Discrimination of Single White Layer Architectural Paints

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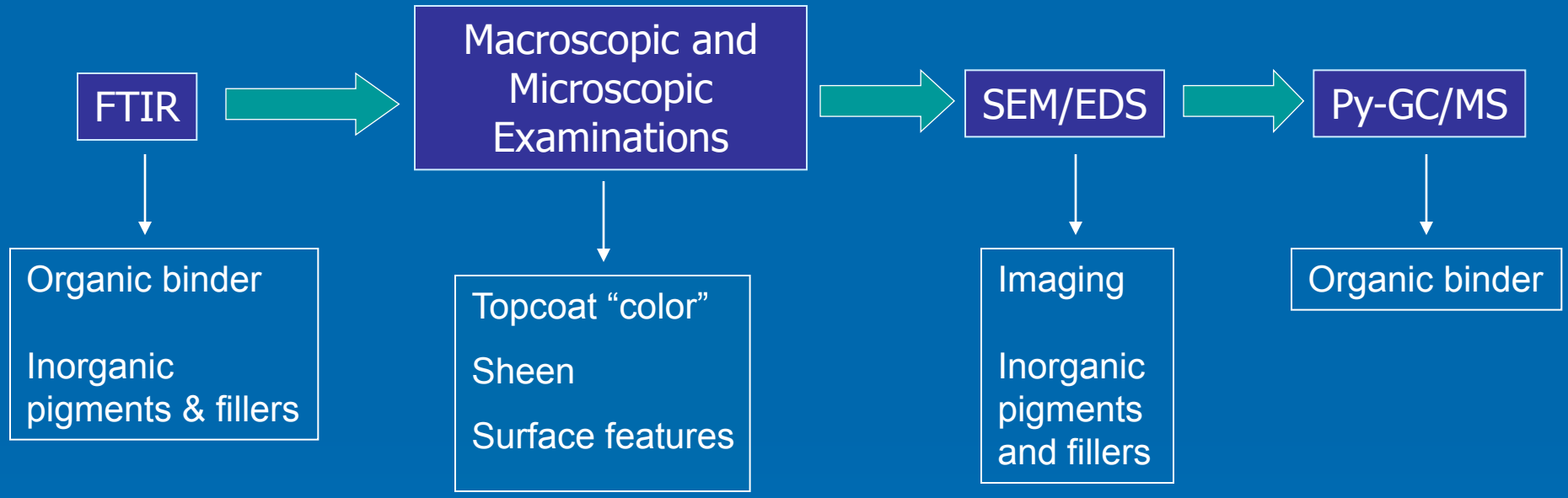
Previous work

- Most recent study published on discrimination of architectural paints
  - Wright, Bradley, and Mehltretter in *For. Sci. Int.*; **209** (2011) pp.86-95.
- Resulted in no random pairs of samples after 464,166 pairwise comparisons
- Suggestions for future work:
  - concentrate on single white layer paints

Purpose of this study

- To determine the discrimination capabilities of standard analytical techniques applied to single white layers of architectural paint
- Attempt to address the significance of associations given the limited points of comparison

Analytical Scheme



Samples

- 199 whites plus 58 neutrals examined previously
- Initially attempted to inter-compare all
- FTIR on the 77 samples not previously analyzed
- Separated all samples based on filler content
  - $CaCO_3$ (74), Kaolin (54), Both (21), Neither (108)
- Standardized classification for discrimination
  - Sheen, color, surface features, ignore underlayers
- Visual and microscopical quickly grew complicated

Plan B

- Identified the best samples from the pool of 257
- Determined how many were suitable for comparison
  - Size (≥ 0.5 cm)
    - sufficient for microscopic comparisons and analysis by all techniques
  - Surface
    - relatively free of external contaminants (e.g., dirt, rust) and imperfections (e.g., gouges, thin coverage that exposes underlayers)

The new and improved sample set

- Identified 60 - 70 samples we all could agree on.
- Cut roughly equivalent aliquots of each sample to form the basis of the new sample set (~ 0.5 cm).
- Asked two colleagues to re-number the samples and randomly select 50.
  - Eliminate pre-conceived biases due to familiarity with the former sample set.
- Decided to replicate five of the 50 samples as a blind verification of discrimination capability.
  - Brought the total sample population to 55.

FTIR analysis

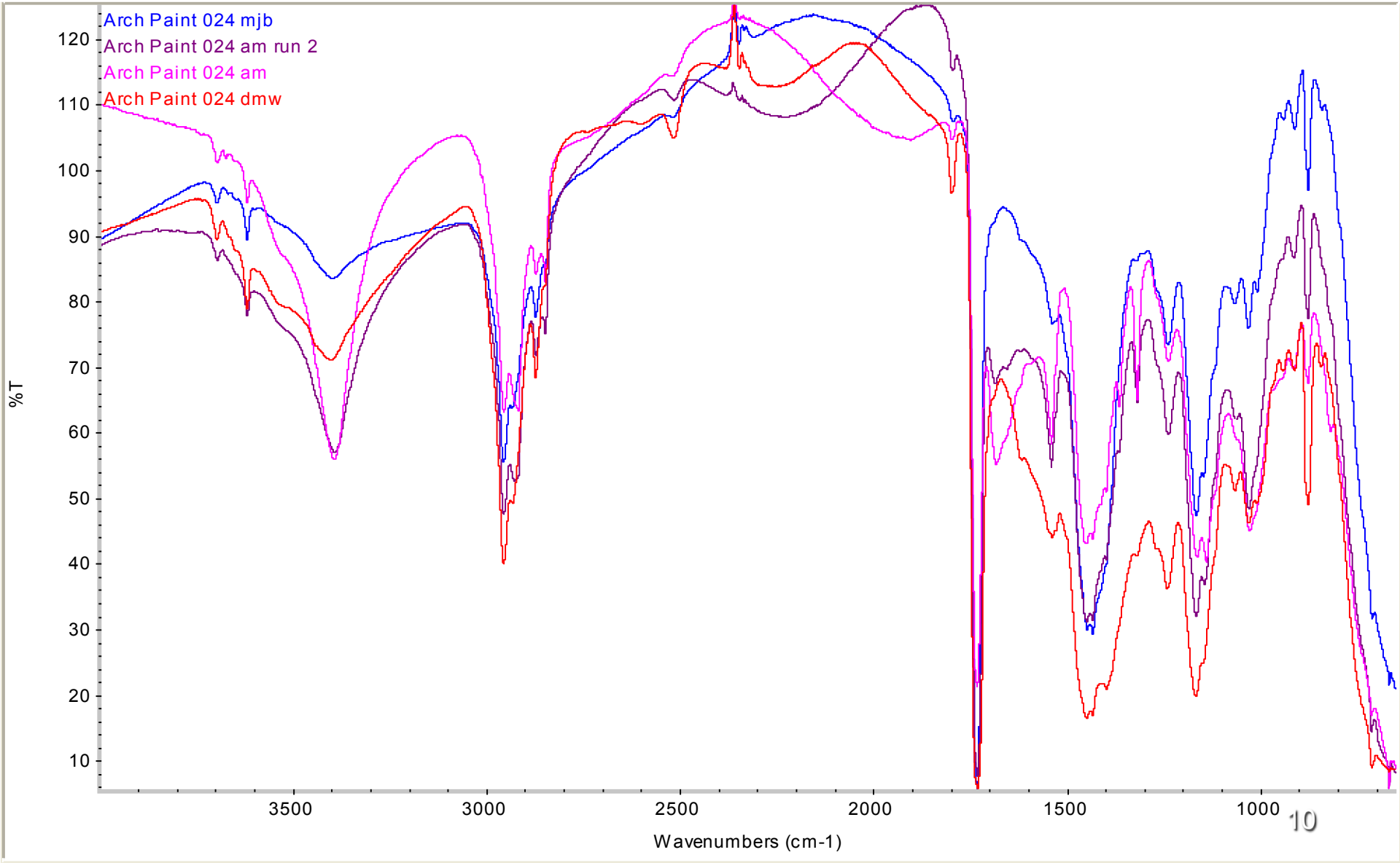
- Analyzed each sample in triplicate (once per analyst).

- Used two identically configured FTIR instruments.
  - Microscope accessory
  - Diamond compression cell
    - Spectrum collected on one of the diamond windows after sample compression
    - Spectrum collected in %Transmission

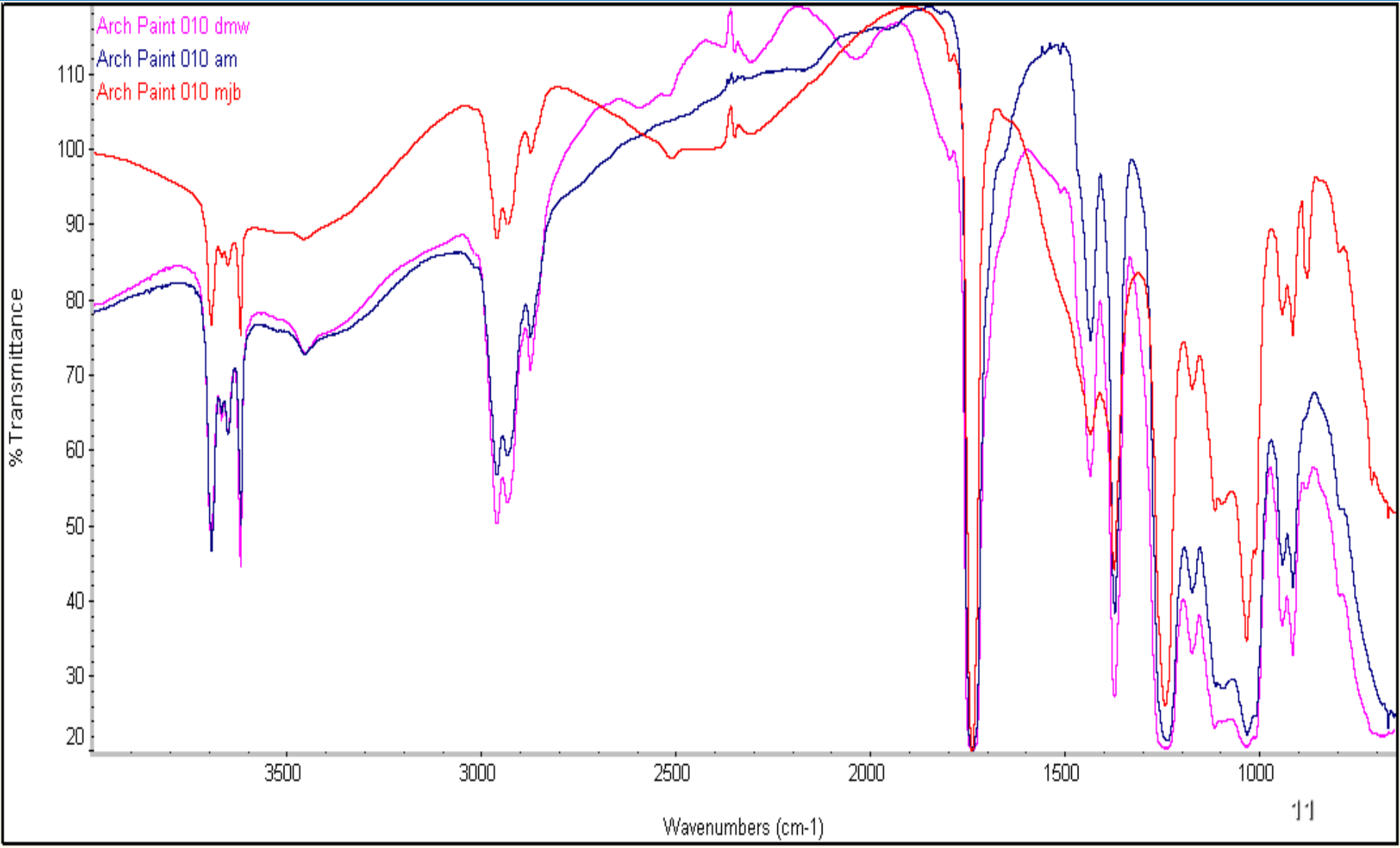
FTIR data analysis

- Data evaluated by two analysts independently.
  - Conservative approach to discrimination utilized.
    - If one analyst would not discriminate a sample pair, the samples were kept together.
- Replicates analyses were critical in evaluating the significance of subtle differences.

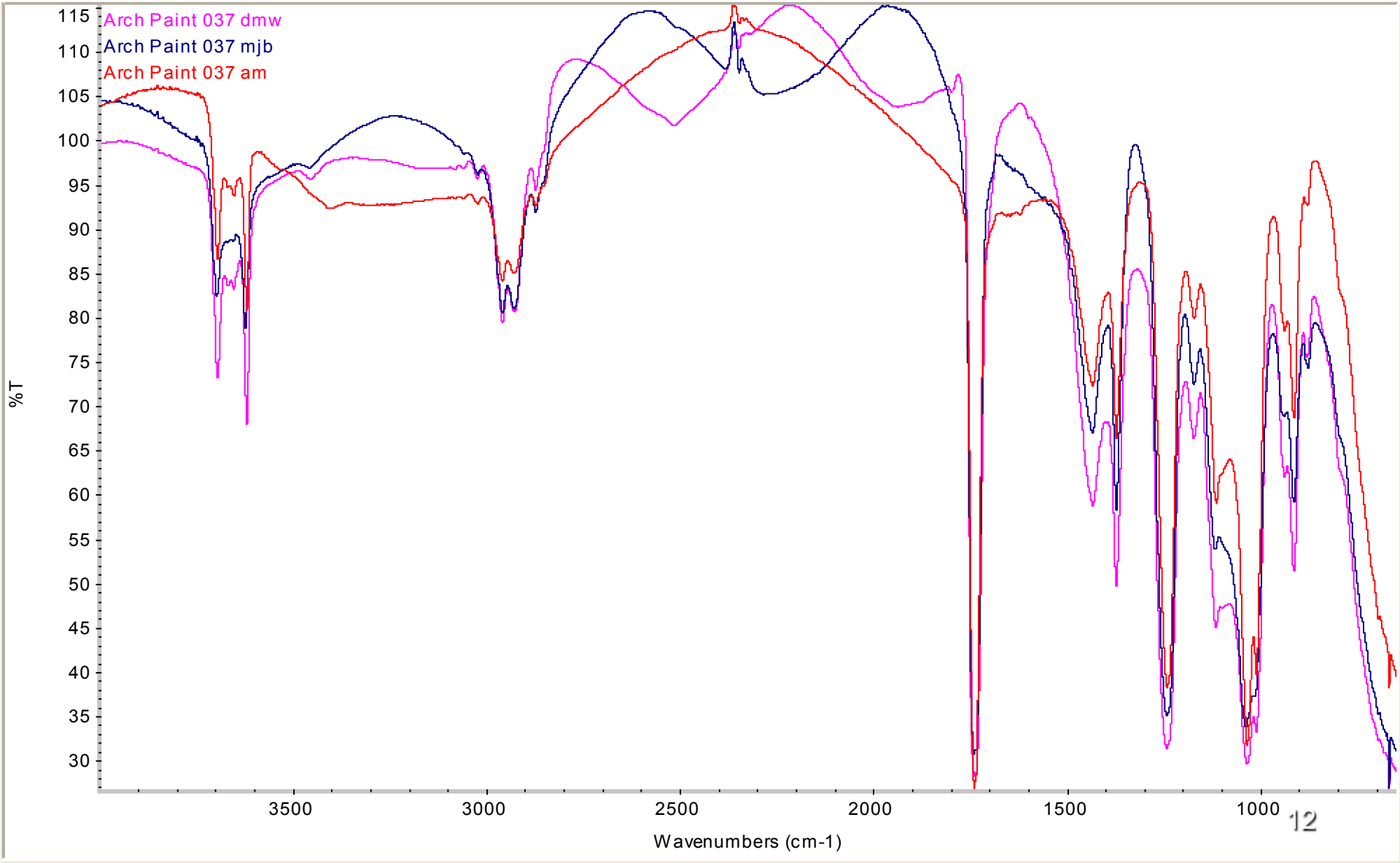
FTIR replicates of Sample 24



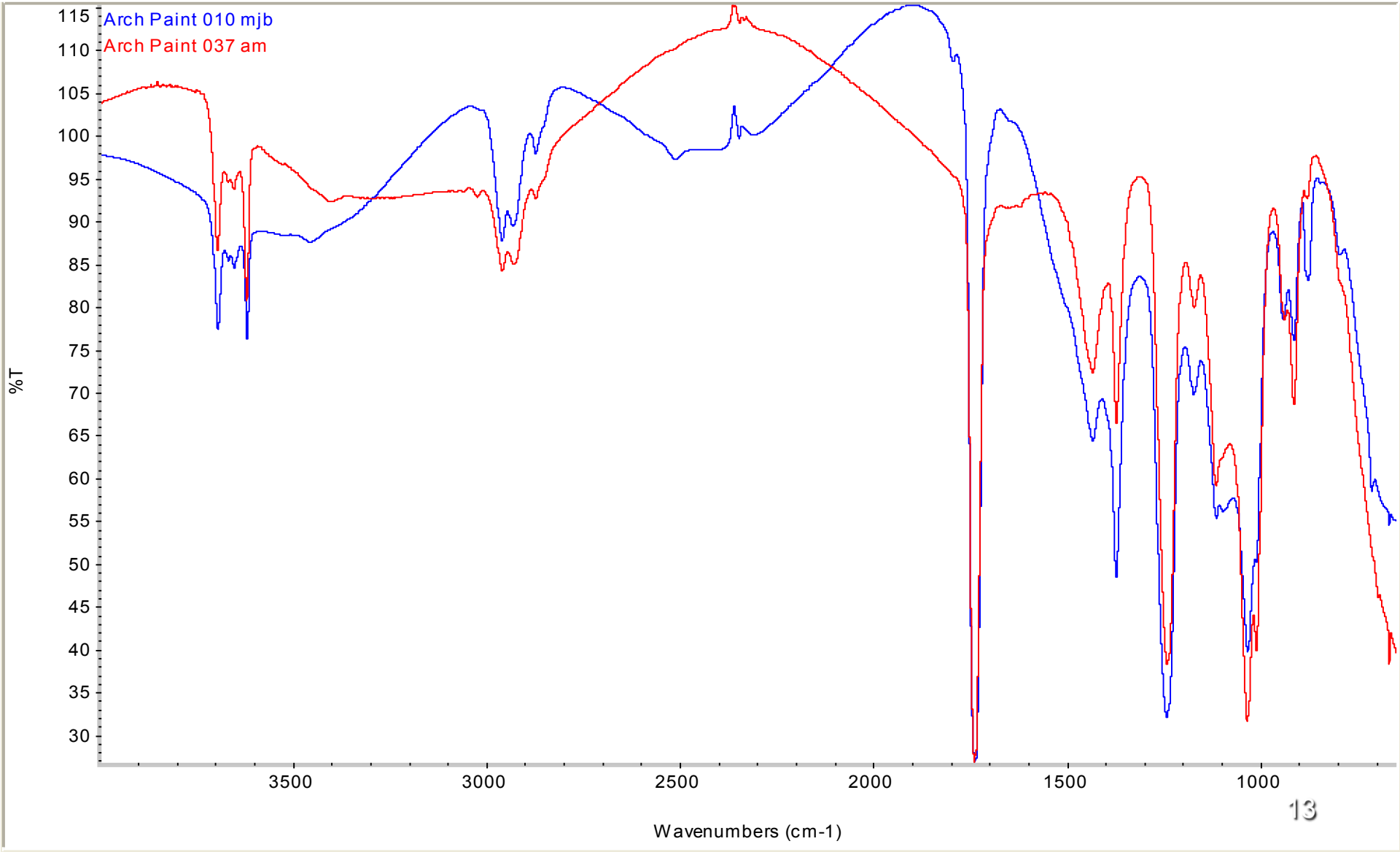
FTIR replicates of Sample 10



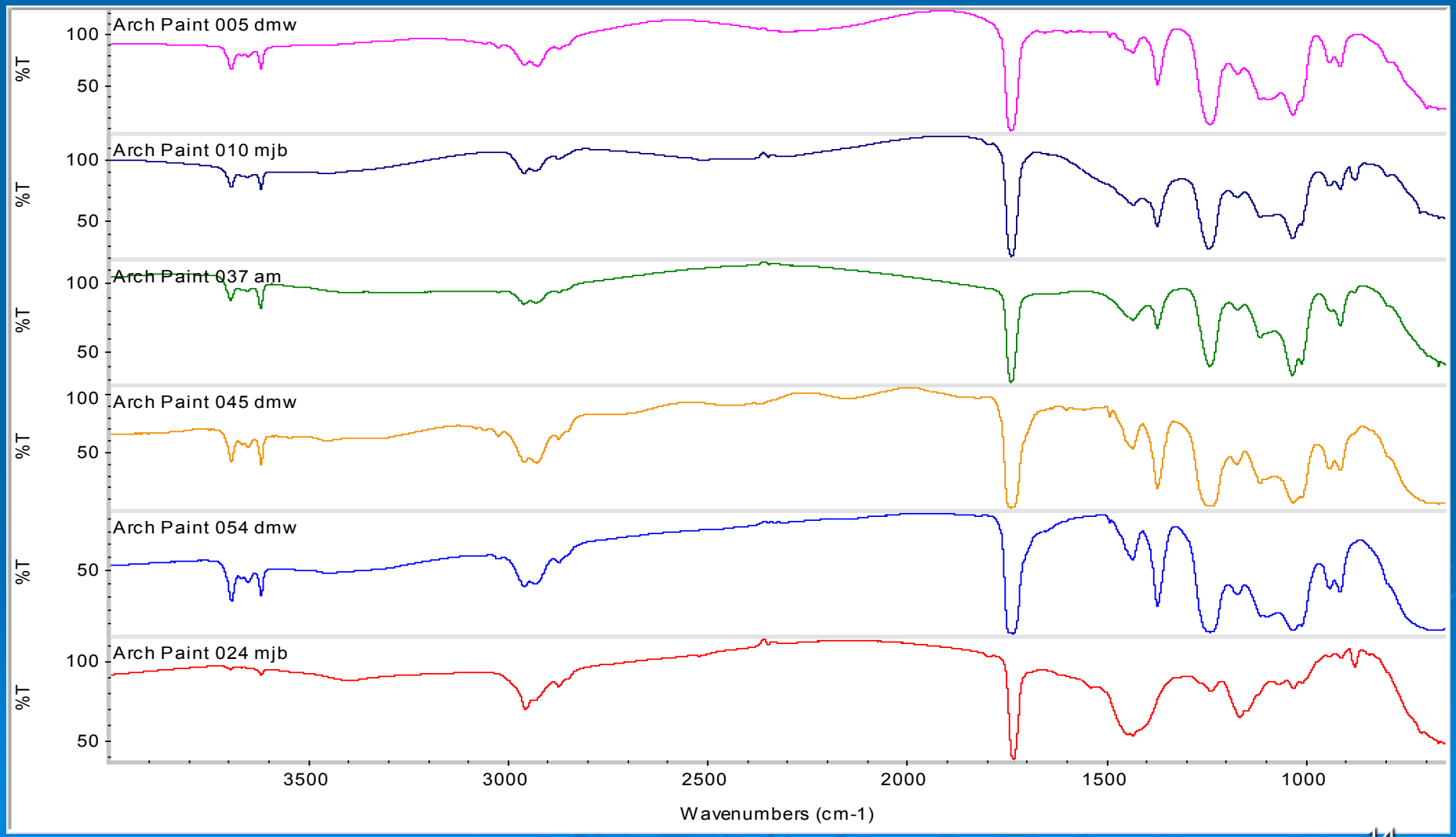
FTIR replicates of Sample 37



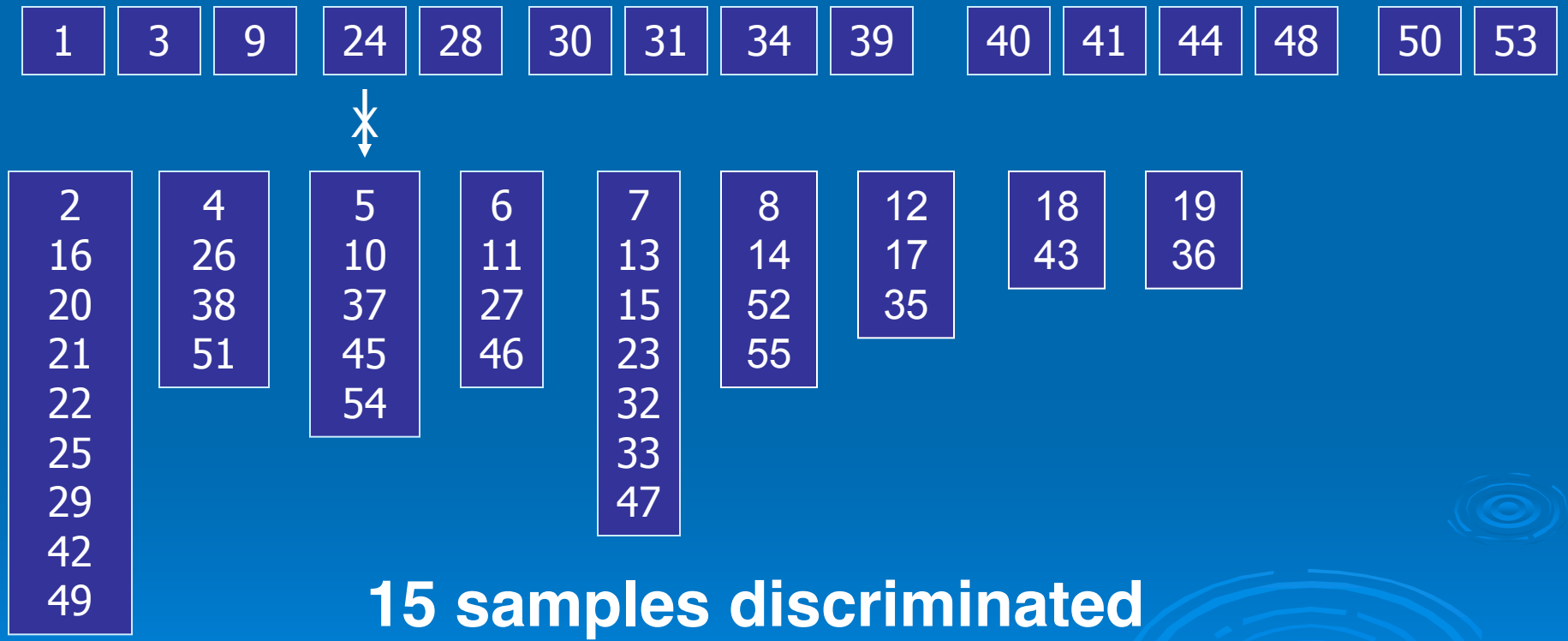
FTIR reps of 10 and 37



FTIR discrimination of 24 vs. 5, 10, 37, 45, & 54



FTIR Groupings



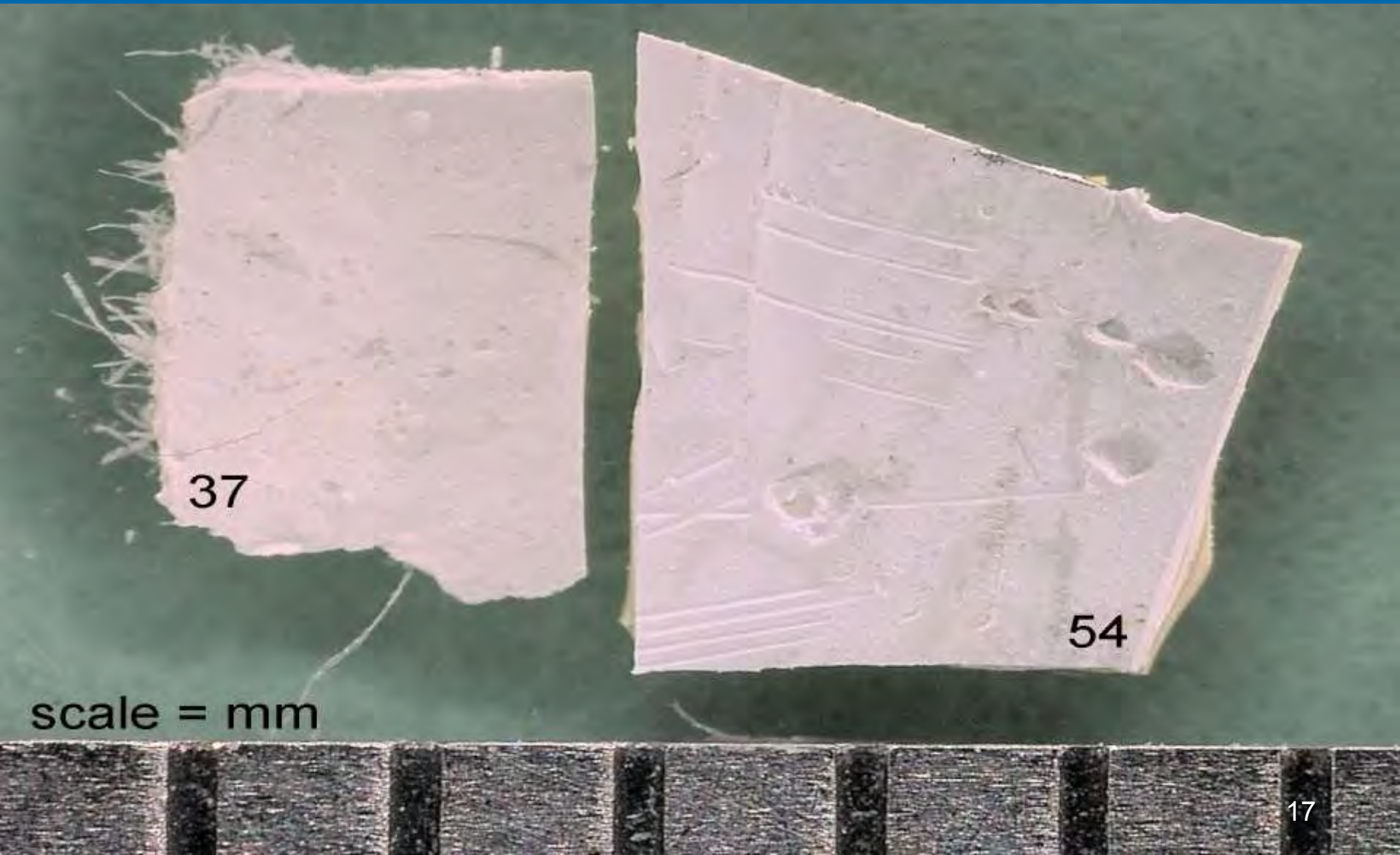
15 samples discriminated

9 groups remain after FTIR analysis

Visual and Microscopical Exams

- Side-by-side pairwise comparisons conducted by two analysts.
  - Sample size differences controlled.
  - Three different light sources used.
  - Third analyst consulted on any discrepancies in the evaluations.
  - Conservative approach again utilized.
    - If one or more analyst(s) would not discriminate a sample pair, samples were kept together.

Sample 37 vs. 54



Visual/Microscopical Groupings

1	3	9	24	28	30	31	34	39	40	41	44	48	50	53

2 16 20 21 22 25 29 42* 42* 49	4 26 38 51	5 10 37 45 54	6 11 27 46	7 13 15 23 32 33 47	8 14 52 55	12 17 35	18 43	19 36

* **42 bridges 2 groups**

5 samples discriminated

13 groups established

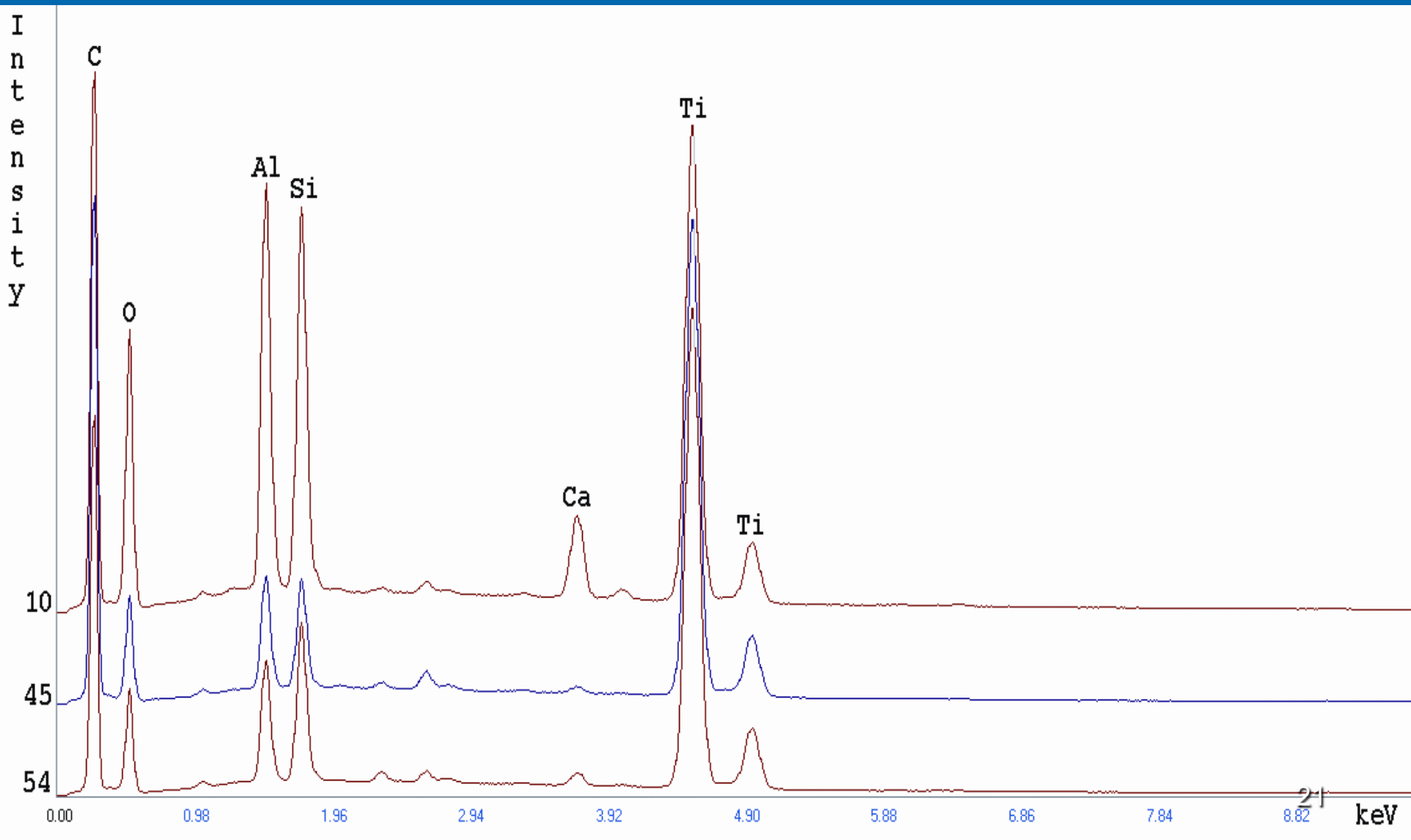
SEM/EDS analysis

- Embedded each paint chip.
  - Utilized backscatter imaging to delineate layer structure, and note homogeneity and relative particle size information.
- All samples analyzed at least twice.
- Spectra imported into SLICE software for overlay and comparison.
- Attempted EDS comparisons using both embedded paint chips and thin peels of the topmost layer.
  - Embedded chips used to evaluate cross sections.
  - Thin peels used to provide larger scanning area.

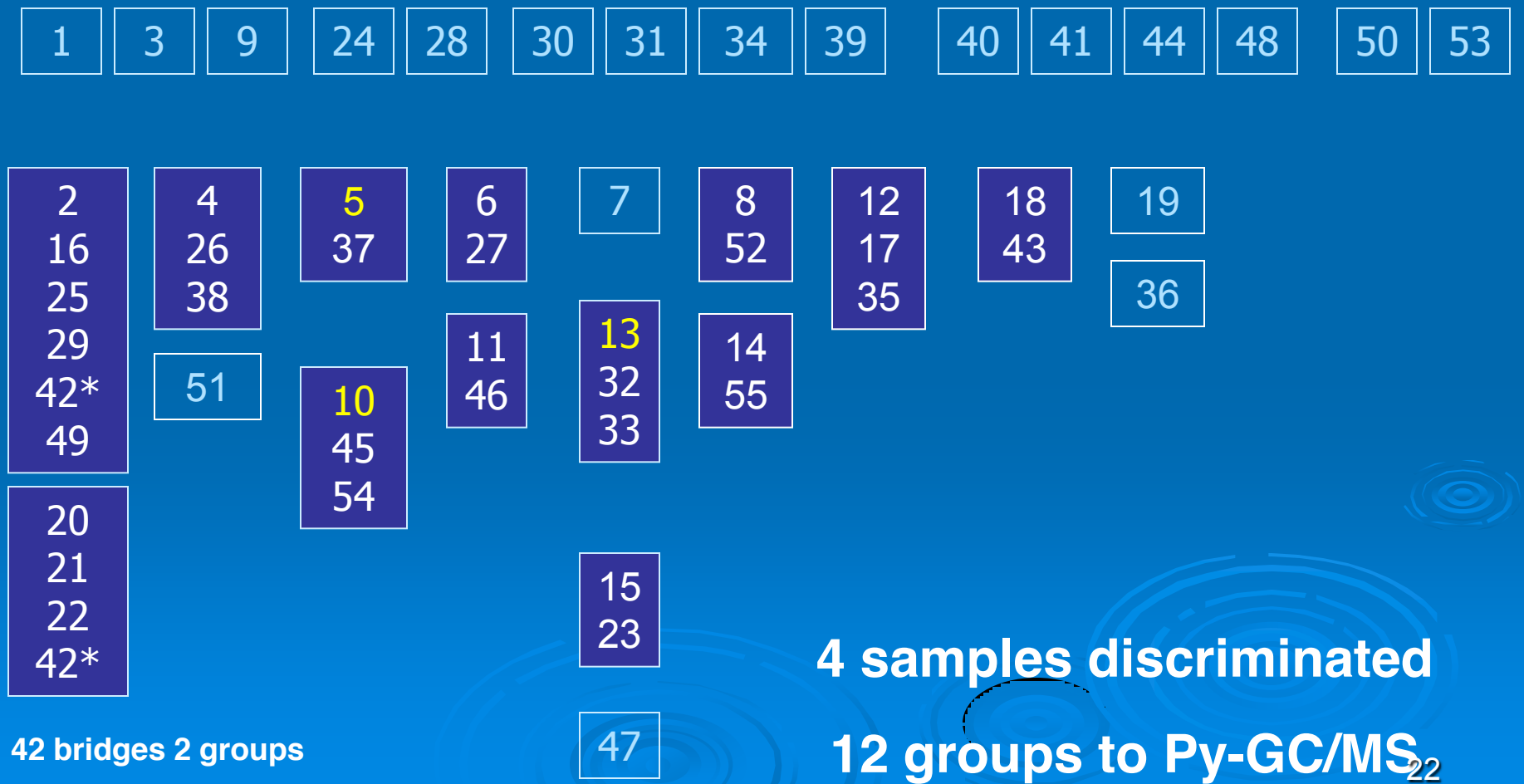
SEM/EDS Groupings

- Six samples discriminated.
  - Element absent or present (e.g., Mg or Zn)
  - Ratio differences (e.g., Ca/Ti, or Al/Si)

SEM/EDS results: 10 vs. 45/54



SEM/EDS Groupings



* 42 bridges 2 groups

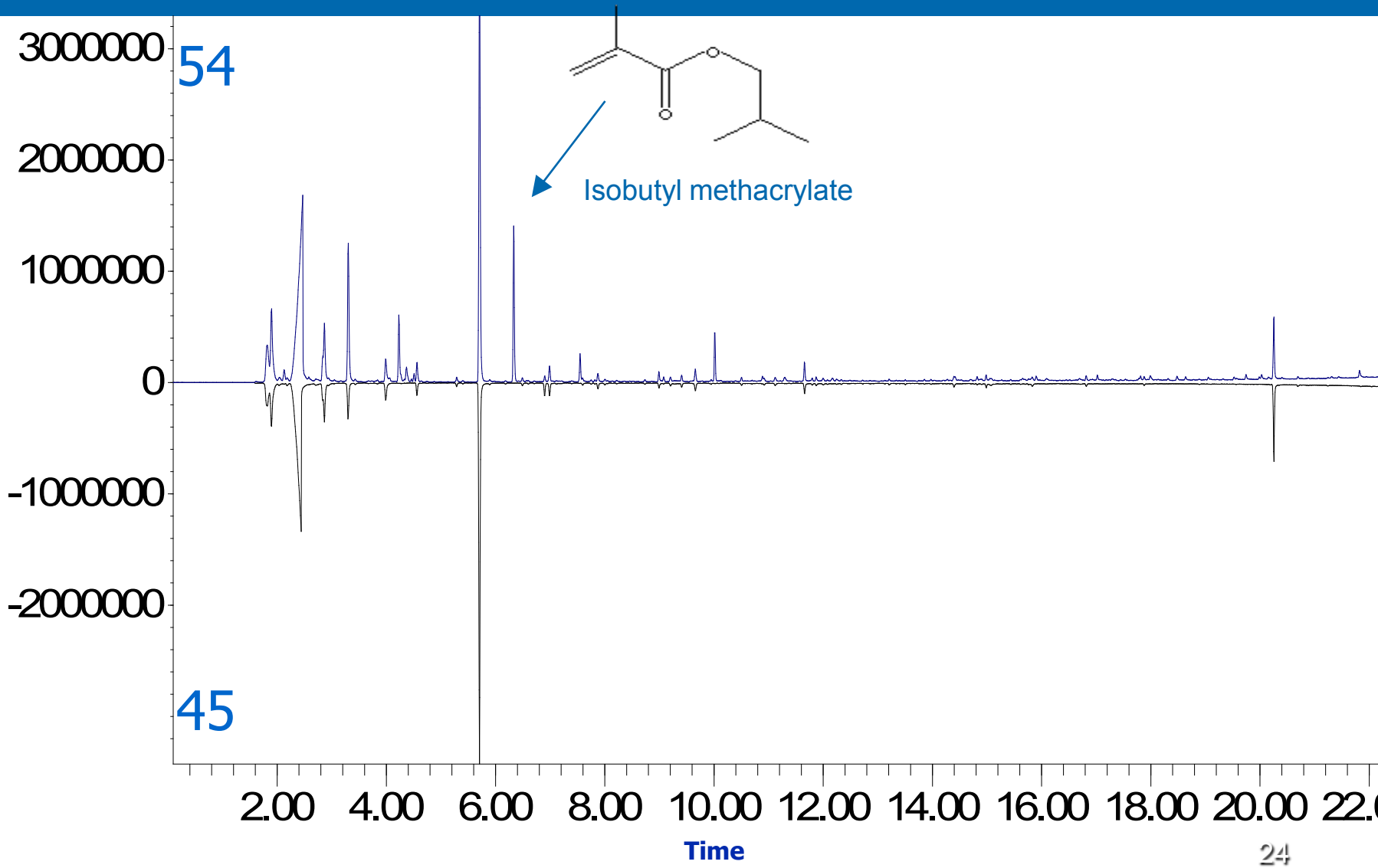
4 samples discriminated

12 groups to Py-GC/MS

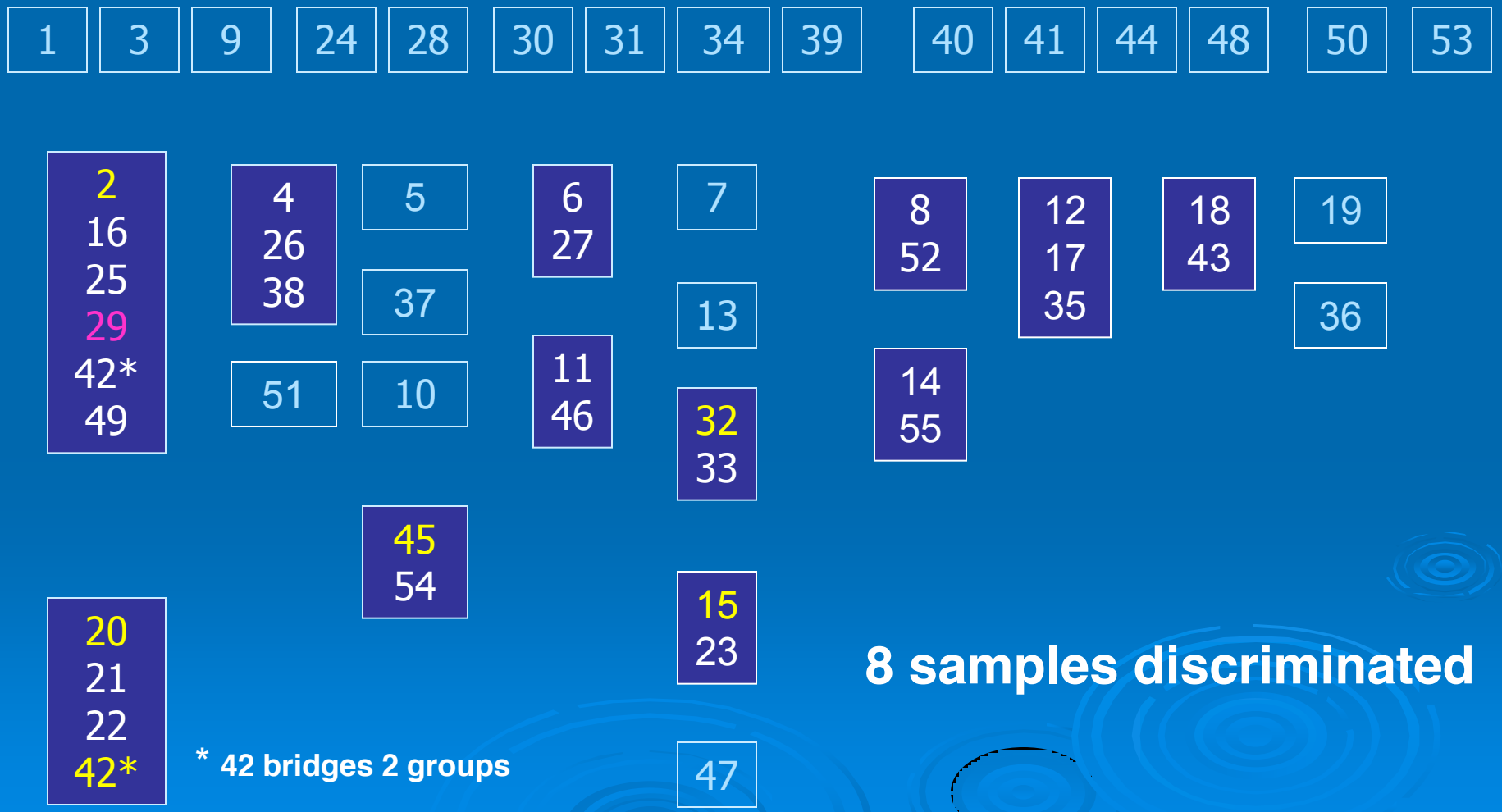
Py-GC/MS analysis

- Samples were analyzed with the following conditions:
  - Microscopically estimated sample size.
  - Used an autosampler for sample introduction.
  - Used quartz wool as a spacer within the quartz sample tube.
  - Pyrolysis chamber ramped up to 880^{o} C.
  - No sample derivitization.
  - Standard GC/MS configuration.
  - Replicate analyses performed when necessary to confirm discrimination.

Sample 45 vs. 54



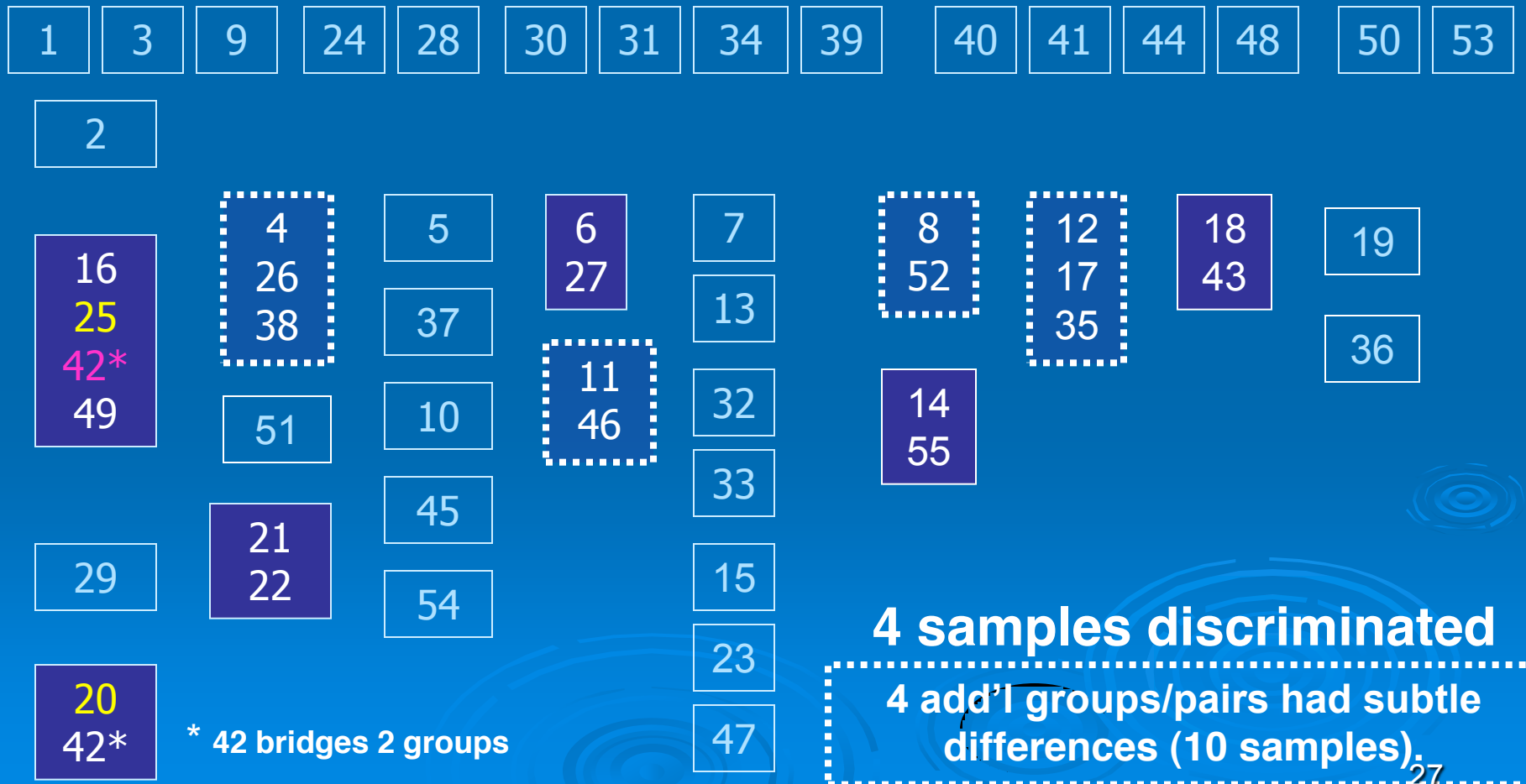
Py-GC/MS Groupings



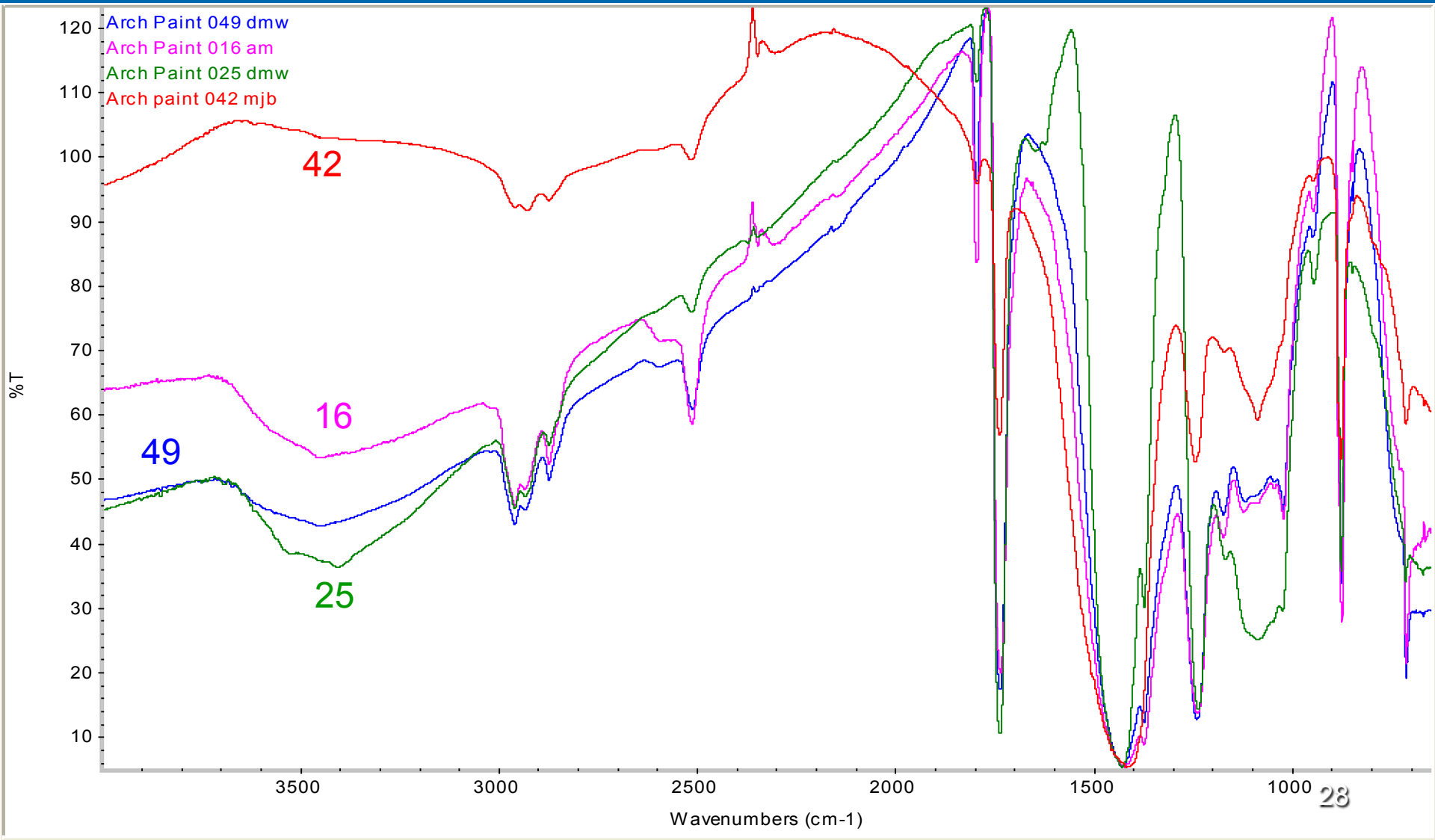
Techniques combined

- Undiscriminated samples evaluated using a combination of the results from all techniques.
- Order of evaluation of data was:
  - FTIR
  - SEM/EDS
  - Py-GC/MS
  - Vis/micro - conducted last to prevent bias from substrate observation.

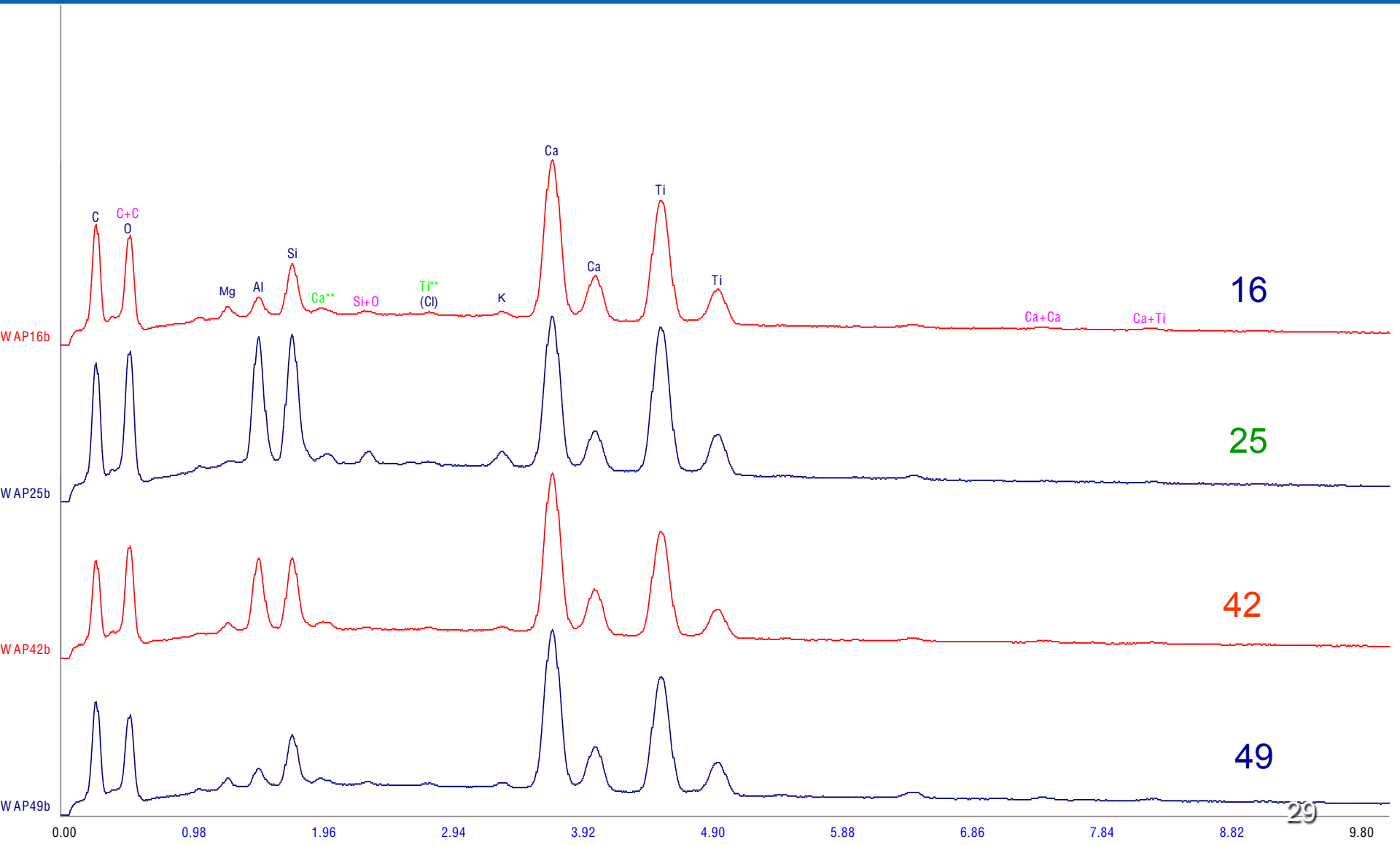
Discrimination from combined techniques



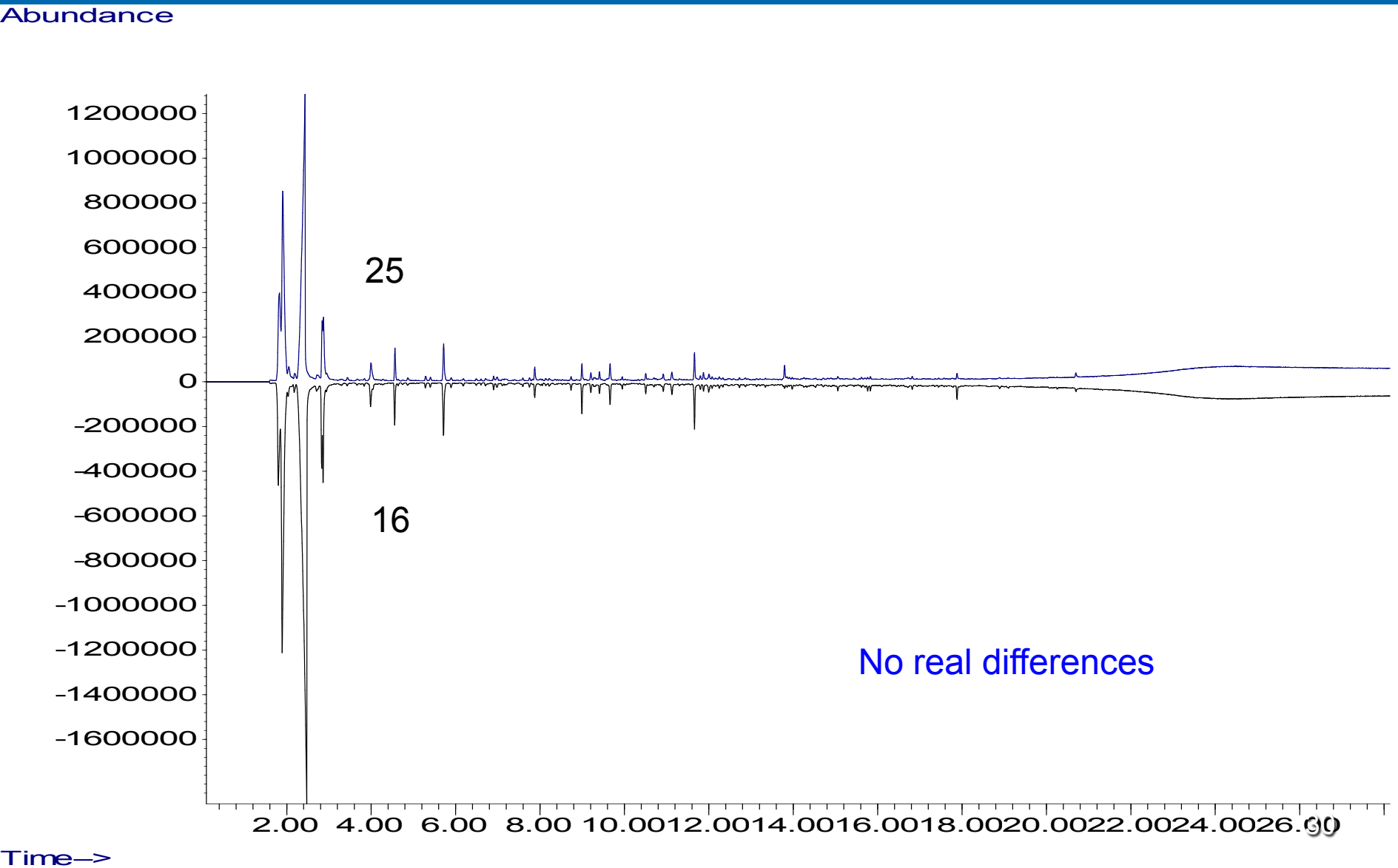
FTIR: 16, 25, 42, 49



SEM/EDS: 16, 25, 42, 49



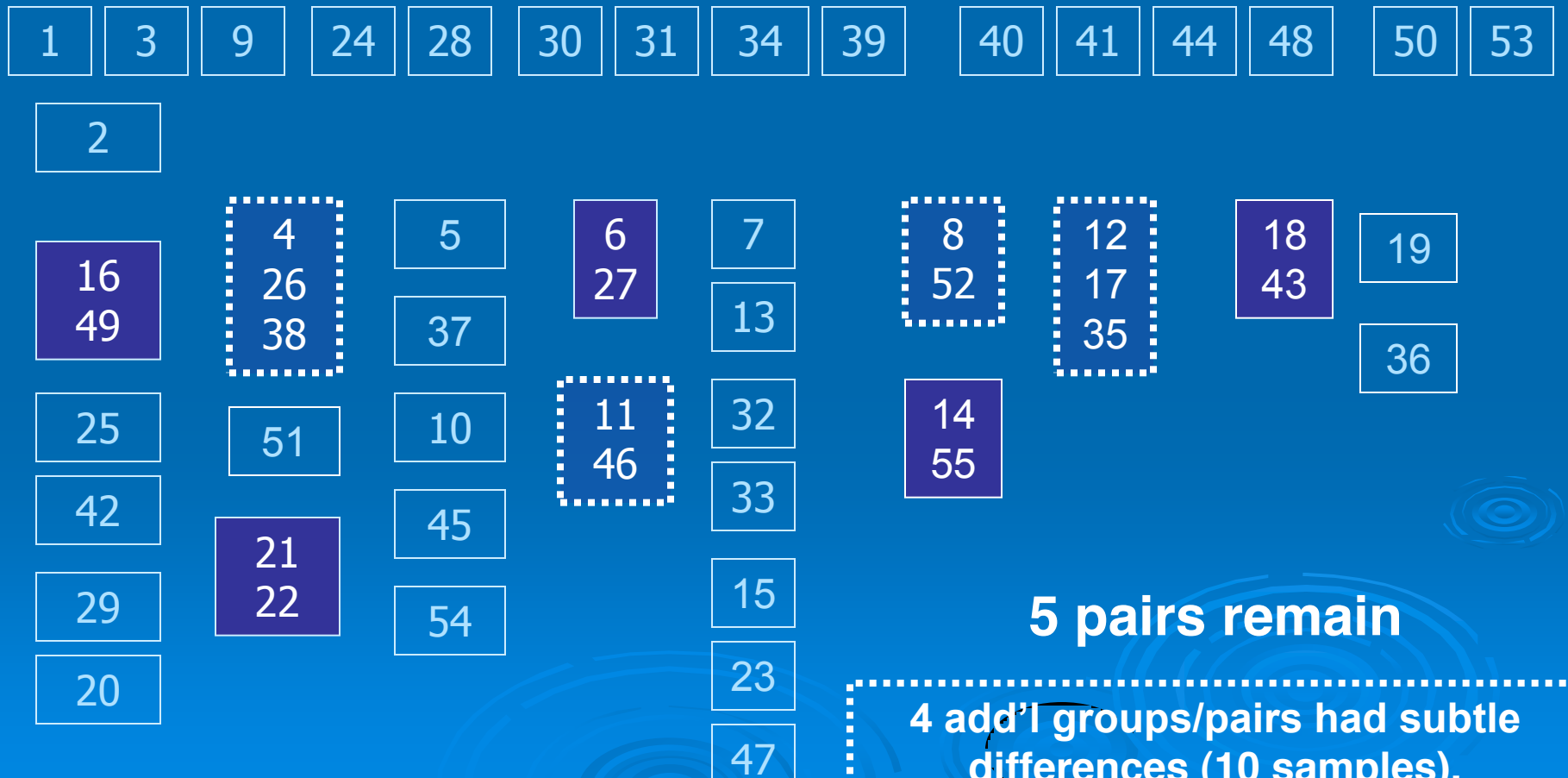
Py-GC/MS: 16 vs 25



Techniques combined summary: (16, 25, 42, 49)

- Pairwise comparison
  - FTIR overlay: diffs observed for 25 and 42
  - SEM/EDS: poss. ratio diffs for 25 and 42
  - Py-GC/MS: no real differences
  - Visual/Micro:
    - Macro exam: 16 = 49; 25~42
    - Micro exam: 16 = 49; 25 ≠ 42
- Final opinion: 25 and 42 discrim from 16/49

Techniques combined - discrimination



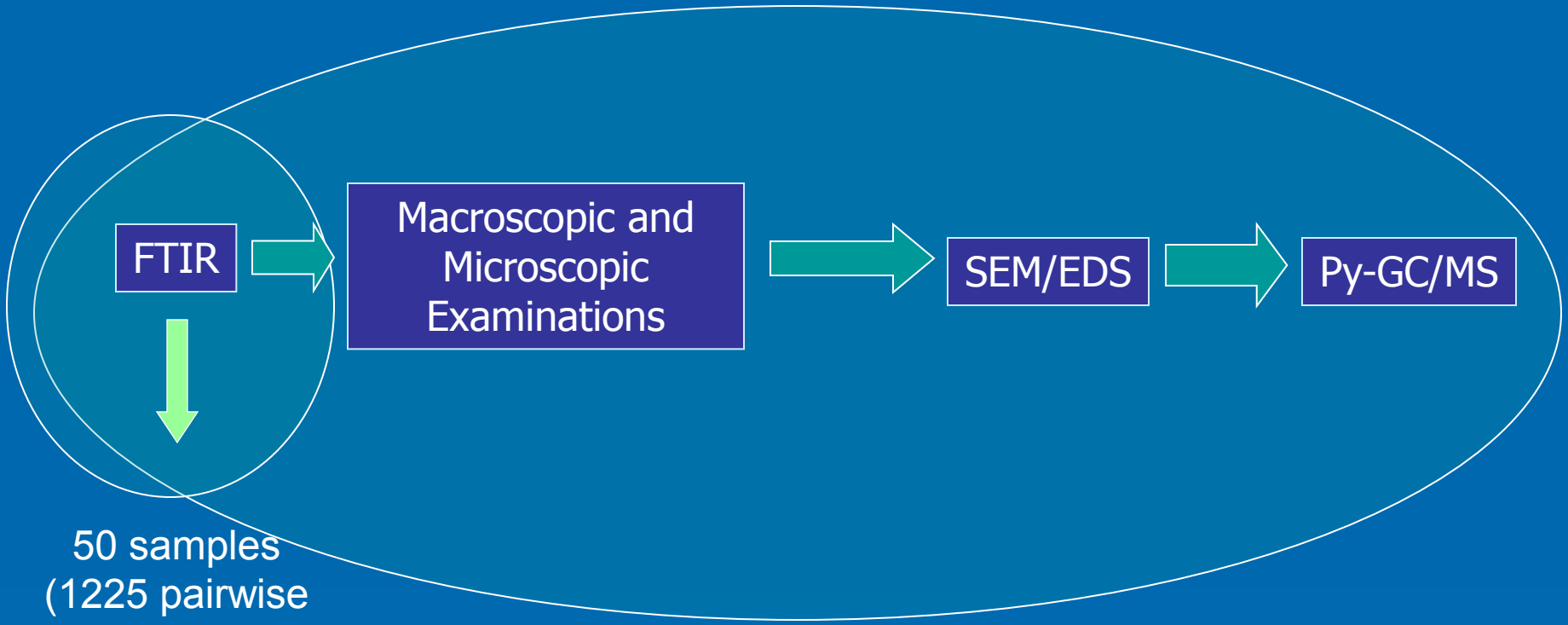
5 pairs remain

4 add'l groups/pairs had subtle differences (10 samples).

Summary of discrimination

- Nine groups/pairs remained.
  - Included five blind verification pairs (10 samples)
  - Two additional pairs (four samples)
  - Two groups of three samples each (six add'l pairs – six samples)
- Latter 4 pairs/groupings are aforementioned sets with subtle differences.
- The only pairs with **no** indications of physical or chemical differences were those samples that originated from the same source.

Discrimination Power



*does not include the 5 replicate pairs

Conclusions

- Overall discrimination using the reported analytical scheme is 99.35%.
- FTIR discrimination alone is 94.45%.

- The ability to differentiate samples of single layer white architectural paints is far greater than previously anticipated.

Future Work

Introduce Raman spectroscopy into FBI Lab's paint SOP

Explore PLM for architectural paints

Acknowledgements

Scott Ryland and Chris Bommarito who suggested this study.