Comments on Present Status of CWS PHC Method

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Comments on CWS PHC Method Status

3 Topics:

- The PHC Round Robin
- Equivalence Protocols
- Recommendations for Improvement of CWS PHC Method

PHC Round Robin Comments

- Primary Objective of RR:

  "1st CAEAL interlab study should provide an assessment of the method" (Red Deer Workshop)

- Was this objective met?
- Very few labs followed the reference method!
  - Maybe only 3 of 36 datasets for F1
  - Maybe only 9 of 39 datasets for F2-4

PHC Round Robin Comments

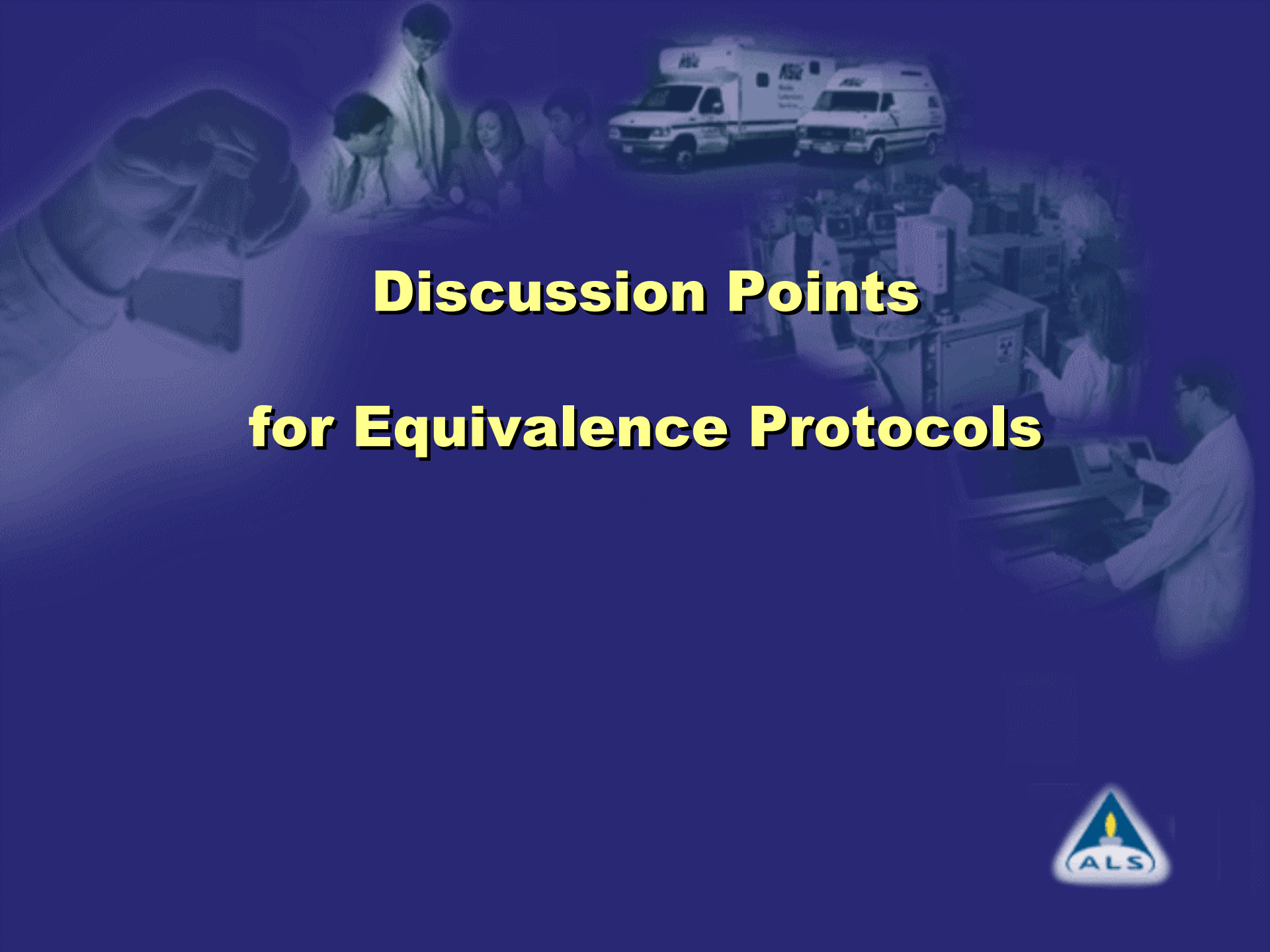
Important information is missing in report:

- Missing information should be obtained & report updated.
- Can't tell whether method followed for ½ of all datasets!
- Relative response information should be tabulated.
- Additional detail on methods should be included.
  - e.g. extraction method, GC injection mode, silica gel option used

PHC Round Robin Comments

Data from Reference Method that met all requirements should be compiled separately.

- Now indicates variability of different methods.
- Re-compilation would give truer indication of CWS method variability.
- Would allow comparison of modified methods to Reference Method population.



Discussion Points

for Equivalence Protocols

A Premise for Equivalence Protocols

Any lab that believes it's modified method is equivalent should have the opportunity to prove or disprove this belief.

Equivalence Protocol Pre-Requisite

- The method needs to be better-defined; we need a definitive reference for comparison.

- Currently there are too many options.

  Examples:

  - Silica gel options.
  - GC parameters, etc.

Potential Components of an Equivalence Testing Scheme

1. In-house Equivalence Tests.
2. Round Robin Equivalence Study?
3. Audit & Approval of Equivalence.
4. Ongoing CAEAL PT studies.

Equivalence Study Components

1. In-house Evaluation Studies:

- Rigorous, well-designed protocol is needed. It must define:
  - Number and types of samples to test.
    - include challenging samples (clays, high moisture).
  - Degree of replication required.
  - Criteria for “equivalence”.

Equivalence Study Components

2. Round Robin Based Equivalence Study?

- A lot of extra effort, but adds credibility.
- Last study probably not that useful for this purpose, since not enough labs followed the method.
- Design the study to estimate both bias & precision of modified methods.
  - Replicate data needed for modified methods.
  - Large population needed for reference method.

Equivalence Study Components

3. Audit and Approval of Equivalence

- CAEAL could assess In-House & Round Robin outputs against pre-determined criteria.

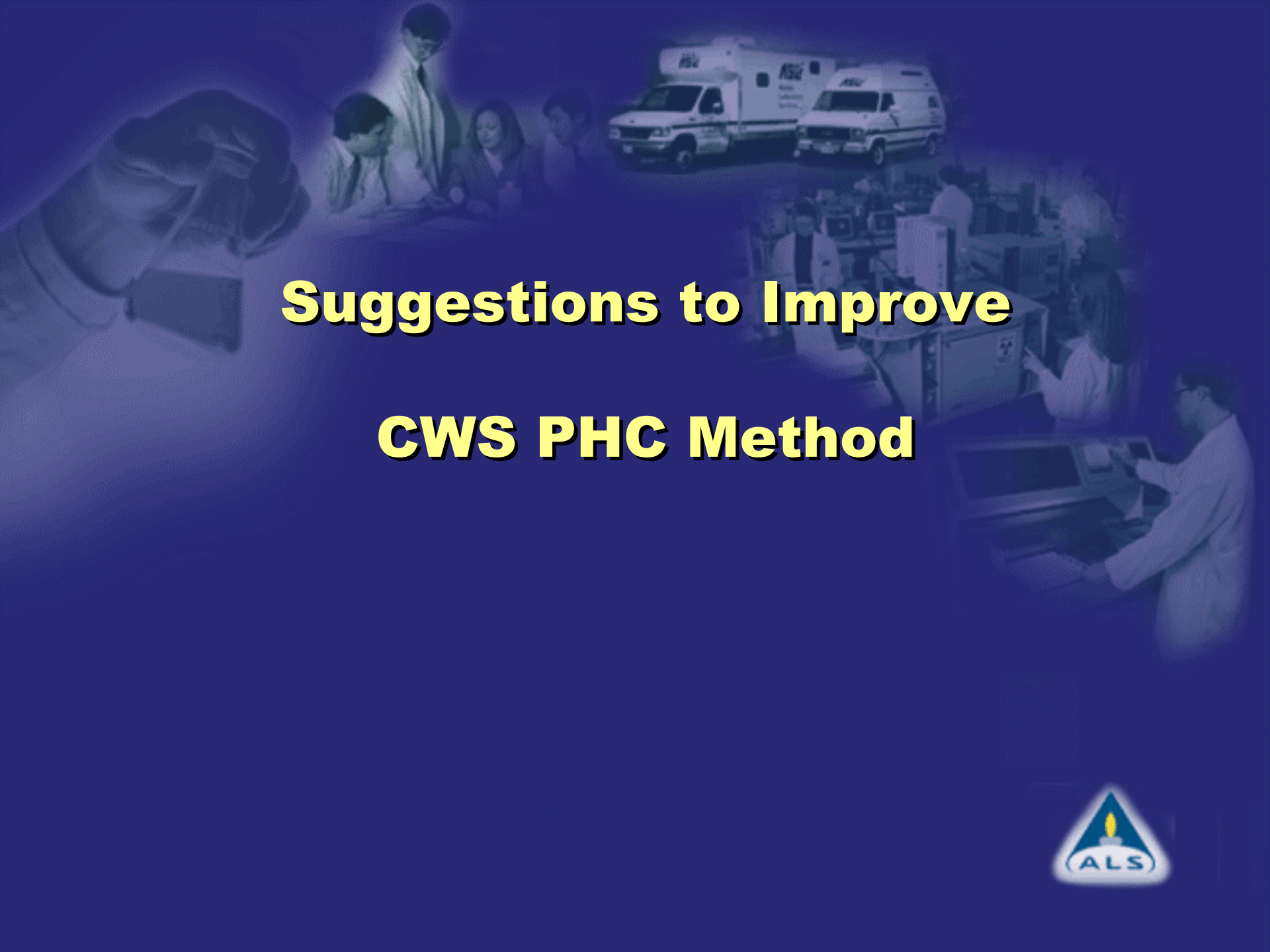
- If acceptable, CAEAL could then accredit the lab for the modified method.

Equivalence Study Components

4. Ongoing CAEAL PT Studies

- Monitor ongoing performance using the regular CAEAL PT approach.

- Only the reference method and modified methods of demonstrated equivalence should be used.



Suggestions to Improve

CWS PHC Method

Issues With Analysis of F4

Analysis costs for F4 are too high compared to its relevance.

- F4 is the least toxic of PHC fractions.
- Lowest F4 criteria is 2800 mg/kg.
- There is only one criteria value for F4, but there are 3 different F4 methods.
  - For many samples, all three F4 methods are required.
- There is redundancy here (note: F4Gsg is virtually always ∞ F4 by GC).
- Biggest problem: F4 by GC requires on-column GC (very costly technique).

Ideas to Improve F4 Issues:

- Eliminate analysis of F4 by GC.
- Analyze for F4G only if GC chromatogram indicates material >C34 is present.
  - HTGC could be substituted if provincial jurisdiction allows.
- Relax C10/16/34 relative response criteria to ✂ 20% to permit splitless GC.
  - Splitless GC = lower analytical costs.

Silica Gel Cleanup

- Silica Gel Cleanup makes method extremely cumbersome.
  - adds to cost of analysis
  - adds to variability
  - questionable benefits
  - typically no effect due to Hex/DCM solvent

- Is the silica gel cleanup necessary?
  - We would like to see an evaluation of the impact of the current cleanup.

Other Issues with the Method

- The F4G “return to baseline” criteria needs to take concentration into account.
  - F4G is now often required when F2-4 is <DL!
- The 10 gram minimum weight requirement is unnecessary for combined F2-4 + F4G extractions.
  - 5g is sufficient for homogeneity considerations.
  - MDL requirements address sensitivity needs.
  - ASE cells can’t always hold 10g samples.

Next Method Revision?

We would like to see the AMTAG committee re-formed to address these issues and revise the method well before the scheduled review in 2005.

- Definition of “reference method” options needs to be done before equivalence testing begins.