Performance Based Method

1. MDL – LOQ
2. Replicate Precision
3. Audit Accuracy

Basis for a single sample confidence level

ALBERTA RESEARCH COUNCIL

QA for Field Sites

- QA for method based on defining a confidence level for a single sample.
- QA for a field site is based on field sampling and analysis protocol – confidence level based on multiple samples.
- QA specified in field sampling protocols

Detection Limit Criteria

- For regulatory purposes usually LOQ at ten times the standard deviation of a low level standard or sample. The confidence level is expressed as +/- 30% with 99% confidence for numbers reported at the LOQ.
- The MDL is a false positive criteria – a number at the MDL with 99% confidence is greater than zero
- Important that the definition and method of determination be defined. (Assumptions – accuracy, distribution, and others)

PHC-CWS MDL

- Low level spiked soil samples used to determine the MDL
- 7 replicate spiked soil samples required to determine the Standard Deviation
- 99% confidence level is 3*standard deviation.
- Assumes – accuracy (unbiased), Gaussian distribution, independent.

PHC-CWS MDL

- MDL upper limits
- F1, C6 to C10 Hyd 10.7 mg/kg
- F2, C10 to C16 Hyd 3.9 mg.kg
- F3, C16 to C34 Hyd 9.0 mg/kg
- F4, C34 to C50 Hyd 8.0 mg/kg
- F4G grav. On motor oil 290 mg/kg

Tier 1 Remedial Standard mg/kg

Land U	Soil T	F1	F2	F3	F4
Agric.	Coarse	130	450	400	2800
Resid.	Coarse	30	150	400	2800
Comm.	Coarse	310	760	1700	3300
Indus.	Coarse	310	760	1700	3300
PHC MDL		10.7	3.9	9.0	8.0 F4G 290

Replicate Precision

- Replicate precision from repeated analysis of single homogeneous sample greater than 10 times the MDL. (real sample)
- Replicate precision criteria defined from a preliminary reference lab verification study or a Round Robin validation study.

PHC-CWS Replicate Precision

- F1, C6 to C10 hyd +/- 30%
- F2, C10 to C16 hyd +/- 20%
- F3, C16 to C34 hyd +/- 20%
- F4, C34 to C50 hyd +/- 20%
- F4G, grav. heavy hyd +/- 30%

PHC-CWS Replicate Precision

- Replicate precision refined from:
  - Round robin studies
  - reference laboratory studies.

Audit Accuracy

- Not required in the CWS method
- +/- 30% typical - to be refined from network samples – CCME – CAEAL RR Study.
- Based on those labs that followed the reference method. Reanalyze of the RR study may be necessary.

Recoveries

Standard Reference Materials
SRMs,
Diesel, Motor oil, Crude oil (30 API Cardium etc.)

Calibration Standards
SRM
in solvent

Calibration Standard
Extract from SRM
in Matrix (Clay)

Recovery
To account for
The difference

Prescribed Elements – F1

- F1 GC/FID
- Methanol Extraction –ensure soil is dispersed
- Analyze within 48 Hrs of receipt, within 7 days of sampling
- Run Acceptance Criteria - Response factors within 30% of toluene std. For nC6 and nC10. Replicate accuracy 30%
- Perform BTEX when required

Performance Based Elements - F1

- F1, Benchmark (Reference procedure) – Purge and trap – (BC method – on column)
- If headspace method used – salting will improve recovery of aromatics
- Minimize methanol and maintain sufficient sample to achieve MDL.

Prescribed Elements – F2,F3,F4

- GC/FID cap column
- Calibration std - nC10, nC16, nC34
- Run acceptance criteria – nC50 RF >70% of nC10, nC16, nC34 Ave RF & nC10, nC16, nC34 RF within 10% of each other.
- Silica gel clean up 0.6 gm of silica gel per gm of sample.

Prescribed Elements – F2,F3,F4

- Run Acceptance criteria
  - Calibrate with nC10, nC16, nC34 SRM in toluene – 3 point calib. Linearity within 15% overall, and within 10% for each compound.
  - Use nC50 SRM in toluene as a Ret.time & RF check
  - Low and mid calib. Standard as sensitivity check must be within 20% and 15% respectively.
  - Replicate accuracy 20% F4G 30%

Performance Based Elements F2,F3,F4,

- Injection method: split/splitless, on column or other.
- Soxhlet extraction with n-Hexane-Acetone (benchmark), other extractions require validation.
- Other elements – rotovap, turbovap, shakers, ovens require validation. Temp?

Performance Based Elements F2,F3,F4,

- Toluene keeper in the concentration step, must demonstrate nC10 retention. (BC isooctane keeper)

Prescribed Elements F4G (Gravimetric)

- 50:50 hexane:acetone solvent
- Gravimetric

Performance Based Elements - F4G (Gravimetric)

- Soxhlet extraction is benchmark, others require validation.
- Cleanup - Separation of polar – nonpolar fractions by hexane:DCM and silica gel.

Prescribed Elements
Moisture Determination

- Oven dry at 101-110 Deg. C.
- Performance based options
  - none

QA for Field Sites

- Concerns - Method turnaround too slow.
- Use of more automated method, with a percentage of samples run against the Reference Method for acceptance.

Performance Based Options Summary

- FI
  - On column injections
  - Headspace injections
  - SPME

Performance Based Options Summary

- F2, F3, F4
  - Injection method
  - Extraction procedure
    - ASE procedure
    - Sonication
    - Cold Shaking
    - Supercritical fluid extraction
    - Microwave extraction

Performance Based Options Summary

- F2, F3, F4
  - Isooctane keeper
  - Isooctane calibration std solvent
- F4G
  - Extraction procedures
  - Cleanup procedures