Data from Online Chromium-6 Analyzer Helps Monitor Performance of Chromium Remediation in Real-time

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GRA 2017 Conference

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Background

CA Water sources with elevated Cr(VI) levels above 10 ppb

- Regulation introduced in 2014 with **(planned)** Regulatory compliance deadline 1 January 2020
- May 2017 Judge announces final results of lawsuit brought by Solano County Taxpayers Association and the California Manufacturers & Technology Association that the State Water Resources Control Board (SWRB) and Regulation is returned to 50 ppb Total Cr
- August 2017 SWRCB announces they are planning to reconsider the costs and will be working towards a plan for a new regulation. Expected to take 18 months to 2 years

http://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/Chromium6sampling.shtml

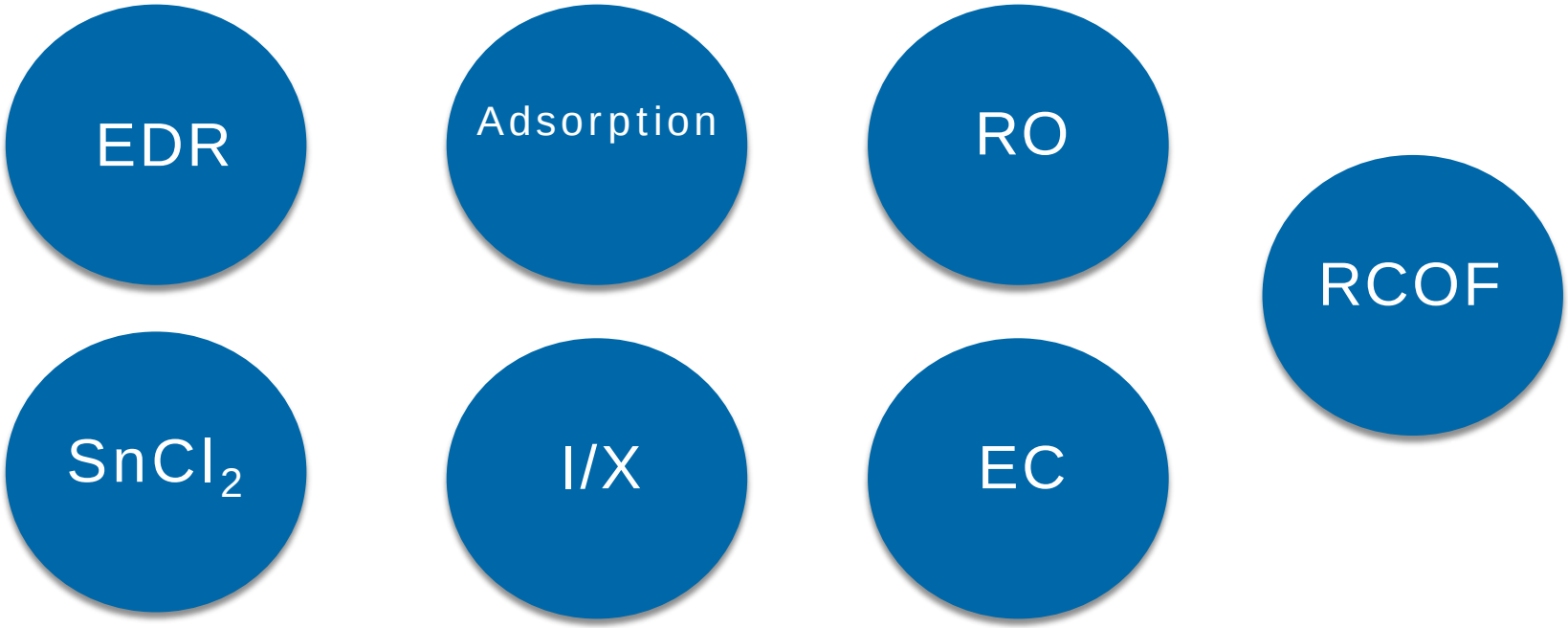
Options to Address Cr(VI) Contamination

Remediation Option	Cost
Remove Well From Use	-
Blending (Dilution)	$
Drill New Well	$$
Purchase Water	$$
Install Treatment	$$$$

Dilution is the most cost effective treatment solution.

Installing treatment is expensive, utilities on the edge of regulatory compliance should explore blending with clean or partially treated sources.

Cr(VI) Treatment Options



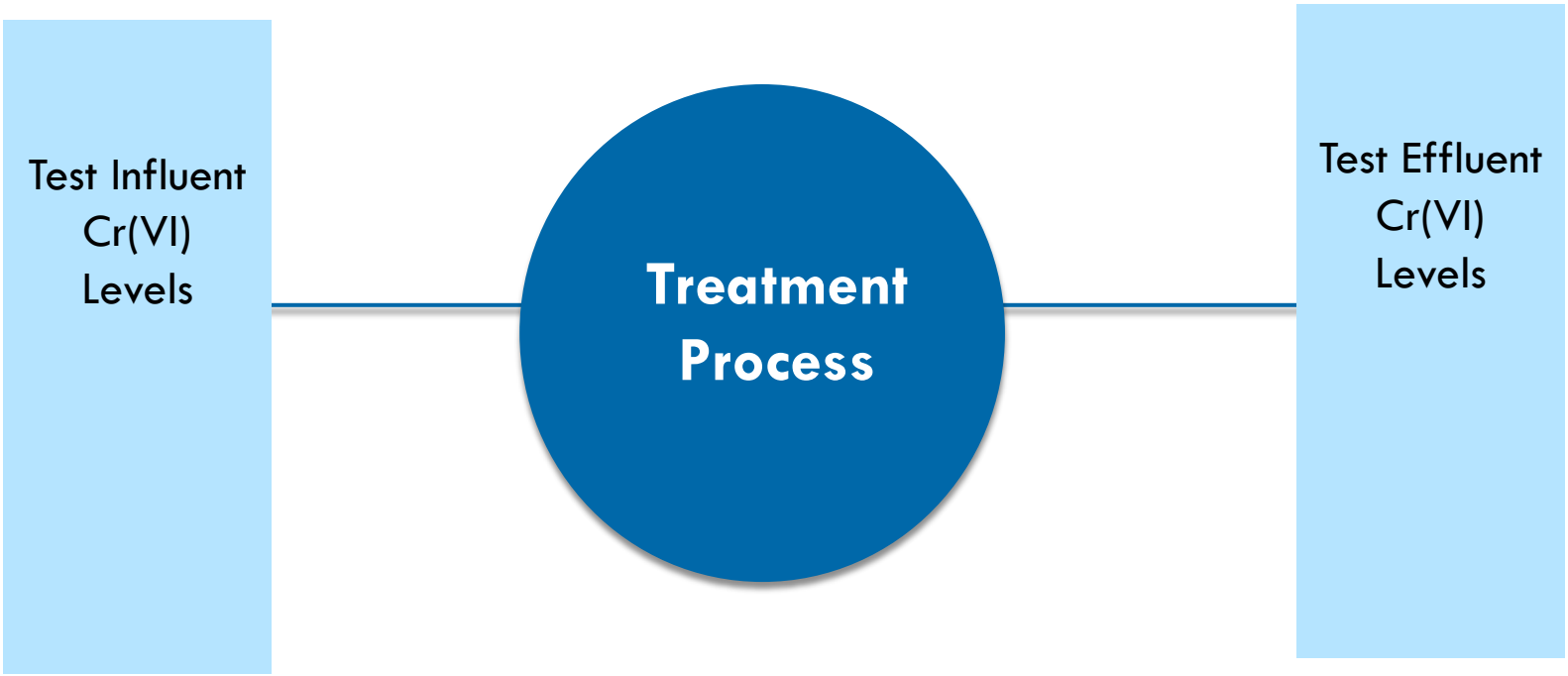
To economically and effectively meet Cr(VI) regulatory levels, contaminated water can be blended with a clean or partially treated source to reduce overall concentration.

Process Validation

For the utility to consistently deliver water below regulatory levels from their treatment process or blending scheme they must be able to accurately and reliably measure influent/effluent Cr(VI) levels in real time.

Labs Cannot Provide Data in Real Time

Process Validation & Role of Online Cr(VI) Monitoring



Real time analysis and high frequency data permits rapid assessment and validation of process schemes.

Use of online monitors aided process validation for As MCL compliance and should be part any viable strategy for Cr(VI) compliance.

Analyzing Cr(VI) Influent/Effluent Levels

Laboratory

EPA method 218.7 recommended lab-based Cr(VI) test approach

- Requires analysts skilled in the operation of ion chromatographic instrumentation and interpretation of associated data
- Results take approximately 2 weeks to be returned, leading to costly project delays

Online

A new instrument based on voltammetric analytical method developed for real-time Cr(VI) analysis

- 2016 - First commercial application at California Utility to validate RCOF (Reduction Coagulation Oxidation Filtration) treatment process using ferric chloride at Watsonville, CA
- 2016 - Used to validate stannous chloride treatment processes for small, unchlorinated systems at Coachella Valley Water District, CA

The Value of High Frequency Real-time Cr(VI) Data

BASELINE DATA	Extensive data stream to enable the design of cost-effective remediation processes
PILOT AND WHAT IF STUDIES	Simulation ("what if ?") of the impact of multi-parameter operational changes on contaminant levels
VENDOR VALIDATION	Fast feedback permits rapid assessment and validation of remediation process
PROCESS OPTIMIATION	Captures changes in contaminant levels to enable timely and cost effective remediation
RISK MANAGEMENT	Captures non-compliance risk to enable timely action before non compliance occurs, ensures regulatory and contract compliance

Voltammetric Analytical Method

Voltammetry, subset of amperometry, measures electric current through an electrode at specific potentials.

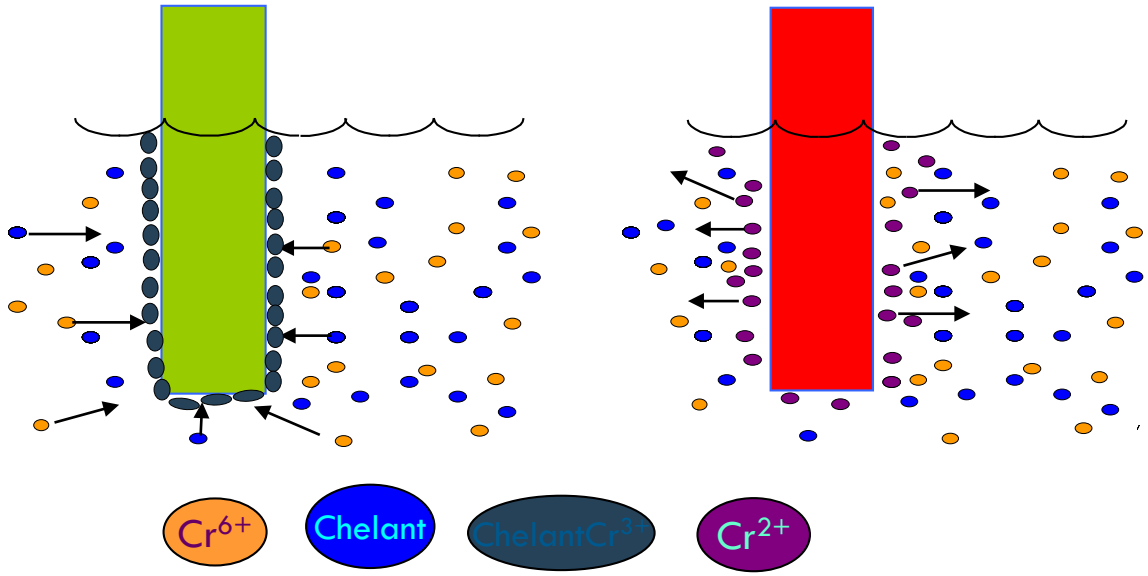
Step 1- Accumulation

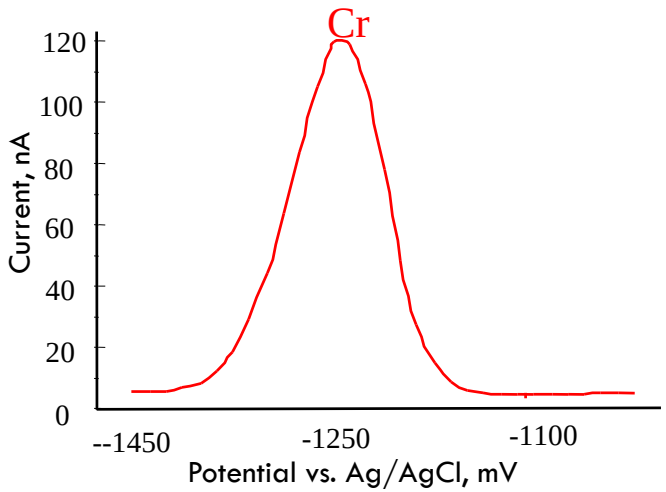
$Chel + Cr^{6+} + 3e^- \rightarrow ChCr^{3+}$

Step 2- Stripping

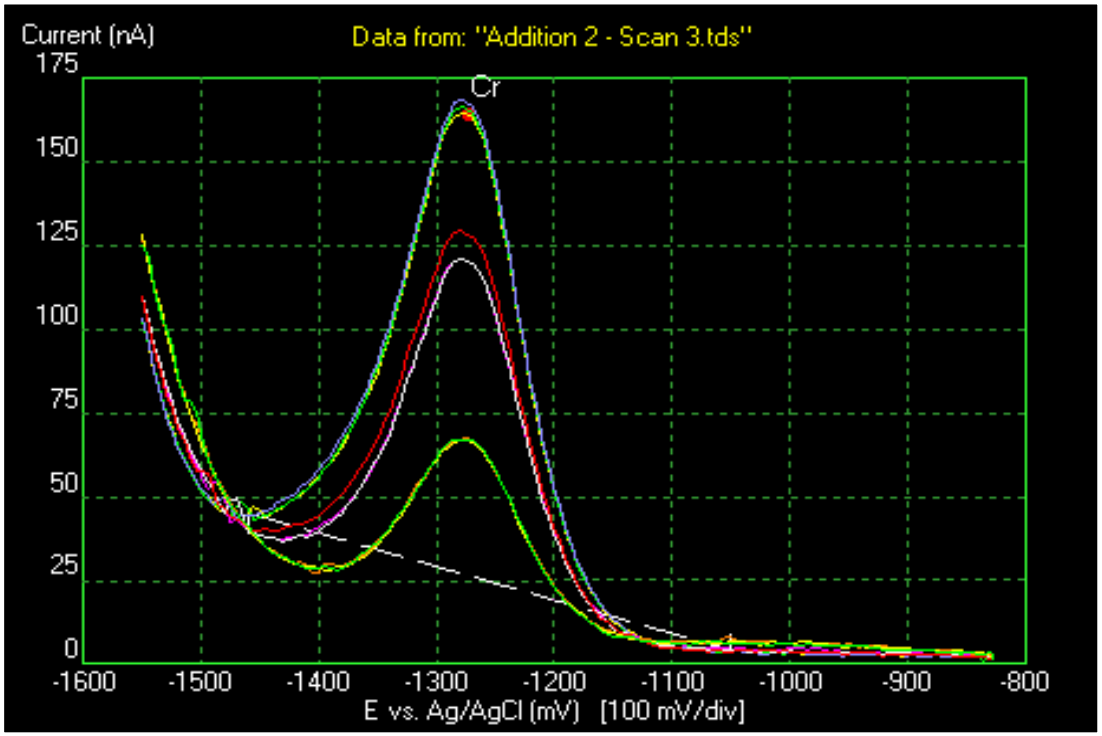
$ChelCr^{3+} + e^- \rightarrow ChelCr^{2+}$

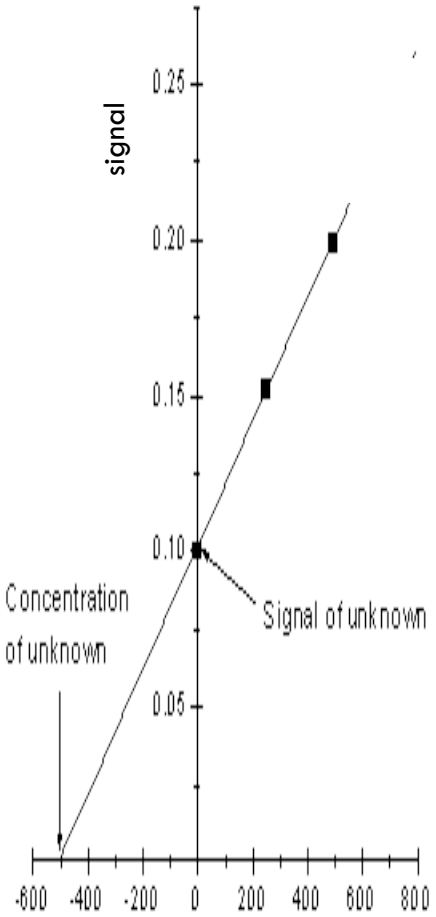
Resulting Signal





Cr(VI) Quantification by Method of Standard Addition





- Calibration approach compensates for sample matrix and temperature effects
- Each measurement quality is ensured by calibration curve fit factor
- System maintains calibrated status without any operator interference for virtually unlimited time

Elements Available by ASV and AdASV

Enabling Process Control with On-line Monitoring

Multi-stream Online Cr(VI) Monitor

Automated online operation

- Eliminates operator variability
- Accuracy to 1 ppb
- Measurement time less than 40 min
- Correlation with standard method +/- 15% typical
- Multiple streams including grab sample port

Comprehensive data acquisition

- Easy-to-use front panel HMI
- Programmable on-board data acquisition

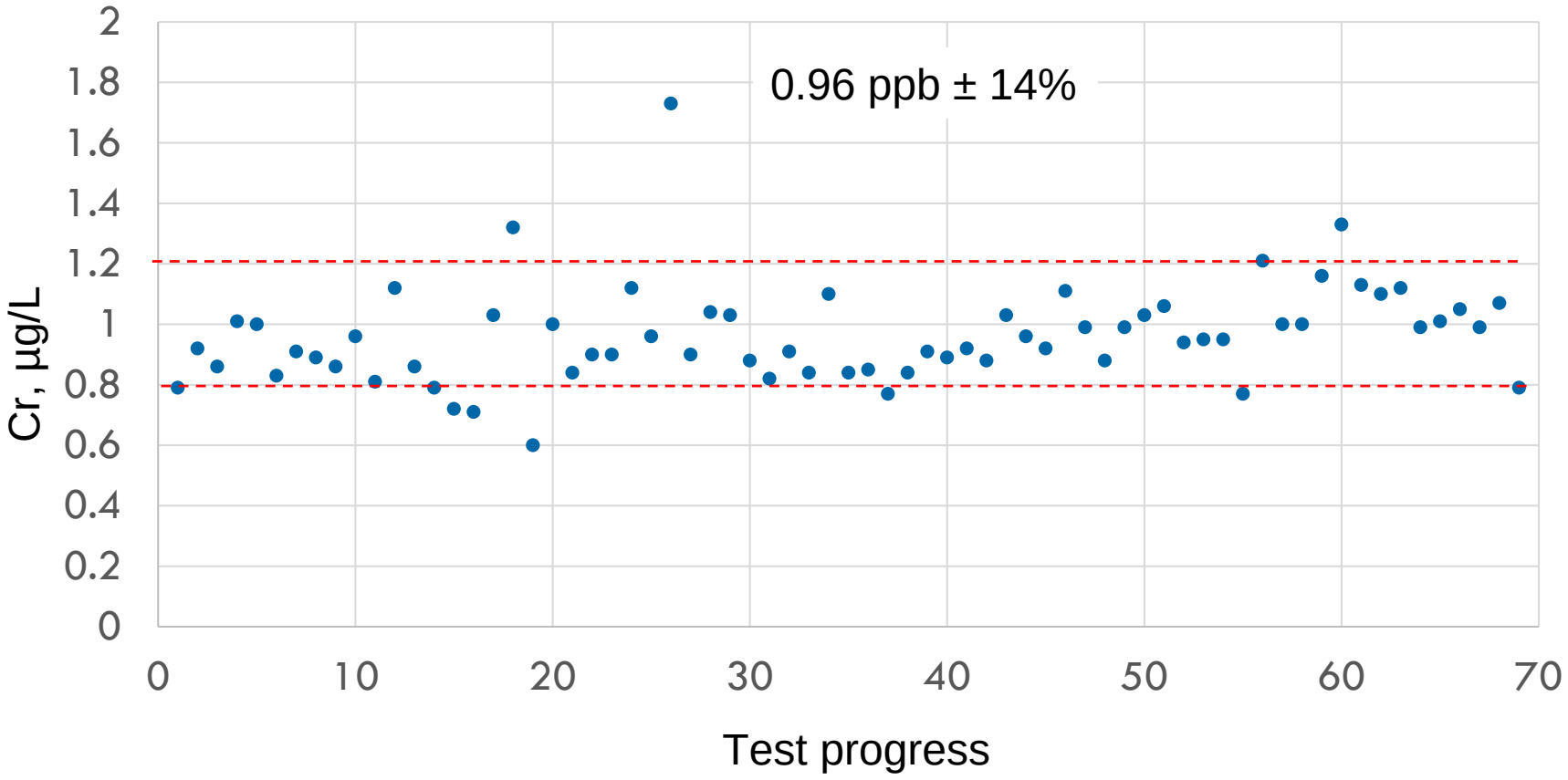
Low operational costs

- Replaceable reagent tray provides up to 1,000 measurements
- Employs a self-regenerating sensor and is auto-calibrating
- NEMA 4X enclosure, climate control

MetalGuard™
Chromium

Repetitive Cr(VI) Determination (Spiked Tap H_20)

Measurement of 1.0 ppb Cr(VI) Synthetic sample)

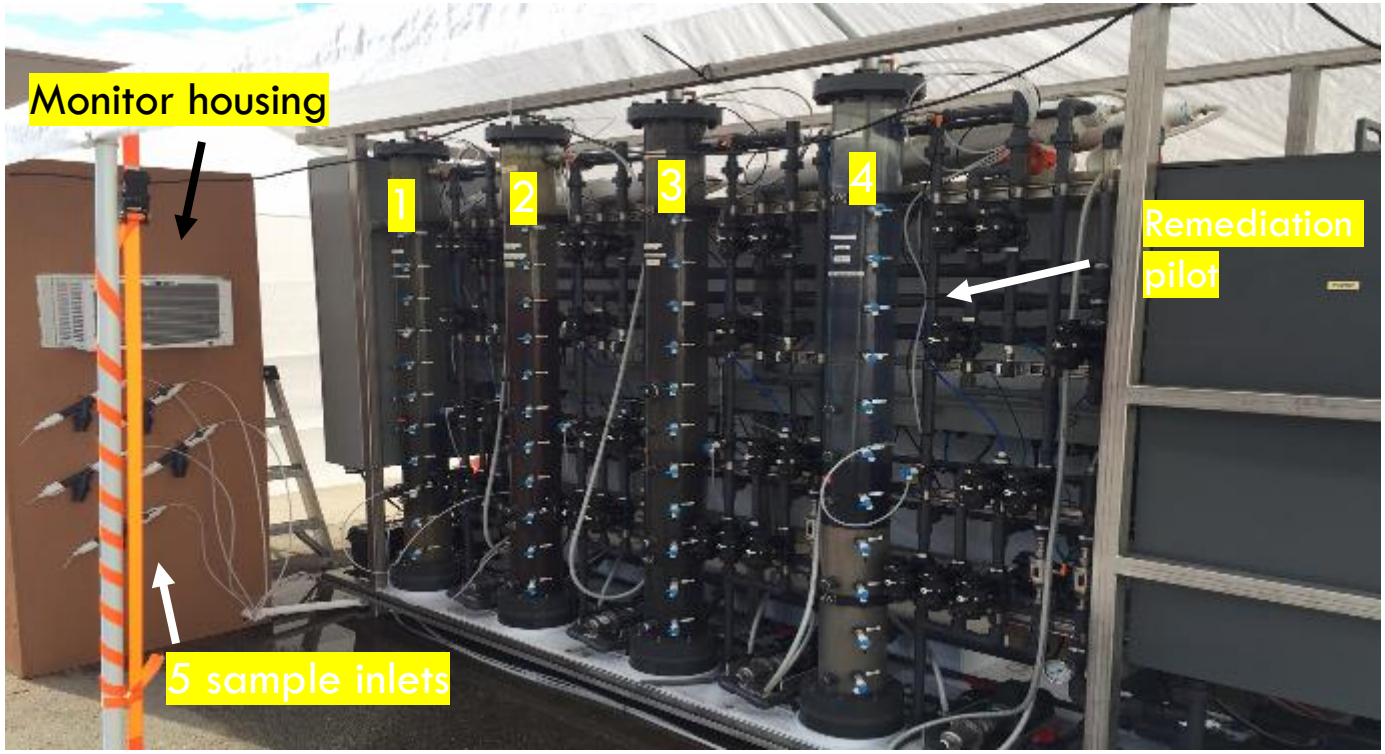


Case Study

The first commercial application of the real-time Cr(VI) monitor was undertaken at Watsonville, CA. The City receives 85% of their water supply from a groundwater source where hexavalent chromium is a naturally occurring mineral.

Online Cr(VI) Monitor Aided RCOF Pilot

- System was tested under a variety of simulated operational conditions at 4 of the Utility's 8 affected water wells
- Online Cr(VI) monitor used to provide real-time and multi-stream analysis of influent and effluent chromium levels

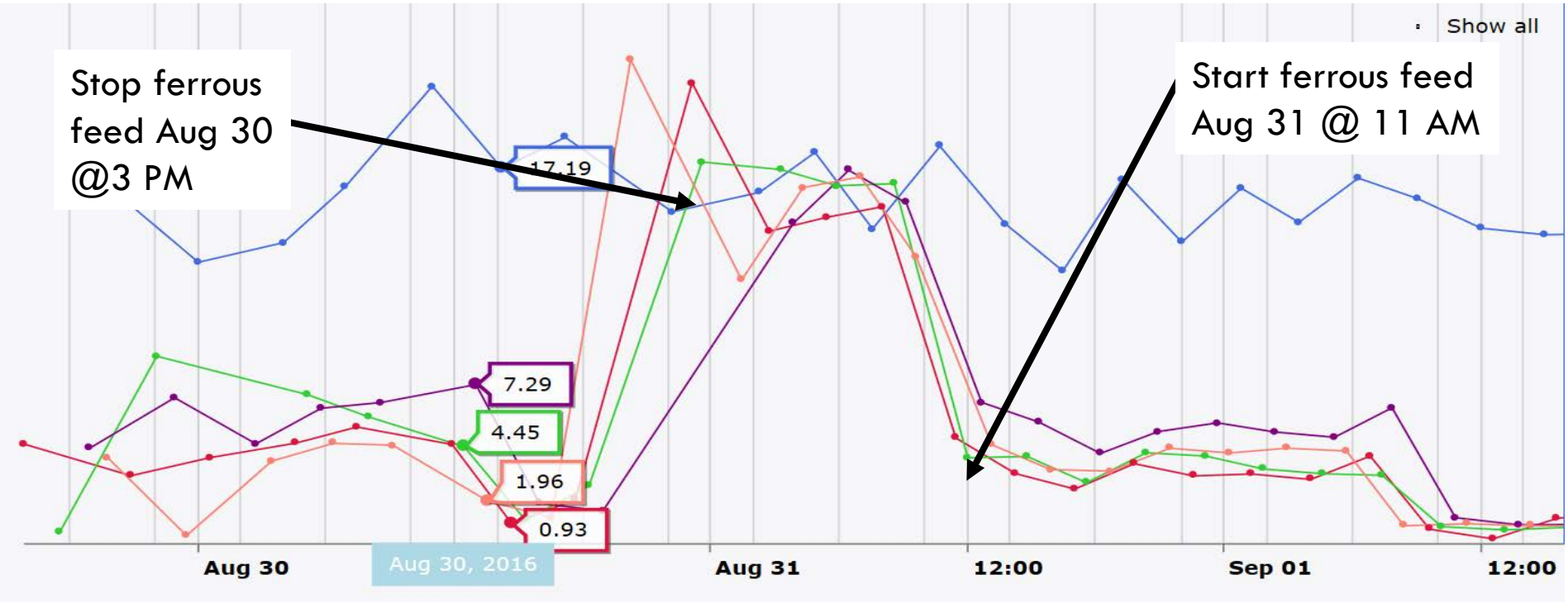


Advantages of Voltammetric Cr(VI) Analysis

- Extremely high method sensitivity down to 100 ppt due to proprietary probe
- High method selectivity: common metal ions and anions naturally exist in the sample or added during treatment process have no effect on hexavalent chromium determination
- Short analysis time (as low as 40 min)
- Highly robust self-calibrated detector with virtually unlimited lifetime
- Unattended, economical and environmentally friendly. Low reagent consumption and waste
- The online Cr(VI) monitor provided more insight into the RCOF treatment process and effect of operational conditions than what would have been possible from a laboratory

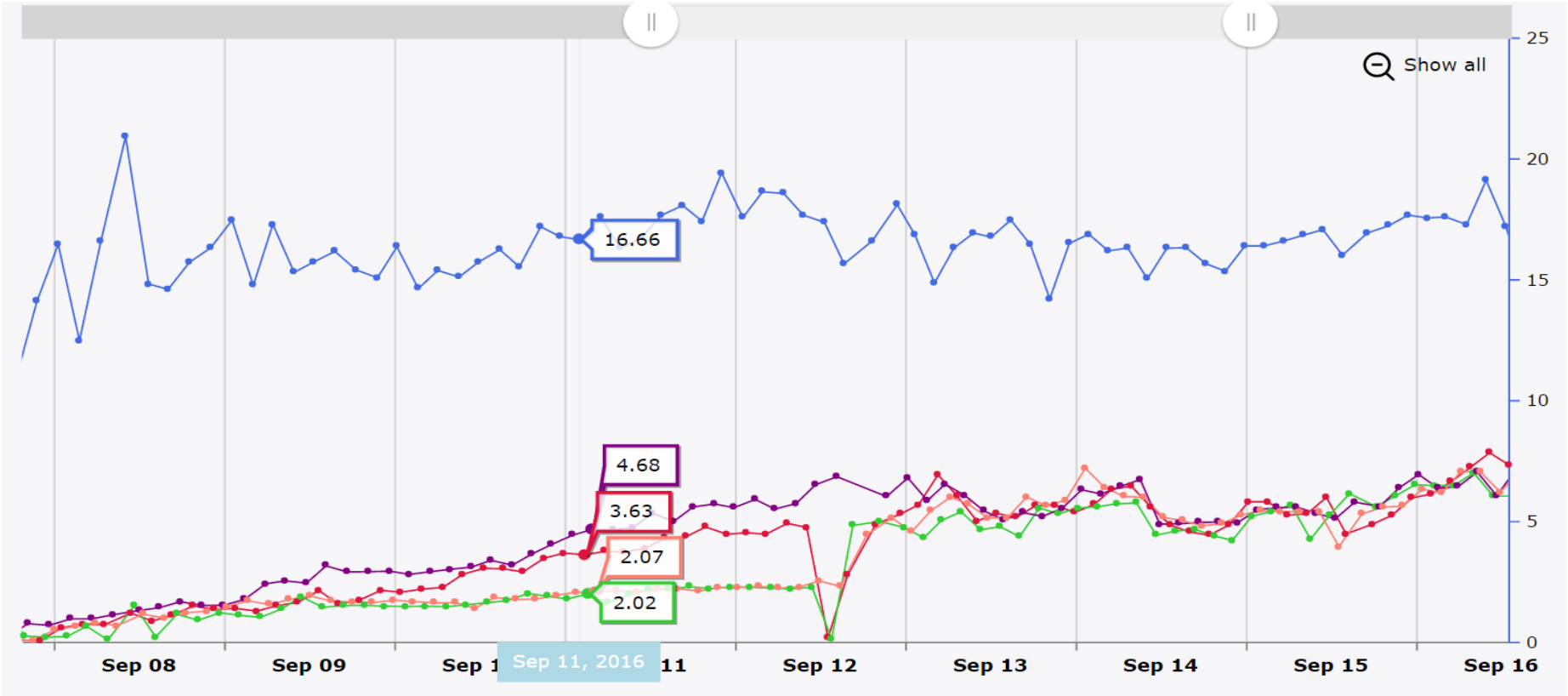
Insight into RCOF Process

Cr(VI) Monitor Response on Ferrous Sulfate Feed Pump Failure



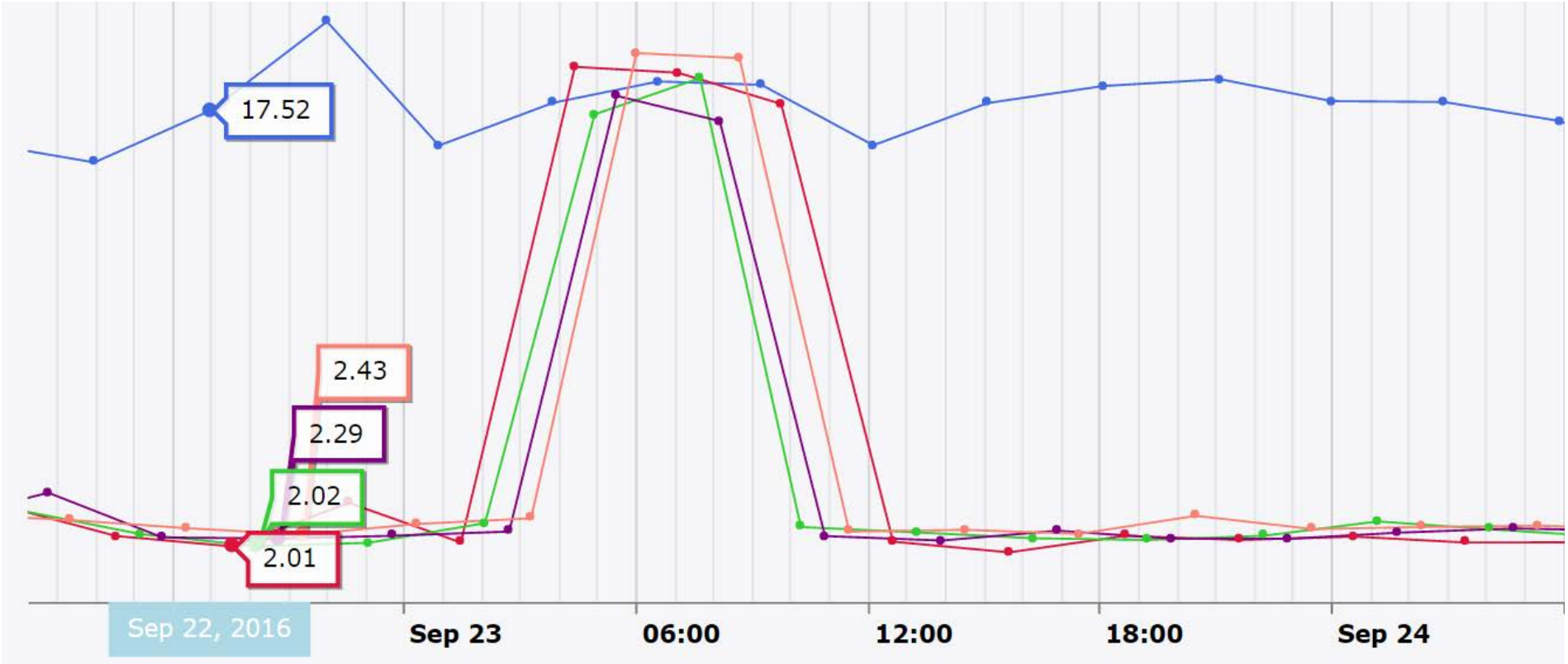
Insight into RCOF Process

Long-term Performance of Online Cr(VI) Monitor



Insight into RCOF Process

Cr Monitor Capturing Feed Pump Failure on 23 Sep 2016



Conclusions from Online Cr(VI) Monitor in RCOF Pilot

- Reduced costs by accelerating evaluation of plant and process
- Permitted real-time optimization of Cr(VI) remediation processes (e.g. chemical feed, pH, backflush, etc…)
- Allowed rapid identification of operational trends and better understanding of treatment process behavior
- Significantly reduced sampling costs and time to receive results
- Eliminated sampling and sample handling error

Case Study

Online Cr(VI) monitor has been aiding the research, development and optimization of $SnCl_2$ treatment providing baseline data on influent and effluent chromium levels in real time.

New Data on Benefits of $SnCl_2$ for Cr(VI) Removal

- Economical treatment approach with potential to significantly reduce capital, operations, and maintenance costs compared to BATs which have been surrounded in controversy due to their high capital/operating expenses.
- Coachella Valley Water District (CVWD) had an estimated $250 million price tag to construct a BAT-based Cr(VI) treatment solution at a third of their wells and they are now exploring the use of $SnCl_2$ with a potential savings of $155 million from original estimates.

Category	Potential Savings
Capital Cost Savings	$135 M
Operating & Maintenance Cost Savings	>$5 M in annual savings (less than half the current plan)
Well Replacement Costs	$12-15 M saved by preventing stranded well assets

Conclusions

- Online Cr(VI) monitoring will help drive effective chromium treatment & blending schemes
- Online Cr(VI) monitors produce accurate and reliable high frequency data in real time

LABS CANNOT PROVIDE Cr(VI) DATA IN REAL TIME.

Acknowledgements

- Corona Environmental Consulting
- California Environmental Protection Agency- State Water Resources Control Board- Division of Drinking Water Programs
- City of Watsonville, CA
- City of Coachella, CA

Thank you

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