

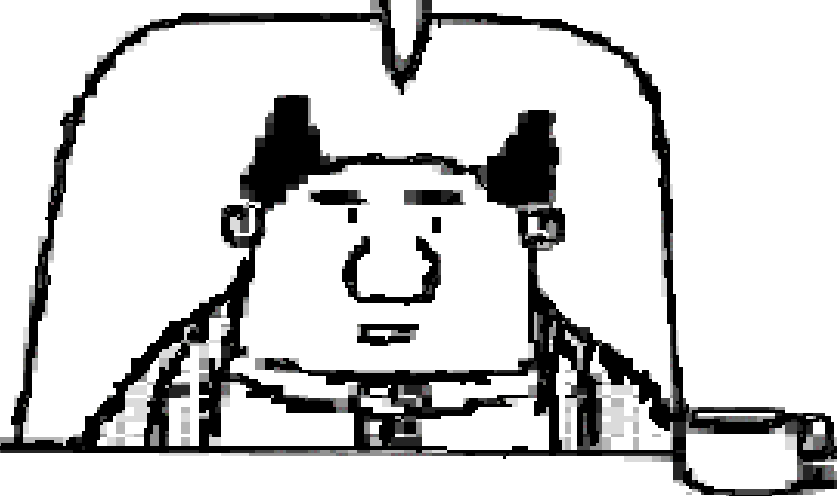
Development of PHC CWS Method



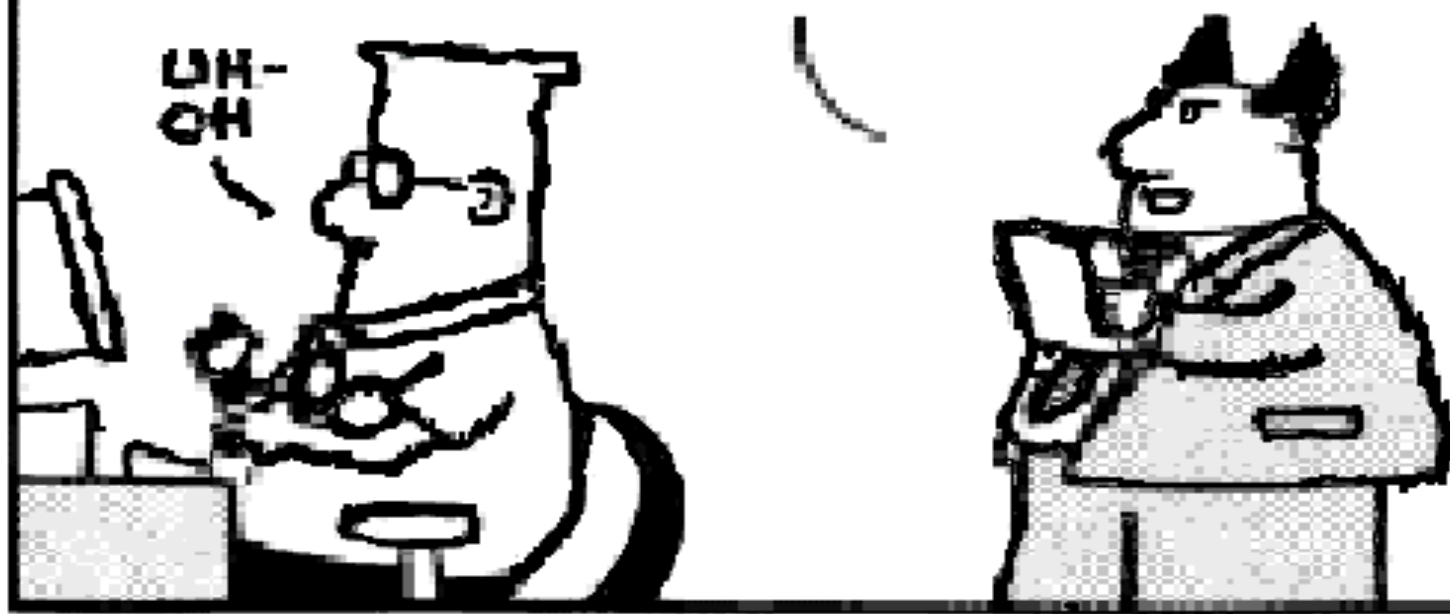
Richard Turle

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Environmental Technology Centre
Environment Canada

I HAVE FOUND
A NEW USE FOR
HYDROCARBONS



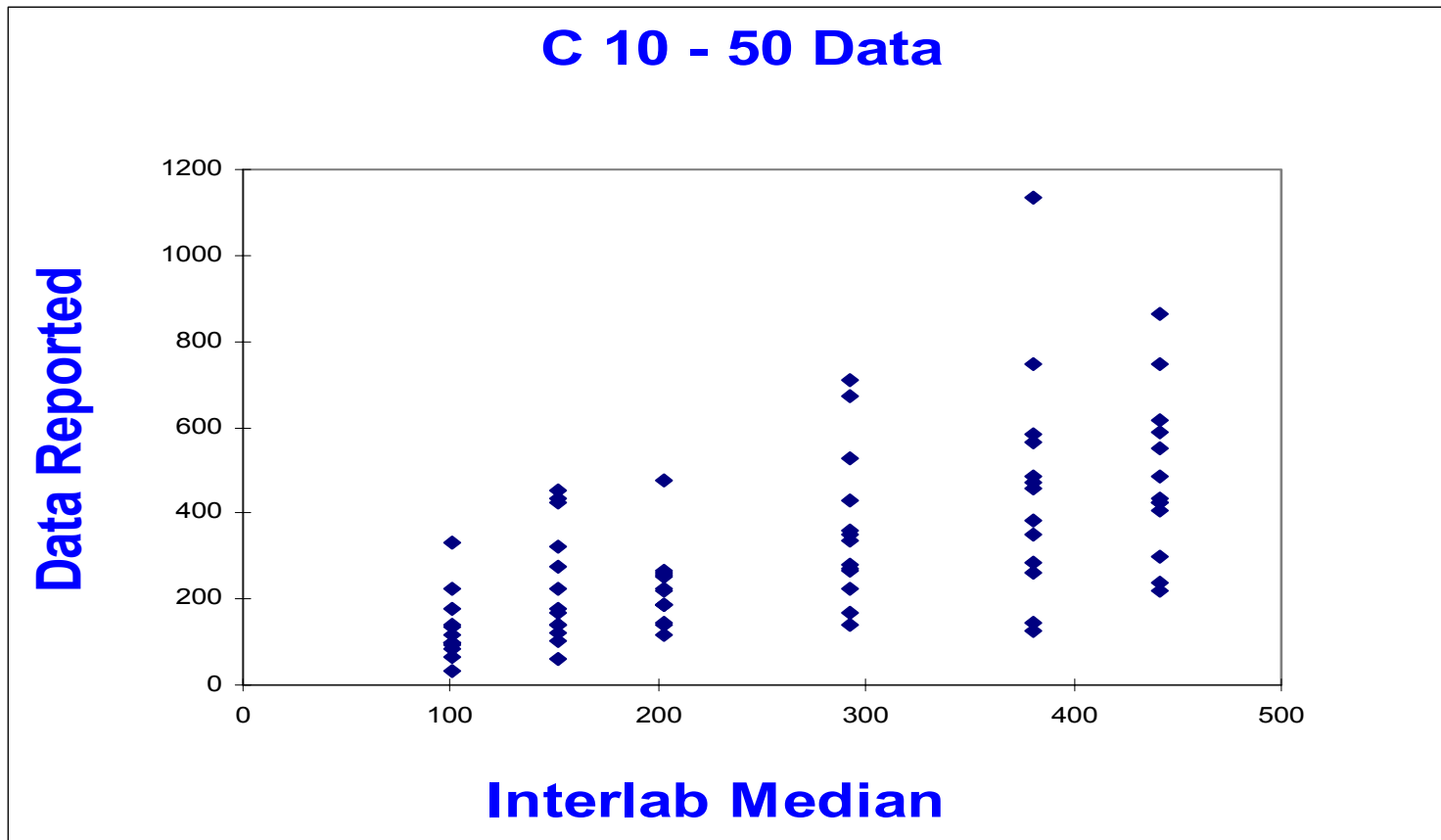
FIRST WE SPILL SOME,
THEN WE TAKE LOTS OF
SAMPLES FOR ANALYSIS



THEN WE CAN MAKE
MILLIONS FIGURING
OUT WHAT IT MEANS



Before the CWS Process CAEAL did a PHC Round Robin (1997)





Conclusion was.....

- No uniform methodology
- No definition of analyte
- No standardized calibration
- Thus:
 - Results incomparable
 - Needed a new approach
 - Hence the CWS PHC method

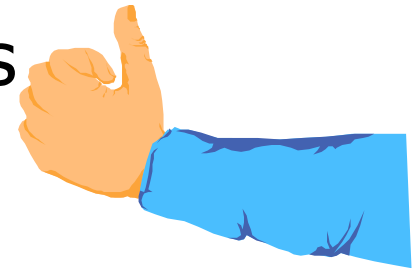


Recommendation from the October 1997 PHC Workshop

- **Harmonize PHC Analysis Methods**
- **Major issues to be resolved**
 - **Carbon ranges**
 - **MDLs and DQOs**
 - **Single or multiple methods**
 - **Method options allowed**
 - **What about the heavy fraction?**

What We Have (AMTAG ++) Accomplished?

- Wide consultation on method - Job Done!
- Agreed on hydrocarbon fractions
- Agreed on analytical method
- Carried out 2 Round Robins
- Single lab validation & method development
- Published method



Hydrocarbon Fractions

- F1 : C6 - C10 - BTEX
- F2 : C10 - C16 - Naphthalene
- F3 : C16 - C34 - 9 PAHs
- F4 : C34 - C50

or Gravimetric Heavy
Hydrocarbons,

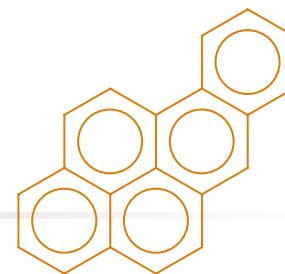
(silica gel cleanup optional)

or High temperature GC

- % Moisture



Aromatics



- BTEX and specific PAHs
- Correct rather than double count if analyzed

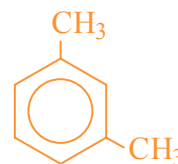
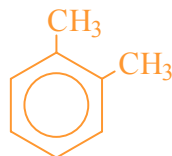
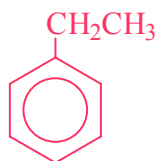
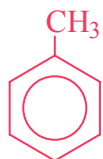
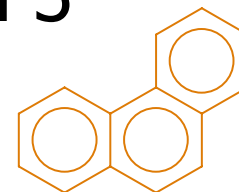
- Subtract BTEX from F1



- Subtract Naphthalene from F2

- Subtract other specified PAHs from F3

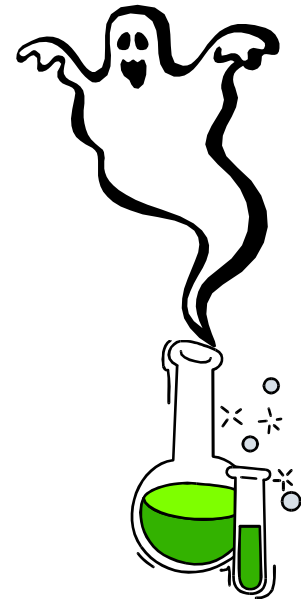
- Analyze 1 sample to show absence



Analytical Method

F1 C6 - C10

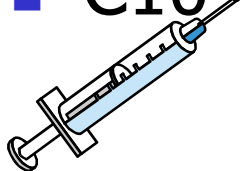
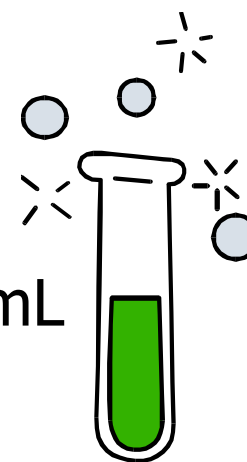
- Extract with methanol
- Extract within 2 days (if possible)
- Purge and Trap
- GCFID - DB1 column
- Calibrate against toluene
- Integrate beginning of C6 to apex of C10



Analytical Method

F2, F3, F4 (C10 - C50)

- Dry with diatomaceous earth
 - Soxhlet with hexane + acetone
 - Dry with sodium sulfate
 - Add 3 - 5 mL toluene, reduce to 1 - 2 mL
 - Clean up with silica gel
 - GCFID - DB1 column
 - Calibrate against nC10 + nC16 + nC34
 - C10 - C16, C16 - C34, C34 - C50
- 70% recovery for nC50



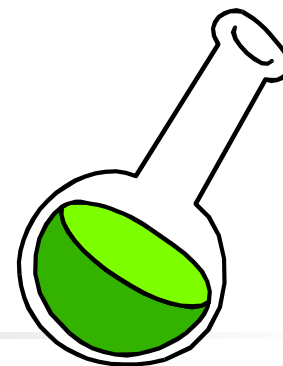
How to Recover C50?



- Need 70% recovery for nC50
- On column or splitless works
- Need high injector temperature
- Electronic pressure program helps
- Keep injector clean and silanized
 - Difficult, but it can be done

Silica Gel Options

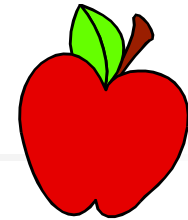
C10 - C50



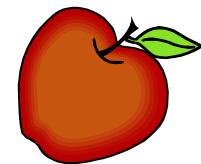
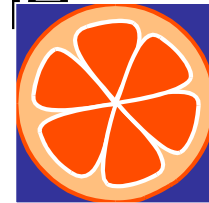
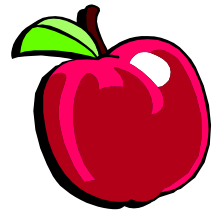
- In - situ cleanup (**no longer recommended**)
 - ⦿ add 20 mL 50 / 50 n-hexane / DCM
 - ⦿ add 0.6 g 100% Activated Silica Gel per g dry sample
 - ⦿ shake or stir 5 minutes
 - ⦿ add 1 - 2 mL toluene, evaporate to 1 mL
- Column cleanup (**recommended**)
 - ⦿ glass column 15 - 20 mm id
 - ⦿ 1 cm Na_2SO_4 , 20 mm (5g) 100% Activated Silica Gel
 - ⦿ add sample extract
 - ⦿ elute with 20 mL 50 / 50 n-hexane / DCM

Analytical Method

F4 GHH



- Cannot be added to GC results
- Soxhlet with hexane + acetone
- Evaporate and weigh
- Reconstitute in DCM + hexane
- Clean up with silica gel
- Evaporate and weigh again



F4!

- If chromatogram returns to baseline at C50 then report C34 - C50 as F4
- If it does not return to baseline
 - must do gravimetric heavy hydrocarbons
 - if <50% of limit, report F4G
 - if >50% of limit, do silica gel, report F4G-SG
 - report the higher of C34 - 50 or GHH-SG as F4
- If jurisdiction permits,
 - do high temperature GC characterization
 - report that result as F4-HTG



Report all results!

F4!

**Chromatogram returns to
baseline at C50?**

Yes

**Report C34 – C50
as F4**

**Result is < 50% of
CWS PHC Criteria**

**Report GHH as
F4G**

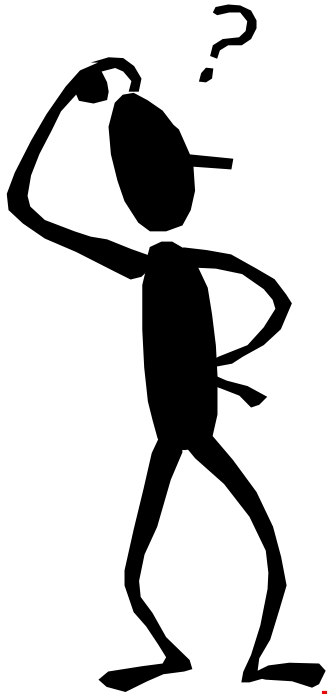
No

Do GHH

**Result is > 50% of
CWS PHC Criteria**

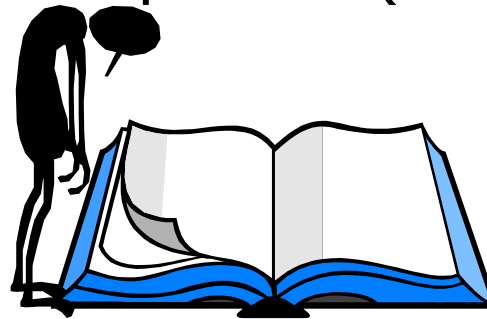
**Do Silica Gel and
report F4G-SG**

Province allows High Temp GC? Report F4-HTG!



Reporting

- F1 or F1 - BTEX (if analyzed)
- F2 or F2 - Naphthalene (if analyzed)
- F3 or F3 - particular PAHs (if analyzed)
- F4 greater of C34 - C50 with Silica Gel OR GHH with Silica gel OR F4-HTG maybe)
- % Moisture
- Total organic carbon (if analyzed)
- MDL
- Professional judgement about the product (if asked)



• *Report all F4 results*

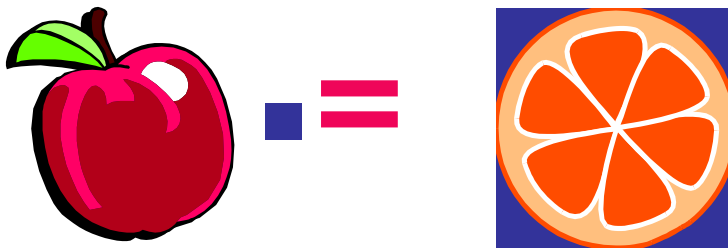
Reporting

- Name and address of client and lab
- Dates, report number, sample ID, validator
- Statement that GHH cannot be added to C6 - C50
- Statement that method complies with CWS PHC method and is validated
- Deviations from method used
- Did chromatogram return to baseline at C50?
- Were all Quality Criteria met?
- Note that QC sample data is available



Equivalent Alternatives

- Some aspects of method are prescriptive
- Technical progress is allowed using a performance based approach
- Soxhlet, purge and trap, silica gel, etc. can be changed if validated
- Validation includes analysis of 4 soils including peaty and clay soils by CCME and proposed method
- Data must be within 20% and all QC criteria met!





Special Soil Types

- Judgement of regulators and experts paramount
- High organic content soils can give false positives - confirm PHCs using GCMS or subtract a "blank" comparison soil. Measure TOC
- Manure amended bioremediation soils - compare PHC results to a control site
- Soils containing partially degraded PHCs requires careful Silica Gel cleanup and might compare a contaminated and uncontaminated soil
- Wet soils dried using diatomaceous earth



Single Lab Validation

- Linearity: excellent for all standards
- Precision for standards (%RSD)
 - ⦿ nC6 12%
 - ⦿ benzene 8.5%
 - ⦿ toluene 4.0 %
 - ⦿ nC10 9.0%
 - ⦿ nC8 - nC30 less than 4%
 - ⦿ nC50 7.3%



Single Lab Validation

- Gasoline spiked soil
 - at 50 mg/kg Recovery = 82%, RSD = 7.5%
 - at 400 mg/kg Recovery = 88%, RSD = 8.4%
- Diesel and motor oil spike soil
 - Recovery about 95% for sum of F2 + F3 + F4
 - Precision 5% RSD for F2, 3.4% for F3, 3.5% for F4
- nC6, toluene and nC10 standards stable for 38 days (15% loss after 38 days)
- nC10 - nC50 standards stable for 57 - 62 days.



Single Lab Validation

Detection Limits and CCME Tier 1 Levels for Residential / Parkland

■ CCME Levels (mg/kg)

☪ F1	30
☪ F2	150
☪ F3	400
☪ F4	2800

■ Single Lab MDL (mg/kg)

☪ F1	12
☪ F2	3.9
☪ F3	9.0
☪ F4	8
☪ GHH	290

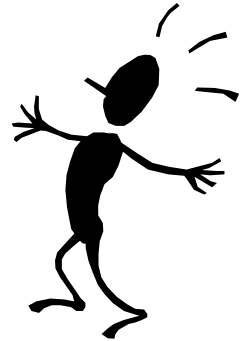
Round Robin July 1999

- 33 labs participated
- 7 Injectable standards and products
- 4 Soil samples
- Questionnaire



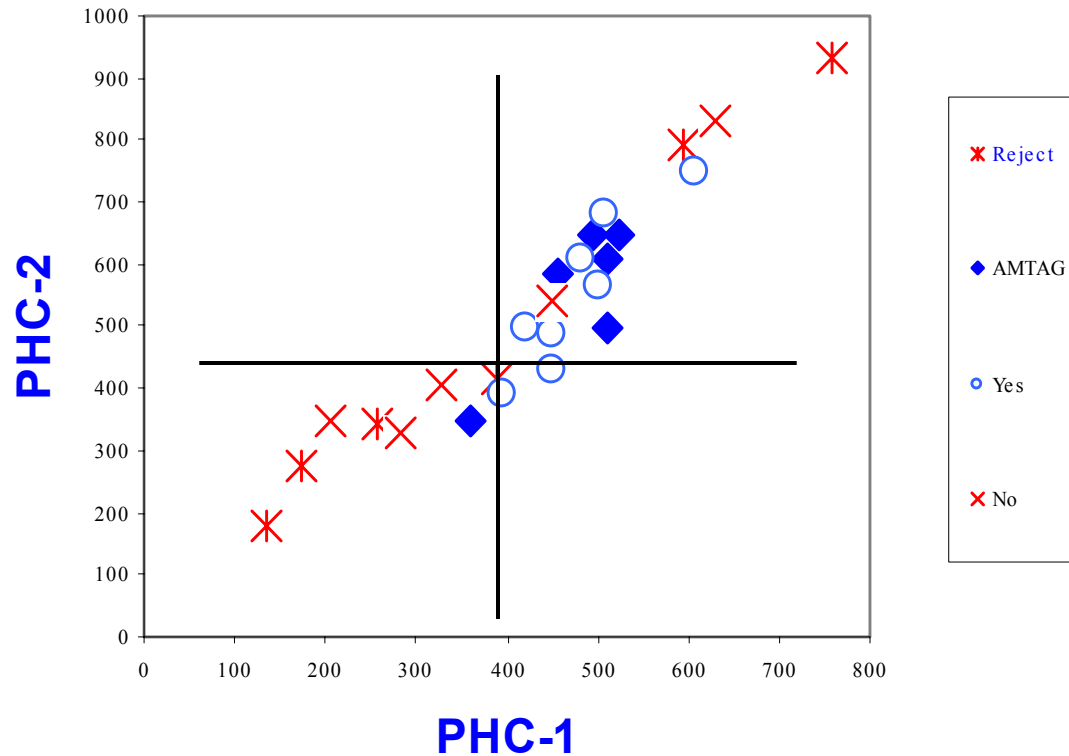
Round Robin July 1999

- Some used CWS PHC method, some didn't
- Less variability when CWS PHC method used
- Lots of GC problems encountered
- Good data for C10 - 16 and C16 - C34
- Poor data for C5 - 10, C>34 - 50 and GHH

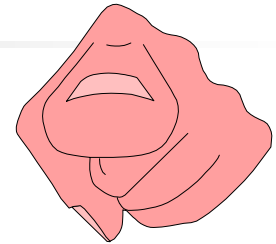


Round Robin July 1999

PHC-1 vs PHC-2 C10-16



Lessons Learned from the Round Robin

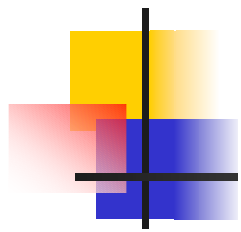


- Must use CWS PHC method
- This is a difficult method to learn correctly so experience with the method is needed
 - Must meet QC criteria in method
 - Must get GC analysis right
- Updated method based on feedback
- Needed a second round robin



Method published

- Published April 2001 (English and French)
- Addendum issues in April 2002
 - (sent out with interlab study)
- Multi-lab validation Study summer 2002



MOM SAID TO CALL THE
CCME BECAUSE ALL THE
PROBLEMS ARE SOLVED!
ALMOST.

