

Analytical Chemistry and EQUIS

A Few Challenging Concerns

Presented by
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CDM

A Few Topics for Today's Discussion

- A Little About Analytical Method Codes or:
“Why did the lab analyze my SOM01.2 VOA samples by method E624?”
- Trouble With SIM Analyses
- One Particular Challenge With Dioxin Data
- What Is a Co-eluting Peak and Why Should I Care

A Little About Me

WHO IS THIS GUY

By Day and Sometimes Night

- Analytical Chemist and Lab Services Coordinator
- Data Validation for 18+ years
- Data Management 12 years
- Other Hats (Sampler/Field Team Leader/Project Manager)
- Analytical Chemist for Commercial Laboratory
 - Wet Chemistry and Metals Analyst/Supervisor
 - GC/MS Analyst



Analytical Method Codes

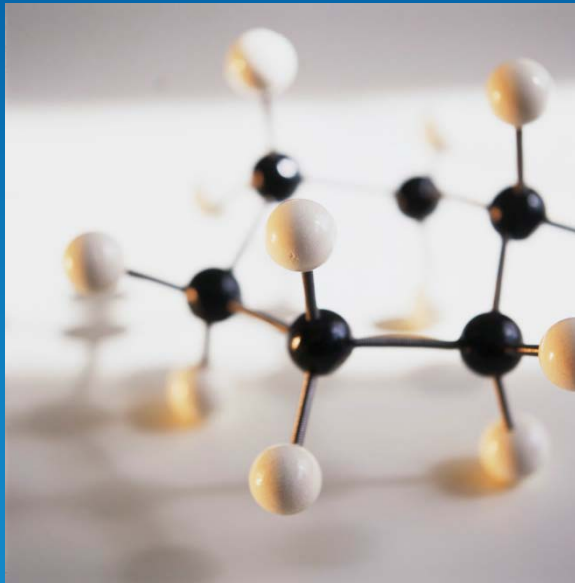
THE GREY AREA BETWEEN ANALYTICAL METHODS

Analytical Method Codes

- Labs need to maximize their analytical runs (batches)
- Many methods have overlapping requirements
 - Instrument conditions
 - QC requirements
 - Sequencing protocols
- One analytical run (instrument method) can satisfy
 - CLP SOWs low/medium or trace level analysis
 - Organics method series 600, SW846 (8260) or 500 series
- CLP seems to be particularly susceptible to variations in method codes

Analytical Method Codes

- Bottom Line
 - Do not be captive to the method code on the EDD
 - Confirm that the requested method was performed
 - Edit it or have the Lab provide the desired codes

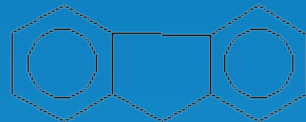
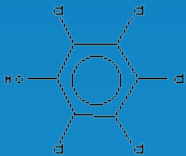
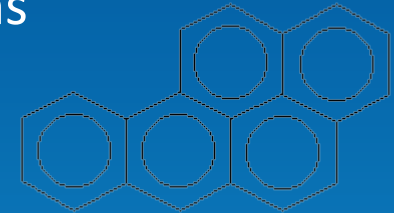
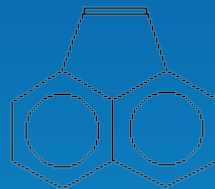
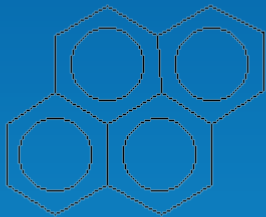


Trouble With SIM Analysis

SELECT ION MONITORING ANALYSIS

Trouble With SIM Analysis

- Select Ion Monitoring
 - Mass spectroscopy method
 - Improved sensitivity on organic compounds
 - Used on samples with no or minimal detections



Trouble With SIM Analysis

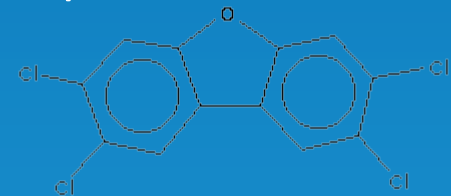
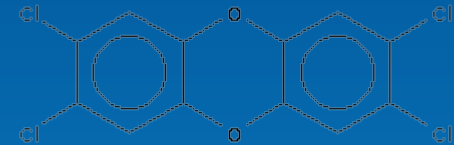
- Problems for Data Management
 - Generally presented as independent method
 - Yields 2 results for a compound
 - Is performed on samples regardless of need
 - Dual results are a problem for risk statistics
- Resolutions
 - Application of reportable result flag
 - Preparation of a “combined” result set

One Particular Challenge with Dioxin Data

THE ESTIMATED MAXIMUM POSSIBLE CONCENTRATION (EMPC)

The EMPC

- The EMPC differs from a reporting limit
 - It is a worst-case estimate of concentration (SW846 8290A, rev1, 2007)
 - This difference needs to be communicated
- Problems for data management
 - Not usually listed as a common qualifier
 - Contains more than 2 character (i.e. UJ) breaks business rule
- Resolution
 - Enter E, M, P & C as valid qualifiers
 - Bring it in as a comment and move it over after post
 - Or wait until the next EQUS release



EMPC Data Dance

Inserted for demonstration

| CAS_RN | CHEMICAL_NAME | RESULT_VALUE | ERROR_DELTA | RESULT_CODE | REPORTABLE_RESULT | DETECT_FLAGS | LAB_QUALIF_IERS | VALIDATOR_QUALIFIERS | INTERPRETED_QUALIFIERS | DETECTIO_N_LIMIT | Form 1 EMPC/EDL | RESULT_UNIT |
|------------|---------------------|--------------|-------------|-------------|-------------------|--------------|-----------------|----------------------|------------------------|------------------|-----------------|-------------|
| 51207-31-9 | 2,3,7,8-TCDF | 0.58 | | TRG | Yes | Y | J | J | J | 0.25 | | ng/kg |
| 1746-01-6 | 2,3,7,8-TCDD | 0.29 | | TRG | Yes | Y | J | J | J | 0.17 | | ng/kg |
| 57117-41-6 | 1,2,3,7,8-PeCDF | | | TRG | Yes | N | U | | | 0.18 | 0.176 | ng/kg |
| 57117-31-4 | 2,3,4,7,8-PeCDF | | 2 | TRG | Yes | Y | J | J | J | 0.16 | | ng/kg |
| 40321-76-4 | 1,2,3,7,8-PeCDD | | | TRG | Yes | N | | | EMPC | 0.19 | 0.334 | ng/kg |
| 70648-26-9 | 1,2,3,4,7,8-HxCDF | 0.65 | | TRG | Yes | Y | J | J | J | 0.14 | | ng/kg |
| 57117-44-9 | 1,2,3,6,7,8-HxCDF | 0.54 | | TRG | Yes | Y | J | J | J | 0.13 | | ng/kg |
| 60851-34-5 | 2,3,4,6,7,8-HxCDF | 1.1 | | TRG | Yes | Y | J | J | J | 0.14 | | ng/kg |
| 72918-21-9 | 1,2,3,7,8,9-HxCDF | | | TRG | Yes | Y | JB | | | 0.18 | 0.198 | ng/kg |
| 39227-28-6 | 1,2,3,4,7,8-HxCDD | | | TRG | Yes | N | | | EMPC | 0.17 | 0.258 | ng/kg |
| 57653-85-7 | 1,2,3,6,7,8-HxCDD | | | TRG | Yes | N | | | EMPC | 0.18 | 0.547 | ng/kg |
| 19408-74-3 | 1,2,3,7,8,9-HxCDD | 0.48 | | TRG | Yes | Y | J | J | J | 0.16 | | ng/kg |
| 67562-39-4 | 1,2,3,4,6,7,8-HpCDF | 3.9 | | TRG | Yes | Y | J | J | J | 0.18 | | ng/kg |
| 55673-89-7 | 1,2,3,4,7,8,9-HpCDD | | | TRG | Yes | N | | | EMPC | 0.32 | 0.523 | ng/kg |
| 35822-46-9 | 1,2,3,4,6,7,8-HpCDD | 10 | | TRG | Yes | Y | | | | 0.22 | | ng/kg |
| 39001-02-0 | OCDF | 9.4 | | TRG | Yes | Y | JB | J | J | 0.45 | | ng/kg |
| 3268-87-9 | OCDD | 88 | | TRG | Yes | Y | B | | | 0.62 | | ng/kg |

| TARGET ANALYTE | SELECTED IONS | PEAK RT | ION RATIO # | CONCENTRATION | Q | EMPC/EDL |
|----------------|---------------|---------|-------------|------------------|---------------|----------|
| 2378-TCDD | 320/322 | 27.30 | 0.65 | 0.291 | J | |
| 2378-TCDF | 304/306 | 25.90 | 0.76 | 0.579 | J | |
| 12378-PeCDF | 340/342 | | | | U | 0.176 |
| 12378-PeCDD | 354/356 | 33.40 | 0.77 * | | J | 0.334 |
| 23478-PeCDF | 340/342 | 33.00 | 1.50 | 1.96 | J | |
| 123478-HxCDF | 374/376 | 36.10 | 1.33 | 0.646 | J | |
| 123678-HxCDF | 374/376 | 36.22 | 1.43 | 0.536 | J | |
| 123478-HxCDD | 390/392 | 36.90 | 0.95 * | | J | 0.258 |
| 123678-HxCDD | 390/392 | 37.01 | 1.52 * | | J | 0.547 |
| 123789-HxCDD | 390/392 | 37.26 | 1.25 | 0.478 | J | |
| 234678-HxCDF | 374/376 | 36.77 | 1.43 | 1.12 | J | |
| 123789-HxCDF | 374/376 | 37.52 | 1.21 | 0.198 | JB | 0.198 |
| 1234678-HpCDF | 408/410 | 38.95 | 1.05 | 3.87 | J | |
| 1234678-HpCDD | 424/426 | 39.86 | 1.03 | 10.0 | J | |
| 1234789-HpCDF | 408/410 | 40.25 | 1.41 * | | J | 0.523 |
| OCDD | 458/460 | 42.52 | 0.86 | 87.9 | B | |
| OCDF | 442/444 | 42.68 | 0.85 | 9.40 | JB | |

Reported on EDD correctly

Not an EMPC issue

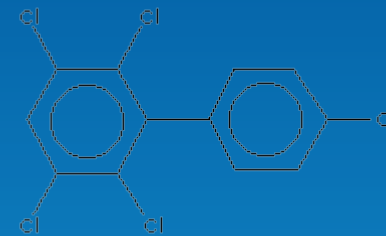
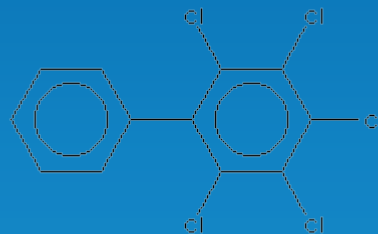
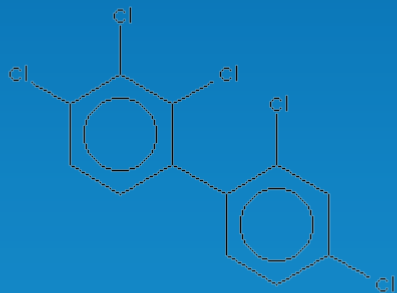
NOTE: Concentrations, Estimated Maximum Possible Concentrations (EMPCs), and Estimated Detection Levels (EDLs) for solid samples are calculated on a dry weight basis (except tissues, which are reported on a wet weight basis with % Lipids).

Co-Eluting Peaks from PCB Congener Analysis

SOME THOUGHTS ON DEALING WITH CO-ELUTING PEAKS

Co-Eluting Peaks

- Co-eluting peak is:
 - A chromatographic peak that consists of 2 or more compounds
 - PCB congener analysis generally causes most confusion
 - 209 congeners
 - 30+ co-eluting peak sets
 - Up to 5 compounds in one co-elution



Method 1668B November 2008

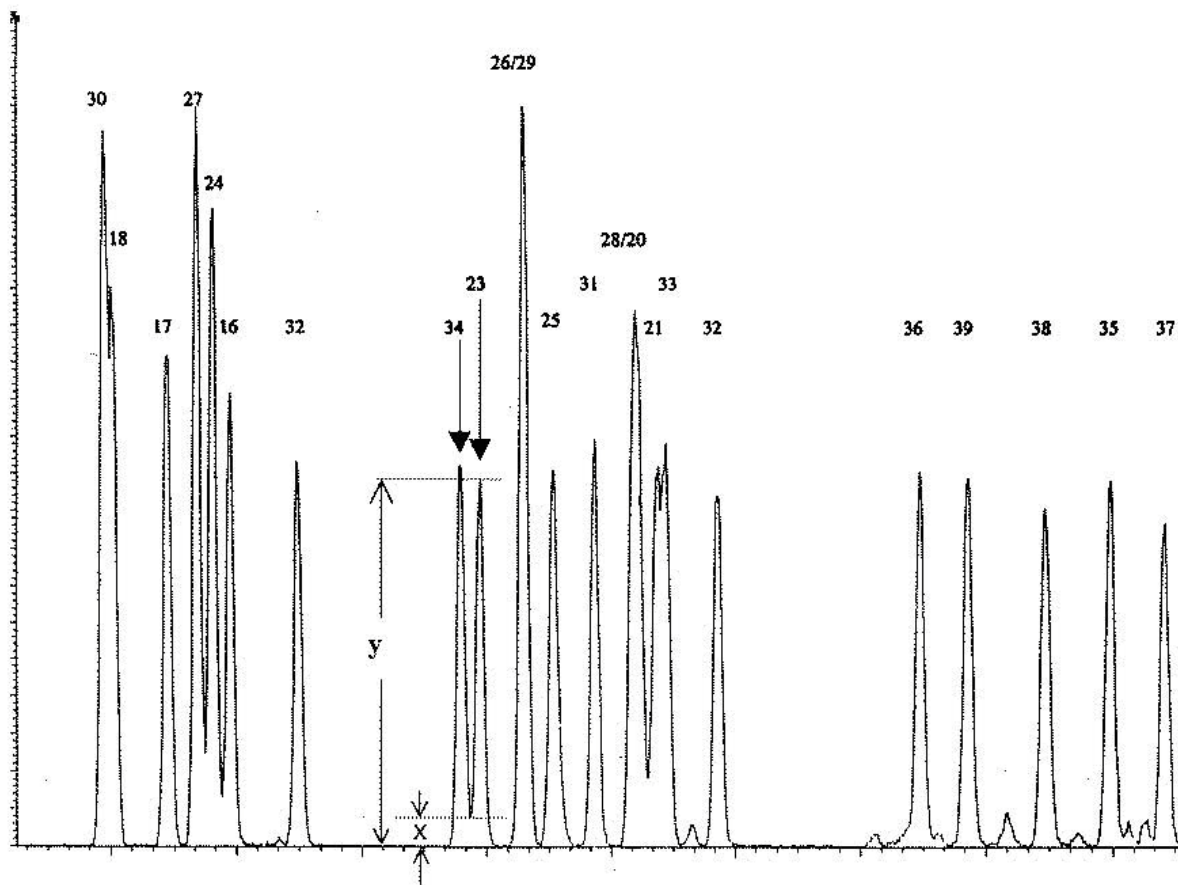
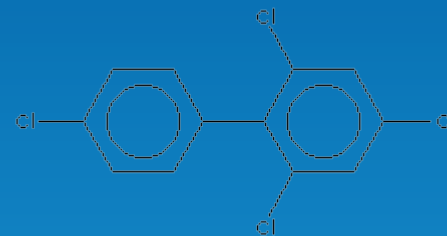
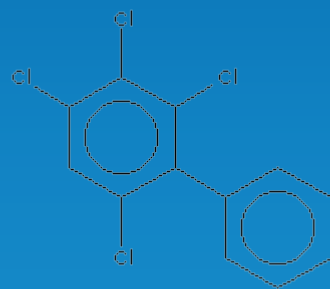
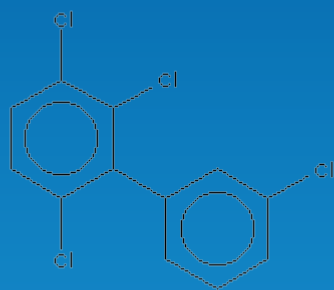


Figure 6 Octyl column resolution test #1: Separation of Cl-3 congeners 34 and 23 with valley <40% (i.e. $100x/y < 40\%$)

Co-Eluting Peaks

- Co-eluting compound relationship identified by lowest congener
 - PCB-59, 62 & 75
 - PCB-59 should have concentration reported sometimes with a “C” qualifier
 - PCB-62 & PCB-75 should both have “null” in result with “C59” qualifier



Co-Eluting Peaks in EDDs

- Example of PCB Congener Co-eluting Compounds EDD

Inserted for demonstration

| #sys_sample_code | lab_anl_m | chemical_name | result_value | | reportable_result | detect_flag | lab_qualifiers | validator_qualifiers | interpreted_qualifiers | reporting_detection_limit | result_unit | minimum_detectable_conc |
|------------------|-----------|---------------|--------------|--------|-------------------|-------------|----------------|----------------------|------------------------|---------------------------|-------------|-------------------------|
| | E1668A | PCB-59 | 64500 | 64500 | Yes | Y | C59 | J | J | 552 | ng/kg | Validated |
| | E1668A | PCB-62 | 64500 | | Yes | Y | C59 | J | J | 552 | ng/kg | Validated |
| | E1668A | PCB-75 | 64500 | | Yes | Y | C59 | J | J | 552 | ng/kg | Validated |
| | E1668A | PCB-83 | 355000 | 355000 | Yes | Y | C83 | J | J | 797 | ng/kg | Validated |
| | E1668A | PCB-99 | 355000 | | Yes | Y | C83 | J | J | 797 | ng/kg | Validated |
| | E1668A | PCB-116 | 116000 | | Yes | Y | C85 | J | J | 656 | ng/kg | Validated |
| | E1668A | PCB-117 | 116000 | | Yes | Y | C85 | J | J | 656 | ng/kg | Validated |
| | E1668A | PCB-85 | 116000 | 116000 | Yes | Y | C85 | J | J | 656 | ng/kg | Validated |

Total PCB 1251500

Total PCB 535500

Difference 716000

| #sys_sample_code | lab_anl_m | chemical_name | result_value | reportable_result | detect_flag | lab_qualifiers | validator_qualifiers | interpreted_qualifiers | reporting_detection_limit | result_unit | minimum_detectable_conc |
|------------------|-----------|---------------|--------------|-------------------|-------------|----------------|----------------------|------------------------|---------------------------|-------------|-------------------------|
| | E1668A | PCB-59 | 64500 | Yes | Y | C59 | J | JC | 552 | ng/kg | Validated |
| | E1668A | PCB-62 | | Yes | Y | C59 | J | JC59 | 552 | ng/kg | Validated |
| | E1668A | PCB-75 | | Yes | Y | C59 | J | JC59 | 552 | ng/kg | Validated |
| | E1668A | PCB-83 | 355000 | Yes | Y | C83 | J | JC | 797 | ng/kg | Validated |
| | E1668A | PCB-99 | | Yes | Y | C83 | J | JC83 | 797 | ng/kg | Validated |
| | E1668A | PCB-116 | | Yes | Y | C85 | J | JC | 656 | ng/kg | Validated |
| | E1668A | PCB-117 | | Yes | Y | C85 | J | JC85 | 656 | ng/kg | Validated |
| | E1668A | PCB-85 | 116000 | Yes | Y | C85 | J | JC85 | 656 | ng/kg | Validated |

Co-Eluting Peaks

- Problems for data management
 - Not a single standard for EDD
 - Result = Null
 - Identifying qualifier > than 2 characters (i.e. C59)
 - Problems with reporting/calculating total PCB
- Resolution
 - Enter character “-” for result
 - Enter C59 (and others) as valid qualifiers
 - Bring it in as a comment and move it over after post
- Or wait until the next EQUS release

QUESTIONS, COMMENTS, OR
DISCUSSION