



The Practicality (Necessity) of Use of Clean-up Techniques for the Analysis of D/F and PCB Congeners

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Clean-up Methods

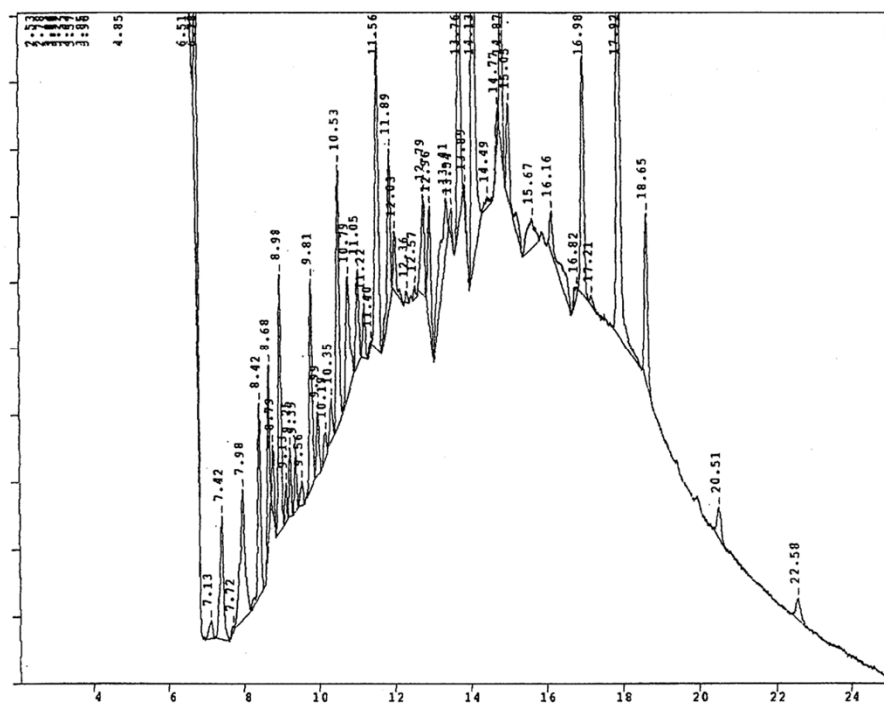


In today's competitive environmental lab market, we are constantly tasked with;

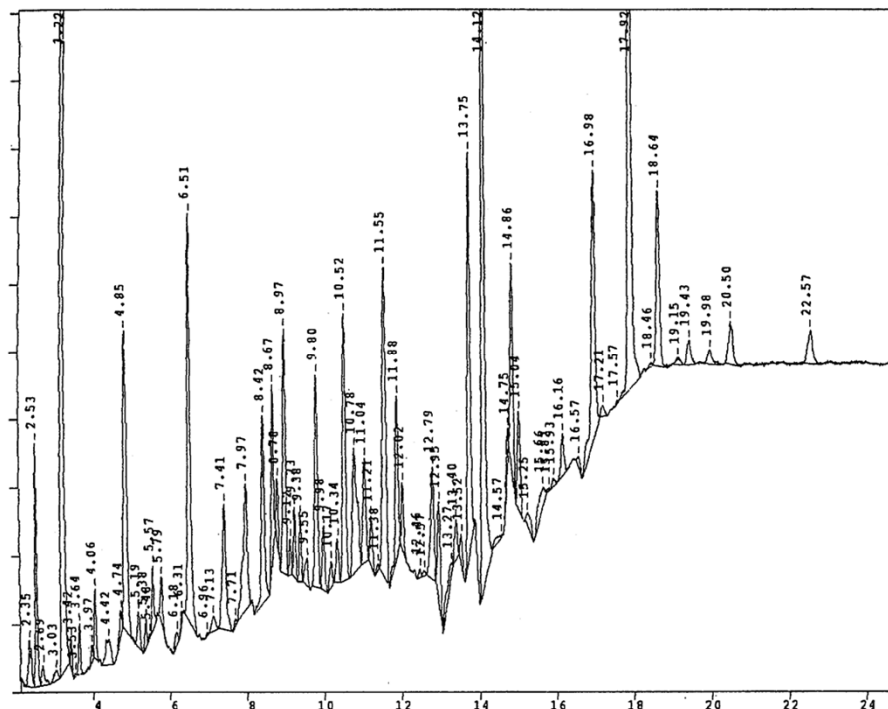
1. Doing our work faster
2. Generating analytical results for less cost
3. But increasing and improving the quality of the analytical result

The use of clean-up methods helps #3, but goes against #1 and #2

Example #2



Before Sulfur Clean-up



After Sulfur Clean-up

Why Use Clean-up Methods



SW-846 Method 3600 states that the purpose of a clean-up method is to remove interferences and high boiling material that may;

- Result in errors in quantitation
- False positives
- False negatives caused by retention time shifts
- Rapid reduction in performance of chromatography columns
- Instrument downtime

Available Clean-up Methods



Method No.	Method Name	Cleanup Type
3610	Alumina Cleanup	Adsorption
3611	Alumina Cleanup and Separation of Petroleum Wastes	Adsorption
3620	Florisil Cleanup	Adsorption
3630	Silica Gel Cleanup	Adsorption
3640	Gel-Permeation Cleanup (GPC)	Size-Separation
3650	Acid-Base Partition Cleanup	Acid-Base Partitioning
3660	Sulfur Cleanup	Oxidation/Reduction
3665	Sulfuric Acid/Permanganate Cleanup	Oxidation/Reduction

Clean-up Chemistries



Mechanism	Characteristic
Adsorption	Useful for separating analytes of relatively narrow polarity from interferences of different polarity
Acid-base partitioning	Separate acidic or basic organics from neutral organics
Size Exclusion	Separate high molecular weight (high boiling, non-volatile) organics from a wide range of organics
Oxidation/Reduction	Chemically change the solubility or adsorption properties of interferences

HRMS Analyses



Polychlorinated Dibenzodioxins and Polychlorinated Dibenzofurans (D/F)

- SW-846 Method 8290
- EPA Method 1613

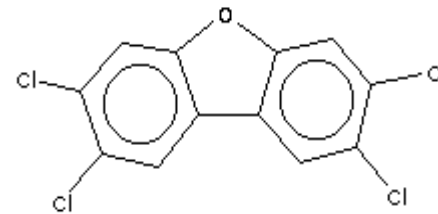
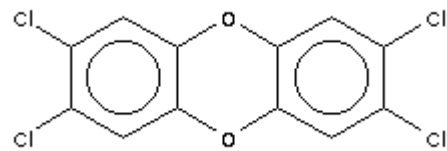
Polychlorinated Biphenyl Congeners (PCB congeners)

- EPA Method 1668

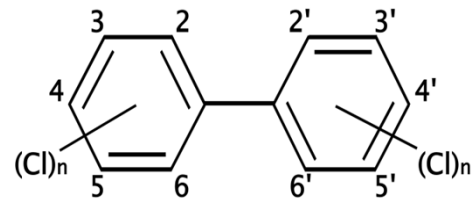
HRMS Analyses



Dioxins/Furans



PCB Congeners



HRMS Analyses



- For most or many of the situations where the 3600 series clean-ups are applied, target analytes are present or being detected in nanogram (ng) and microgram (ug) masses
- The interferences that are being removed are typically in the high milligram (mg) or low gram level
- For the HRMS method applications, target analytes are present or being detected at picogram (pg) and in some instances high femtogram (fg) masses
- Therefore, the use of more than one clean-up method and combination of clean-up mechanisms is needed.

HRMS Analyses



Multi-tiered Approach

1. Use Gel Permeation Chromatography as a broad sweep to remove the high mass co-extractants
2. Exploit the fact that D/F and PCB congeners are groups of compounds with slightly different but similar range of polarity
3. Also, exploit the fact that many of the possible co-extractants are compounds that can be oxidized or reduced to change their adsorption and solubility characteristics

HRMS Analyses



- After GPC, use combined characteristics to optimize the clean for trace analysis
- Use adsorption (silica gel), with chemical oxidation (acid) to effect a more thorough clean-up
- Add in adsorption (silica gel), with base to catch those organics unaffected by the acid
- Combine that with an additional adsorption chemistry (alumina, Florisil) to more full polish the extract.
- Use of adsorption media also allows for fractionation of constituents

HRMS Analyses



Multiple sorbents with different chemical modifiers

- Silica gel
- Silica gel w/ H₂SO₄
- Silica gel w/ NaOH
- Alumina
- Florisil



HRMS Analyses



Columns with samples loaded.

Note the various degrees of reaction occurring

Results



- Without the “extra” clean-up routine analytical systems unable to detect PFK lockmass for certain MID mass windows.
- The requirements for relative retention time (RRT) within each method, Method 1668 is much more sensitive to, are more difficult to maintain.
- Without RRT within specifications, quality of detections can be questioned.
- More frequent maintenance required on system
- Ability to pass shift ending calibration check standards (8290) reduced

Conclusions



- There is no doubt that the use of broad and extensive clean-ups adds to cost of analysis.
- The use of clean-ups can also add time to the sample preparation step of the analysis.
- The use of clean-ups reduces re-analysis on the instrument.
- The use of clean-ups helps to assure the quality of the data.
- The use of clean-ups increases instrument uptime.
- In the final analysis, the use of clean-ups improves analysis TAT and improves client satisfaction

Thank you



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