



Civil & Environmental Consultants, Inc.

# Analytical Methods and Industrial Wastewater

Recognizing when a Method is Generating  
Bad Results or Causing False  
Exceedances

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# Sources for Analytical Methods

- USEPA Clean Water Act Analytical Methods
  - EPA publishes laboratory analytical methods, or test procedures that are used by industries and municipalities to analyze the chemical, physical and biological components of wastewater and other environmental samples that are required by the Clean Water Act (CWA). Most of these methods are published in the Code of Federal Regulations at 40 CFR Part 136.
- Standard Methods for the Examination of Water and Wastewater
  - A compilation of current analytical test methods and best practices
  - Jointly published by the American Public Health Association (APHA), the American Water Works Association (AWWA), and the Water Environment Federation (WEF).



# Analytical Method Considerations

- Test Matrix
  - Typically drinking water or municipal wastewater
- Interferences
  - Method typically lists common interferences and how to address them
- MDL and RL
  - Defined / validated during the method development
  - Matrix specific / dependent
  - Must be periodically reevaluated

# MDL and RL

- Method Detection Limit (MDL)
  - The minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results.
- Reporting Limit (RL)
  - The minimum concentration of an analyte that can be measured within specified limits of precision and accuracy.
    - Either the lowest acceptable calibration point used by a laboratory; or calculated by multiplying the MDL by a factor of 3
    - EPA considers the terms “reporting limit,” “quantitation limit,” and “minimum level” to be synonymous

# General Rule

- When faced with unexpected results:
  - **Step #1: question the method**

# Past Experience with Method Issues

- Total Suspended Solids (TSS)
- Chemical Oxygen Demand (COD)
- Oil & Grease (HEM)
- 5-day Biochemical Oxygen Demand (BOD<sub>5</sub>)
- Total Organic Carbon (TOC)
- Inductively Coupled Plasma (ICP) Metals
- Methylene Blue Active Substances (MBAS)
- Cobalt Thiocyanate Active Substances (CTAS)
- Polycyclic Aromatic Hydrocarbons (PAHs)

# What to do, if you suspect an analytical issue?

- Review the analytical report
  - Qualifiers
  - Quality control samples
- Review the common method interferences
- Contact the analytical lab
- Test / audit the analytical lab
  - Blind samples
  - Split samples with a second lab
- Contact USEPA and/or Standard Methods
  - Clean Water Act (CWA) Methods Team
  - CWA Alternate Test Procedure (ATP) Program
  - Standard Methods Technical Information Manager
- Method validation study

# Decoding Analytical Reports

- Quality Control Samples:
  - Blanks
  - Calibration Standards
  - Duplicates
  - Matrix spikes
  - Matrix spike duplicates
  - Surrogate standard spiking
- What is the lab's tolerance for QC samples?
  - Duplicate Relative Percent Difference (RPD)
  - Matrix Spike Recoveries
- What is the lab policy for failed QC?
- Is the lab doing duplicates and matrix spikes on your samples?



# Decoding Analytical Reports

- Qualifier Flags

- J - The reported result is an estimate. The value is less than the minimum calibration level but greater than the estimated detection limit (EDL)
- U - The analyte was not detected in the sample at the estimated detection limit (EDL)
- E - Exceeds calibration range.
- D - Dilution data. Result was obtained from the analysis of a dilution
- B - Analyte found in sample and associated blank
- NR - Analyte not reported because of problems in sample preparation or analysis
- V - Surrogate recovery is not within method control limits
- EMPC - Estimated maximum possible concentration. Indicates that a peak is detected but did not meet all the method required criteria

# USEPA Does Allow for Method Modification

- §136.6 Method modifications and analytical requirements
  - (4) Equivalent performance means that the modified method produces results that meet or exceed the QC acceptance criteria of the approved method
- USEPA Guidance Document
  - Solutions to Analytical Chemistry Problems with Clean Water Act Methods (2007)
  - For chemical methods, you may demonstrate that there is interference and implement corrective action

# Case History #1

- Chemical industry client
- Wastewater from process cleaning between production batches
- Many products contain surfactants
- Industrial pretreater
  - Pretreatment system consisting of pH control and antifoam addition
- Exceedances for oil & grease

# Background

- Initial project scope
  - Site visit
  - Data review
  - Report on options for reducing effluent oil & grease
- Discovery
  - Client does not process any plant or animal fats, or, in general, mineral / petroleum oils
  - Identified potential method issues
- Consultation with USEPA on Method 1664B
- Meeting with the POTW to discuss method issues

# Oil and Grease Definitions

- Oil
  - a) Any of numerous unctuous combustible substances that are liquid or can be liquefied easily on warming, are soluble in ether but not in water, and leave a greasy stain on paper or cloth;
  - b) Petroleum
- Grease
  - a) Rendered animal fat;
  - b) Oily matter;
  - c) A thick lubricant

(Merriam-Webster Definition)

# How are Oil and Grease measured

- Oil & grease is an aggregate parameter
  - Parameter is defined by the test method
  - Some other aggregate parameters: BOD<sub>5</sub>, COD, TOC
- Test Method: USEPA Method 1664B
  - n-Hexane Extractable Material (HEM)
  - Measures compounds that are soluble in n-hexane
- Method 1664B replaced EPA Method 413.1
  - Method 413.1 used Freon-113
  - "EPA acknowledges that, due to the diverse nature of discharges, there may be instances in which n-hexane will extract an amount of oil and grease greater or less than the amount extracted by Freon-113"

# Method 1664B Analytical Method Learnings

- Surfactants can cause emulsions to occur during this extraction. The method allows multiple techniques to “break” any significant emulsions.
- Emulsions and the technique used to break that emulsion can impact the repeatability and accuracy of the method.
- The degree of “polarity” of a surfactant impacts its “solubility” in the hexane phase and the aqueous phase during the separation step of the method.

# Method 1664B Analytical Method Learnings

- According to Clean Water Act (CWA) Alternate Test Procedure (ATP) Coordinator (Lemuel Walker, Jr.)
  - “Yes, surfactants may be determined by Method 1664 Revision A and Revision B”
  - “Any materials extracted by n-hexane which do not volatilize at 85 C are considered HEM or SGT-HEM”
  - “It is known that detergents can be an interference due to the formation of emulsions in the extraction”



# Current Project Status

- Agreement with the POTW that Method 1664B is likely not appropriate for measuring actual fats, oils and/or grease in the client's discharge to the POTW
  - As it appears that the majority of HEM is due to compounds other than fats, oils and grease
- Method study currently in progress
  - 70+ blind samples (blanks, standards, duplicates, matrix spikes with standards and products, serial dilutions)
  - Evaluating which raw materials and/or products are extracted as HEM
  - Evaluating which raw materials and/or products interfere with the method
- Client evaluating potential sources of oil & grease and potential routes into the plant's sewers
- Agreement to develop an alternative means for assuring that the client is not discharging significant concentrations of actual fats, oils and greases to the POTW



# Case History #2

- OCPSF chemical industry (plastics materials and resins)
- 7 MGD process effluent
- Treatment system
  - pH adjustment (metals precipitation)
  - Primary clarification
  - Equalization
  - Conventional activated sludge
  - Granular media filtration
  - Disinfection
  - Step aeration
- Client on target for monthly average mass exceedance of TSS

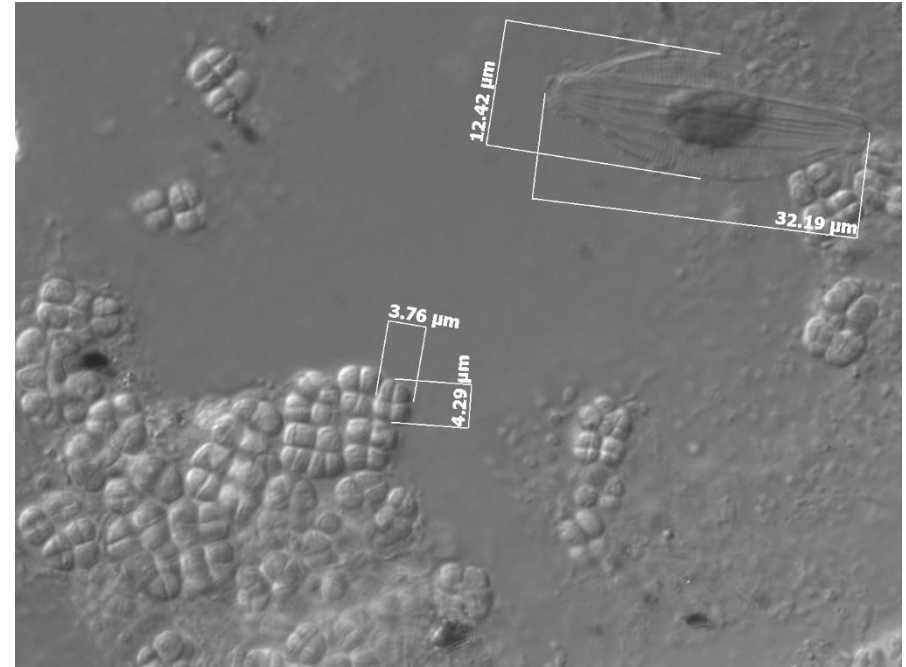
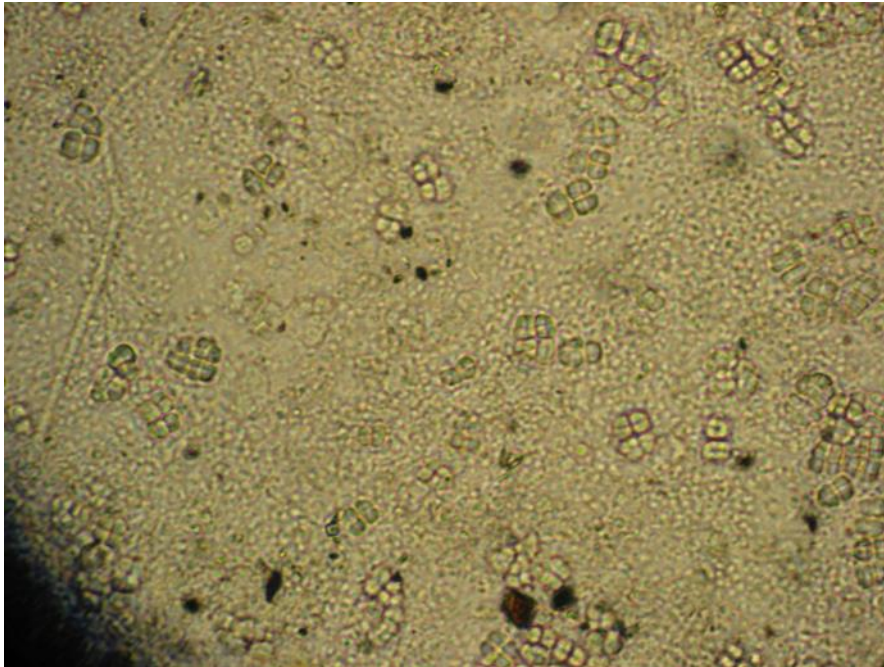


# Site Visit

- Performed TSS analysis in client's onsite lab
- Discussed issue with plant personnel
  - Learned that the filtration was taking longer than normal
- Performed microscopic analysis
- Initial findings
  - Something in the effluent is causing the TSS filters to rapidly blind off. This may also be causing additional matter (or TDS), which would otherwise pass through the filter paper, to be retained on the filter, thereby biasing the result.
  - Testing using varying volumes of DI rinse show that rinsing is critical for achieving accurate and repeatable results. Samples that were rinsed with a DI volume of less than 100% of the sample volume showed as significant error.
  - Per Standard Methods, if it takes longer than 10 minutes to filter the sample, then the lab should either use a larger diameter filter or a smaller sample volume.



# Chroococcus (cyanobacteria) or Zooglea?



# Analytical Laboratory Audit

- Findings:
  - Lab was filtering 1L samples
    - Followed by 30 mL rinse
  - Lab reported filtration times of 45 minute for the 1L samples
    - Stopped rinsing samples when filtration times got too long

# Recommendations

- Recommendations for the lab:
  - Smaller sample volumes (50 mL)
  - Consider using larger diameter filters to reduce filter times
  - Rinse volume should be at least 200% of the sample volume
  - Rinses should be added in portions allowing each portion to drain
  - Perform 4 replicates on all client samples
    - Target a relative percent difference of 10% (20% at worst)
    - For samples of less than 50 mg/L TSS, the absolute difference between the duplicates should be less than 4 mg/L
- Recommendations for the plant:
  - Reduce residual phosphorous (i.e., nutrient phosphorous addition)
  - Increase F/M by wasting less sludge
  - Coagulant addition to address related WAS dewatering issue



# Key Points from TSS Method

- SM 2540 D. Total Suspended Solids Dried at 103–105°C
- b. Interferences:
  - For samples high in dissolved solids thoroughly wash the filter to ensure removal of dissolved material.
  - Prolonged filtration times resulting from filter clogging may produce high results owing to increased colloidal materials captured on the clogged filter.
- c. Sample analysis:
  - While stirring, pipet a measured volume onto the seated glass-fiber filter.
  - Wash filter with three successive 10-mL volumes of reagent-grade water, allowing complete drainage between washings, and continue suction for about 3 min after filtration is complete.
  - Samples with high dissolved solids may require additional washings.

# Case History #3

- Chemical industry client
- Singapore
- High strength wastewater
  - Significant fraction of non-degradable organics
  - Percent levels of sodium chloride
- Treatment system:
  - Membrane activated sludge
  - Activated carbon
- Issue with effluent COD compliance





# COD as a Regulatory Parameter

- Due to the expense and complexity of the BOD<sub>5</sub> test, many developing countries have substituted COD for BOD<sub>5</sub> as the regulated parameter by assuming a correlation
- Because many industrial facility effluents contain non-biodegradable / inert compounds that do not contribute to oxygen depletion in the receiving stream, COD is not an appropriate regulatory parameter for industrial discharges
- In the US, only two industries are regulated based on effluent COD (one is the pharmaceutical industry)

# Issue with Measuring Effluent COD

- Singapore NEA Trade Effluent Standards
  - 50 mg/L BOD<sub>5</sub>
  - 100 mg/L COD
- Unable to measure compliance with 100 mg/L COD limit
  - Wastewater contains between 2.5% to 3.8% chlorides
  - Based on the chloride concentration, the COD test method would have an MDL of about 600 mg/L

Parameter	Units	Influent	MBR Effluent	Carbon Effluent
COD	mg/L	13,000	2,000	700
TOC	mg/L	4,500	800	300
BOD <sub>5</sub>	mg/L	--	12	12

# COD and Chlorides

- Chloride is the most common interference with the COD method
  - Reacts with silver ion to precipitate silver chloride, and thus inhibits the catalytic activity of silver
  - Is unpredictably oxidized by potassium dichromate to produce chlorine
  - SM 5220: Do not use the test for samples containing more than 2,000 mg Cl-/L
- Chloride interference can be overcome largely, though not completely, by complexing with mercuric sulfate ( $\text{HgSO}_4$ ) before the refluxing procedure
- May be removed by precipitation with silver ion and filtration before digestion
  - This approach may introduce substantial errors due to the occlusion and carrydown of COD matter

# Approach

- Research and whitepaper on the history of BOD and COD as regulatory parameters worldwide and the development of the COD method
- Consultation with Standard Methods into research performed on using the COD method with high chloride wastewaters
- Meetings with Singapore NEA
- Method validation study for using USEPA Method 410.3
  - Method proposed by NEA
  - Minimum accepted value for COD of 250 mg/L for chloride level exceeding 1,000 mg/L
  - No existing precision and accuracy data for method
  - Mercuric sulfate is added in the ratio of 10 mg to 1 mg chloride
  - Chloride correction factor (CCF) applied, based on analyzing blanks at various chloride levels, and adjusted for chemistry of chloride oxidation

# Outcomes

- USEPA Method 410.3 Method validation study
  - A PQL of 250 mg/L is obtainable at chloride concentrations of 20,000 mg/L and 25,000 mg/L
  - The method can obtain accuracy and precision based on achieving 80 to 120 percent recoveries and less than 20% relative percent difference for replicates or duplicates
  - However, these PQLs and the ability to reliably achieve accuracy and precision criteria are contingent upon consistent and constant determination of the chloride correction factor.
  - Not comfortable with the safety and health issues presented by use of this Method on a routine basis, particularly the exposure to mercury and the disposal of mercury-laden waste.
- Variance granted by NEA for elevated effluent COD limit



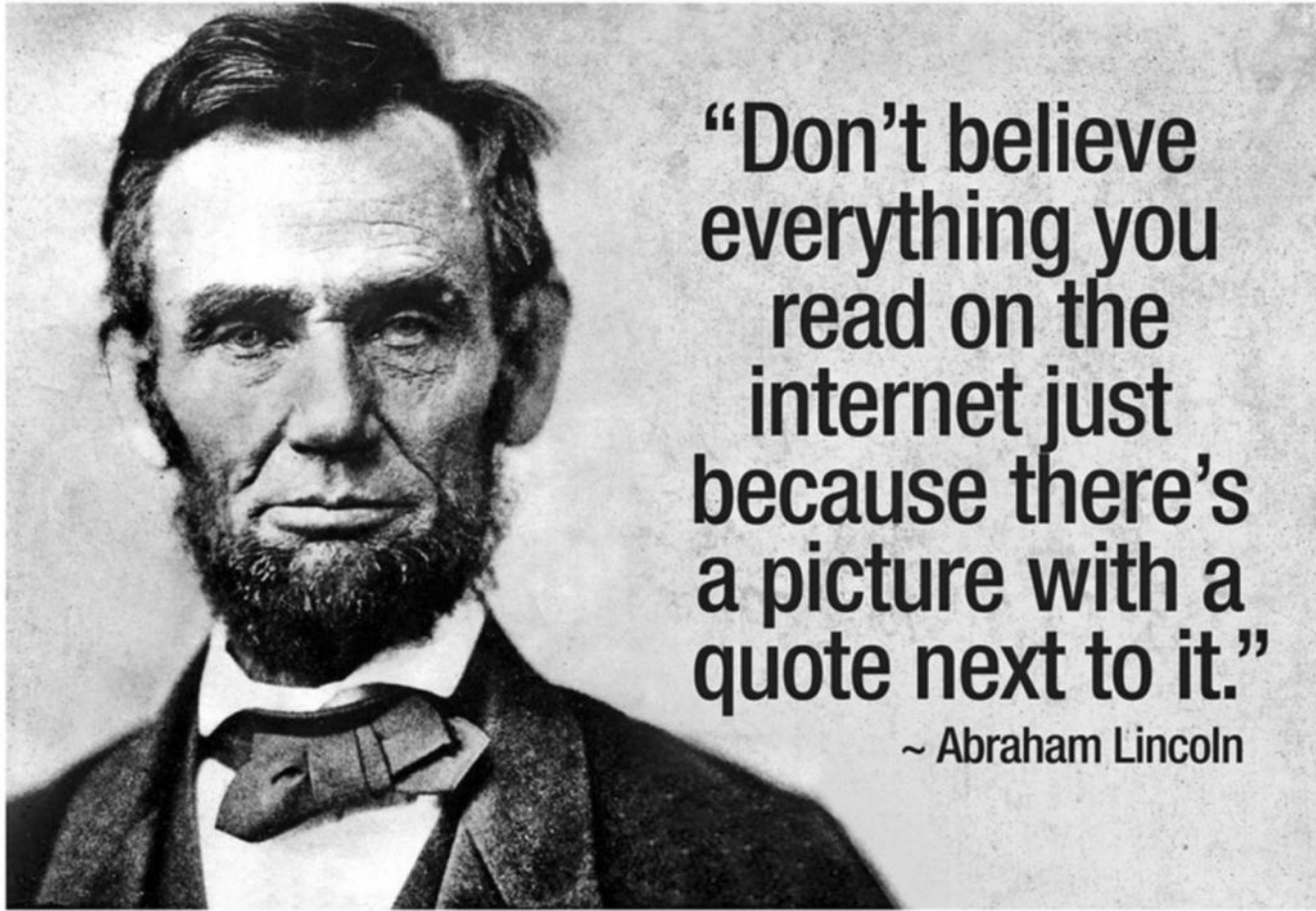
# Responses from Standard Methods

- “not at all surprised that existing COD methods yield scurrilous data in the presence of chlorides up to, at times, greater than twice the chloride concentration of seawater”
- “no amount of mercuric sulfate can overcome the chloride interference at those chloride levels”
- “other methods rely on 'diluting out' the chloride interference - which, of course, also dilutes out the analyte”
- “This problem has also been seen from food processors that utilize high levels of salt in their process, (Pickles or Kosher meats)”
- “method cannot be modified to cope with "low“ levels of organic in the presence of such high chloride. In fact, I can't think of a reason why COD is even a discharge issue in such a waste stream; the salt content itself is the biggest potential issue in a receiving water”

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- Cobalt Thiocyanate Active Substances (CTAS)
- Polycyclic Aromatic Hydrocarbons (PAHs)
- Microscopy

**Next time you receive an analytical report...**





# Questions?

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