Monitoring Quality of Wastewater and Storm Water Data – Dealing with Multiple Permits, States, and Analytical Laboratories

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Introduction

- Koppers is a multi-national producer of coal tar distillates, pitches, and wood preservatives.
- Each manufacturing facility has wastewater and storm water permits for effluent discharge (NPDES Permits).
- Several facilities have permit limits set at or near method quantitation limits (QLs) or method detection limits (DLs).
- Any detected or quantitated value could result in a Notice of Violation (NOV).

Koppers Wastewater Treatment Program

- **Program objective: improve performance of its industrial wastewater treatment plants (WWTPs)**
  - 2006 Benchmark: Koppers received 46 NOVs for exceeding effluent permit discharge limits at multiple WWTPs.
  - WWTPs ranged 20-40 years old treating wastewaters containing tar and wood-treating chemicals, often high in organic concentrations with separate phase liquids present (e.g., creosote, tar, oils)
- **CES contracted to assist with program in late 2006**
  - WWTP technology effort included evaluation of WWTPs, update of operating procedures to optimize and update of operator training
  - Analytical effort addressed the entire analytical program for WWTP process control and effluent compliance monitoring

Millions of dollars worth of added wastewater treatment technology cannot solve an analytical problem: You must start with a chemist on analytical procedures!

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Koppers Wastewater Analytical Program

- **Program objective: accurate analysis of Koppers industrial wastewaters for process control and for compliance monitoring**
- **Use of certified reference materials (CRMs) was a key element of this program in two efforts:**
  - Evaluation of analyses onsite at WWTP for process control with corrective actions
  - Evaluation of analyses by external laboratories with corrective actions

Evaluation of Analyses Onsite at WWTP for Process Control

- **Parameters of Interest**
  - Total Phenolics
  - Ortho-Phosphorus (as P)
  - Ammonia-Nitrogen (as N)
  - Nitrate-Nitrogen (as N)
  - Chemical Oxygen Demand (COD)
  - pH
  - Dissolved Oxygen
- **CRMs were prepared for each WWTP for analysis.**
- **CRMs were prepared in DI water.**
- **Results showed inconsistent performance across WWTPs.**

Onsite WWTP Evaluation Findings for CRMs in DI Water

- Improper ranges being used for test kits.
- Phosphorus and Nitrogen Results were not being reported as proper species.
- Instruments were not being calibrated correctly
  - expired reagents,
  - no 2nd source verification, and
  - improper maintenance of oxygen electrode.

WWTP Corrective Action Based on CRM Results

- Operators given training in proper performance of methods.
- Equipment and methodologies standardized across all plants.
- Spiked CRMs into WWTP process wastewater samples
- Repeat evaluations
- Plants with unacceptable results given additional training
- Most issues involved not filtering samples and correcting for color
- Periodic training and equipment upgrades continuing today

Results After Initial Work

- 2008 Benchmark: 34 NOVs down from 46 in 2006
- Management re-emphasized goal of no NOVs
- CES began evaluation of external analytical laboratories
  - A number of the NOVs in 2008 appeared to be due to matrix interferences, variations among laboratories, problematic methods, non-optimal quality control samples
  - Each WWTP selected a laboratory to perform compliance monitoring and often sampling, typically a local laboratory certified in the state resulting in more than 15 laboratories being used at the time

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External Lab Evaluations Using CRMs in Double Blind Samples

- CES engaged Environmental Resource Associates (ERA) to prepare a series of double blind samples:
  - Type 1 water blanks, substitute wastewater blanks, spikes of compounds at levels between 0.5 -5 times permit levels for problematic compounds
  - Sent to laboratories where facilities had NOVs.
- Known interferences from chemical treatment compounds or manufacturing operation were also spiked into the samples.
- Selected laboratories received samples of blank water, substitute wastewater, spiked blank water, and spiked substitute wastewater.
- Samples submitted as a double blind.

Compounds Chosen for Spiking in External Lab Evaluations Using CRMs

- Trace metals: arsenic, cadmium, hexavalent chromium, and zinc
- Polynuclear aromatic hydrocarbons (PAHs)
- Pentachlorophenol (PCP)
- Oil and Grease
- Phenols (colorimetric)
- BOD_5 (Type 1 water only)
- Total Suspended Solids (Type 1 water only)
- Total Cyanides

ASTM Substitute Wastewater (ASTM D5905-98) Preparation for 2 liters of Sample

- Place 500 mL of Type 1 Water in a blender
- Add 0.400 grams of flour (dried at 103^{o}C)
- Add 2.000 grams of ocean salts (dried at 103^{o}C)
- Add 0.080 grams Kaolin, USP grade (dried at 103^{o}C)
- Add 20.0 mL of Triton X-100 Solution , and
- Add 120.0 mL of light beer (de-carbonated for 24 hours)
- Blend on lowest setting for 30 seconds. Allow foam to dissipate.
- Dilute to volume with Type I water in a 2-liter volumetric flask.

General Result of External Laboratory Evaluations with Double Blind Samples

More Specific Discussion of Results of External Laboratory Evaluation 1

- No laboratory that used USEPA Method 610 showed a clean blank for either the Type 1 or Substitute Wastewater Blank. There was little difference between the results of the blanks and the spiked blanks for low level PAHs.
- PCP was not detected in the spiked samples over 75% of the time.

More Specific Discussion of Results of External Laboratory Evaluation 2

- Arsenic was found at levels above permit limits in blanks that contained high iron. Zinc also recovered high.
- Interestingly, acceptable recovery was obtained on the spiked samples, if you corrected for the amount in the blank.
- In many cases, the substitute wastewater blank was diluted prior to analysis, resulting in elevated QL that would have resulted in an NOV. (Hexavalent Chromium, PCP)

More Specific Discussion of Results of External Laboratory Evaluation 3

- Surprisingly poor performance for total phenols and oil and grease in Type 1 Water. Failure rate was 67% with the majority of the result reported high. All missed total phenols results were high.
- Total cyanides recovered high in samples with organic nitrogen compounds.

Other Issues with of External Laboratory Evaluation

- There was inconsistency between quantitation limits between laboratories.
- Some labs made no distinction between detection limits, quantitation limits, and reporting limits.
- Rules for reporting significant figures were not being followed
- Dilution of samples because of “matrix interferences” with no attempt to perform sample clean-up.
- General recovery ranges for data acceptance

Does anybody generate control charts anymore?

Conclusions from External Laboratory Evaluation Using CRMs

- A number of analytical procedures being used for Koppers wastewater samples were not appropriate for the matrix.
- Standard QC procedures used at the analytical laboratory were not sufficient to ensure that results were suitable for compliance monitoring of these wastewater samples.
- Laboratories detection limits, and quantitation limits were not realistic for these wastewater samples.
- At times, specific interferences listed in EPA methods were not checked for or removed.

Laboratory Corrective Actions as a Result of CRM Testing

- 2009 – Consolidation of all effluent compliance monitoring to a single external laboratory.
- Thorough review of analytic procedures to select methods appropriate for Koppers matrices.
- Define spiking levels and acceptance criteria for each test.
- Dilution of samples because of matrix interferences is not acceptable.
- Prepare detailed QA manual for sampling and analysis.

Method Specific Changes Based on CRM Testing 1

- Method 200.7 not used for metals analysis. All trace metals testing done using EPA method 200.8.
- Method 610 not used for PAH analyses. All specific organic procedures require GC/MS.
- USEPA method 625 had to be modified to reach detection limits comparable to EPA 610. Method development and validation was done and approved by regulatory agency as an alternative method at 2 WWTPs.

Method Specific Changes Based on CRM Testing 2

- Low level determinations require dedicated glassware, columns, and instruments.
- Implemented strict criteria on the use of instrument blanks.
- Use ion chromatography (USEPA Method 218.6) for hexavalent chromium.
- Implemented cleanup procedure for PCP analysis to remove interferences from aliphatic oils.
- Required use of sulfamic acid to remove interferences from organic nitrogen in cyanide determinations.

Retesting and Verification Using CRMs

- All method changes were verified by the use of CRMs spiked into substitute wastewater and WWTP effluent samples.
- CRMs are submitted to the contract laboratories at least annually as double blind samples.
- Any failures trigger a laboratory audit with a formal corrective action required. If a failure occurs, additional CRMs are submitted.

Results

- Number of Kopper's NOV's since implementation of CRMs and QA Program

Year	Number of Exceedances
2008	34
2009	17
2010	4
2011	4
2012	3
2013	1
2014 (YTD)	1

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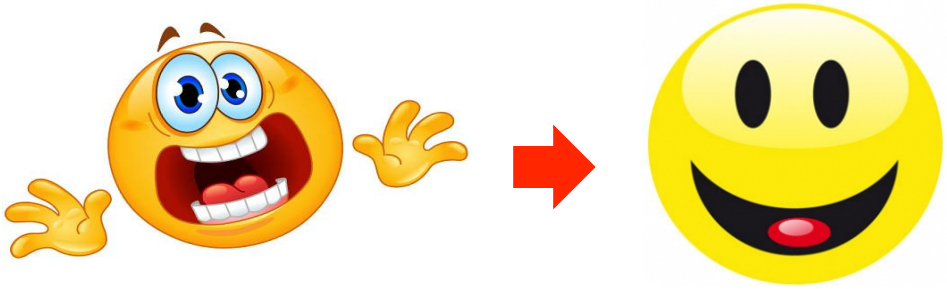
Takeaway

- The use of CRMs in an appropriate matrix at appropriate levels submitted as a double blind allows careful evaluation of laboratory methodologies.
- The use of CRMs has become an integral part of the Koppers overall QA program, ensuring consistent quality both internally and externally.
- Koppers was able to decrease the number of NOV's from 46 in 2006 to 1 in 2013 without capital spending for additions to upgrade existing WWTPs in large part due to the use of CRMs in the analytical program



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Looking to the Future and Uses of CRMs

- Permit limits continue to decrease.
  - Latest Draft permits require QLs of 1 ppb for semivolatiles, including phenolics. (Method development)
- Trace metals and mercury require special sampling techniques (USEPA 1669).
  - Need to incorporate Certified Reference materials into sampling procedures
- Use of CRMs for International Facilities

Challenges for Wastewater Effluent Compliance Monitoring

- NPDES testing does not generally create a large volume of samples for an analytical laboratory.
  - Sampling may be weekly, quarterly, or semi-annually making it difficult to find a laboratory willing to perform extra steps (i.e., dedicated glassware, special spiking levels, additional clean-up, method development) to generate quality data at low permit levels.
- Traditionally, samples are run in large batches, with samples of other wastewater samples, with different interferences and permit requirements.
- The current procedures for determining detection and quantitation limits create difficulties
- Different QLs and DLs between States

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Thank You for Your Time!

Open Discussion