Analytical Challenges to Identify and Quantitate p-Chlorobenzene Sulfonic Acid in Wastewater

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Presentation Topics

- **Advanced Water Quality Assurance Laboratory**
- **Advanced Water Purification Process in Orange County, CA**
- **History and Monitoring experience for p-CBSA**
- **Analytical Methods for p-CBSA using SPE**
- **Development of direction injection method**
- **Method validation and QA/QC data**
- **Conclusion and further investigation**

Advanced Water Quality Assurance Laboratory

- **Key to managing water quality**

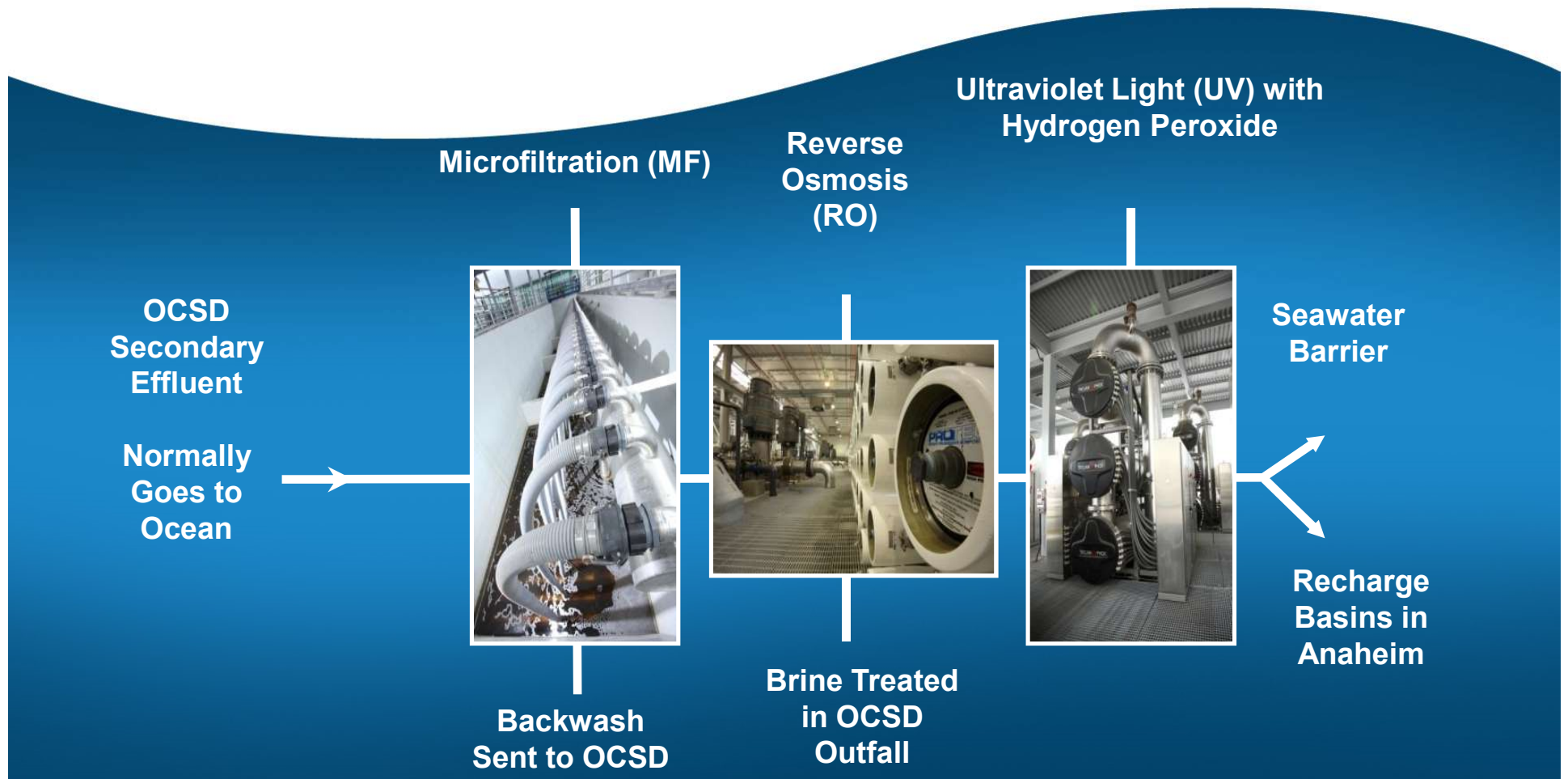- **Proactive testing for 500+ individual constituents**
- **Over 400,000 individual analyses**

GWRS

GROUNDWATER REPLENISHMENT SYSTEM

- **100 million gallons (379,000 m^3)/day advanced water purification facility**

- **33 billion gallons (127 million m^3)/year per year source of water → enough for 850,000 people**

- **Takes treated wastewater that otherwise would be wasted to the ocean and purifies it to near-distilled quality**

- **Operational since January 2008**

GWRS Advanced Water Purification Process

Ultraviolet Light (UV) with Hydrogen Peroxide

Microfiltration (MF)

Reverse Osmosis (RO)

OCSD Secondary Effluent

Normally Goes to Ocean

Seawater Barrier

Backwash Sent to OCSD

Brine Treated in OCSD Outfall

Recharge Basins in Anaheim

Stringfellow Super Fund Site, CA

- 1956 - 1972 Waste Disposal Period

- 1985 Pre-Treatment Plant (PTP) built

- 1991 Lower Canyon Treatment Facility (LCTF) built

- 1996 Department of Toxic Substance Control operates all sites
  1998 Direct PTP to Santa Ana River (SAR) connection built

- 2000 ClO4, NDMA, 1,4-dioxane: concerns started emerging

- 2005 Proposed future standards for ClO4, NDMA, 1,4-dioxane

- 2003-9 Bench-and pilot-scale testing of treatment technologies

Stringfellow Site View

Original disposal areas

Pre-Treatment Plant

Treatment Technology

- **State-of-the-art membrane technologies: Removal by various membranes**
- **Combined UV and Hydrogen peroxide**
- **Granular Activated Carbon (GAC)**

4-chlorobenzenesulfonic acid (p-CBSA)

CAS #	98-66-8
Molecular weight	192.62
Formula	$C_6H_5ClO_3S$
Melting Point	102 ^{O} C
Boiling Point	149 ^{O} C @ 22 mm Hg
Stability	Stable. Incompatible with strong oxidizing agents
Source	Byproduct of the manufacture of DDT
Found	Environmental contamination. Municipal drinking water wells and wastewater

Perchlorate Analysis by LC/MS/MS or IC/MS

	EPA 314	EPA 331/332
MRL (ug/L)	2.5	0.1
Detector	Conductivity	Mass Spectrometer
Identification	Retention time	Quan ion (101) Retention time
Sample prep	filtration	Less sample prep cost & time
QA/QC	False positive	High accuracy Less resample
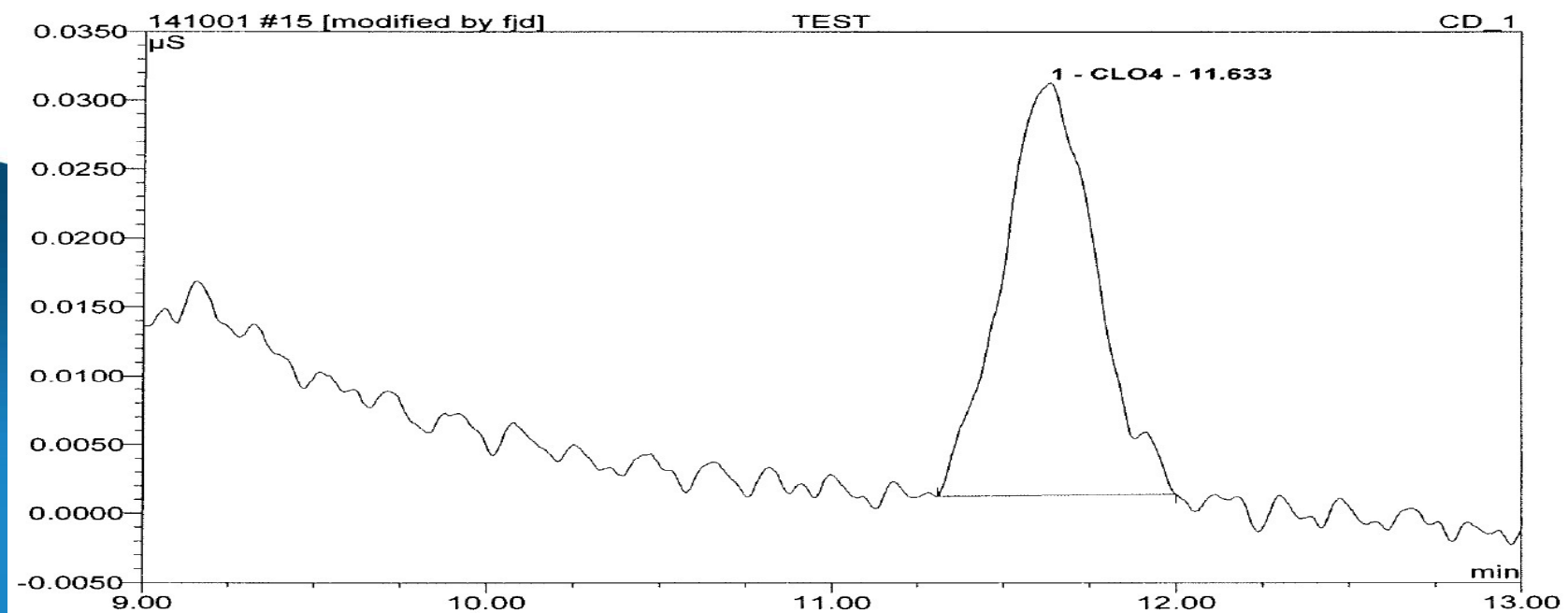
No.	Ret.Time min	Peak Name	Height µS	Area µS*min	Rel.Area %	Amount ppb	Type
1	11.63	CLO4	0.0300	0.0095	100.00	1.669	BMB*
Total:			0.030	0.009	100.00	1.669	

4.0 ppb p-CBSA standard was identified as 1.7 ppb perchlorate by Ion Chromatography (IC) system.

Direct Injection Technique;

Sample Volume: 10mL
Calibration standards: 5 ppb - 200ppb
Internal Standard (IS): Ibuprofen $^{13}C_3$
Spike ICAL, QCs and samples with 100uL of 1ug/mL IS

Isotopic dilution/ SPE technique

Sample Volume: 500 mL

6mL HLB Cartridge containing 200mg sorbent
Concentrate the extract to 1mL using Turbo Vap

Analytical Method for p-CBSA

- **ABSciex: QTRAP5500**
- **Analytical Column:**
  - **Phenomenex-Gemini C6 Phenyl (2.0 x 150mm, 5um)**
  - **Column temperature: 50^0C**
- **Mobile Phase – 5 mM Ammonium Acetate in Milli-Q water (0.385g NH_4OAC) to 1L HPLC grade water**
- **LC/MS grade methanol**
- **10 μL injection volume**

pCBSA Direct Inject
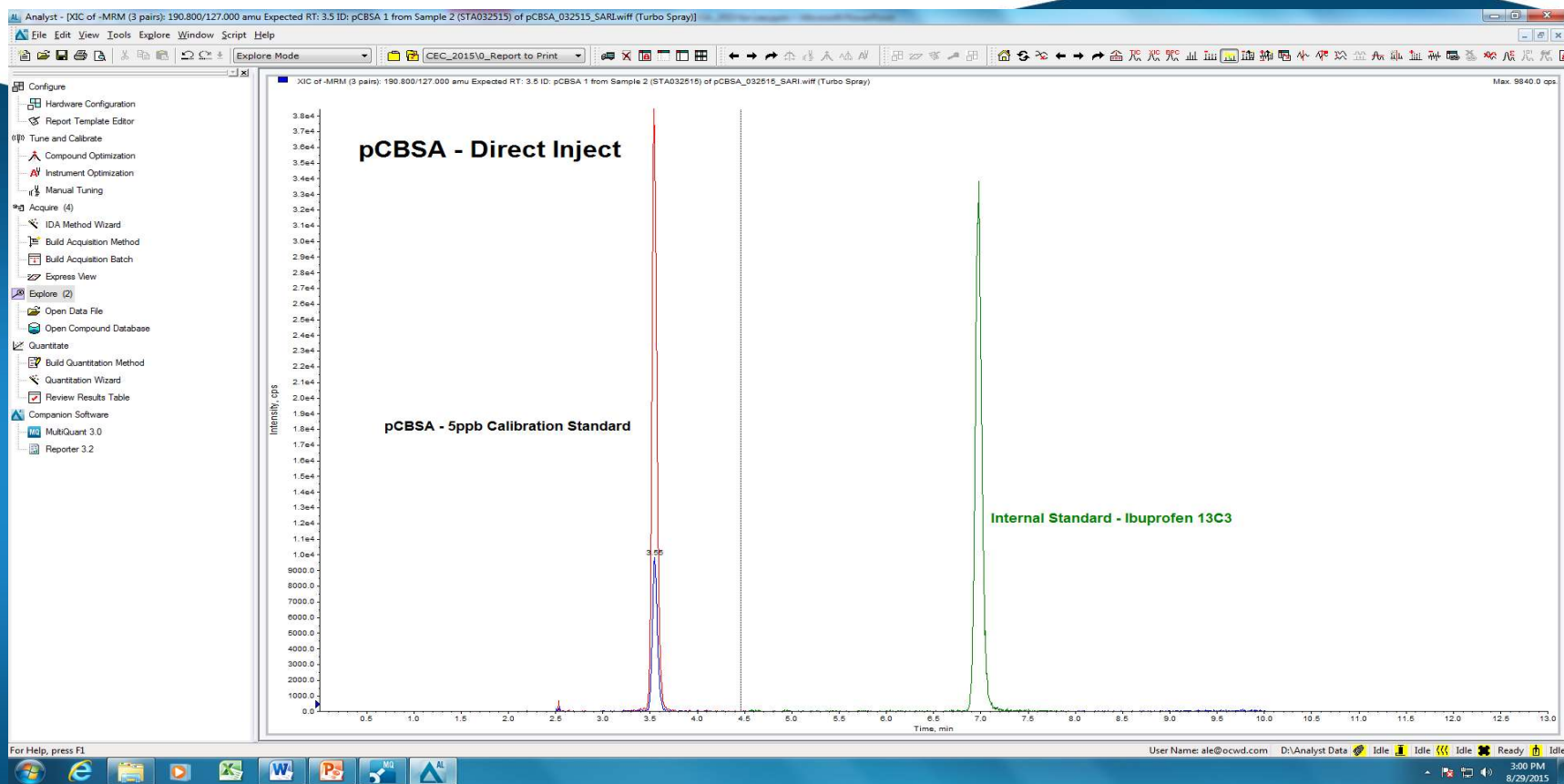
pCBSA Direct Inject - Calibration Curve: 5ppb to 200ppb
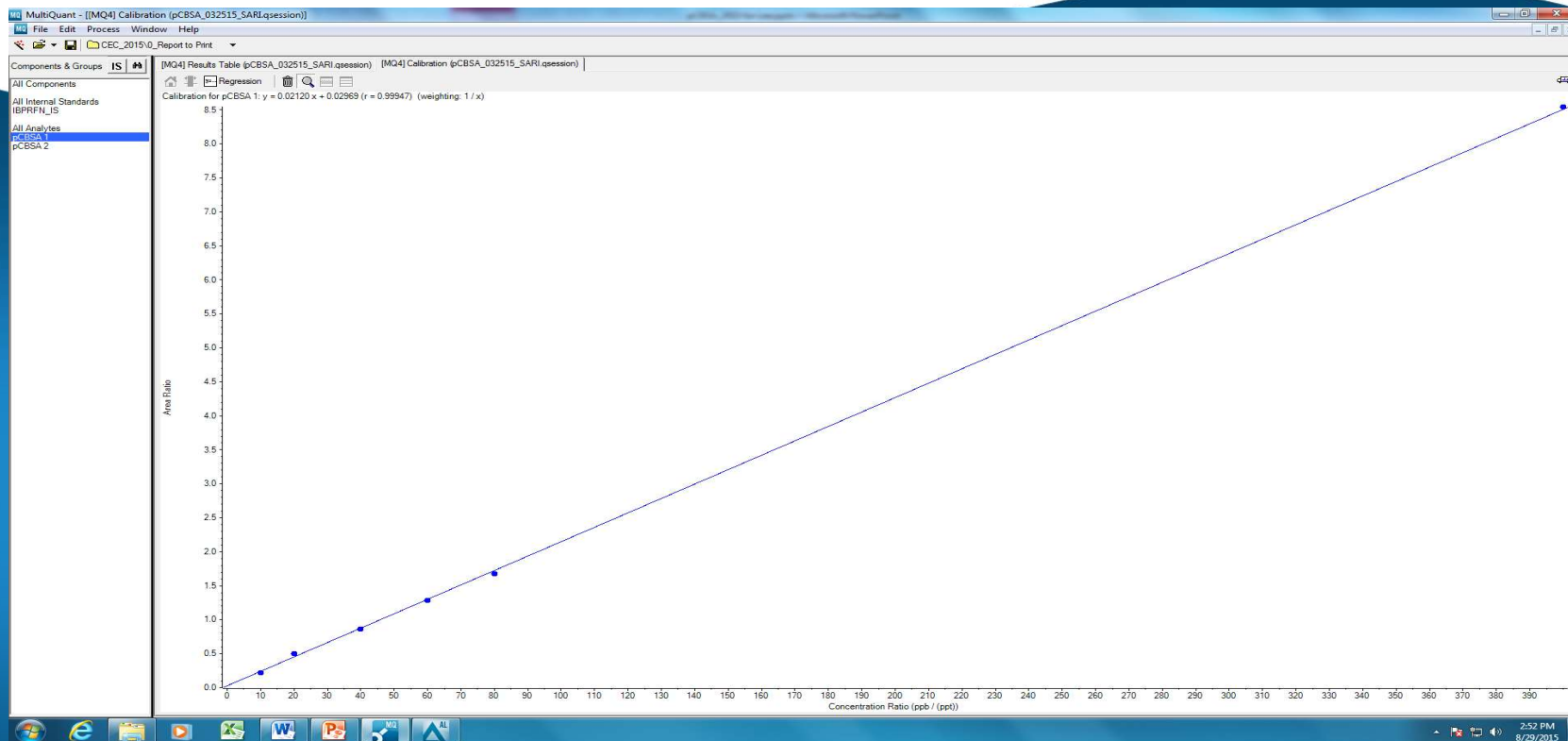
Orange County Water District
## Method: CEC – Negative Pharma

Analyte Name: pCBSA 1
Internal Standard: IBPRFN_IS

Data File	NP_061815_CEC-R.wiff	Result Table	NP_061815_CEC-R
Acquisition Date	6/18/2015 6:17:59 PM	Algorithm Used	IntelliQuan
Acquisition Method	CEC_NP_PHE_041015.dam	Instrument Name	QTRAP 5500
Project	CEC_2015	Analyst	Le, Anh-Tu

Regression Equation: $y = -1.15900e\text{-}8\ x^2 + 4.64972e\text{-}4\ x + 0.02591$ (r = 0.99935) (weighting: 1 / x)

Expected Concentration	Number of Values	Mean Calculated Concentration	% Accuracy	Std. Deviation	%CV
100.000	1 of 1	86.297	86.3	N/A	N/A
200.000	1 of 1	225.015	112.5	N/A	N/A
500.000	1 of 1	519.912	104.0	N/A	N/A
1000.000	1 of 1	986.150	98.6	N/A	N/A
2000.000	1 of 1	1961.564	98.1	N/A	N/A
4000.000	1 of 1	4021.610	100.5	N/A	N/A
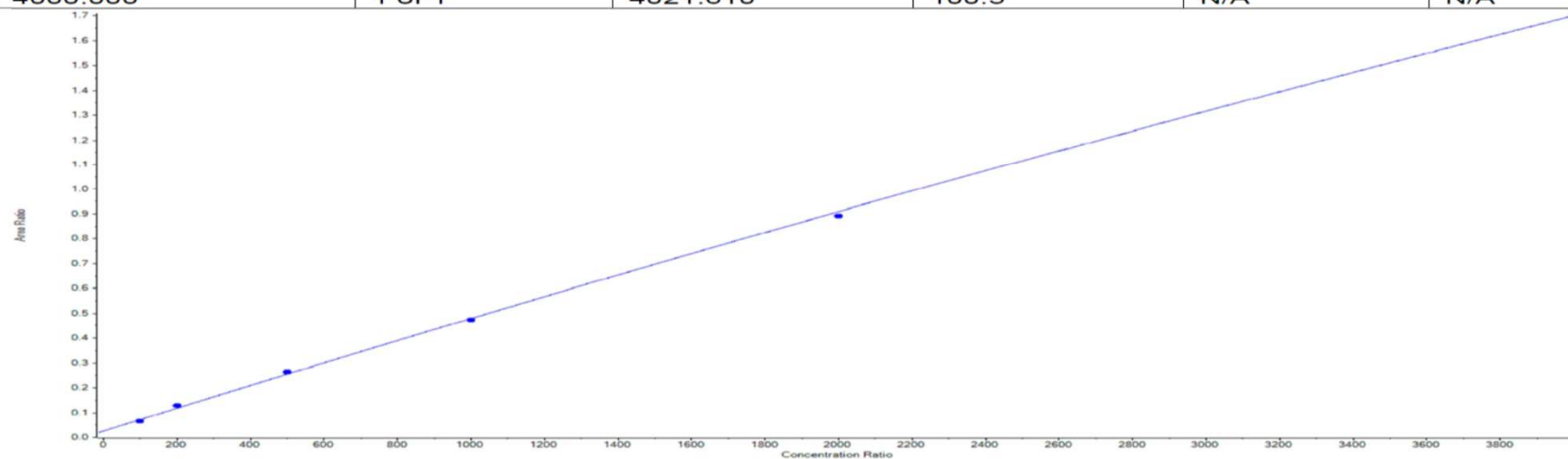
pCBSA – Isotopic Dilution CEC Method
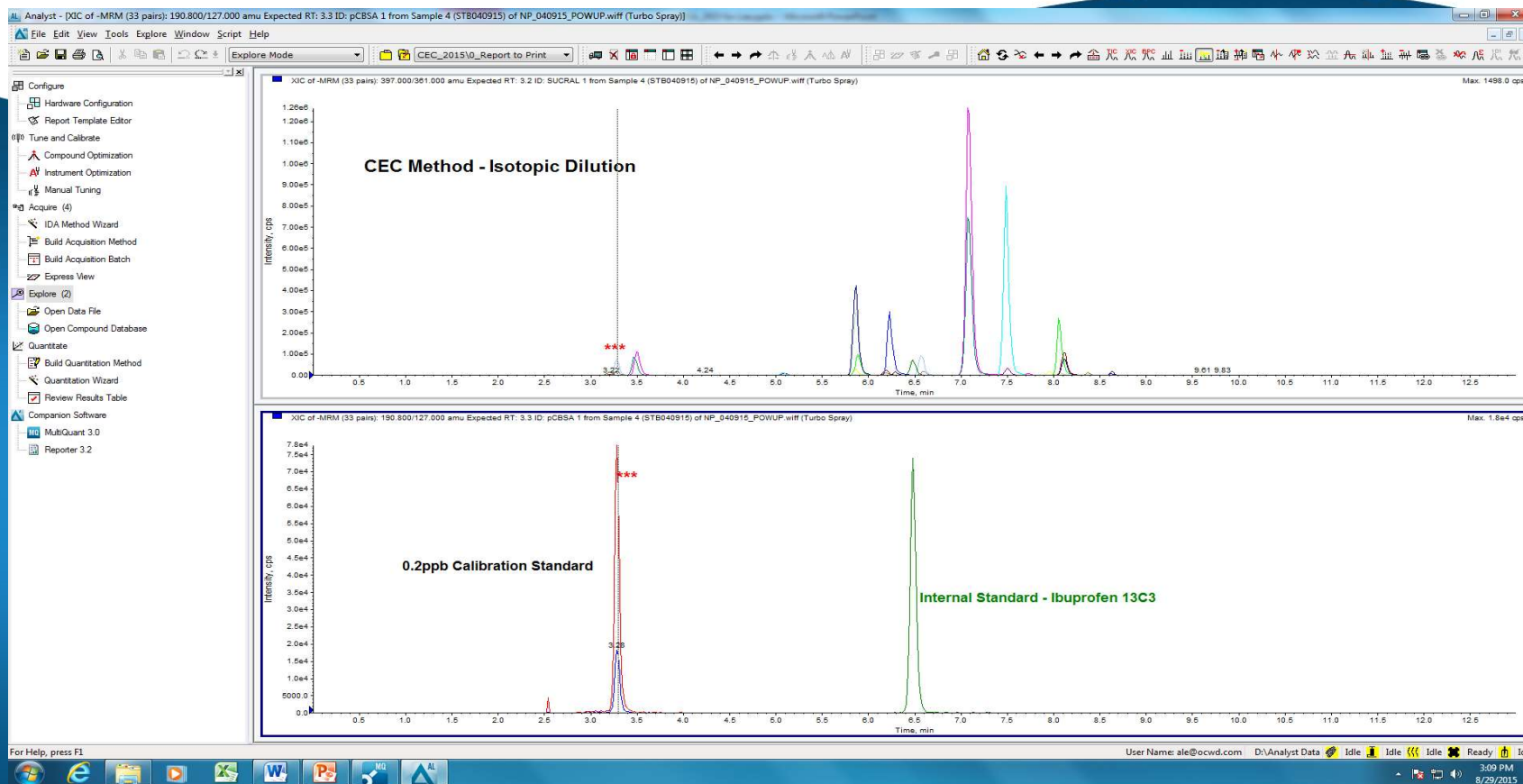
pCBSA – Isotopic Dilution CEC Method
 Calibration Curve: 0.1ppb to 40ppb
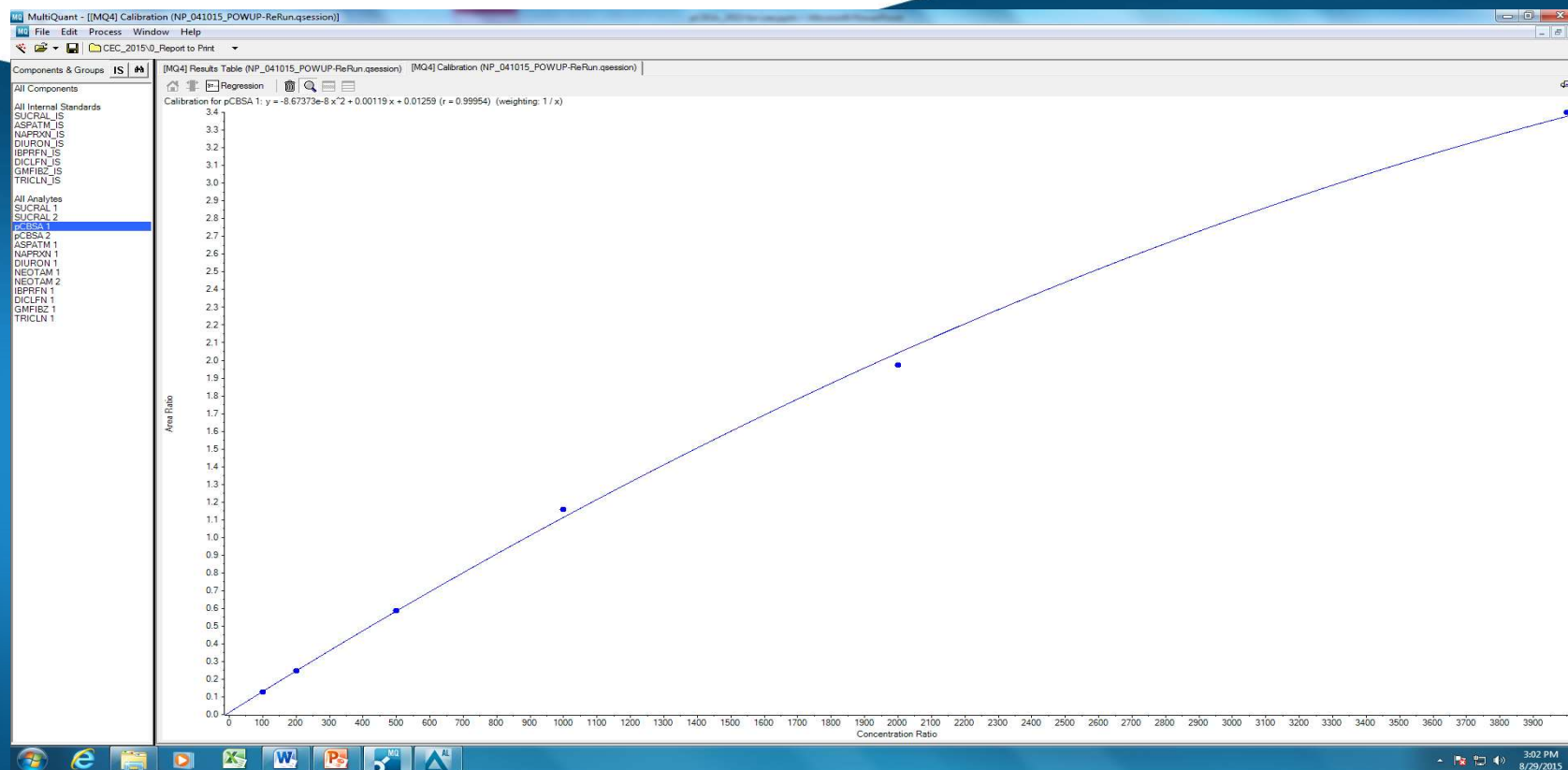
p-CBSA analyzed by LC/MS/MS & IC/MS/MS

6 Weeks Study for Stringfellow Effluent, Super Fund Site, California

Date	LC/MS/MS	IC/MS/MS	Units
12/8/14	**26,100**	**54,000**	ug/L
12/15/14	17,300	26,000	ug/L
12/22/14	44,800	54,000	ug/L
12/29/14	4,520	6,100	ug/L
1/5/15	46,400	52,000	ug/L
1/12/15	47,700	52,000	ug/L

Conclusion

- **P-CBSA is co-eluting with Perchlorate by Ion Chromatography**
- **LC/MS/MS (EPA 331) and IC/MS (EPA 332) methods for preventing false positive report and detection sensitivity by 20-50 times**
- **Direct Injection Technique is more reliable than SPE for p-CBSA**
- **Isotopic method using ibupropane or p-CBSA improved analytical accuracy and reliability**
- **Developed simultaneous detection method for p-CBSA and Perchlorate using IC/MS for wastewater monitoring program**