -	- -	- -	- -	- -	- -	- -	
10A	- -	- -	- -	- -	- -	- -	- -	- -	
10B	0.118 0.124	0.973 1.03	1.78 1.84	3.68 2.58	0.958 0.952	4.14 5.87	2.11 1.65	1.05 0.904	

U: The result has been excluded by flagging in the data file

C_6H_6 - C_{10} mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level E	Level G	Method
	Assigned value mg/kg 2.5	Assigned value mg/kg 2.5	
1	- <2.5	- <2.5	111
2A	- -	- -	
2B	<2.5 <2.5	<2.5 <2.5	1213
3	<2 <2	<2 <2	191
4	<2 <2	<2 <2	311
5	- -	- -	
6	- -	- -	
7	- -	- -	
8A	<2.0 <2.0	<2.0 <2.0	111
8B	<2.0 <2.0	<2.0 <2.0	111
9	- 2.7	- 2.4	111
10	- -	- -	

>C_{10} - C_{25} mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level E	Level G	Method
	Assigned value mg/kg 110	Assigned value mg/kg 370	
1	- 111	- 372	111
2A	- -	- -	
2B	119.7 120.5	386.6 306.9	1213
3	96.69 100.46	411.75 349.64	191
4	135.2 151.0	365.8 338.6	311
5	- -	- -	
6	- -	- -	
7	- -	- -	
8A	76.93 102.84	457.76 456.97	111
8B	93.29 142.55	372.05 442.67	111
9	- 12.8	- 151	111
10	- -	- -	

>C_{25} - C_{40} mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level E	Level G	Method
	Assigned value mg/kg 230	Assigned value mg/kg 54	
1	- 207	- 54	111
2A	- -	- -	
2B	200.5 202.3	42.5 35.5	1213
3	253.91 282.41	55.59 54.75	191
4	310.3 347.6	40.2 45.0	311
5	- -	- -	
6	- -	- -	
7	- -	- -	
8A	233.35 228.22	77.54 71.54	111
8B	235.38 307.63	58.71 69.42	111
9	- 89.0	- 39.9	111
10	- -	- -	

Total hydrocarbons mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level E	Level G	Method
	Assigned value mg/kg 330	Assigned value mg/kg 430	
1	- 318	- 426	111
2A	- -	- -	
2B	320.5 323.2	429.7 343.0	1213
3	350.60 382.87	467.34 404.39	191
4	445.5 498.6	406.0 383.6	311
5	- -	- -	
6	- -	- -	
7	- -	- -	
8A	310.28 331.06	535.30 528.50	111
8B	328.68 450.18	430.77 512.08	111
9	- 105	- 193	111
10	- -	- -	

Fluoranthene mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level E	Level G	Method
	Assigned value mg/kg -	Assigned value mg/kg 0.02	
1	- -	0.02 -	929
2A	- -	0.029 0.023	929
2B	- -	- -	
3	- -	- -	
4	- -	0.020 0.011	321
5	- -	0.11 0.03	929
6	- -	- -	
7	- -	- -	
8A	- -	0.0206 0.0349	929
8B	- -	0.0227 0.0157	929
9	- -	<0.05 -	121
10	- -	- -	

Benzo(b+j+k)fluoranthene mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level E	Level G	Method
	Assigned value mg/kg -	Assigned value mg/kg 0.026	
1	- -	<0.02 -	929
2A	- -	0.036 0.034	929
2B	- -	- -	
3	- -	- -	
4	- -	0.028 0.020	321
5	- -	0.07 0.04	929
6	- -	- -	
7	- -	- -	
8A	- -	0.0295 0.0397	929
8B	- -	0.0323 0.0204	929
9	- -	<0.05 -	121
10	- -	- -	

Benzo(a)pyrene mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level E	Level G	Method
	Assigned value mg/kg -	Assigned value mg/kg 0.016	
1	- -	0.02 -	929
2A	- -	0.018 0.017	929
2B	- -	- -	
3	- -	- -	
4	- -	0.015 0.011	321
5	- -	0.06 0.02	929
6	- -	- -	
7	- -	- -	
8A	- -	0.0203 0.0220	929
8B	- -	0.0258 0.0131	929
9	- -	0.01 -	121
10	- -	- -	

Indeno(1,2,3-cd)pyrene mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level E	Level G	Method
	Assigned value mg/kg -	Assigned value mg/kg 0.012	
1	- -	<0.02 -	929
2A	- -	0.015 0.016	929
2B	- -	- -	
3	- -	- -	
4	- -	0.014 0.012	321
5	- -	0.06 0.02	929
6	- -	- -	
7	- -	- -	
8A	- -	0.0212 0.0137	929
8B	- -	0.0203 0.0142	929
9	- -	<0.05 -	121
10	- -	- -	

Dibenz(a,h)anthracene mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level E	Level G	Method
	Assigned value mg/kg -	Assigned value mg/kg 0.003	
1	- -	<0.02 -	929
2A	- -	<0.005 <0.005	929
2B	- -	- -	
3	- -	- -	
4	- -	<0.005 <0.005	321
5	- -	<0.05 <0.05	929
6	- -	- -	
7	- -	- -	
8A	- -	0.0056 0.0039	929
8B	- -	0.0062 0.0038	929
9	- -	<0.01 -	121
10	- -	- -	

Sum of naphthalenee mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level E	Level G	Method
	Assigned value mg/kg 0.5	Assigned value mg/kg 0.2	
1	- -	- -	
2A	- -	- -	
2B	- -	- -	
3	- -	- -	
4	0.468 0.469	0.149 0.100	321
5	- -	- -	
6	- -	- -	
7	- -	- -	
8A	- -	- -	
8B	- -	- -	
9	- -	- -	
10	- -	- -	

Sum of phenanthrenes mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level E	Level G	Method
	Assigned value mg/kg 1	Assigned value mg/kg 0.2	
1	- -	- -	
2A	- -	- -	
2B	- -	- -	
3	- -	- -	
4	1.18 1.12	0.165 0.114	321
5	- -	- -	
6	- -	- -	
7	- -	- -	
8A	- -	- -	
8B	- -	- -	
9	- -	- -	
10	- -	- -	

17alfa(H),21beta(H)-Hopane mg/kg
ISO5725, table A: Results from participating laboratories:

Laboratory	Level E	Level G	Method
	Assigned value mg/kg -	Assigned value mg/kg 0.14	
1	- -	- -	
2A	- -	- -	
2B	- -	- -	
3	- -	- -	
4	0.177 0.197	0.104 0.099	321
5	- -	- -	
6	- -	- -	
7	- -	- -	
8A	- -	- -	
8B	- -	- -	
9	- -	- -	
10	- -	- -	

n-C17/pristane
ISO5725, table A: Results from participating laboratories:

Laboratory	Level E	Level G	Method
	Assigned value 3.3	Assigned value 0.1	
1	- -	- -	
2A	- -	- -	
2B	- -	- -	
3	- -	- -	
4	3.5 3.8	0.094 0.099	
5	- -	- -	
6	- -	- -	
7	- -	- -	
8A	- -	- -	
8B	- -	- -	
9	- -	- -	
10	- -	- -	

n-C18/phytane
ISO5725, table A: Results from participating laboratories:

Laboratory	Level E	Level G	Method
	Assigned value - -	Assigned value 0.05 -	
1	- -	- -	
2A	- -	- -	
2B	- -	- -	
3	- -	- -	
4	4.2 3.9	0.032 0.14	
5	- -	- -	
6	- -	- -	
7	- -	- -	
8A	- -	- -	
8B	- -	- -	
9	- -	- -	
10	- -	- -	

Pristane/phytane
ISO5725, table A: Results from participating laboratories:

Laboratory	Level E	Level G	Method
	Assigned value 0.8	Assigned value 1.3	
1	- -	- -	
2A	- -	- -	
2B	- -	- -	
3	- -	- -	
4	1.05 0.87	1.3 1.2	
5	- -	- -	
6	- -	- -	
7	- -	- -	
8A	- -	- -	
8B	- -	- -	
9	- -	- -	
10	- -	- -	

CPI(15-21)
ISO5725, table A: Results from participating laboratories:

Laboratory	Level E	Level G	Method
	Assigned value 1.0	Assigned value -	
1	- -	- -	
2A	- -	- -	
2B	- -	- -	
3	- -	- -	
4	1.03 0.99	4.7 2.7	
5	- -	- -	
6	- -	- -	
7	- -	- -	
8A	- -	- -	
8B	- -	- -	
9	- -	- -	
10	- -	- -	

CPI(25-33)
ISO5725, table A: Results from participating laboratories:

Laboratory	Level E	Level G	Method
	Assigned value 1.0	Assigned value -	
1	- -	- -	
2A	- -	- -	
2B	- -	- -	
3	- -	- -	
4	0.92 0.90	0.93 0.94	
5	- -	- -	
6	- -	- -	
7	- -	- -	
8A	- -	- -	
8B	- -	- -	
9	- -	- -	
10	- -	- -	

KVALITATIV VURDERING

Laboratorium	Prøve A1	Prøve A2	Prøve B
"Nominel værdi"			*Ren jord uden muld spiket med blanding af diesel og fuelolie*
1			Gasolie + smøre-/hydraulikolie
4			Gasolie - frisk + tung olie (Heavy fuel oil)
8A og B			Gasolie (ikke nedbrudt)/motorolie evt. bunkerolie
10A			Blanding af diesel- og fuelolie

Laboratorium	Prøve C	Prøve D	Prøve E
"Nominel værdi"	*Blanding af ren jord uden muld og kompost*	*Prøve fra jordrensefirma (prøve B fra præstation-sprøvning 2003-5) spiket med BTEX*	*Prøve C spiket med fu-elolie*
1	Naturlige komponenter	Forvitret gasolie + natur-lige komponenter	Smøreolie + naturlige komponenter
4	Tungere olie + naturligt forekommende kul-brinter.	Gasolie - nedbrudt	Heavy fuel oil
8A og B	Helt eller delvist naturligt forekommende kul-brinter. Spor af petro-gene kulbrinter.	Gasolie (kraftigt ned-brudt). Spor af naturlige kulbrinter.	Fuelolie (ikke nedbrudt). Tegn på naturlige kul-brinter (phytosteroler).
10A	Tørv/spagnum	Weatheret diesel	Blanding af fuelolie og tørv/spagnum

Laboratorium	Prøve F	Prøve G	Prøve H
"Nominel værdi"	*Vejopfej*	*Prøve fra jordrensefirma*	*Prøve C spiket med diesel*
1	Smøreolie og naturlige komponenter.	Forvitret gasolie.	Gasolie.
4	Tungere olie	Blanding af nedbrudt olie og en tungere olie.	Gasolie
8A og B	Højt indhold af 17α(H),21β(H)-hopan indikerer motorolie eller lignende. Indhold af naturlige kulbrinter. CPI >>1	Gasolie (kraftigt nedbrudt). Spor af naturlige kulbrinter.	Gasolie (ikke nedbrudt).
10A	-	Weatheret diesel	Diesel

Laboratorium	Prøve E (egen metode)	Prøve G (egen metode)
1	Smøreolie	Forvitret gasolie.
4	Heavy fuel oil	Nedbrudt gasolie
8A og B	Fuelolie (ikke nedbrudt)	Gasolie (kraftigt nedbrudt)
10A	-	-

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A N N E X J

Participants' comments

Laboratory number	Parameter/ Sample	Comment received on result forms
1	A-H	One of sample G was broken in the centrifuge. It was difficult to obtain a free pentane phase.
	A-H C_6H_6-C_{10}	Re. GC-FID-analyses: In the hydrocarbon fraction, C_6H_6-C_{10}, appeared a number of components that the laboratory at present is not sure if they are true components of the samples. These components are not seen when analysing using the laboratory's present method.
	E-G (laboratory's own method)	PAH-MSD: Pyrophosphate + toluene GC-FID: Pyrophosphate + pentane Please note that the laboratory's own method includes hydrocarbons only till C_{35}
2	D PAH	Sample D: Internal standards for PAH-analysis are absorbed by the sample material.
	A-H Benzene	GC-FID: Benzene was not analysed due to problems with the acetone.
4	A-H CPI(25-33)	C_{30} is used as internal standard. Therefore the conc. of C_{28} in the samples is used instead of C_{30} for calculation of CPI(25-33).
	A-E C_{17}/pristane, C_{18}/phytane, pristane-/phytane, CPI(15-21), CPI(25-33)	In sample C the results for the 5 last parameters are marked with an asterisk meaning: Alkanes and pristane / phytane concentrations are very close to the limit of detection. Therefore these values are **very** uncertain.
	E-G (laboratory's own method) CPI(25-33)	C_{30} is used as internal standard. Therefore the conc. of C_{28} in the samples is used instead of C_{30} for calculation of CPI(25-33).
6	A-H	The laboratory uses ISO/DIS 16703 for analysis of soil. Therefore no results are reported for "the laboratory's own method". It was difficult to close the sample glasses sufficiently to avoid leaking. Also, supply of extra lids and membranes would have facilitated addition of solvent.
7	A-H	It was difficult, and for some samples impossible to separate the pentane phase. Even high speed centrifugation did not help. For this reason only single measurements are reported for sample A2, B, D and G.
	D	One sample was analysed using GC-FID and one using GC-MS.

Laboratory number	Parameter/ Sample	Comment received on result forms
8B	A-H	No results are reported for one D-sample because the lid leaked during extraction. Therefore no pentane phase was left.
	A-H BTEX	Re. BTEX: The results are highly variable from bottle to bottle. This is probably because the lids did not close properly.

Laboratory number	Parameter/ Sample	Comment received after distribution of preliminary data report
2	E $>C_{10}$ - C_{25}, $>C_{25}$ - C_{40}	The data reported from the laboratory were accidentally mixed so that the second result for $>C_{10}$ - C_{25} was reported as $>C_{25}$ - C_{40} and vice versa. Eurofins comment: the data are corrected in the final report.
3	A - E BTEX, C_6H_6 - C_{10}, $>C_{10}$ - C_{25}, $>C_{25}$ - C_{40}	The laboratory's data are missing from the preliminary report. Eurofins comment: The error was Eurofins' and the data are added for the final report.
6	C and E C_6H_6 - C_{10}	All results should be <2,5 mg/kg. Eurofins comment: the data are corrected in the final report.
	G Dibenz(a,h)-anthracene	The results should be <0,005 mg/kg. Eurofins comment: the data are corrected in the final report.
8	H Total hydro-carbons	The GC used was probably not linear till 4000 mg/kg. The extracts have been analysed again giving improved values, included in a spreadsheet. Eurofins comment: the data are corrected in the final report.
	C C_{17}/pristane, C_{18}/phytane, pristane-/phytane	The concentrations for C_{17}, C_{18}, pristane and phytane are below the limit of detection. The values reported for sample C for the three parameters are withdrawn. Eurofins comment: the data are corrected in the final report.

A N N E X K

Methods

ANALYSIS OF SAMPLE A, B, C, D, E, F, G, H (METHOD EVALUATION STUDY)

GC-analysis

Method no.	Principle
1	GC-FID
2	GC-MS Sim
3	GC-MS Scan
9	Other methods

ANALYSIS OF SAMPLE E AND G USING THE LABORATORY'S OWN METHOD

Ekstraction

Method no.	Principle	Reference
1	With pentane and pyrophosphate for 16 hours	VKI: Bestemmelse af olie i jord, gaschroma-tografisk metode, July 1998
2	With pentane and pyrophosphate for 2 hours	OM's QA-manual of 1.8.97
3	With dichlormethane	
4	With acetone + n-heptane	ISO/DIS 16703, February 2001
9	Other methods	

GC-analysis

Method no.	Principle	Reference
1	GC-FID	VKI: Bestemmelse af olie i jord, gaschroma-tografisk metode, July 1998
2	GC-MS	
3	GC-FID	ISO/DIS 16703, February 2001
9	Other methods	

Forbindelser/produkter som anvendes til kalibrering af indholdet af olie

Method no.	Principle	Reference
1	Selected specific substances	VKI: Bestemmelse af olie i jord, gaschroma-tografisk metode, July 1998
2	Prescribed products such as gasoline, diesel and fuel oil	OM's QA-manual of 1.8.97
3	Individual products corresponding to content of samples	
4	Mixture of equal weights diesel and lubricating oil containing no additives	ISO/DIS 16703, February 2001
9	Other methods	

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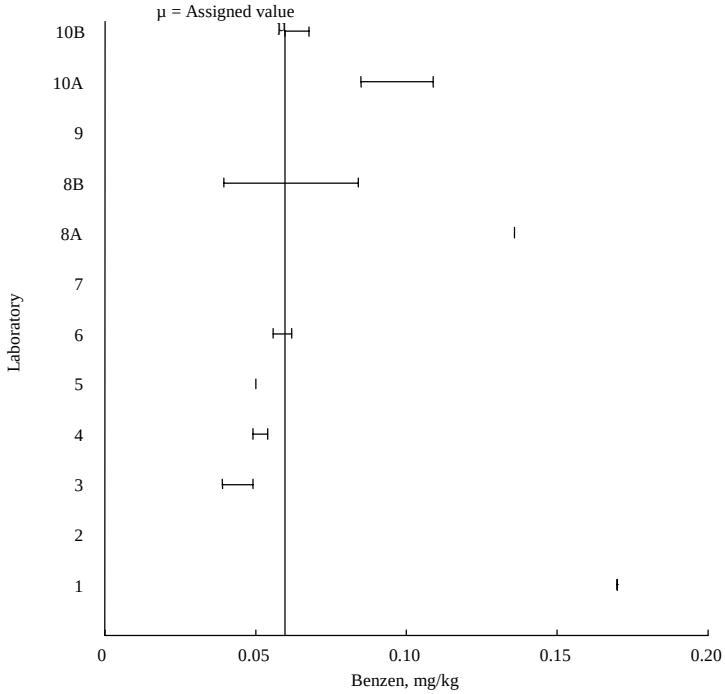
A N N E X L

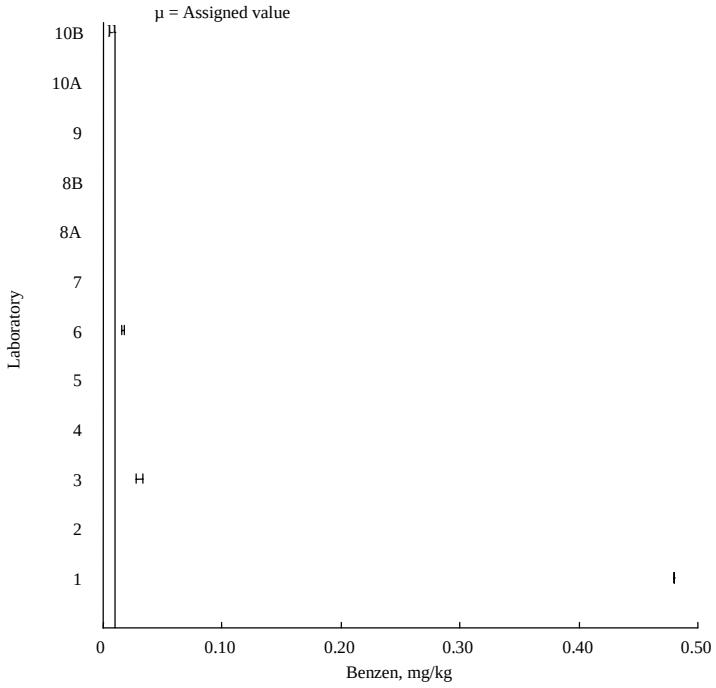
Plots of participants' results

Level A



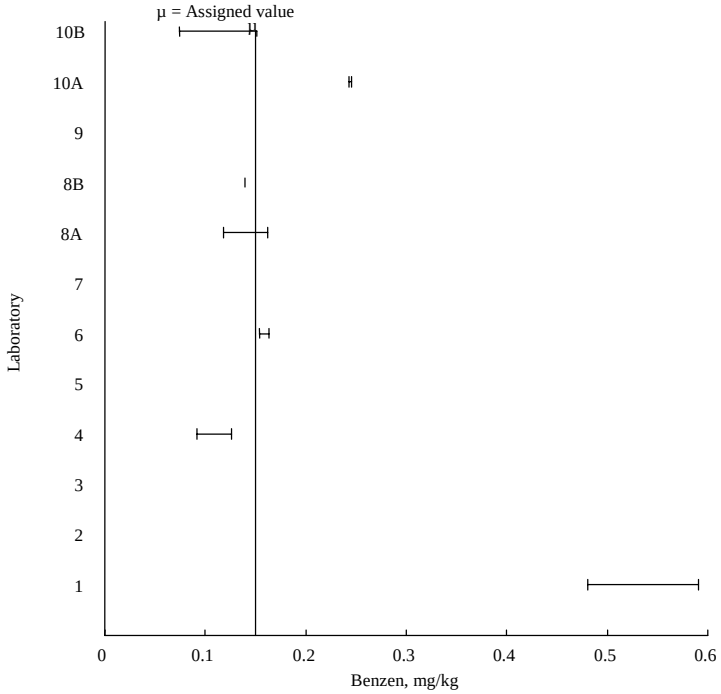
All results including outliers: n = 16 Mean = 0.080
Std.dev = 0.044
All results excluding outliers: n = 16 Mean = 0.080
Std.dev = 0.044

Level B



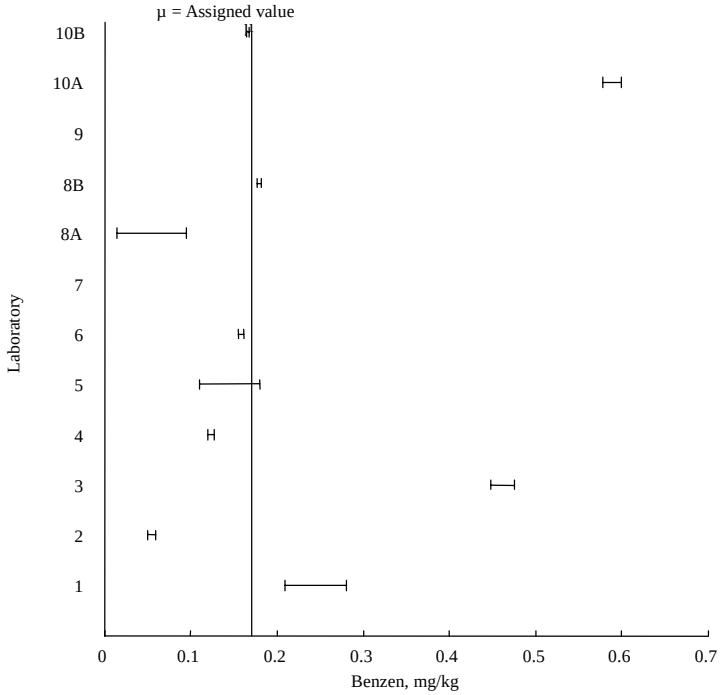
All results including outliers: n = 6 Mean = 0.180
Std.dev = 0.240
All results excluding outliers: n = 6 Mean = 0.180
Std.dev = 0.240

Level D



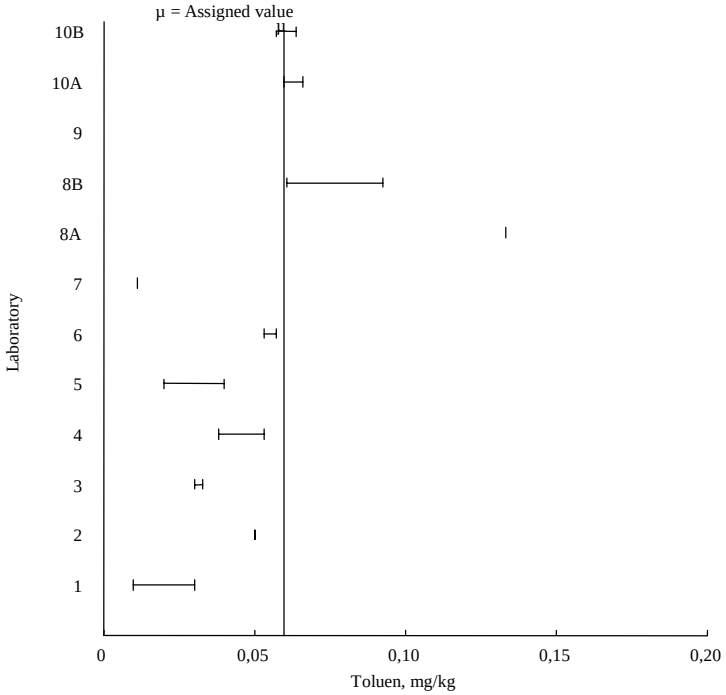
All results including outliers: n = 13 Mean = 0.210
Std.dev = 0.150
All results excluding outliers: n = 13 Mean = 0.210
Std.dev = 0.150

Level H



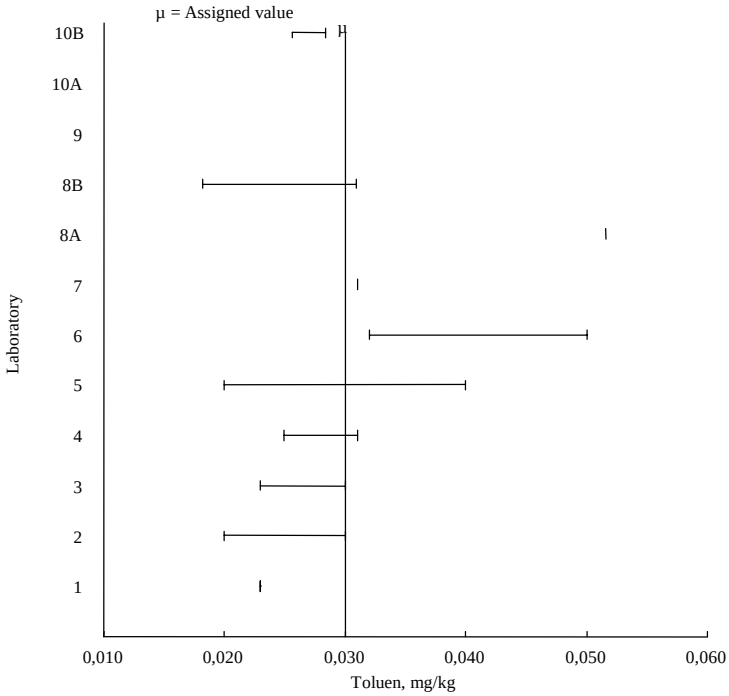
All results including outliers: n = 20 Mean = 0.220
Std.dev = 0.170
All results excluding outliers: n = 20 Mean = 0.220
Std.dev = 0.170

Level A



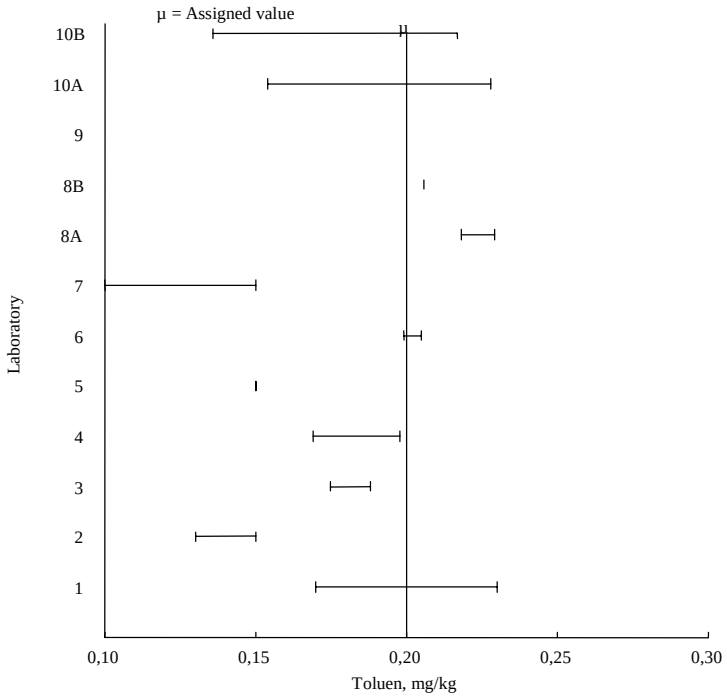
All results including outliers: n = 20 Mean = 0,050
Std.dev = 0,028
All results excluding outliers: n = 20 Mean = 0,050
Std.dev = 0,028

Level B



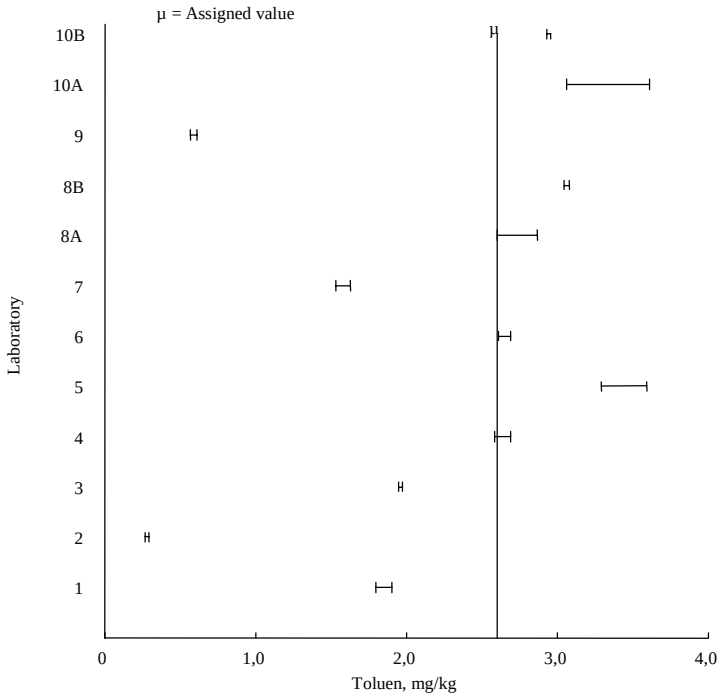
All results including outliers: n = 18 Mean = 0,030
Std.dev = 0,009
All results excluding outliers: n = 18 Mean = 0,030
Std.dev = 0,009

Level D



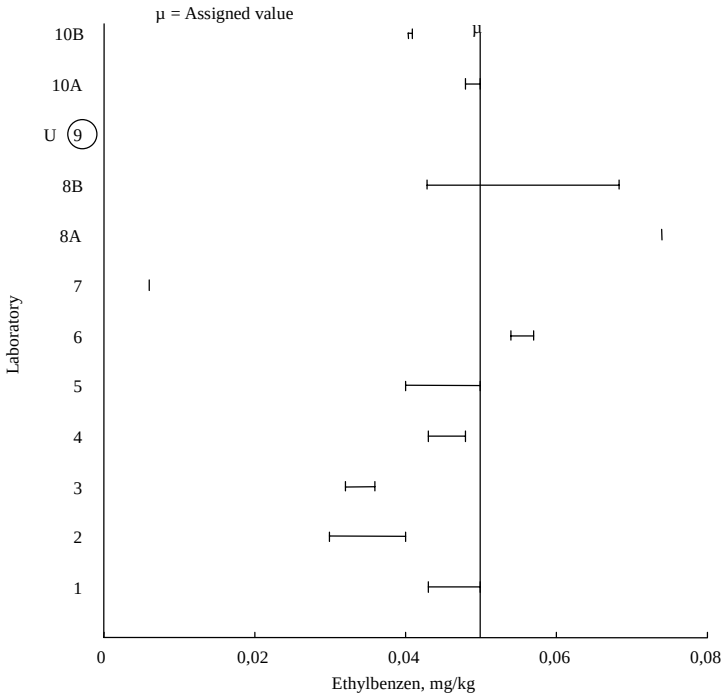
All results including outliers: n = 21 Mean = 0,180
Std.dev = 0,037
All results excluding outliers: n = 21 Mean = 0,180
Std.dev = 0,037

Level H



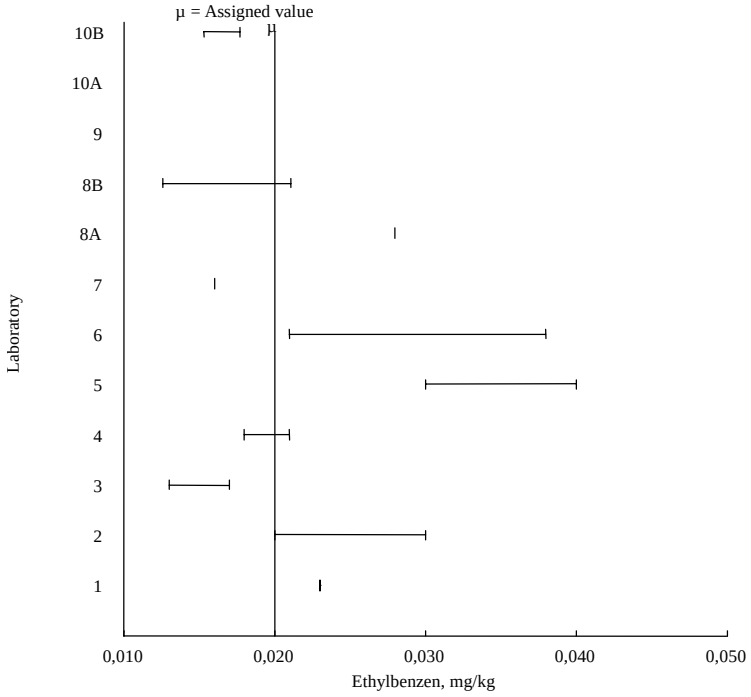
All results including outliers: n = 24 Mean = 2,30
Std.dev = 1,00
All results excluding outliers: n = 24 Mean = 2,30
Std.dev = 1,00

Level A



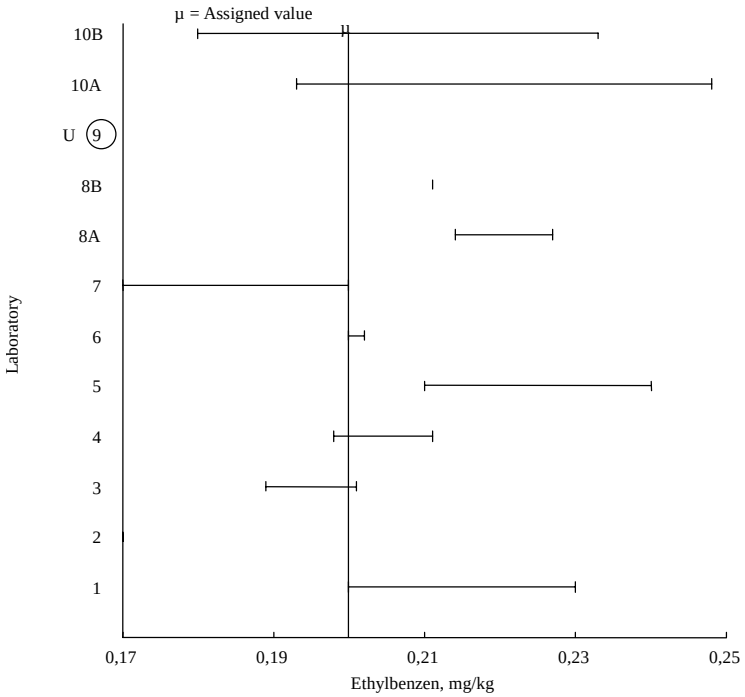
All results including outliers: n = 20 Mean = 0,045
Std.dev = 0,014
All results excluding outliers: n = 20 Mean = 0,045
Std.dev = 0,014

Level B



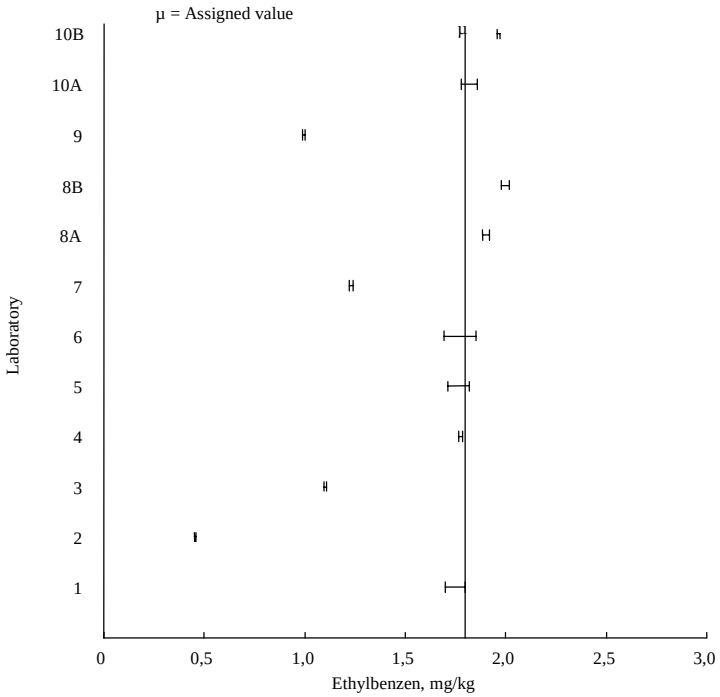
All results including outliers: n = 18 Mean = 0,022
Std.dev = 0,008
All results excluding outliers: n = 18 Mean = 0,022
Std.dev = 0,008

Level D



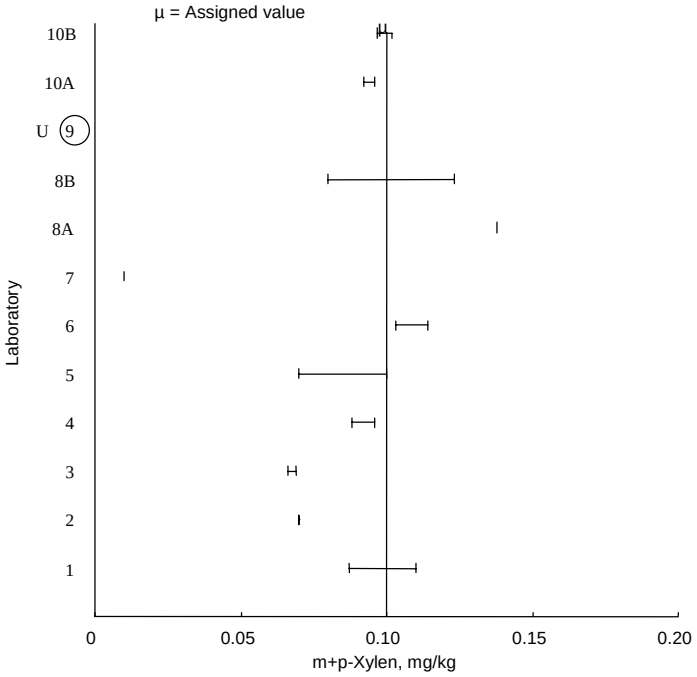
All results including outliers: n = 21 Mean = 0,200
Std.dev = 0,022
All results excluding outliers: n = 21 Mean = 0,200
Std.dev = 0,022

Level H



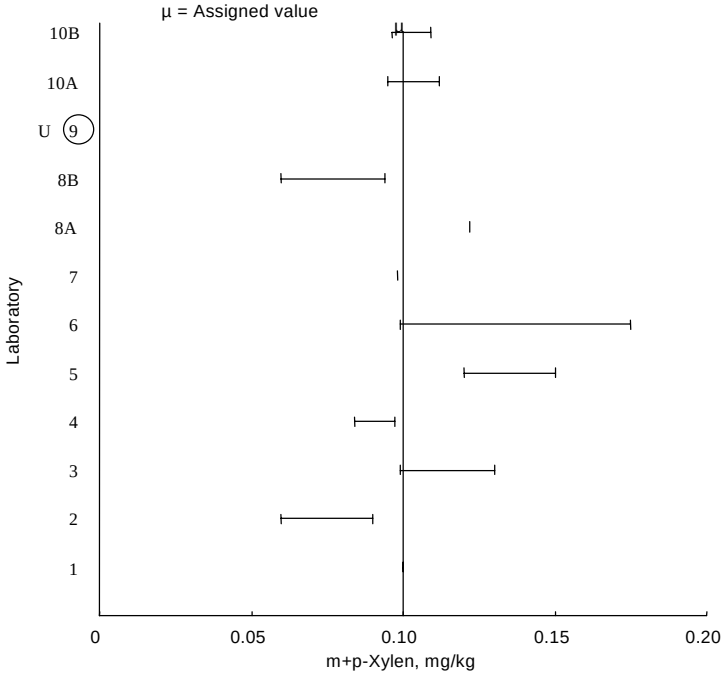
All results including outliers: n = 24 Mean = 1,50
Std.dev = 0,47
All results excluding outliers: n = 24 Mean = 1,50
Std.dev = 0,47

Level A



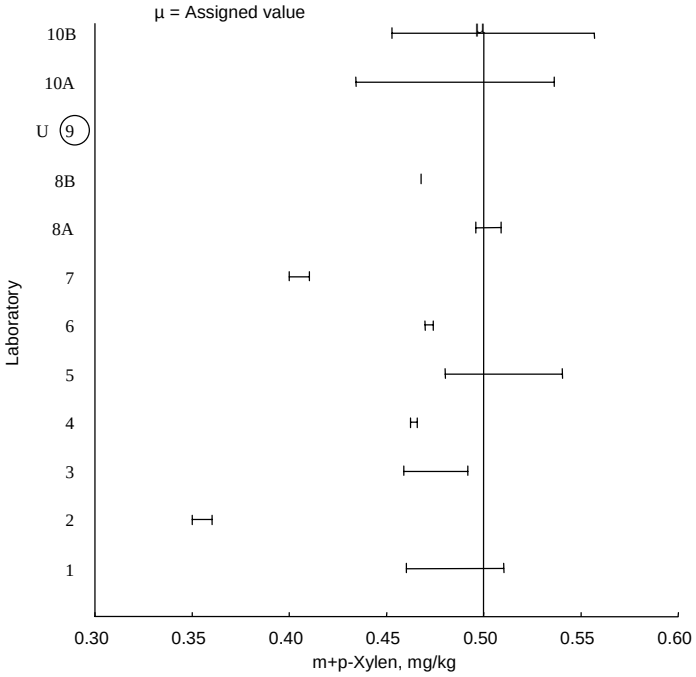
All results including outliers: n = 20 Mean = 0.089
Std.dev = 0.027
All results excluding outliers: n = 20 Mean = 0.089
Std.dev = 0.027

Level B



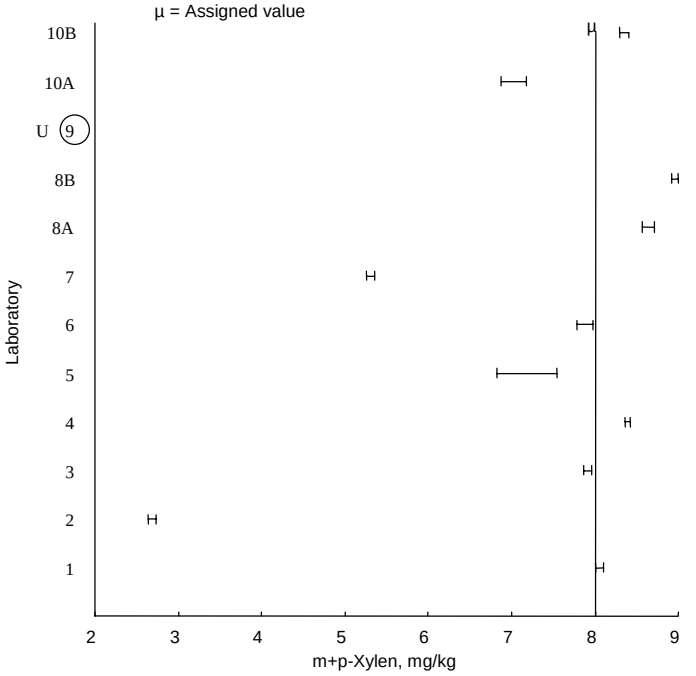
All results including outliers: n = 20 Mean = 0.100
Std.dev = 0.027
All results excluding outliers: n = 20 Mean = 0.100
Std.dev = 0.027

Level D



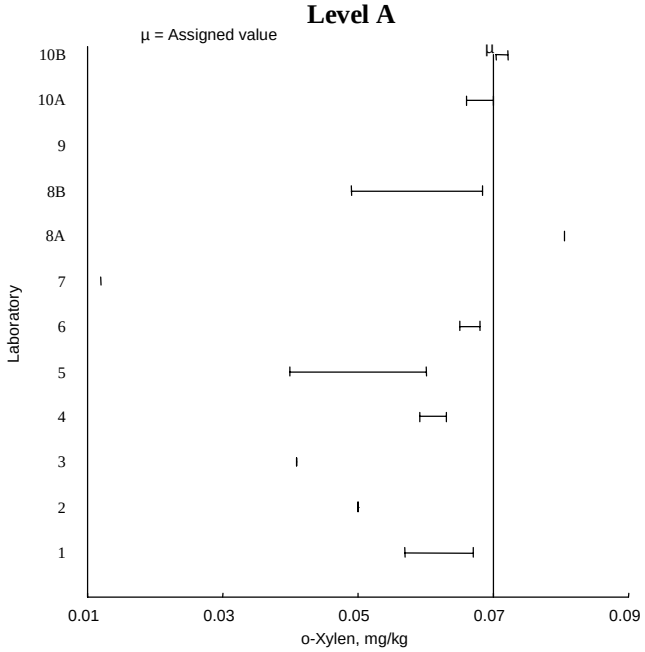
All results including outliers: n = 21 Mean = 0.470
Std.dev = 0.054
All results excluding outliers: n = 21 Mean = 0.470
Std.dev = 0.054

Level H



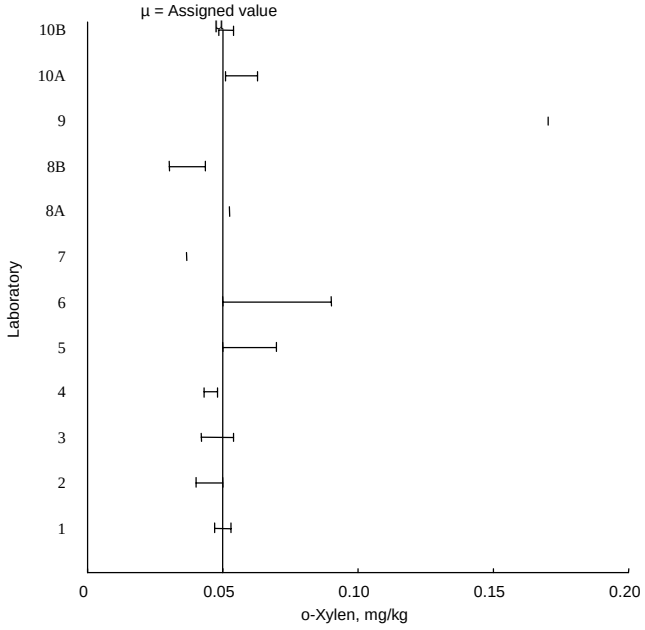
All results including outliers: n = 22 Mean = 7.30
Std.dev = 1.80
All results excluding outliers: n = 22 Mean = 7.30
Std.dev = 1.80

Level A



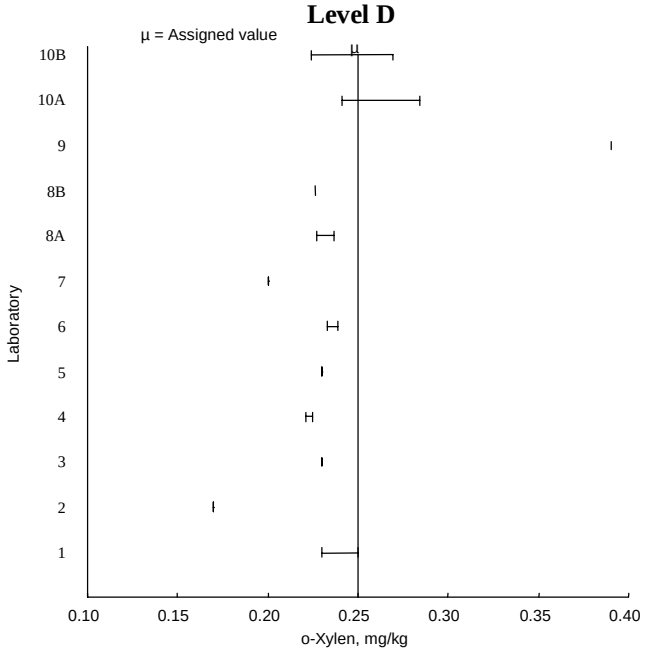
All results including outliers: n = 20 Mean = 0.057
Std.dev = 0.016
All results excluding outliers: n = 20 Mean = 0.057
Std.dev = 0.016

Level B



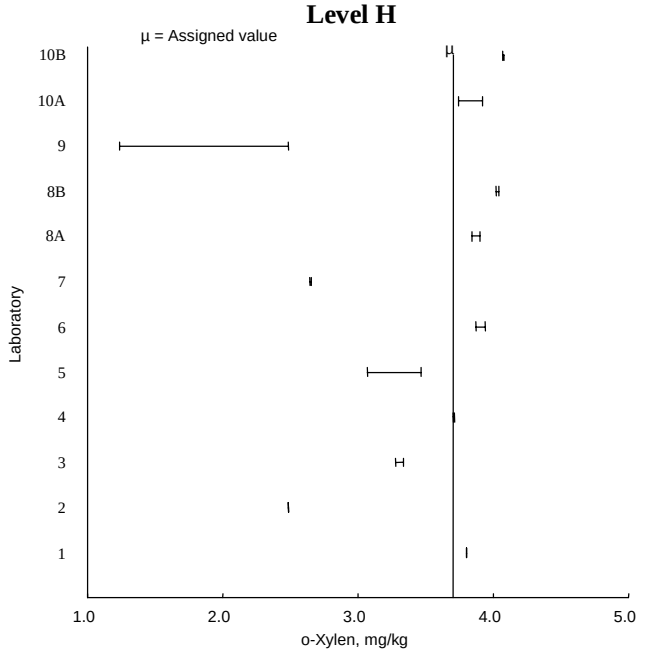
All results including outliers: n = 21 Mean = 0.057
Std.dev = 0.029
All results excluding outliers: n = 21 Mean = 0.057
Std.dev = 0.029

Level D



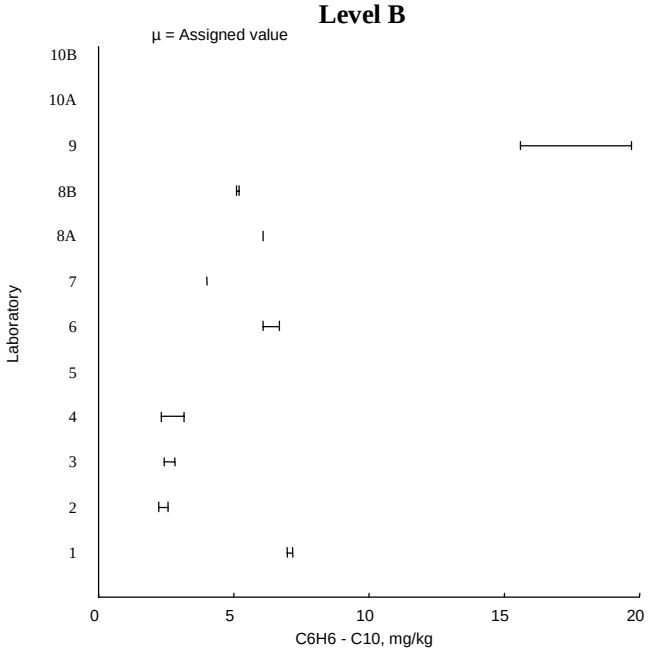
All results including outliers: n = 22 Mean = 0.230
Std.dev = 0.043
All results excluding outliers: n = 22 Mean = 0.230
Std.dev = 0.043

Level H



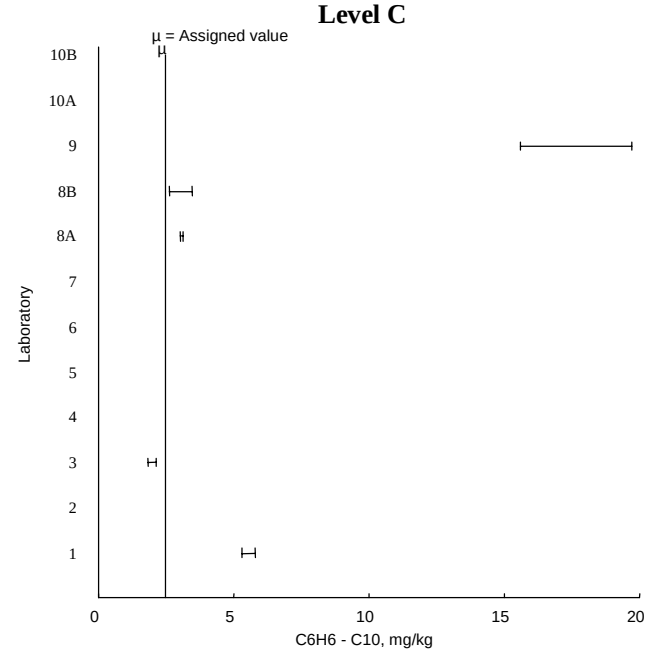
All results including outliers: n = 24 Mean = 3.40
Std.dev = 0.72
All results excluding outliers: n = 24 Mean = 3.40
Std.dev = 0.72

Level B



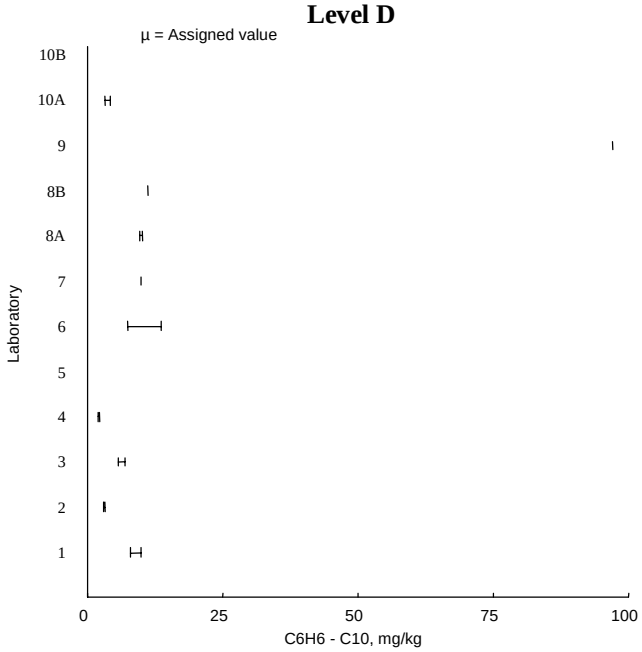
All results including outliers: n = 16 Mean = 6.10
Std.dev = 4.90
All results excluding outliers: n = 16 Mean = 6.10
Std.dev = 4.90

Level C



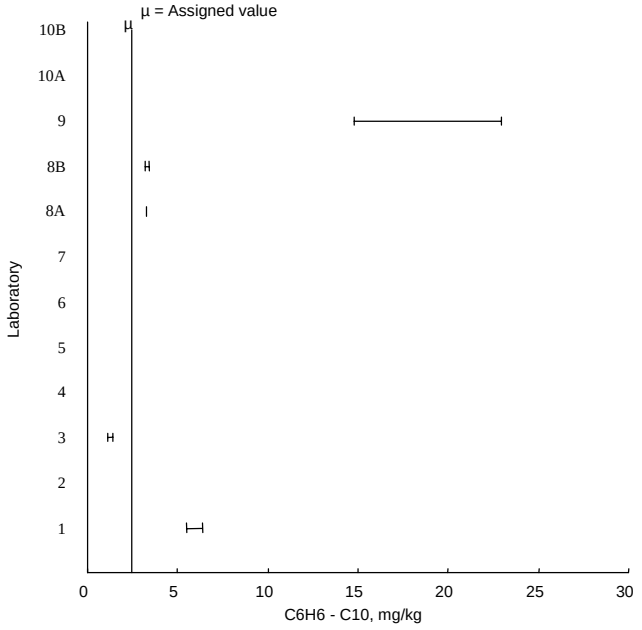
All results including outliers: n = 10 Mean = 6.30
Std.dev = 6.20
All results excluding outliers: n = 10 Mean = 6.30
Std.dev = 6.20

Level D



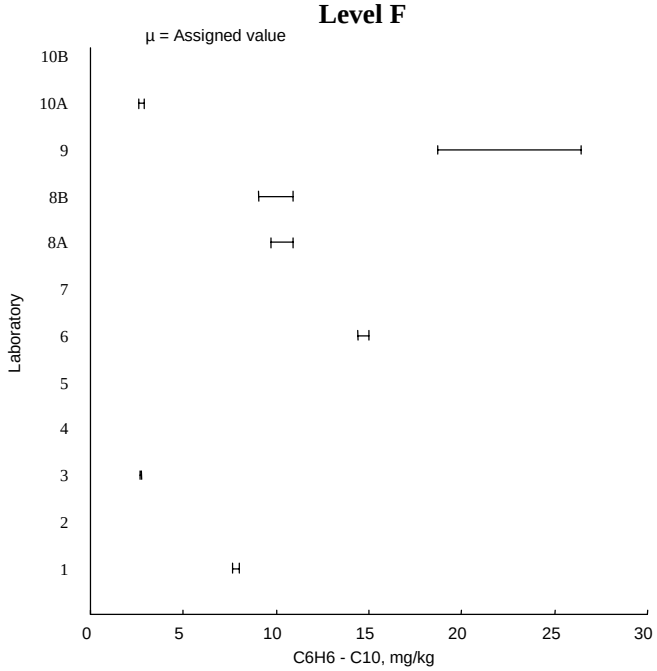
All results including outliers: n = 17 Mean = 12.00
Std.dev = 22.00
All results excluding outliers: n = 17 Mean = 12.00
Std.dev = 22.00

Level E



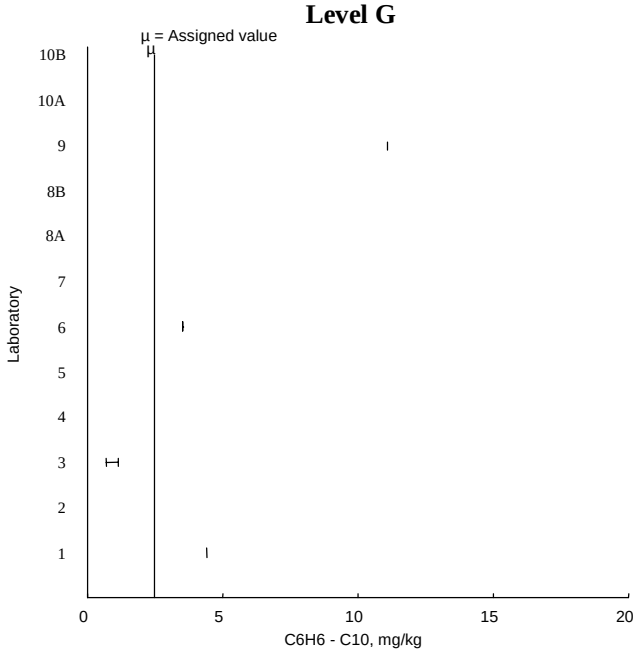
All results including outliers: n = 9 Mean = 6.90
Std.dev = 7.30
All results excluding outliers: n = 9 Mean = 6.90
Std.dev = 7.30

Level F



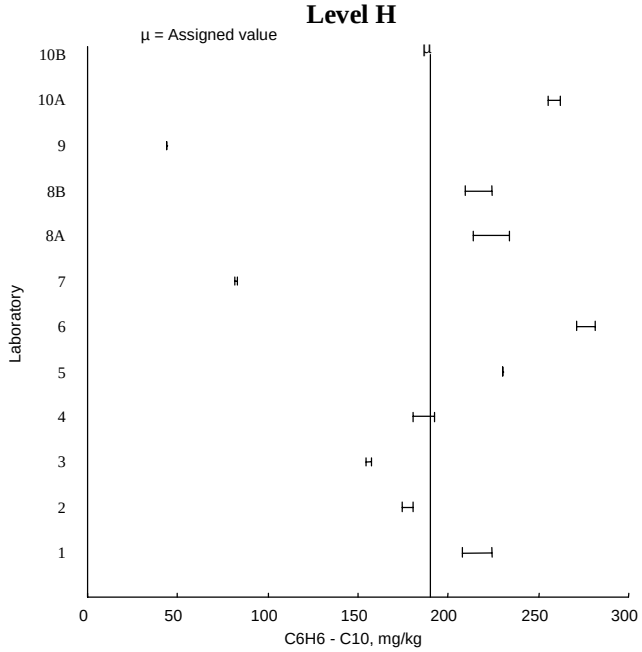
All results including outliers: n = 14 Mean = 10.00
Std.dev = 6.80
All results excluding outliers: n = 14 Mean = 10.00
Std.dev = 6.80

Level G



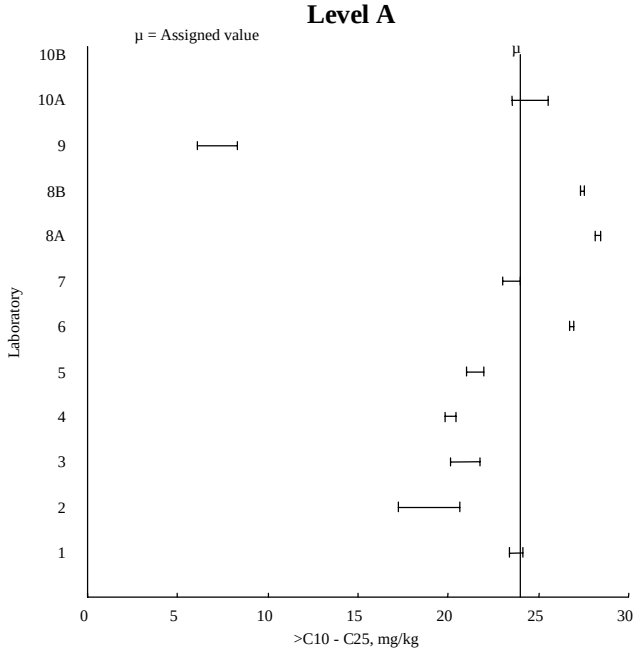
All results including outliers: n = 6 Mean = 4.10
Std.dev = 3.70
All results excluding outliers: n = 6 Mean = 4.10
Std.dev = 3.70

Level H



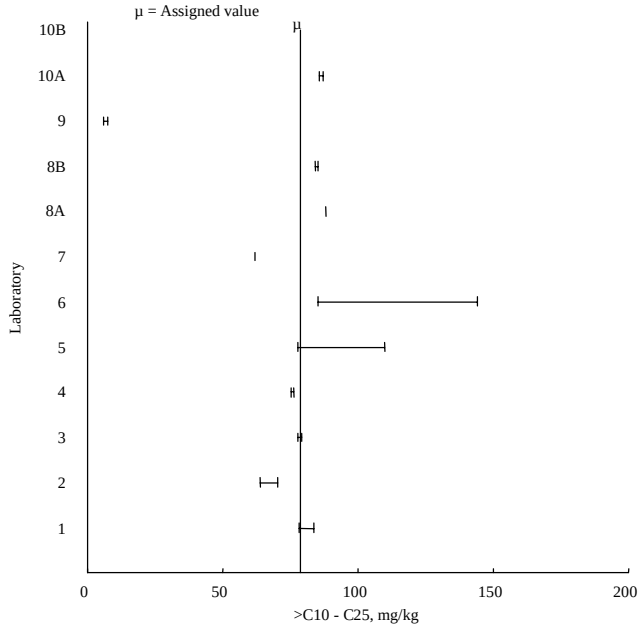
All results including outliers: n = 22 Mean = 1.9E2
Std.dev = 69.0
All results excluding outliers: n = 22 Mean = 1.9E2
Std.dev = 69.0

Level A



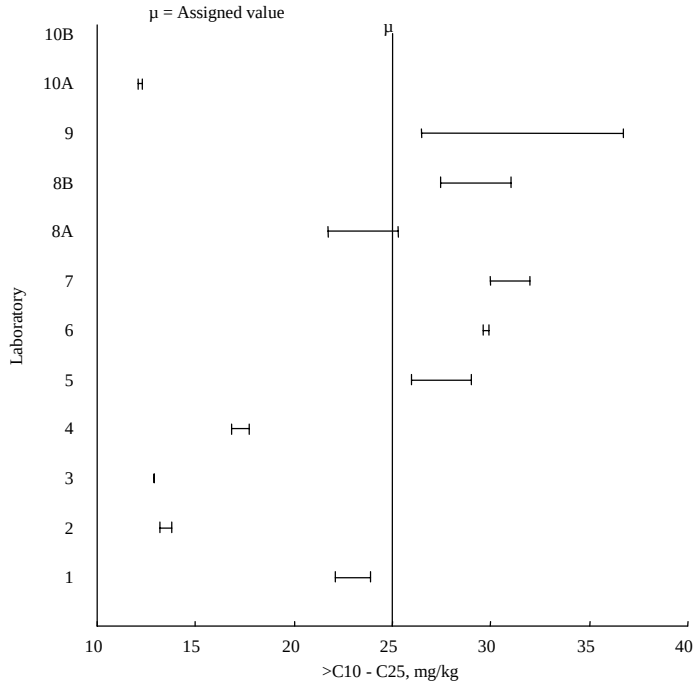
All results including outliers: n = 22 Mean = 22.0
Std.dev = 5.7
All results excluding outliers: n = 22 Mean = 22.0
Std.dev = 5.7

Level B



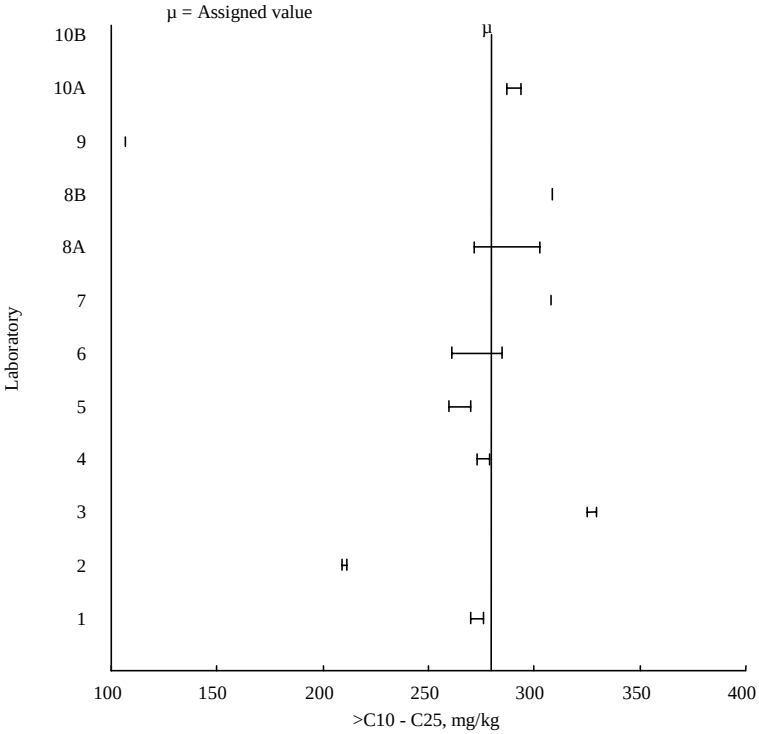
All results including outliers: n = 20 Mean = 76.0
Std.dev = 29.0
All results excluding outliers: n = 20 Mean = 76.0
Std.dev = 29.0

Level C



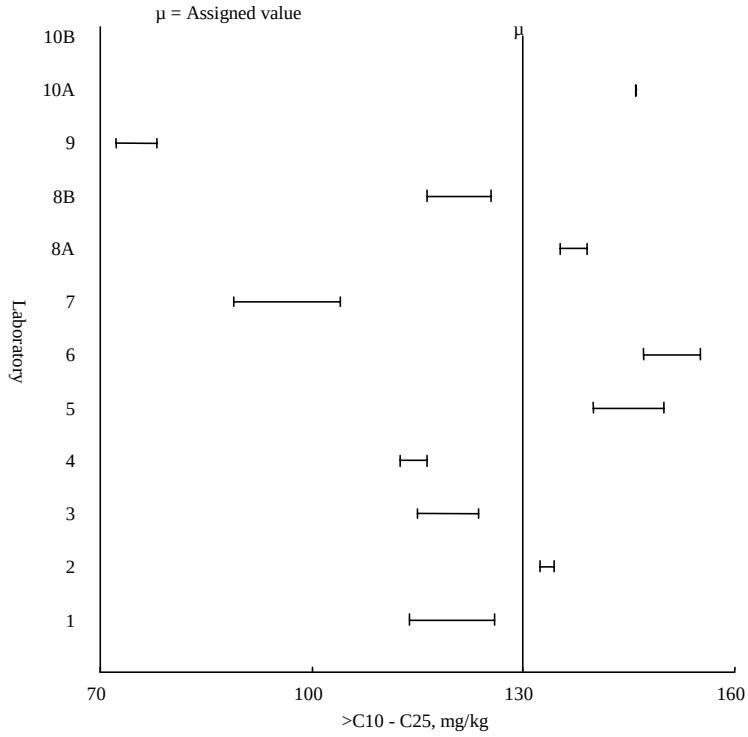
All results including outliers: n = 22 Mean = 23.0
Std.dev = 7.7
All results excluding outliers: n = 22 Mean = 23.0
Std.dev = 7.7

Level D



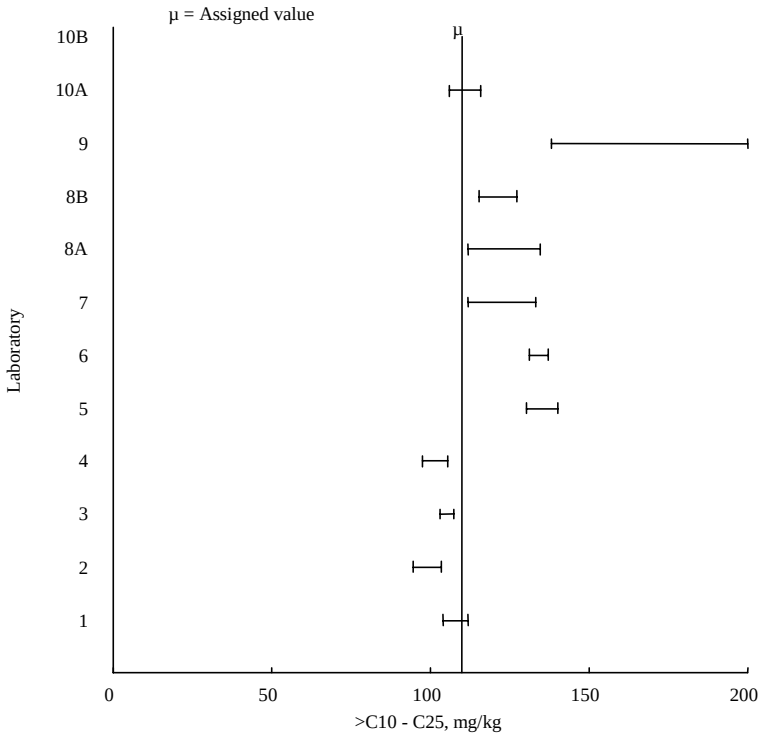
All results including outliers: n = 19 Mean = 2.7E2
Std.dev = 50.0
All results excluding outliers: n = 19 Mean = 2.7E2
Std.dev = 50.0

Level E



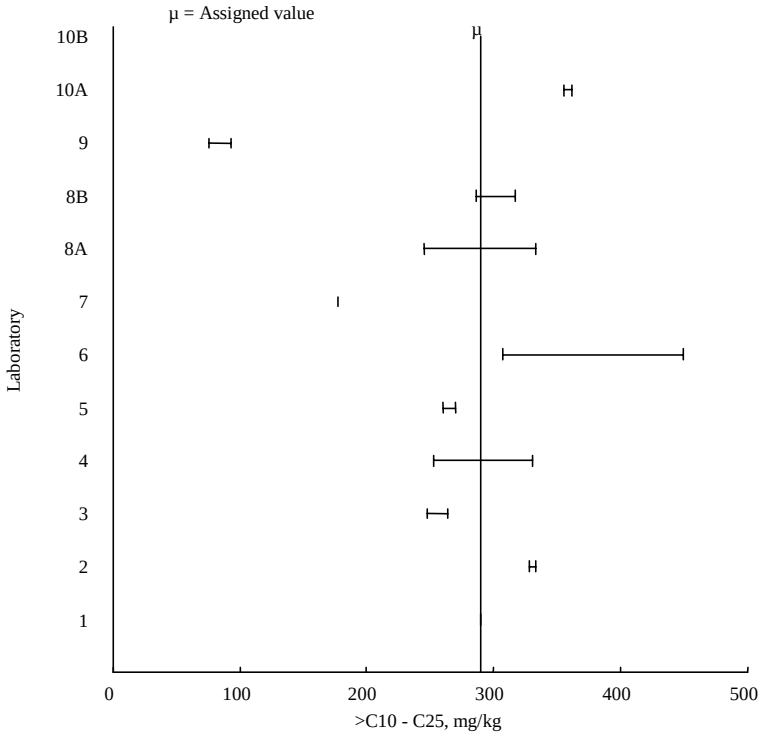
All results including outliers: n = 22 Mean = 1.2E2
Std.dev = 23.0
All results excluding outliers: n = 22 Mean = 1.2E2
Std.dev = 23.0

Level F



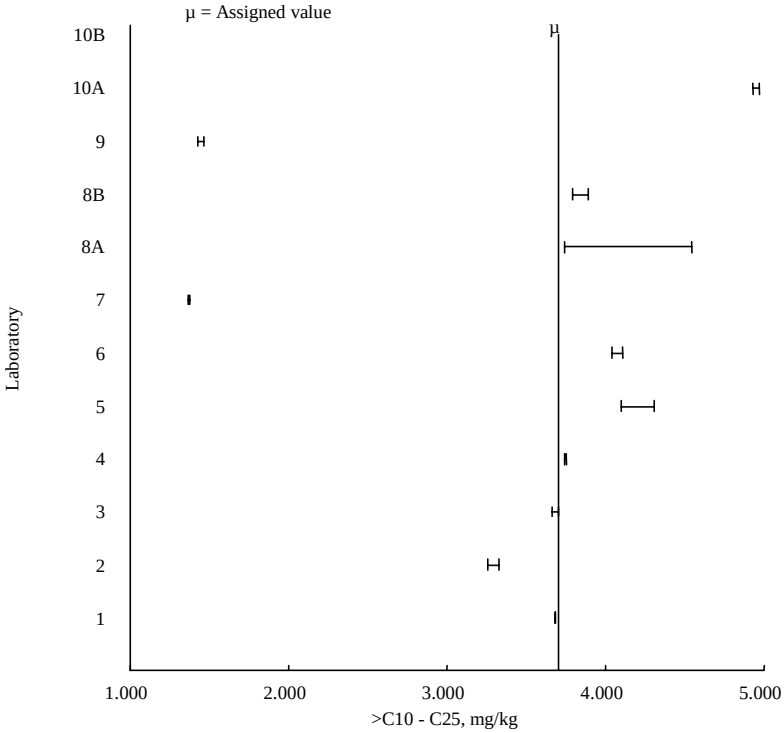
All results including outliers: n = 22 Mean = 1.2E2
Std.dev = 23.0
All results excluding outliers: n = 22 Mean = 1.2E2
Std.dev = 23.0

Level G



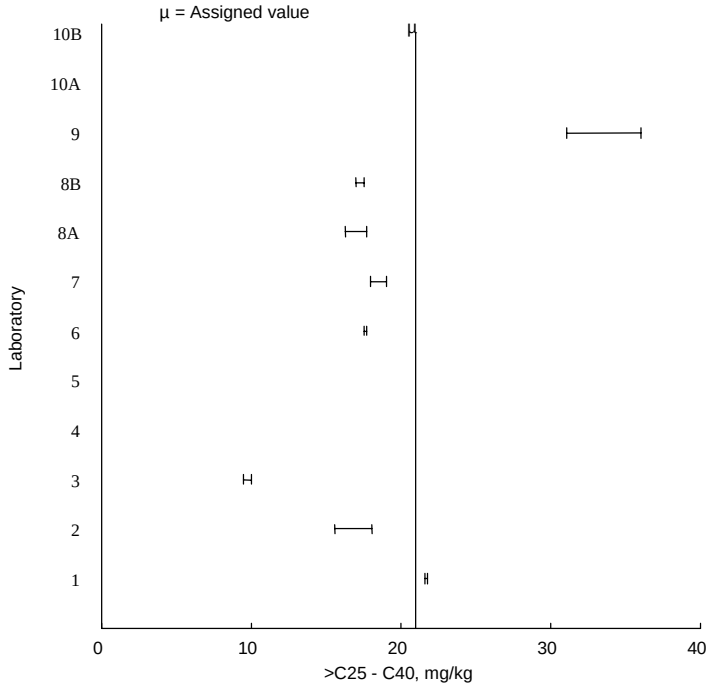
All results including outliers: n = 20 Mean = 2.8E2
Std.dev = 87.0
All results excluding outliers: n = 20 Mean = 2.8E2
Std.dev = 87.0

Level H



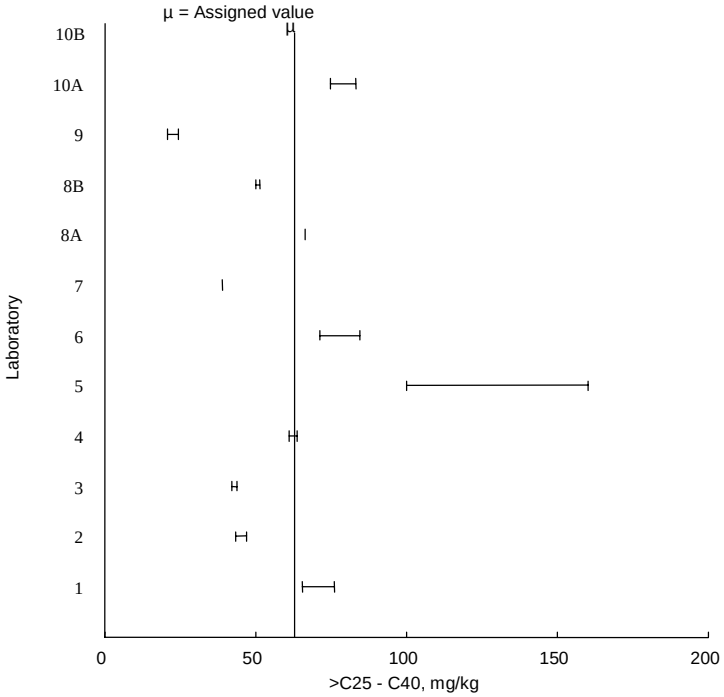
All results including outliers: n = 22 Mean = 3.5E3
Std.dev = 1.1E3
All results excluding outliers: n = 22 Mean = 3.5E3
Std.dev = 1.1E3

Level A



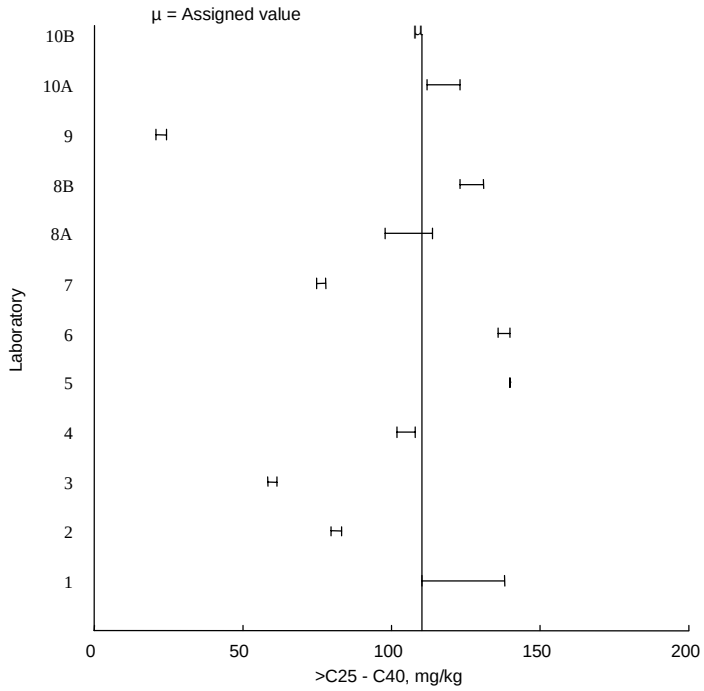
All results including outliers: n = 16 Mean = 19.0
Std.dev = 6.6
All results excluding outliers: n = 16 Mean = 19.0
Std.dev = 6.6

Level B



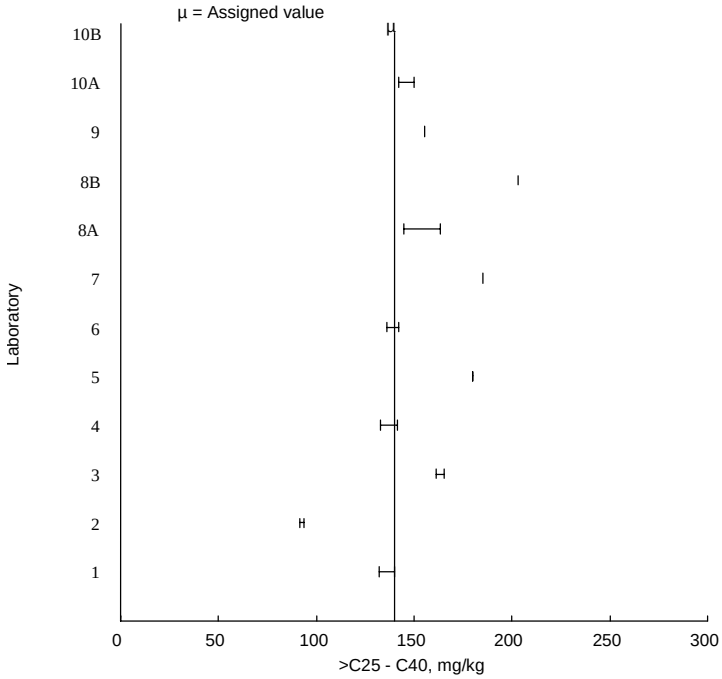
All results including outliers: n = 20 Mean = 63.0
Std.dev = 30.0
All results excluding outliers: n = 20 Mean = 63.0
Std.dev = 30.0

Level C



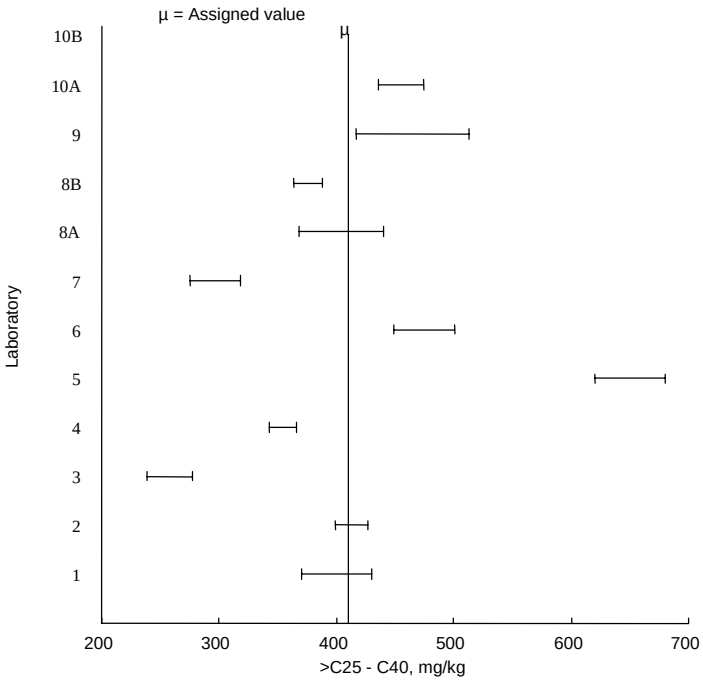
All results including outliers: n = 22 Mean = 1E2
Std.dev = 36.0
All results excluding outliers: n = 22 Mean = 1E2
Std.dev = 36.0

Level D



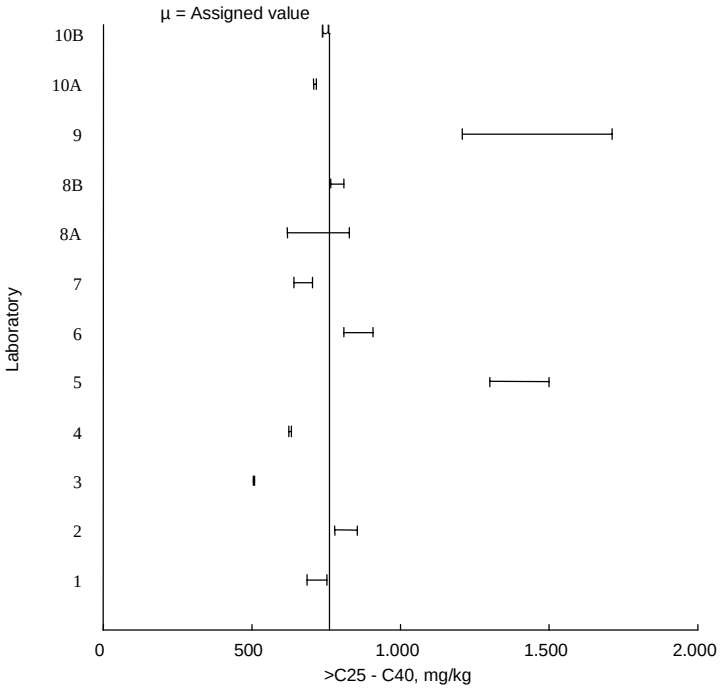
All results including outliers: n = 19 Mean = 1.5E2
Std.dev = 28.0
All results excluding outliers: n = 19 Mean = 1.5E2
Std.dev = 28.0

Level E



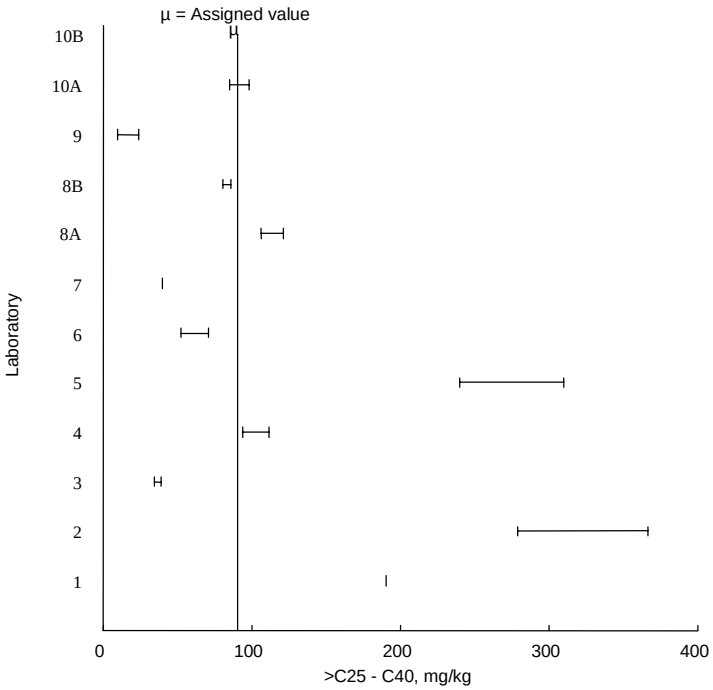
All results including outliers: n = 22 Mean = 4.1E2
Std.dev = 1E2
All results excluding outliers: n = 22 Mean = 4.1E2
Std.dev = 1E2

Level F



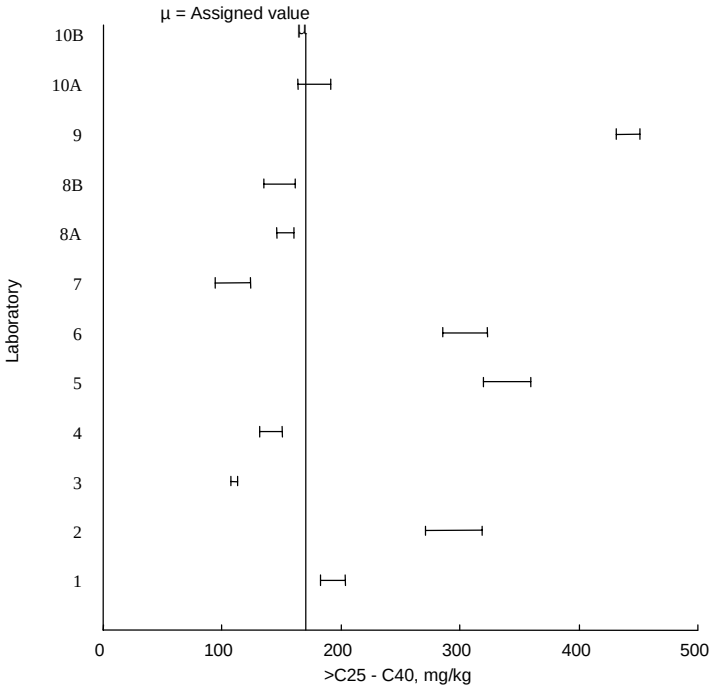
All results including outliers: n = 22 Mean = 8.4E2
Std.dev = 3.1E2
All results excluding outliers: n = 22 Mean = 8.4E2
Std.dev = 3.1E2

Level G



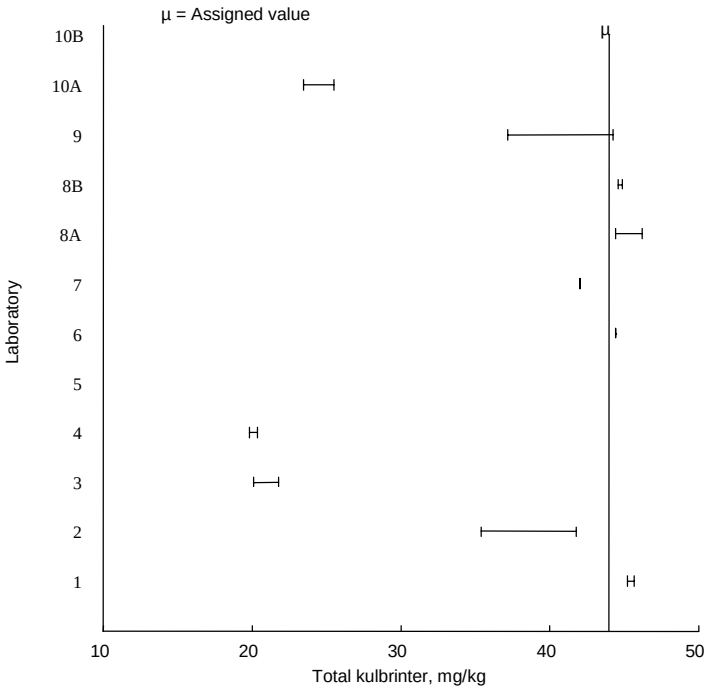
All results including outliers: n = 20 Mean = 1.2E2
Std.dev = 1E2
All results excluding outliers: n = 20 Mean = 1.2E2
Std.dev = 1E2

Level H



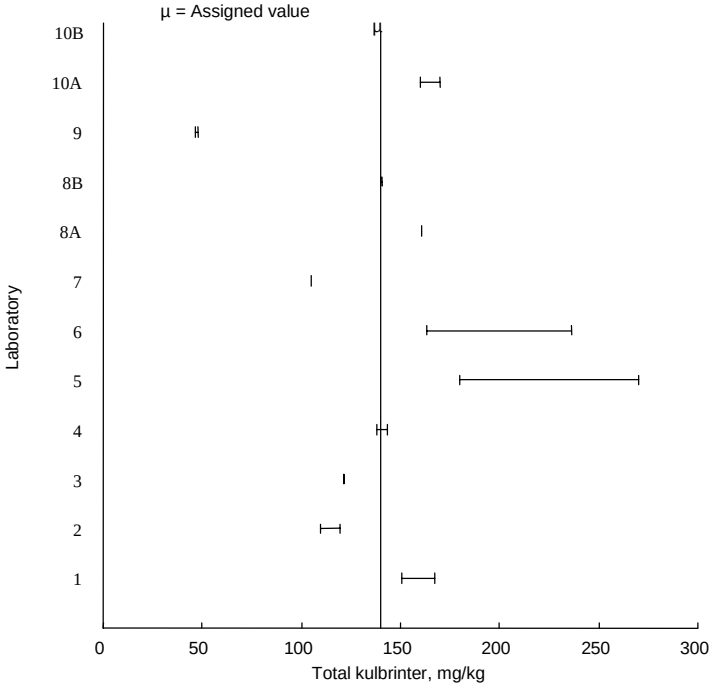
All results including outliers: n = 22 Mean = 2.2E2
Std.dev = 1.1E2
All results excluding outliers: n = 22 Mean = 2.2E2
Std.dev = 1.1E2

Level A



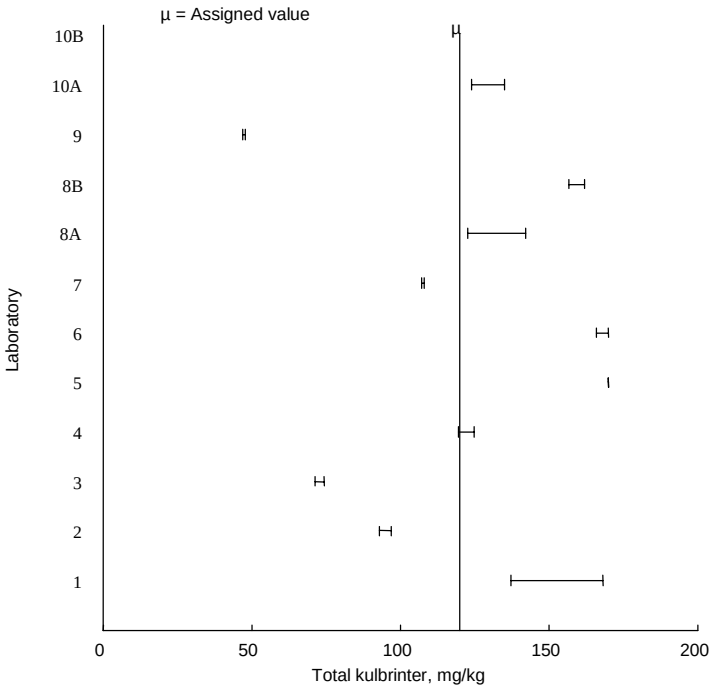
All results including outliers: n = 20 Mean = 37.0
Std.dev = 10.0
All results excluding outliers: n = 20 Mean = 37.0
Std.dev = 10.0

Level B



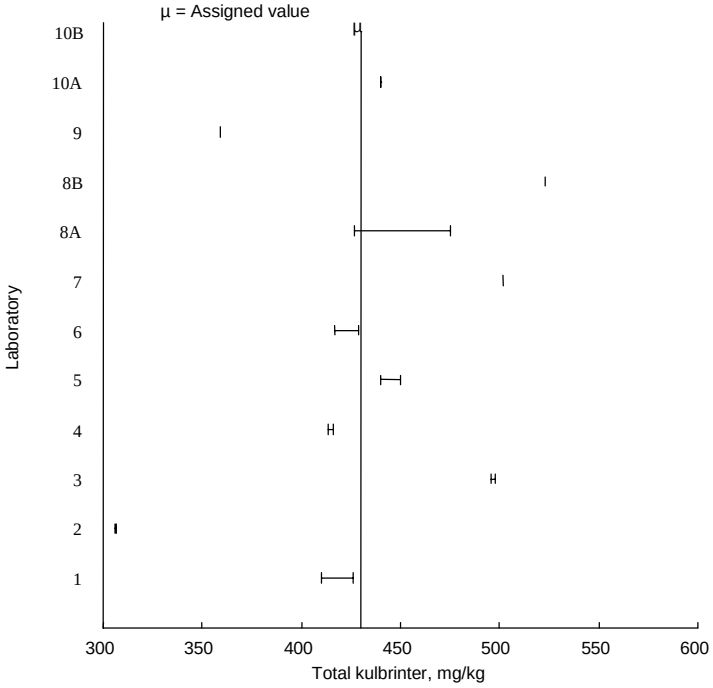
All results including outliers: n = 20 Mean = 1.4E2
Std.dev = 52.0
All results excluding outliers: n = 20 Mean = 1.4E2
Std.dev = 52.0

Level C



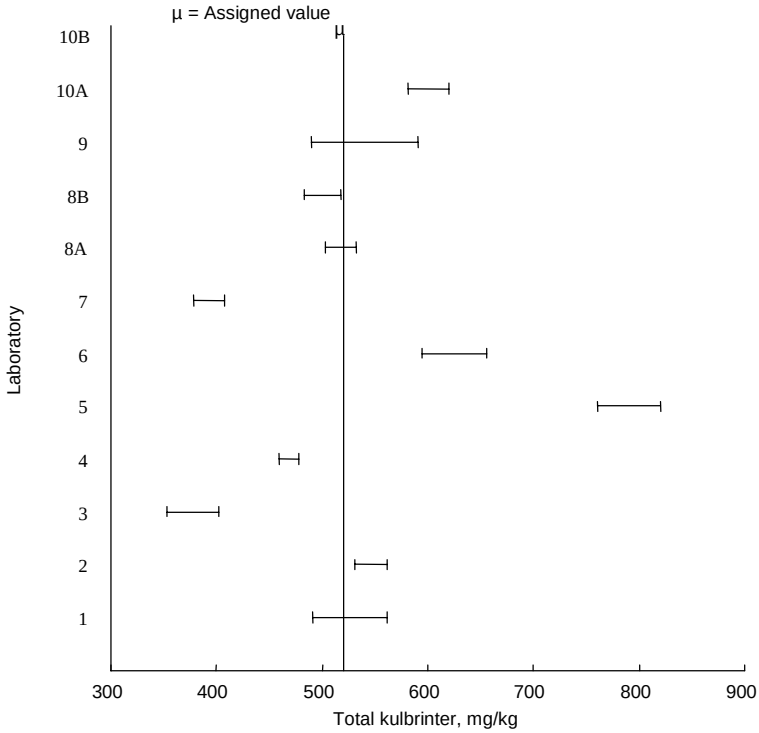
All results including outliers: n = 22 Mean = 1.2E2
Std.dev = 39.0
All results excluding outliers: n = 22 Mean = 1.2E2
Std.dev = 39.0

Level D



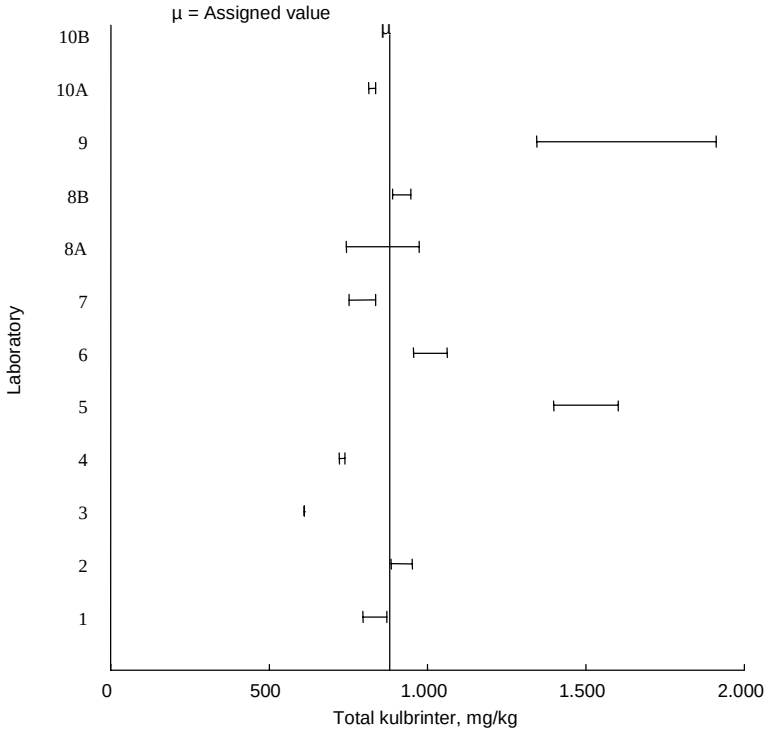
All results including outliers: n = 19 Mean = 4.3E2
Std.dev = 59.0
All results excluding outliers: n = 19 Mean = 4.3E2
Std.dev = 59.0

Level E



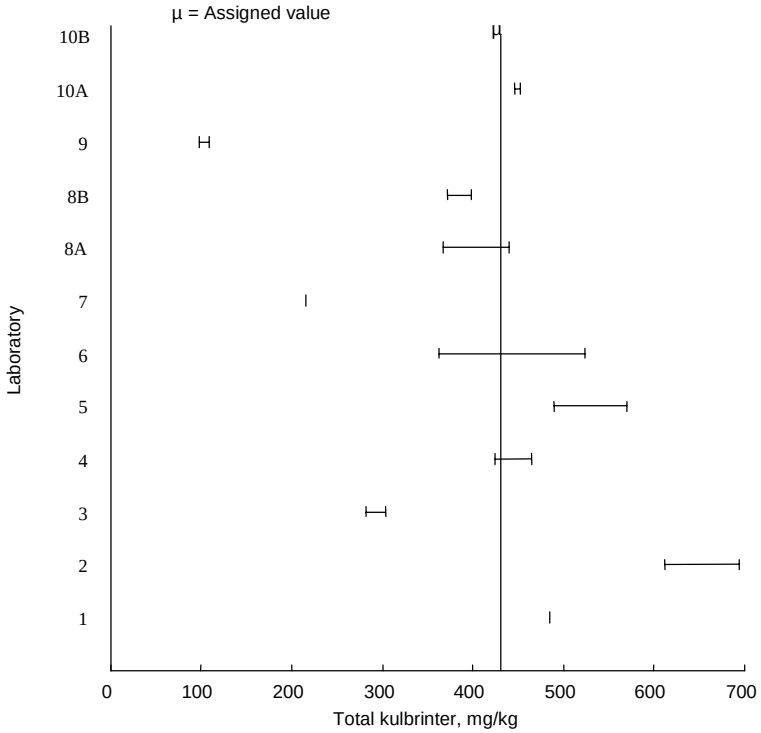
All results including outliers: n = 22 Mean = 5.4E2
Std.dev = 1.1E2
All results excluding outliers: n = 22 Mean = 5.4E2
Std.dev = 1.1E2

Level F



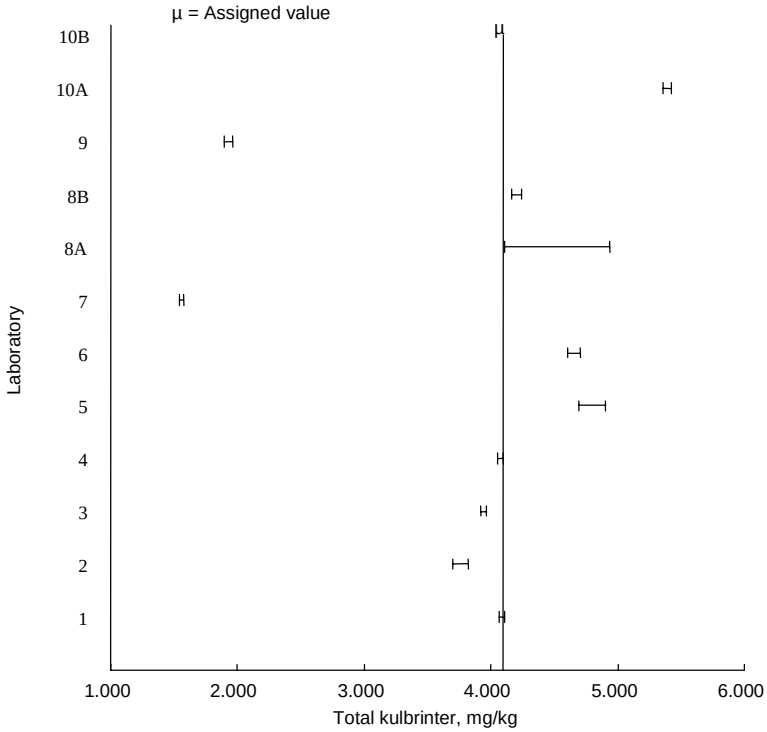
All results including outliers: n = 22 Mean = 9.7E2
Std.dev = 3.2E2
All results excluding outliers: n = 22 Mean = 9.7E2
Std.dev = 3.2E2

Level G



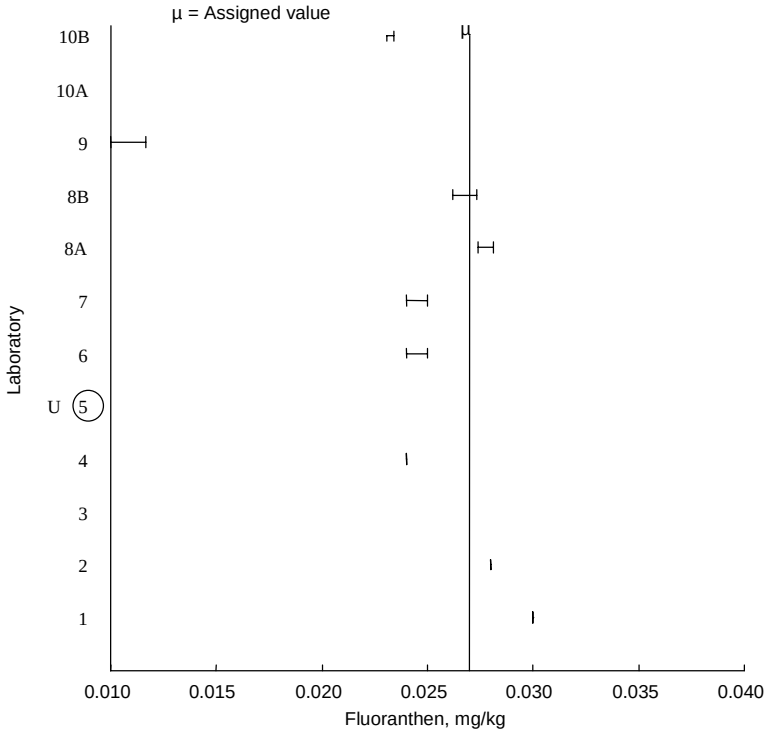
All results including outliers: n = 20 Mean = 4.1E2
Std.dev = 1.5E2
All results excluding outliers: n = 20 Mean = 4.1E2
Std.dev = 1.5E2

Level H



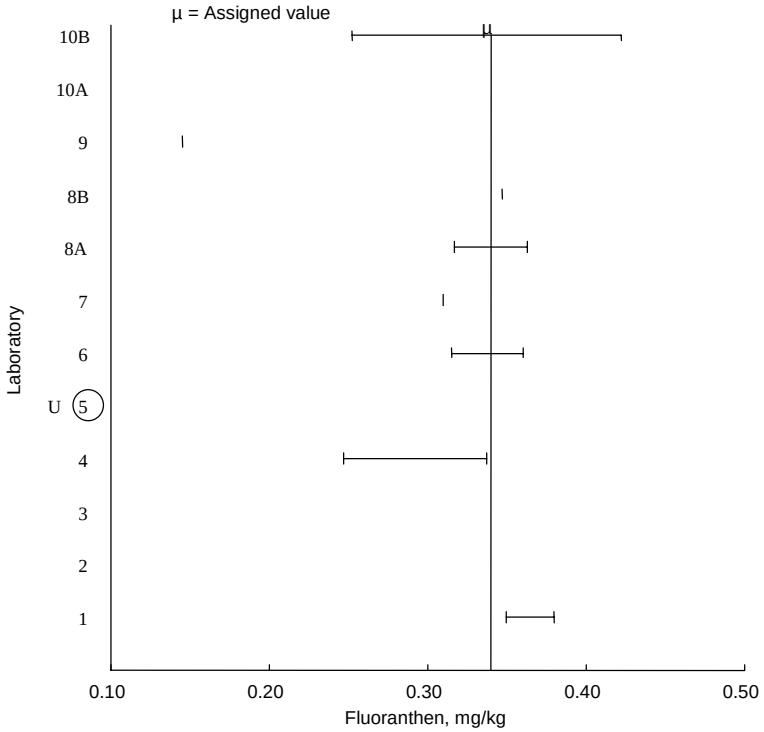
All results including outliers: n = 22 Mean = 3.9E3
Std.dev = 1.1E3
All results excluding outliers: n = 22 Mean = 3.9E3
Std.dev = 1.1E3

Level A



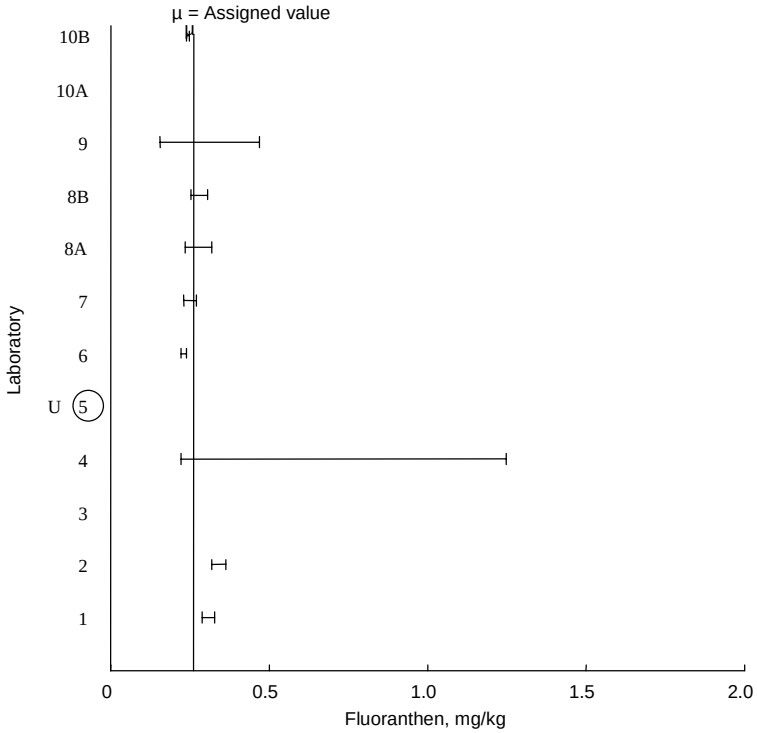
All results including outliers: n = 18 Mean = 0.024
Std.dev = 0.005
All results excluding outliers: n = 18 Mean = 0.024
Std.dev = 0.005

Level D



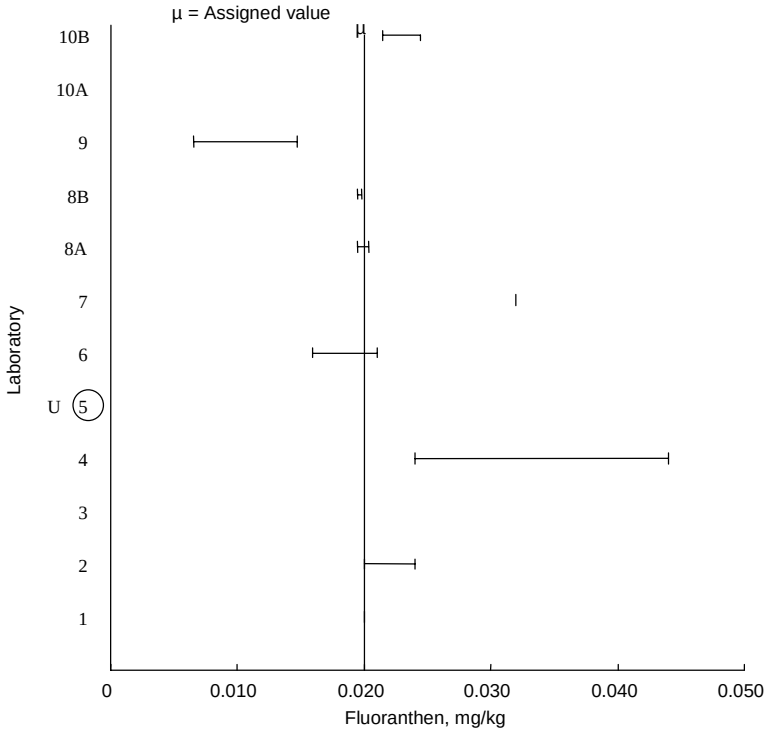
All results including outliers: n = 13 Mean = 0.320
Std.dev = 0.071
All results excluding outliers: n = 13 Mean = 0.320
Std.dev = 0.071

Level F

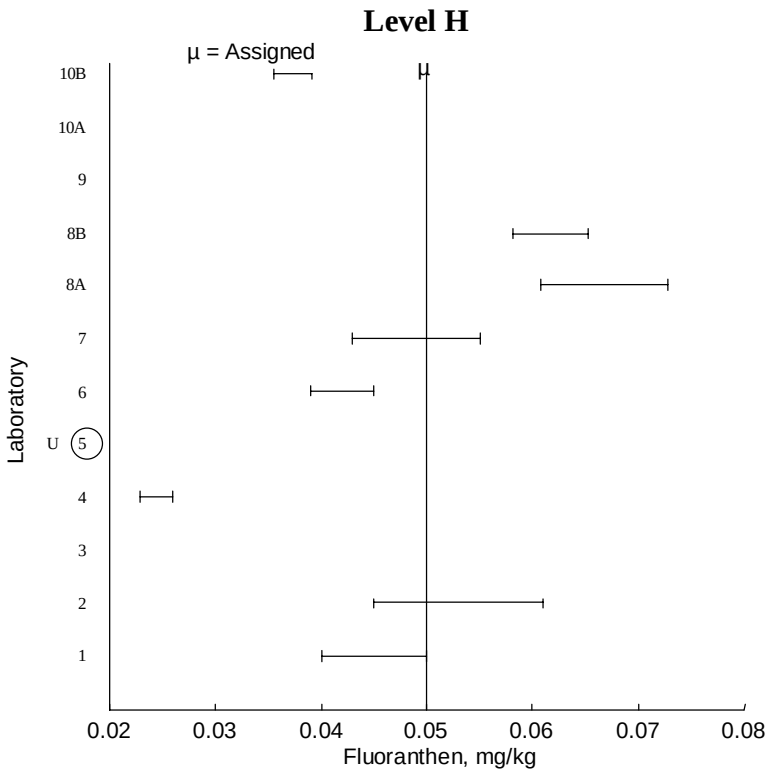


All results including outliers: n = 18 Mean = 0.330
Std.dev = 0.240
All results excluding outliers: n = 18 Mean = 0.330
Std.dev = 0.240

Level G

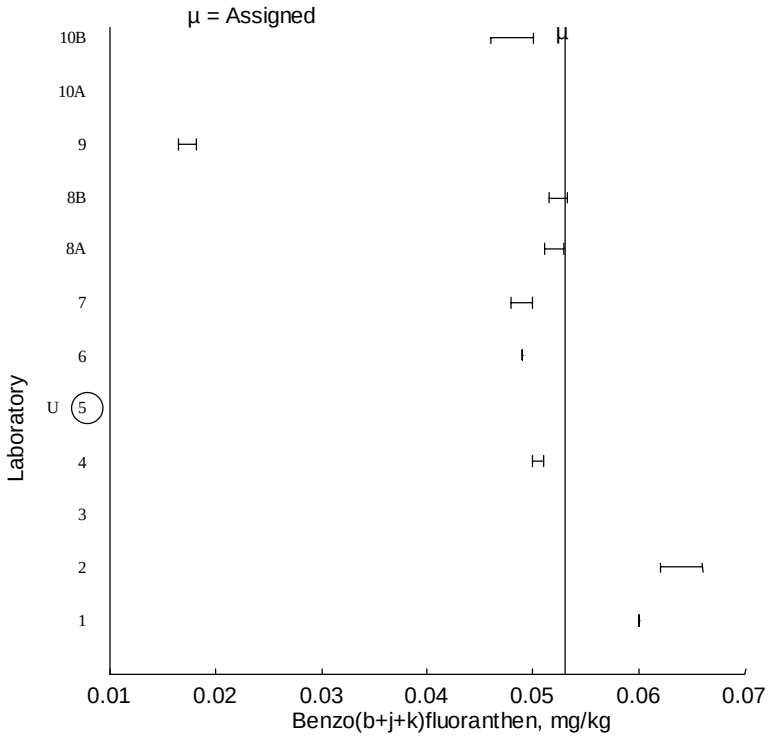


All results including outliers: n = 16 Mean = 0.022
Std.dev = 0.008
All results excluding outliers: n = 16 Mean = 0.022
Std.dev = 0.008



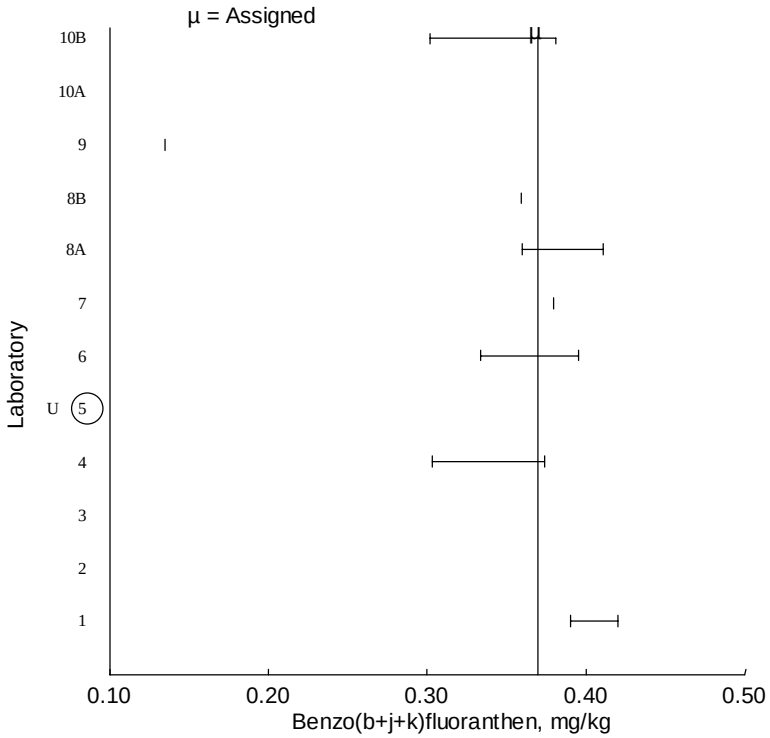
All results including n = 16 Mean = 0.047
Std.dev = 0.014
All results excluding n = 16 Mean = 0.047
Std.dev = 0.014

Level A



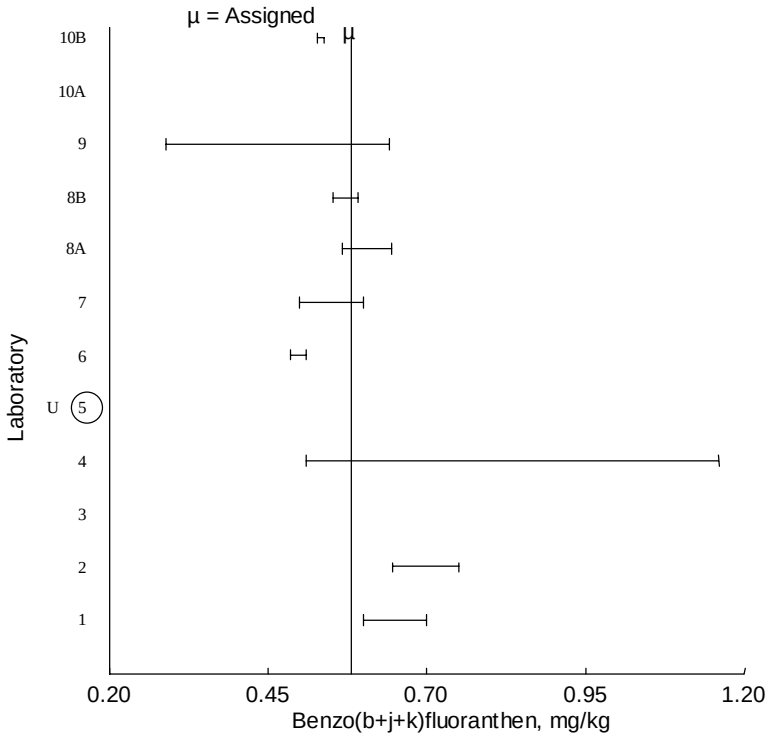
All results including n = 18 Mean = 0.049
Std.dev = 0.013
All results excluding n = 18 Mean = 0.049
Std.dev = 0.013

Level D



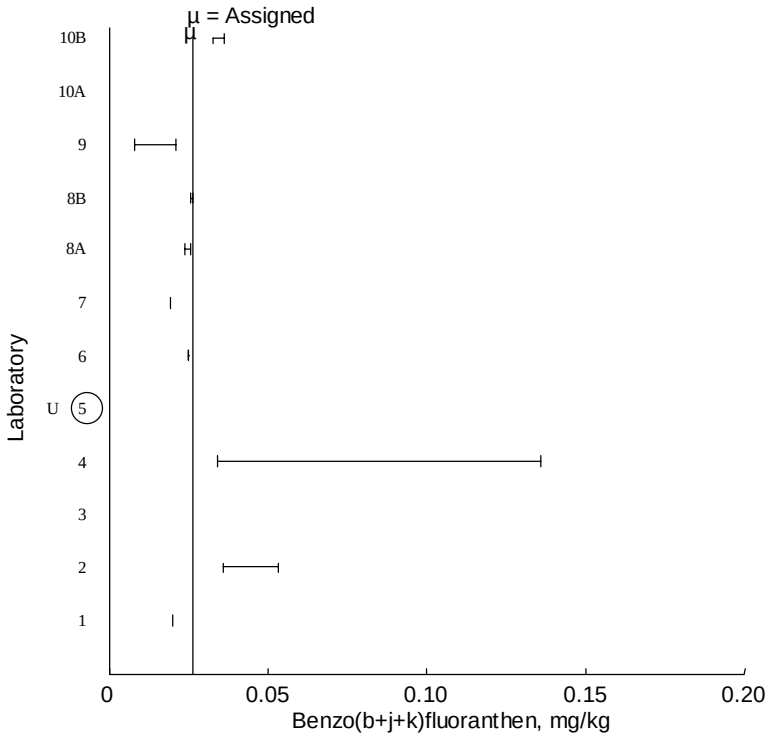
All results including n = 13 Mean = 0.350
Std.dev = 0.074
All results excluding n = 13 Mean = 0.350
Std.dev = 0.074

Level F



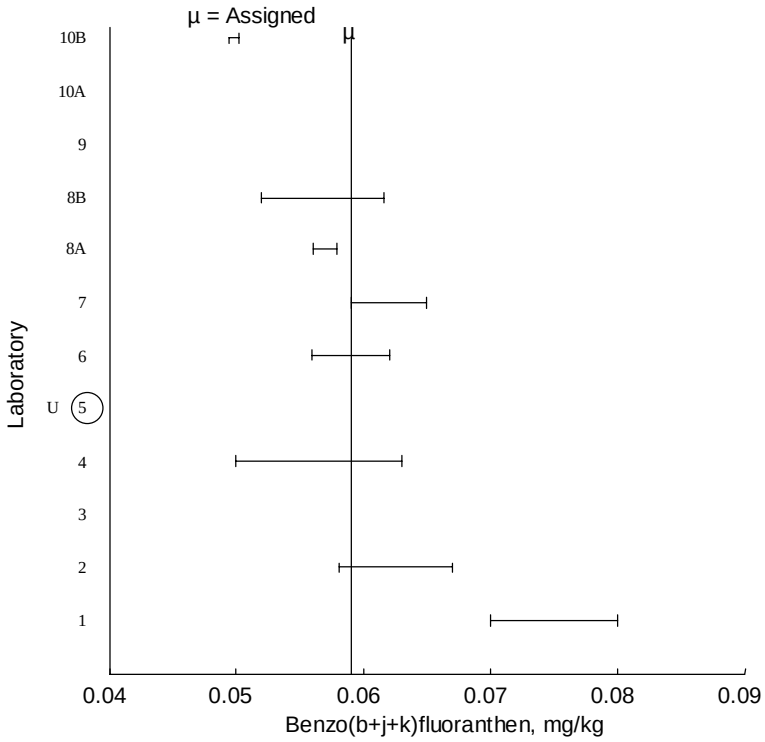
All results including n = 18 Mean = 0.600
Std.dev = 0.170
All results excluding n = 18 Mean =
Std.dev = 0.170

Level G



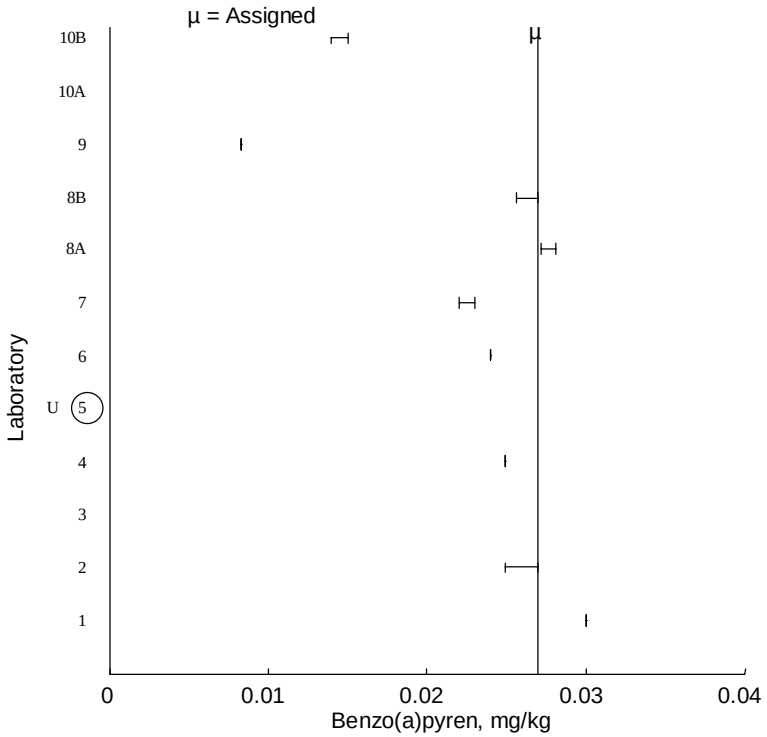
All results including n = 16 Mean = 0.034
Std.dev = 0.029
All results excluding n = 16 Mean = 0.034
Std.dev = 0.029

Level H



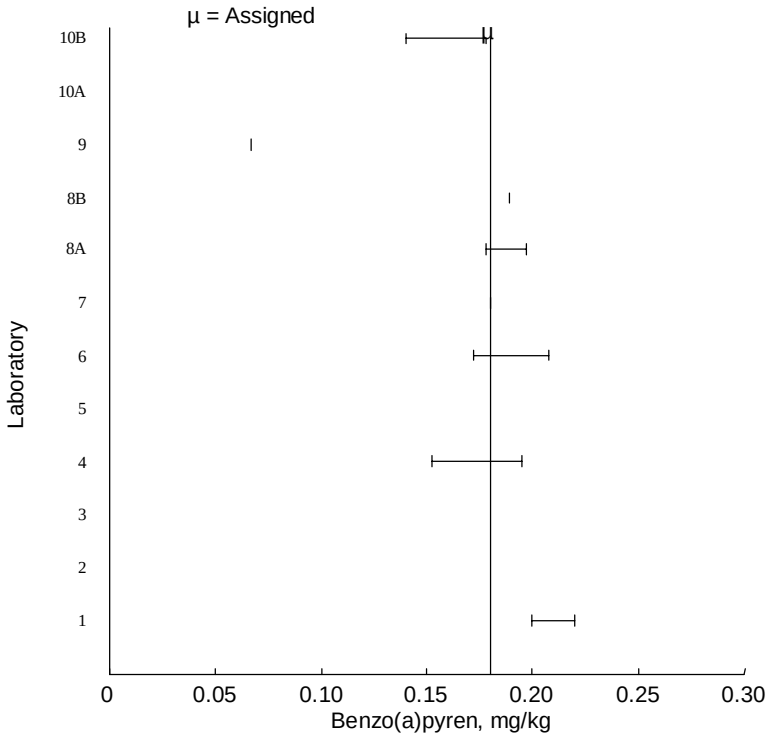
All results including n = 16 Mean = 0.060
Std.dev = 0.008
All results excluding n = 16 Mean = 0.060
Std.dev = 0.008

Level A



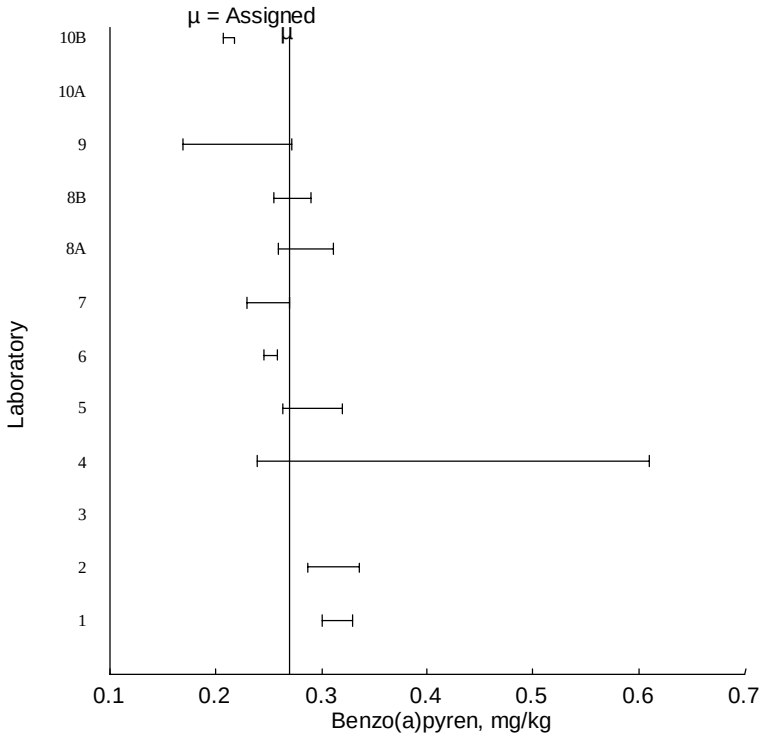
All results including n = 18 Mean = 0.023
Std.dev = 0.007
All results excluding n = 18 Mean = 0.023
Std.dev = 0.007

Level D



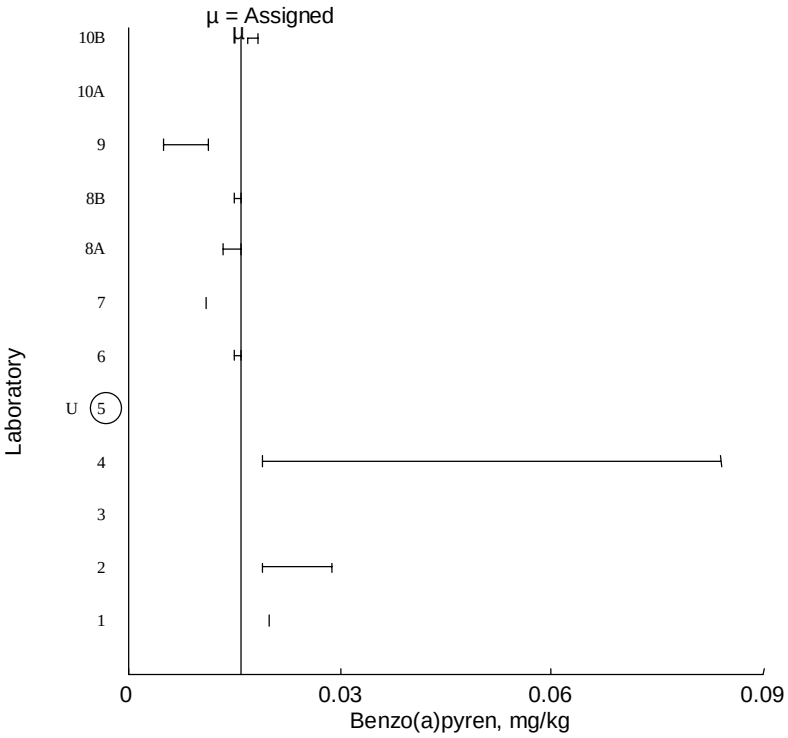
All results including n = 13 Mean = 0.180
Std.dev = 0.039
All results excluding n = 13 Mean = 0.180
Std.dev = 0.039

Level F



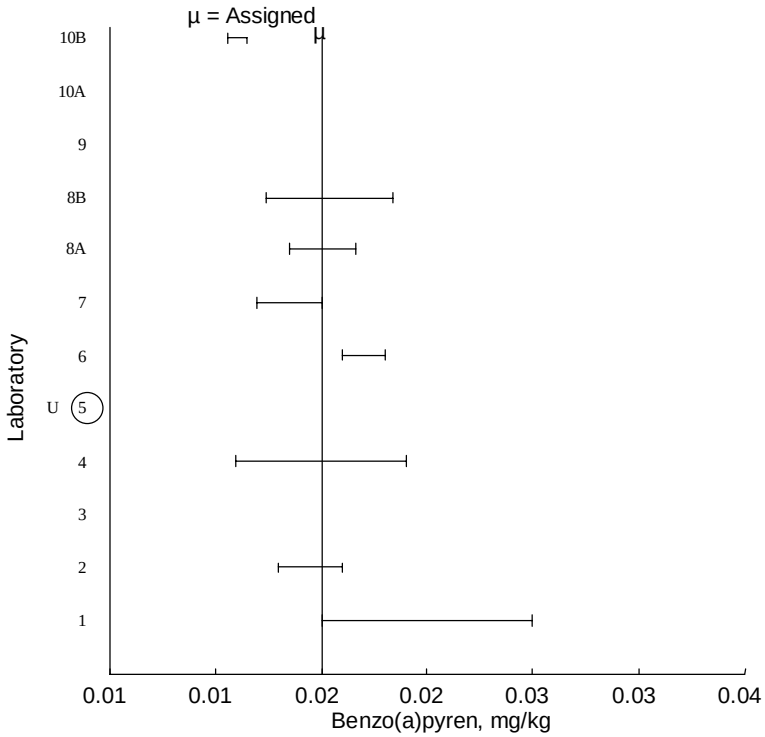
All results including n = 20 Mean = 0.280
Std.dev = 0.087
All results excluding n = 20 Mean = 0.280
Std.dev = 0.087

Level G



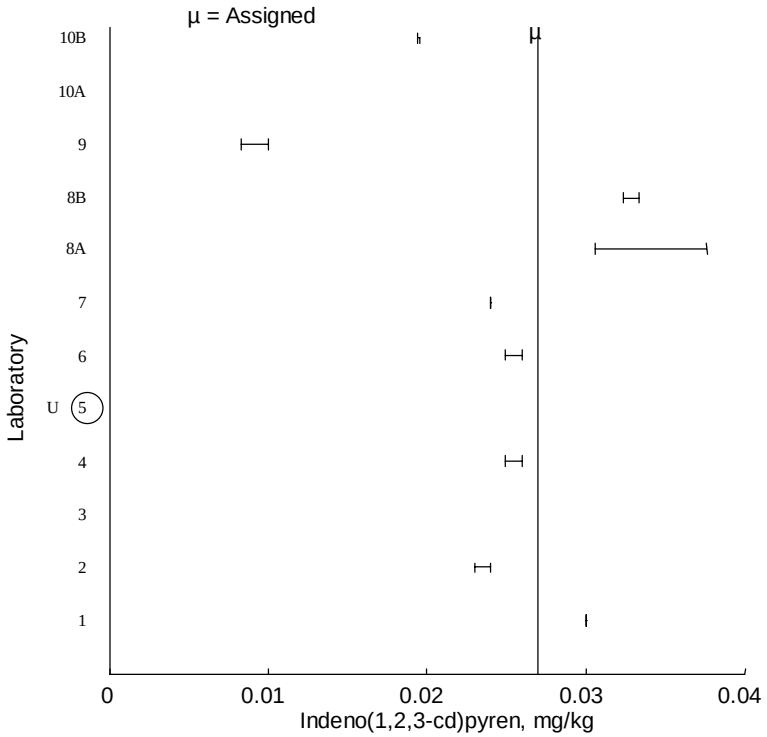
All results including n = 16 Mean = 0.020
Std.dev = 0.018
All results excluding n = 16 Mean = 0.020
Std.dev = 0.018

Level H



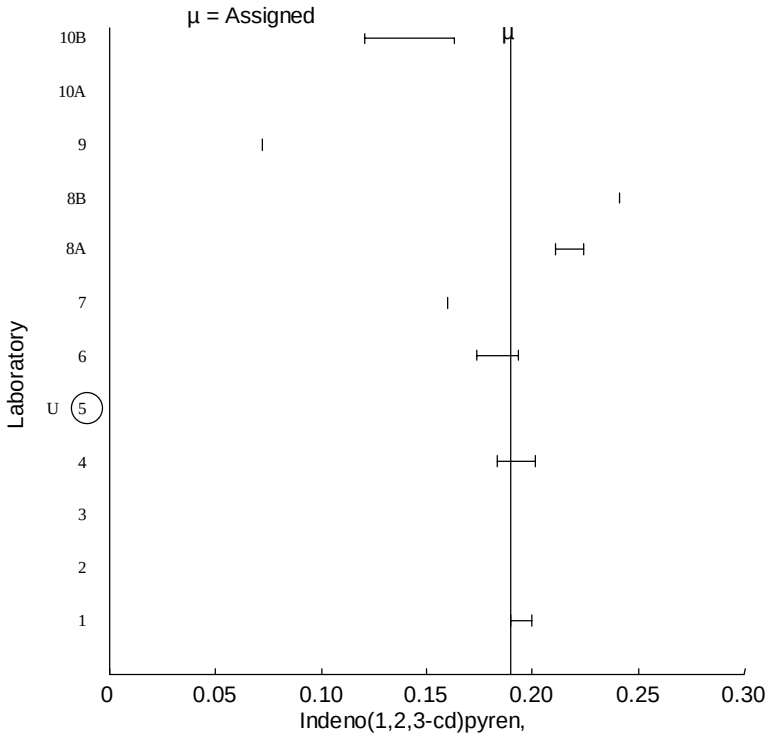
All results including n = Mean = 0.020
Std.dev = 0.004
All results excluding n = Mean = 0.020
Std.dev = 0.004

Level A



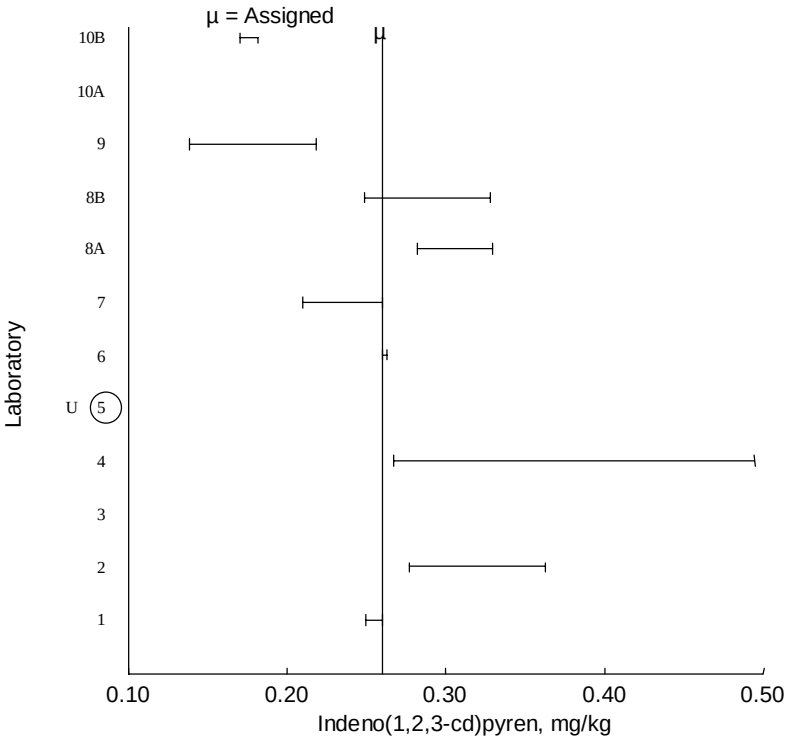
All results including n = 18 Mean = 0.025
Std.dev = 0.007
All results excluding n = 18 Mean = 0.025
Std.dev = 0.007

Level D



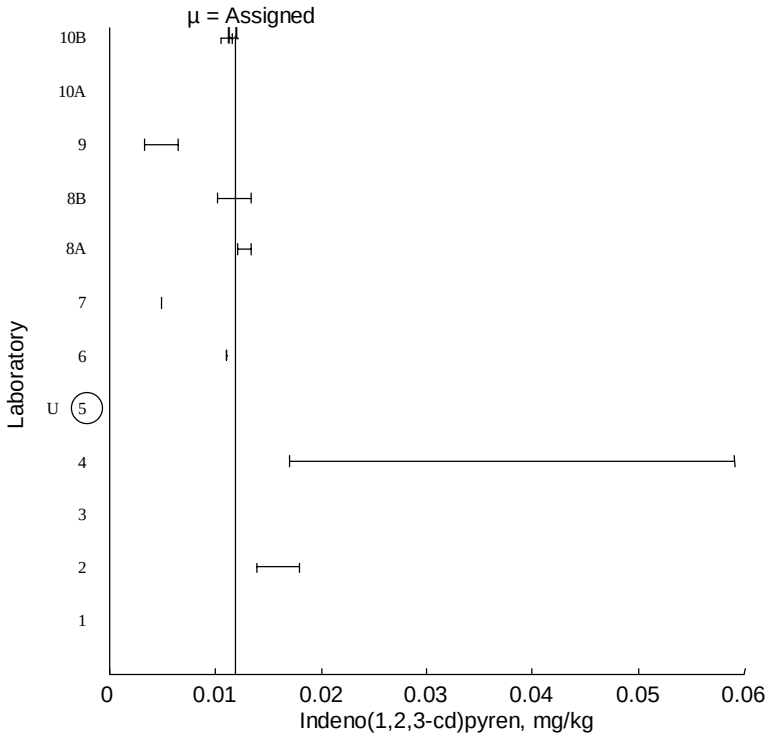
All results including n = 13 Mean = 0.180
Std.dev = 0.044
All results excluding n = 13 Mean = 0.180
Std.dev = 0.044

Level F



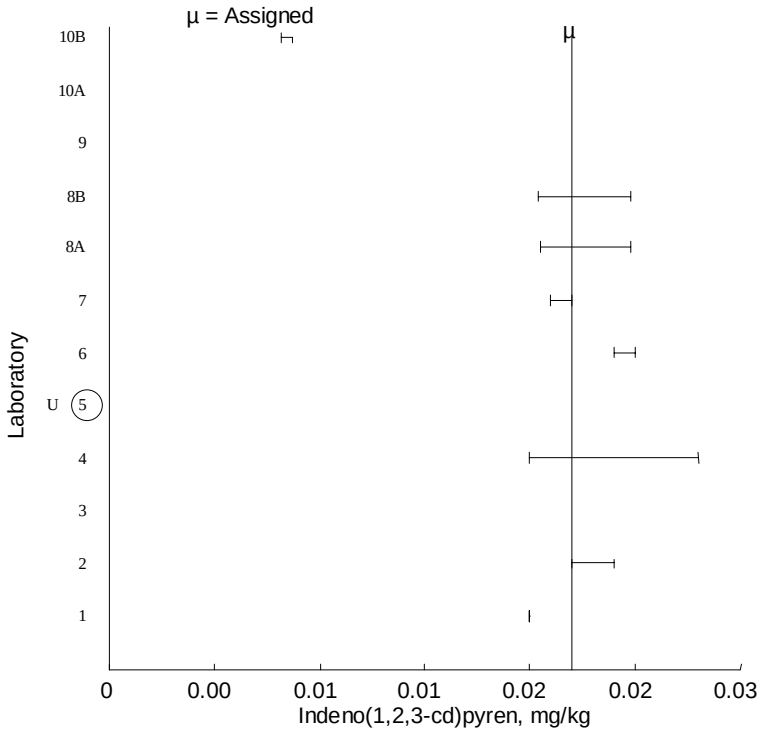
All results including n = 18 Mean = 0.270
Std.dev = 0.080
All results excluding n = 18 Mean = 0.270
Std.dev = 0.080

Level G



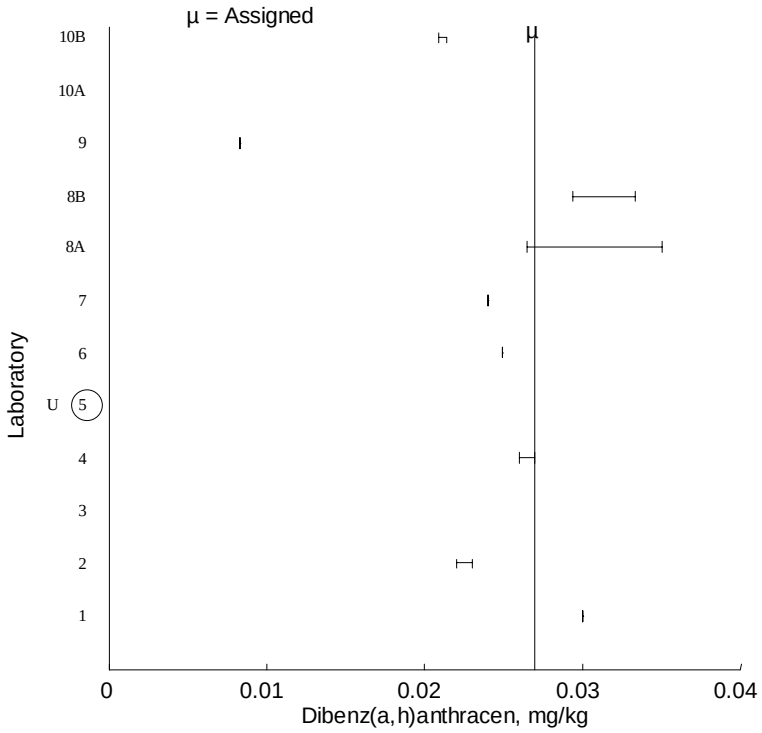
All results including n = 15 Mean = 0.014
Std.dev = 0.013
All results excluding n = 15 Mean = 0.014
Std.dev = 0.013

Level H



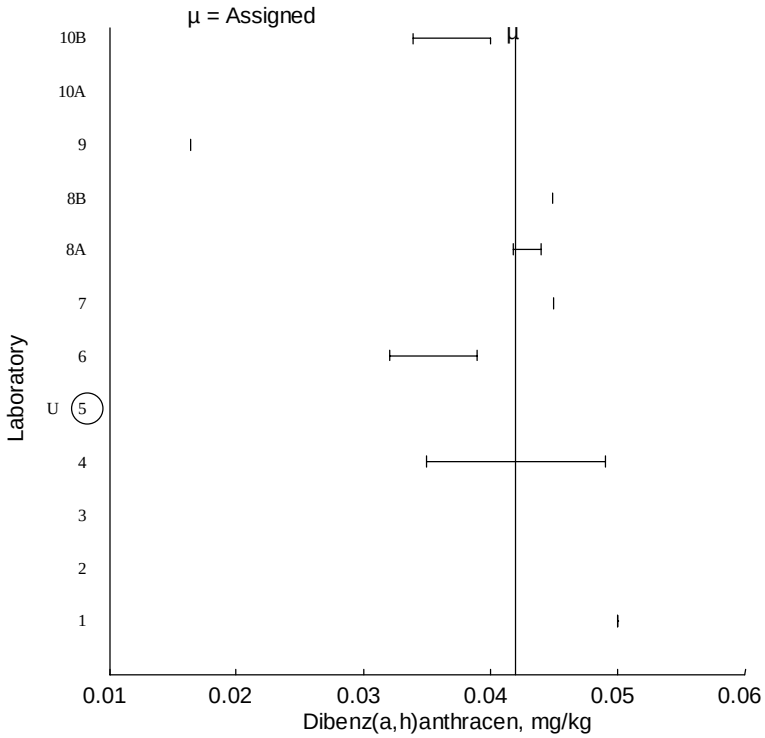
All results including n = 16 Mean = 0.021
Std.dev = 0.005
All results excluding n = 16 Mean = 0.021
Std.dev = 0.005

Level A



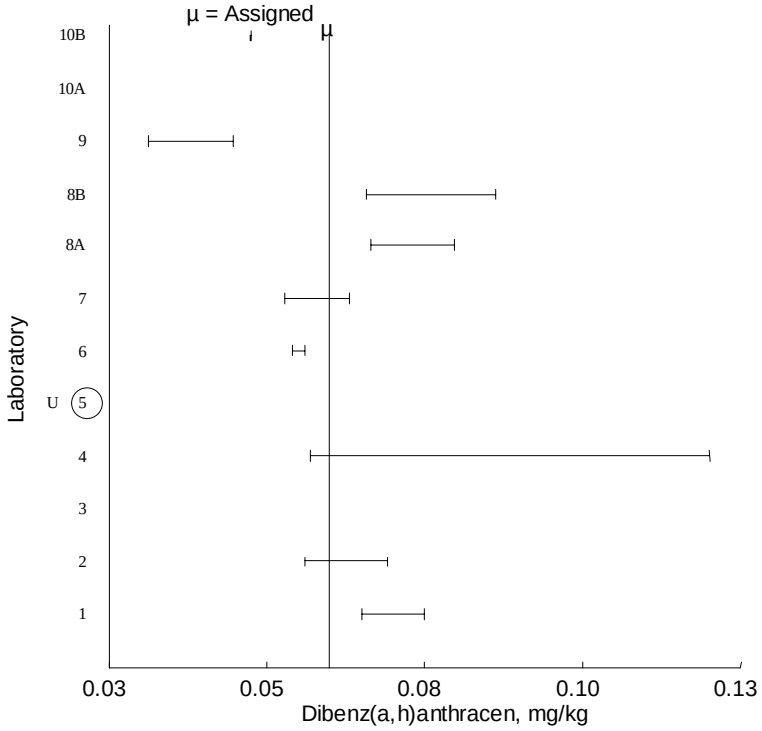
All results including n = 18 Mean = 0.024
Std.dev = 0.007
All results excluding n = 18 Mean = 0.024
Std.dev = 0.007

Level D



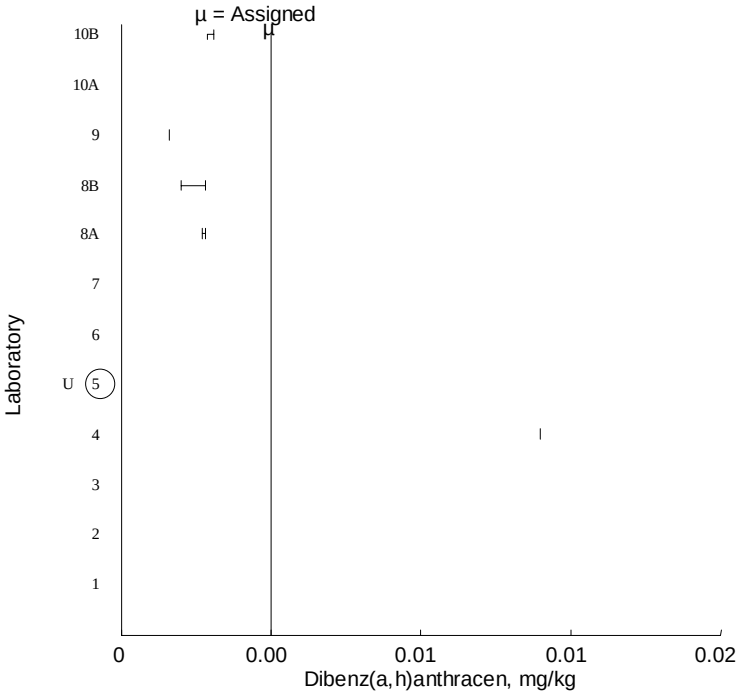
All results including n = 13 Mean = 0.040
Std.dev = 0.009
All results excluding n = 13 Mean = 0.040
Std.dev = 0.009

Level F



All results including n = 18 Mean = 0.068
Std.dev = 0.019
All results excluding n = 18 Mean = 0.068
Std.dev = 0.019

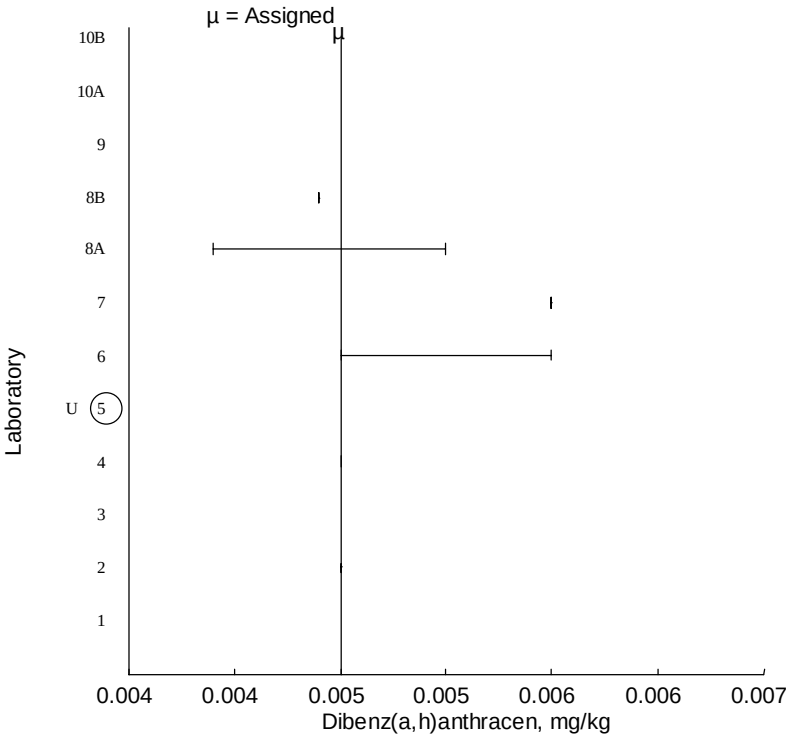
Level G



All results including n = 9 Mean = 0.004
Std.dev = 0.004
All results excluding n = 9 Mean = 0.004
Std.dev = 0.004

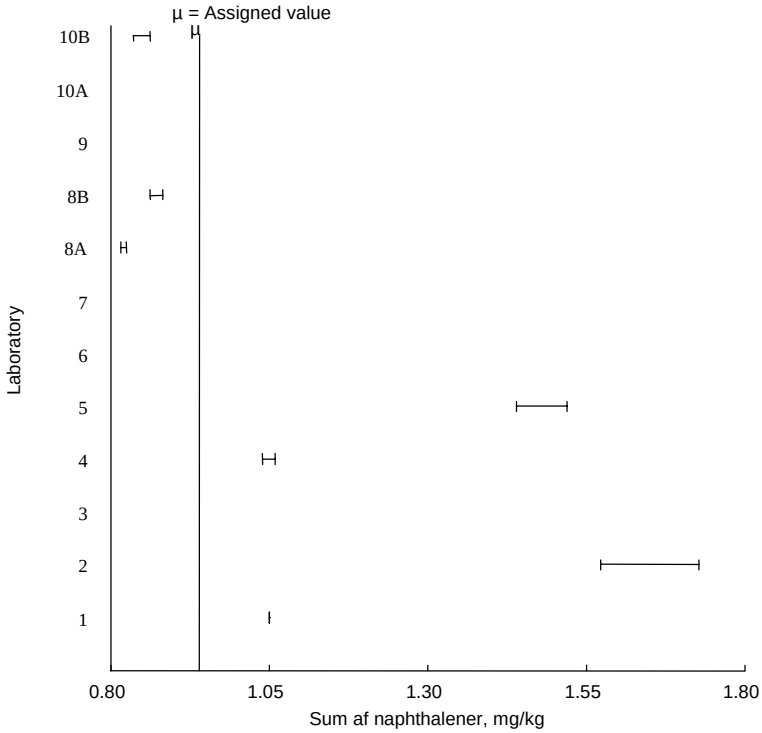
Results not included in the above
Laboratory 9, result=0

Level H



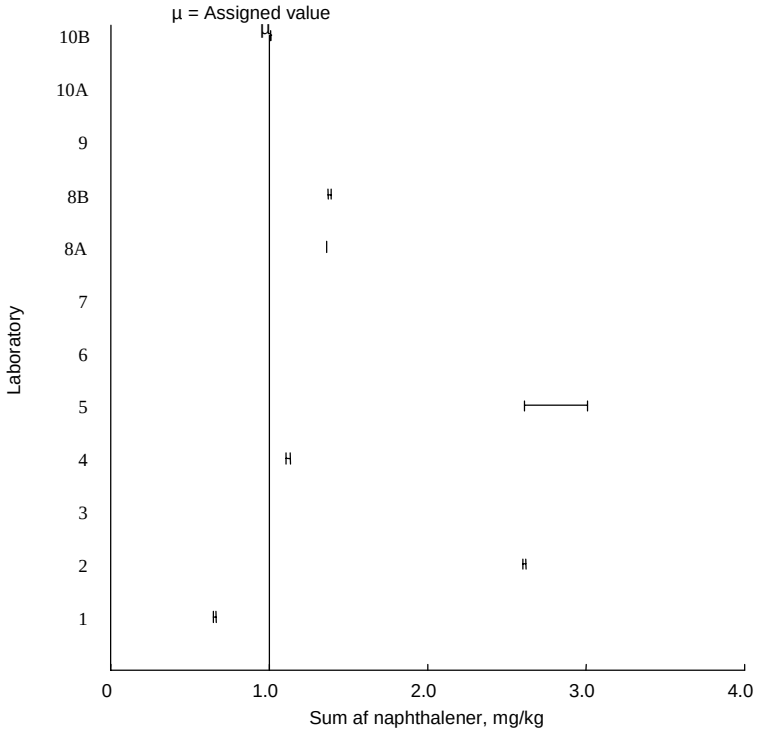
All results including n = 11 Mean = 0.005
Std.dev = 0.001
All results excluding n = 11 Mean = 0.005
Std.dev = 0.001

Level A



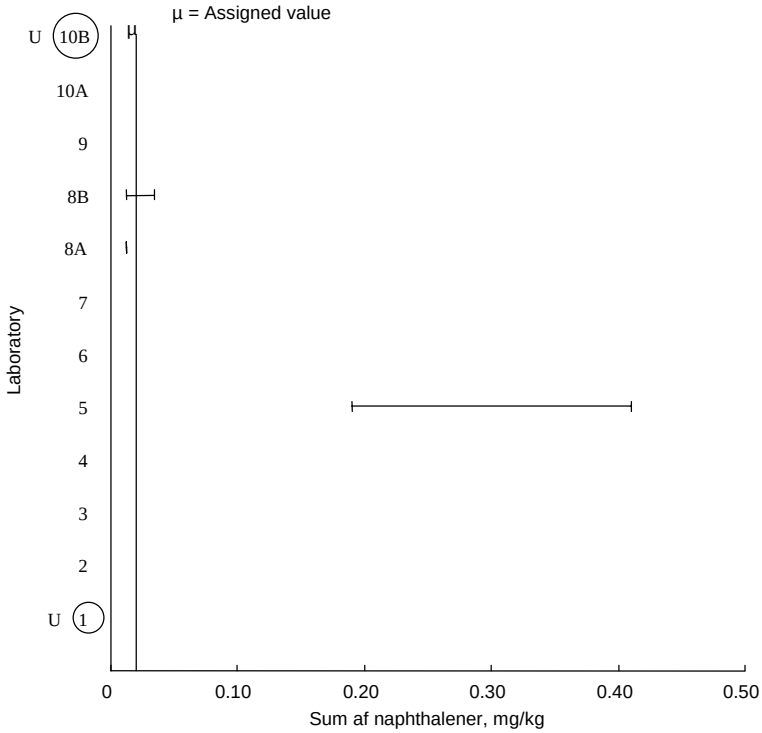
All results including outliers: n = 14 Mean = 1.100
Std.dev = 0.320
All results excluding outliers: n = 14 Mean = 1.100
Std.dev = 0.320

Level B



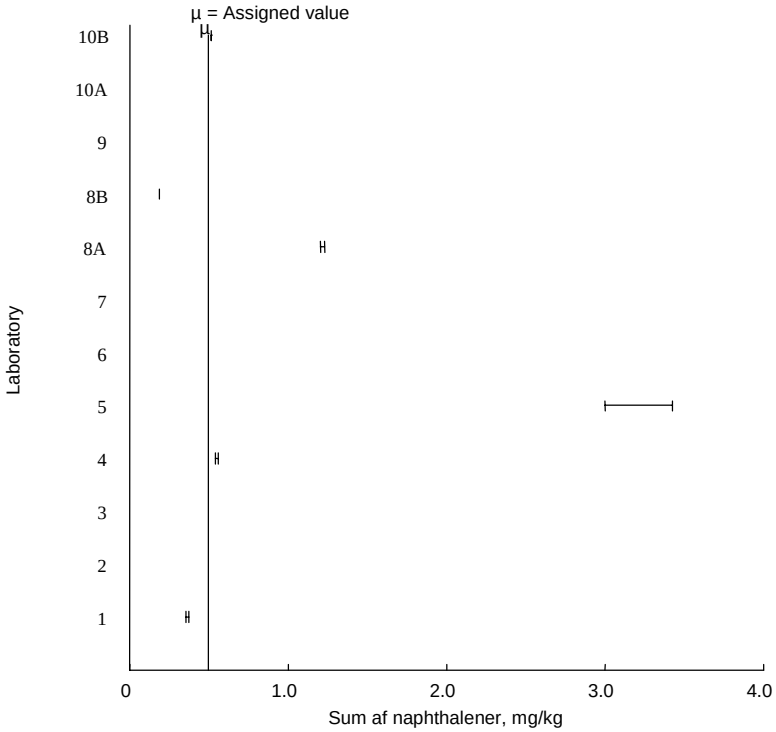
All results including outliers: n = 13 Mean = 1.600
Std.dev = 0.820
All results excluding outliers: n = 13 Mean = 1.600
Std.dev = 0.820

Level C



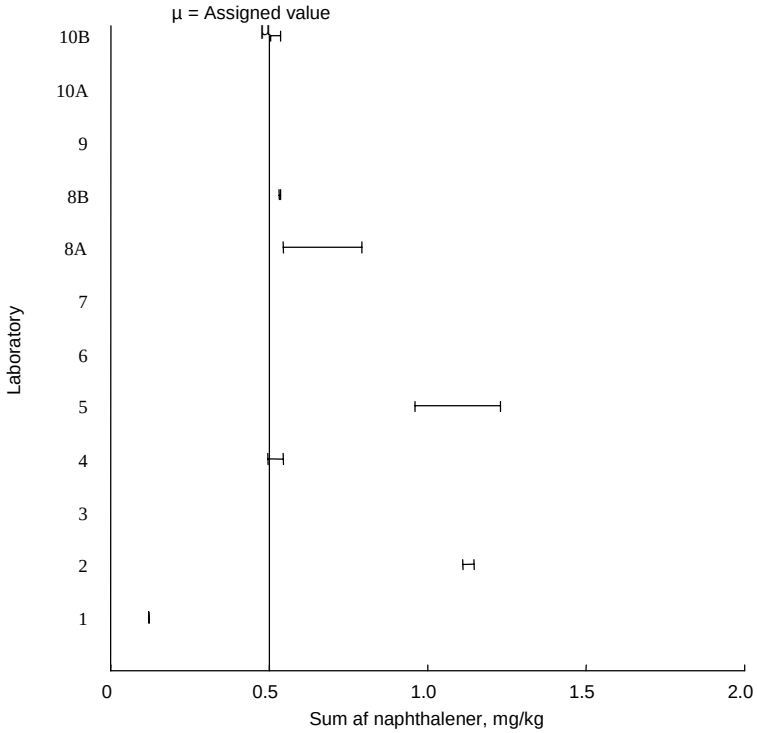
All results including outliers: n = 6 Mean = 0.11
Std.dev = 0.16
All results excluding outliers: n = 6 Mean = 0.11
Std.dev = 0.16

Level D



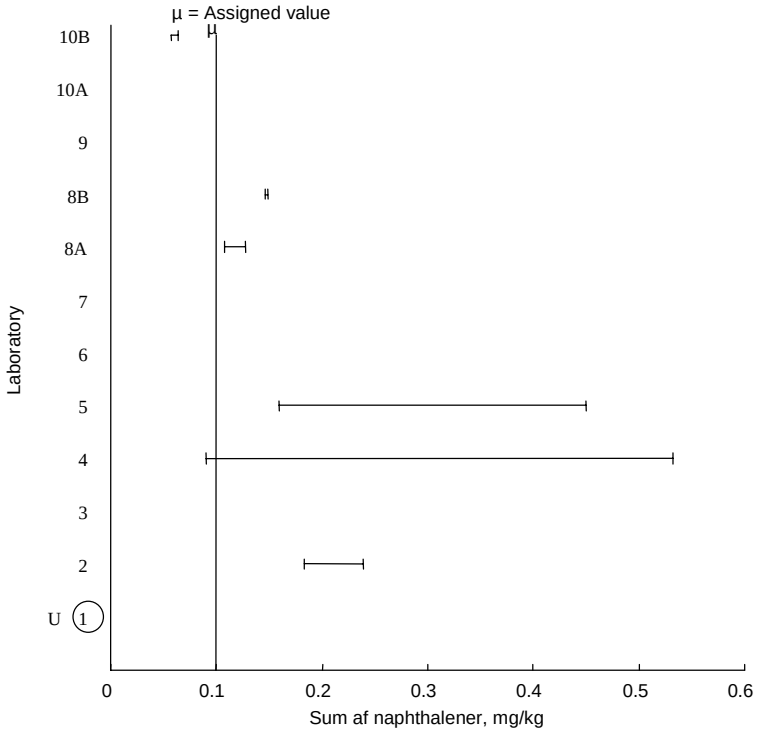
All results including outliers: n = 11 Mean = 1.100
Std.dev = 1.100
All results excluding outliers: n = 11 Mean = 1.100
Std.dev = 1.100

Level E



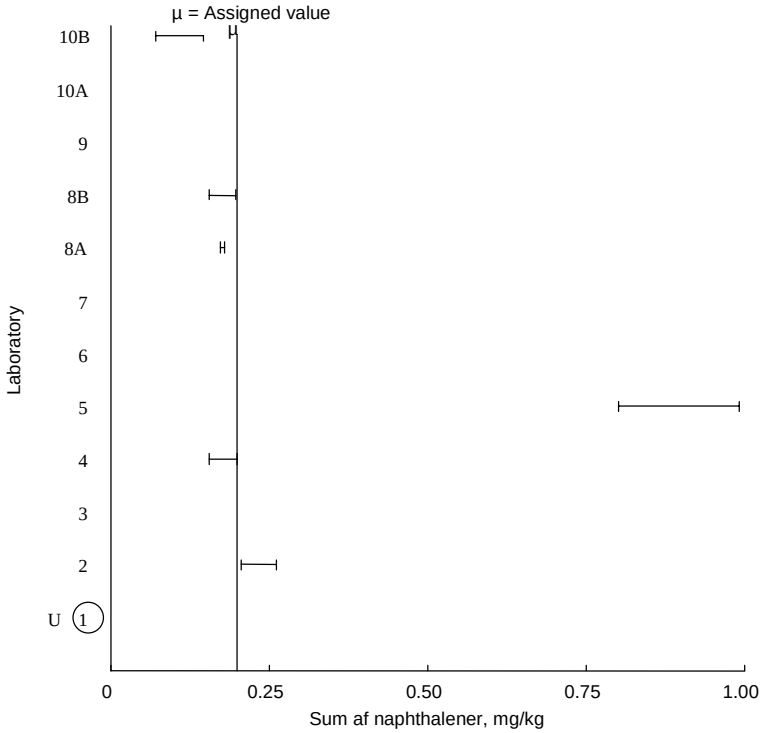
All results including outliers: n = 14 Mean = 0.660
Std.dev = 0.350
All results excluding outliers: n = 14 Mean = 0.660
Std.dev = 0.350

Level F



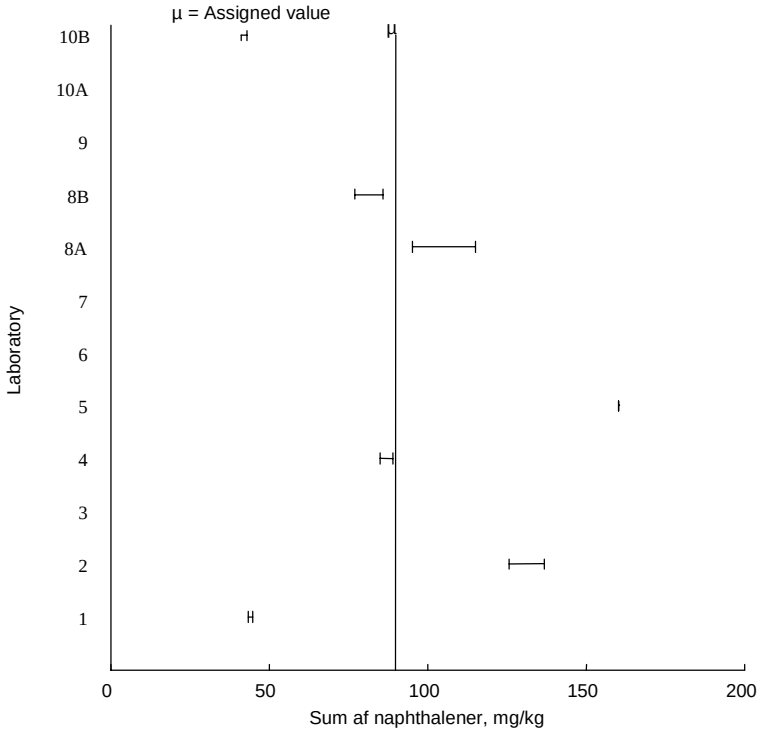
All results including outliers: n = 12 Mean = 0.190
Std.dev = 0.150
All results excluding outliers: n = 12 Mean = 0.190
Std.dev = 0.150

Level G



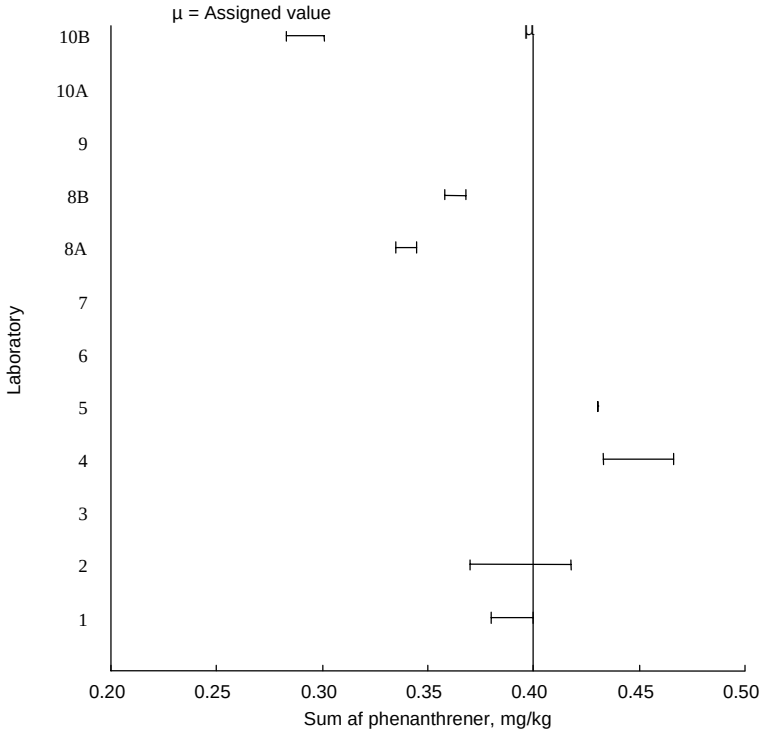
All results including outliers: n = 12 Mean = 0.290
Std.dev = 0.290
All results excluding outliers: n = 12 Mean = 0.290
Std.dev = 0.290

Level H



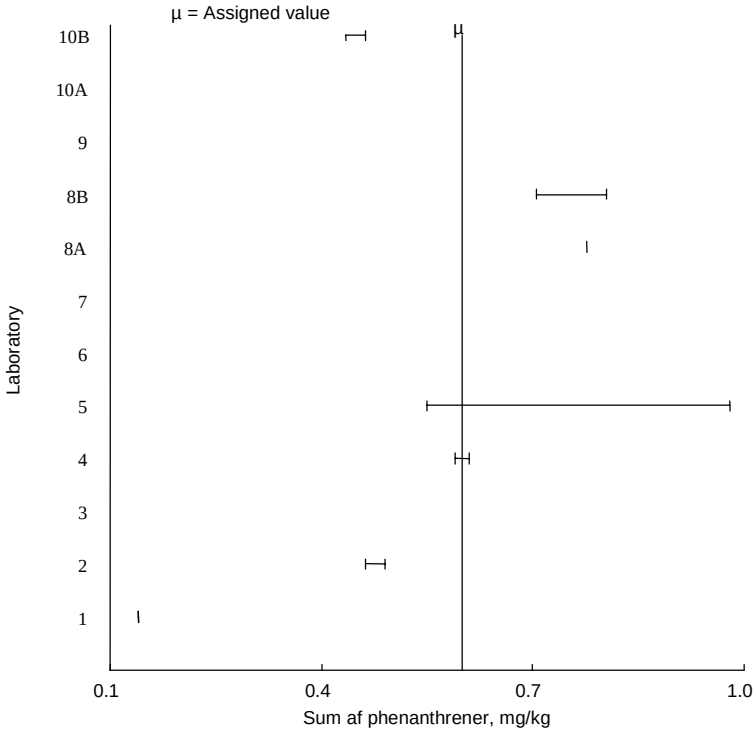
All results including outliers: n = 14 Mean = 93.00
Std.dev = 42.00
All results excluding outliers: n = 14 Mean = 93.00
Std.dev = 42.00

Level A



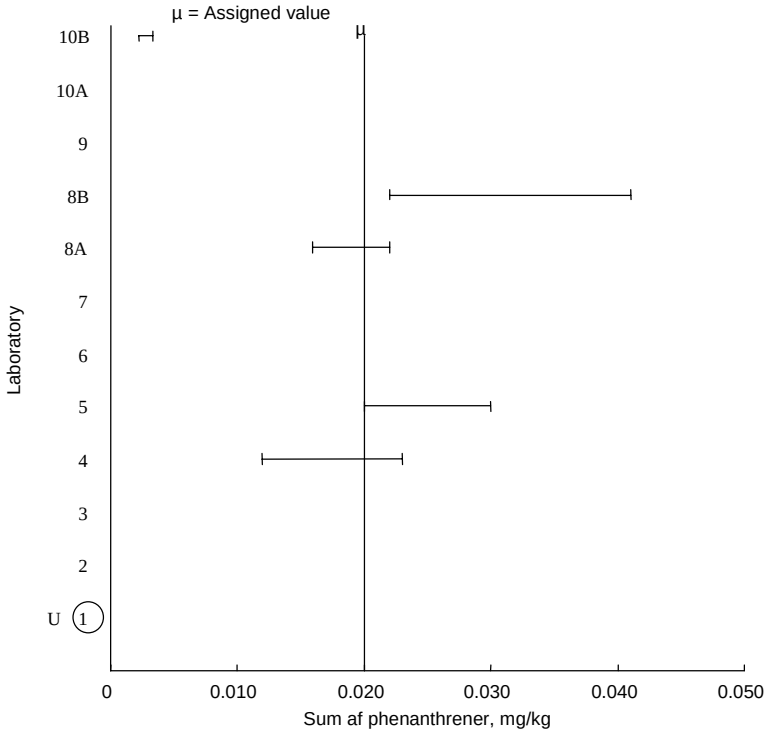
All results including outliers: n = 14 Mean = 0.380
Std.dev = 0.053
All results excluding outliers: n = 14 Mean = 0.380
Std.dev = 0.053

Level B



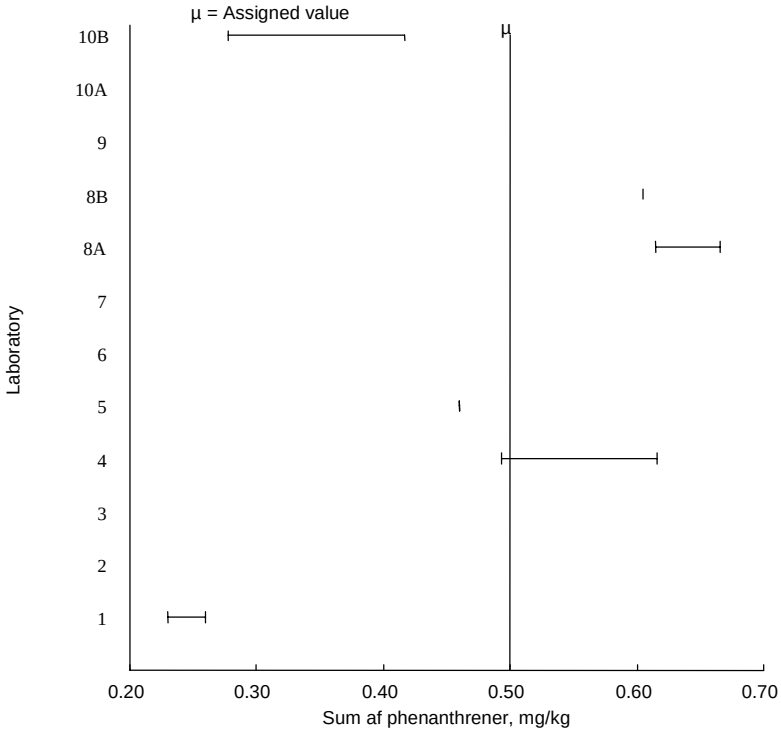
All results including outliers: n = 13 Mean = 0.550
Std.dev = 0.240
All results excluding outliers: n = 13 Mean = 0.550
Std.dev = 0.240

Level C



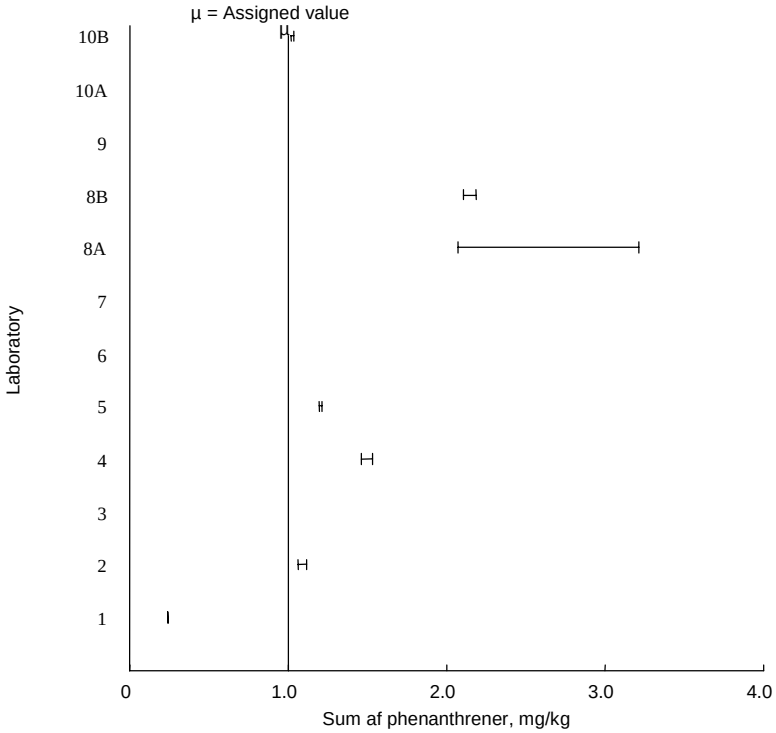
All results including outliers: n = 10 Mean = 0.019
Std.dev = 0.012
All results excluding outliers: n = 10 Mean = 0.019
Std.dev = 0.012

Level D



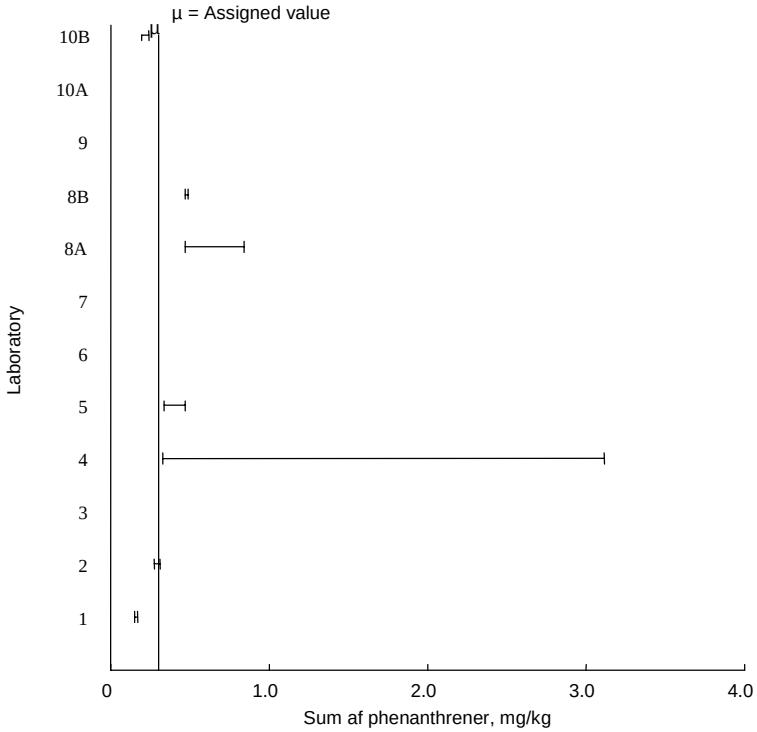
All results including outliers: n = 11 Mean = 0.460
Std.dev = 0.160
All results excluding outliers: n = 11 Mean = 0.460
Std.dev = 0.160

Level E



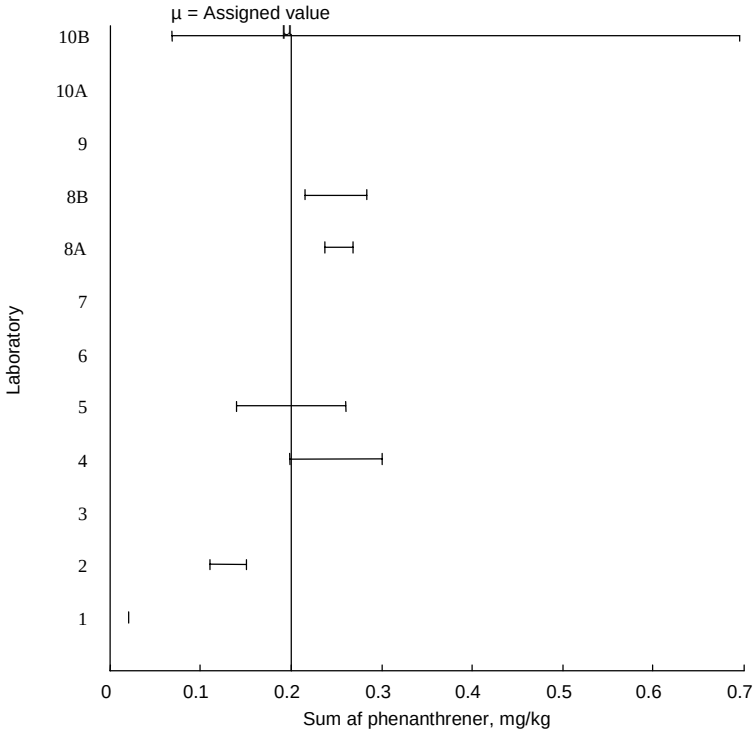
All results including outliers: n = 14 Mean = 1.400
Std.dev = 0.790
All results excluding outliers: n = 14 Mean = 1.400
Std.dev = 0.790

Level F



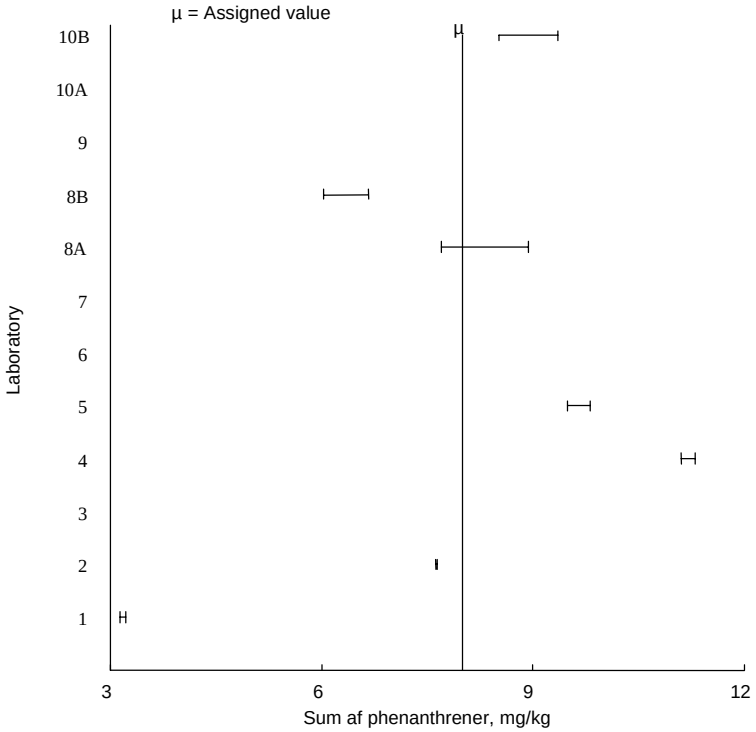
All results including outliers: n = 14 Mean = 0.560
Std.dev = 0.760
All results excluding outliers: n = 14 Mean = 0.560
Std.dev = 0.760

Level G



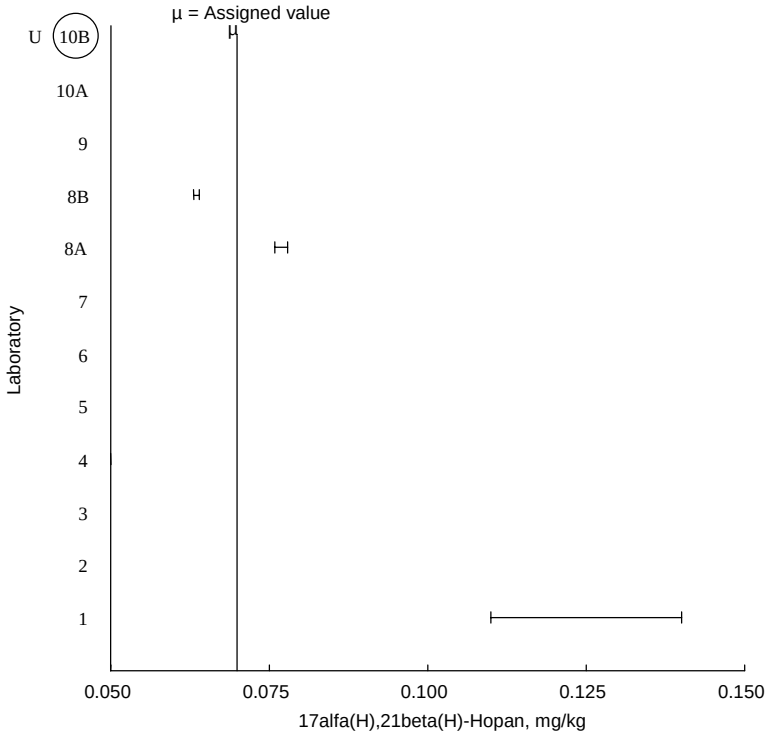
All results including outliers: n = 13 Mean = 0.230
Std.dev = 0.170
All results excluding outliers: n = 13 Mean = 0.230
Std.dev = 0.170

Level H



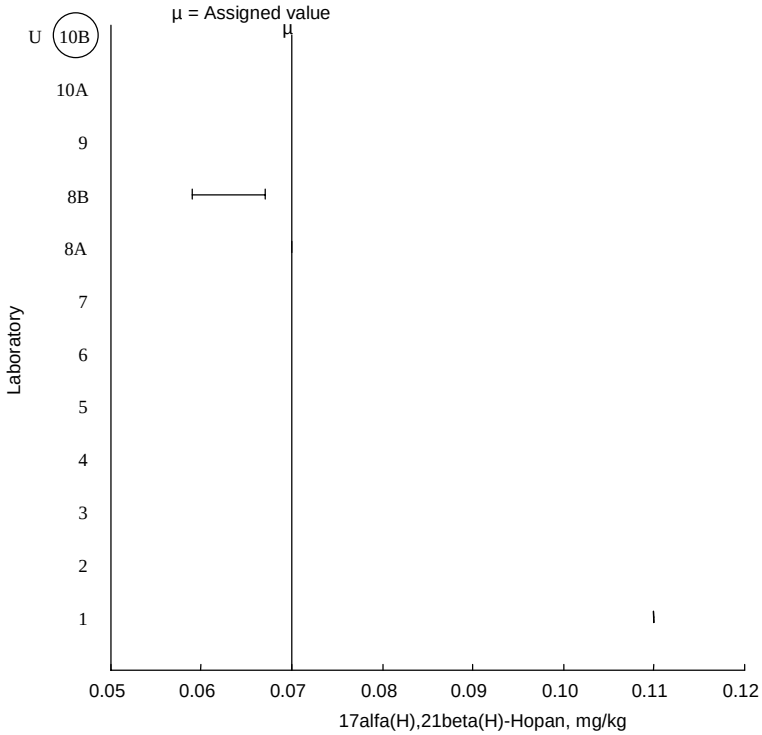
All results including outliers: n = 14 Mean = 7.90
Std.dev = 2.50
All results excluding outliers: n = 14 Mean = 7.90
Std.dev = 2.50

Level A



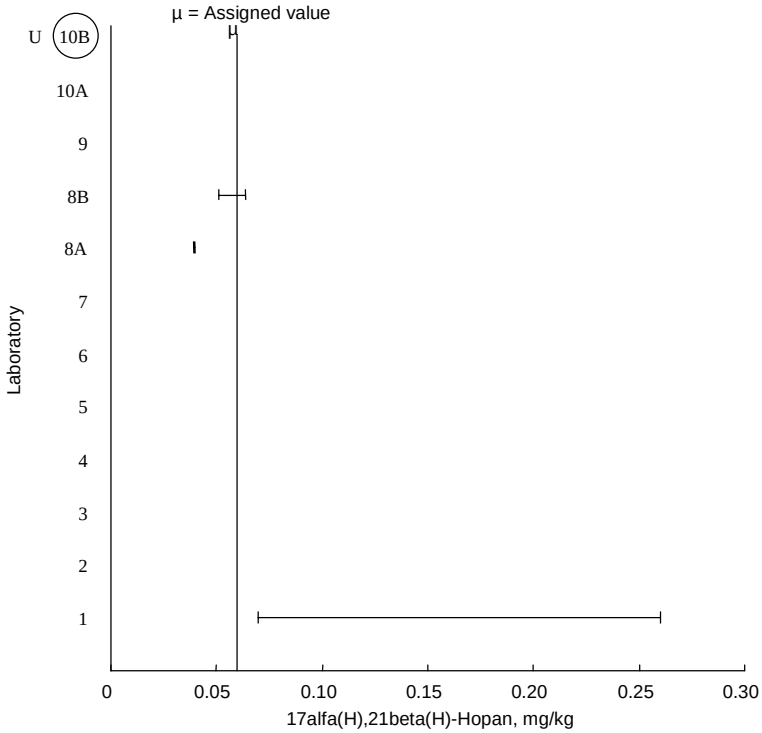
All results including outliers: n = 7 Mean = 0.08
Std.dev = 0.03
All results excluding outliers: n = 7 Mean = 0.08
Std.dev = 0.03

Level B



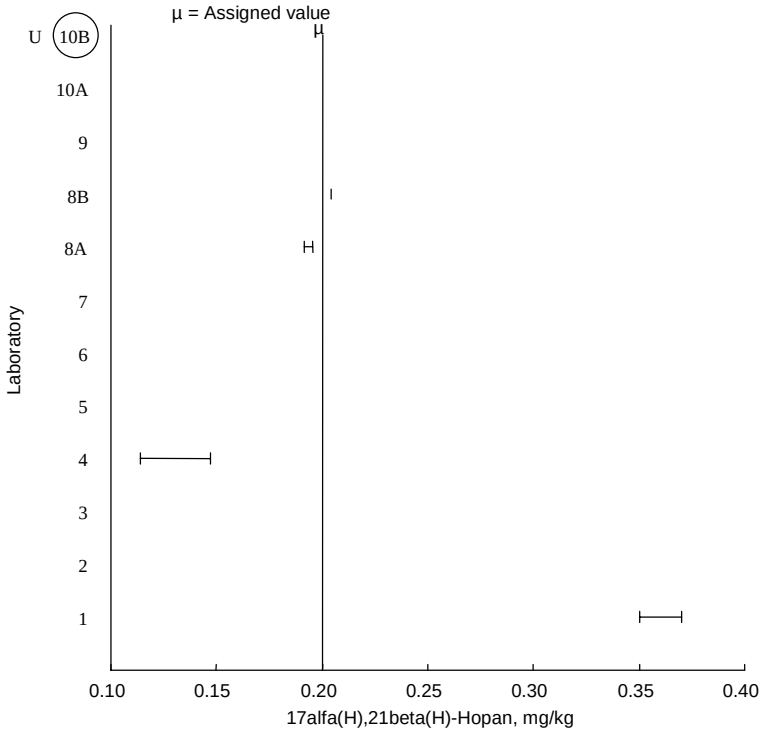
All results including outliers: n = 5 Mean = 0.08
Std.dev = 0.02
All results excluding outliers: n = 5 Mean = 0.08
Std.dev = 0.02

Level C



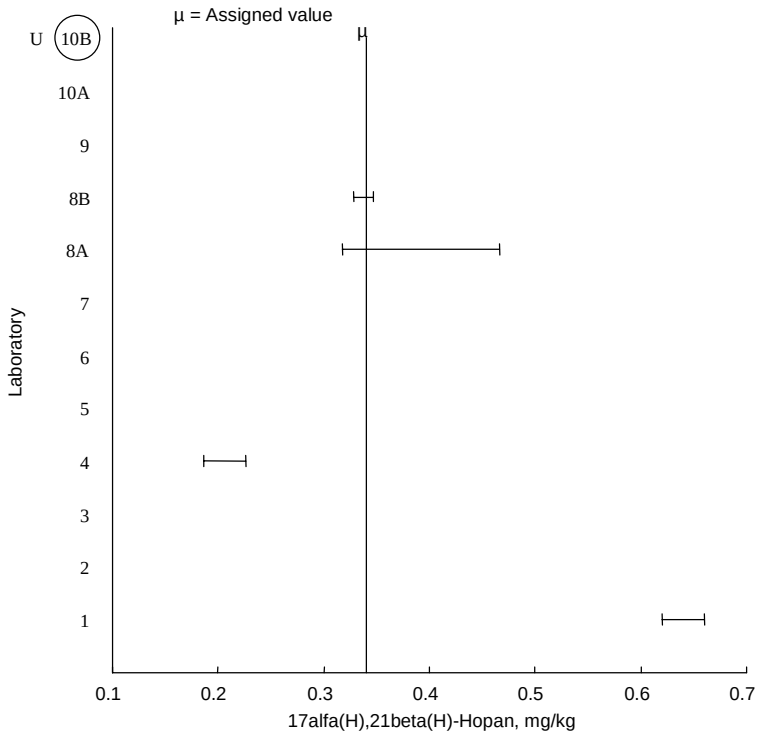
All results including outliers: n = 6 Mean = 0.09
Std.dev = 0.09
All results excluding outliers: n = 6 Mean = 0.09
Std.dev = 0.09

Level D



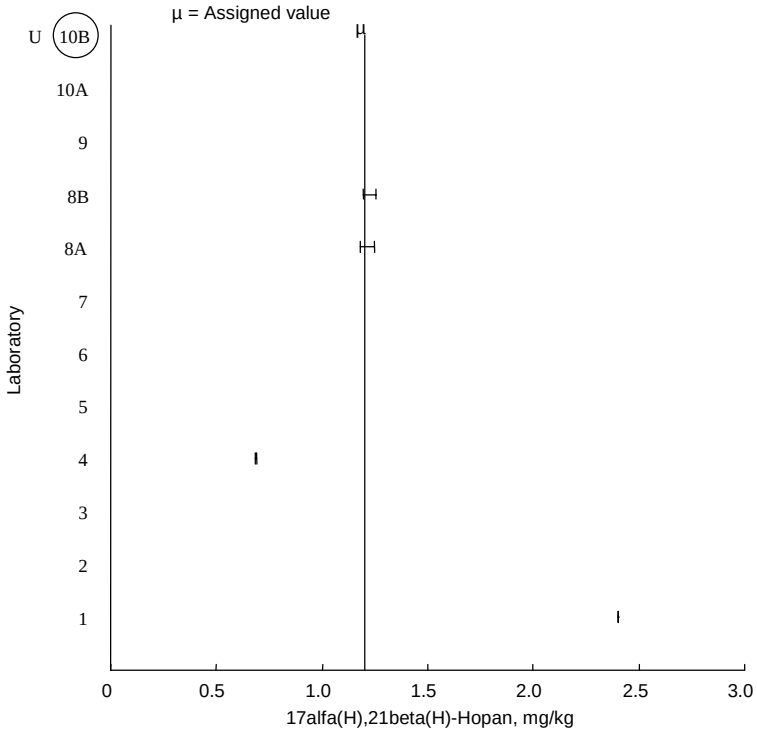
All results including outliers: n = 7 Mean = 0.22
Std.dev = 0.10
All results excluding outliers: n = 7 Mean = 0.22
Std.dev = 0.10

Level E



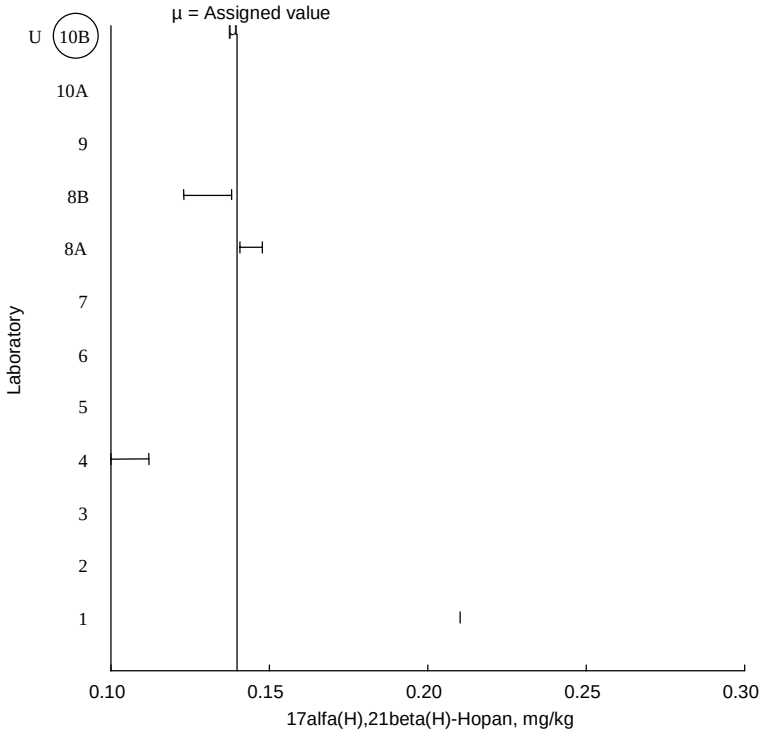
All results including outliers: n = 8 Mean = 0.39
Std.dev = 0.17
All results excluding outliers: n = 8 Mean = 0.39
Std.dev = 0.17

Level F



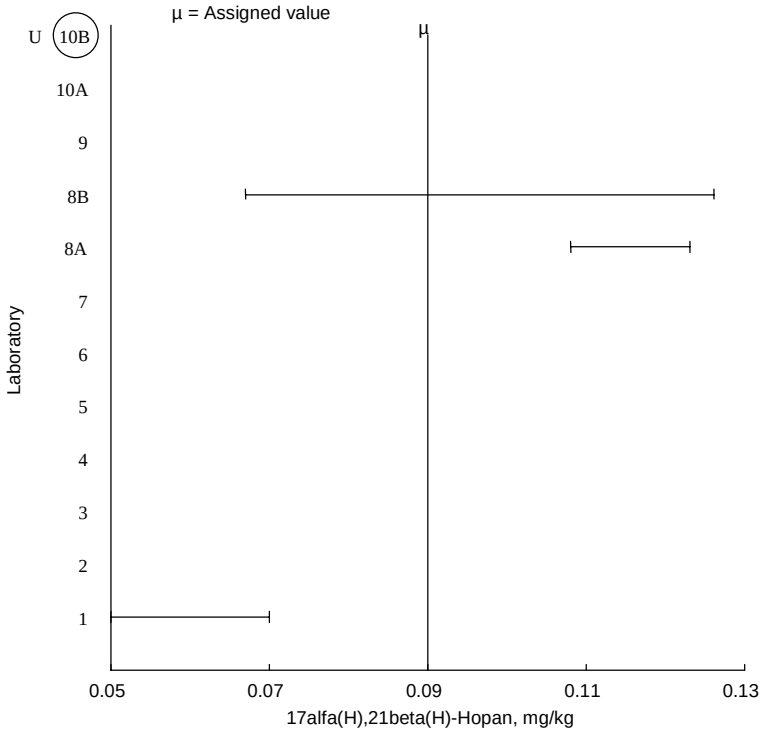
All results including outliers: n = 8 Mean = 1.40
Std.dev = 0.67
All results excluding outliers: n = 8 Mean = 1.40
Std.dev = 0.67

Level G



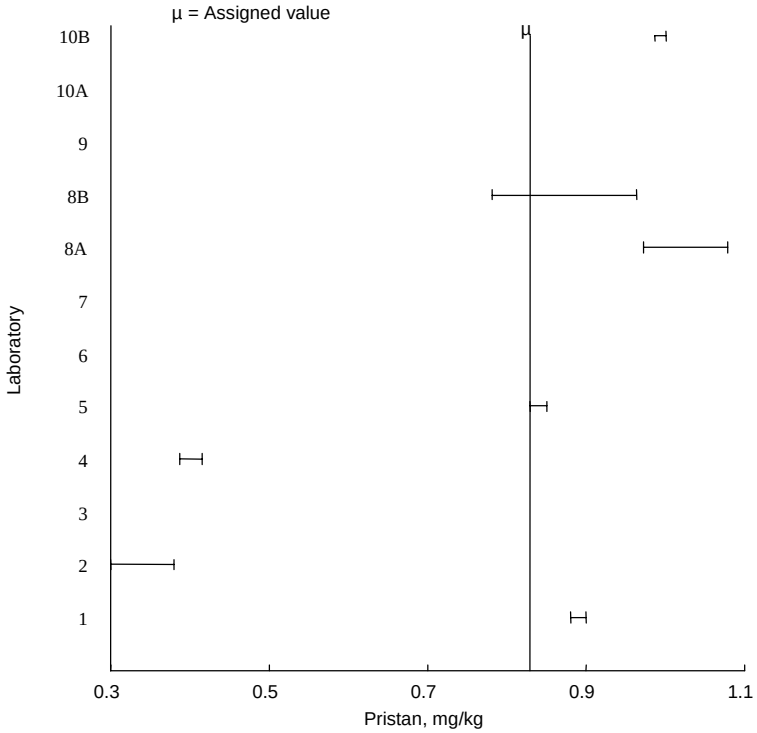
All results including outliers: n = 7 Mean = 0.14
Std.dev = 0.04
All results excluding outliers: n = 7 Mean = 0.14
Std.dev = 0.04

Level H



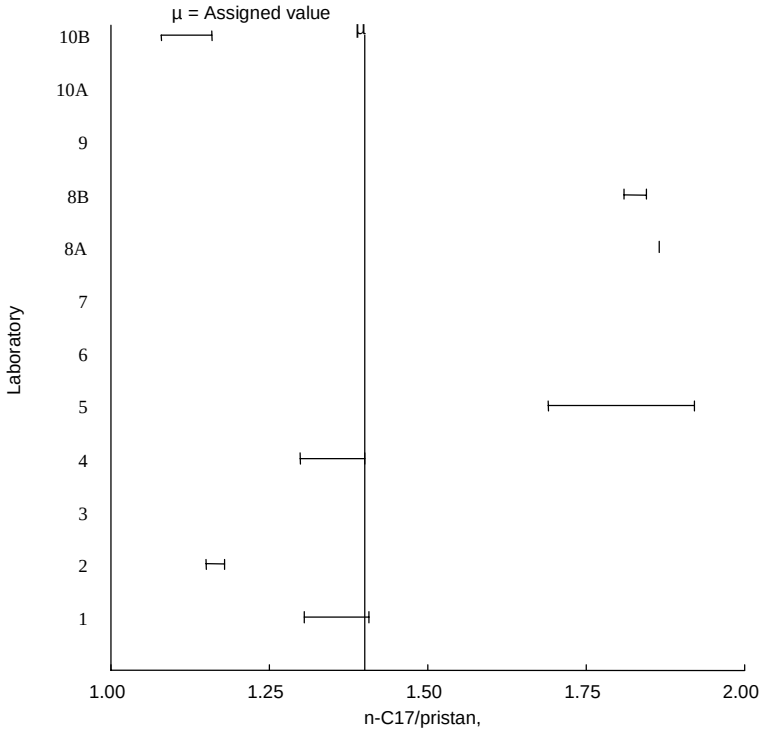
All results including outliers: n = 6 Mean = 0.09
Std.dev = 0.03
All results excluding outliers: n = 6 Mean = 0.09
Std.dev = 0.03

Level A



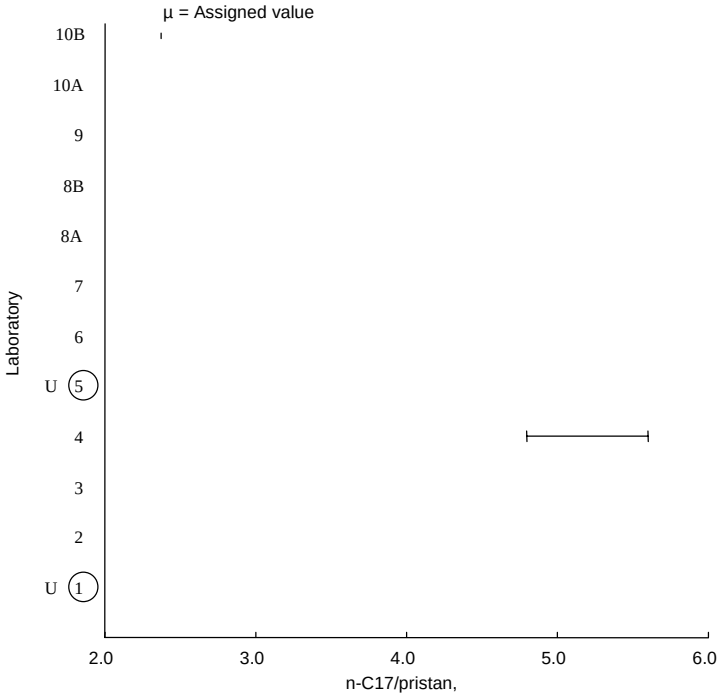
All results including outliers: n = 14 Mean = 0.77
Std.dev = 0.27
All results excluding outliers: n = 14 Mean = 0.77
Std.dev = 0.27

Level B



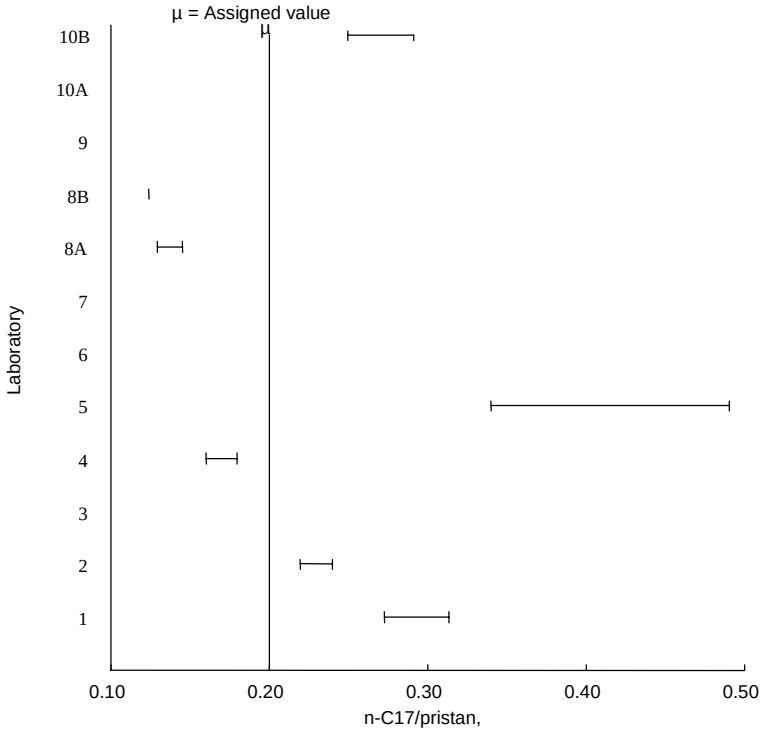
All results including outliers: n = 13 Mean = 1.50
Std.dev = 0.31
All results excluding outliers: n = 13 Mean = 1.50
Std.dev = 0.31

Level C



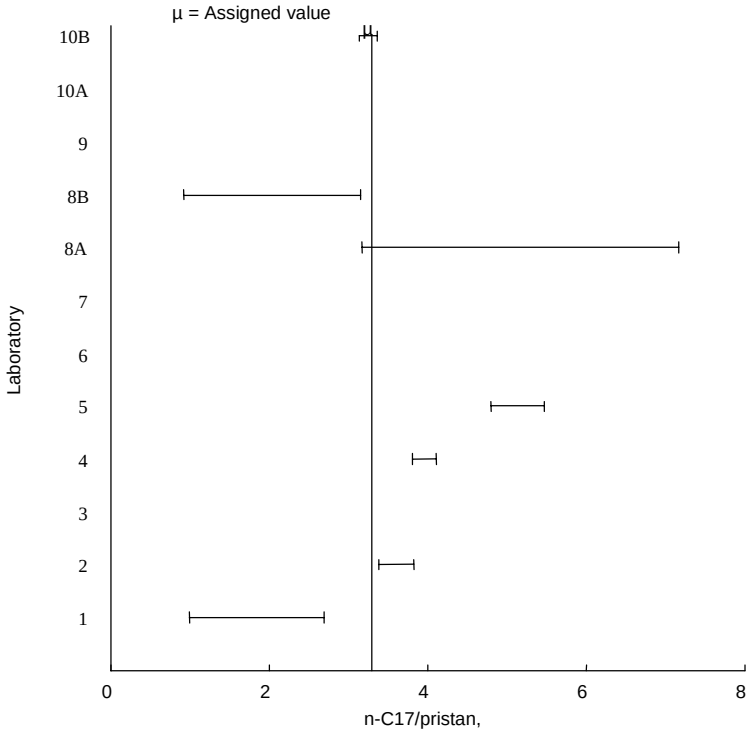
All results including outliers: n = 3 Mean = 4.3
Std.dev = 1.7
All results excluding outliers: n = 3 Mean = 4.3
Std.dev = 1.7

Level D



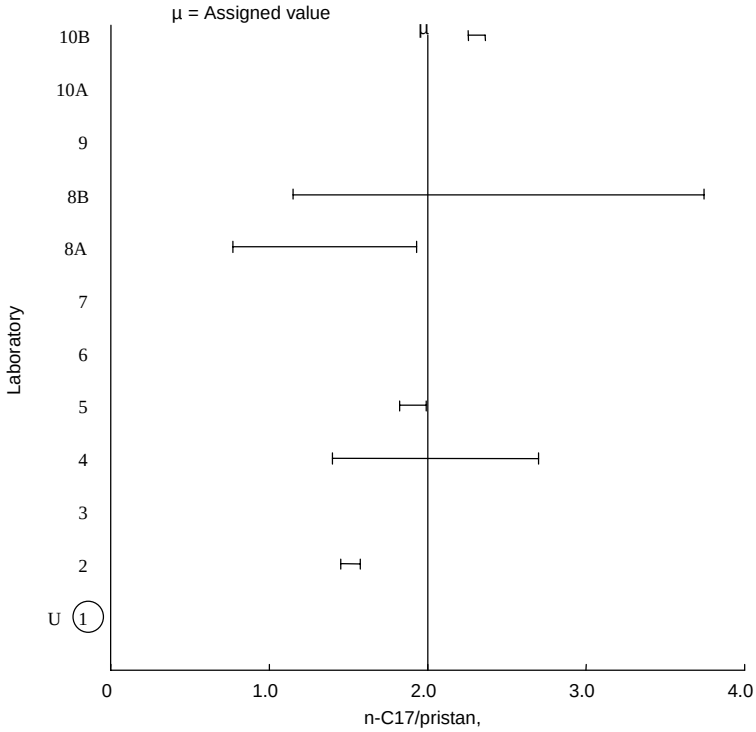
All results including outliers: n = 13 Mean = 0.240
Std.dev = 0.100
All results excluding outliers: n = 13 Mean = 0.240
Std.dev = 0.100

Level E



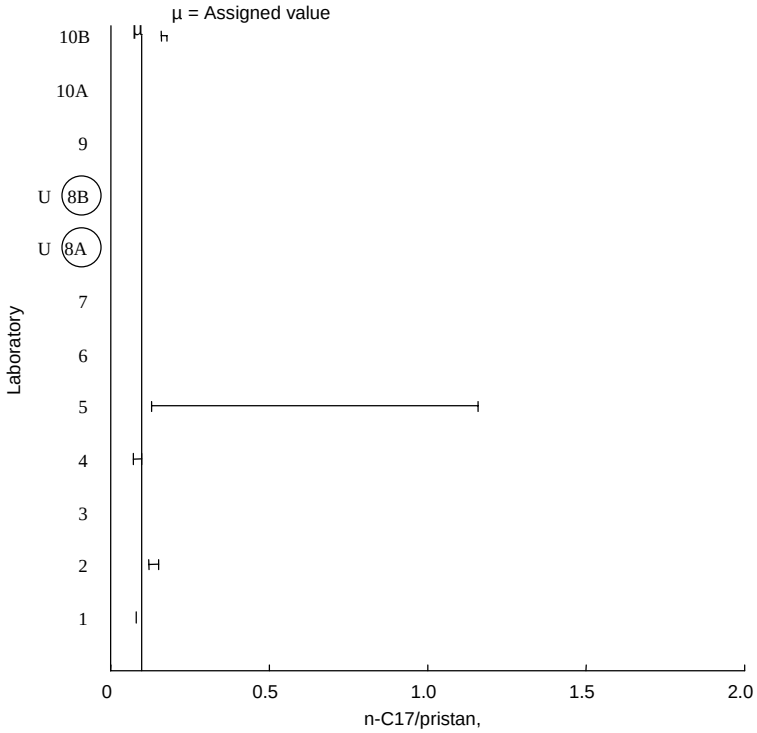
All results including outliers: n = 14 Mean = 3.60
Std.dev = 1.60
All results excluding outliers: n = 14 Mean = 3.60
Std.dev = 1.60

Level F



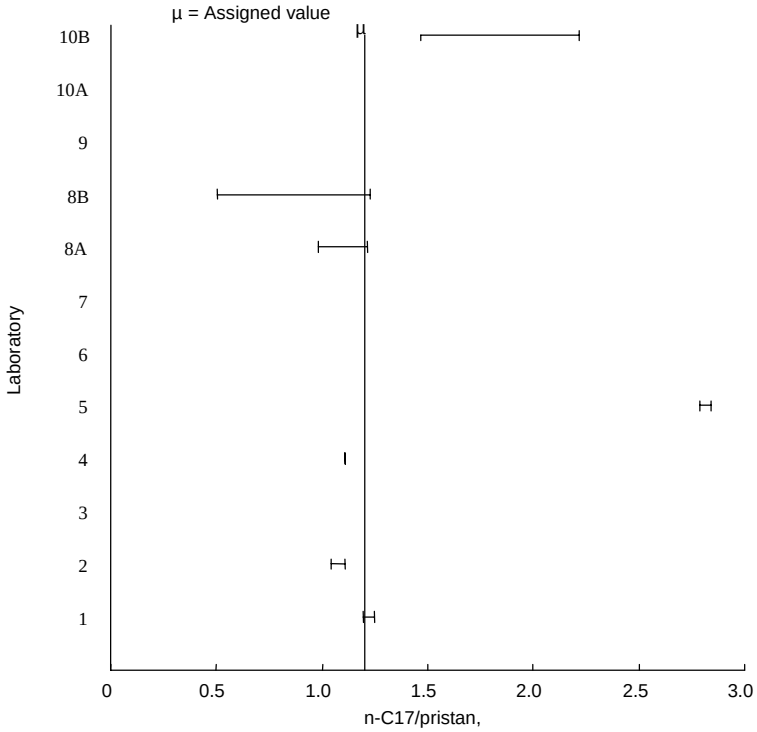
All results including outliers: n = 12 Mean = 1.90
Std.dev = 0.79
All results excluding outliers: n = 12 Mean = 1.90
Std.dev = 0.79

Level G



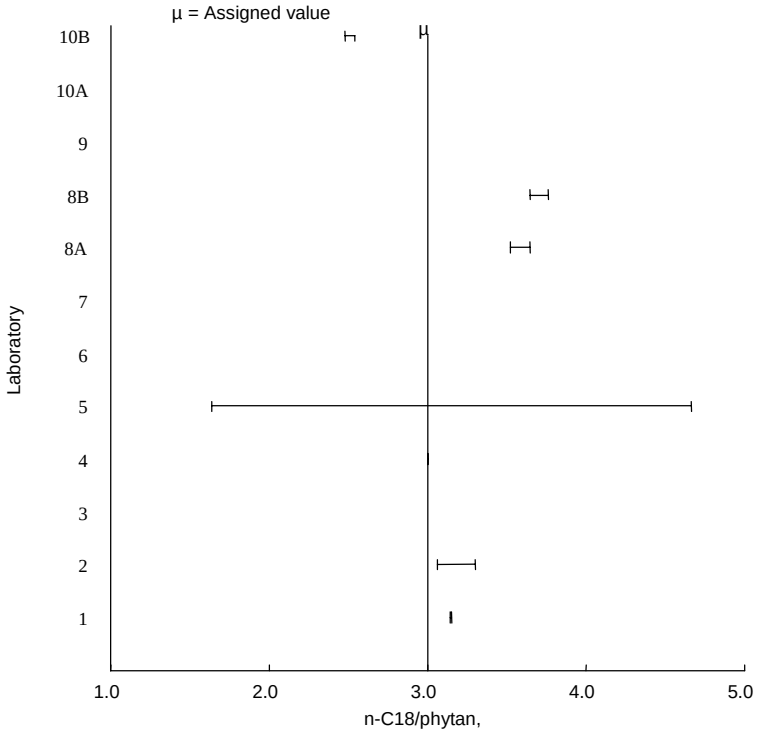
All results including outliers: n = 9 Mean = 0.24
Std.dev = 0.35
All results excluding outliers: n = 9 Mean = 0.24
Std.dev = 0.35

Level H



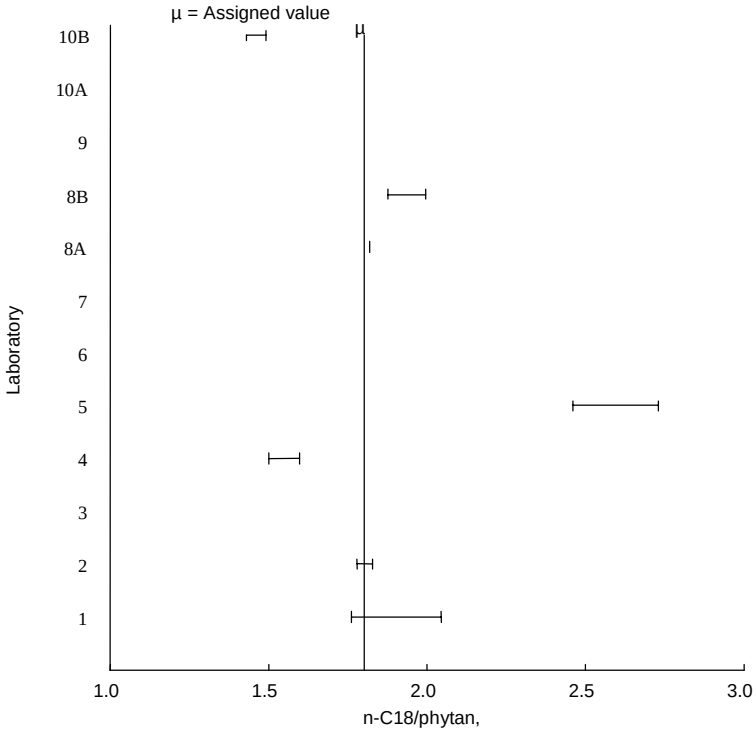
All results including outliers: n = 14 Mean = 1.40
Std.dev = 0.69
All results excluding outliers: n = 14 Mean = 1.40
Std.dev = 0.69

Level A



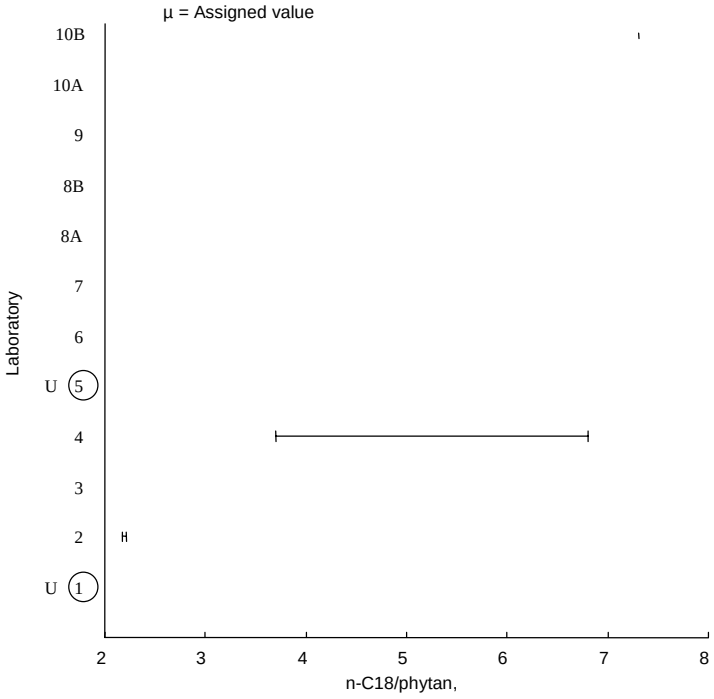
All results including outliers: n = 14 Mean = 3.20
Std.dev = 0.70
All results excluding outliers: n = 14 Mean = 3.20
Std.dev = 0.70

Level B



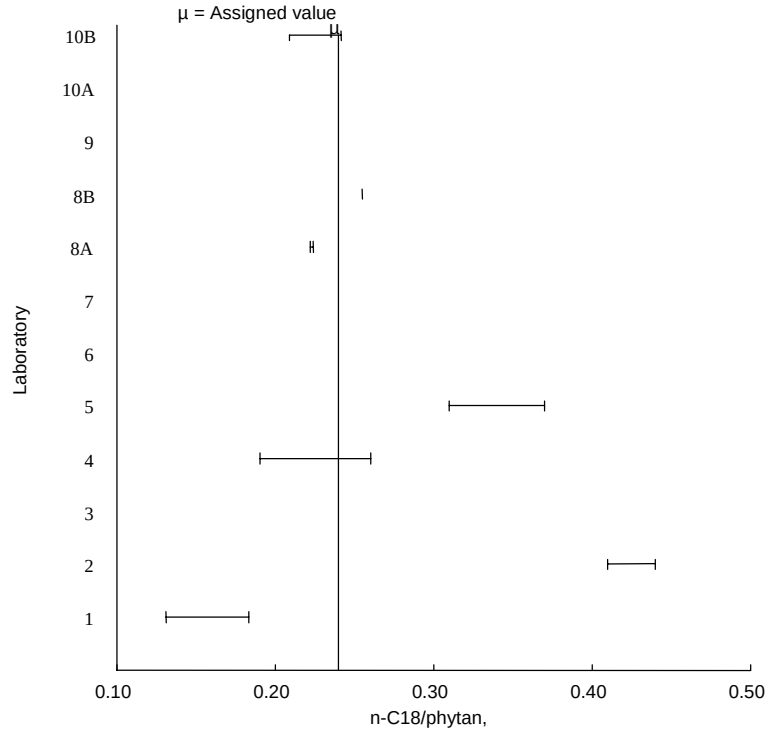
All results including outliers: n = 13 Mean = 1.90
Std.dev = 0.38
All results excluding outliers: n = 13 Mean = 1.90
Std.dev = 0.38

Level C



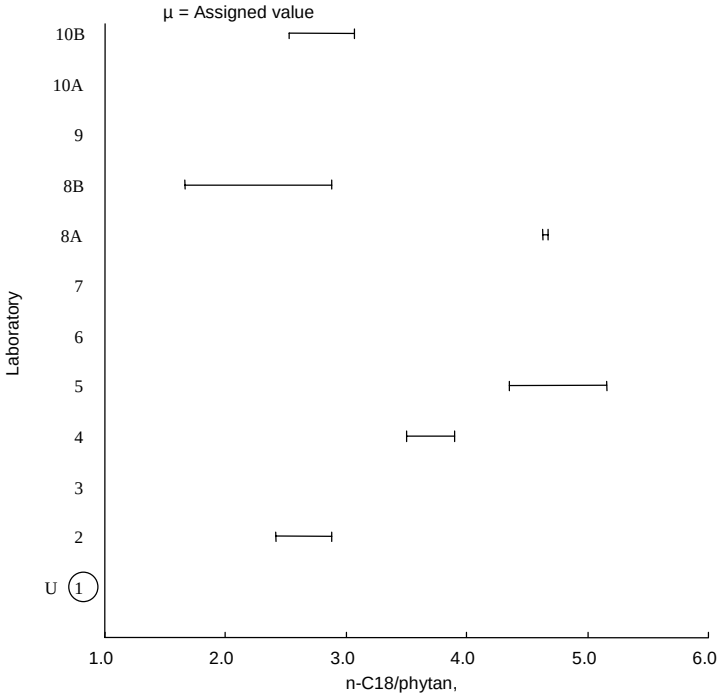
All results including outliers: n = 5 Mean = 4.4
Std.dev = 2.5
All results excluding outliers: n = 5 Mean = 4.4
Std.dev = 2.5

Level D



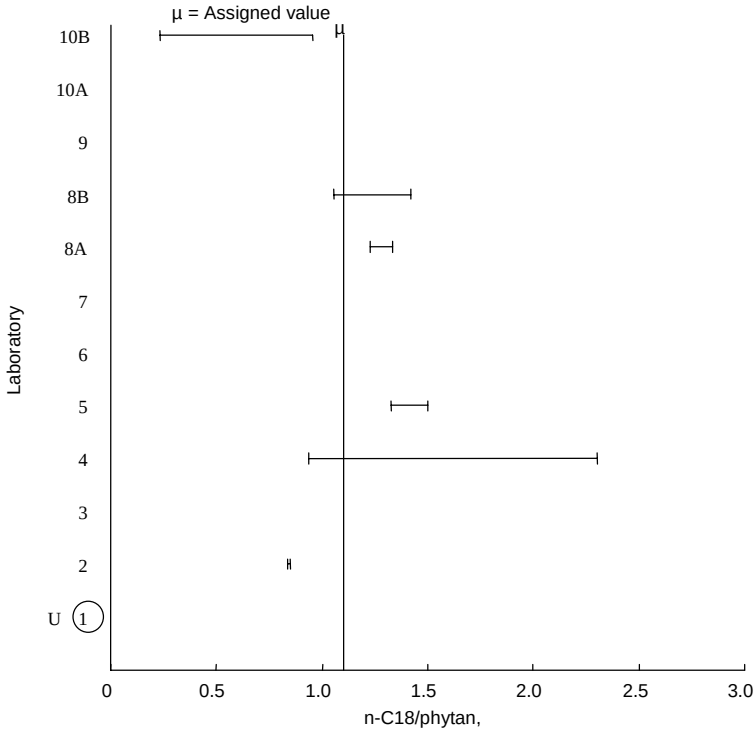
All results including outliers: n = 13 Mean = 0.270
Std.dev = 0.092
All results excluding outliers: n = 13 Mean = 0.270
Std.dev = 0.092

Level E



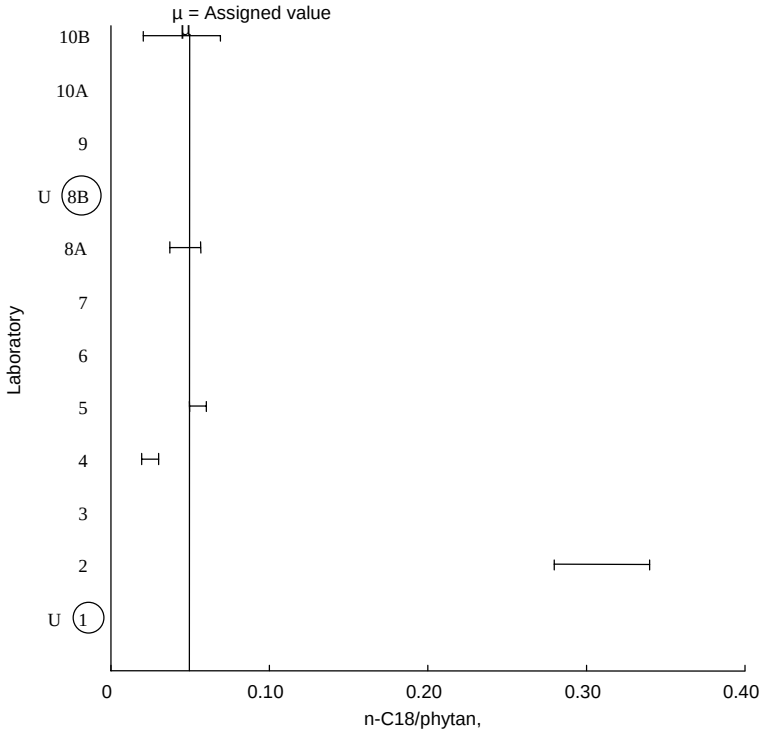
All results including outliers: n = 12 Mean = 3.50
Std.dev = 1.10
All results excluding outliers: n = 12 Mean = 3.50
Std.dev = 1.10

Level F



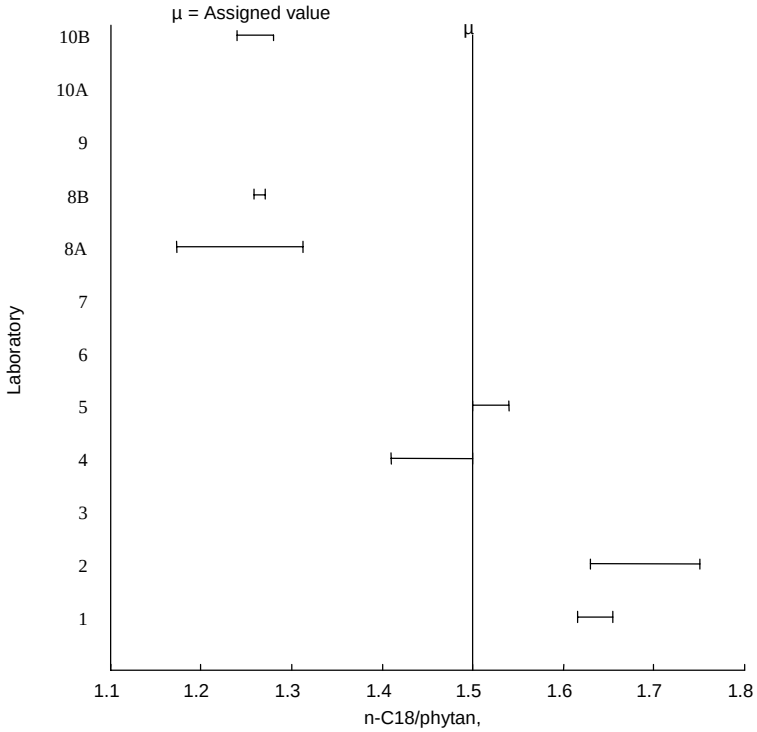
All results including outliers: n = 12 Mean = 1.20
Std.dev = 0.50
All results excluding outliers: n = 12 Mean = 1.20
Std.dev = 0.50

Level G



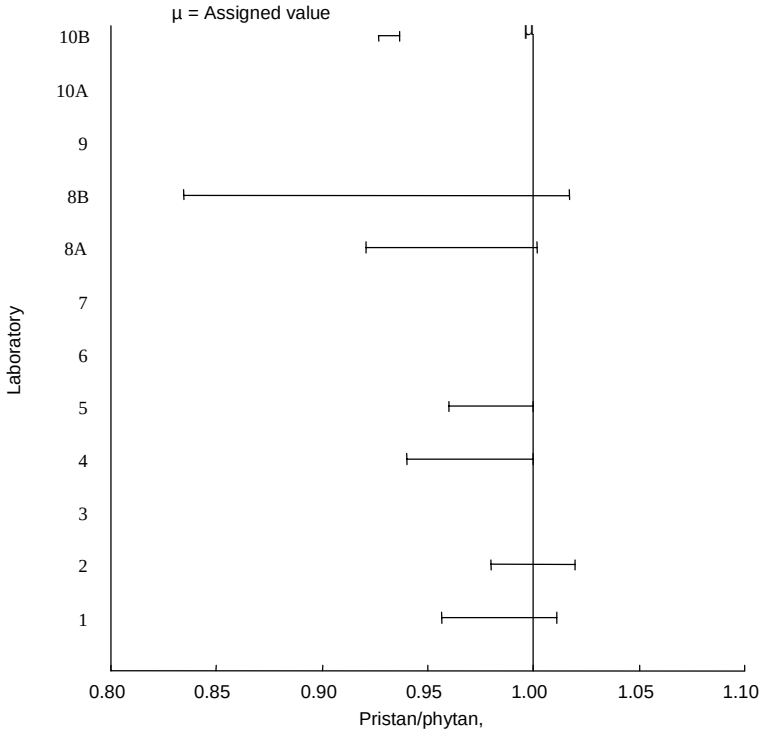
All results including outliers: n = 10 Mean = 0.10
Std.dev = 0.11
All results excluding outliers: n = 10 Mean = 0.10
Std.dev = 0.11

Level H



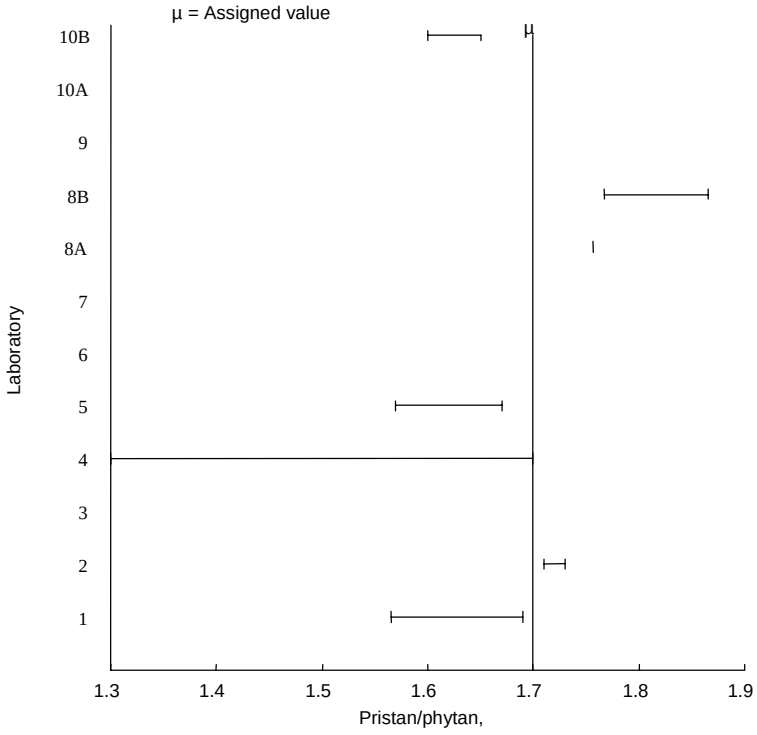
All results including outliers: n = 14 Mean = 1.40
Std.dev = 0.18
All results excluding outliers: n = 14 Mean = 1.40
Std.dev = 0.18

Level A



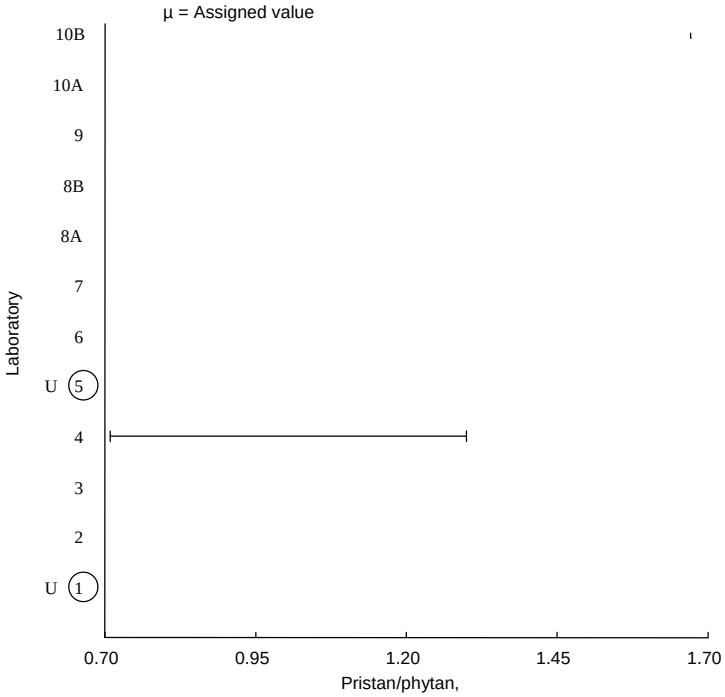
All results including outliers: n = 14 Mean = 0.96
Std.dev = 0.05
All results excluding outliers: n = 14 Mean = 0.96
Std.dev = 0.05

Level B



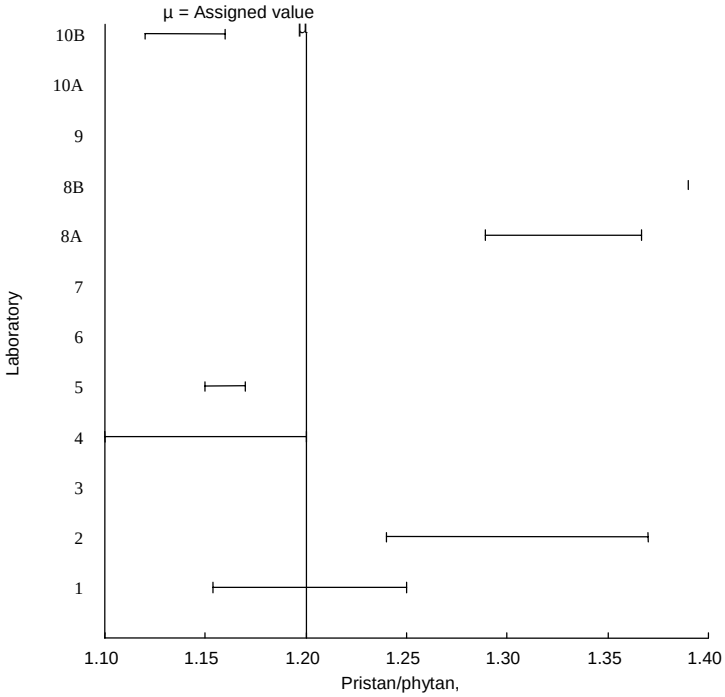
All results including outliers: n = 13 Mean = 1.70
Std.dev = 0.14
All results excluding outliers: n = 13 Mean = 1.70
Std.dev = 0.14

Level C



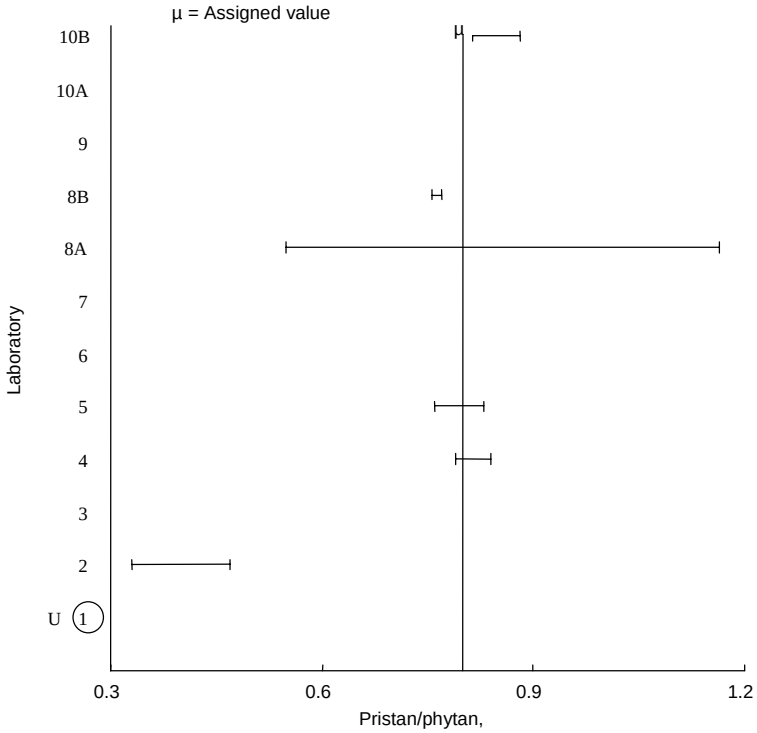
All results including outliers: n = 3 Mean = 1.2
Std.dev = 0.5
All results excluding outliers: n = 3 Mean = 1.2
Std.dev = 0.5

Level D



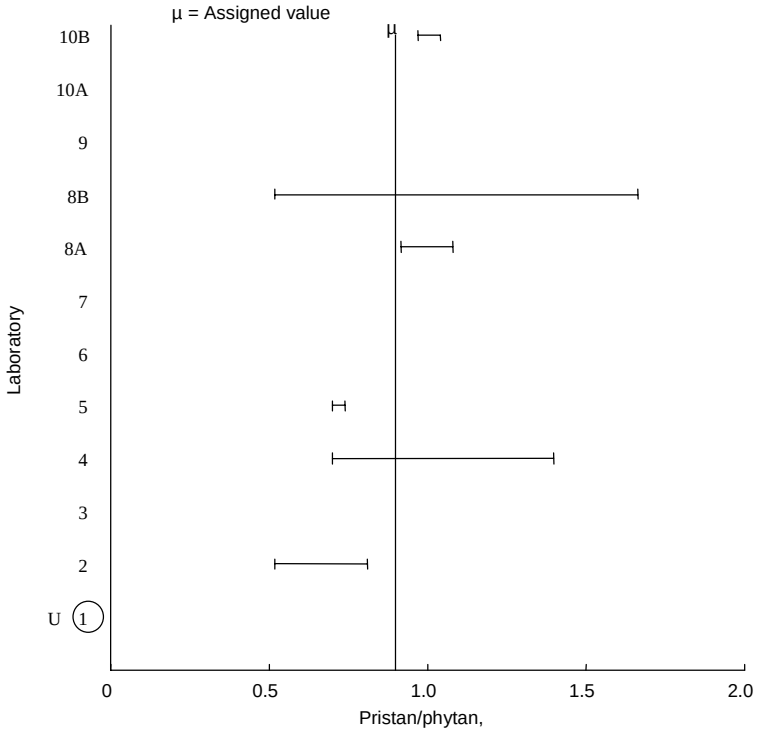
All results including outliers: n = 13 Mean = 1.20
Std.dev = 0.10
All results excluding outliers: n = 13 Mean = 1.20
Std.dev = 0.10

Level E



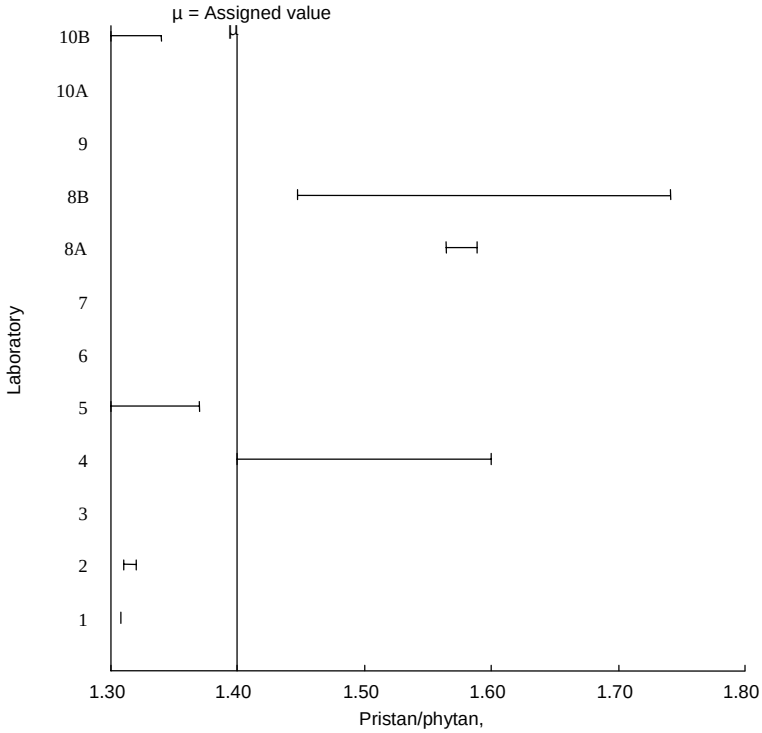
All results including outliers: n = 12 Mean = 0.75
Std.dev = 0.21
All results excluding outliers: n = 12 Mean = 0.75
Std.dev = 0.21

Level F



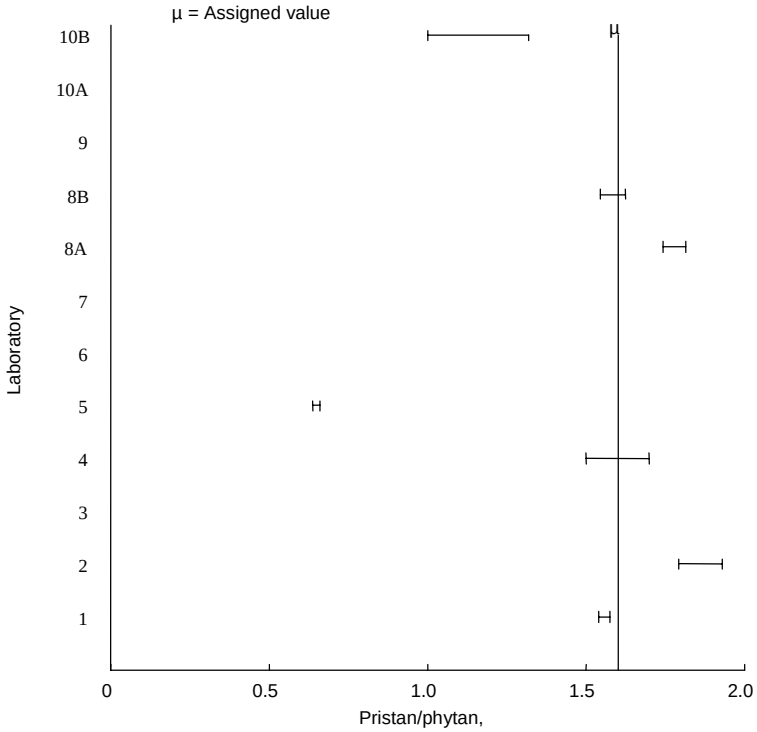
All results including outliers: n = 12 Mean = 0.92
Std.dev = 0.34
All results excluding outliers: n = 12 Mean = 0.92
Std.dev = 0.34

Level G



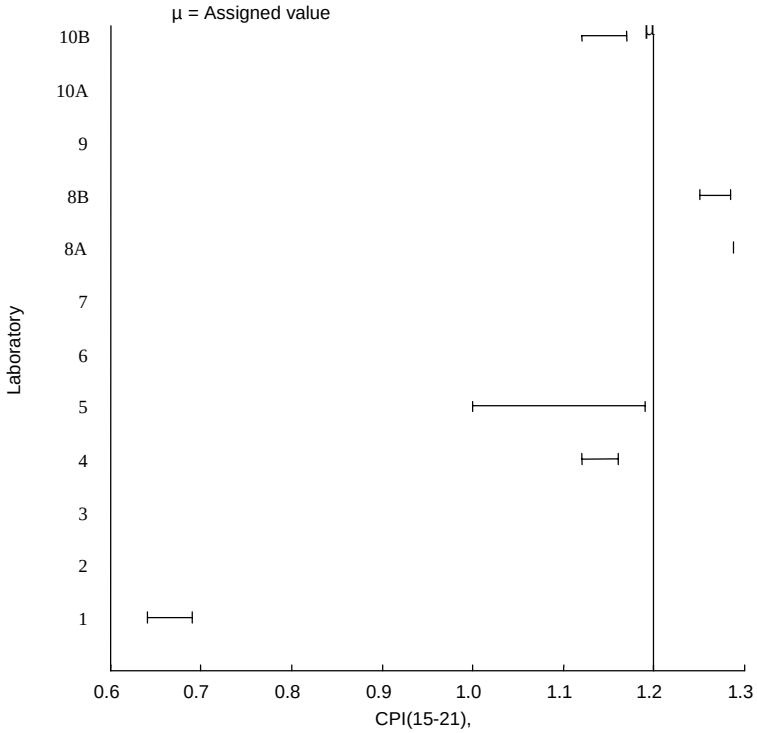
All results including outliers: n = 13 Mean = 1.40
Std.dev = 0.15
All results excluding outliers: n = 13 Mean = 1.40
Std.dev = 0.15

Level H



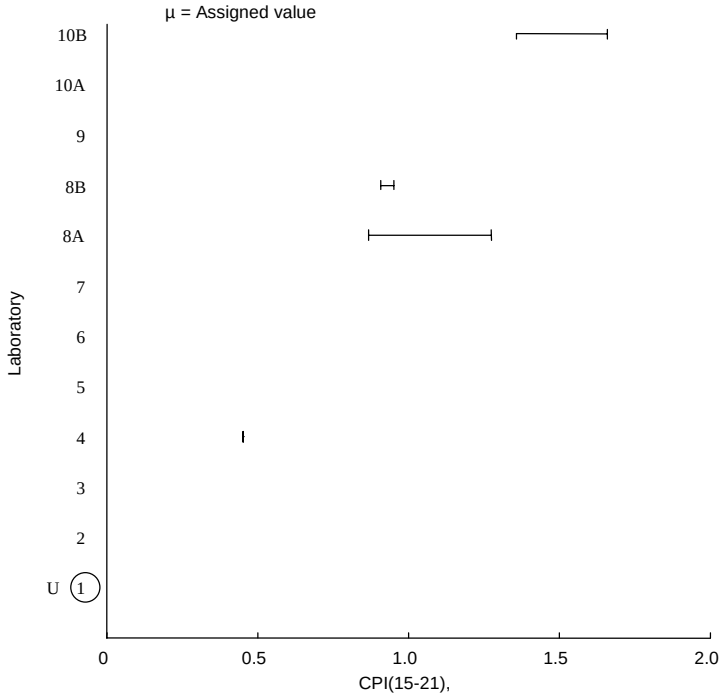
All results including outliers: n = 14 Mean = 1.50
Std.dev = 0.41
All results excluding outliers: n = 14 Mean = 1.50
Std.dev = 0.41

Level B



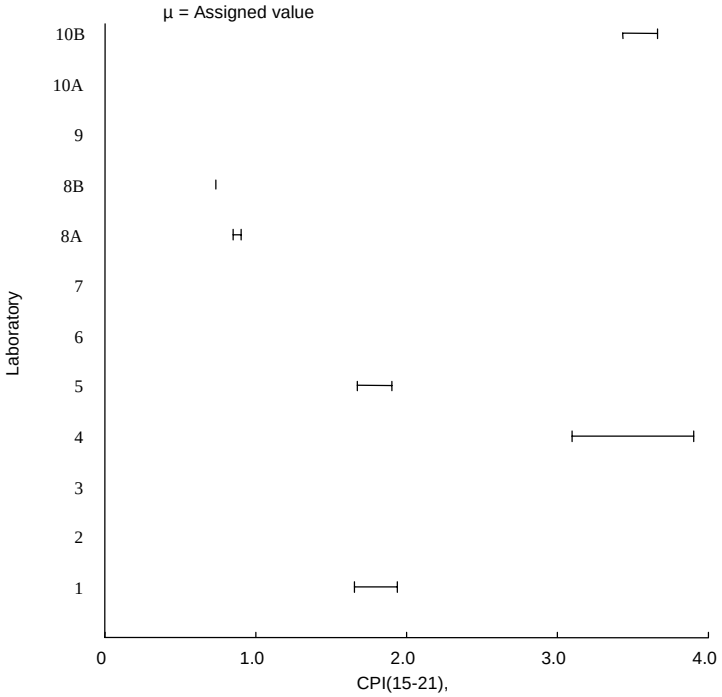
All results including outliers: n = 11 Mean = 1.10
Std.dev = 0.22
All results excluding outliers: n = 11 Mean = 1.10
Std.dev = 0.22

Level C



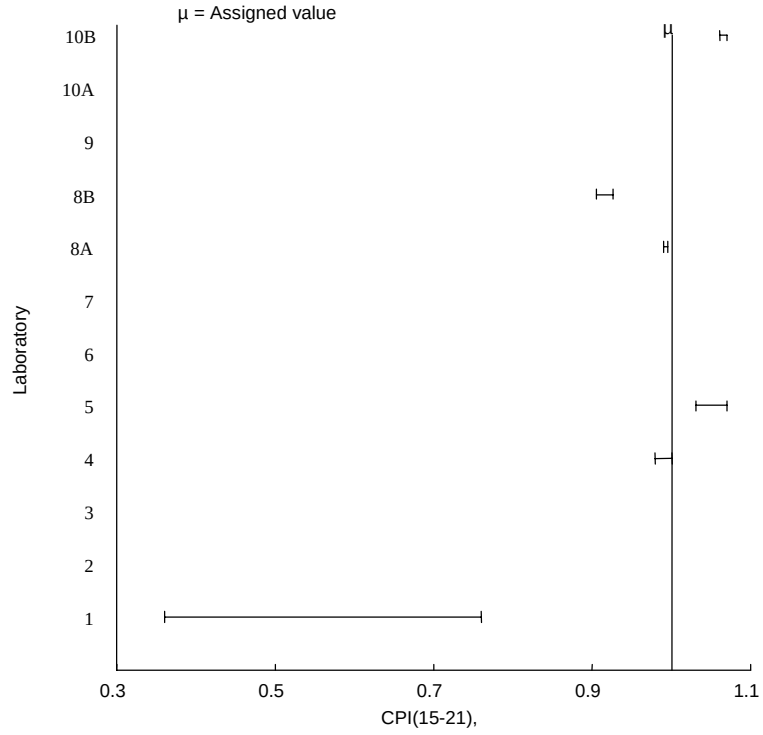
All results including outliers: n = 8 Mean = 0.99
Std.dev = 0.43
All results excluding outliers: n = 8 Mean = 0.99
Std.dev = 0.43

Level D



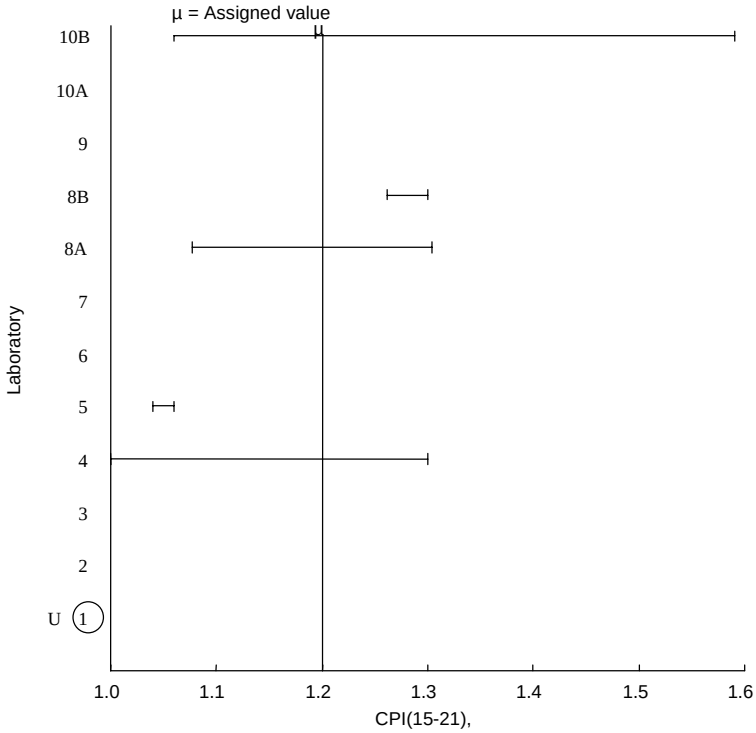
All results including outliers: n = 11 Mean = 2.20
Std.dev = 1.20
All results excluding outliers: n = 11 Mean = 2.20
Std.dev = 1.20

Level E



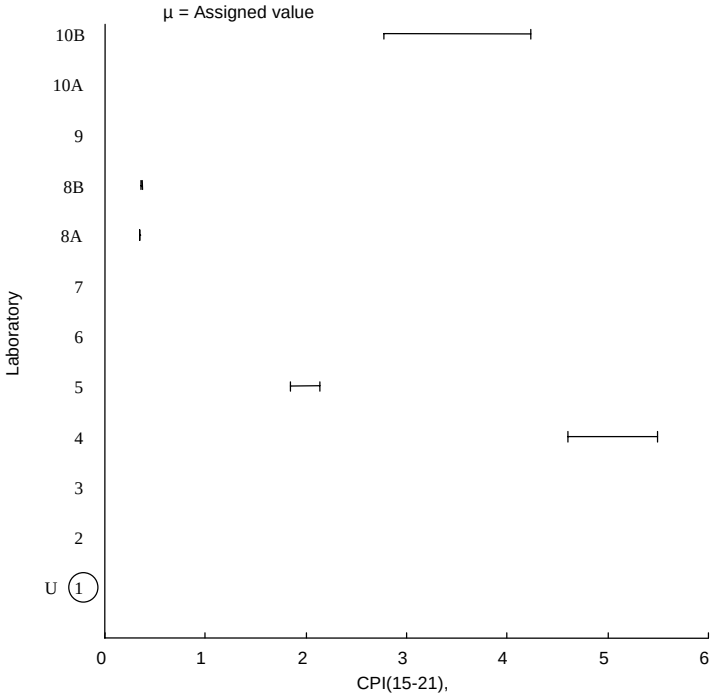
All results including outliers: n = 12 Mean = 0.93
Std.dev = 0.20
All results excluding outliers: n = 12 Mean = 0.93
Std.dev = 0.20

Level F



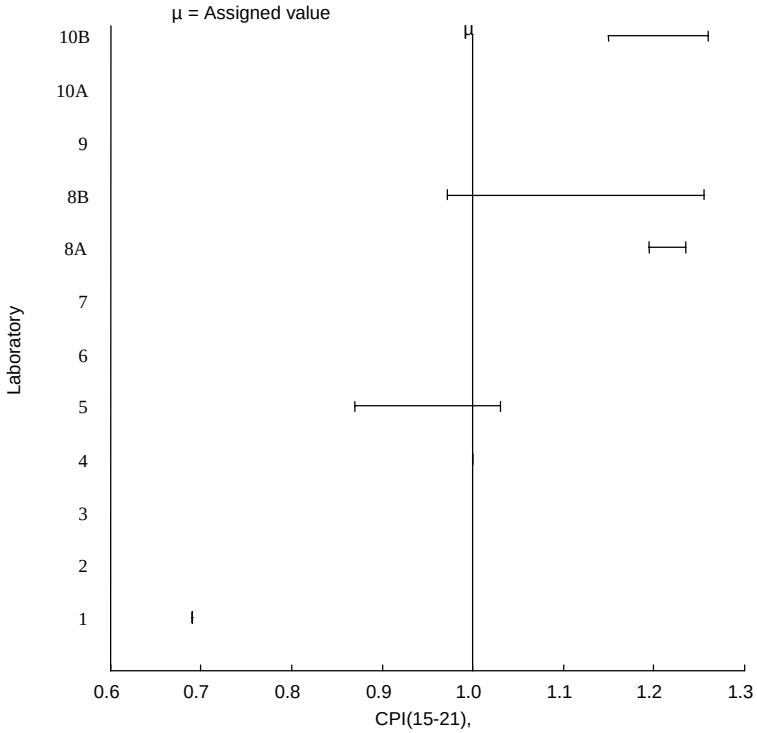
All results including outliers: n = 10 Mean = 1.20
Std.dev = 0.18
All results excluding outliers: n = 10 Mean = 1.20
Std.dev = 0.18

Level G



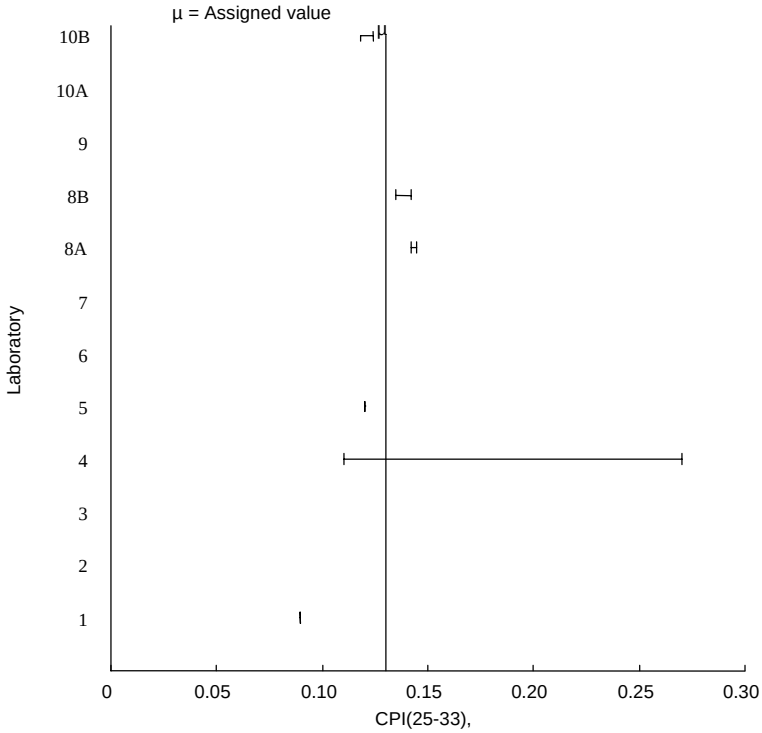
All results including outliers: n = 10 Mean = 2.30
Std.dev = 2.00
All results excluding outliers: n = 10 Mean = 2.30
Std.dev = 2.00

Level H



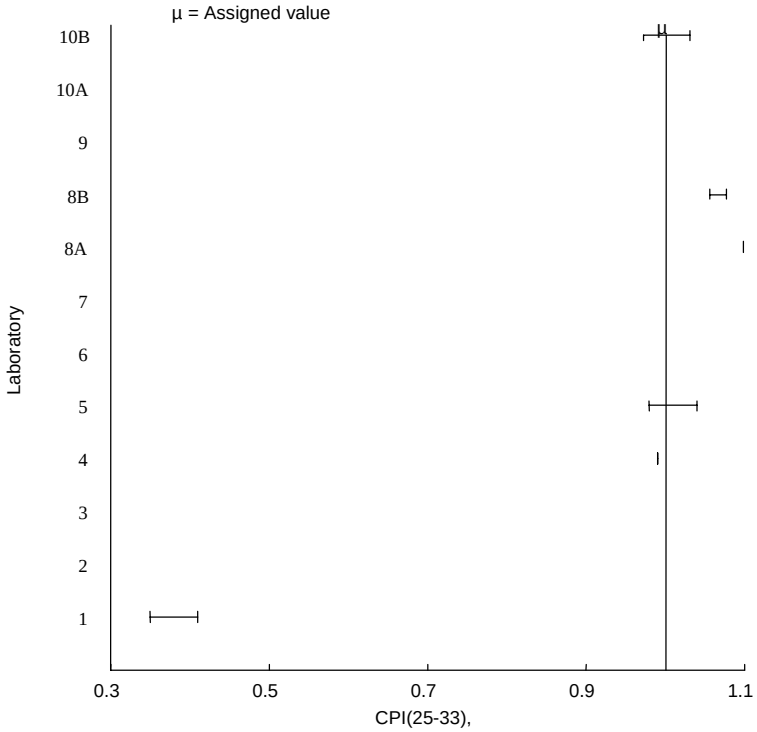
All results including outliers: n = 12 Mean = 1.00
Std.dev = 0.20
All results excluding outliers: n = 12 Mean = 1.00
Std.dev = 0.20

Level A



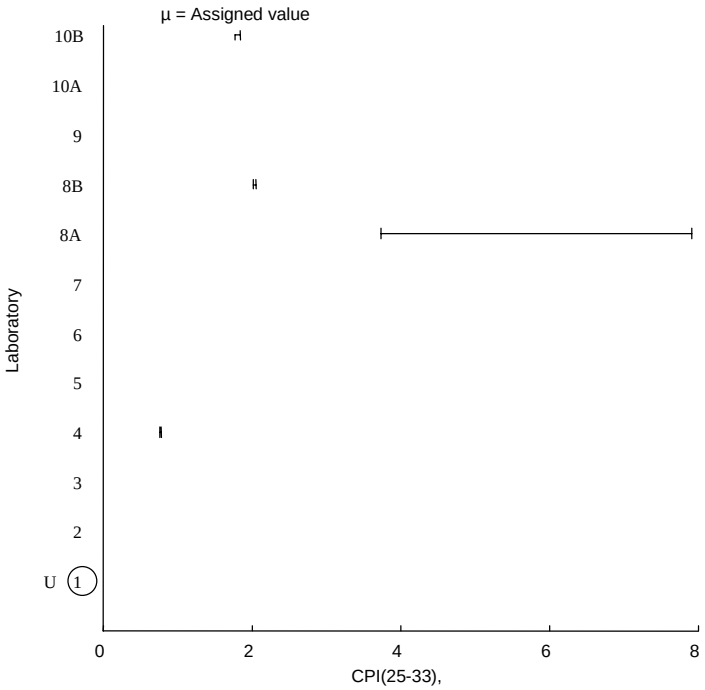
All results including outliers: n = 12 Mean = 0.13
Std.dev = 0.05
All results excluding outliers: n = 12 Mean = 0.13
Std.dev = 0.05

Level B



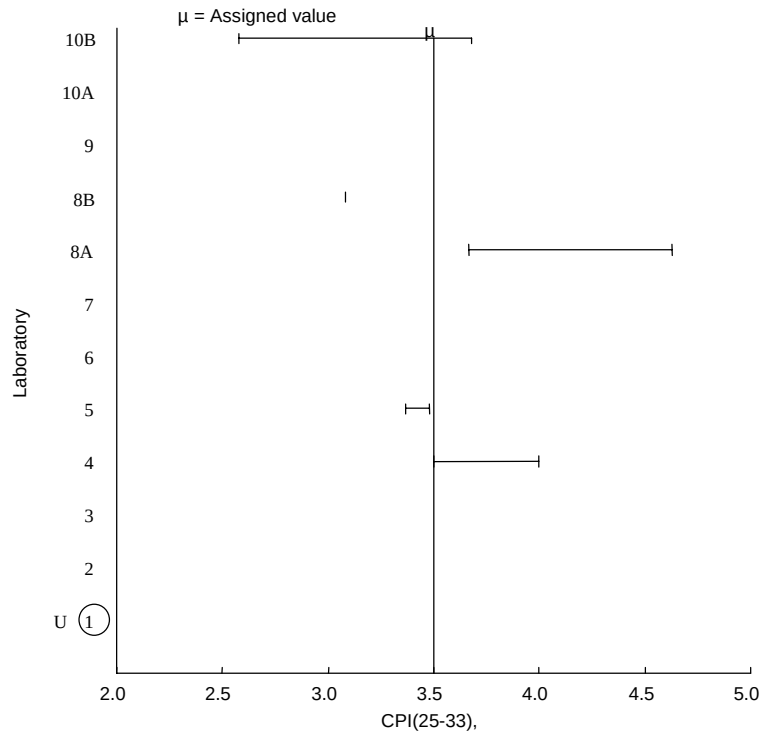
All results including outliers: n = 11 Mean = 0.91
Std.dev = 0.26
All results excluding outliers: n = 11 Mean = 0.91
Std.dev = 0.26

Level C



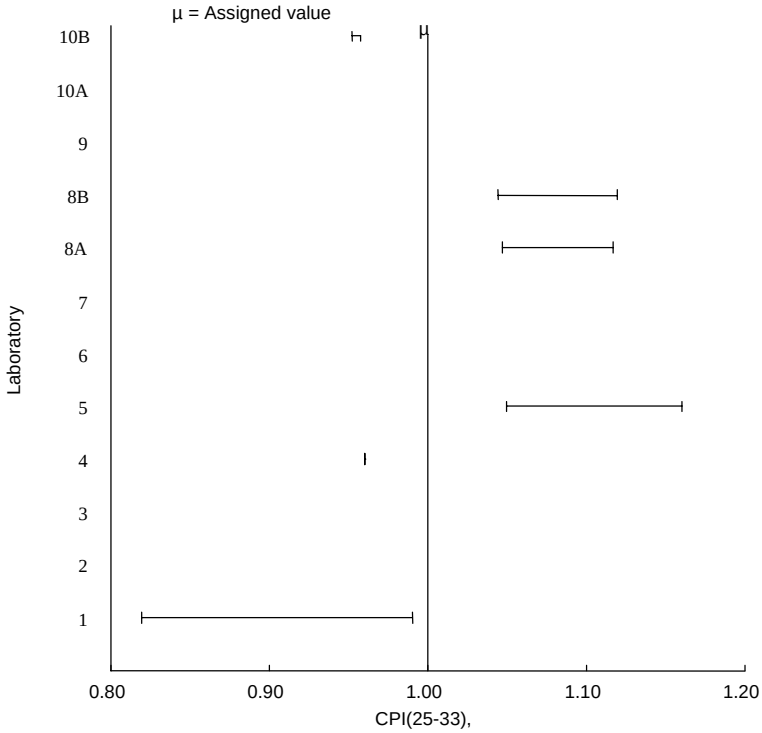
All results including outliers: n = 8 Mean = 2.60
Std.dev = 2.30
All results excluding outliers: n = 8 Mean = 2.60
Std.dev = 2.30

Level D



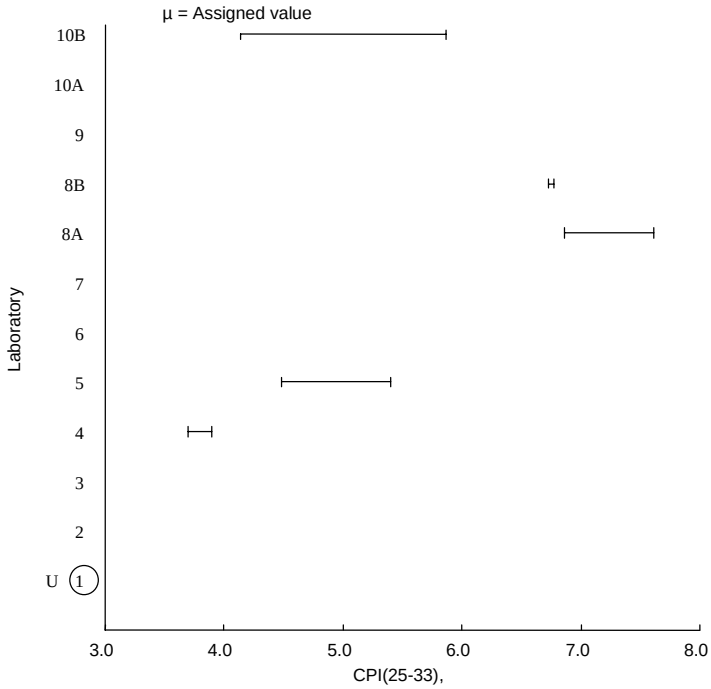
All results including outliers: n = 9 Mean = 3.60
Std.dev = 0.57
All results excluding outliers: n = 9 Mean = 3.60
Std.dev = 0.57

Level E



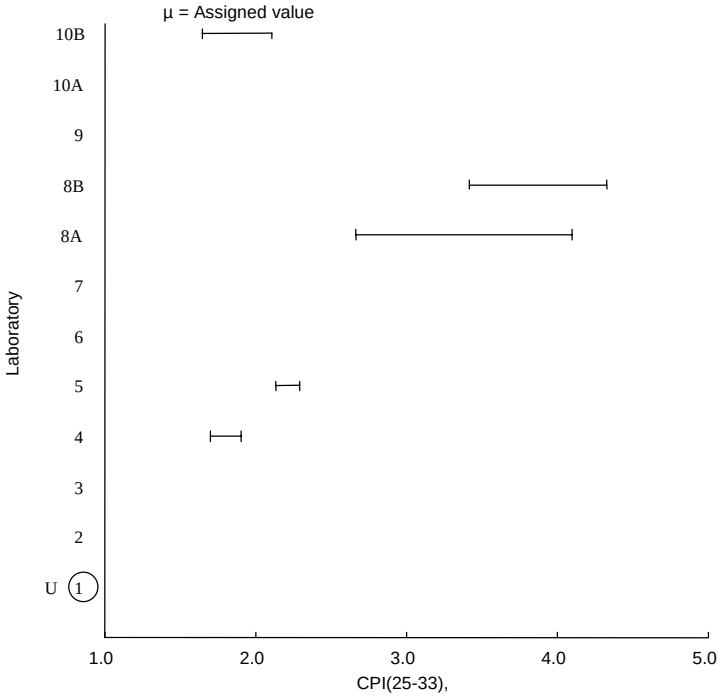
All results including outliers: n = 12 Mean = 1.00
Std.dev = 0.09
All results excluding outliers: n = 12 Mean = 1.00
Std.dev = 0.09

Level F



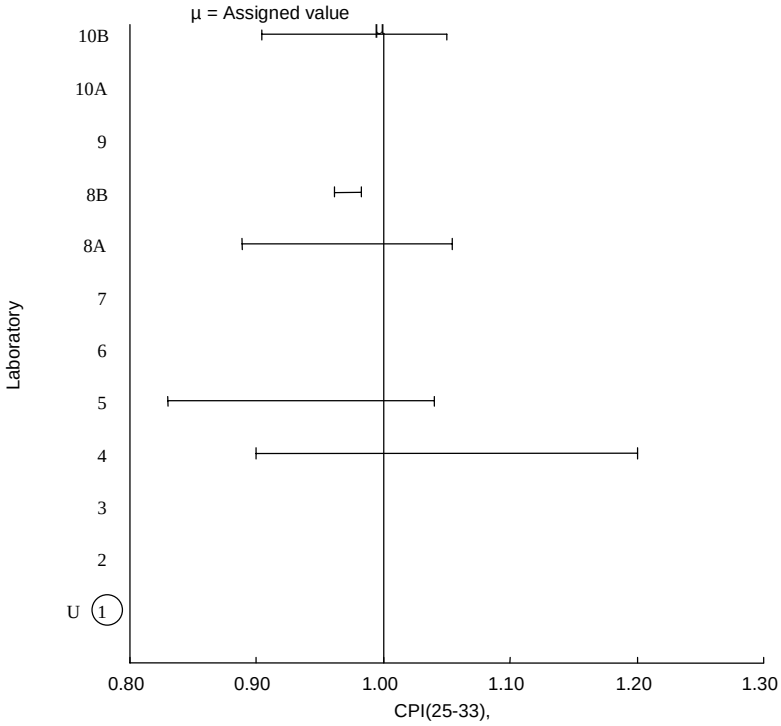
All results including outliers: n = 10 Mean = 5.50
Std.dev = 1.40
All results excluding outliers: n = 10 Mean = 5.50
Std.dev = 1.40

Level G



All results including outliers: n = 10 Mean = 2.60
Std.dev = 0.98
All results excluding outliers: n = 10 Mean = 2.60
Std.dev = 0.98

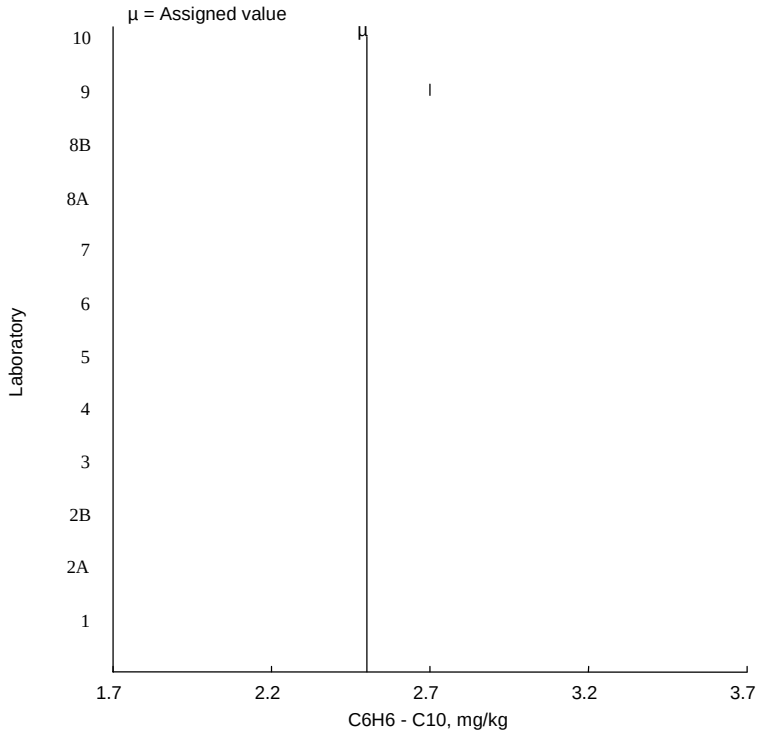
Level H



All results including outliers: n = 10 Mean = 0.98
Std.dev = 0.11
All results excluding outliers: n = 10 Mean = 0.98
Std.dev = 0.11

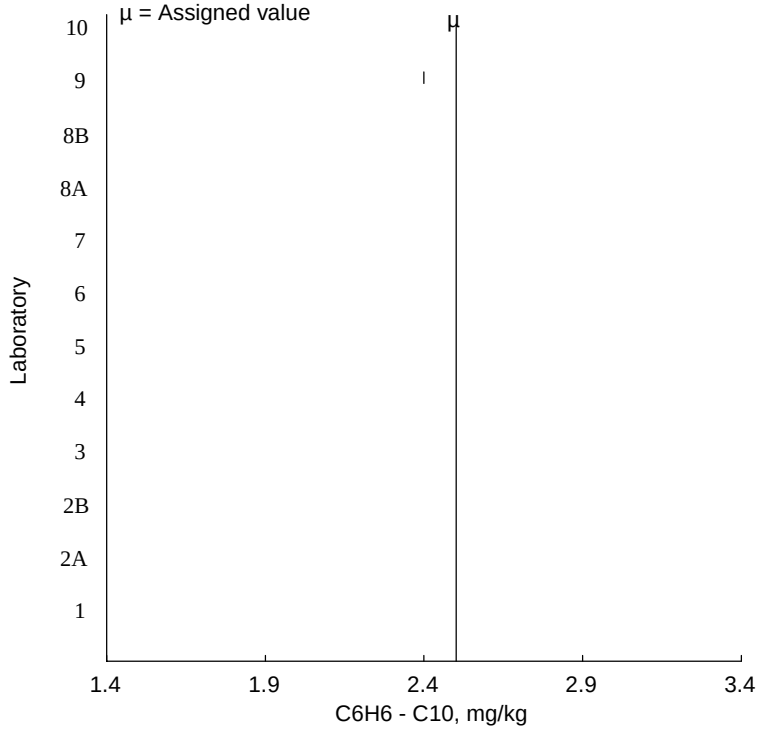
Plots - own method

Level E



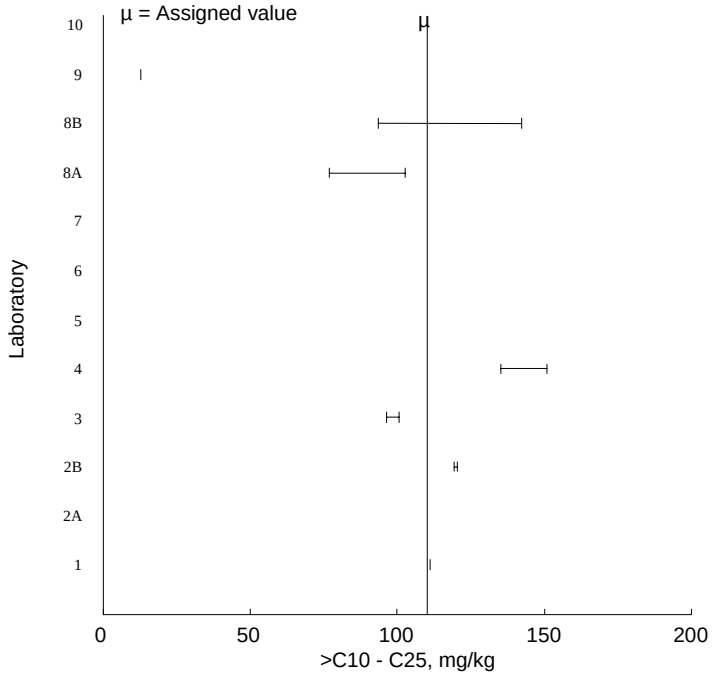
All results including outliers: n = 1 Mean = 2.7
Std.dev = 0.0
All results excluding outliers: n = 1 Mean = 2.7
Std.dev = -

Level G



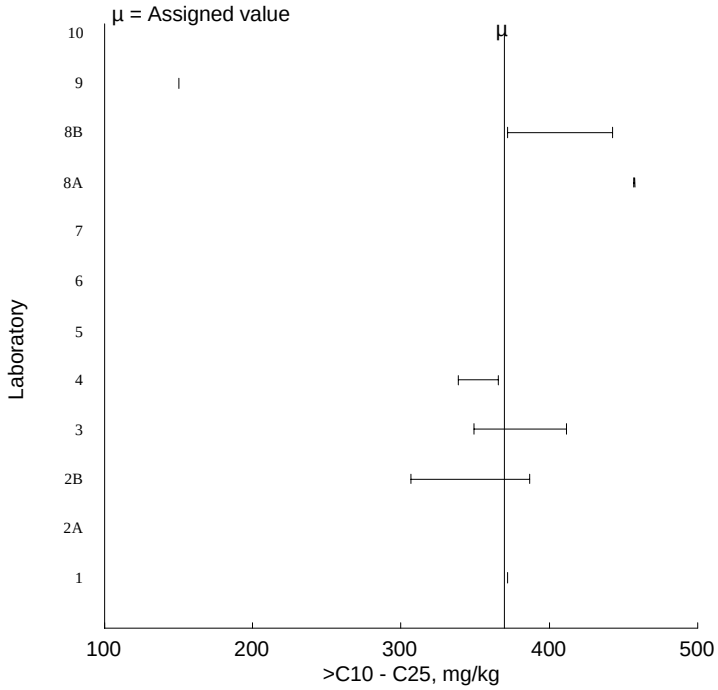
All results including n = Mean = 2.4
Std.dev = 0.0
All results excluding n = Mean = 2.4
Std.dev = -

Level E



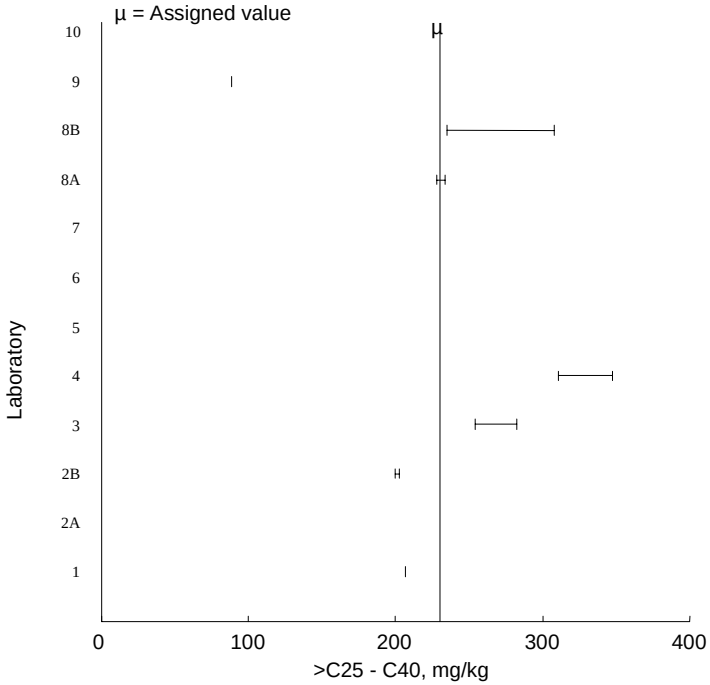
All results including n = 12 Mean = 1.1E2
Std.dev = 36.0
All results excluding n = 12 Mean = 1.1E2
Std.dev = 36.0

Level G



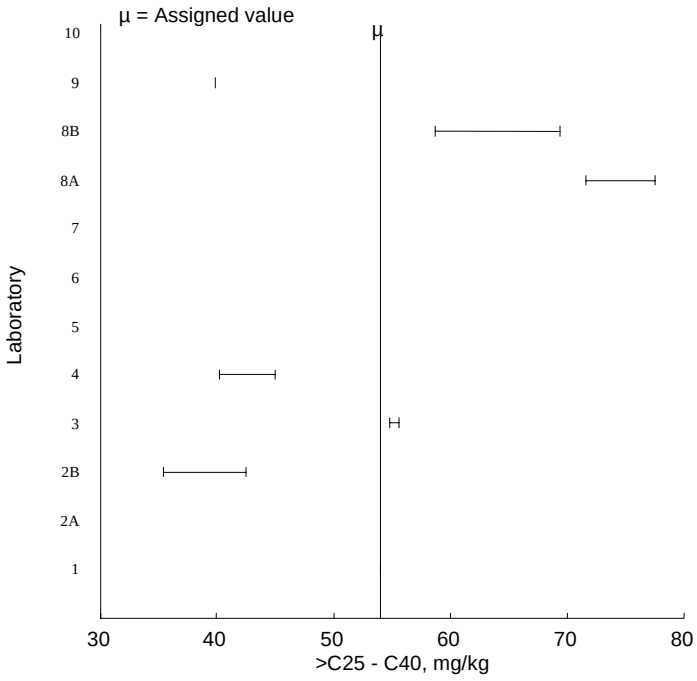
All results including n = 12 Mean = 3.7E2
Std.dev = 83.0
All results excluding n = 12 Mean = 3.7E2
Std.dev = 83.0

Level E



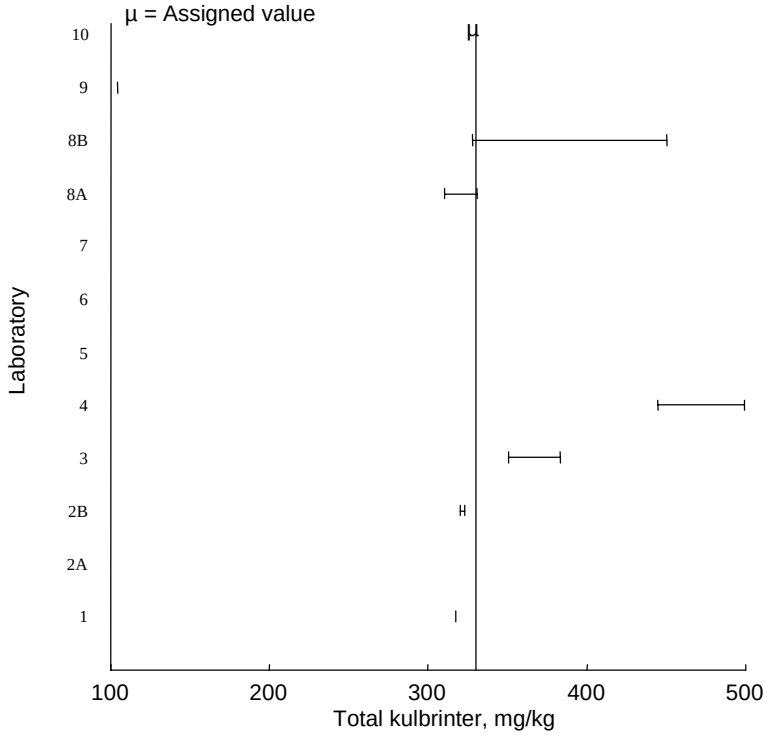
All results including n = 12 Mean = 2.4E2
Std.dev = 68.0
All results excluding n = 12 Mean = 2.4E2
Std.dev = 68.0

Level G



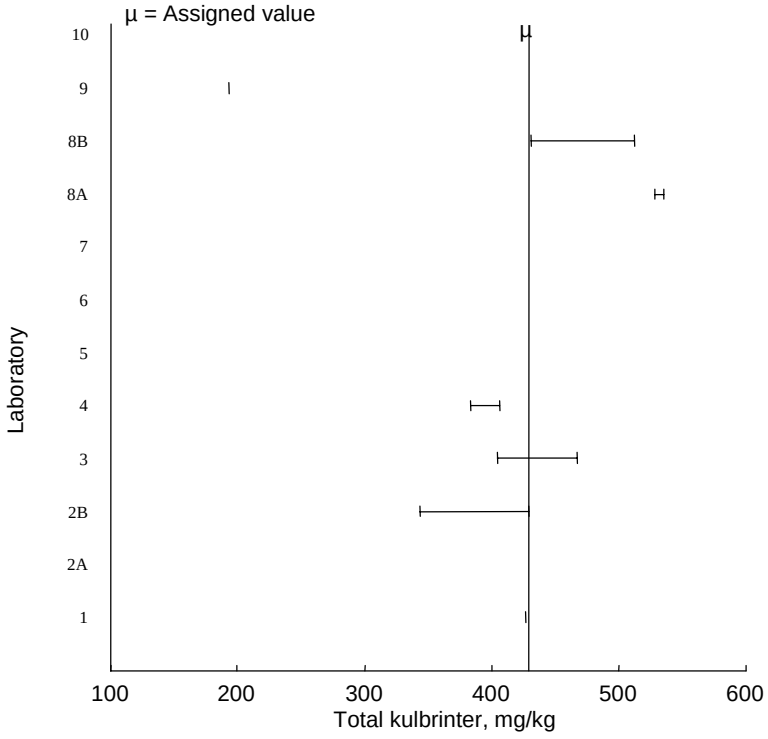
All results including n = 12 Mean = 54.0
Std.dev = 14.0
All results excluding n = 12 Mean = 54.0
Std.dev = 14.0

Level E



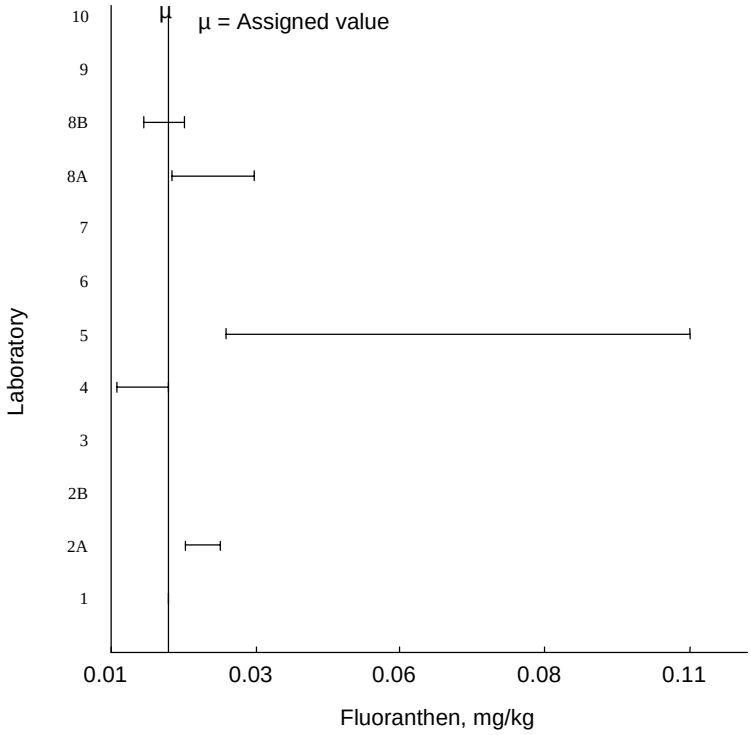
All results including n = 12 Mean = 3.5E2
Std.dev = 99.0
All results excluding n = 12 Mean = 3.5E2
Std.dev = 99.0

Level G



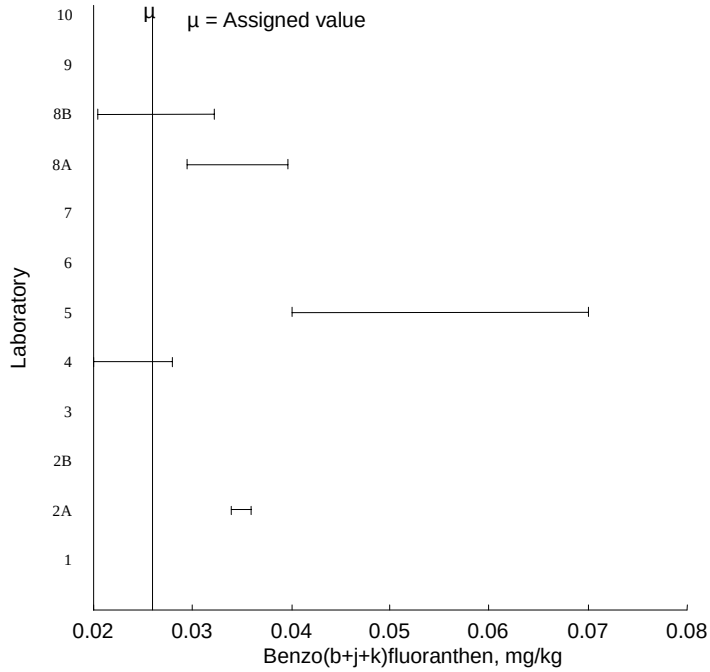
All results including n = 12 Mean = 4.2E2
Std.dev = 93.0
All results excluding n = 12 Mean = 4.2E2
Std.dev = 93.0

Level G



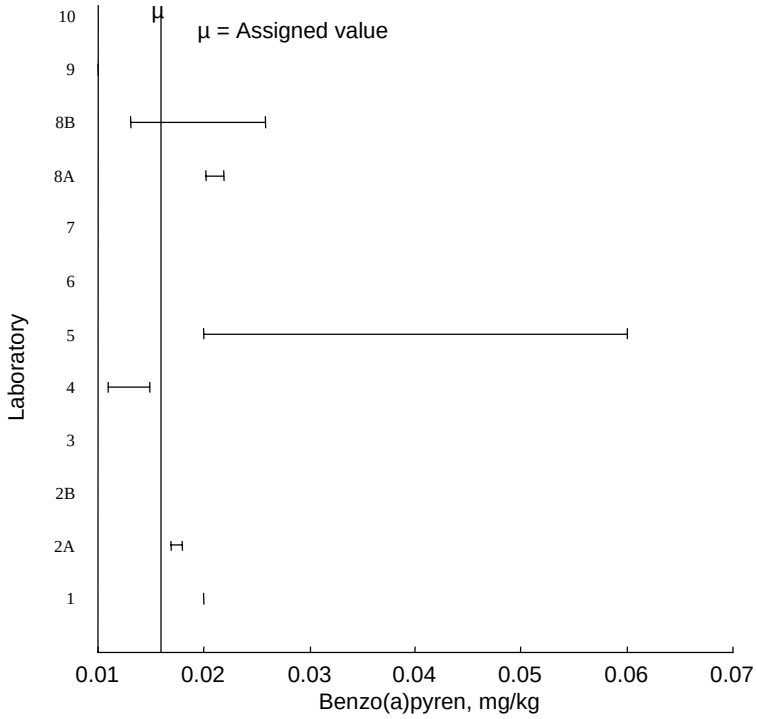
All results including n = 11 Mean = 0.031
Std.dev = 0.027
All results excluding n = 11 Mean = 0.031
Std.dev = 0.027

Level G



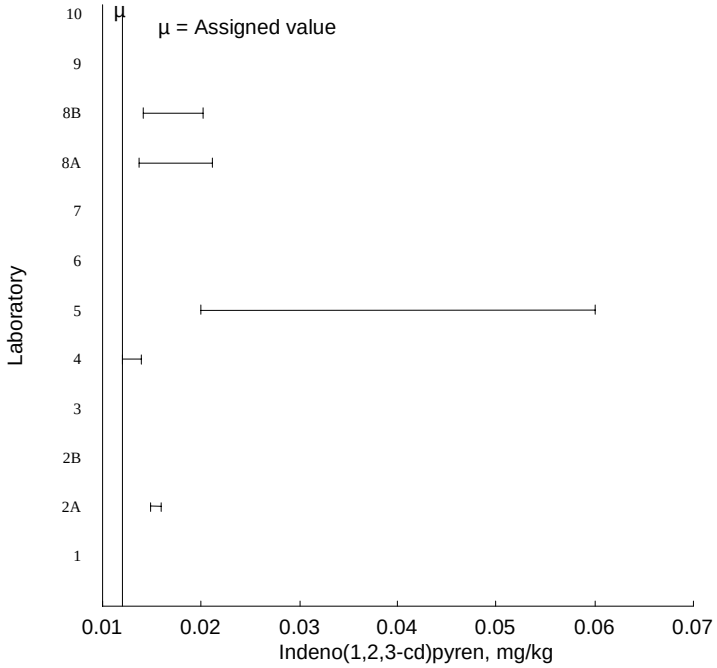
All results including n = 10 Mean = 0.035
Std.dev = 0.014
All results excluding n = 10 Mean = 0.035
Std.dev = 0.014

Level G



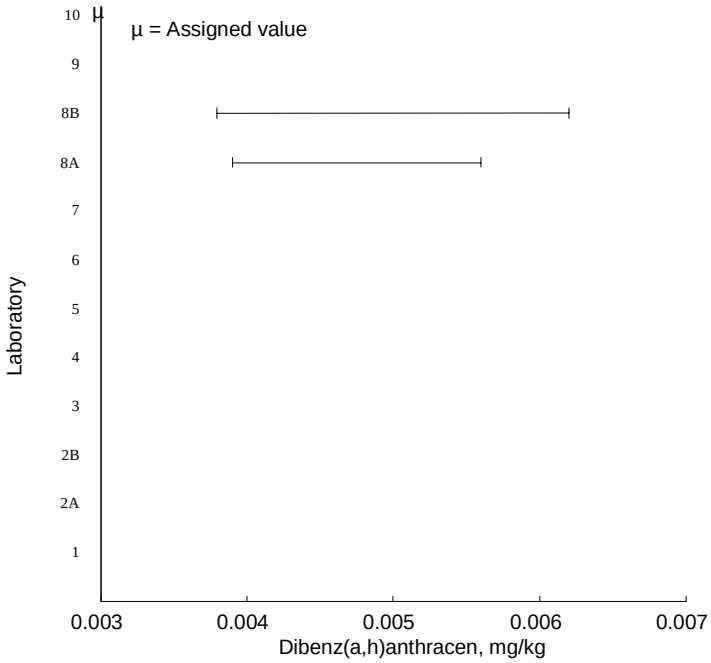
All results including n = 12 Mean = 0.021
Std.dev = 0.013
All results excluding n = 12 Mean = 0.021
Std.dev = 0.013

Level G



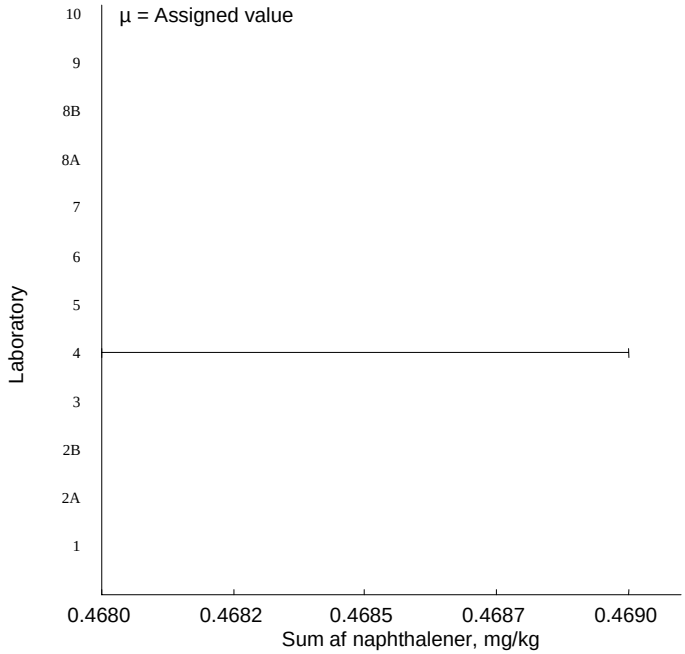
All results including n = 10 Mean = 0.021
Std.dev = 0.014
All results excluding n = 10 Mean = 0.021
Std.dev = 0.014

Level G



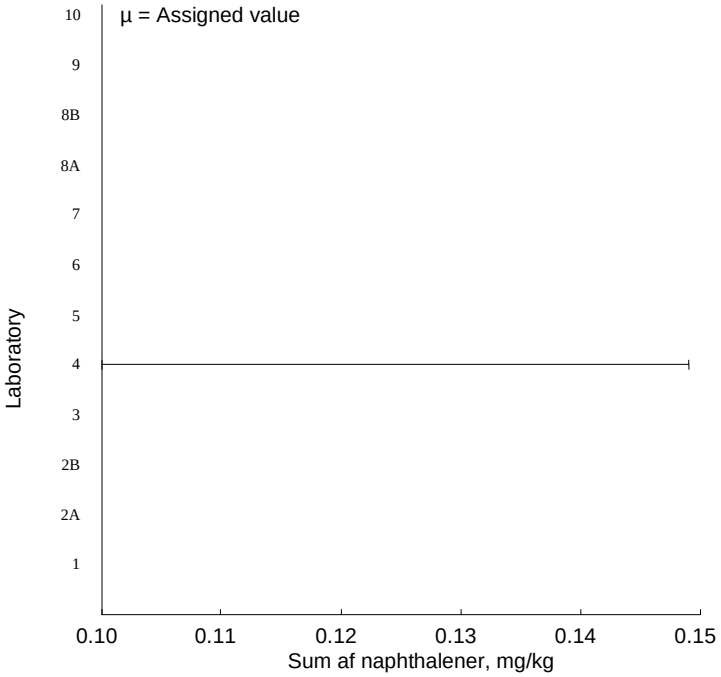
All results including n = 4 Mean = 0.0049
Std.dev = 0.0012
All results excluding n = 4 Mean = 0.0049
Std.dev = 0.0012

Level E



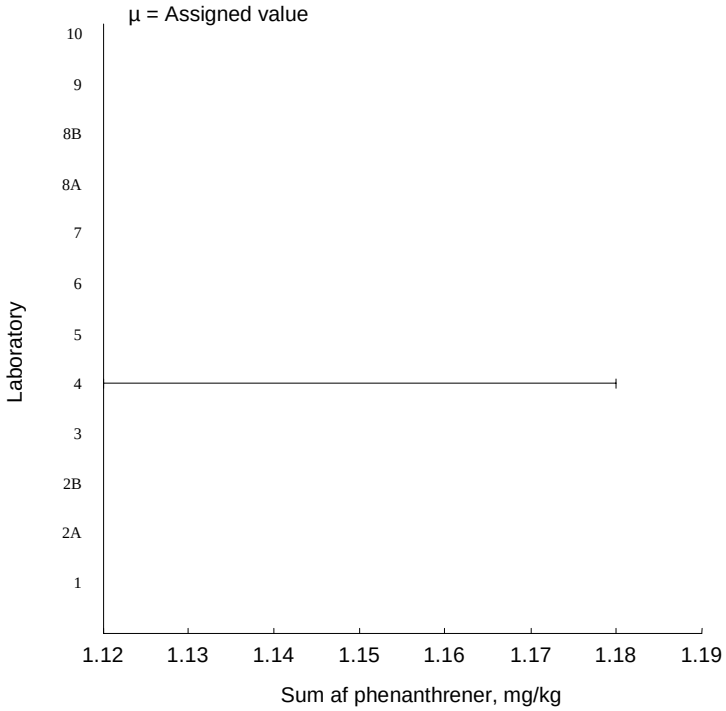
All results including n = 2 Mean = 0.470
Std.dev = 0.001
All results excluding n = 2 Mean = 0.470
Std.dev = 0.001

Level G



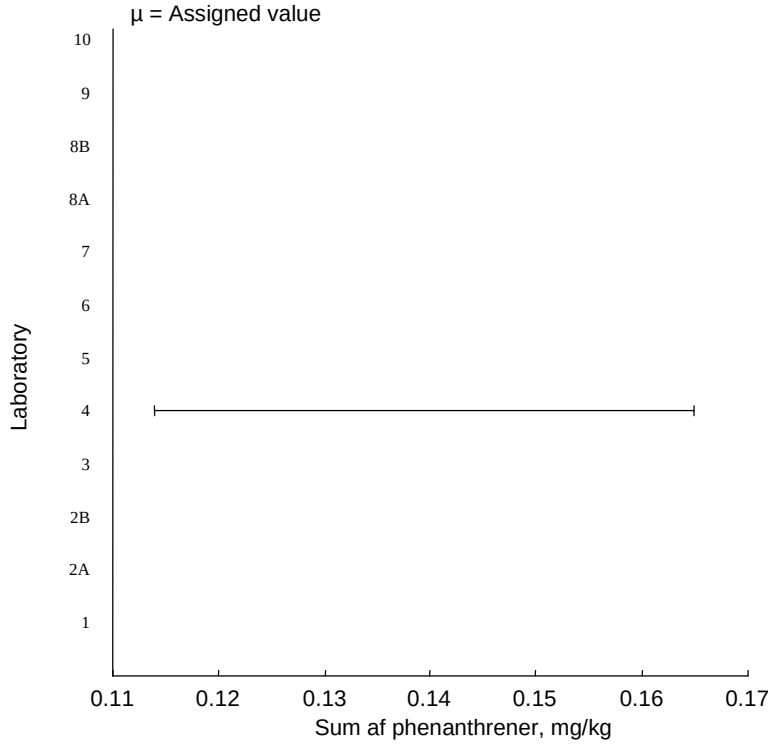
All results including n = 2 Mean = 0.120
Std.dev = 0.035
All results excluding n = 2 Mean = 0.120
Std.dev = 0.035

Level E



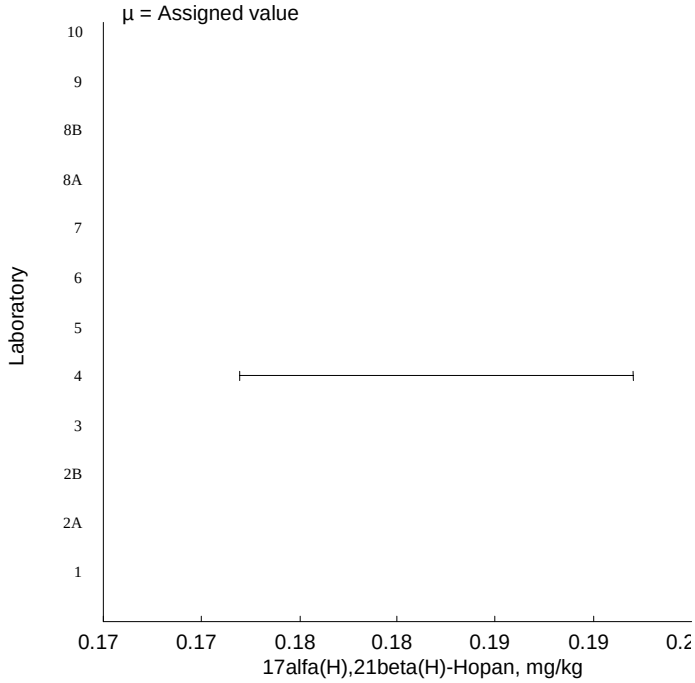
All results including n = 2 Mean = 1.10
Std.dev = 0.04
All results excluding n = 2 Mean = 1.10
Std.dev = 0.04

Level G



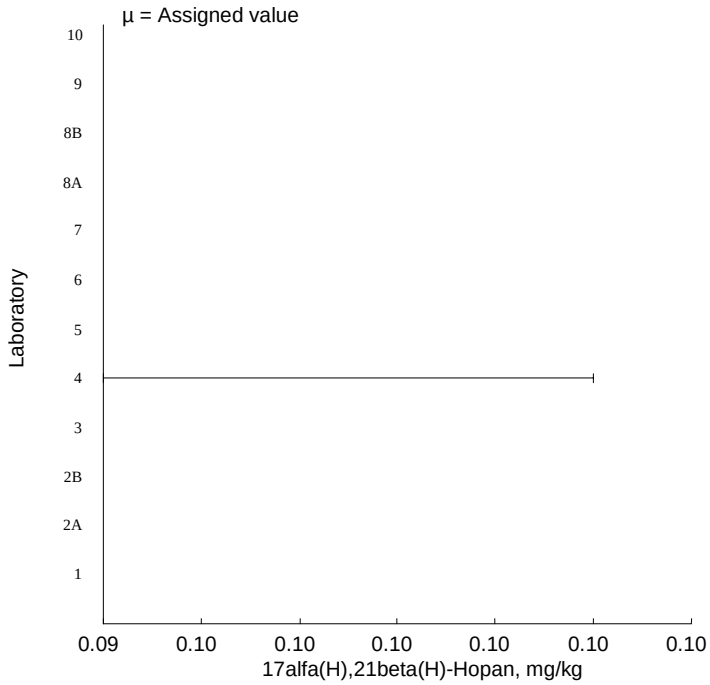
All results including n = 2 Mean = 0.140
Std.dev = 0.036
All results excluding n = 2 Mean = 0.140
Std.dev = 0.036

Level E



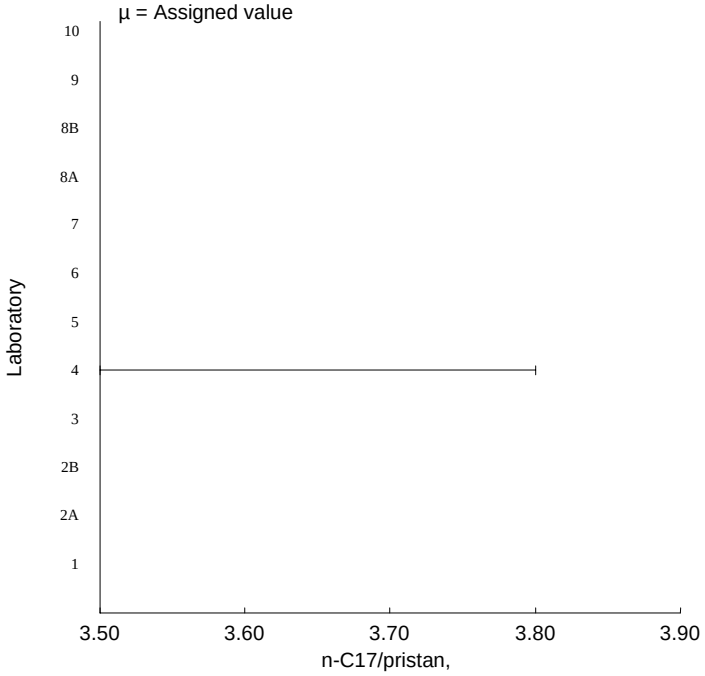
All results including n = 2 Mean = 0.190
Std.dev = 0.014
All results excluding n = 2 Mean = 0.190
Std.dev = 0.014

Level G



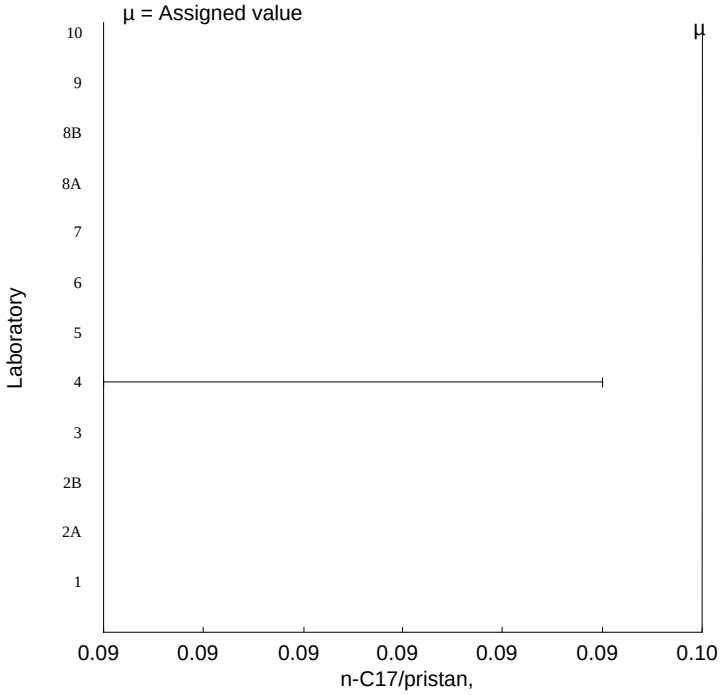
All results including n = 2 Mean = 0.100
Std.dev = 0.004
All results excluding n = 2 Mean = 0.100
Std.dev = 0.004

Level E



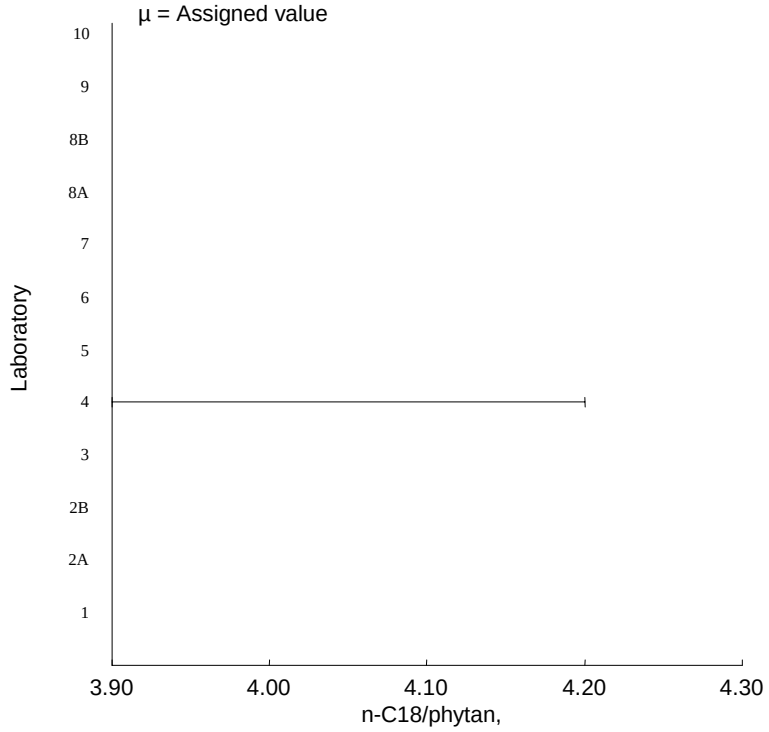
All results including n = 2 Mean = 3.6
Std.dev = 0.2
All results excluding n = 2 Mean = 3.6
Std.dev = 0.2

Level G



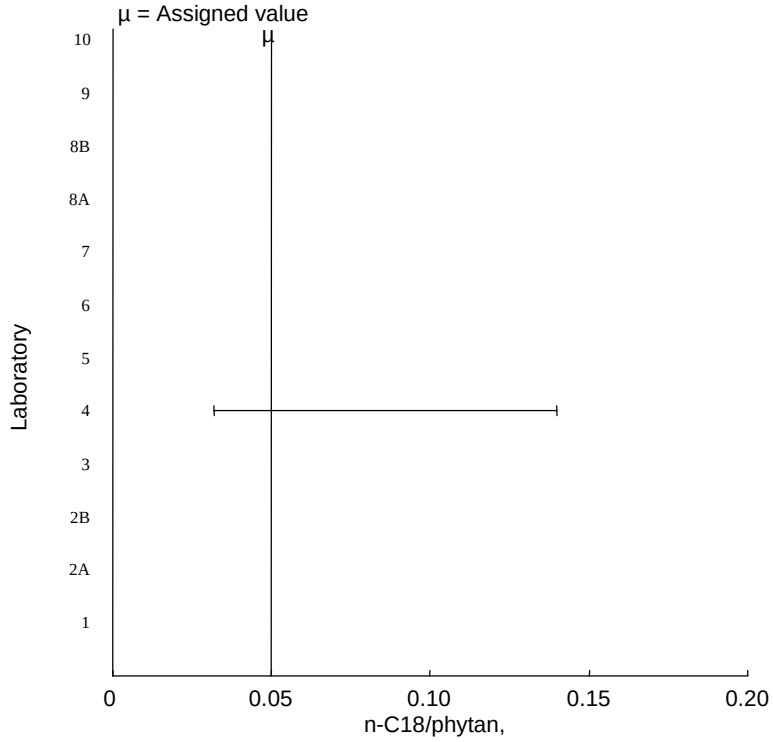
All results including n = 2 Mean = 0.097
Std.dev = 0.004
All results excluding n = 2 Mean = 0.097
Std.dev = 0.004

Level E



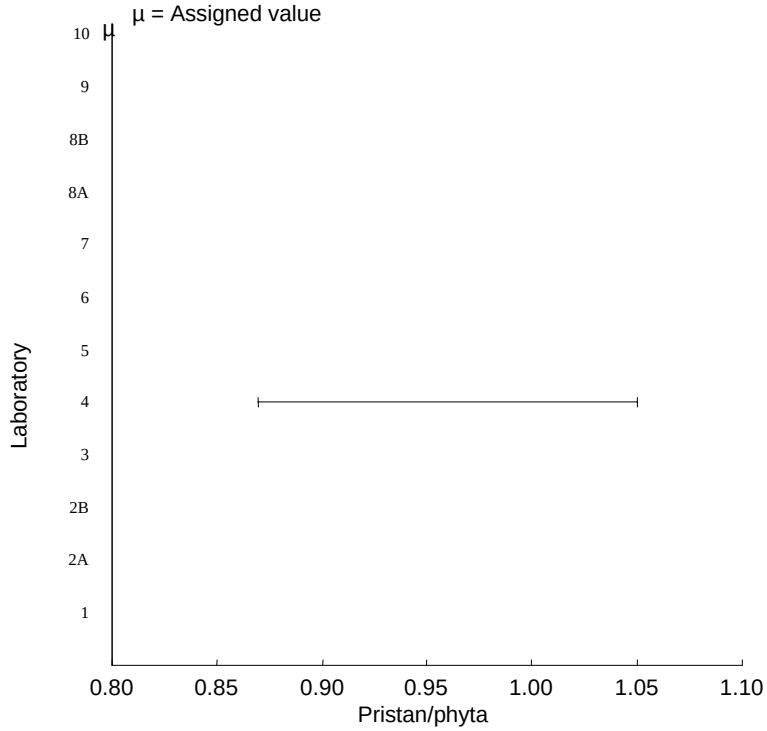
All results including n = 2 Mean = 4.0
Std.dev = 0.2
All results excluding n = 2 Mean = 4.0
Std.dev = 0.2

Level G



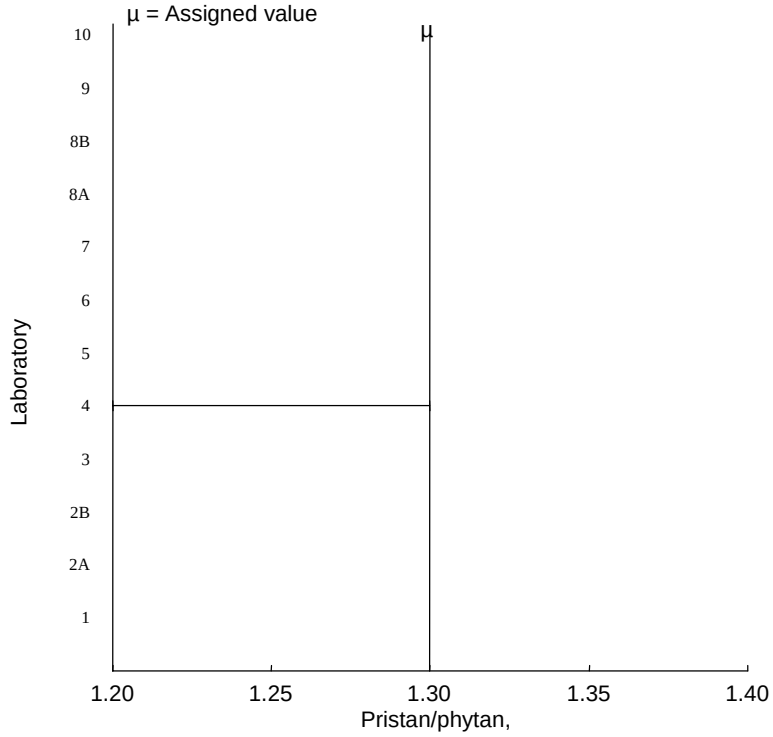
All results including n = 2 Mean = 0.09
Std.dev = 0.08
All results excluding n = 2 Mean = 0.09
Std.dev = 0.08

Level E



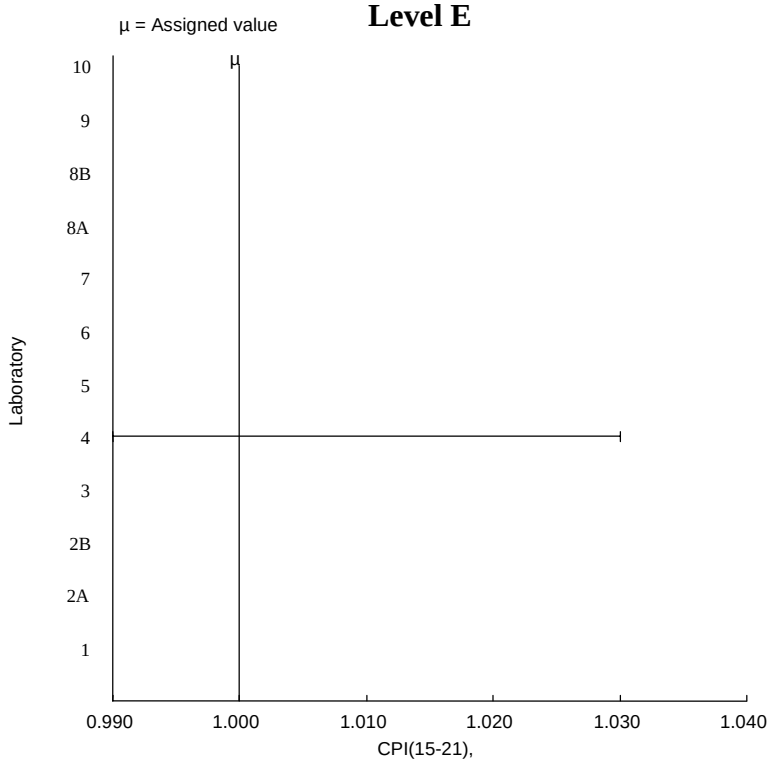
All results including n = 2 Mean = 0.96
Std.dev = 0.13
All results excluding n = 2 Mean = 0.96
Std.dev = 0.13

Level G



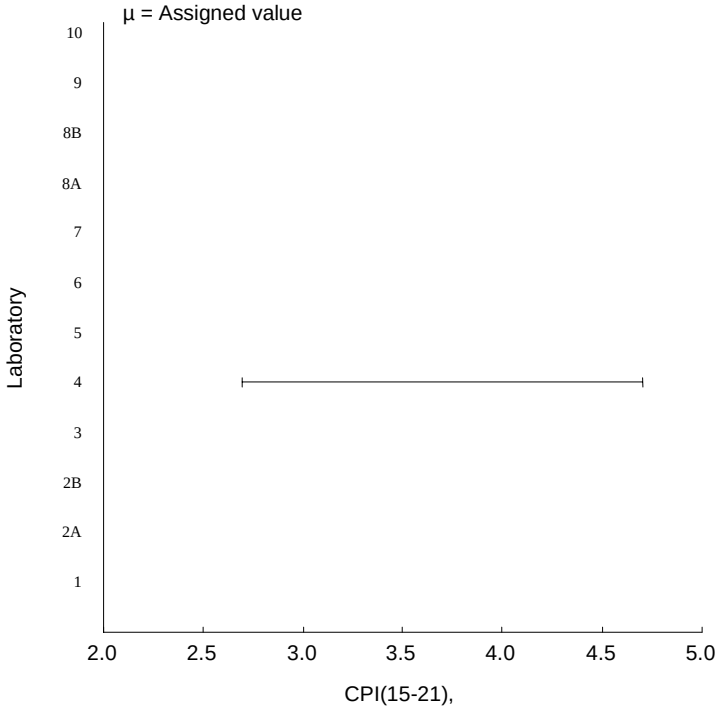
All results including n = 2 Mean = 1.3
Std.dev = 0.1
All results excluding n = 2 Mean = 1.3
Std.dev = 0.1

Level E



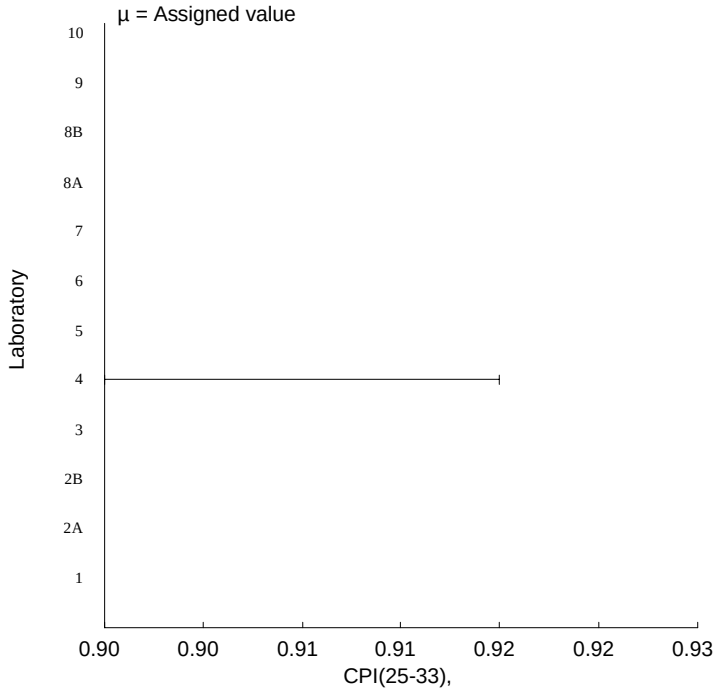
All results including outliers: n = 2 Mean = 1.00
Std.dev = 0.03
All results excluding outliers: n = 2 Mean = 1.00
Std.dev = 0.03

Level G



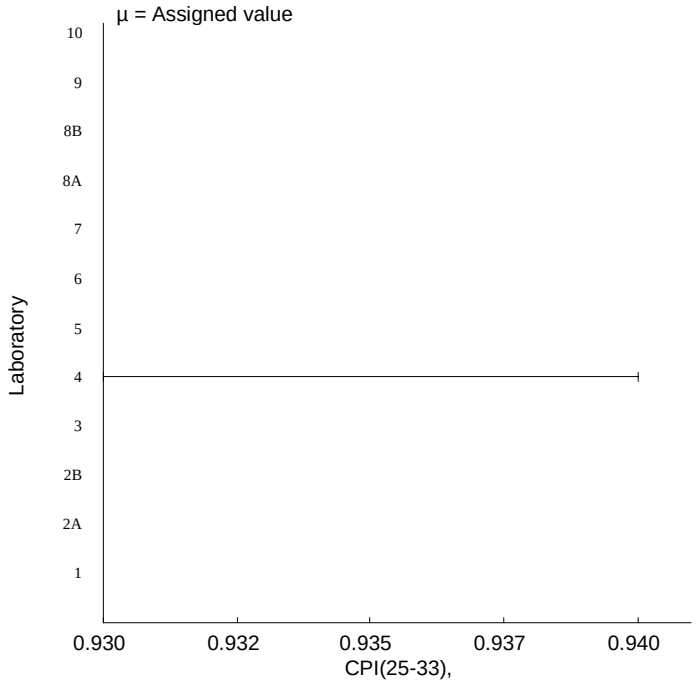
All results including n = 2 Mean = 3.7
Std.dev = 1.4
All results excluding n = 2 Mean = 3.7
Std.dev = 1.4

Level E



All results including n = 2 Mean = 0.91
Std.dev = 0.01
All results excluding n = 2 Mean = 0.91
Std.dev = 0.01

Level G



All results including n = 2 Mean = 0.94
Std.dev = 0.01
All results excluding n = 2 Mean = 0.94
Std.dev = 0.01

A N N E X M

Final procedure - REFLAB Metode 4:2004 (in Danish)

Reflab metode 4:2004
1. udgave
Godkendt: 29-03-2006

Bestemmelse af olieindhold, BTEX og PAH i jord ved gaskromatografi

1 Orientering og anvendelsesområde

Denne metode benyttes til at bestemme indholdet af totalkulbrinter, BTEX og PAH-forbindelser i jord samt indikatorparametre for petrogene kulbrinter.

1.1 BTEX

Enkeltkomponenterne benzen, toluen, ethylbenzen, meta+para-xylen og ortho-xylen omtales samlet som BTEX.

Denne metode omfatter bestemmelse af BTEX ved GC-FID i koncentrationsområdet mellem 0,1 og 3 mg/kg TS og ved GC-MS mellem 0,02 og 3 mg/kg TS.

1.2 Total kulbrinter

Metoden bestemmer indholdet af sammensatte produkter som olie, fuelolie og nogle smøreolier. Det svarer til et kogepunktsinterval fra 80°C til 525°C og begrænses af benzen og n-C_{40}-alkan, tetracontan.

Totalkulbrinter defineres i denne metode som summen af organiske stoffer, der ekstrahereres fra en given jordprøve med acetone/pentan (1:1), samt detekteres med GC-FID.

Meget flygtige forbindelser med kogepunkt under 80 °C medregnes således ikke, da de vil skjules under solventtoppen.

Kulbrinterne beregnes i fire fraktioner som dog rapporteres i tre fraktioner samt som total kulbrinter, som er en sum af de fire fraktioner. Fraktionerne opdeles udfra visse n-alkaners kogepunkt, som beskrevet i Tabel 1-1. Resultaterne angives i analyserapporten som de anførte fraktioner.

Tabel 1-1. Kulbrinte fraktioner.

Fraktion	Indhold	Måleområde [mg/kg TS]
Benzen – C_{10}	Benzen – C_{10}	2,5 -
> C_{10} – C_{25}	> C_{10} – C_{25}	5 -
> C_{25} – C_{40}	>C_{25} – C_{35} + >C_{35} – C_{40} → C_{25} – C_{40}	15 -
Total kulbrinter	Benzen – C_{10} + >C_{10} – C_{25} + >C_{25} – C_{35} + >C_{35} – C_{40} = Benzen – C_{40}	30 - 5000

På basis af mønsteret i gaskromatogrammet og kogepunktet for individuelle n-alkaner kan uddrages det omtrentlige kogepunktområde for mineralolien i en given prøve og der kan uddrages kvalitativ information om forureningens sammensætning.

1.3 PAH

Metoden kan benyttes til bestemmelse af Poly Aromatiske Hydrocarboner (PAH). PAH-forbindelser er komponenter i tjære og i mindre mængder i de tungere olieprodukter.

Metoden kan benyttes til bestemmelse af alle PAH´er i Tabel 1-2.

Metoden er afprøvet på ét laboratorium til alle 16 PAH, men er kun valideret ved interlaboratoriundersøgelse til de 7 forbindelser som kontrolleres i forbindelse med de danske jordkvalitetskrav, der er fastlagt i Vejledning fra Miljøstyrelsen /1/.

Tabel 1-2. PAH-forbindelser.

Afprøvet	Valideret ved inter-laboratorundersøgelse
Naphthalen	
Acenaphthylen	
Acenaphthen	
Fluoren	
Phenanthren	
Anthracen	
Fluoranthen	Fluoranthen
Pyren	
Benz(a)anthracen	
Chrysen/triphenylen	
Benzo(b+j+k)fluoranthener	Benzo(b+j+k)fluoranthener
Benz(a)pyren	Benz(a)pyren
Indeno(1,2,3-cd)pyren	Indeno(1,2,3-cd)pyren
Dibenz(a,h)anthracen	Dibenz(a,h)anthracen
Benzo(ghi)perylen	

Måleområdet er fra 0,005 mg/kg TS til 3 mg/kg TS.

1.4 Indikatorer for petrogene kulbrinter

Petrogene kulbrinter er komponenter, der indgår i mineralolie, og som er karakteristiske for mineralolie. Metoden er afprøvet til bestemmelse af en række petrogene kulbrinter /3/, og de i Tabel 1-3 nævnte er afprøvet ved interlaboratorieundersøgelse.

Tabel 1-3. Petrogene kulbrinter.

Komponent
Sum af naphthalener:
Naphthalen
C_1-naphthalener[1]
C_2-naphthalener[2]
C_3-naphthalener[3]
Sum af phenanthrener:
Phenanthren
C_1-phenanthrener[4]
C_2-phenanthrener[5]
17α(H),21β(H)-Hopan
n-Alkaner[6]
Pristan, phytan

Metoden kan yderligere anvendes til bestemmelse af andre acykliske isoprenoider[7] og hopaner[8].

1.5 Naturlige kulbrinter

Ekstraktionsmetoden og de gaskromatografiske betingelser kan benyttes til bestemmelse af bidrag af naturlige kulbrinter til total kulbrinteindholdet jf. /3/.

[1] methylnaphthalener og andre forbindelser, der detekteres med ionspor 142
[2] dimethylnaphthalener og andre forbindelser, der detekteres med ionspor 156
[3] trimethylnaphthalener og andre forbindelser, der detekteres med ionspor 170
[4] methylphenanthrener og andre forbindelser, der detekteres med ionspor 192
[5] dimethylphenanthrener og andre forbindelser, der detekteres med ionspor 206
[6] n-Alkanerne C_{14}; C_{15}; C_{16}; C_{17}; C_{18}; C_{19}; C_{20}; C_{21}; C_{22}; C_{24}; C_{25}; C_{26}; C_{27}; C_{28}; C_{29}; C_{30}; C_{31}; C_{32}; C_{33} og C_{34}.
[7] Farnesan og nor-pristan
[8] Ts, Tm, 29ab, 31abS og 31abR

Disse omfatter phytosteroler og ulige n-alkaner, der skønnes at stamme fra naturligt forekommende kulbrinter, og som interfererer med total kulbrinteindholdet.

Metoder hertil er ikke afprøvet ved interlaboratorieundersøgelse, og denne metode indeholder alene en vejledning for kvantificering.

2 Reference

"ISO/DIS 16703 Soil Quality – Determination of hydrocarbon content in the range C_{10} - C_{40} by gas chromatography", udkast august 2003.

3 Interferenser

3.1 BTEX

3.1.1 FID
Andre enkeltkomponenter med samme retentionstid kan fejlagtigt identificeres som en af BTEX'erne. F.eks. har cyclohexan og benzen stort set samme retentionstid ved den her anvendte kolonne.

3.1.2 MS
Der er ikke konstateret problemer med interferens på BTEX ved GC-MS.

3.2 Total kulbrinter
Apolære og svagt polære forbindelser f.eks. stammende fra plantemateriale, mosejord eller gammel havbund vil give bidrag til indholdet af totalkulbrinter, og vil interferere på identifikationen af olieproduktet.

Polære fedtstoffer, vegetabilske- og animalske olier der medekstraheres fra en given jordprøve kan give interferens ved kromatografering, men vil være let genkendelige for en erfaren kemiker.

Chlorerede opløsningsmidler samt andre forbindelse, der ikke er rene kulbrinter, vil blive medbestemt i totalkulbrinteindholdet, men detekteres med lavere respons pga. FI-detektoren svagere respons overfor chlor, ilt mm.

3.3 PAH
Mange PAH-forbindelser har identisk molekylvægt samt en struktur og fysisk-kemiske egenskaber, der ligner hinanden meget. Derfor er det vanskeligt fuldstændigt at undgå interferens i bestemmelsen af PAH. Det er derfor af stor vigtighed, at laboratoriet ved GC-MS-bestemmelsen benytter optimale kromatografiske betingelser for at opnå størst mulig separation mellem muligt interfererende forbindelser.

Da forskellige kromatografiske kolonner har forskellig separation af individuelle PAH-forbindelser, og da separationen desuden er stærkt afhængig af den brugte ovntemperaturprogram, er det op til det enkelte laboratorium at sikre mindst mulig interferens i bestemmelserne. I de tilfælde, hvor interferens ikke kan undgås, bør der angives en sum af de individuelle forbindelser samt klart angives, hvilke forbindelser det drejer sig om. De bedst kendte interferenser på normal GC-kolonner er chrysen og triphenylen samt benzo(b)fluoranthen, benzo(j)fluoranthen og benzo(k)fluoranthen. Disse forbindelser angives normalt som en sum af benzo(b+j+k)fluoranthen og chrysen/triphenylen.

4 Princip
En prøve af ca. 60 gram jord ekstraheres ved mekanisk rystning med acetone og pentan i 12 – 16 timer. Herefter tilsættes vand og det organiske lag separeres. En passende mængde af

dette ekstrakt analyseres til bestemmelse af totalkulbrinter ved anvendelse af kapillar gaskromatografi med flammeionisationsdetektion. Kvantificeringen udføres ved at sammenligne det kromatografiske areal fra benzen til n-C_{40}-alkan med nogle specifikke forbindelser. Indholdet af olie opdeles i tre fraktioner efter komponenternes flygtighed. En anden del af ekstraktet kan analyseres for BTEX eller PAH ved kapillar gaskromatografi med massespektrometrisk detektion i SIM-mode. Ekstraktet kan yderligere analyseres for petrogene og naturlige kulbrinter ved kapillar gaskromatografi med massespektrometrisk detektion i Scan-mode.

5 Reagenser og standarder

5.1 Kemikalier

De anvendte kemikalier skal være af analytisk renhedsgrad og velegnede til formålet.

5.1 Acetone

5.2 Pentan

5.3 Vand, vandhanevand eller tilsvarende uden målelige indhold af de forbindelser eller produkter, som skal bestemmes.

5.4 Afprøvning af opløsningsmidler
Der anvendes pentan og acetone af analysekvalitet. Når pentan og acetone modtages på laboratoriet afprøves deres renhed med hensyn til BTEX og PAH. Vandet, der anvendes, afprøves sammen med acetone.

5.4.1 Pentan
Der fyldes en vial med pentan, som analyseres på GC-FID og GC-MS efter metoderne beskrevet i afsnit 9 og 10. Pentan kan godkendes til analyse, når den ikke indeholder BTEX eller PAH i koncentrationer over detektionsgrænsen for hver enkelt komponent.

5.4.2 Acetone og vand
20 mL acetone håndrystes med 20 mL afprøvet pentan (5.4.1) i ca. 1 min. Der tilsættes 30 mL vand, og der rystes 1 min. Der tappes en vial fra pentanfasen, som analyseres på GC-FID og GC-MS efter metoderne beskrevet i afsnit 9 og 10. Acetone og vand kan godkendes til analyse, når den pentan, det er rystet med, ikke indeholder BTEX eller PAH i koncentrationer over detektionsgrænsen for hver enkelt komponent. Hvis der opstår problemer i forhold til dette, afprøves acetone og vand hver for sig.

5.5 Interne standarder:
Monobrombenzen
o-Terphenyl
Squalan
Såfremt der foretages bestemmelse ved GC-MS anvendes yderligere:
Phenanthren-d10
Fluoranthen-d10
Benz(a)pyren-d12

5.6 Standarder til kalibrering:
Der anbefales brug af færdigkøbte ampuller[9] som kalibreringsstandarder og kontrolopløsninger. Følgende stoffer anvendes:

5.6.1 BTEX: benzen, toluen, ethylbenzen, xylener (3 isomere).

5.6.2 n-Alkaner: C_{12}, C_{14}, C_{16}, C_{18}, C_{20}, C_{22}, C_{24}, C_{26}, C_{28}, C_{30}, C_{32}, C_{34}, C_{36} og C_{38}.

[9] Med certifikater.

5.6.3 PAH: Fluoranthen, benzo(b)fluoranthen, benz(a)pyren, indeno(1,2,3-cd)pyren, dibenz(a,h)anthracen og eventuelle andre som laboratoriet ønsker at bestemme kvantitativt.

5.6.4 Petrogene kulbrinter: naphthalen, 1-methylnaphthalen, 2-methylnaphthalen, 2,6-dimethylnaphthalen, 2,3,5-trimethylnaphthalen, phenanthren, 2-methylphenanthren, 3,6-dimethylphenanthren, 17α(H),21β(H)-hopan, pristan, phytan.

5.7 Standarder til kontrol:
Der anbefales brug af færdigkøbte ampuller[9] som kalibreringsstandarder og kontrolopløsninger. Følgende stoffer anvendes:

5.7.1 BTEX: benzen, toluen, ethylbenzen, xylener (3 isomere). Hvis færdigkøbt ampul anvendes skal den være af andet fabrikat end anvendt til kalibrering.

5.7.2 Mineralolie standard.

5.7.3 PAH: Fluoranthen, benzo(b)fluoranthen, benz(a)pyren, indeno(1,2,3-cd)pyren, dibenz(a,h)anthracen og eventuelle andre som laboratoriet ønsker at bestemme kvantitativt. Hvis færdigkøbt ampul anvendes skal den være af andet fabrikat end anvendt til kalibrering.

5.7.4 Fuelolie standard.

5.8 Stamopløsninger af interne standarder:

5.8.1 IS Stamopløsning GC-FID (IS Stam 1, 2 og 3)
Der afvejes 1 g $\pm$ 0,001 g af henholdsvis monobrombenzen, o-terphenyl og squalan til hver sin 100 mL målekolbe. De nøjagtige afvejede mængder noteres. Målekolberne fyldes til mærket med afprøvet pentan (5.4.1). De tre stamopløsninger kaldes henholdsvis *IS Stam 1, 2 og 3*.
Koncentrationen i hver opløsning er 10000 mg/L.

5.8.2 IS Stamopløsning GC-MS (IS-MS)
Der afvejes 0,1 g $\pm$ 0,001 g af henholdsvis phenanthren-d10, fluoranthen-d10 og benz(a)pyren-d12 i samme 100 mL målekolbe. Den nøjagtige afvejede mængde noteres. Målekolben fyldes til mærket med afprøvet pentan (5.4.1).
Koncentrationen i opløsningen *IS-MS* er 1000 mg/L.

5.8.3 Intern standard opløsning (IS-opl.)
En 100 mL målekolbe fyldes halvt med afprøvet pentan (5.4.1). Der udtages med fuldpipette 1 mL $\pm$ 0,01 mL af hver af *IS Stam 1, 2 og 3* (5.8.1) samt 1 mL $\pm$ 0,01 mL af *IS-MS* (5.8.2) som tilsættes ned i pentanen i målekolben. Målekolben fyldes op til mærket med afprøvet pentan og mærkes *IS-opl*.
Koncentrationen i opløsningen er 100 mg/L for interne standarder til FID og 10 mg/L for interne standarder til MS.

5.9 Pentan med intern standard (Pentan IS)
En 2000 mL målekolbe fyldes halvt op med afprøvet pentan (5.4.1). Der tilsættes 1 mL af hver af *IS Stam 1, 2 og 3* (5.8.1) samt 1 mL af *IS-MS* (5.8.2) ned i pentanen i målekolben. Målekolben fyldes op til mærket med afprøvet pentan.
Koncentration i opløsningen er 5 mg/L for de interne standarder til FID og 0,5 mg/L for de interne standarder til MS[10].
Det er vigtigt at Pentan IS (5.9) og IS opl. (5.8.3) er fremstillet ud fra samme IS-Stam (5.8.1) og IS-MS (5.8.2).

[10] Dette gør sig også gældende for alle standarder og kontroller.

5.10 Sekvensblind
Der fyldes en række vials af den til prøverne anvendte pentan IS (5.9). Disse opbevares på køl indtil analysetidspunktet.

5.11 Standard til kalibrering: total kulbrinter og BTEX (STD-opl.)
En 100 mL målekolbe fyldes halvt med afprøvet pentan (5.4.1). Der afpipetteres koncentrerede BTEX- og alkan-standarder (5.6.1 og 5.6.2) til kalibrering til en færdig koncentration på 5 mg/L. Der afpipetteres desuden 5 mL af IS-opl. (5.8.3) over i målekolben. Der fyldes op med afprøvet pentan (5.4.1) til mærket. Den færdige opløsning fordeles på vials uden headspace over væsken. Opbevares på køl indtil analyse.

5.12 Standard til kalibrering: PAH-forbindelser (PAH-STD)
En 200 mL målekolbe fyldes halvt med afprøvet pentan (5.4.1). Der afpipetteres koncentrerede standarder (5.6.3) til kalibrering til en færdig koncentration på 5 mg/L. Der tilsættes desuden 1 mL af IS-MS (5.8.2) over i målekolben. Der fyldes op med afprøvet pentan (5.4.1) til mærket. Den færdige opløsning fordeles på vials uden headspace over væsken. Opbevares på køl indtil analyse.

5.13 Standard til kalibrering: Petrogen kulbrintestandard
En 50 mL målekolbe fyldes halvt op med pentan IS (5.9). Der afpipetteres stamopløsninger af standardene for petrogene kulbrinter (5.6.4) i målekolben sådan at koncentrationerne bliver som anført i Tabel 5-1. Der fyldes op med pentan IS (5.9) til mærket.

Tabel 5-1. Koncentrationer i petrogen kulbrintestandard.

Komponent	Koncentration i Petrogen kulbrintestandard
1- og 2-Methylnaphthalen	10 mg/L
2,6-Dimethylnaphthalen	10 mg/L
2,3,5-Trimethylnaphthalen	10 mg/L
2-Methylphenanthren	10 mg/L
3,6-Dimethylphenanthren	5 mg/L
Pristan og phytan	10 mg/L
17α(H),21β(H)-Hopan	1,0 mg/L

5.14 Kontroloplø sninger

5.14.1 Kontrol total kulbrinter (KNT-opl.)
Stamopløsning knt.:
En ampul af mineral olie (5.7.2) tempereres til stuetemperatur. Der afvejes ca. 0,8 g med 0,001 g nøjagtighed mineral olie i en 100 mL målekolbe. Den nøjagtige vægt noteres. Målekolben fyldes til mærket med afprøvet pentan (5.4.1). Kolben rystes omhyggeligt. Koncentrationen af olien i *Stamopløsning knt*. er ca. 8000 mg/L.

KNT-opl.:
En 100 mL målekolbe fyldes halvt med afprøvet pentan (5.4.1). Der udtages 10 mL $\pm$ 0,1 mL af tempereret *stamopløsning knt*. til 100 mL målekolben. Der afpipetteres desuden 5 mL $\pm$ 0,05 mL af *IS-opl*. (5.8.3) over målekolben. Der fyldes op med afprøvet pentan til mærket. Koncentrationen af *KNT-opl* er ca. 800 mg/L, koncentrationen skal beregnes nøjagtigt, før indsættelse i kontrolkort. *KNT-opl.* hældes på vials uden headspace over væsken. Opbevares på køl indtil analyse.

5.14.2 Kontrol BTEX (BTEX-knt.)
En 100 mL målekolbe fyldes halvt op med afprøvet pentan (5.4.1). Der afpipetteres et volumen af BTEX ampul til kontrol (5.7.1) til målekolben, således at koncentrationen bliver 1,0 mg/L pr. enkeltkomponent. Der afpipetteres desuden 5 mL $\pm$ 0,05 mL af *IS-opl*. (5.8.3) over i målekolben. Der fyldes op med afprøvet pentan til mærket. *BTEX-knt*. hældes på vials uden headspace over væsken. Opbevares på køl indtil analyse.

5.14.3 Kontrol PAH (PAH-knt.)
En 100 mL målekolbe fyldes halvt op med afprøvet pentan (5.4.1). Der afpipetteres et volumen af PAH ampul til kontrol (5.7.3) til målekolben, således at koncentrationen bliver 1,0 mg/L pr. enkeltkomponent. Der tilsættes desuden 500 µL ± 5 µL af *IS-MS* (5.8.2) over i 100 mL målekolben. Der fyldes op med afprøvet pentan til mærket. *PAH-knt*. hældes på vials uden headspace over væsken. Opbevares på køl indtil analyse.

5.14.4 Kontrol petrogene kulbrinter
Fuelolieopløsning
Afvej 100 mg fuelolie (5.7.4) i en 100 mL målekolbe. Fyld op til mærket med pentan IS (5.9). Koncentrationen er 1000 mg/L.

6 Apparatur

6.1 Prøveglas

Der skal anvendes membranglas[11]. Et glas volumen på 100 mL er passende til både jord, opløsningsmidler samt plads til omrystning. Det anbefales at anvende 100 mL Duranglas.

Glasudstyr rengøres[12] ved normal opvask efterfulgt af varmebehandling ved 400-500 °C i min. 2 timer. Renheden af glasvarerne skal være dokumenteret.

Der skal en ny membran i glassene imellem hver anvendelse. Membranen skal være teflonbelagt på indersiden.

Det er en fordel at kende glassets vægt, før disse sendes ud til kunden. Således kan denne glasvægt subtraheres fra vægten af det fyldte glas.

6.2 Rysteapparat

Et apparat der anvendes til at ryste prøverne i membranglassene. Det anbefales, at placere glassene i vandret liggende position, mens de rystes, således at de rystes i samme retning som centeraksen af glassene, altså på langs. Det er vigtigt, at anvende kraftig rystning for at opnå ligevægt inden for den angivne ekstraktionstid. Der anbefales en amplitude på 7 cm og en rystefrekvens på 200 slag pr. minut. Andre specifikationer kan være tilfredsstillende, men dette skal valideres af det enkelte laboratorium inden brug.

6.3 Centrifuge

En centrifuge til separation af faserne efter ekstraktion. Det er hensigtsmæssigt, hvis centrifugen har mulighed for at centrifugere membranglassene for at undgå overførsel af prøverne til nyt glasudstyr.

6.4 Gaskromatografer

6.4.1 GC-FID

Gaskromatografisk system med kapillarkolonne og flammeionisationsdetektor (FID). FID er karakteristisk ved, at alle kulbrinter stort set giver samme respons, hvilket er essentielt for metodens anvendelighed. GC-system med temperatur- og trykstyring, kapillarkolonne og splitless injektion anbefales. Et datasystem til beregning af kromatografiske arealer ved brug af tvungen basislinieprojektion, og som er i stand til at gemme og reintegrere kromatografiske data skal benyttes.

[11] Forsynet med et låg, hvori der sidder et septum, som tillader at opløsningsmidler injiceres igennem membranen.
[12] Med mindre der anvendes engangsglasvarer.

6.4.2 GC-MS

Et gaskromatografisk system med kapillarkolonne og massespektrometrisk detektion (MS). MS er karakteristisk ved at detektere ioner i forhold til deres masse/ladningsforhold (m/z), hvilket gør detektionen mere specifik i forhold til enkeltstoffer.

GC-system bør have temperaturstyring, splitless injektion og anvende kapillarkolonne. Trykstyring af bæregassen anbefales for bedre reproducerbarhed.

Massespektrometret skal have mulighed for anvendelse af SIM (single ion monitoring) og Scan (scaning over alle ioner) samt være tilkoblet et datasystem, der tillader dataopsamling og lagring af alle data, der optages i det kromatografiske forløb. Datasystemet skal kunne søge datafilerne for ioner med specifikke masser og skal kunne udskrive ionresponset i forhold til tiden eller scan-nummer. Datasystemet skal kunne integrere såvel som reintegrere signalet for ethvert udtrukket ionspor.

6.5 GC-kolonne

Følgende kolonnedimensioner anbefales: 30 m, 0,25 mm ID og 0,25 μm filmtykkelse, 5 % phenylmethylsiloxan. Kolonner med lav blødning og mulighed for høje temperaturer anbefales.

Kolonnes skal leve op til kravene om kromatografisk ydeevne (9.1.2).

7 Prøvetagning og opbevaring

7.1 Prøven

7.1.1 Prøveudtagning

Der henvises til Miljøstyrelsen: Vejledning om prøveudtagning og analyse af jord /3/.

Der udtages 60 g jord, som hurtigt overføres til et membranglas (6.1), der lukkes umiddelbart herefter. Det er vigtigt at sikre, at glaskanten og gevindet er fri for jordpartikler, for at sikre en tæt lukning af membranglasset. Prøveudtagningskeen skal have en diameter, som er mindre end åbningen af membranglasset for at forhindre partikler på glaskant og gevind.

Membranglasset må maksimalt fyldes halvt op for at tillade tilsætning af opløsningsmiddel og vand, og for at sikre tilfredsstillende bevægelser i forbindelse med ekstraktionen.

Der skal udtages en parallel prøve til bestemmelse af tørstof. Hertil kan enhver tætsluttende emballage benyttes. Tørstof bestemmes i henhold til DS 204:1980, idet der tages en større mængde jord i anvendelse: 10-20 g.

7.1.2 Forholdsregler

Jordprøven skal normalt ankomme til laboratoriet i membranglas som beskrevet i 7.1.1.

Hvis prøver modtages i anden emballage end membranglas, skal dette opgives på analysecertifikatet, idet tab af flygtige forbindelser kan forventes i forbindelse med prøvehåndteringen.
Hvis mængden af jordprøve er for lille, under 30 g, skal det kommenteres på analysecertifikatet. Om nødvendigt skal detektionsgrænsen hæves.

Hvis prøven er på mere end 100 g, skal beholderen åbnes og overskydende jord fjernes, således at der gøres plads til opløsningsmidler samt sikres plads til optimal omrystning. Dette skal rapporteres sammen med resultaterne.

7.1.3 Opbevaring

Prøven skal opbevares ved ca. 4 °C i mørke. Prøven skal transporteres til laboratoriet så hurtigt som muligt og inden for et døgn efter udtagning.

8 Procedure

Ekstraktion af prøverne skal påbegyndes indenfor et døgn efter modtagelse på laboratoriet.

8.1 Metodeblind

Der udrystes mindst et prøveglas om dagen, præcis som om det var en prøve (8.2.2 - 8.2.4). Pentanen aftappes og analyseres som en prøve. Denne må ikke give indhold over detektionsgrænsen for de enkelte parametre.

8.2 Ekstraktion

8.2.1 Afvejning

Det halvt fyldte membranglas vejes og mængden af jord bestemmes ved at subtrahere glasvægten. Hvis glasvægten ikke kendes, vejes den tomme flaske efter ekstraktion, rengøring og tørring. Det er en fordel, at kunden anvender forvejede glas, jvf. 6.1.

Hvis prøver modtages i en anden type beholder, afvejes der 60 g prøve i et 100 mL membranglas. Det skal sikres ved homogenisering at den afvejede prøve repræsenterer den samlede prøve, og der udtages delprøver jævnt fordelt over den totale prøve.

8.2.2 Tilsætning af acetone/pentan

Der injiceres 20 mL af den afprøvede acetone (5.4.2) til prøven gennem membranen i låget. Ryst glasset kort i hånden. Injicer 20 mL pentan med intern standard (5.9) til prøven gennem membranen. Skru låget af og skift membranen. Dette sikrer, at glasset er helt tæt under udrystning. Ryst glasset kraftigt i hånden, indtil en ensartet suspension er nået[13].

8.2.3 Rystning

Glassene lægges ned på langs på rysteapparatet og spændes fast. Rysteapparatet indstilles på en rystefrekvens 200 slag pr. min. med en amplitude på 7 cm. Prøverne rystes i 12 til 16 timer. Derefter tages de af rysteapparatet og tappes umiddelbart herefter.

8.2.4 Aftapning

Når prøverne er taget af rysteapparatet tilsættes 30 mL vand (5.4.2). Prøverne rystes 1 min. og henstilles et kort øjeblik. Ved mange prøver dannes en fri klar pentanfase øverst i glasset, denne kan umiddelbart tappes i vials. I andre tilfælde kan det være nødvendigt at centrifugere glasset for at få faserne til at adskille.

Der aftappes det antal vials, der skal benyttes til analysen[14] samt en ekstra til opbevaring. Vials opbevares på køl indtil analysetidspunktet.

9 Gaskromatografisk bestemmelse – total kulbrinter og BTEX ved GC-FID

9.1 Klargøring og kalibrering af GC-FID

9.1.1 Klargøring/opstart af GC

Gaskromatografen skal være klargjort og vedligeholdt før opstart af prøvesekvens. Kolonnen skal opretholde tilfredsstillende adskillelse af enkeltkomponenter (se krav under metode/betingelser, 9.1.2), samt have minimal kolonne blødning.

9.1.2 Metode/betingelser

Der skal vælges betingelser, så der opnås en tilfredsstillende kromatografering af hele området fra benzen til n-alkan C_{40}.

Kravene til ydeevne er:

[13] For visse jordtyper samt referencematerialer kan det være nødvendigt at tilsætte ekstra acetone eller vand for at opnå suspension.
[14] Afhængigt af antal analyseparametre.

- Der skal kunne opnås ensartet respons for de enkelte n-alkaner i hele det kromatografiske område. Enkelttoppene skal have en pæn kromatografisk form. Bedømmes visuelt.

- Der skal være basislinieseparation for n-alkan C_{17} og pristan.

- For hver fraktion ($>C_{10} – C_{25}$, $>C_{25} – C_{35}$, $>C_{35} – C_{40}$) skal det laveste respons udgøre mindst 2/3 af det største.

- Der må ikke være uhensigtsmæssig diskriminering af tungere forbindelser: arealet af C_{40} skal udgøre mindst 60% af arealet for C_{20}.

I tabel 9-1 ses et eksempel på GC-betingelser, som kan anvendes.

Tabel 9-1. Eksempel på GC-betingelser.

Betingelser	GC-FID
Injektionsbetingelser	350 °C Tryk 11,7 psi. Splitless-tid 1,0 min. Helium som bæregas.
Ovnprogram	Starttemp 35 °C. Starttemp holdes 3 min, herefter 15 °C/min til 315 °C. Sluttemp holdes 18 min.
Kolonne	HP5 MS 30.0 meter 250 µm ID 0,25 µm filmtykkelse. Flow 1,0 ml/min
Detektor	Temperatur 315 °C Hydrogen 30 ml/min. Luft 400 ml/min. Makeup 30 ml/min.

9.1.3 Sekvens/prøveserie

Det anbefales at analysere en *sekvensblind (5.10),* en *STD-opl*. (5.10), en *KNT-opl.* (5.14.1) og en *BTEX-knt*[15].(5.14.2) først og sidst i hver prøveserie. Desuden en sekvensblind efter 10 prøver. Der er erfaring for, at en sekvens ikke bør være længere end 20 prøver af hensyn til GC'ens performance. Der skal for hver serie ekstraktioner analyseres en *metodeblind (8.1)*.

9.1.4 Kalibrering og kontrol

Der anvendes ét-punkt kontrol af kalibrering ved daglig analyse. Når metoden anvendes første gang samt når kolonnetype, apparat eller operatør skiftes udføres en basiskalibrering med mindst fem forskellige koncentrationer af kalibreringsopløsning.

9.1.4.1 Total kulbrinter

Det kontrolleres, at:

- der ikke er megen kolonneblødning eller overslæb på blindprøverne.

- forholdet af C_{40}/C_{20} i standarden (*STD-opl*. (5.11)) er mindst 60%.

[15] Kun nødvendigt hvis der skal kvantificeres BTEX på prøverne.

- indholdet i kontrolprøven (*KNT-opl.* (5.14.1)) ligger indenfor kontrolgrænserne i laboratoriets kontrolkort. Kontrolgrænserne må maksimalt være fra 80% - 120% af nominel værdi[16].

9.1.4.2 BTEX på GC-FID
Det kontrolleres, at:

- der ikke er indhold af BTEX i blindprøverne (5.10 og 8.1) højere end detektionsgrænsen.

- arealet af de enkelte BTEX'er i standarden (*STD-opl*. (5.10)) er fornuftige i forhold til hinanden. Arealet af toluen ≅ ethylbenzen ≅ ½*m-p-xylen ≅ o-xylen, benzen ned til 80% af toluen/ethylbenzen/o-xylen.

- indholdet i kontrolprøven *BTEX-knt.*(5.14.2) ligger indenfor kontrolgrænserne i laboratoriets kontrolkort. Kontrolgrænserne må maksimalt være fra 80-120% af nominel værdi.

9.2 Resultater

9.2.1 Beregning

9.2.1.1 Total kulbrinter
Retentionstiden for benzen, C_{10}, C_{25}, C_{35} og C_{40} i standarden *(STD-opl*. (5.10)) findes. Disse tider plus 0,2 min[17] benyttes til at opdele kromatogrammet af prøver og blindprøver i fraktioner.

Responset af en given prøve fratrækkes metodeblind (8.1), som er fratruklet arealet af intern standard i metodeblinden, og arealerne af de interne standarder i prøven inden koncentrationen beregnes. Dette gøres for de enkelte fraktioner.

Indholdet i prøverne beregnes efter følgende formel.

$$Indhold\ [mg/kg\ TS] = \frac{(A_{frak.} / A_{ISfrak.}) * C_{std} * V_{ext} * 100}{(A_{std.} / A_{ISstd.}) * m * TS\%}$$

Hvor,
$A_{frak.}$: Arealet for den pågældende fraktion.
$A_{IS\ frak.}$: Arealet for den interne standard i pågældende fraktion.
$A_{std.}$: Summen af arealet for de n-alkaner i standarden, der hører til pågældende fraktion, se Tabel 9-2.
$A_{IS\ std.}$: Arealet for den tilsvarende interne standard i standarden.
$C_{std.}$: Koncentrationen af standarden i mg/L
V_{ext} : Volumen af ekstraktionsmiddel i mL
m : Prøvens vægt i gram
TS % : Procent tørstof

Resultater opgives med to betydende cifre. I koncentrationsområdet op til 5 gange detektionsgrænsen dog kun 1 betydende ciffer.

Tabel 9-2. Beregning af de enkelte fraktioner.

Beregning af fraktioner				
Beregnes som total-arealet	Beregnes overfor sum-arealet af	Beregnes i forhold til intern standard	Opgives som	Totalindholdet [mg/kg TS]:
Benzen – C_{10}	Toluen	monobrombenzen	benzen – C_{10}	fra benzen til og med C_{10}

[16] Beregnet udfra den nøjagtige afvejede mængde.
[17] Benzen minus 0,2 min.

> C_{10} – C_{25}	C_{12} + C_{16} +C_{20} +C_{24}	o-terphenyl	> C_{10} – C_{25}	fra C_{10} til og med C_{25}
> C_{25} – C_{35}	C_{28} + C_{30} + C_{32} +C_{34}	o-terphenyl	>C_{25} – C_{40}	fra C_{25} til og med C_{35} summeret med fra C_{35} til og med C_{40}
> C_{35} – C_{40}	C_{36} + C_{38}	o-terphenyl		
			Total kulbrinter benzen – C_{40}	Fra og med benzen til og med C_{10} summeret med fra C_{10} til og med C_{25}, fra C_{25} til og med C_{35} og fra C_{35} til og med C_{40}

Hvis der forekommer interferens på o-terphenyl, således at dens areal afviger mere end 20% i forhold til det gennemsnitlige areal for o-terphenyl i sekvensblind, beregnes i forhold til squalan.

9.2.1.2 BTEX på GC-FID

BTEX'ernes retentionstider identificeres i standardkromatogrammet (*STD-opl*. (5.10)). BTEX i prøverne integreres udfra retentionstiden af standarden +/- 0,2 min. Arealet for den enkelte BTEX fratrækkes eventuelt blindindhold (8.1).

Indholdet af enkeltkomponenter beregnes efter følgende formel:

$$Indhold\ [mg/kg\ TS] = \frac{(A_{komp.} / A_{ISpr.}) * C_{std} * V_{ext} * 100}{(A_{std.} / A_{ISstd.}) * m * TS\%}$$

Hvor,

$A_{komp.}$: arealet for den enkelte komponent.
$A_{IS\ pr.}$: arealet for interne standard (monobrombenzen) i prøven.
$A_{std.}$: arealet for samme komponent i standarden.
$A_{IS\ std.}$: arealet for intern standard (monobrombenzen) i standarden.
$C_{std.}$: koncentrationen af standarden i mg/L
V_{ext} : volumen af ekstraktionsmiddel i mL
m : prøvens vægt i gram
TS % : procent tørstof

Resultater opgives med to betydende cifre.

10 Gaskromatografisk bestemmelse – PAH og BTEX ved GC-MS SIM

10.1 Klargøring og kalibrering af GC-MS

10.1.1 Klargøring/opstart af GC

GC vedligeholdes og klargøres som i afsnit 9.1.1. Kolonnen skal opretholde tilfredsstillende adskillelse af enkeltkomponenter[18].

10.1.2 Metode/betingelser

I tabel 10-1 ses et eksempel på GC-MS betingelser, som kan anvendes til bestemmelse af PAH og BTEX ved GC-MS.

Tabel 10-1. Eksempel på GC-MS betingelser.

[18] Kontrolleres let ved adskillelse af indeno(1,2,3-cd)pyren og dibenz(ah)anthracen

Betingelser	GC-MS
Injektionsbetingelser	300 °C Tryk 6,77 psi. Splitless-tid 0,30 min. Helium som bæregas.
Ovnprogram	Starttemp 35 °C. Starttemp holdes 3 min, herefter 15 °C/min til 315 °C. Sluttemp holdes 8 min
Kolonne	HP5 MS 30.0 meter 250 µm ID 0,25 µm filmtykkelse. Flow 1,0 ml/min
Detektor	Electron Impact Mode

10.1.3 Sekvensopbygning

10.1.3.1 BTEX på MS
Det anbefales at analysere en metodeblind (8.1), en *STD-opl*. (5.10) og en *BTEX-knt*. (5.14.2) først og sidst i hver prøveserie. Desuden en sekvensblind (5.10) og en *BTEX-knt*. (5.14.2) efter hver 10 prøver.

10.1.3.2 PAH på MS
Det anbefales at analysere en metodeblind (8.1), en *PAH-std*. (5.12) og en *PAH-knt.* (5.14.3) først og sidst i hver prøveserie. Desuden en sekvensblind (5.10) og en *PAH-knt.* (5.14.3) efter hver 10 prøver.

10.1.4 Kalibrering og kontrol
Kvantificeringsdelen i MS skal opdateres i forhold til standard (*std-opl.(5.10)/PAH-std.(5.12))*, således at retentionstider og forholdet mellem target og qualifierion passer i forhold til den aktuelle standard.

Det kontrolleres, at:

- der ikke er indhold af BTEX/PAH i blindprøven højere end detektionsgrænsen (sekvensblind 5.10).

- indholdet i kontrolprøven (*BTEX-knt.*(5.14.2)/*PAH-knt.* (5.14.3) ligger indenfor kontrolgrænserne i laboratoriets kontrolkort. Kontrolgrænserne må maksimalt være fra 80-120% af nominel værdi.

10.2 Resultater

10.2.1 Beregning
PAH/BTEX i prøverne integreres udfra retentionstiden af standarden. Det kontrolleres at target/qualifierion forholdet er tilsvarende forholdet i standarden, normalt 80-120%. Dette kan dog fraviges specielt i nærheden af detektionsgrænsen, hvor en visuel vurdering kan godtages.

Arealet for den enkelte PAH/BTEX fratrækkes eventuelt blindindhold (8.1).

Indholdet af enkeltkomponenter beregnes efter følgende formel:

$$Indhold\ [mg/kg\ TS] = \frac{(A_{komp.} / A_{ISpr.}) * C_{std} * V_{ext} * 100}{(A_{std.} / A_{ISstd.}) * m * TS\%}$$

Hvor;

$A_{komp.}$: arealet for den enkelte komponent.
$A_{IS\ pr}$: arealet for den interne standard i prøven.
$A_{std.}$: arealet for samme komponent i standarden.
$A_{IS\ std.}$: arealet for den interne standard i standarden.
$C_{std.}$: koncentrationen af standarden i mg/L
V_{ext} : volumen af ekstraktionsmiddel i mL
m : prøvens vægt i gram
TS % : procent tørstof

Alle BTEX beregnes overfor monobrombenzen som intern standard. I Tabel 10-2 kan det ses hvilken intern standard de enkelte PAH'er beregnes overfor.

Tabel 10-2. Interne standarder til PAH-MS.

Intern standard	Phenanthren-d10	Flouranthen-d10	Benz(a)pyren-d12
PAH-forbindelser	Naphtalen Acenaptylen Acenaphten Fluoren Phenanthren Anthracen	Fluoranthen Pyren Benz(a)anthracen Chrysen/triphenylen	Benzo(b+j+k)fluoranthen Benz(a)pyren Indeno(1,2,3-cd)pyren Dibenz(a,h)anthracen Benzo(ghi)perylen

Resultater opgives med to betydende cifre.

11 Gaskromatografisk bestemmelse – petrogene kulbrinter ved GC-MS-Scan

11.1 Klargøring og kalibrering af GC-MS

11.1.1 Klargøring/opstart af GC

GC vedligeholdes og klargøres som i afsnit 9.1.1. Kolonnen skal opretholde tilfredsstillende adskillelse af enkeltkomponenter[19].

11.1.2 Metode/betingelser

I Tabel 11-1 ses et eksempel på GC-MS betingelser, som kan anvendes til bestemmelse af petrogene kulbrinter.

Tabel 11-1. Eksempel på GC-MS betingelser.

Betingelser	GC-MS
Injektionsbetingelser	300 °C Tryk 6,77 psi. Splitless-tid 0,30 min. Helium som bæregas.
Ovnprogram	Starttemp 35 °C. Starttemp holdes 3 min, herefter 15 °C/min til 315 °C. Sluttemp holdes 8 min
Kolonne	HP5 MS 30.0 meter 250 µm ID 0,25 µm filmtykkelse. Flow 1,0 ml/min
Detektor	HP standard, scan ion 35 m/z – 500 m/z

[19] Kontrolleres let ved adskillelse af indeno(1,2,3-cd)pyren og dibenz(ah)anthracen

11.1.3 Sekvensopbygning

11.1.3.1 Petrogen kulbrintestandard
Det anbefales at analysere en metodeblind (8.1), en *std. opl.* (5.10) en *petrogen kulbrintestandard* (5.13) og fuelolieopløsning (5.14.4) først og sidst i hver prøveserie. Desuden en sekvensblind (5.10) og en *fuelolieopløsning* (5.14.4) efter hver 10 prøver.

11.1.4 Kalibrering og kontrol
Kvantificeringsdelen i MS skal opdateres i forhold til standard (*std-opl.5.10/Petrogen kulbrintestandard. 5.13)*, således at retentionstider passer i forhold til den aktuelle standard.

11.2 Resultater

11.2.1 Petrogene kulbrinter. Beregning
Kulbrinterne i prøverne integreres udfra retentionstiden af standarden og de homologe rækker af naphthalener og phenanthrener integreres udfra retentionstider fundet i fuelolien. Tilsvarende integreres hopaner udfra retentionstider opnået fra fuelolien.

Følgende ionspor anbefales:

Tabel 11-2. Valg af kalibrant og ionspor

Komponent	Kalibrant	MS ion (m/z)
Naphthalen	Naphthalen	128
1- og 2-Methylnaphthalen	1- og 2-Methylnaphthalen	142
Dimethylnaphthalener	2,6-Dimethylnaphthalen	156
Trimethylnaphthalener	2,3,5-Trimethylnaphthalen	170
Phenanthren	Phenanthren	178
Methylphenanthrener	2-Methylphenanthren	192
Dimethylphenanthrener	3,6-Dimethylphenanthren	206
Hopaner	17α(H),21β(H)-Hopan evt. n-alkan C30, areal std*0,23	191
n-alkaner	Lige; overfor n-alkaner Ulige; overfor nærmeste foregående lige n-alkan	113
Pristan	Pristan	113
Phytan	Phytan	113

Alle komponenter beregnes overfor o-terphenyl som intern standard.

Indholdet af enkeltkomponenter beregnes efter følgende formel:

$$Indhold\ [mg/kg\ TS] = \frac{(A_{komp.} / A_{ISpr.}) * C_{std} * V_{ext} * 100}{(A_{std.} / A_{ISstd.}) * m * TS\%}$$

Hvor;
$A_{komp.}$: arealet for den enkelte komponent.
$A_{IS\ pr}$: arealet forden interne standard i prøven.
$A_{std.}$: arealet for samme komponent i standarden.
$A_{IS\ std.}$: arealet for den interne standard i standarden.
$C_{std.}$: koncentrationen af standarden i mg/L
V_{ext} : volumen af ekstraktionsmiddel i mL
m : prøvens vægt i gram
TS % : procent tørstof

Resultater opgives med to betydende cifre.

Følgende forhold og koncentrationer beregnes (Tabel 11-3).

Tabel 11-3: Kvalitativ bestemmelse af petrogene kulbrinter

Parameter
Sum af naphthalener
Sum af phenanthrener
17α(H),21β(H)-Hopan
Isoprenoidforhold:
n-alkan C_{17}/pristan
n-alkan C_{18}/phytan
CPI-indeks:
CPI(15 - 21)
CPI(25 - 33)
Øvrige hopaner

Der skal udvises forsigtighed for stærkt nedbrudte olieforureninger eller prøver uden olieindhold, hvor koncentrationerne af n-alkaner mv. er meget lave. Koncentrationerne kan reelt være under detektionsgrænsen eller stærkt påvirket af interferens. Isoprenoidforhold og CPI-indeks bør i sådanne tilfælde ikke beregnes.

CPI[20] beregnes som følger:

$$CPI(15\text{-}21) = \frac{2*(C15+C17+C19+C21)}{(C14+C16+C18+C20)+(C16+C18+C20+C22)}$$

$$CPI(25\text{-}33) = \frac{2*(C25+C27+C29+C31+C33)}{(C24+C26+C28+C30+C32)+(C26+C28+C30+C32+C34)}$$

11.2.2 Naturlige kulbrinter. Vejledende metode til beregning

Nedenstående er beskrevet en metode for tilnærmet korrektion af indhold af total kulbrinter for indhold af naturlige kulbrinter. Metoden er ikke afprøvet ved interlaboratorieundersøgelse.

Sitosterol lokaliseres udfra ionspor af ion 93 m/z, samt udfra massespektrum. Phytosterolerne lokaliseres ved ionspor 93 m/z, og integreres og beregnes ved GC-FID. Integrering foretages ved at trække basislinie umiddelbart under phytosteroltoppene (ikke til basisliniebund). Phytosterolerne kvantificeres over for de standarder, der anvendes for kulbrintefraktioner i det pågældende kogepunktsinterval. Summen af phytosteroler kan trækkes fra totalkulbrinteindholdet fundet ved GC-FID for at korrigere for indhold af naturlige kulbrinter.

Indholdet af phytosterol i prøverne beregnes efter følgende formel.

$$\text{Indhold}\,[\text{mg/kg TS}] = \frac{(A_{phytosterol.}/A_{ISfrak.})*C_{std}*V_{ext}*100}{(A_{std.}/A_{ISstd.})*m*TS\%}$$

Hvor,

$A_{phytosterol}$: Arealet af phytosteroler ved GC-FID.
$A_{IS\ frak.}$: Arealet for den interne standard i pågældende fraktion.
$A_{std.}$: Summen af arealet for de n-alkaner, der hører til pågældende fraktion, se Tabel 9-2.

Fordelingen af ulige hhv. lige n-alkaner samt summen af de ulige n-alkaner fremgår af beregningen af enkeltkomponenterne jf. 11.2.1.

De ulige n-alkaner, der kan trækkes fra totalkulbrinteindholdet fundet ved GC-FID, beregnes som differencen mellem den ulige n-alkan fratrukket indholdet af den lige n-alkan umiddelbart før.

[20] "Carbon preference indeks", giver som navnet antyder et udtryk for foretrukne kulstofforbindelser. Se afsnit 12.8 i □/3/ for yderligere forklaring.

Ulige n-alkaner fra naturlige kulbrinter =

$$(C25-C24)+(C27-C26)+(C29-C28)+(C31-C30)+(C33-C32)$$

11.3 Vejledning

11.3.1 Petrogene kulbrinter

De fundne indhold anvendes til vurdering af, hvorvidt der er indhold af petrogene kulbrinter i jordprøven /7/.

Til vurdering anvendes følgende retningslinier:

Parameter	Indikator for
Sum af naphthalener	Kulbrinter af petrogen oprindelse fra et olieprodukt med kogepunktsinterval under n-C_{25}. Naphthalener nedbrydes forholdsvis hurtigt, hurtigere end andre PAH.
Sum af phenanthrener	Kulbrinter af petrogen oprindelse. Phenanthrener nedbrydes langsommere end naphthalener.
17α(H),21β(H)-Hopan	Kulbrinter af petrogen oprindelse fra et olieprodukt med relativt højt kogepunktsinterval, fra 300°C. 17α(H),21β(H)-Hopan er meget resistent overfor nedbrydning.
n-C_{17}/pristan	Tilstedeværelse af n-alkan C_{17} og pristan er tegn på kulbrinter af petrogen oprindelse. Empiriske værdier for n-C_{17}/pristan: ikke-nedbrudt olie f.eks diesel: ca. 1 (fra 1 - 3) nedbrudt olie: mindre end 1 stærkt nedbrudt olie: ikke målelig (C_{17} ikke til stede).
n-C_{18}/phytan	Tilstedeværelse af n-alkan C_{18} og phytan er tegn på kulbrinter af petrogen oprindelse. Empiriske værdier for n-C_{18}/phytan: ikke-nedbrudt olie f.eks diesel: ca. 1 (fra 1 – 4) nedbrudt olie: mindre end 1 stærkt nedbrudt olie: ikke målelig (C_{18} ikke til stede).
CPI(15-21) and CPI(25-33)	CPI ≈ 1 indikerer tilstedeværelse af et olieprodukt (fra Mellemøsten eller Nordsøen). Høje værdier tyder på tilstedeværelse af kulbrinter fra planter. CPI bestemmes kun for det aktuelle olieprodukts kogepunktinterval.

12 Kvalitetsparametre

12.1.1 Detektionsgrænse, præcision og nøjagtighed

Kvalitetsparametre er undersøgt ved en interlaboratorieundersøgelse /4/ med deltagelse af 10 laboratorier fra Danmark, Finland, Norge og Sverige samt opfølgning med deltagelse af 5 laboratorier fra Danmark. Resultatet heraf ses som oversigt i Tabel 12-1. Detaljer, herunder værdier fundet for de enkelte stoffer kan forefindes i rapport for interlaboratorieundersøgelsen. Metoden er desuden valideret på ét laboratorium ved afslutning af metodeudvikling. Kvalitetsparametre for denne undersøgelse kan ses i valideringsrapporten for analysemetoden /3/. Kvalitetsparametrene bør eftervises regelmæssigt på det enkelte laboratorium, fortrinsvis ved intern kvalitetskontrol, samt når metoden tages i brug.

Tabel 12-1. Detektionsgrænse, præcision og korrekthed.

Prøve	Detektions-grænse [mg/kg TS]	Præcision		Korrekthed
		Repeterbarhed relativ standard-afvigelse, %	Reproducerbarhed relativ standard-afvigelse, %	Genfinding, %
Benzen - C10	2,5	5 (0,5 mg/kg TS)**	30 (5 mg/kg TS)**	-
C10 – C25	5	9	23	-
C25 – C40	10 - 15	11	32	-
Total kulbrinter, benzen - C40	30	9	25	100

BTEX – FID:	0,1*			
BTEX – MS:	0,02 – 0,05	4 (0,02 mg/kg TS)**	30	70 – 90
PAH – MS:	0,005	15	30	90
Sum af naphthalener og sum af phenanthrener	0,2	5 (0,05 mg/kg TS)**	57 – 90	>90
17α(H),21β(H)-Hopan	0,05	13	67	>90
n-C17/pristan og n-C18/phytan	-	20	48	>90
CPI(15-21) og CPI(25-33)	-	13	18	>90

* undersøgt ved metodevalidering /3/, men ikke ved interlaboratorieundersøgelse /4/

** Værdier opgivet som mg/kg TS gælder ved lave koncentrationer.

12.1.2 Linearitet

Der er under valideringen vist koncentrationsområder, hvori der er en lineær sammenhæng mellem respons og koncentration. I disse områder kan metoden anvendes med ét-punktskalibrering (som i denne forskrift). Lineariteten skal eftervises af de enkelte laboratorier, der anvender denne metode, når metoden anvendes første gang samt når kolonnetype, apparat eller operatør ændres.

13 Analyserapport

Analyserapporten skal som minimum indeholde følgende:

- Henvisning til denne metode.
- Nøjagtig identifikation og prøvemærkning af den enkelte prøve.
- Angivelse af tidspunktet for prøvernes modtagelse på laboratoriet, og hvornår ekstraktionen er indledt.
- Koncentrationen i mg/kg TS for hver komponent, der er bestemt.
- Afvigelser fra analyseforskriften skal angives, herunder modtagelse af prøverne i andre beholdere end foreskrevet, åbning af prøveglas for udtagning af overskydende jord mv. (jvf. 7.1.2)
- Hvis BTEX er bestemt ved GC-FID skal det anføres at identifikationen alene er udført ud fra retentionstid.
- Detektionsgrænse og usikkerhed for den enkelte analyseparameter.
- Kvalitativ information udfra GC-FID kromatogrammet, f.eks. angivelse af olietype, nedbrydningsgrad og indhold af petrogene kulbrinter, tegn på PAH eller chlorerede opløsningsmidler.
- Udspecificering ved hjælp af vejledning (11.3.1) af indhold af kulbrinter, der ikke umiddelbart kan henføres til mineralolieprodukter.

14 Litteratur

/1/ Vejledning fra Miljøstyrelsen: Prøveudtagning og analyse af jord, nr. 13. 1998.

/2/ DS 204:1980. Vandundersøgelser. Tørstof og glødetest.

/3/ Videreudvikling af metoder til analyse af olie i jord. Miljørapport nr. 905, 2003.

/4/ Method evaluation study – Oil in soil, Miljøstyrelsens Referencelaboratorium for Kemiske Miljøanalyser, juni 2004.