NATIONAL ENVIRONMENTAL MONITORING CONFERENCE

2008 PROCEEDINGS

Section 7:
Inorganic Methods
Organic Methods

Washington DC
August 10 – 16, 2008

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INDEPENDENT LABORATORIES INSTITUTE

ELAB

THE NELAC INSTITUTE

NEMC

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NEMC 2008
CONFERENCE HIGHLIGHTS

The Environmental Measurement Symposium, a combined meeting of the National Environmental Monitoring Conference (NEMC) and The NELAC Institute (TNI) was held August 10 – 16, 2008 in Washington DC, just blocks from the nation's capitol. The conference was co-sponsored by the US Environmental Protection Agency, the Independent Laboratories Institute, and The NELAC Institute.

A total of 469 people attended the 2008 Forum, which was a 9% increase in attendance over 2007. The meeting included:

- 19 technical breakout sessions with 100 presentations;
- a 2-day poster program with 23 posters;
- 4 keynote presentations;
- 3 EPA general sessions with 13 presentations;
- 13 TNI committee meetings;
- an assessment forum;
- a laboratory mentoring session;
- an accreditation body forum;
- a meeting of the Environmental Laboratory Advisory Board;
- 5 training workshops; and
- a 3-day exhibit program with 43 exhibitors and sponsors.

Highlights of the week included the following keynote speakers:

- Dr. Jorg Feldman from the University of Aberdeen who spoke on elemental speciation in environmental monitoring;
- Dr. Heidelore Fielder from the UN Environmental Program who spoke on global monitoring of persistent organic pollutants;
- Dr. J. Clarence Davies from Resources for the Future who spoke on EPA and nanotechnology; and
- TNI's own Bob Wyeth who spoke on moving forward on national accreditation.

NATIONAL ENVIRONMENTAL MONITORING CONFERENCE PROCEEDINGS 2008

SECTION 7 TABLE OF CONTENTS

INORGANIC METHODS

ORGANIC METHODS

SECTION 7 TABLE OF CONTENTS cont.

2008 NEMC Proceedings

INORGANIC METHODS

Cyanide Preservation and Interferences

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ABSTRACT

Recent developments in cyanide analysis procedures have lead to new discoveries on interferences, sample pretreatment, and sample storage. Requirements for lower cyanide reporting limits necessitate greater understanding of holding times, and the effects of sample storage and analytical methods on the final result generated.

This presentation will discuss the cyanide preservation and interference procedures outlined in the EPA Method Update Rule of March 12, 2007. Problems with the rule will be discussed along with some potential solutions. Topics will include analysis of solid samples, sulfide abatement and mitigation, and the analysis of free, available, and total cyanide.

Preservation and Interferences in Cyanide Analysis

William Lipps
OI Analytical

O·I·Analytical
A World of Solutions

Analysis of Cyanide Species

- Free Cyanide
  - HCN + CN^- + (NaCN, KCN)
- Weak And Dissociable (WAD, CATC)
  - Free Cyanide + Cu, Ni, Ni, Zn, Ag
- Total Cyanide
  - Free Cyanide + WAD Cyanide + Fe, Co, Au, Pt

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Potential Interferences

- Reduced Sulfur Species
  - S^{-2}, S_n^{-2} (n = 2-7)
- Oxidized Sulfur Species
  - Sulfur +1 to +4 oxides
- NO3-N, NO2-N, NH3-N, SCN
- Amines, chloramines, aldehydes, sugars, alcohols, etc

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Table II 40 CFR Part 136.3

Parameter No./name	Container[1]	Preservation[2,3]	Maximum holding time[4]
23–24. Cyanide, total or available (or CATC)	P, FP, G	Cool, ≤6 °C[18], NaOH to pH>12[6], reducing agent[5]	14 days.

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Holding Time

- Cyanide must be taken as a "grab" sample.
- Grab samples must be preserved within 15 minutes of collection.
- The Holding Time begins at the time of collection.
- Analyze ASAP after collection.

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Preservation

- Oxidizers.
  - Residual Chlorine, peroxides, etc.
  - Treat sample immediately to avoid loss of cyanide.
  - Chloramine and CN^- can coexist.
- Treat for oxidizers only if present.

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Reducing Agents for Oxidizers

- Ascorbic Acid
  - Carbon source that can generate CN^-
  - Holding time < 2 days
  - Can cause significant negative bias
  - Can cause positive bias

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Ascorbic Acid decreases CN

- Ascorbic Acid + NaOH with Cyanide present in sample.
  - Holding time decreased to 1 day!
  - A synthetic sample containing 200 ppb CN + ascorbic acid held for 3 days at pH 12 resulted in a 24 % recovery.

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Ascorbic Acid increases CN

- Ascorbic Acid + NaOH and no CN present.
  - Ascorbic acid along with a nitrogen source, or thiocyanate can react at pH 12 to create CN.
  - Synthetic samples containing a nitrogen source, ascorbic acid, adjusted to pH 12 with NaOH generated 5.0 – 50 ppb CN upon storage.

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Reducing Agents for Oxidizers

- Sodium Thiosulfate.
  - Oxidized Sulfur– an interference.
  - Negative interference with distillation/colorimetric methods.
  - Positive interference with UV gas diffusion-amperometry method.

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Sodium Thiosulfate decreases CN

- Distillation with Sodium Thiosulfate results in negative bias.
  - Distilled synthetic samples spiked with 200 ppb CN and 200 ppm thiosulfate varied from **0 – 80 %** recovery depending on operator.

Sodium Thiosulfate increases CN

- UV Irradiation, gas diffusion – amperometry (OIA1678) produces a slight positive bias with excess thiosulfate.
  - 200 ppm thiosulfate produced a 14 ppb apparent CN.
  - **Can be corrected** by modifying the acidification reagent.

Reducing Agents for Oxidizers

- Sodium Arsenite.
  - Recommended, but frowned upon because of arsenic toxicity.
- Sodium Borohydride.
  - Mostly untested.
  - Releases Hydrogen gas on acidification.

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Preservation – footnote 6

- Footnote 6 describes guidance/actions to take if the following potential interferences are present:
  - Elemental Sulfur
  - Sulfide
  - Sulfite, thiosulfate, thiocyanate
  - Aldehydes
  - Carbonate
  - Oxidizers
  - Particulates

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Preservation – Sulfide present?

- Collect a volume sufficient for the method used.
- Adjust to pH >12 if no Sulfide
  - Analyze within 48 hours
- Otherwise treat for interferences, adjust to pH >12 and analyze within 14 days
  - Treatment must be within 15 minutes.

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Elemental Sulfur

- Removed by filtration.
- Filter paper is extracted for particulate CN.
- Extract concentration is added to concentration detected in the filtrate.

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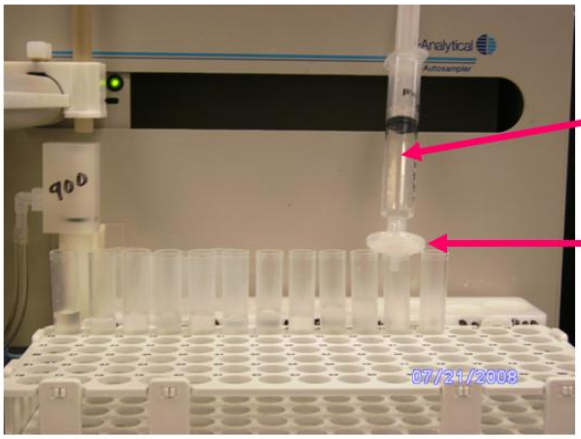
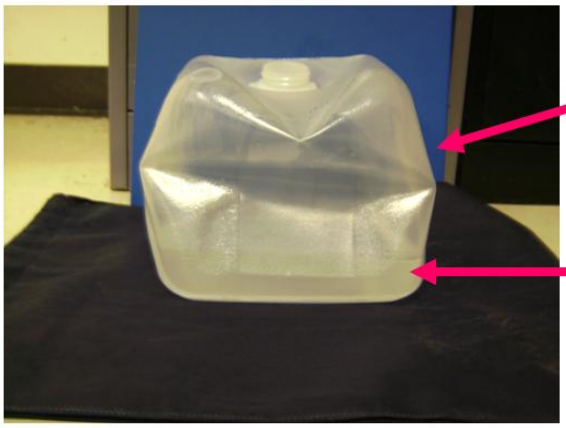
Example of Filtration



Sulfide Treatment

- Test sample for presence of S^{-2} with lead acetate test strips.
  - Sensitive to about 50 ppm S^{-2}.
- Remove S^{-2} by one of the following:
  - Headspace Expelling.
  - Dynamic Stripping.
  - Precipitation.

Headspace Expelling



4.4 L collapsible cubitainer

0.75 L acidified sample

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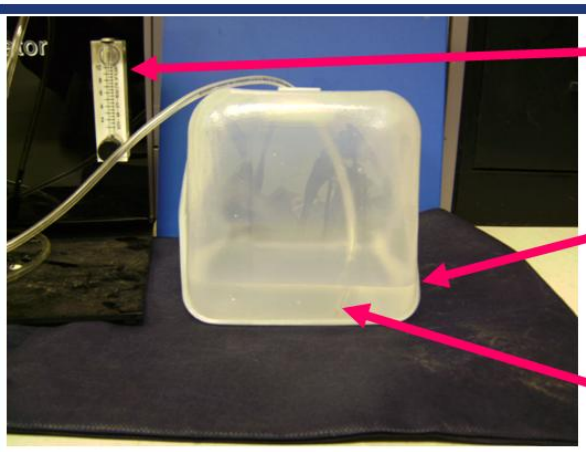
Dynamic Stripping



Aerator at 2.25 ml/min

0.75 L of acidified sample

Glass frit

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Sulfide Precipitation

- Any particulates present must be filtered first.
  - The filter is extracted and analyzed.
- Adjust pH >12 with NaOH.
- Add $CdCl_2$ (1mg per ml).
- Shake, then filter through 0.45 um.

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Problems with Sulfide Removal Methods in Footnote 6

- They don't work.
- Headspace and Stripping.
  - Residual sulfide remains.
  - Attempts to remove S^{-2} remove cyanide.
  - Difficult as a field procedure.
- Precipitation with Cd.
  - Precipitates iron cyanide (total CN).

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Recoveries After Sulfide Removal

Sample Pretreatment 200 ppm S + 200ppb CN	Recovery after 2 days storage at 4 C
Headspace	48%
Dynamic Stripping	55%
Cadmium Chloride	50%
Dilution	**101%**

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Best way to remove Sulfide

- Dilute the sample
  - Analyze available CN by ASTM D6888-04
  - Analyze distilled total CN by ASTM D7284 –08
  - Analyze total CN by OIA 1678

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Sulfite, Thiosulfate, and Thiocyanate

- If sulfite, thiosulfate, or thiocyanate are known or thought to be present use:
  - UV digestion at > 290 nm (Kelada 01 mentioned in parentheses)
  - OIA 1677

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Sulfite, thiosulfate, or thiocyanate

- Sulfite – dechlorinate effluents
- Thiosulfate – dechlorinate samples
  - Older thiosulfate solutions contain many other interfering sulfur oxides
- Thiocyanate – reaction by product of CN

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Flexibility Text within Footnote 6

- "There may be interferences that are not mitigated by approved procedures. Any procedure for removal or suppression of an interference may be employed, provided the laboratory demonstrates that it more accurately measures cyanide."

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But, ...

- How does one determine whether interferences are present?
- How do you know if a method is more accurately measuring cyanide?
- Most common approach – matrix spikes.

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Using Matrix Spikes to Demonstrate Accuracy

Method	Technique	Recovery
335.4	Distillation/GD-amperometry	98 %
335.3	Automated distillation/colorimetry	98 %

Both methods detected 15 – 30 ppb CN^- in a synthetic sample containing no CN^-.

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Verify Accuracy Using Interference Free Methods

- Use methods demonstrated by literature and multiple users to be interference free
  - OIA 1677 or ASTM D6888-04
  - ASTM D 7284-08*
  - OIA 1678 (ASTM WK 8854)*

* Not currently EPA approved

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What isn't mentioned in the footnotes.

- Nitrite.
  - Abundant literature suggests field treatment.
  - Can cause CN^- concentrations to increase on storage.

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What else isn't mentioned.

- The dangers of pH 12 with NaOH.
  - CN^- reacts with SO^-_3 rapidly oxidizing to OCN^-.
    - Without NaOH, CN^- is stable in SO^-_3 solutions.
    - With NaOH, CN^- disappears almost immediately.

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What else isn't mentioned

- Chloramines react at pH 12 generating CN^-
  - Numerous literature reports
  - Results in non compliance
  - Results in fines

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OI Suggestions – Sampling cyanide

- Fill an amber 40 ml VOA vial with sample, refrigerate, and ship to the lab.
- Adjust pH, add ligands, and analyze Available CN by OIA 1677 or ASTM D6888-04.
- Analyze Total CN by OIA 1678 (ASTM WK8854) or ASTM D 7284.

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OI suggestions - Interferences

- Sulfide > 50 ppm.
  - Dilute to less than 50 ppm.
  - Fill an amber 40 ml VOA vial with sample, refrigerate, and ship to the lab.
  - Analyze Available CN by OIA 1677 or ASTM D6888-04.
  - Analyze Total CN by OIA 1678 (ASTM WK8854) or ASTM D 7284.

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OI suggestions - Interferences

- Particulates > 1%.
  - Filter 40 ml into a VOA vial, refrigerate, and ship sample and filter to the lab.
  - Extract filter by with 10 ml of 0.1 M NaOH.
  - Analyze filtrate and extract for CN by OIA 1678, or ASTM D7284-08.

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OI suggestions - Interferences

- Oxidizers.
  - Add just enough fresh Sodium Thiosulfate to remove oxidizer, fill an amber 40 ml VOA vial with sample, refrigerate, and ship to laboratory.
  - Add ascorbic acid, adjust pH to 12 with NaOH and Analyze Available CN by OIA 1677 or ASTM D6888-04 within 8 hours.
  - Analyze Total CN by OIA 1678 (ASTM WK8854) or add ascorbic acid and analyze by ASTM D 7284.

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What can you do?

- ASTM D 7365-07 Guide for sampling and mitigating cyanide interferences.
  - Recently (2007) published
  - A living document
  - www.epa.gov/waterscience/methods/

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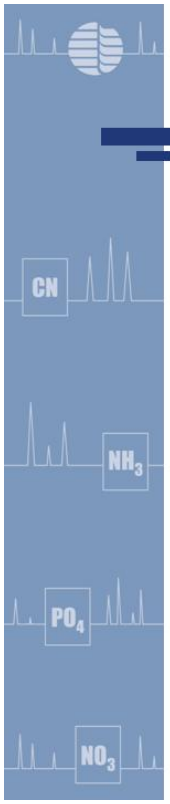

Thank You!

Questions?

O·I·Analytical

Evaluating Discrete Analyzer Methods for Inorganic Analysis of Waste and Water in Environmental Samples

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ABSTRACT

Discrete analyzer technologies have many applications in the clinical industries. In recent years, methods based on the technology have seen a marked increase in the environmental field. A number of classical inorganic methods using the technology are now employed in various environmental laboratories. Comparison of discrete analyzer methods with one of the widely used automated techniques was examined for total cyanide, ammonia nitrogen, total kjeldahl nitrogen, and total phosphorus. Data obtained indicate that methods based on the discrete analyzer technology could produce equivalent results. Additionally, the technique produced significant reduction in overall analytical waste generated in the course of an analysis.

EVALUATING DISCRETE ANALYZER METHODS FOR WASTE AND WATER QUALITY INORGANIC ANALYSIS OF

ENVIRONMENTAL SAMPLES

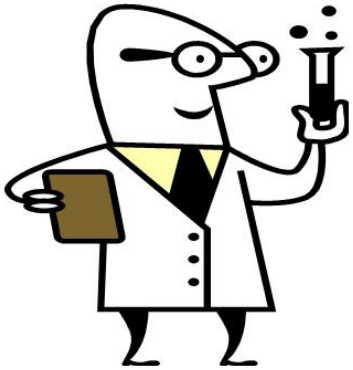
EPA REGION 5,
CHICAGO REGIONAL LAB

OBJECTIVE

- Acquire an instrument that can deliver analytical results of known quality to support on-going clients efforts.
- Maintain or improve the Region 5 CRL ability to deliver those results.
- Reduce laboratory waste in the process.

Why the Discrete Analyzer?

- Mr. Joe I. M. Chemist.



Other considerations

- Flow injection analyzers (FIA).
- Segmented flow analyzers (SFA).
- Manual spectrophotometers.
- Ion chromatography (IC).

Approach

- Prepare samples using existing or approved methods.
- Analyze prepared samples by both continuous flow and discrete analyzer technique.
- Compare results using students t-test.

Sample Preparation Procedures

- Cyanide (CN) EPA Method 335.4 & Microdist (Hach Company)
- Total Phosphorus (TP) EPA Method 365.4
- Total Kjeldahl Nitrogen (TKN) EPA Method 351.2
- Ammonia Nitrogen (Ammonia-N), EPA Method 350.1

Instrumental Analysis

- Continuous flow analyzer methods; Same as referenced in preparation procedure.
- Discrete analyzer procedures; Technical Bulletin, from EST Analytical; CN-EPA method 335.2 (EST V080105), TKN-EPA 351.2 Rev2 (EST V010208) TP-EPA method 365.4, and Ammonia-N by EPA 350.1 Rev2 (EST V04072004).

Discrete Analyzer Instrumental Procedure

- TKN by EPA Method 351.2.
- Sample (32µL) additional volume (20µL).
- Buffer reagent (80µL) additional volume (20µL).
- Salicylate-nitroprusside reagent (32µL) additional volume (20µL).
- Sodium hypochlorite reagent (32µL) additional volume (20µL).
- Measurement by absorbance at 660 nm wavelength.

RESULTS

- Where is the data?

Calibration archive

aquakem Labmedics | Cyanide | Samples | Results | Reagents | Main

Con

Accepted 30/01/2008 14:20

Factor 0.930

Bias 0

Coeff. of det. 0.999358

Errors

Resp. (A)

0.600

0.000

0 0.5

Conc. (mg/l)

Cuv

Tem

	Calibrator	Response	Calc. con.	Conc.	Errors
1	CN-0	0.001	0.001558	0.000000	
2	CN - 500	0.008	0.007497	0.005000	
3	CN - 500	0.013	0.011939	0.010000	
4	CN - 500	0.028	0.026242	0.025000	
5	CN - 500	0.053	0.049911	0.050000	
6	CN - 500	0.104	0.097116	0.100000	
7	CN - 500	0.259	0.240555	0.250000	
8	CN - 500	0.543	0.505182	0.500000	

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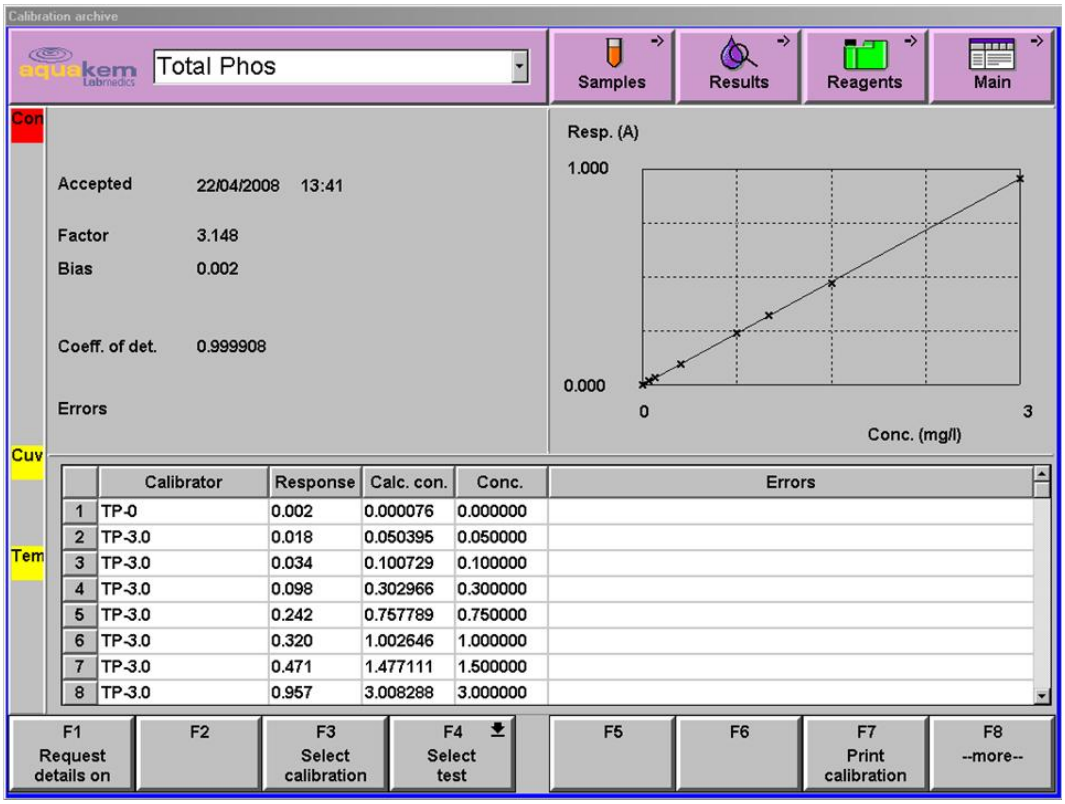
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aquakem Labmedics
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0.000
0
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Conc. (mg/l)
Cuv
Tem
Calibrator Response Calc. con. Conc. Errors
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3 TP-3.0 0.034 0.100729 0.100000
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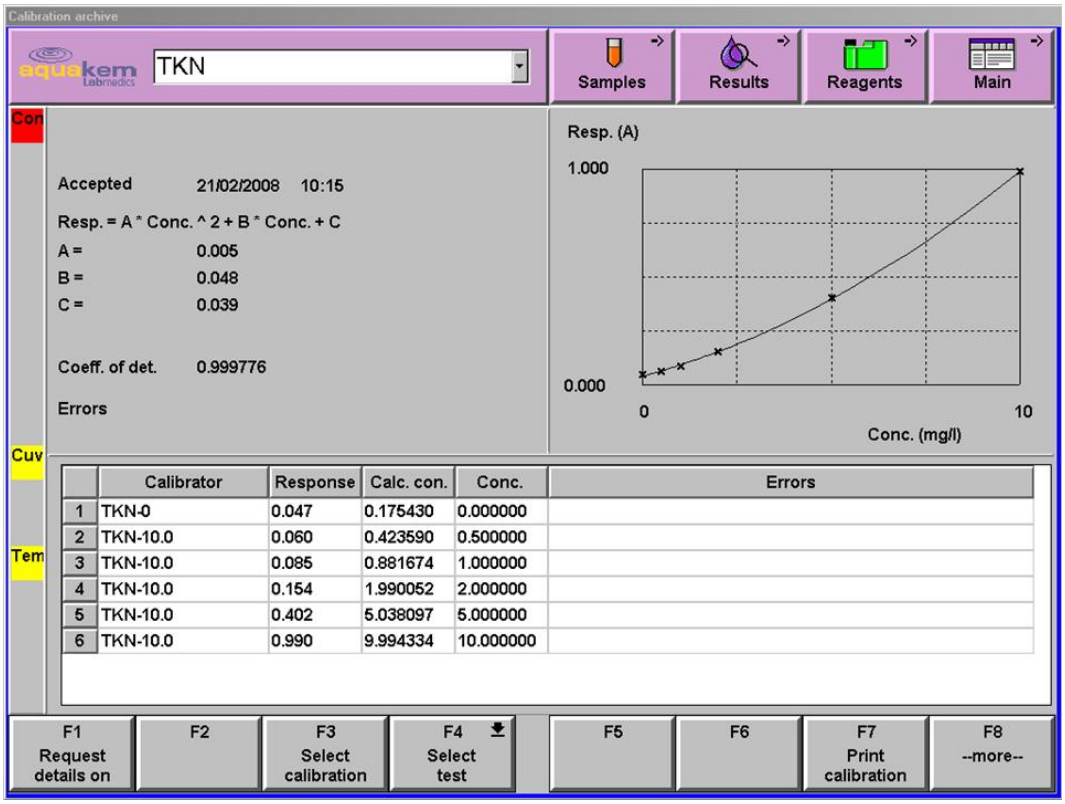
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TKN
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A = 0.005
B = 0.048
C = 0.039
Coeff. of det. 0.999776
Errors
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0.000
0
10
Conc. (mg/l)
Cuv
Tem
Calibrator Response Calc. con. Conc. Errors
1 TKN-0 0.047 0.175430 0.000000
2 TKN-10.0 0.060 0.423590 0.500000
3 TKN-10.0 0.085 0.881674 1.000000
4 TKN-10.0 0.154 1.990052 2.000000
5 TKN-10.0 0.402 5.038097 5.000000
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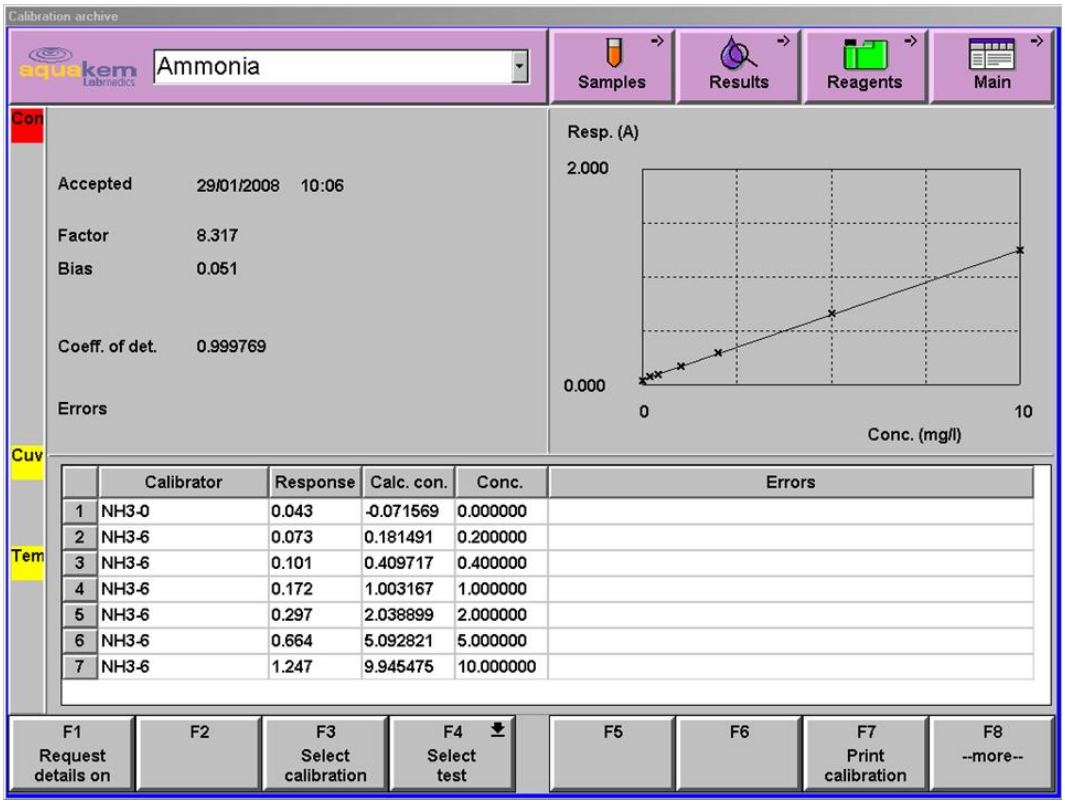
F2
F3 Select calibration
F4 Select test
F5
F6
F7 Print calibration
F8 --more--



CYANIDE

Sample ID	Continuous Flow (mg/L)	Discrete Analyzer (mg/L)
E803004-07	0.0520	0.0514
E803004-09	0.0813	0.0906
E803004-10	0.0670	0.0746
E803004-16	0.0195	0.0138
E803004-17	0.0256	0.0190
E803004-20	0.0764	0.0793
E803004-22	0.1060	0.1103

Total Phosphorus (TP)

Sample ID	Continuous Flow (mg P/L)	Discrete Analyzer (mg P/L)
0801010-01A	4.50	4.61
0801010-02A	7.56	7.69
0711016-03B	3.59	3.69
0712002-01A	0.99	1.27
0712002-02A	1.12	1.37
0712002-06A	2.45	2.96
0712002-18A	1.08	1.35

Total Kjeldahl nitrogen (TKN)

Sample ID	Continuous Flow (mg/L)	Discrete Analyzer (mg/L)
0801010-01A	17.3	15.7
0801010-02A	51.5	43.3
0711016-03B	11.5	8.86
0712002-01A	1.82	1.95
0712002-02A	1.87	1.98
0712002-06A	3.83	4.02
0712002-18A	1.83	1.91

Ammonia Nitrogen

Sample ID	Continuous Flow (mg/L)	Discrete Analyzer (mg/L)
0711015-01A	-0.021	0.055
0711016-01B	0.068	0.132
0711016-02B	2.330	2.083
0711016-03B	2.680	2.322
0711016-04B	-0.133	0.026
0712002-01A	-0.047	0.045
0712002-05A	0.327	0.406
0712002-06A	0.484	0.226

Summary Statistics

Analysis	Pop. (n)	CI	t	t-Calc.
Cyanide				0.676
TP	7			4.36
		95%	1.943	
TKN		99%	3.143	1.464
Ammonia	8	95%	1.895	0.687
		99%	2.998	

Total Phosphorus (TP) P & A

Sample ID	Spiked Conc. (mg P/L)	Measured Conc. (mg P/L)	Recovery (%)
0807027-01	1.0	1.03	103
0807027-01	1.0	1.01	101
0807027-01	1.0	1.02	102
0807027-01	1.0	1.03	103

Total Phosphorus MDL

Sample ID	Spiking Conc. (mg P/L)	Measured Conc. (mg P/L)	Recovery (%)
0802010-01	0.200	0.205	102
0802010-02	0.200	0.200	100
0802010-03	0.200	0.200	100
0802010-04	0.200	0.204	102
0802010-05	0.200	0.202	101
0802010-06	0.200	0.202	101
0802010-07	0.200	0.205	103

Total Phosphorus (TP) Summary Statistics

- P&A
  - Mean Recovery = 1.02 mg P/L (102%)
  - Standard deviation = 0.011 mg P/L
- MDL
  - Mean recovery = 0.203 mg P/L (102%)
  - Standard deviation = 0.007 mg P/L
  - MDL = 0.02 mg N/L

Ammonia-N P&A

Sample I.D	Spiked Conc. (mg N/L)	Measured Conc. (mg N/L)	Recovery (%)
0807021-01	2.00	2.07	103
0807021-01	2.00	2.03	101
0807021-01	2.00	2.02	101
0807021-01	2.00	2.02	101

Ammonia-N MDL

Sample ID	Spiking Conc. (mg N/L)	Measured Conc. (mg N/L)	Recovery (%)
0807021-05	0.10	0.114	114
0807021-06	0.10	0.102	102
0807021-07	0.10	0.097	96.5
0807021-08	0.10	0.095	94.7
0807021-09	0.10	0.092	92.3
0807021-10	0.10	0.103	103
0807021-11	0.10	0.102	102

Ammonia-N P&A

Sample ID	Spiked Conc. (mg N/L)	Measured Conc. (mg N/L)	Recovery (%)
0807021-01	2.00	2.07	103
0807021-01	2.00	2.03	101
0807021-01	2.00	2.02	101
0807021-01	2.00	2.02	101

Ammonia Nitrogen Summary Statistics

- P&A
  - Mean Recovery = 2.03 mg N/L (102%)
  - Standard deviation = 0.023 mg N/L
- MDL
  - Mean recovery = 0.101 (101%)
  - Standard deviation = 0.022 mg N/L
  - MDL = 0.02 mg N/L

CONCLUSION

- Cyanide and Ammonia nitrogen results were found to be comparable by both techniques.
- TKN calibration was non-linear using the discrete analyzer determinative procedure. But sample results were found to be comparable.
- TP analysis indicate possible bias between the two techniques. The bias appears to have no significant impact on precision as demonstrated by PE sample analysis.

CONCLUSION

- TP PE Sample (Target 8.27 mg P/L, found 8.59 mg/L, recovery = 104%).
- Observed bias in TP results could be investigated futher on multiple days, resource permitting.
- Immediate reduction in reagent consumption and waste production.
- Calibration range does not limit efficiency.

ACKNOWLEDGEMENTS

- Region 5, Chicago Regional Laboratory.
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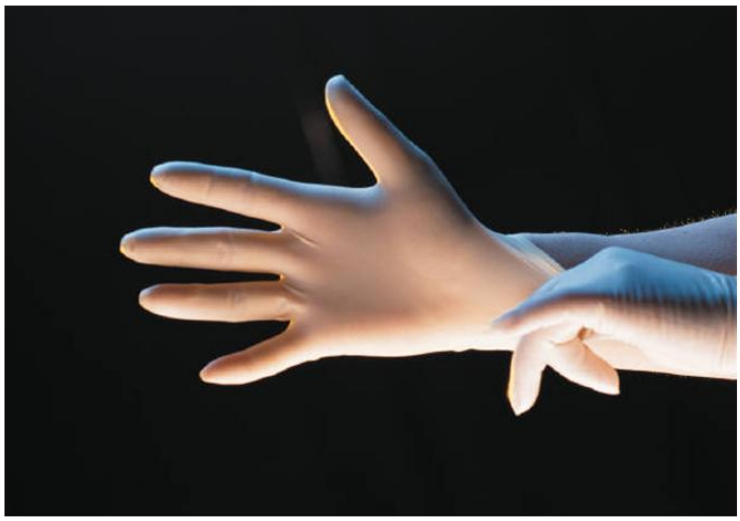
- George Schupp, Deputy Director USEPA Region 5 (CRL).
- Dennis Wesolowski, Director, USEPA, Region 5 (CRL).

Questions & Suggestions



Accurate Preparation of TOC Standards

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ABSTRACT

As we screen our samples at lower and lower levels the importance of accuracy in standards preparation cannot be overlooked. Since organic carbon is essentially everywhere, it is almost impossible to obtain reagent water and/or laboratory glassware that is Total Organic Carbon (TOC) free. The end result is that all calibrations are essentially standard additions forcing tight control over what is often considered "routine' laboratory practices. This presentation will discuss observations made by OI Analytical on common mistakes that can lead to incorrect results, or difficulties in obtaining adequate low level TOC calibrations. The solutions that OI Analytical have found to be effective will be presented.

Accurate Preparation of TOC Standards

2008

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A World of Solutions

What Are Standards?

- Standards means many things to different people.
  - Official Method (ASTM Standard).
  - Standard Operating Procedure (SOP).
  - Certified Reference Material (SRM).
  - Calibration Solutions.

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Standardization of Calibration

- Calibration procedures in existing methods are poorly defined.
  - Use easily oxidized KHP
- Variability in calibration severely effects results.
- Especially evident at lower concentrations.

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Method 5310B - HTC

- SM 5310B says:
  - Prepare standards to cover instrument linear range
  - Inject, and record peak response from standards and blank
  - Plot mgC versus response
- Validation Data – ASTM D 2579-93

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ASTM D2579-93

- Prepare at least 4 standards at concentrations encompassing sample range.
- Inject, and record response from standards and blanks.
- Plot mg /L C versus response.
- Analyzer used in validation not HTCO
  - Teal's apparatus
  - MDL = 2 ppm

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Method 5310C- Wet Oxidation

- SM5310C says:
  - Prepare standards to cover expected sample range.
  - Inject, and record peak response from standards and blank.
  - Subtract blank response and plot concentration versus response.

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ASTM D4839-94

- Calibrate according to the manufacturer's instructions.
- Plot standard concentration versus instrument reading.
- Establish instrument blank according to manufacturer's instructions.

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The Point Is….

- The Standardized Methods say what to do without saying how.
  - Especially important is advice on blank correction
  - Instructions are too general
  - Rely on manufacturers – vary by instrument

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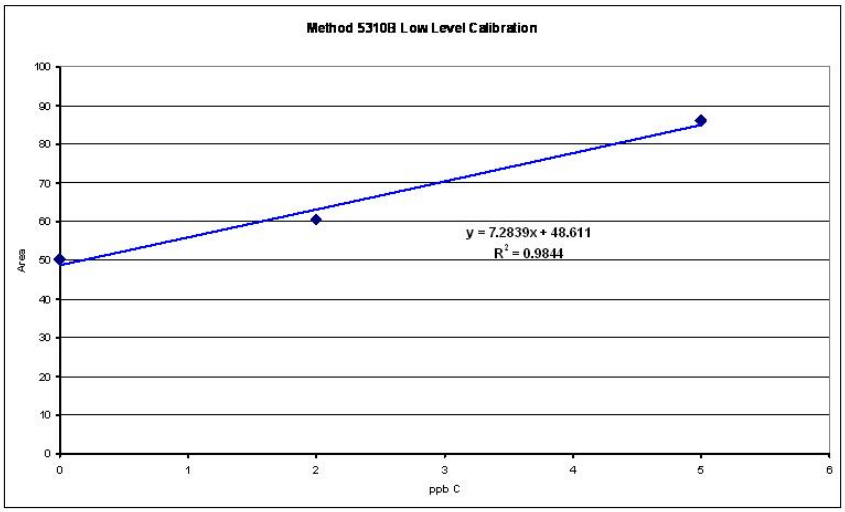
Low Level Calibration – 5310B



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Things to Note About the Calibration

- It does not pass through zero
- Imprecision
- Estimated Blank (zero) concentration
  - [5 ppb / (86.09-50.2)] x 50.2 = **7 ppb**
- TOC calibrations are always Standard Additions
  - Remember – high point was 5 ppb
  - Actual Carbon – 12 ppb

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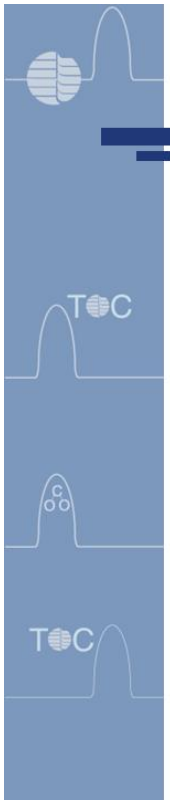

Some Definitions

- RB = Reagent Blank
  - Amount of carbon from reagents and system
- RW = Reagent Water
  - Amount of carbon from water used to prepare standards

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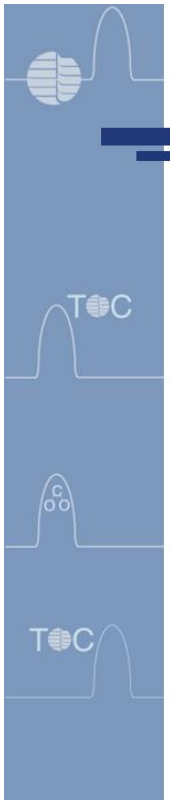

The Calibration Signal

- $A_T = A_{STD} + A_{RW} + A_{RB}$
  - A_T = Instrument Response from calibrant
  - A_{STD} = Instrument Response from carbon added (calibration concentration)
  - A_{RW} = Instrument Response from the reagent water
  - A_{RB} = Instrument Response from reagents and system

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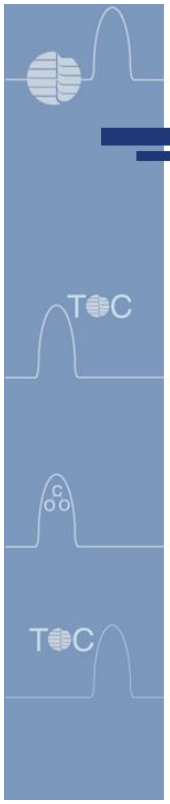

Things to Assume

- There will always be Carbon present in the RW and the RB.
  - RB usually subtracted by software.
- Lower Concentration calibration standards have higher uncertainty in actual concentration value.
  - Variability from glassware.
  - Variability from RB.
  - Variability from RW.

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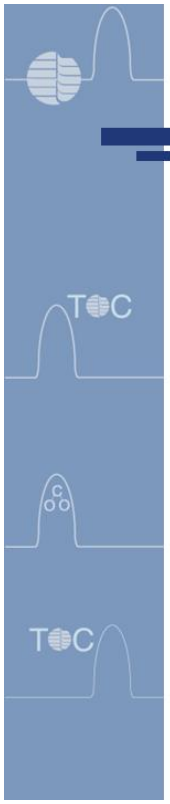

Remember the Curve

- RW was 7 ppb
- Calibrants were 0 ppb, 2 ppb and 5 ppb
- Actual levels were 7 ppb, 9 ppb and 12 ppb
- Suppose +/- 1 ppb precision
  - 1/9 x 100 = 11% variation

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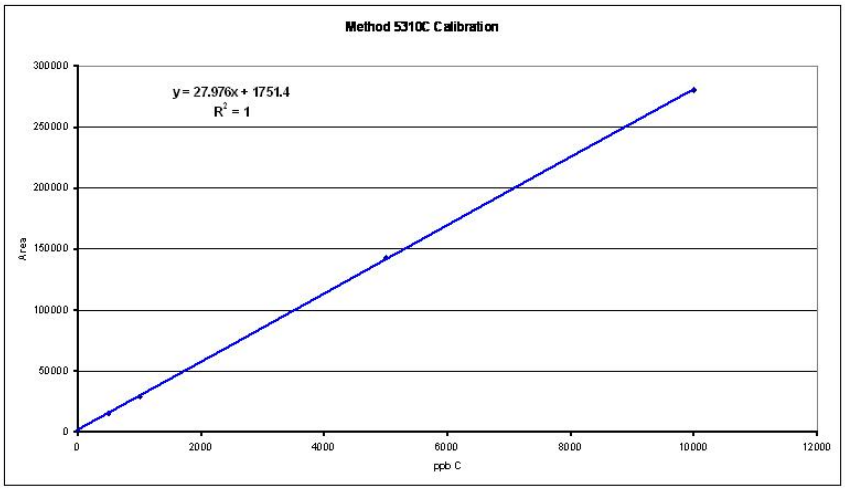
Method 5310C Calibration



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Things to Note About the Calibration

- RB = 28ppb Carbon
- RW = 32 ppb Carbon
- Lowest calibrant = 500 ppb
- Actual calibrant concentration = 560 ppb
- Suppose +/- 1 ppb precision
  - 1 / 560 x 100 = 0.2 % variation

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More Realistically

- The average standard deviation of multiple readings taken under "clean conditions" was 4 ppb.
- The error was +/- 3 ppb.
- Worst case = 7/500 x 100 = 1.4 %.

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What Does This Mean?

- There must be control over RW and RB.
- Glassware must be clean.
- Calibrations standards must be significantly higher than RW.
- Written Standards need to say more.

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Sample and Standard Vials

- Sample vials are a significant contributor
  - Vial supplier A = 5 – 20 ppb C
  - Vial supplier B = 3 – 10 ppb C
  - Vial supplier C = > 150 ppb C
    - Supplier C "VOC " vials
- Must use TOC clean vials!

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Impact of Vials on Calibration

	Vial Type	Vial 1	Vial 2	Difference ppb C
500 ppb	Low TOC	524	536	12
500 ppb	Reg. VOC	544	730	186

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Impact of Vials on MDL (VOC Vials)

Run 1	57
Run 2	46
Run 3	45
Run 4	98
Run 5	49
Run 6	80
Run 7	52
Standard Deviation	20.2
MDL	63 ppb

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Impact of Vials on MDL (Low TOC Vials)

Run 1	33
Run 2	28
Run 3	22
Run 4	21
Run 5	31
Run 6	28
Run 7	26
Standard Deviation	4.397
MDL	14 ppb

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Purity of Reagent Water

Reagent Water	Max TOC (ppb)
ASTM Type I	50
ASTM Type II	50
ASTM Type III	200

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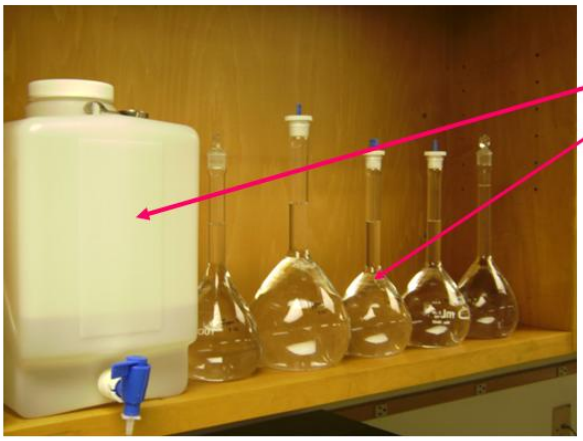
Water and Glassware Control



Same RW must be used in all calibration standards.

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Contamination Control

- Artifacts in glassware
  - Remnants from previous usage
  - Cross contamination
- Atmospheric
  - CO_2
  - VOC

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Calibrant Levels

- Recommend no lower than 500 ppb C.
  - 5 ppb error = 1% error.

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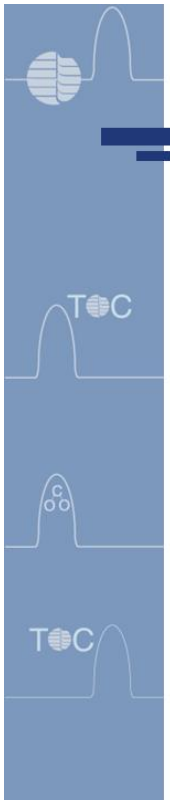

New Written Standards

- EPA 415.3.
  - Extensive coverage of calibration and blanks.
  - Good source of information.
- ASTM D2579-93.
  - Withdrawn.
  - New Work item.
  - Will contain info similar to 415.3.

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Comparison of Three Methods for the Determination of Mercury in Water and Wastewater

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ABSTRACT

Mercury measurement is of importance in water quality and treatment. Commonly applied analytical techniques for total concentration of mercury in water and wastewater include cold vapour atomic absorption spectrometry (CVAAS), inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES). This paper addresses our laboratory's comparison of the three methods in various aspects, such as potential interference, analytical characteristics, sample preparation and applicability to various sample matrices. The results will provide a guideline to method choice for different applications.

The CVAAS method, using a PerkinElmer FIMS-100 flow injection mercury system, is highly selective because of mercury vapour formation and its separation from aqueous solution. It has a method detection limit (MDL) of 30 ng/L for treated water and wastewater matrices, and a dynamic range up to 20 µg/L (with a sample loop of 500 µL). When the method is applied to water samples with a high concentration of chloride, such as wastewater, seawater and marine catchment water, its sample preparation procedure still functions well but care should be taken to add more permanganate solution prior to the addition of persulfate.

ICP-MS is able to simultaneously quantify multi-elements, including mercury. When using an Agilent 7500a quadrupole ICP mass spectrometer, the method has a MDL of 26 ng/L for treated water matrix and its calibration range is linear up to at least 100 µg/L. Since mercury in drinking water is regulated with a maximum contaminant level of 2 µg/L in the United States and 1 µg/L in the European Union, a smaller calibration range, e.g., 0-5 µg/L, is preferred for drinking water, NEWater, surface water and seawater. Carry-over was observed during mercury determination at µg/L level. The rinse period between samples should be long enough to eliminate significant carry-over. Addition of Au(III) solution to the rinse blank was found to effectively reduce carry-over and shorten the rinse period. As a preservative, Au(III) should be added to a sample prior to acid digestion. An appropriate digestion procedure is EPA method 3005A, which uses nitric acid, hydrochloric acid and a heating temperature of 90-95 °C to avoid volatile mercury loss.

ICP-OES is also a multi-element quantitation technique. However, compared with the other two methods, its sensitivity is much poorer. Using a PerkinElmer Optima 5300DV ICP-OES system, a MDL of 5.1 µg/L was obtained using emission wavelength of 194.168 nm for treated matrix and the calibration range was linear up to 5.0 mg/L. Similarly, the carry-over effect was found when Au(III) was not added to a sample. Obviously, ICP-OES method is not suitable for mercury measurement in drinking water, reservoir water and seawater, but it is useful for wastewater examination and emergency screening of other waters for heavy inorganic contamination.

Certified reference materials and a number of water samples were analysed by the three methods, and their results were statistically compared.

Comparison of Three Methods for the Determination of Mercury in Water and Wastewater

Zhongxian Guo, Wei Zhang, Wei Ning Yap, Zhaoguang Yang

Centre for Advanced Water Technology
PUB Consultants, Singapore

Washington, DC, USA
12 August 2008

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Outline

- ❖ Background
- ❖ Summary of mercury analytical methods
- ❖ Laboratory comparison of three methods
  - ❑ CVAAS
  - ❑ ICP-MS
  - ❑ ICP-OES
- ❖ Conclusions

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Mercury in drinking water

- Sources
  - Erosion of natural deposits (rocks, soils);
  - Discharge from refineries & factories (power plants);
  - Runoff from landfills and croplands
- Toxic metal: Inorganic Hg (including Hg^{2+}, $Hg(OH)_2^0$, Hg^0) , Methyl mercury (highly toxic, can concentrate in aquatic food chain), causing kidney damage
- Maximum contaminant level (MCL):

  2 ug/L (USEPA), 1 ug/L (EU), 1 ug/L (WHO)

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Analytical methods of mercury in water

- CVAAS
  - Method of choice for all samples, EPA 245.1, 245.2, SM3112B
  - Equipment available in ways of continuous flow, FIA & discrete analysis
  - Detection limit improvable with gold amalgamation unit
- ICP-MS
  - May be successfully applied in some cases
  - Listed as an analyte in more standard methods (USEPA 6020A, 200.8), but not in SM3125, ASTM D5673-05, ISO17294)
- ICP-OES
  - Applied to water, wastewater
  - Listed as an analyte in USEPA 200.7 (Rev. 5.0, 2001), 6010B/C, but not in SM3120, ASTM D1976-02, ISO11885:2007

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Analytical methods of mercury in water

- CVAFS (cold vapor atomic fluorescence spectrometry)
  - Brominating digestion, CVAFS with ultrapure argon as carrier gas
  - Higher sensitivity than CVAAS, detection limit down to 1 ng/L
  - Applied to drinking, surface, ground and rain water, may be applied to industrial and municipal wastewater
  - EPA 245.7, 1631 (purge and trap), ISO 17852:2006, EPA 7474 (for sediment and tissue)

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Samples Tested at CAWT Laboratory

Supporting projects of PUB (Singapore's national water agency) and other water industry players

- Source water
  - Reservoir water
  - Catchment water
  - Feed water of NEWater plants (wastewater)
  - Sea water (feed water of desalination plant)
- Treated water
  - Drinking water
  - NEWater
  - Desalinated water
- Sediments, sludges, and others

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Mercury testing equipment at CAWT

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Questions raised

- How to test samples with reliable results, compliance with regulations and high throughput?
- How to help customers to choose an appropriate method and reduce testing cost?

Comparative study here on three methods
(CVAAS, ICP-MS, ICP-OES)

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What to be Compared?

- Potential interferences
- Sample preparation procedure
- Analytical characteristics
- Applicability to different matrices
- Samples analysis

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Typical Parameters of FIA-CVAAS

Flow injection	Sample volume:	500 uL
	Preconcentration:	No
	Peristaltic pump	1
	Reagents	6 ml/min $SnCl_2$ in HCl; 10 ml/min HCl
	Loading & injection time	40 s
Carrier gas system	High purity argon	Pressure: ~360 kPa; Flow rate: 70 ml/min
	Gas-liquid separator	
Atomic absorption system	Mercury lamp:	Wavelength: 253.7 nm Slit width: 0.7 nm
	Atomic absorption cell	Length: 260 mm Diameter: 4 mm
	Detection time	15 s per injection

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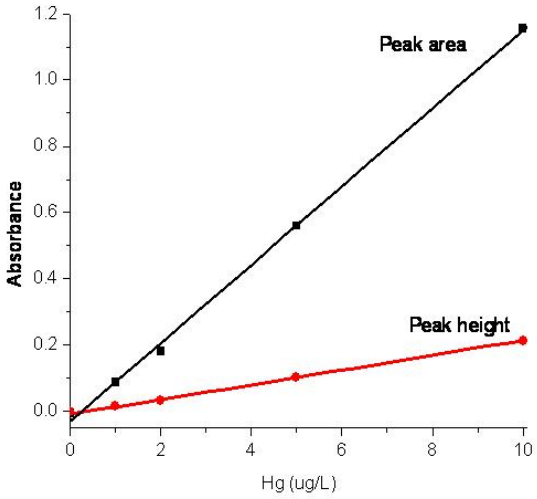
FIA-CVAAS

- Peak area / height can be used for construction of a calibration graph. Peak area way is preferred.
- Good linearity is readily obtained (R>0.997).
- Linear range up to 20 ug/L
- IDL: 10 ng/L
- MDL: 30 ng/L



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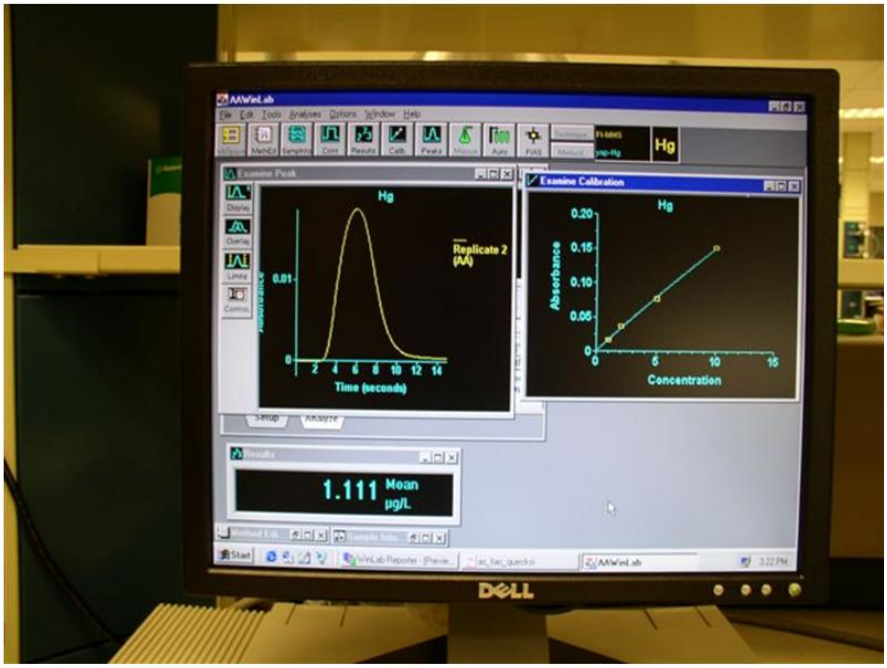
11



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ICP-MS Instrument parameters

Radio-frequency power	1500 W
Carrier gas	Argon, 1.19 L/min
Plasma gas	Argon, 15 L/min
Auxiliary gas	Argon, 0.9 L/min
Torch	Standard quartz, 2.5 mm i.d.
Nebulizer	Quartz concentric
Spray chamber	Double pass quartz Scott type, 2 °C
Sampling/skimmer cones	Nickel
Detector mode	Pulse
Isotopes monitored	202, 200 (199, 201)
Washout	2 mg/L Au(III) in 2% HNO_3 - 1% HCl, wash 40 s

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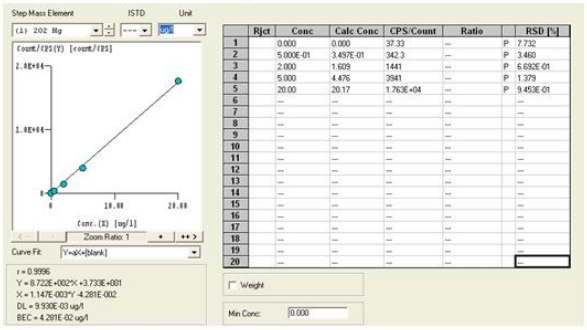
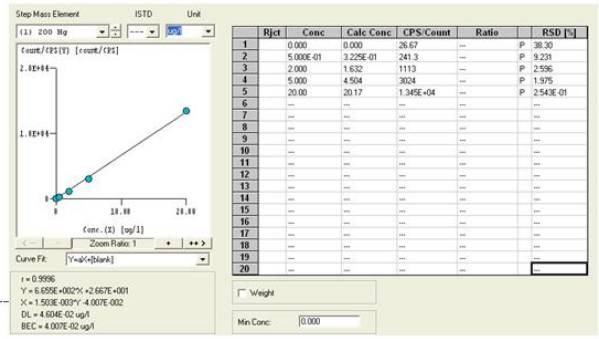
13

Calibration at m/z 202 and 200 by ICP-MS





Range: 0-20 ug/L,

IDL: 9.93 ng/L
MDL: 26 ng/L

For seawater,
10-fold dilution
MDL: 0.3 ug/L

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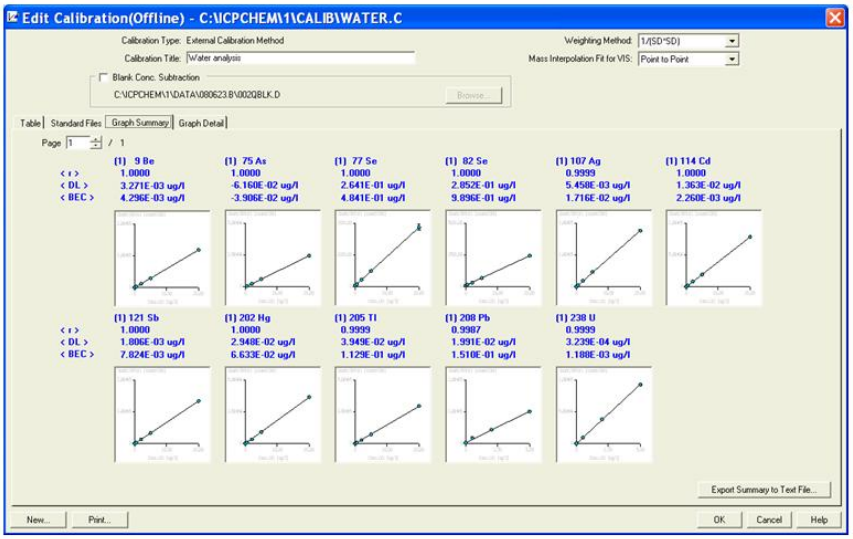
Calibration for Multi-elements by ICP-MS



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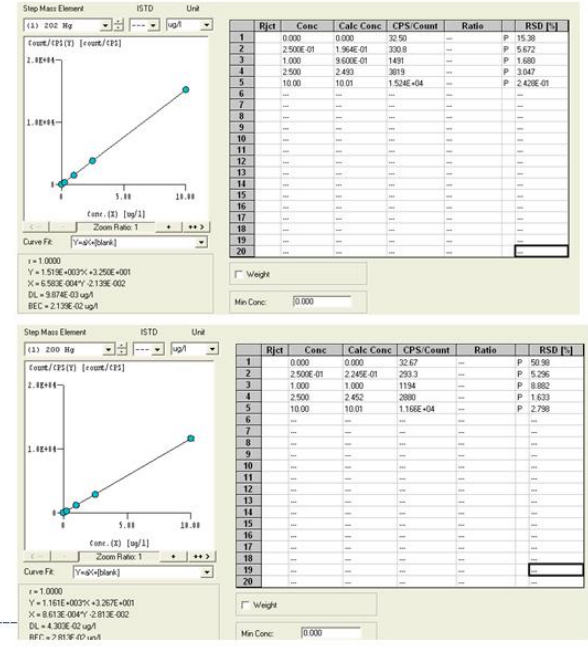
Calibration at m/z 202 and 200 by ICP-MS



Range: 0-10 ug/L

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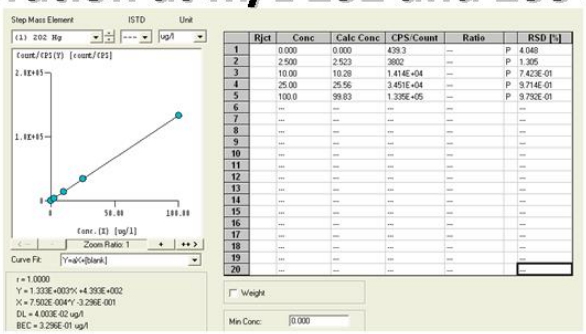
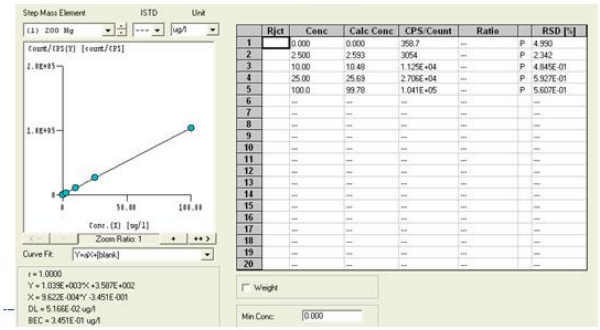
Calibration at m/z 202 and 200 by ICP-MS



Range: 0-100 ug/L



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ICP-OES Instrument parameters

Spectrometer system	PerkinElmer Optima 5300DV with AS-93 autosampler
Radio-frequency power	1300 W
Plasma gas	Ar, 15 L/min
Auxiliary gas	0.2 L/min
Nebulizer gas	0.8 L/min
Plasma view	Axially viewed, distance: 15.0 mm
Wavelength (nm)	194.168, 253.652, 184.886
Data processing	Peak area algorithm, 3 points/peak
Resolution	Normal
Purge gas flow	Normal
Read delay	30 sec

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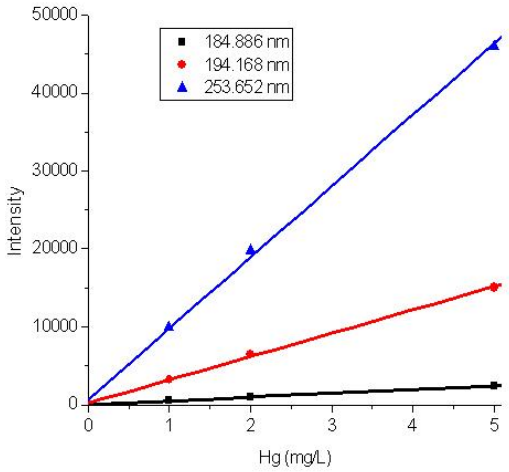
18

Typical Calibration of ICP-OES

- Good linearity is readily obtained at each wavelength (R>0.999).
- Strongest intensity at 253.652 nm
- IDL: 1.8 ug/L (194.168 nm)
- IDL: 2.0 ug/L (253.652 nm)
- MDL: 5.1 ug/L (NEWater matrix, 194.168 nm)



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19

Sample Preparation

	FIA-CVAAS	ICP-MS	ICP-OES
Sample collection and preservation	Preservation by acidification with HNO_3 to pH<2, holding time at about 4 °C and in glass containers 5 weeks (compared with 14 d in plastic containers). For dissolved Hg only, filtration through 0.45 um membrane is necessary		
Digestion	Permanganate-persulfate oxidation in H_2SO_4 -HNO_3 matrix at 95°C	$AuCl_3$ solution added at a final level of 2 mg/L, HNO_3-HCl digestion at 95°C (a gentle reflux action occurs)	
Reagents and gas supplies	Reduce excess $KMnO_4$ with NaCl-(NH_2OH)-HCl solution; $SnCl_2$ in HCl to reduce Hg^{2+} to Hg^0	Rinse blank containing Au(III), or multi-rinse blanks	
Reagents purity	Higher purity reagents (including acids) and gases		

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20

Potential Interferences

FIA-CVAAS	ICP-MS	ICP-OES
Contaminated glassware, especially previously exposed to high levels of Hg		
Carry-over of residual $SnCl_2$, causing Hg reduction and loss	Carry-over (long time rinse or flush to minimize it)	Carry-over (long time rinse or flush to minimize it)
Free chlorine absorbing at 253 nm (from oxidation of chloride, need sparging removal before Hg reduction)	Polyatomic (molecular) ions, e.g., WO	Spectral interferences (spectral line overlaps, broadened wings of intense spectra lines, molecular band emission, scattered light)
Stannous solution decomposition with aging	Signal suppression in the case of high TDS. Dilution is necessary for seawater.	Nonspectral interferences (changes in physical properties, and chemical interference highly dependent on sample matrix)

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21

Analytical Characteristics

Method	FIA-CVAAS	ICP-MS	ICP-OES
Signal monitored	Light absorption of Hg vapour in flow cell at 253.7 nm	Intensity (counts) of Hg ions at m/z=202 or 200	Light emission of Hg excited atoms / ions at 194.168 nm, 253.652 nm, etc.
Linear range	0-10 (20) ug/L	0-5 (10, 20, 40, 100 ug/L)	0-5.0 mg/L
MDL (treated water matrix)	30 ng/L (for 500-uL sample injection)	26 ng/L	5.1 ug/L (using 194.168 nm)
Simultaneous determination	Hg alone	Yes	Yes
Selectivity	High selectivity, vapour-liquid separation, matrix-interference free	High selectivity, element-specific	Good selectivity, but not good as CVAAS and ICP-MS
Analytical speed	Minutes after digestions (hours)		

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22

Analysis of Certified Water Supply Samples

Sample	Certified value (ug/L)	FIA-CVAAS		ICP-MS	
		Found (ug/L)	RSD (%)	Found (ug/L)	RSD (%)
RTC QCI-016-1	5.94	6.13±0.19	3.1	5.65±0.24	4.2
RTC PEI-016-1	2.64	2.77±0.04	1.3	2.60±0.15	5.7
APG WS #5070	2.66	2.62±0.05	2.0	2.45±0.11	4.5

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23

Applications of Three Methods at CAWT

- CVAAS
  - Long-time (10 years) sole choice for all water and wastewater samples
  - Also used for analysis of sediments, waste oils, pharmaceuticals
- ICP-MS
  - As an alternative to CVAAS, its applications at CAWT started in 2005
  - Multi-analyte monitoring of drinking water, reservoir water, wastewater, seawater
  - Supports water treatment projects, which produce samples containing mercury from mg/L to ng/L (Saving cost for customers)
- ICP-OES
  - Seldom used, mainly for wastewater
  - Screening of source/treated water in emergencies for contaminants

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24

Analysis of an Aqueous Sample by ICP-OES

Wavelength (nm)	Total Hg found (mg/L)	
	500-fold dilution	1000-fold dilution
Hg 184.886	4.30±0.05	2.06±0.02
Hg 194.168	4.66±0.02	2.36±0.01
Hg 253.652	4.65±0.02	2.34±0.01

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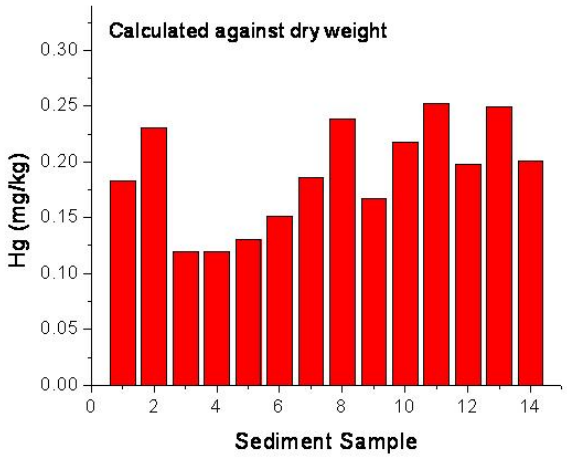
25

Analysis of Sediments by FIA-CVAAS



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26

Conclusions

- ICP-MS: Applicable, high throughput, cost-effective for water and wastewater analysis
- CVAAS: Classical
- ICP-OES: Emergency screening, very high level samples.

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Thank you!

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Analysis of Regulated Inorganic Anions in Waters by LC/ESI/MS/MS

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ABSTRACT

The U.S. Environmental Protection Agency (EPA) has regulated nitrate, nitrite, bromate, and chlorite in drinking water. The current maximum contamination levels (MCLs) are 10 mg/L for nitrate measured as nitrogen, 1 mg/L for nitrite measured as nitrogen, 0.010 mg/L for bromate, and 1 mg/L for chlorite, respectively. Perchlorate contamination mainly originates from the manufacturing of rocket fuels. It has been found in various waters and several types of foods. It has been reported that the exposure to perchlorate contamination may have potential adverse effects on human health. EPA has not yet established an MCL for perchlorate because the impact level on human health is still in debate. However, two states have recently regulated perchlorate with an MCL of 0.006 mg/L in California and 0.002 mg/L in Massachusetts. EPA recently included perchlorate as a high-priority contaminant of concern on the draft Contaminant Candidate List 3 (CCL3).

It was recently found that nitrate and perchlorate concentrations obtained from the reference methods were significantly different from those obtained from the in-house methods using LC/ESI/MS/MS for a number drinking water samples. The reference methods included EPA Methods 353.2, 300.1, and 314.0. The root cause might be due to matrix interferences as well as the lack of specificity in colorimetry and ion chromatography/conductivity detection. It is very important to have accurate analytical results because biased results could cause misidentified MCL violations and put public health at risk. The presentation will cover the following three aspects: (1) LC/ESI/MS/MS method development, (2) performance evaluation and application, and (3) performance comparison. The developed LC/ESI/MS/MS method will be compared with the reference methods to investigate the impact of various sample matrix interferences on the analytical accuracy in a wide range of concentrations.

Trace Level Bromate Analysis in Drinking Water: Is Multi-Dimensional Approach Really Necessary?

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281-484-5000
jay@mp-ic.com

ABSTRACT

Bromate is regulated as a carcinogen in drinking water. New technologies are available for the analysis of Bromate in drinking water, bottled water. New regulations throughout the world are forcing lower detection limits. Do we really need multi-dimensional approach for the analysis? This presentation will discuss current and emerging new instrumentation for the Bromate Analysis.

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Trace Level Bromate Analysis in Drinking Water – Is Multi-Dimensional Approach Necessary?

Jay Gandhi, Technical Manager
Metrohm-Peak, LLC
Houston TX

Metrohm International Headquarters

Outline

- USEPA Method 300.0 and 300.1 part B – review
- USEPA Method 317.0 and 326.0 – review
- USEPA Method 326.X review
- 2D IC - overview
- Bromate without 2D IC
- Summary

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USEPA Method 300.0 and 300.1 part B review

page 1

EPA Method 300 (Revision 2.1 - August 1993)
TITLE: Determination of Inorganic Anions by Ion Chromatography

PART B.

Bromate Chlorite
Chlorate

Loop size for 4 mmID column = 200 microliters

METHOD 300.1

DETERMINATION OF INORGANIC ANIONS IN DRINKING WATER BY ION CHROMATOGRAPHY

PART B.-- Inorganic Disinfection By-products

Bromate Chlorite
Bromide Chlorate

Loop size for 4 mmID column = 200 microliters

Loop Size for 2mmID column = 50microliters

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C-grams from the current method

Method B

Peak	Ret. Time	Ion	mg/L
1	2.75	ClO_2^-	0.1
2	3.23	BrO_3^-	0.1
3	3.63	Cl^-	0.1
4	7.08	ClO_3^-	0.1

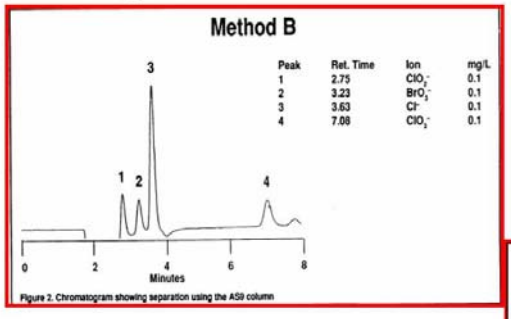
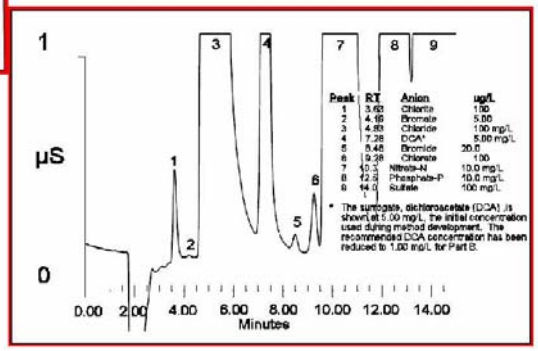


Figure 2. Chromatogram showing separation using the AS9 column

Method 300.0 part B

Method 300.1 part B



Peak	RT	Anion	µg/L
1	3.62	Chlorite	100
2	4.16	Bromate	5.00
3	4.69	Chloride	100 mg/L
4	7.28	DCA*	5.00 mg/L
5	8.48	Bromide	20.0
6	9.28	Chlorate	100
7	10.3	Nitrate-N	10.0 mg/L
8	12.8	Phosphate-P	10.0 mg/L
9	14.0	Sulfate	100 mg/L

* The surrogate, dichloroacetate (DCA), is shown at 5.00 mg/L, the initial concentration used during method development. The recommended DCA concentration has been reduced to 1.00 mg/L for Part B.

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Other methods for Bromate Analysis

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USEPA Method 317.0 and 326.0 (UV/PCR)

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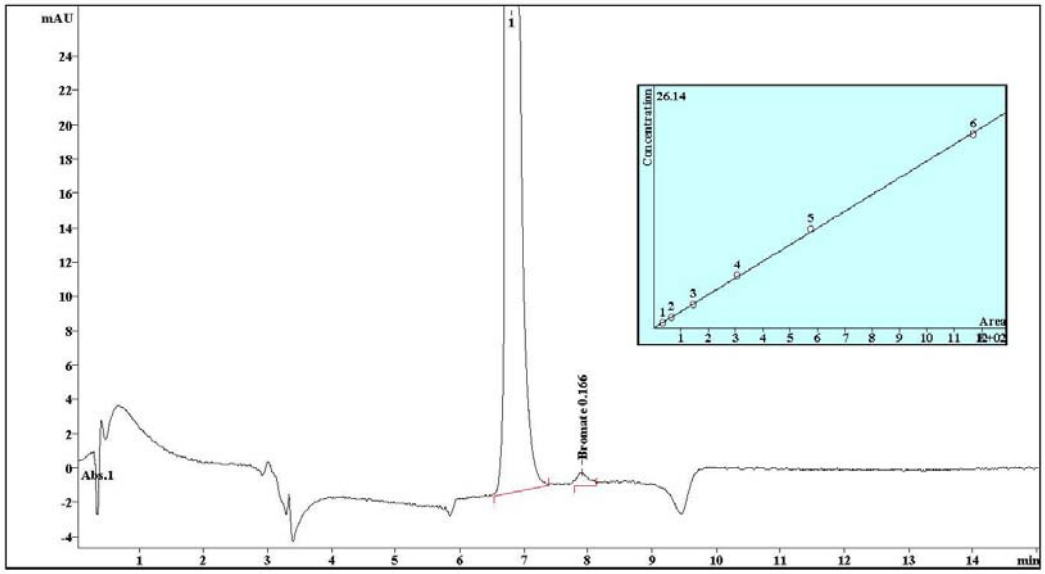
USEPA Method 326 – Triiodide method



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Also there is existence of Bromate method using IC/ICPMS for the analysis

USEPA modified method 321.8

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2D Ion Chromatography

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2D IC - Concept

- In 1975, Originally two column approach for Ion Chromatography started with the invention
- Multi-dimensional IC started back in 1990 – 1991 with the idea of matrix elimination, pre-concentration with suppressed anion chromatography.

Back in 2004 Metrohm fully investigated 2D IC for Perchlorate analysis
(paper presented at International Ion Chromatography Symposium in Trier Germany)

NEMC – 2008 (Tuesday)
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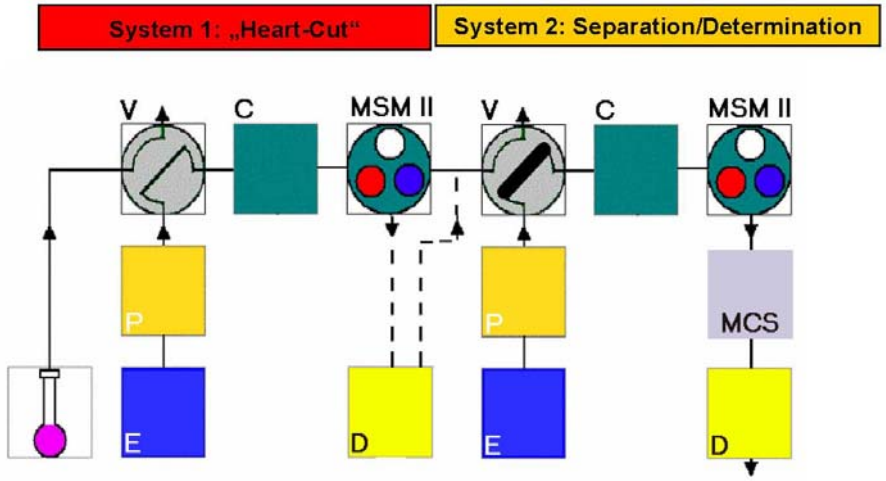
Using IC "heart-cut" Technique (USEPA 314.1)



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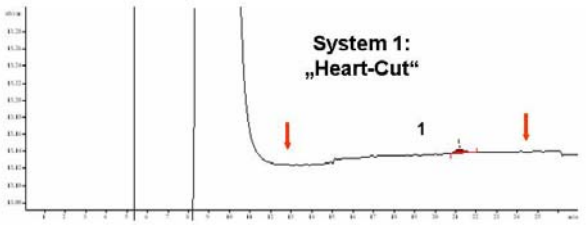
2D IC Technique

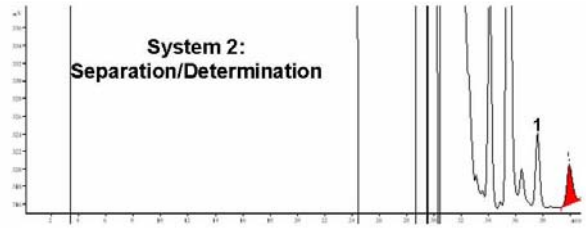
0.5 ppb Perchlorate in Ultra Pure Water

Metrosep A Supp 5 – 150 mm

1	Perchlorate in UPW	0.5 ppb

Na_2CO_3/acetone; 10/15 mM/%; 0.8 mL/min; 3.5 mL





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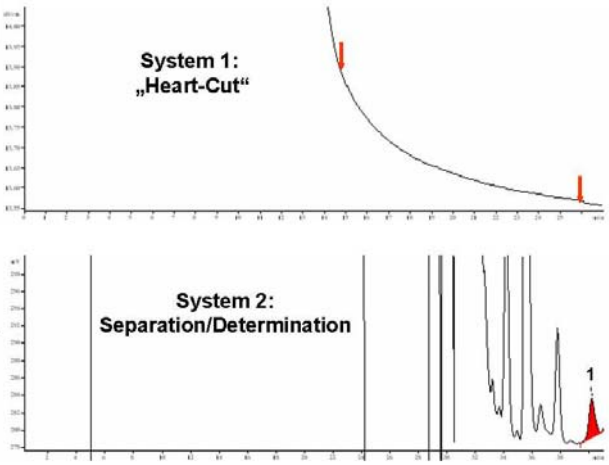
2D IC Technique

0.5 ppb Perchlorate in High Ionic Matrix

Metrosep A Supp 5 – 150 mm

	Chloride	1'000 ppm
	Carbonate	1'000 ppm
	Sulfate	1'000 ppm
1	Perchlorate	0.5 ppb

Na_2CO_3/acetone; 10/15 mM/%; 0.8 mL/min; 3.5 mL



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2D IC Technique

Calibration

Metrosep A Supp 5 – 150

Calibration level

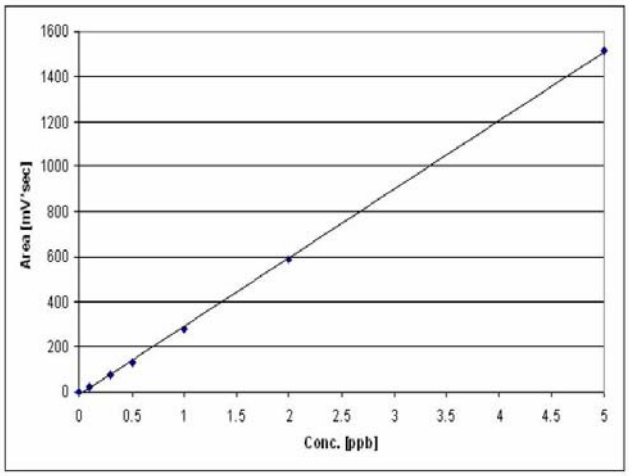
0, 0.1, 0.3, 0.5, 1, 2, 5 ppb

Correlation coefficient

$r^2 = 0.9997$

$y = 304.24x - 13.821$

Na_2CO_3/acetone; 10/15 mM/%; 0.8 mL/min; 3.5 mL



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Comparison (314.0 and 314.1)

	MDL in Ultra Pure Water	MDL in High Ionic Matrix	Robust-ness	Precision Recovery	Auto-mation	Simple Set up
Direct Injection	0.5 ppb	> 1 ppb	+	+	+	+
Pre-separation	0.1 ppb	< 0.5 ppb	+	+	+	-
Monolithic column	0.1 ppb	< 0.5 ppb	+	+	+	+

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Simple Approach for Bromate Analysis

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Method Goals for Bromate

- Achieve less than 1part per billion detection limit for Bromate
- Less than 1ppb Bromate should be achieved in presence of high Chloride, Nitrate, Sulfate
- Method should as green as possible (less waste generation)

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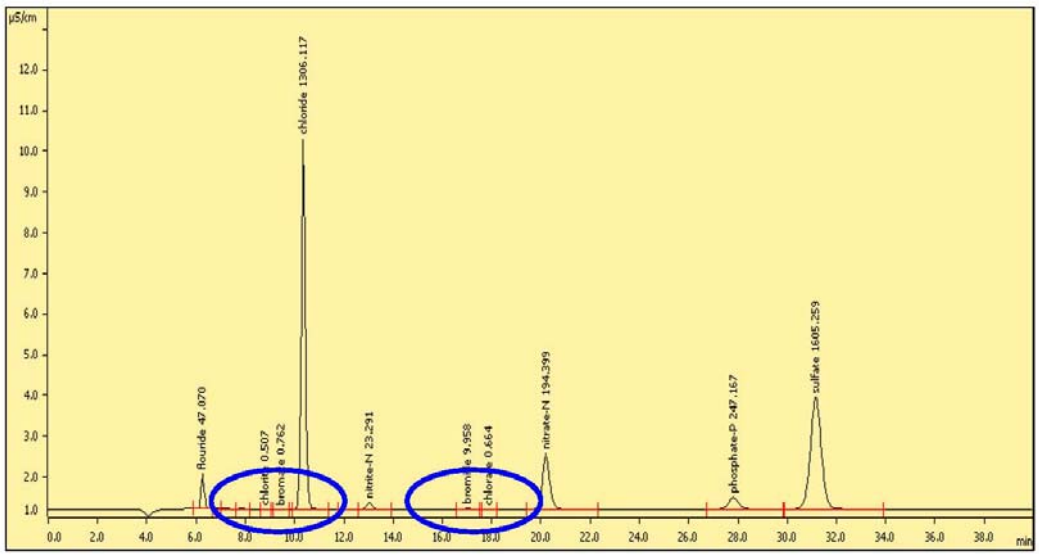
USEPA Method 300.0

Suppressed Ion Conductivity



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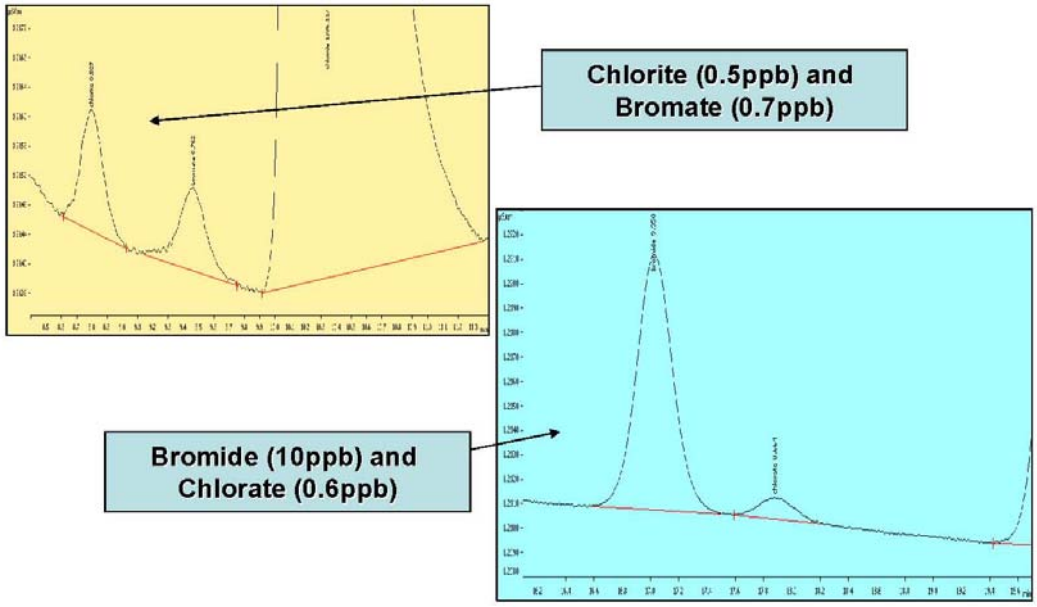
Zoomed Chromatogram



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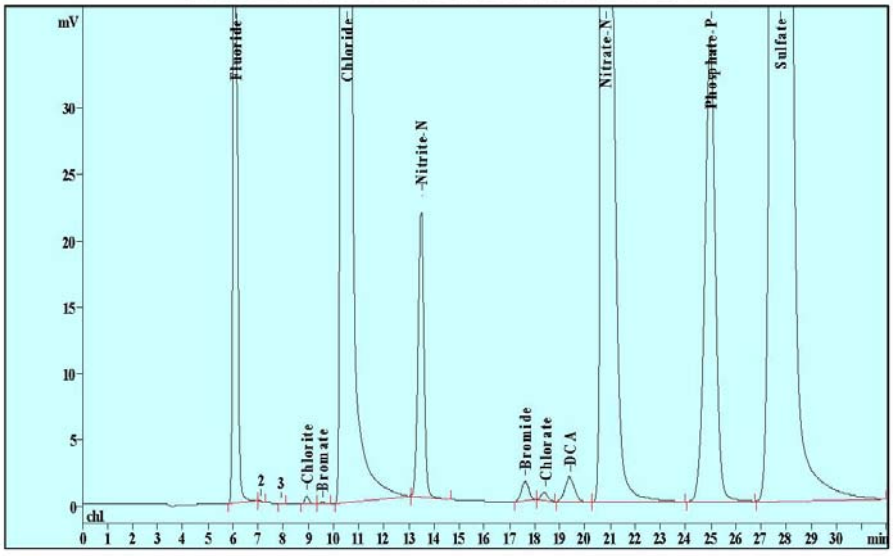
USEPA Method 300.1



Houston Tap Water fortified with 1ppb Bromate and 1ppm DCA (Surrogate)

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Summary

- Multi-dimensional IC is an over kill for this analysis
- Current method 300.0 or 300.1 needs to just modify to include column and eluent chemistry to meet or exceed Bromate analysis regulation (globally).
- If required in-line sample preparation techniques can be incorporated to eliminate high alkalinity or Chloramination cations in the sample matrix

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Thank you for listening…..

Applications of Ion Chromatography Systems with Eluent Regeneration

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ABSTRACT

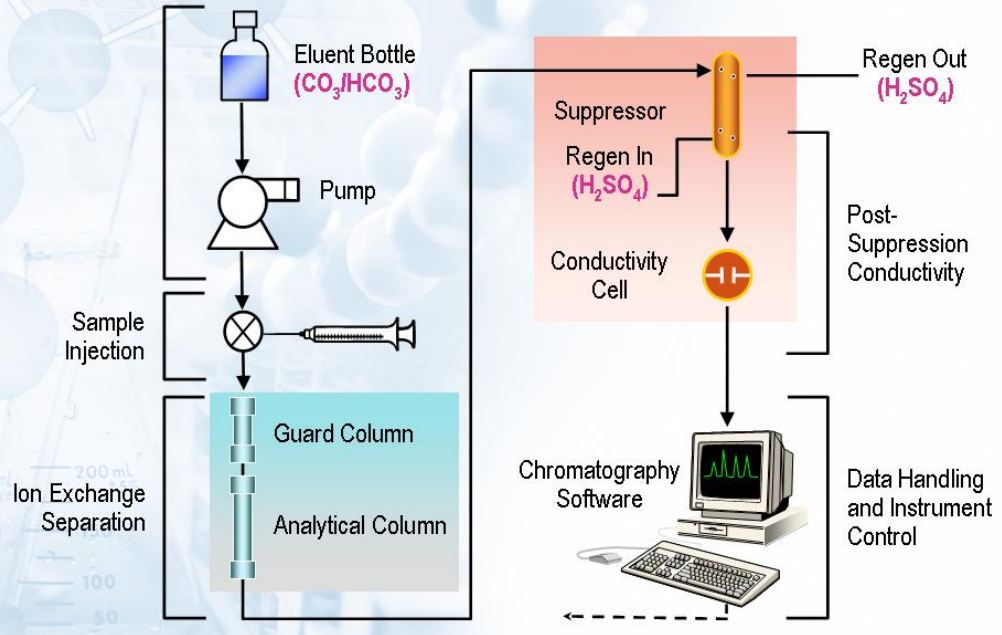
There have been continuing efforts to improve the performance of ion chromatography (IC) systems while developing new capabilities for the determination of anionic and cationic analytes in various sample matrices. We have recently developed a novel and new operation mode for IC systems equipped with electrolytic suppressors. This new mode of IC operation utilizes on the fact that the effluent from an electrolytic suppressor operated in the AutoSuppression® mode consists of mainly the eluent used in the IC separation process. The new IC systems use novel approaches to remove hydrogen and oxygen gases, sample ions, and other trace contaminants. They purify the suppressor regenerant effluent so that it is regenerated back into the pure electrolyte solution for reuse as the ion chromatographic eluents. This IC operation mode is compatible with IC separations using carbonate/bicarbonate and methanesulfonic acid (MSA) eluents. In this paper, we will demonstrate the applications of the IC systems with eluent regeneration in determination of common cations and anions in different sample matrices.

Applications of Ion Chromatography Systems with Reagent Free Ion Chromatography (RFIC)

Richard Jack, Yan Liu, Zhongqing Lu, John Madden, and Chris Pohl
Dionex Corporation, Sunnyvale, CA, USA

25115

Conventional Ion Chromatographic System
Anion Analysis



Advances in Electrolytic Devices for Ion Chromatography

- Electrolytic eluent generators
  - Produce high-purity electrolyte eluents using deionized water as the carrier stream
- Electrolytically regenerated trap columns
  - Remove ionic contaminants in the eluents
- Electrolytically regenerated suppressors
  - Reduce eluent background conductance and maximize analyte conductance prior to detection

Reagent-Free Ion Chromatography (RFIC™) Systems

- RFIC systems are ion chromatography systems that utilize electrolytic devices to generate (EG) or regenerate (ER) eluents in the ion chromatographic separation processes
  - RFIC-EG systems (2003)
  - RFIC-ER systems (2008)

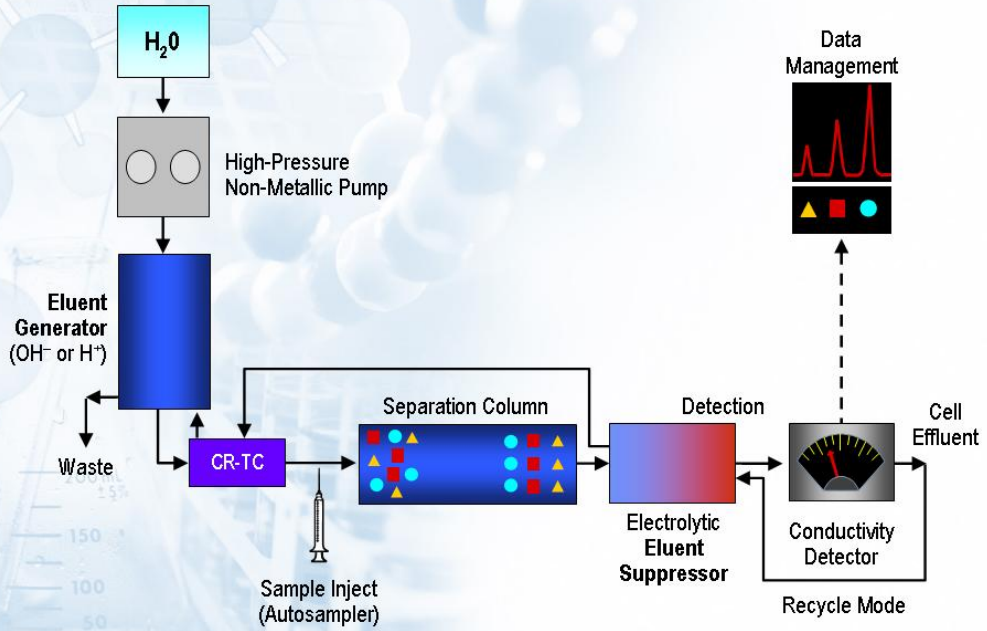
24767

RFIC™-EG Systems

- Use electrolytic eluent generators to produce high purity acid, base, or carbonate eluents on-line using deionized water as the carrier
- Produce eluents of precise and reproducible concentrations through the convenient control of electrical current
- Improve retention time reproducibility for both isocratic and gradient separations
- Compatible with a wide range of high-performance detection methods including conductivity, UV-Vis, electrochemical, and MS
- Improve the ease of use, sensitivity, and performance of IC methods for the determination of target analytes in a wide variety of sample matrices

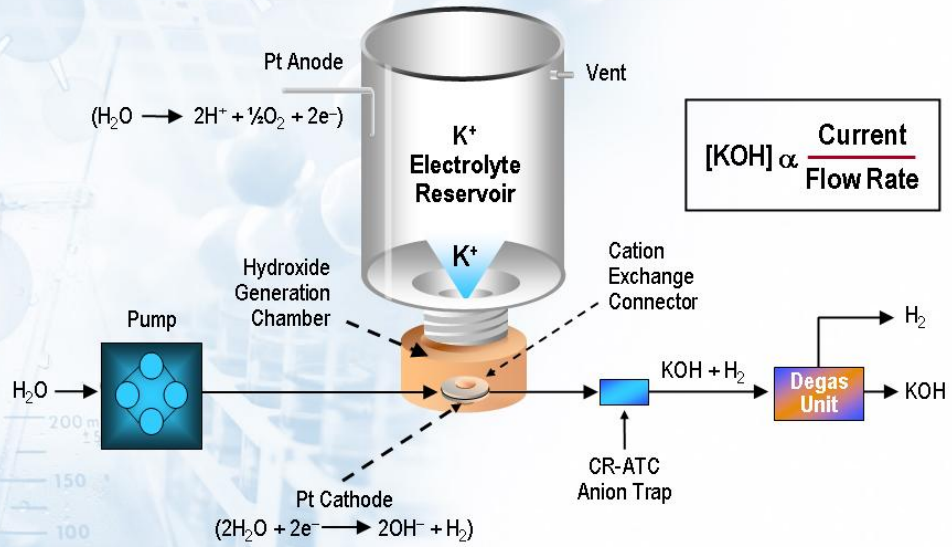
24771

A Reagent-Free™ Ion Chromatography (RFIC) System



25116

Electrolytic Generation of KOH Eluents Using an EGC-KOH Cartridge



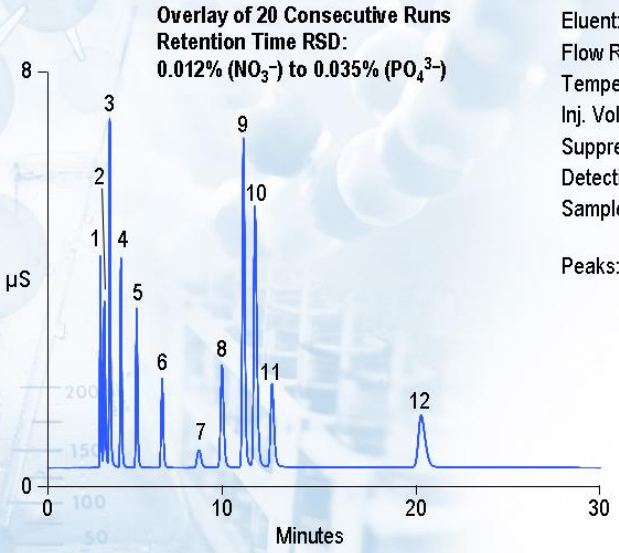
25117

RFIC-EG™ Systems

- RFIC-EG systems provide a number of key advantages
  - Ease of use
  - Reproducibility
  - High levels of sensitivity
  - Flexibility
  - Performance
- RFIC-EG systems are suited to a wide range of applications
- RFIC-EG systems are used successfully for IC determination of target analytes in a wide variety of sample matrices

25119

Highly-Reproducible Separation of Anions on a 4-mm AS18 Column Using an ICS-2000 RFIC-EG™ System



Column:	IonPac® AS18, 4 mm
Eluent Source:	EGC-KOH cartridge with CR-ATC
Eluent:	22–30 mM KOH: 7–8 min
Flow Rate:	1.0 mL/min
Temperature:	30 °C
Inj. Volume:	25 µL
Suppressor:	ASRS® ULTRA II at 100 mA
Detection:	Suppressed conductivity
Sample:	Anion standard

Peaks:		
	1. Fluoride	2.0 mg/L
	2. Acetate	10
	3. Formate	10
	4. Chlorite	10
	5. Chloride	3.0
	6. Nitrite	10
	7. Carbonate	—
	8. Bromide	10
	9. Sulfate	15
	10. Nitrate	10
	11. Chlorate	10
	12. Phosphate	15

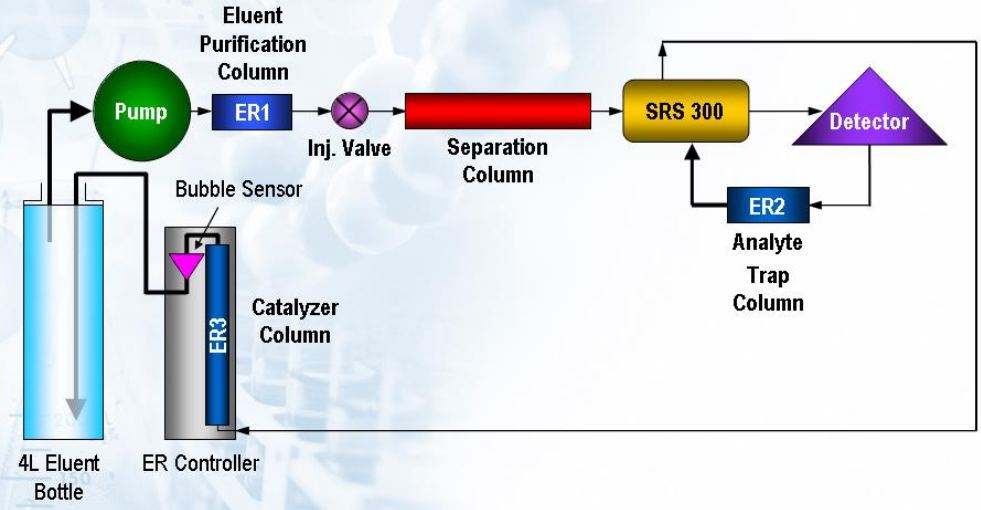
25120

RFIC™-ER Systems

- Operate SRS 300 electrolytic suppressors in the recycle mode to regenerate the starting eluents
- Use novel catalytic columns to recombine H_2 and O_2 generated by the electrolytic suppressors into water
- Use high-performance eluent purification columns to purify the regenerated eluents for reuse
- Compatible with carbonate/bicarbonate and methanesulfonic acid (MSA) eluents for isocratic separation of common anions and cations
- Designed to provide many of the key advantages of RFIC-EG systems desirable for dedicated IC applications

25123

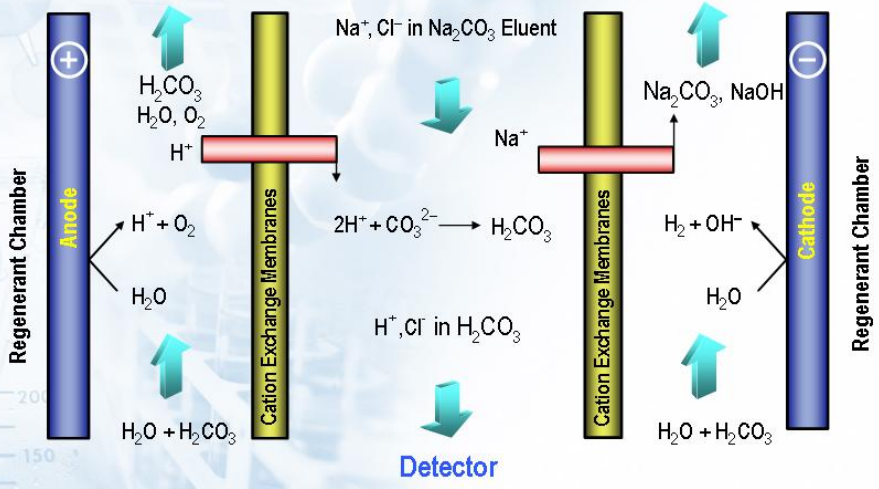
RFIC™-ER System Schematic



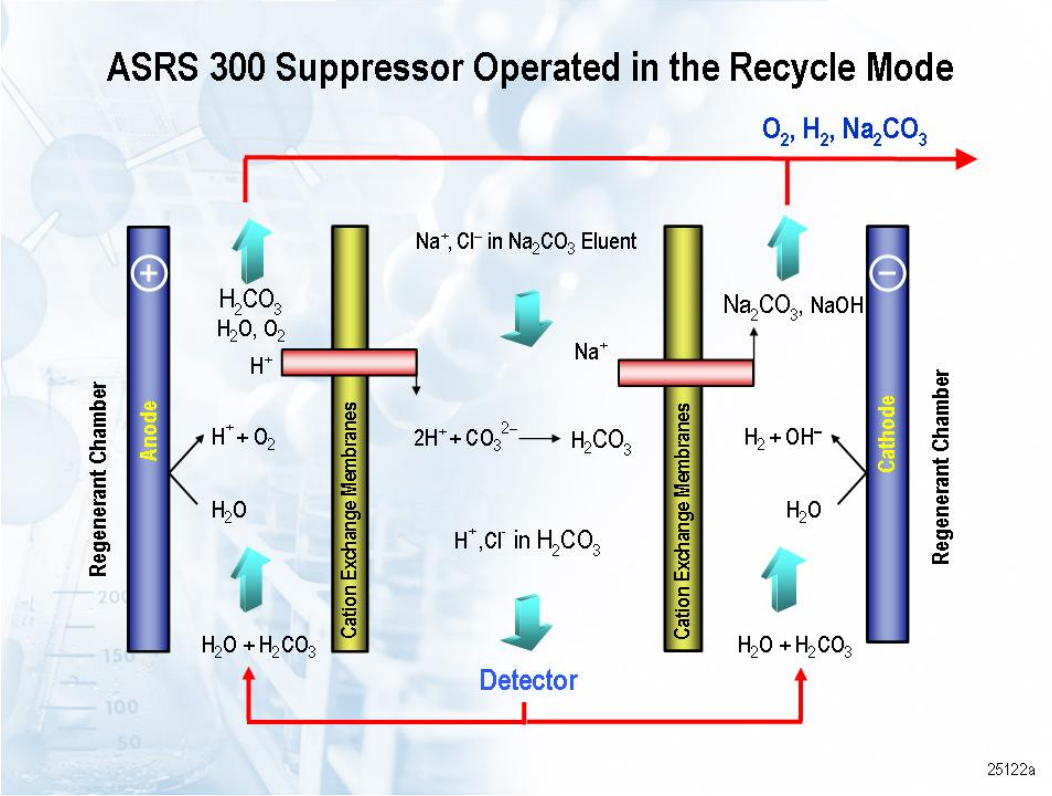
Continuous and Non-stop Operation Up To Four Weeks After the Initial Eluent Is Prepared

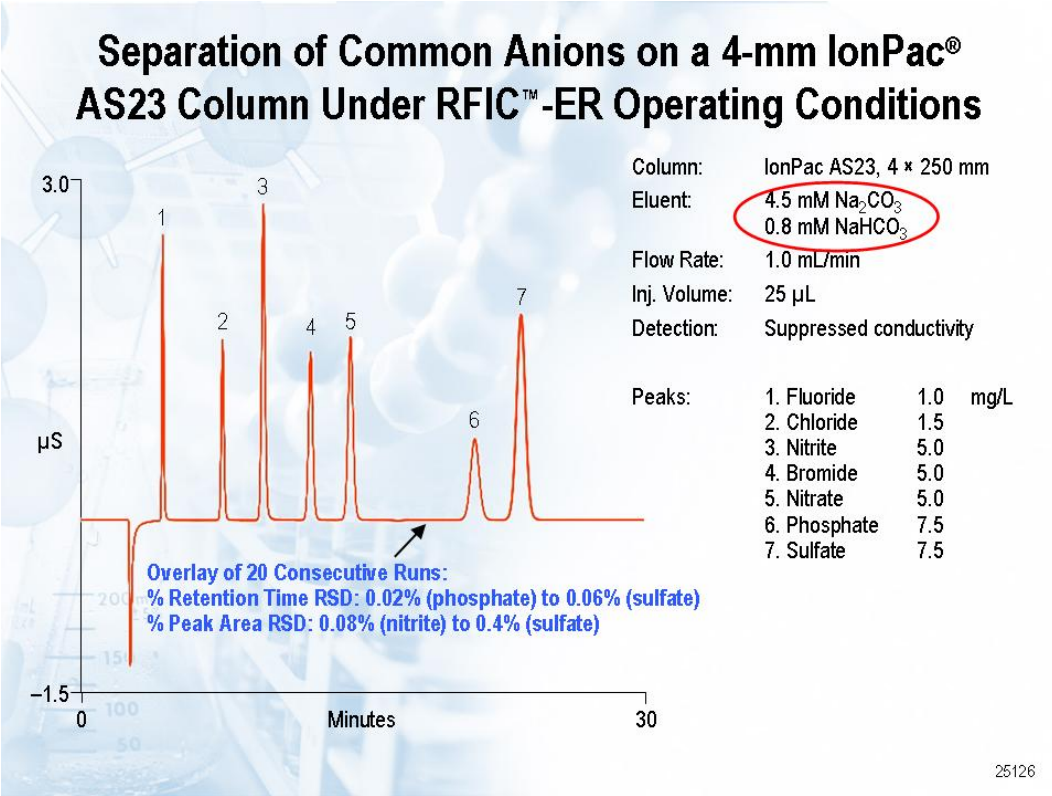
24769

Electrochemical Processes in an ASRS 300 Electrolytic Suppressor for Determination of Anions (Na_2CO_3 as the Eluent)

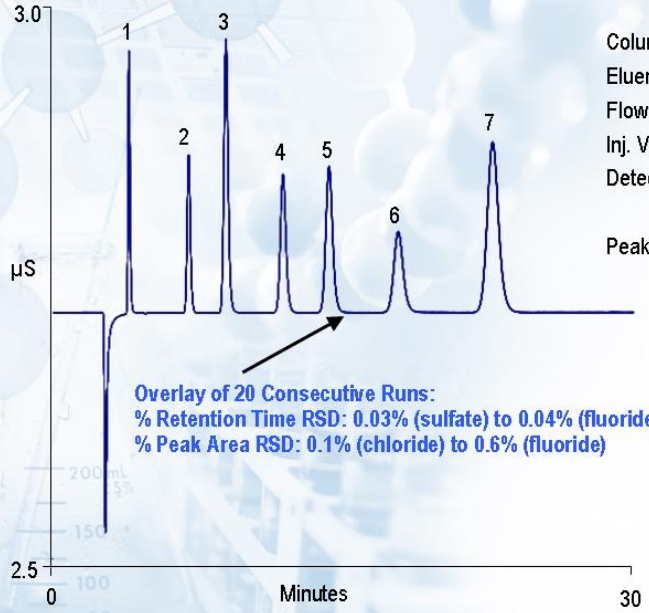


25121


ASRS 300 Suppressor Operated in the Recycle Mode
O_2, H_2, Na_2CO_3
Regenerant Chamber
Anode
H_2CO_3
H_2O, O_2
H^+
$H^+ + O_2$
H_2O
$H_2O + H_2CO_3$
Cation Exchange Membranes
Na^+, Cl^- in Na_2CO_3 Eluent
Na^+
$2H^+ + CO_3^{2-} \rightarrow H_2CO_3$
H^+,Cl^- in H_2CO_3
Detector
Cation Exchange Membranes
Na_2CO_3, NaOH
$H_2 + OH^-$
H_2O
$H_2O + H_2CO_3$
Cathode
Regenerant Chamber
25122a


Separation of Common Anions on a 4-mm IonPac® AS23 Column Under RFIC™-ER Operating Conditions
Column: IonPac AS23, 4 × 250 mm
Eluent: 4.5 mM Na_2CO_3
0.8 mM $NaHCO_3$
Flow Rate: 1.0 mL/min
Inj. Volume: 25 µL
Detection: Suppressed conductivity
Peaks: 1. Fluoride 1.0 mg/L
2. Chloride 1.5
3. Nitrite 5.0
4. Bromide 5.0
5. Nitrate 5.0
6. Phosphate 7.5
7. Sulfate 7.5
3.0
µS
−1.5
0
Minutes
30
Overlay of 20 Consecutive Runs:
% Retention Time RSD: 0.02% (phosphate) to 0.06% (sulfate)
% Peak Area RSD: 0.08% (nitrite) to 0.4% (sulfate)
25126

Separation of Common Anions on a 4-mm IonPac® AS9-HC Column Under RFIC™-ER Operating Conditions

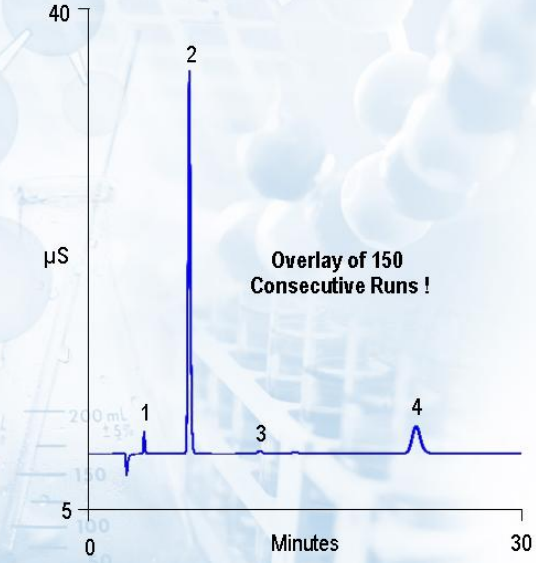


Column: IonPac AS9-HC, 4 x 250 mm
Eluent: 9.0 mM Na_2CO_3
Flow Rate: 1.0 mL/min
Inj. Volume: 25 µL
Detection: Suppressed conductivity

Peaks:			
	1. Fluoride	1.0	mg/L
	2. Chloride	1.5	
	3. Nitrite	5.0	
	4. Bromide	5.0	
	5. Nitrate	5.0	
	6. Phosphate	7.5	
	7. Sulfate	7.5	

25125

Determination of Common Anions in Sunnyvale Drinking Water Using a 4-mm IonPac® AS9-HC Column Under RFIC™-ER Operating Conditions



Column: IonPac AS9-HC, 4 x 250 mm
Eluent: 9.0 mM Na_2CO_3
Flow Rate: 1.0 mL/min
Inj. Volume: 25 µL
Detection: Suppressed conductivity

Peaks:
1. Fluoride
2. Chloride
3. Bromide
4. Sulfate

25127

Reproducibility Data for Determination of Common Anions in Sunnyvale Drinking Water Using a 4-mm IonPac® AS9-HC Column Under RFIC™-ER Operating Conditions

	Retention Time RSD (n = 150)	Peak Area RSD (n = 150)
Fluoride	0.1%	0.2%
Chloride	0.08%	0.3%
Bromide	0.1%	0.9%
Sulfate	0.09%	0.2%

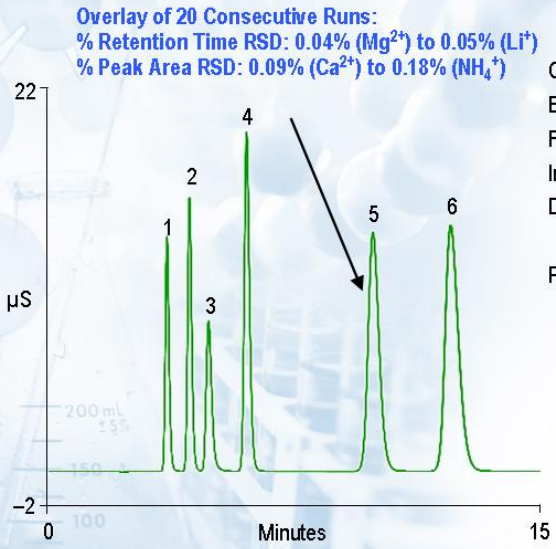
25128

Eluent Consumption Under Conventional IC and RFIC™-ER Operating Conditions

Separation Column	Flow Rate (mL/min)	Eluent	Volume of Eluent Used over 28 Days (L)		Volume of Eluent Saved Per Year Using RFIC-ER System (L)
			RFIC-ER	Conventional IC	
AS4A-SC	2.0	1.8 mM Na_2CO_3/ 1.7 mM $NaHCO_3$	4.0	80.6	998
AS9-HC	1.0	9.0 mM Na_2CO_3	4.0	40.3	472
AS22	1.2	4.5 mM Na_2CO_3/ 1.2 mM $NaHCO_3$	4.0	48.4	577
AS23	1.0	4.5 mM Na_2CO_3/ 0.8 mM $NaHCO_3$	4.0	40.3	472
CS12A	1.0	20 mM MSA	4.0	40.3	472
CS16	1.0	30 mM MSA	4.0	40.3	472

25124

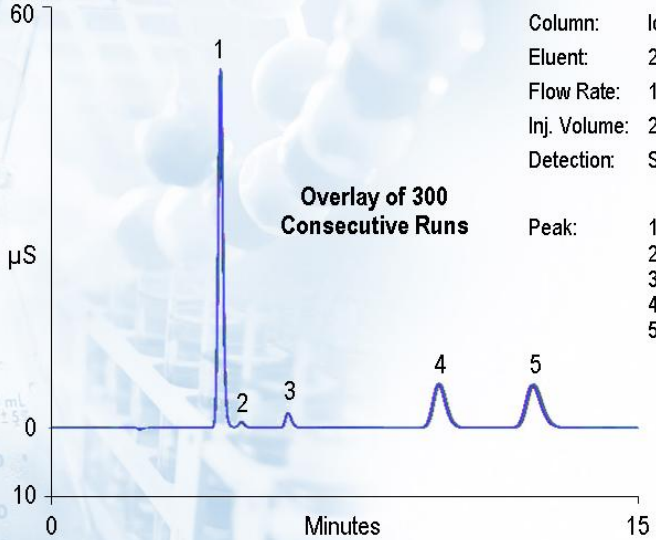
Separation of Common Cations on a 4-mm IonPac® CS12A Column Operated Under RFIC™-ER Operating Conditions



Column:	IonPac CS12A, 4 × 250 mm	
Eluent:	20 mM methanesulfonic acid	
Flow Rate:	1.0 mL/min	
Inj. Volume:	25 µL	
Detection:	Suppressed conductivity	
Peak:	1. Lithium	2 mg/L
	2. Sodium	8
	3. Ammonium	10
	4. Potassium	20
	5. Magnesium	10
	6. Calcium	20

25130

Determination of Common Cations in Sunnyvale Drinking Water Using a 4-mm IonPac® CS12A Column Operated Under RFIC™-ER Operating Conditions



Column:	IonPac CS12A, 4 × 250 mm
Eluent:	20 mM methanesulfonic acid
Flow Rate:	1.0 mL/min
Inj. Volume:	25 µL
Detection:	Suppressed conductivity
Peak:	1. Sodium
	2. Ammonium
	3. Potassium
	4. Magnesium
	5. Calcium

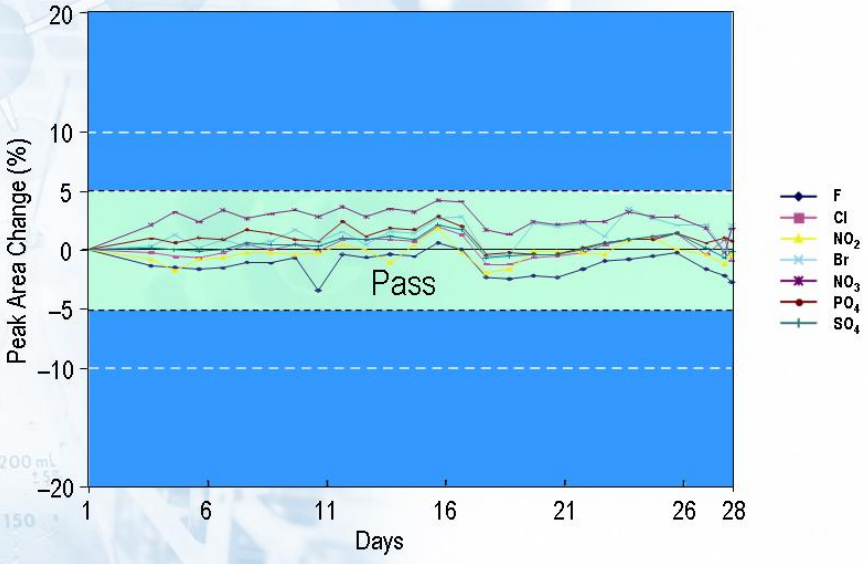
25131

Reproducibility Data for Determination of Common Cations in Sunnyvale Drinking Water Using a 4-mm IonPac® CS12A Column Under RFIC™-ER Operating Conditions

	Retention Time RSD (n=300)	Peak Area RSD (n=300)	Plate Number RSD (n=300)
Na^+	0.09%	0.2%	0.4%
K^+	0.09%	0.4%	0.4%
Mg^{2+}	0.1%	0.4%	0.3%
Ca^{2+}	0.1%	0.4%	0.3%

25132

RFIC™-ER Calibration Performance



Seven Anion Check Standard on an RFIC-ER System Using AS22 Chemistry

24774

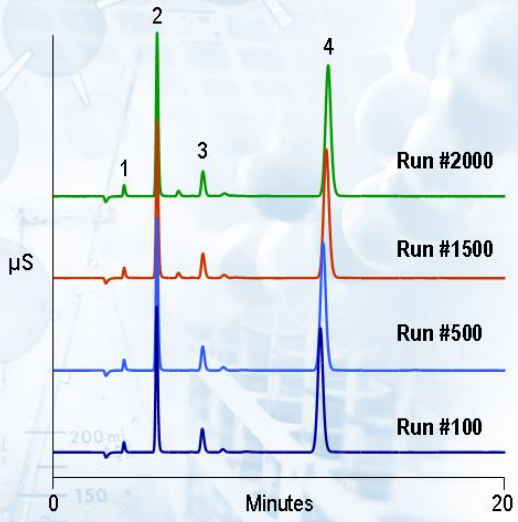
Determination of Chloride in a San Jose Drinking Water Sample Using an RFIC™-ER System

Date	Average Chloride Retention Time (min) (n = 20)	RSD (n = 20)	Average Chloride Concentration (mg/L) (n = 20)	RSD (n = 20)	Average Chloride Peak Plate Number (n = 20)	RSD (n = 20)
12-09-2007	7.193	0.06%	100.97	0.07%	10905	0.45%
12-13-2007	7.200	0.08%	98.34	0.16%	10807	0.62%
12-20-2007	7.210	0.05%	99.89	0.06%	10850	0.23%
12-23-2007	7.215	0.05%	99.55	0.13%	10841	0.43%

Note: 1. 4-mm AG23/AS23 columns were used
2. System calibration was performed on 12-5-2007

25133

Anion RFIC™-ER System Performance



Column:	IonPac® AS22 column, 4 mm × 250 mm
Eluent:	4.5 mM Na_2CO_3/ 1.4 mM $NaHCO_3$
Temperature:	30 °C
Flow Rate:	1.2 mL/min
Inj. Volume:	25 µL
Detection:	Suppressed conductivity
Sample:	Drinking water (Fremont, CA) spiked with 10 mg/L bromide
Peaks:	1. Fluoride 2. Chloride 3. Bromide 4. Sulfate

2000 Runs at 20 min Each Equals Approximately 4 Weeks of Non-Stop Analyses

24772

Summary

- RFIC™-ER systems provide key advantages of RFIC systems including ease of use and improved reproducibility.
- RFIC-ER systems offers additional benefits of non-stop operation, minimal waste generation, increased productivity, and lower cost of ownership.
- RFIC-ER systems target applications for determination of common anions and cations in drinking water, surface water, and groundwater
  - Ideal for EPA Method 300.0 Part A, 300.1 Part A or equivalent applications
  - Not suitable for highly contaminated matrices such as untreated waste waters
- RFIC-EG systems are still recommended for IC applications involving more complex samples or those requiring a wider choice of eluents and gradient separation capabilities

25134

Determination of Nitrate + Nitrite Nitrogen Using Enzymatic Reductase

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ABSTRACT

Conventional methods used for the determination of nitrate plus nitrite nitrogen in aqueous samples employ a cadmium metal reactor that reduces nitrate into nitrite for subsequent quantitation by the very sensitive Greiss reaction. While this method has proved useful over the years it is not without problems. Besides that cadmium metal is toxic and a listed waste, it is a solid reactor prone to surface fouling that causes reduction efficiencies to change over time.

This presentation will discuss the use of nitrate enzyme reductase as an alternative to cadmium reduction for nitrate analysis. The reductase method is made economical by the use of semi automated batch analyzers (Discrete Analyzers) because only small volumes of enzyme are required. Accuracy and precision data on multiple matrices, and comparison data of enzyme reductase versus cadmium reduction will be presented.

Nitrate + Nitrite Analysis by Nitrate Reductase Derived from Higher Plants using Non-toxic NADH as an Electron Donor

2008

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A World of Solutions

Summary of Method

- Reduce NO_3^--N with reductase to NO_2^--N
- Determine NO_2^--N colorimetrically
- Measure NO_3^- + NO_2^--N

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Significance of Reductase Method

- Cadmium Reduction
  - Widely used
  - Well accepted
- Cadmium is not without problems
  - Cadmium metal is oxidized to Cd^{+2}
  - Reaction is heterogeneous
  - Numerous "interferences"

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Cadmium as a Reductor

- Cadmium Reaction
  - $Cd^{\circ} + NO_3^- + 2H^+ \rightarrow NO_2^- + Cd^{+2} + H_2O$
  - Cadmium metal becomes a soluble ion
  - Solution pH increases as reaction proceeds

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Cadmium also Reacts with Oxygen

- $2Cd^{\circ} + O_2 + 4H^{+} \rightarrow 2Cd^{+2} + 2H_2O$
  - Cadmium reacts with dissolved oxygen faster than with nitrate
  - Dissolved oxygen in samples and reagents the major source of Cd in waste
  - Up to 220 ppm Cd^{+2} when not degassed* (decreased to ~ 2 ppm when degassed)

* Gal, Frenzel, and Moller, *Re-examination of the cadmium Reduction Method and Optimization of the Conditions for the Determination of Nitrate by Flow Injection Analysis*, Microchim Acta 146, 155-164, 2004

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Interferences with Cadmium

- Compounds in the samples interfere
  - Sulfide
  - Oil & Grease
  - Chloride
  - Metals

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Nitrate Reductase

- Non-toxic
- Environmentally benign
- Quantitative reduction

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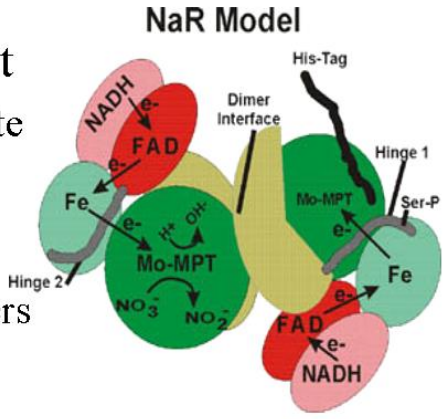
What are Enzymes?

- Biological catalyst
  - Speed reaction rate
  - Selective
- Numerous uses
  - Household cleaners
  - Meat tenderizer



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Reaction Chemistry

- $NO_3^- + NADH + H^+ \xrightarrow{NaR} NO_2^- + NAD^+ + H_2O$
- Once reduced, nitrite is determined by the same color reaction as cadmium reduction methods.
  - Determination step stays the same
  - Only reduction step changes

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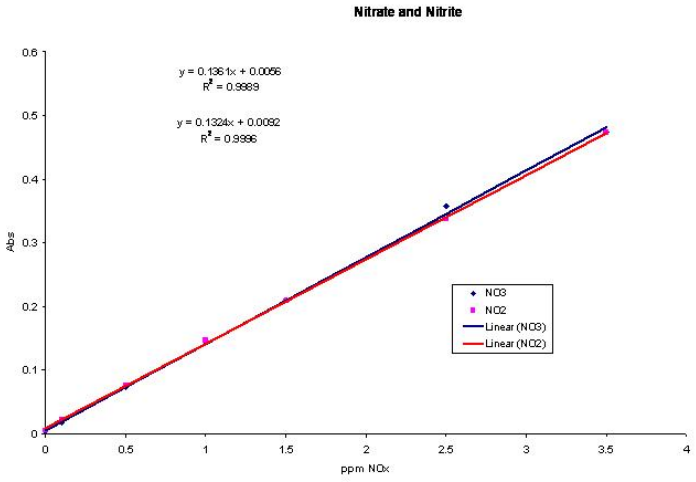
Calibration Examples



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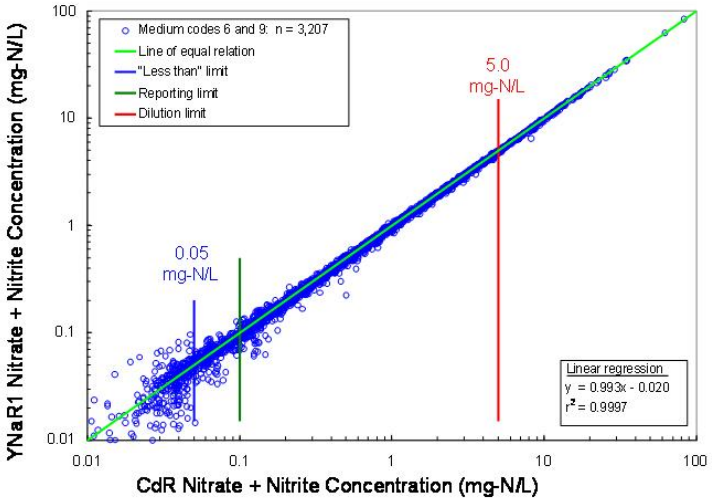
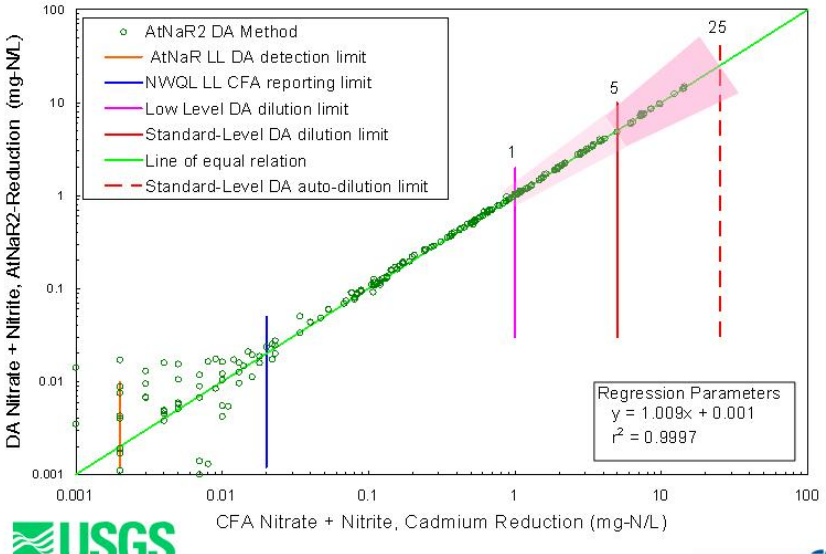
USGS Comparison Data (~ 3000 paired results for CFA CdR and NaR methods)



USGS

O·I·Analytical

USGS Comparison Data



USGS

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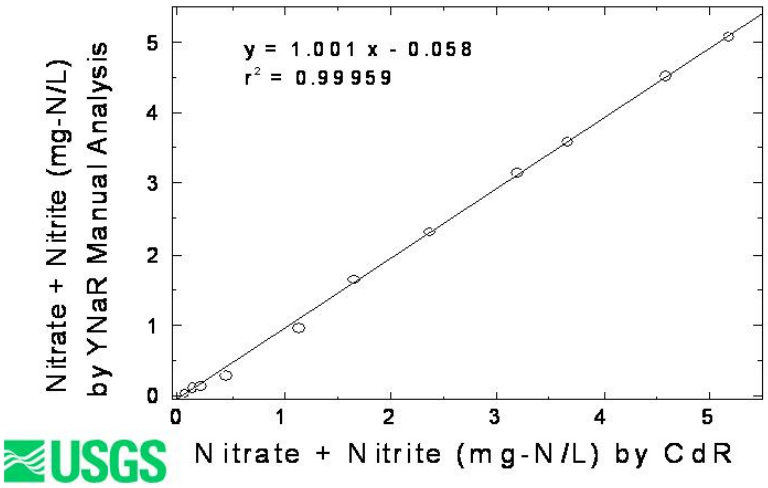
USGS Comparison Data



USGS

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Advantages of Nitrate Reductase Methods

- Results of cadmium reduction and enzymatic reduction are equivalent.
- Applicable to a variety of platforms
  - Continuous Flow (SFA, FIA)
  - Discrete Analyzers
  - Manual Methods
- Non toxic enzyme replaces toxic cadmium.

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More Advantages of Nitrate Reductase

- Fewer interferences
  - Oil & Grease do not interfere
  - Sulfide does not interfere
  - EDTA prevents metal interference
  - Chloride does not interfere
- Micro-liter sample and reagent volumes (50 micro-liters ≈ 1 drop!)

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"Apparent" Disadvantages

- Longer reaction to complete reduction
- Cost of reagent
- Requires expensive equipment to be affordable
- Not EPA approved

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Cost of Reagents – Nitrate Reductase Method

Technique Used	Per test reagent cost
Manual Methods	$0.50
Continuous Flow Analyzer Methods	$0.10 - $0.40
Discrete Analyzer Methods	$0.20 - $0.25

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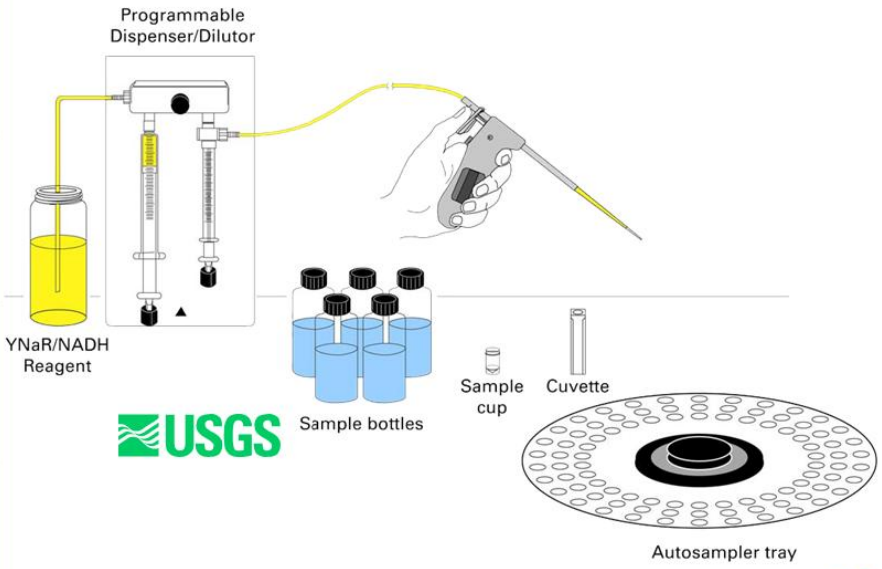
Manual Batch Preparation of Samples



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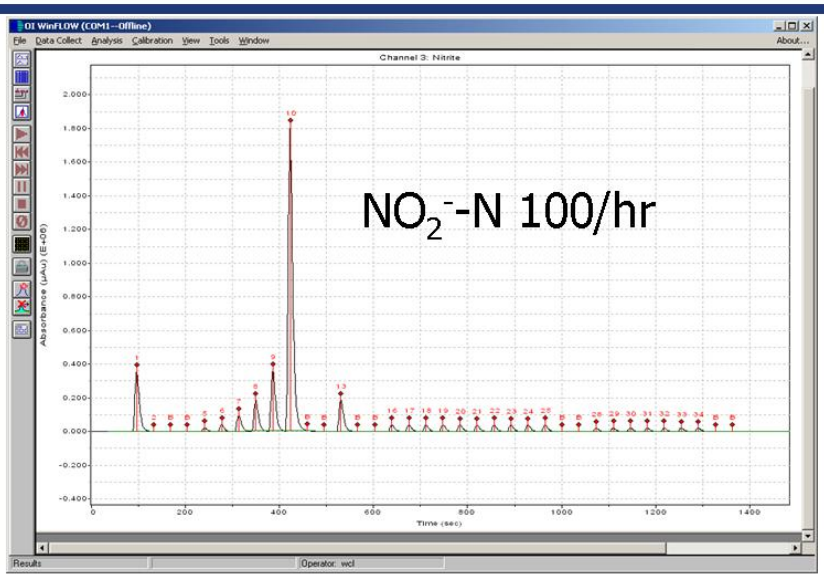
Example of FIA analysis



NO_2^--N 100/hr

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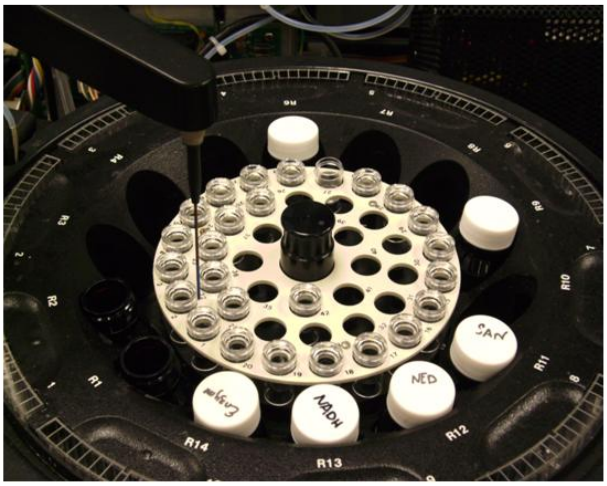
Example of Discrete Analyzer Analysis



Micro-liter sample Volumes

Micro-liter Reagent Volumes

Individual, incubated wells

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Single Laboratory Validation Data

- Discrete Analyzer – fully automated
- Nine Selected Matrices
- 2 – 3 spike levels per matrix

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Matrix – Industrial Effluent

Expected (mg/L)	Found (mg/L)	% Recovery
1.03	0.95	93
5.03	5.19	103

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Matrix – POTW Influent

Expected (mg/L)	Found (mg/L)	% Recovery
0.10	0.10	100
1.00	1.14	114
5.00	4.64	93

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Matrix – POTW Effluent

Expected (mg/L)	Found (mg/L)	% Recovery
1.48	1.61 (10)*	110
5.48	5.19 (2.7)	95

* RPD in parentheses

O·I·Analytical

Matrix - Septic System

Expected (mg/L)	Found (mg/L)	% Recovery
0.12	0.11	93
1.02	1.17	115
5.02	5.34	106

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Matrix – Spiked ASTM Type II Water

Expected (mg/L)	Found (mg/L)	% Recovery
1.06	1.15	109
5.06	5.22	103

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Matrix – Dechlorinated Tap Water

Expected (mg/L)	Found (mg/L)	% Recovery
0.14	0.16	127
1.04	1.25	122
5.04	4.95	98

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Matrix – Synthetic Seawater

Expected (mg/L)	Found (mg/L)	% Recovery
0.15	0.16 (50)*	107
1.05	1.10 (32)	105
5.05	4.71 (10)	93

* RPD in parentheses

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Matrix – Monitoring Well

Expected (mg/L)	Found (mg/L)	% Recovery
1.06	0.99	93
5.06	5.07	100

O·I·Analytical

Matrix – Industrial Effluent

Expected (mg/L)	Found (mg/L)	% Recovery
1.74	1.77 (4.0)*	102
5.74	5.03 (4.4)	88

* RPD in parentheses

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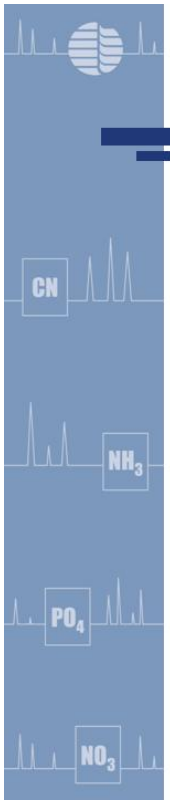

Conclusion

- Nitrate Reductase is a cost effective, accurate, and environmentally friendly replacement to cadmium in routine nitrate determinations in a wide variety of sample matrices.
- Methods on horizon
  - ASTM
  - USGS

O·I·Analytical

Variability of BOD Results Between Split Samples – A Forensic Investigation Case Study

Patrick Conlon, MS and Rock J. Vitale, CEAC, CPC; Environmental Standard, 1140 Valley Forge Road, P.O. Box 393, Valley Forge, PA 08050; 610-935-5577; pconlon@envstd.com

ABSTRACT

As part of routine compliance discharge monitoring, regulatory agencies periodically collect and analyze split samples to determine if the contracted laboratory performing analysis for a permittee is generating accurate data. For an industrial facility in the Mid-Atlantic States, significant variability for BOD results was observed between two laboratories that analyzed split samples of a complex industrial waste water over a one-year period. This presentation will present the investigative approach that was used to identify the cause of the disparate results and to minimize the variability for future events. Details of this case study will include:

- A general discussion of the BOD method and parameters that required control.
- The investigation work plan components that ultimately evolved into the "corrective action plan."
- Details of sampling and laboratory audit findings that revealed the sources of variability.
- The recommendations for improving accuracy and comparability in laboratory results.

This presentation will address issues that are universally applicable to BOD samples and the laboratories performing the analysis as well as project-specific issues. The complexity of the waste water in this project was one of the causes of the variability; ultimately, special sample handling requirements were identified to reduce variability. Finally, the case study will illustrate an approach to forensic investigations when environmental testing anomalies are observed.

Investigation into Observed Split Sample Variability in BOD Results

Patrick A. Conlon
Environmental Standards, Inc.

ENVIRONMENTAL STANDARDS

- Significant variance in split sample industrial effluent BOD results between two commercial labs.
- Variance in split sample results is up to an order of magnitude.
- Variance is unpredictable, and without any apparent trend.

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Audit Plan

The Auditor:

- Observed sampling activities and followed samples back to laboratory A.
- Observed sample log-in, handling and all BOD testing procedures at the laboratory.
- Followed with traditional audit of QA systems
- Repeated process for Laboratory B on a separate event.

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BOD Sampling Findings

- Sample containers not emptied & washed between events
- Very vigorous sample shaking at time of sampling may release volatile and semivolatiles
- Sample bottles had considerable headspace
- Split samples not taken at the same time

ENVIRONMENTAL STANDARDS

Sample Receipt and Holding Time

- LAB A tests for and finds residual chlorine.
- LAB B does not test for the residual chlorine.
- LAB A often will set up BODs a day or two after sampling counting 48 hr from receipt
- LAB B typically sets up BODs on the day of sampling.

Reagent Preparation

- LAB A makes nutrient, buffer, GGA, etc. from dry reagents and uses for several months.
- LAB B uses HACH® powder pillows.
- All reagents were observed to be within expiration dates.

Recommendations:

- Powder pillows are considered to be more reliable and consistent
- Nutrient especially the buffer is prone to support growths. (flock was observed)

Source Water

- LAB B used purchased deionized water.
- Specification for purchase deionized water is only good at time of packaging.
- Purchased deionized water labeled as "non-sterile"

Recommendations

- Source water should be sterilize before use.

ENVIRONMENTAL STANDARDS

Dilution Water Preparation

- Dilution Water Aging is not Required. Aging not recommended for > 24 hours before use.
- Aging **only** recommended where improvement is demonstrated
- Lab A prepared dilution water the day of analysis and Lab B prepared the day before and stored in refrigerator.

Recommendations:

- Aging is not recommend
- Nutrient and buffer should not be added > 8 hours before use.

ENVIRONMENTAL STANDARDS

Dilution Water Aeration Findings

- LAB A aerates dilution water using a pump and aeration stone.
- At LAB A auditor observed air bubbles in samples in the incubator, bubbles in samples are not documented nor are there corrective actions taken.
- LAB B shakes dilution water carboy for ~ 10-15 second after addition of the nutrients and buffer.

ENVIRONMENTAL STANDARDS

Aeration Recommendations

- Mechanical aeration of the dilution water is preferred.
- A natural stone sparger should **not** be used due to potential metals leaching and growths
- The dilution water should sit for a minimum of 15 minutes after aeration and before use.
- A moderate shake during that time is also recommended

ENVIRONMENTAL STANDARDS

Oxygen Probe Calibration

- LAB A does a Daily Winkler Calibration.
- LAB B does a monthly air calibration when membrane is being replaced

Recommendations:

- The O_2 probe must be calibrated every day.
- Winkler Method is reliable and preferred.
- Saturated Air Equilibrium $\geq$ 20 minutes.
- Should record the O_2 drift every 10 samples.

ENVIRONMENTAL STANDARDS

Seed Correction Calculation

- LAB B's seed correction not correctly calculated
- All seed controls were at 2 mL / 300 mL volumes.

Recommendations:

- Seed Correction Factor measurements must meet the same criteria as sample measurements.
- All seed dilutions within range averaged.
- Seed correction factor back calculated from BOD measured in seed control

ENVIRONMENTAL STANDARDS

Seed Preparation Deficiencies

- LAB B seed prepared in DI water and stored overnight
- LAB A seed prepared from dilution water on the day of use
- Neither lab removes the bran from the seed.

Recommendation:

- Seed should be prepared with **dilution**, aerated, and used within 6 hours.
- Bran should be removed by decanting.
- Seed should be stirred during use.

ENVIRONMENTAL STANDARDS

Variable Sequence of Dilutions

- At LAB A sample dilution sequence was
  1) sample dilution aliquots were added
  2) then the seed was added
  3) then the dilution water was added
- At LAB B the bottles were
  1) ½ filled with dilution water
  2) then the sample dilution aliquot was added
  3) then the seed was added
  4) the sample bottles were topped off

ENVIRONMENTAL STANDARDS

Comparisons in Reporting

- LAB A tends to use wide range of dilutions – 1, 3, 10, 25, 50 mL for example
- LAB B for same sample typically would use .3, .5, 1.0, 3.0, 9.0 and 15.0. for example
- On average, LAB B more frequently obtains multiple dilutions within range and LAB A more frequently obtains only one dilution within range.
- 20th Ed. of Standard Methods requires two dilutions within range.

ENVIRONMENTAL STANDARDS

Targeting Dilutions

- Sample had wide range of BOD but was relatively clear with moderate odor.
- Targeting results based on other factors (as COD) recommended in SM 20th Edition.
- Targeting may be done using TOC or COD.
- Ratio of COD or TOC to BOD best established with historical data or from principle component if known.

ENVIRONMENTAL STANDARDS

GGA Recommendations

- Hach ampoules used for GGA by Lab B
- GGA can be a difficult reagent to maintain.
- Unitized GGA ampoule is desirable.
- Hach® Acceptance Limits = 400 ± 30.5 ppm is not equal to Std. Methods 198 ± 30.5 ppm
- Results **should** be divided by 2 and evaluated against Std. Methods limits.

ENVIRONMENTAL STANDARDS

Additional QC Measures

LCS of Potassium Acid Phthalate (KHP)

- KHP is standard used for TOC and demand PTs.
- Performance known for TOC, COD, and BOD.
- 100 ppm TOC = 157 ppm for BOD = 253 for COD
- Acceptance limits based on interlab PT studies should be no greater than ± 50%.
- KHP standard far more stable and reliable than the GGA.

ENVIRONMENTAL STANDARDS

GGA vs. KHP Interpretation

- GGA out and the KHP is acceptable, data may be usable.
- GGA out **and** the KHP is out, the system is not in control and the data are not recommended for use.
- GGA out and KHP is acceptable, data may be reported with qualification.

ENVIRONMENTAL STANDARDS

Reporting of Seed Toxicity

- Neither lab identified and reported seed Toxicity.
- Toxicity is apparent whenever the reported BOD is inversely proportional to the sample volume diluted.
- There are varying recommendations on reporting, but it should always be flagged.
- Toxicity may be caused by sample matrix.
- Toxicity may be corrected by other procedures recommended herein.

ENVIRONMENTAL STANDARDS

Detailed NCM Report

Data review indicated that both labs have had unreported excursions in QC.

- All QC exceedances (NCMs) must be flagged in the report with detail.
- Comprehensive data review checklist with comments and corrective actions.
- Raw data (benchsheet) and NCM summary as important as results report.

ENVIRONMENTAL STANDARDS

Additional Flags Recommended

- Averaging of dilution results where the highest value included in the average is > 2× the lower value.
- Gross exceedance of the method QC limits should result in rejection of the data:
  - Dilution water blank depletion > 1.0 mg/L
  - Seed Control > 2.0 mg/L
  - GGA out of criteria by > 25%

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2008 NEMC Proceedings

ORGANIC METHODS

Improving Environmental Laboratory Productivity Using an Automated Extraction, Clean-up, Sample Concentration System

Andrew Masters, PhD, Edmond McNeil, and Betsy Cliffe; Maxxam Analytics, Inc., 5555 North Service Road, Burlington, Ontario, Canada L7L 5H7; 905-817-5700; andrew.masters@maxxamanalytics.com

ABSTRACT

As a means of improving laboratory productivity, Maxxam Analytics, Inc. purchased a Power-Prep Pressurized Liquid Extraction/Cleanup System (Power-Prep/PLE™). The results of our evaluation of the system demonstrated that, compared to conventional techniques such as Soxhlet and Accelerated Solvent Extraction coupled with open column clean-up, the Power-Prep/PLE™ system was not only accurate and precise but also reduced the time and labor involved in sample preparation. In this paper, the authors will review commonly employed sample preparation procedures, compare them to the Power-Prep/PLE,™ and share their experiences in employing this type of equipment in a commercial environmental laboratory. The paper will also briefly discuss some of the results of a validation study that we conducted on the system.

INTRODUCTION

Given the financial pressures facing both commercial and governmental laboratories, improving laboratory productivity is a critical need. In this regard, an integrated, automated, computer controlled pressurized liquid extraction, clean-up, and extract concentration system was developed by Fluid Management System Inc. (FMS) of Waltham, MA. Given the importance of ensuring accurate results for our clients while reducing analytical costs, Maxxam Analytics, Inc. purchased the Power-Prep/PLE™ Pressurized Liquid Extraction/Cleanup System.

DISCUSSION

In the analysis of solid samples, the first step is to separate out the analytes of interest from the matrix. This is normally performed using one of a number of available liquid-solid extraction procedures such as Soxhlet Extraction (EPA Method 3541), Automated Solvent Extraction (EPA Method 3541), Microwave Assisted Extraction (EPA Method 3546) and Pressurized Fluid Extraction (EPA Method 3545A). In all these procedures, the sample is contacted with an extraction solvent that has a high partition coefficient for the analytes of interest relative to the sample matrix. In the conventional Soxhlet extraction, the sample and extraction liquid are near room temperature during the extraction, while in the other procedures the extraction is carried out at elevated temperatures. In the microwave and PFE systems pressurized system are employed to permit high temperatures to be used. The microwave assisted extraction is a batch procedure where the analyte concentration in the solvent and matrix reach an approximate equilibrium. In a PFE system, a flow thru system is employed which means that the matrix is constantly exposed to fresh solvent during the extraction. The Power-Prep/PLE™ is an

advanced pressurized fluid extraction system that incorporates computer control of the system and automated extract clean-up.

Once the analyte of interest has been removed from its matrix, those components in the extract that will interfere with effective instrumental analysis must be removed before the extract can be analyzed using such techniques as gas chromatography. Common techniques for removing interferences include: Alumina Column Chromatography (EPA Method 3610), Florisil Column Chromatography (EPA Method 3620), Silica Gel Column chromatography (EPA Method 3630), and Size Exclusion or Gel Permeation Chromatography (EPA Method 3640). In classical analysis the extract resulting from the extraction procedure is concentrated, then treated using the appropriate clean-up technique. In some cases, multiple clean-up procedures must be employed.

All the chromatography clean up procedures are similar and involve application of the "dirty" extract to a column containing a material which will separate the analyte of interest from the interfering substances and then eluting the analyte of interest using a flow of solvent. They all require time to clean the columns, prepare the adsorbent, fill the column with adsorbent, apply the dirty extract to the column, extract the analyte of interest using an appropriate solvent, and finally concentrating the resulting clean extract solution. The Power-Prep/PLE™ system eliminates most of the time consuming column preparation steps by integrating in-line adsorption cartridges which serve to remove interfering substances from the sample extracts. In addition to saving most of the time involved in column preparation, elution times are also reduced.

The reason that pressurized fluid extraction is such an effective extraction tool, is because during the extraction process the solvents inside the extraction cell are near their supercritical region which has high extraction properties and a high diffusion rate which permits the solvents to penetrate the solid samples at a much higher rate permitting a fast and efficient extraction process with minimal solvent usage.

To operate the Power-Prep/PLE™, 5 to 100 grams of the sample is mixed with sodium sulfate, loaded in an extraction cartridge of the appropriate size and capped with two disposable filtration end fittings. The extraction cartridges are clamped inside unique and easy to use Power-Prep/PLE™ cartridge seal cups. Up to six extractions can be performed simultaneously. The system is then programmed to select the appropriate solvent or solvent mixture, the amount of solvent to be used for extraction, the solvent flow rate, and the extraction conditions (extraction system pressure and temperature). Upon pressing the start key, the HPLC pump forces the organic solvent of choice, such as Hexane, Dichloromethane, Toluene, etc., into the extraction cartridge(s). The control system then starts the pressurization and heating of the samples. The pressure can be maintained between 1500-3000 PSI, at temperatures of between 70-200 C degrees. The extracted solvent containing target analytes is then either cleaned up using in-cell column clean up, transferred to an in-line Power-Prep/PLE™ column clean up module, or collected in collection vessels for subsequent clean up.

The Power-Prep/PLE™ extraction cell is made of stainless steel and while reusable, they are inexpensive enough to be disposable (approximately $30 for a cell, filters, and end caps). For analyses where low level analyte concentrations are to be measured and analyte carryover is of concern, this feature allows samples containing target analytes at ppq to >ppb levels to be extracted on the same unit. Cells are available to handle sample sizes covering a range of from <5 gms to > 100 gms. The Power-Prep/PLE™ is controlled by means of a PC using software (MS 6000) that shows the pressure, temperature, pump flow rate, solvent mixture, elapsed time,

valve configuration, and status of the cooling system in real time. These parameters can be programmed, controlled, monitored, and recorded prior to or during the extraction run. The software not only controls and records the extraction step but can store directions and setting for multiple methods and thus can reduce operator error while increasing laboratory productivity.

The Power-Prep/PLE™'s clean up module employs disposable absorbent cartridges made from Teflon and is run by the computer software. Available clean up columns include Fluorsil, single and multi layer silica gel, carbon, and alumina. In addition, size exclusion chromatography columns are available for use in removing high molecular weight interfering species (e.g., fats and oils in biological samples).

A Schematic of the PowerPrep/PLE™ system and more information on the equipment is shown in Figure 1.

Laboratory Productivity

Labor

As can be seen in Table 1, when analyzing environmental matrices for trace levels of contamination, the classical Soxhlet sample extraction procedure requires a great deal of technician time. The Soxhlet extractor must be cleaned and conditioned by running the extractor without sample for at least an hour, then the cleaning solvent has to be removed from the extractor and the sample placed in the extractor thimble. The two concentrates are then treated using the appropriate GPC, Alumina, Silica, Carbon or Florisil clean up method. After clean up, the samples are concentrated and analyzed to determine the concentrations of interest and to demonstrate that the system was is clean.

Using the Soxhlet extractor and the appropriate GPC, Alumina, Silica, Carbon or Florisil clean-up method takes approximately 5 days to process the samples and requires about 5 labor-hours of technician labor to process a batch of 6 samples. Processing the same 6 samples using the Power-Prep/PLE™ requires only about 2.4 labor-hours.

The significant savings in labor is a result of the elimination of the system conditioning step, the self-cleaning nature of the Power-Prep/PLE™, and its use of disposable extraction and clean up cartridges. When running a batch of six samples, eliminating the system conditioning saves an hour of labor, while loading the samples into the Soxhlet or PowerPrep/PLE™ extractor cartridge takes about the same amount of time in either system. One save additional technician time since to run the extraction using the preprogrammed, computer-controlled PowerPrep/PLE™, only requires about 3 minutes of technician time. If multiple clean ups are needed, the operator can put multiple clean up cartridges into the PowerPrep/PLE™ and run the clean ups in series.

As can clearly be seen, by using the PowerPrep/PLE™ system a laboratory that analyzes large numbers of environmental samples can reduce its labor cost for the analysis by almost 50%. At the current cost of labor, this constitutes a substantial increase in productivity.

Table 1. Labor Required to Prepare a Batch of Samples for Analysis

	CLASSICAL SAMPLE EXTRACTION AND CLEAN-UP	POWER-PREP/PLE™ SAMPLE EXTRACTION AND CLEAN-UP
Pre-extraction Preparation		
Cleaning and conditioning six Soxhlet units or a six station PLE	60 minutes	0 minutes
Loading samples into extraction unit, extraction of samples, unloading of units (assuming percent moisture or dry weight has already been determined)	140 minutes	118 minutes
Concentration of extracts	30 minutes	30 minutes
GPC or Column Clean-up	90 minutes	30 minutes
Additional clean up if needed (e.g., GPC + Alumina)	90 minutes	0 minutes (columns are run in series)
	320 total labor minutes to process a batch of 6 samples (410 with carbon clean-up)	142 total labor minutes to process a batch of 6 samples

Sample Throughput

A frequently employed procedure in our laboratory is the analysis of soil and other solid samples for chlorinateddibenzo-p-dioxins and furans. Historically we have employed EPA Method 3541 (Soxhlet Extraction) to remove the analytes of interest from the sample, followed by clean up of the extract using a combination of gel permeation chromatography, and silica, alumina and carbon columns. Today we employ the Power-Prep™ for both sample extraction and clean up, saving us a tremendous amount of time.

In Table 1 we compare the time it takes to process 6 samples using the historical and Power-Prep/PLE™ approaches.

Table 2. Time Required to Prepare a Batch of Samples for Analysis

	CLASSICAL SAMPLE EXTRACTION AND CLEAN-UP	POWER-PREP/PLE™ SAMPLE EXTRACTION AND CLEAN-UP
Pre-extraction Preparation		
Cleaning and conditioning six Soxhlet units or a six station PLE	16 hours	12 minutes
Loading samples into extraction unit, extraction of samples, unloading of units	17 hours	73 minutes
Concentration of extracts	60 minutes	60 minutes
GPC Clean-up	8 hours	
Acid/base Silica Clean-up	2 hours	
Alumina Clean-up	2.5 hours	
Carbon column Clean-up	6 hours	
Jumbo Silica + alumina + carbon clean-ups		2 hours
	105.5 hours turnaround time for 6 samples (111.5 hours with carbon clean-up)	4.4 hours turnaround time for 6 samples assuming jumbo silica column was needed.

Using the Power-Prep/PLE™, samples can be prepared for analysis in less than one day, while using the conventional Soxhlet extraction with column clean-up would require a week. As a result, by using the PowerPrep/PLE™ for sample extraction and clean up we are able to substantially increase our equipment productivity while at the same time permitting our laboratory to offer much faster service to our clients which gives us a marketing advantage.

Technician Training and Other

While difficult to quantify with exact numbers, one advantage that I found since switching over to using the PowerPrep/PLE™ is that it has made it much easier and faster to train new technicians on conducting extractions and clean ups. There are several reasons for this. First, the technician has fewer steps to learn and perform. Second, the system is simple to use. Finally, there are fewer things that the technician can do to cause errors. Since the computer can be programmed to remember a number of procedures, it is very easy to switch from one set of extraction conditions to another, and from one extract clean up regime to another. The software remembers the preestablished extraction conditions and parameters and can instantly reprogram the system for the new set of instructions. This reduces the possibility of operator error. The computerization eliminates the possibility of random errors due to incorrect extraction solvent ratios, improper solvent-sample extraction times, and improper clean up column flow rates.

Using the Power-Prep/PLE™ system has also yielded several additional operating advantages. Because the Power-Prep/PLE™ is a computer controlled unit, everything that is done is automatically documented by the software. This includes the system pressure, the extraction temperature, time, and solvent mixture. It prevents inadvertent loss of this valuable documentation due to the technician forgetting to write down what he or she did during the sample preparation steps.

As previously mentioned, the Power-Prep/PLE™ employs disposable extraction cells and preloaded column clean up cartridges. This not only eliminates the time consuming system clean up and conditioning but frees us from the danger of carryover or contamination resulting from less than thorough preparation of conventional extractors and chromatography columns.

Finally, I want to mention that using the Power-Prep/PLE™ system has led to a cost reduction in our cost of solvent since the Power-Prep/PLE™ uses less solvent for extraction and clean up. Not only does this save us on supplies but is also better for the environment and laboratory safety.

Analytical Accuracy

In order to supplement the published literature (1 – 9) which supports the use of the Power-Prep/PLE™ on a variety of solid environmental samples (i.e., soil, sludge, sediment, and waste solids), our laboratory conducted a number of experiments to ensure the validity of the system when used for a variety of common environmental analyses.

Maxxam Analytics, Inc. first spiked samples of garden soil and municipal sewage sludge with a mixture of chlorinated dibenzo-p-dioxins and chlorinated dibenzofurans. Each matrix was spiked at three levels. One sample was spiked at a level twice the expected Limit of Quantitation (LOQ) either 5ng/g (PCDD) or 10 ng/g (PCDF), one at 50 or 100 ng/g (20X LOQ) and one at 500 or

1000 ng/g (200XLOQ). The three samples were then extracted and cleaned up using the Power-Prep and the extracts analyzed by GC-MS using the appropriate EPA methods.

The average recovery found for the PCBs was 90%. At the lowest spiking level the recovery was 89.9% and at the 500 ng/g was 97%. For reasons that we cannot discern, the mid-level spiking recoveries (average was 84.4%) were lower than at the low or high levels. Since the relative standard deviations of the mid-level spiking data were almost twice that of the low and high-level spikes, this may be part of the problem. However, even including the mid-level samples, the recovery of PCBs from soil was essentially quantitative.

Similarly, for the PCDDs and PCDFs, the average recovery over the three levels was over 96%. The same anomolous result was found for the PCDDs and PCDFs as was found for the PCBs. The mid-level spikes yielded recoveries that were a bit lower (94.1%) than the low and high-level spikes. But in all cases, quantitative recoveries were obtained.

We also analyzed several natural matrix certified reference materials obtained from the RTC Company in Laramie, WY using the Power-Prep/PLE™ system. These presented the system with a real world challenge and the Power-Prep/PLE™ again demonstrated its validity as a sample preparation/clean up tool. As the data (see Tables 1 – 5) demonstrate, not only did the Power-Prep/PLE™ yield accurate data for the semi-volatile and polynuclear aromatic compounds in loamy soil, silty clay soil, sewage sludge, river sediment and garden soil, but in all cases yielded data that were as accurate or better than that obtained using the conventional Soxhlet procedure (EPA Method 3540C). For example, for the semi-volatile organics in loamy soil (Table 3), in 26 of the 38 analytes, results within 1 Standard Deviation of the reference value was obtained using the Soxhlet and using the Power-Prep/PLE™ values within 1 SD were obtained 27 out of 38 times. Looking at the results for the organochlorine pesticides (Table 8) in sewage sludge, a difficult matrix to analyze, the Power-Prep/PLE™ recoveries average 113% of the certified values. Since the certified values were based on Soxhlet extraction, this further demonstrates the improved extraction efficiencies that can be obtained when the pressurized liquid extraction technique is applied correctly.

Even in the case of the organophosphorus pesticides in soil sample (Table 7), where we encountered some unknown difficulty in carrying out the analyses, the Soxhlet and the Power-Prep/PLE™ yielded equivalent results. The Soxhlet extractions yielded an average recovery of 35% while the Power-Prep/PLE™'s average recovery was 34%.

CONCLUSION

In conclusion, we have found that the Power-Prep/PLE™ Pressurized Fluid Extraction and Automated Column Chromatography Clean Up gives accurate results when analyzing environmental samples of interest to the solid waste program for a wide variety of compound classes. In addition, by switching from the conventional Soxhlet extraction/column clean up techniques to Pressurized Fluid Extraction with Automated Clean up we have seen significant increases in laboratory productivity.

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Table 3
CRM125-100 Semi-volatile Organics in Loamy Soil

Analyte	RTC Certified Values (ug/g)	Soxhlet Conc. (ug/g)	Data Accep	PLE Conc. (ug/g)	Data Accep
Acenaphthene	2.12	2.10	OK	2.00	OK
Anthracene	1.19	0.76	M	0.71	M
Benzo(a)pyrene	1.56	1.70	OK	1.50	OK
Benzo(b)fluoranthene	3.93	4.80	OK	4.40	OK
Benzo(g,h,i)perylene	2.83	3.40	OK	3.20	OK
Benzo(k)fluoranthene	1.78	2.20	OK	2.00	OK
Benzyl alcohol	3.33	4.20	OK	3.10	OK
Bis(2-chloroethoxy) methane	5.35	7.30	M	6.80	OK
Bis(2-chloroethyl) ether	0.97	1.30	OK	1.00	OK
Bis(2-ethylhexyl)phthalate	3.10	4.20	OK	10.0	F
4-Bromophenyl-phenyl ether	8.04	11.0	M	10.0	M
Butyl benzyl phthalate	7.27	11.0	M	7.90	OK
4-Chloro-3-methylphenol	3.36	3.70	OK	3.60	OK
4-Chlorophenyl-phenyl ether	6.40	8.40	M	7.60	OK
Chrysene	1.21	1.50	OK	1.40	OK
Dibenz(a,h)anthracene	1.23	1.50	OK	1.30	OK
Dibenzofuran	1.75	2.20	M	2.10	M
Di-n-butyl phthalate	7.33	12.0	M	8.70	OK
1,2-Dichlorobenzene	1.08	1.00	OK	ND	OK
1,3-Dichlorobenzene	0.50	ND	F	ND	OK
2,4-Dichlorophenol	4.70	5.70	OK	5.60	OK
Diethyl phthalate	8.06	11.0	OK	7.10	OK
2,4-Dinitrophenol	1.97	1.10	OK	2.00	OK
2,4-Dinitrotoluene	7.84	11.0	M	8.70	OK
Fluoranthene	5.10	6.30	M	6.00	OK
Indeno(1,2,3-cd)pyrene	1.31	1.60	OK	1.30	OK
Hexachlorobutadiene	1.17	1.40	OK	1.00	OK
Isophorone	3.31	4.50	OK	3.30	OK
2-Methylphenol (o-cresol)	1.90	1.50	OK	1.70	OK
4-Nitroaniline	1.84	2.40	OK	ND	F
Nitrobenzene	5.60	7.40	M	6.50	OK
2-Nitrophenol	4.88	4.10	OK	7.20	OK
N-Nitroso-n-propylamine	6.48	9.30	M	6.40	OK
Phenanthrene	0.06	0.10	OK	0.13	OK
Phenol	5.90	7.70	OK	6.60	OK
1,2,4- Trichlorobenzene	2.38	3.10	M	2.20	OK
2,4,5-Trichlorophenol	5.31	6.90	OK	6.30	OK
2,4,6-Trichlorophenol	3.17	4.00	OK	3.70	OK
OK/TOTAL			26/38		27/38

OK = Within 1 Standard Deviation of RTC Certified Value
M = Between 1 and 2 Standard Deviation of RTC Certified Value
F = Value more than 2 Standard Deviation from RTC Certified Value

Table 4
CRM123-100 Semi-volatile Organics in Silty Clay

Analyte	RTC Certified Values (ug/g)	Soxhlet Conc (ug/g)	Data Accep	PLE Conc (ug/g)	Data Accep
Acenaphthene	7.5	7.1	OK	7.1	OK
Acenaphthalene	7.2	4.2	M	3.7	M
Anthracene	6.9	5.3	OK	4.5	M
Benzo(a)pyrene	7.8	6.3	OK	5.5	M
Benz(a)anthracene	8.4	7.5	OK	7.7	OK
Benzo(b)fluoranthene					
Benzo(g,h,i)perylene					
Benzo(k)fluoranthene					
Benzyl alcohol					
Bis(2-chloroethoxy) methane					
Bis(2-chloroethyl) ether					
Bis(2-ethylhexyl)phthalate	8.9	5.4	M	24.0	
4-Bromophenyl-phenyl ether	13.0	13.0	OK	13.0	OK
Butyl benzyl phthalate					
4-Chloro-3-methylphenol	7.6	7.0	OK	7.7	OK
2-Chloronaphthalene	7.4	6.8	OK	6.2	OK
2-Chlorophenol	8.5	8.6	OK	7.0	OK
4-Chlorophenyl-phenyl ether	9.4	8.8	OK	9.1	OK
Chrysene	11.3	11.0	OK	12.0	OK
Dibenz(a,h)anthracene					
Dibenzofuran	8.2	8.1	OK	8.0	OK
Di-n-butyl phthalate	16.8	14.0	OK	19.0	OK
1,2-Dichlorobenzene	5.2	3.0	OK	2.8	OK
1,3-Dichlorobenzene	4.3	2.0	M	1.7	M
1,4-Dichlorobenzene	4.0	2.0	M	1.6	M
2,4-Dichlorophenol	10.6	10.0	M	12.0	OK
Diethyl phthalate					
2,4-Dimethylphenol	9.3	5.5	OK	5.3	OK
Dimethyl phthalate	9.6	9.3	OK	10.0	OK
2,4-Dinitrophenol	6.4	14.0	F	ND	F
2,4-Dinitrotoluene	17.4	17.0	OK	15.0	OK
Di-n-octyl phthalate	11.4	6.7	M	12.0	OK
Fluoranthene	9.3	8.0	OK	9.2	OK
Fluorene	6.9	6.4	OK	6.7	OK
Indeno(1,2,3-cd)pyrene					
Hexachlorobenzene	6.8	6.2	OK	6.7	OK
Hexachlorobutadiene					
Isophorone	8.1	7.3	OK	8.3	OK
2-Methylphenol (o-cresol)	7.7	7.1	OK	7.0	OK
Naphthalene	9.7	9.9	OK	6.6	M
4-Nitroaniline					
Nitrobenzene	10.6	11.0	OK	11.0	OK
2-Nitrophenol	6.3	11.0	M	7.6	OK
N-Nitroso-n-propylamine					
Phenanthrene	7.9	7.3	OK	8.1	OK
Phenol					
Pyrene	6.8	6.1	OK	6.7	OK
1,2,4- Trichlorobenzene					
2,4,5-Trichlorophenol	5.3	5.7	OK	6.7	OK
2,4,6-Trichlorophenol					
OK/TOTAL			26/34		26/34

OK = Within 1 Standard Deviation of RTC Certified Value
M = Between 1 and 2 Standard Deviation of RTC Certified Value
F = Value more than 2 Standard Deviation from RTC Certified Value

Table 5

CRM827-150 Organophosphorus Pesticides in Soil

Analyte	RTC Certified Values (ug/Kg)	Soxhlet Conc (ug/Kg)	PLE Conc (ug/Kg)
Demeton-S	525	ND	37.2
Dichlorvos	887	ND	ND
Fenchlorophos (Ronnel)	830	421	429
Phorate	480	ND	3.6
Diazinon	3760	470	399
Parathion Ethyl	4880	4800	4146
Malathion	8020	6776	6827
Guthion		1535	1244

Table 6

CNS312-04-050 Organochlorine Pesticides, Polyaromatic Hydrocarbons (PAHs) and Polychlorinated Biphenyls (PCBs) in Sewage Sludge

Analyte	RTC Certified Values (ug/g)	PLE Conc (ug/g)	Data Accep
PCBs			
PCB-28	0.205	0.279	OK
PCB-52	0.263	0.329	OK
PCB-101	0.257	0.195	OK
PCB-118	0.074	0.088	OK
PCB-138	0.136	0.109	OK
PCB-153	0.214	0.153	OK
PCB-180	0.232	0.595	F
PAHs			
Acenaphtene	2.99	3.52	OK
Acenaphthalene	2.42	1.66	OK
Anthracene	1.67	2.11	OK
Benzo(a)anthracene	1.45	1.93	M
Benzo(g,h,i)perylene	0.835	ND	F
Benzo(a)pyrene	0.872	ND	F
Chrysene	1.12	1.40	OK
Dibenz(a,h)anthracene	0.407	ND	F
Fluoranthene	4.19	5.09	OK
Fluorene	2.01	2.18	OK
Naphthalene	2.58	2.67	OK
Pyrene	4.17	5.06	OK
Organochlorine Pesticides			
Aldrin	.221	.184	OK
Lindane	.578	.573	OK
2,4'-DDD (o,p)	.625	.682	OK
2,4'-DDE (o,p)	.258	.276	OK
2,4"-DDT (o,p)	.223	.3	OK
4,4'-DDD (p,p)	.809	.947	OK
4,4"-DDE (p,p)	.229	.272	OK
Dieldrin	.569	.554	OK
Endosulfan I	.296	.431	OK
Endrin	.336	.379	OK
Heptachlor	.197	.185	OK
Heptachlor epoxide	.104	.139	OK

OK = Within 1 Standard Deviation of RTC Certified Value
M = Between 1 and 2 Standard Deviation of RTC Certified Value
F = Value more than 2 Standard Deviation from RTC Certified Value

Table 7

CRM104-100 Semi-volatile Organics in River Sediment

Analyte	RTC Certified Values (ug/g)	Soxhlet Conc (ug/g)	PLE Conc (ug/g)
Bis(2-ethylhexyl) phthalate	1.34	OK	1.4
4-Bromophenyl phenyl ether	1.98	OK	2.1
Butyl benzyl phthalate	0.49	OK	0.5
Di-n-butyl phthalate	0.47	OK	0.5
Diethyl phthalate	6.25	OK	7.1
2,4-Dinitrotoluene	1.73	OK	1.8
2-Nitrophenol	0.36	OK	0.3
2,4,5-Trichlorophenol	1.60	OK	1.4
2,4,6-Trichlorophenol	0.91	M	0.5

Table 8

CRM135-100 Semi-volatile Organics in Soil

Analyte	RTC Certified Values (ug/g)	PLE Conc* (ug/g)	Data Accep
Acenaphthene	1.39	1.3	OK
Acenaphthalene	1.21	ND	F
Aniline	2.31	0.58	M
Anthracene	0.85	0.32	F
Benzo(a)pyrene	0.35	0.27	OK
Benz(a)anthracene	3.52	3.8	OK
Benzoic Acid	1.9	4.1	F
Benzyl alcohol	1.56	1.8	OK
Bis(2-chloroethyl) ether	0.69	0.38	
4-Bromophenyl-phenyl ether	5.26	5.7	OK
Butyl benzyl phthalate	3.13	3.3	OK
Carbazole	5.4	4.1	OK
4-Chloroaniline	0.75	ND	F
4-Chloro-3-methylphenol	0.6	0.5	OK
2-Chloronaphthalene	2.03	0.32	F
2-Chlorophenol	1.67	1.4	OK
4-Chlorophenyl-phenyl ether	7.62	8.7	OK
Dibenzofuran	5.1	5.6	OK
Di-n-butyl phthalate	4.6	5.2	OK
1,2-Dichlorobenzene	0.63	ND	F
2,4-Dichlorophenol	1.55	1.3	OK
Diethyl phthalate	0.25	1.9	
2,4-Dimethylphenol	3.27	ND	F
Dimethyl phthalate	3.78	3.9	OK
2,4-Dinitrophenol	2.22	1.7	OK
Di-n-octyl phthalate	5.14	7.6	M
Fluoranthene	0.33	0.31	OK
2-Methyl-4,6-dinitrophenol	4.28	3.9	OK
2-Methylphenol (o-cresol)	3.5		
Naphthalene	0.64	.37	M
2-Nitroaniline	5.09	5.8	OK
3-Nitroaniline	4.93	3.0	OK
4-Nitroaniline	1.73	.58	F
Nitrobenzene	4.37	4.1	OK
2-Nitrophenol	3.82	3.9	OK
4-Nitrophenol	3.68	4.2	OK
Pentachlorophenol	3.42	2.9	OK
Phenanthrene	2.01	2.2	OK
1,2,4- Trichlorobenzene	1.71	0.7	M

OK = Within 1 Standard Deviation of RTC Certified Value
M = Between 1 and 2 Standard Deviation of RTC Certified Value
F = Value more than 2 Standard Deviation from RTC Certified Value
*** = Average of 2 runs. When 1 run yields a non-detect and the other a value > RDL, "Conc" is equal to (.5xRDL + Measured Concentration)/2**

Automated Extraction Procedure for Improved Recovery of Phenols and Phenoxy Herbicides

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ABSTRACT

Accelerated Solvent Extraction (ASE) is a rapid sample preparation technique that uses common organic solvents to extract solid or semi-solid samples. Using ASE, pressurized solvents are heated at or above their boiling points. The use of hot, pressurized solvents has many favorable extraction properties as compared to traditional extraction techniques such as Soxhlet or sonication. For example, as temperature increases the solution viscosity is reduced, resulting in less resistance to mass transfer as analytes diffuse between solid and liquid phases. It is well known that diffusion coefficients and analyte solubility increase with temperature. The effect of reduced solution viscosity, higher analyte solubility, and increased diffusion accelerates the extraction process resulting in rapid, efficient sample preparation. ASE has been applied to many different analytes and numerous matrices. In general, ASE methods are complete in 15 to 25 minutes and consume 20 to 40-mL solvent per extraction. ASE is fully automated and can facilitate in-line clean-up of some samples using resins and sorbents to retain some co-extractables. ASE can be used for environmental applications such as the extraction of pesticides, PAHs, PCBs, TPH, dioxins, phenols and phenolic herbicides in environmental matrices.

Due to the polar nature of phenols and phenoxy herbicides, the extraction and the commensurate recovery for analytical determination of these compounds can be challenging. Often acidic pre-treatment of samples is required for efficient extraction of these compounds. A discussion of pre-treatment techniques such as adding HCl prior to ASE as means to improve the recoveries of phenols and phenoxy herbicides will be presented.

Comprehensive Analysis of Polycyclic Aromatic Hydrocarbons by Liquid Chromatography and Gas Chromatography

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are a group of chemicals that are known or suspected carcinogens. Exposures to PAHs usually occurs by eating charbroiled foods, inhaling burning coal, tar, garbage, exhaust fumes and smoke but are also present in medicines, plastics and pesticides. National and international regulation agencies such as the United States Environmental Protection Agency (EPA) and the European Union (EU) have recommended several targeted PAH analyte lists.

Many chromatographic methods are available to analyze PAHs. Both liquid chromatography (LC) and gas chromatography (GC) have been utilized to analyze PAHs. Several phases for both LC and GC have been evaluated. Phases were analyzed to optimize selectivity and optimum speed. The target analyte list evaluated includes the 18 EPA 610 mandated target PAHs along with the 15 EU 256/2005 recommended PAH analytes. These compounds were also analyzed out of a food matrix.

In addition to phase evaluation, several different LC column dimensions were also optimized. Previous HPLC analyses of PAHs have been analyzed on a 4µm particle size C18 column with a typical analysis time of twenty minutes. Optimization of the alkyl phase has increased selectivity of PAHs while column dimension optimization has decreased analysis time to five minutes or less.

The gas chromatographic techniques typically used for the analysis of PAHs are often coupled with mass spectrometry. Laboratories performing low-level PAH analyses often utilize the single ion monitoring (SIM) function of GC/MS because of the sensitivity required to achieve typical regulatory or monitoring levels. Flame ionizer detectors (FID) are also widely used for the analysis of PAHs.

Comprehensive Analysis of Polycyclic Aromatic Hydrocarbons by Liquid Chromatography and Gas Chromatography

Michelle Misselwitz, Julie Kowalski, PhD, Jason Thomas
Restek Corporation
Bellefonte, PA

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Outline

- **Background of PAHs**
  - Exposure and Toxic Effects
  - Regulating agencies
- **Liquid Chromatography**
  - Optimization of stationary phase
  - Small Particle advantage – faster throughput
- **Gas Chromatography**
  - Evaluation of stationary phases
  - Choosing the best column
  - Analysis of PAHs in Olive Oil

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Exposure of PAHs

- **Environment**
  - Naturally occurring fumes from, crude oil, coal tar, wildfires
  - Man-made asphalt, vehicle exhaust, cigarette and tobacco smoke
- **Food**
  - Foods grown in contaminated soil: vegetables, fruits
  - Grilled or charred food
  - Contaminated cereals, processed or pickled foods

Toxic Effects of PAHs

- **Targets fat tissue**
  - Kidneys and liver
  - Exposure linked to cancer
- **Animal studies**
  - Reproductive problems
  - Birth defects
  - Tumors
  - Damage to skin, and immune system

Regulations of PAHs

- **US Environmental Protection Agency, Method 610**
  - Determination of PAHs in municipal and industrial discharge
- **European Union, Commission Recommendation 256/2005**
  - Monitoring levels of certain PAHs in foodstuffs
- **Occupational Safety and Health Administration**
  - Sets permissible exposure limits for workplace air levels

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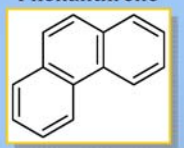
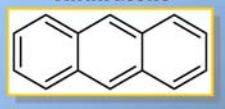
Stationary Phase Optimization

- **Pinnacle II PAH**
  - particle size: 4µm, spherical
    pore size: 110Å
    pH range: 2.5 to 10
    temperature limit: 80°C
- **Pinnacle DB PAH**
  - particle size: 1.9µm
    pore size: 140Å
    pH range: 2.5 to 7.5
    temperature limit: 80°C

Phenanthrene



Anthracene



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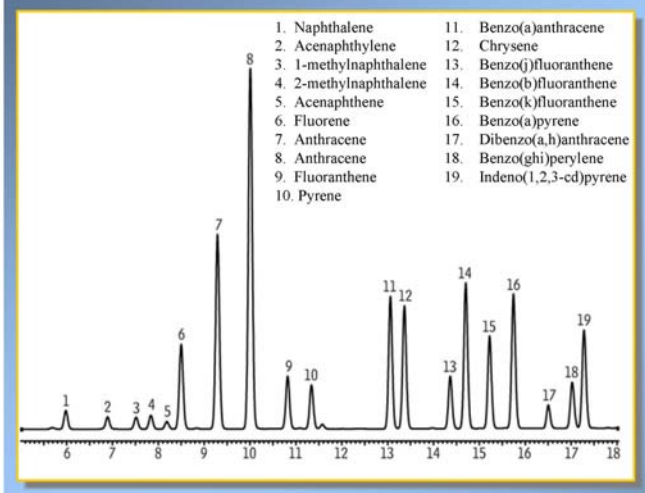
Analyzing PAHs by LC



Pinnacle II PAH
150mm x 3.2mm, 4µm

Mobile Phase:
A: water
B: acetonitrile

Flow: 1.2 mL/min

UV Detector @ 254nm

Time	%B
0	40
7	60
16	100
19	100

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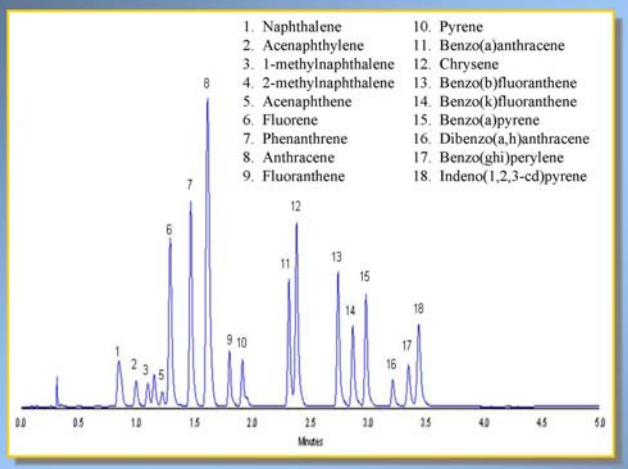
Small Particle Advantage-Faster Throughput



Pinnacle DB PAH
50mm x 2.1mm, 1.9µm

Mobile phase:
A: Water
B: Acetonitrile

Flow: 0.6 mL/min

UV detector @ 254nm

Time	%B
0	50
1	60
3	100
5	100

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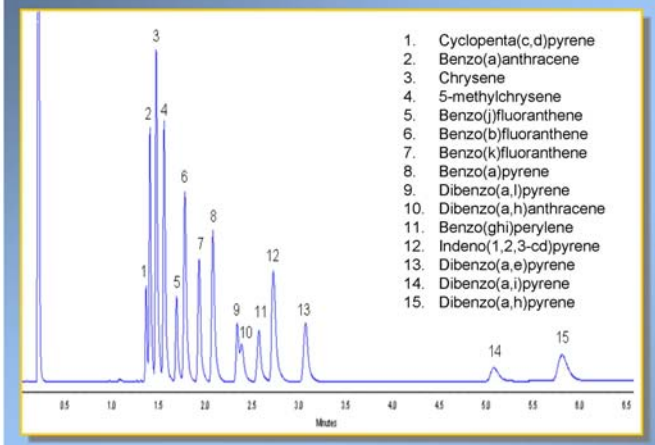
Small Particle Advantage-Faster Throughput



Pinnacle DB PAH
50mm x 2.1mm, 1.9µm

Mobile phase:
A: Water
B: Acetonitrile

Flow: 0.6 mL/min

UV detector @ 254nm

Time	%B
0	50
1	90
2	95
5	100
7	100

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Analysis of PAHs by Gas Chromatography

- Column Evaluation
  - Rt-PAH (polar liquid-crystalline phase)
  - Rxi-17 (crossbonded 50%diphenyl / 50% dimethyl polysiloxane)
  - Rxi-50 (crossbonded 100% methylphenyl polysiloxane)
  - Rxi-5sil MS (crossbonded silarylene phase)

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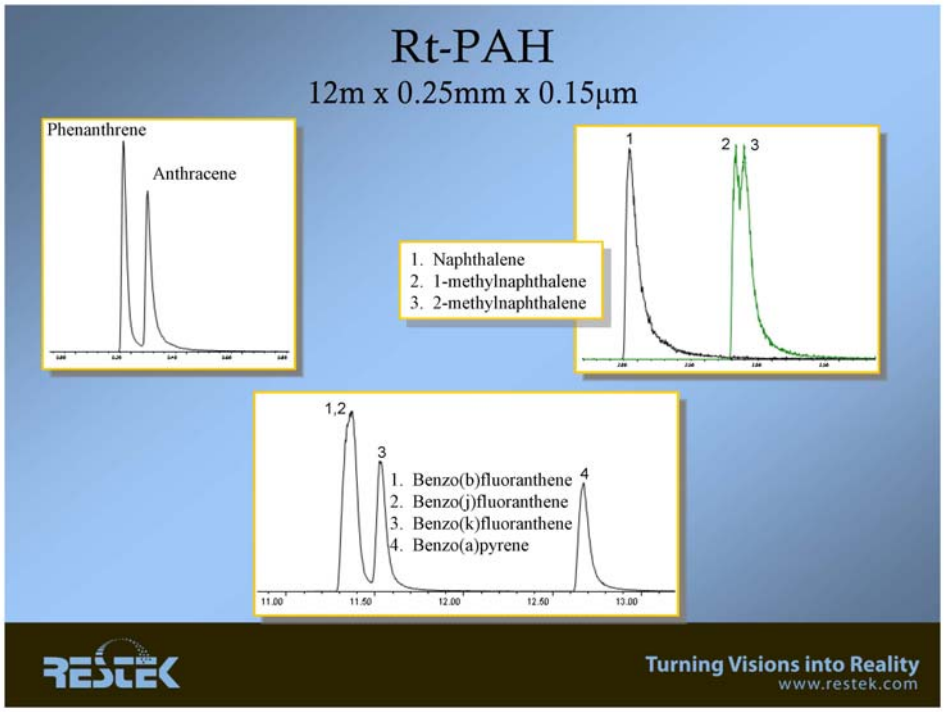
Rt-PAH
12m x 0.25mm x 0.15µm
Phenanthrene
Anthracene
1. Naphthalene
2. 1-methylnaphthalene
3. 2-methylnaphthalene
1,2
3
1. Benzo(b)fluoranthene
2. Benzo(j)fluoranthene
3. Benzo(k)fluoranthene
4. Benzo(a)pyrene
4
11.00
11.50
12.00
12.50
13.00
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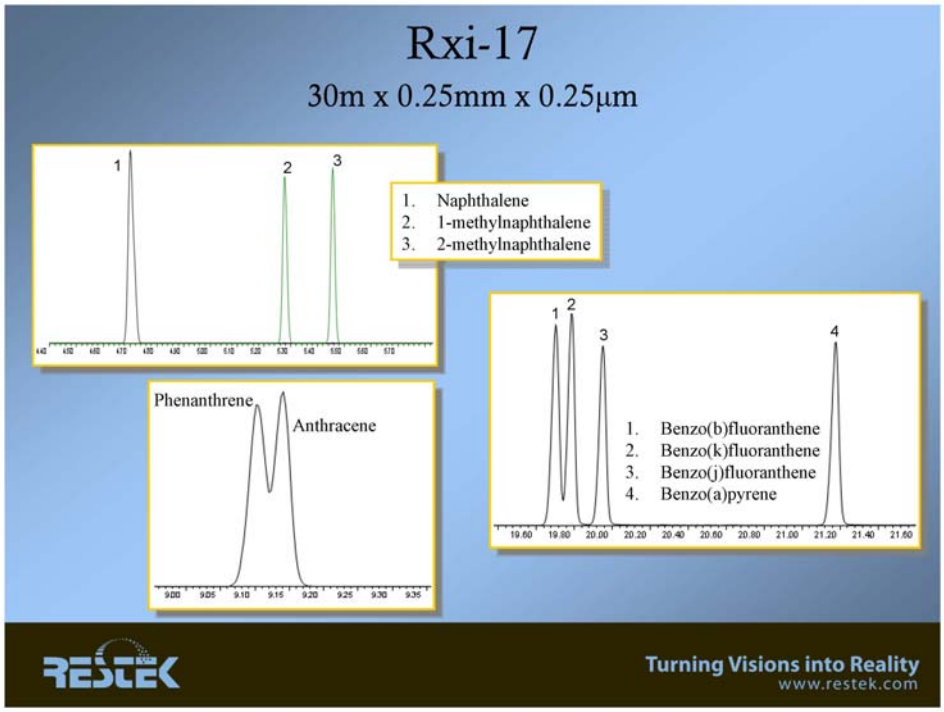
Rxi-17
30m x 0.25mm x 0.25µm
1. Naphthalene
2. 1-methylnaphthalene
3. 2-methylnaphthalene
Phenanthrene
Anthracene
1. Benzo(b)fluoranthene
2. Benzo(k)fluoranthene
3. Benzo(j)fluoranthene
4. Benzo(a)pyrene
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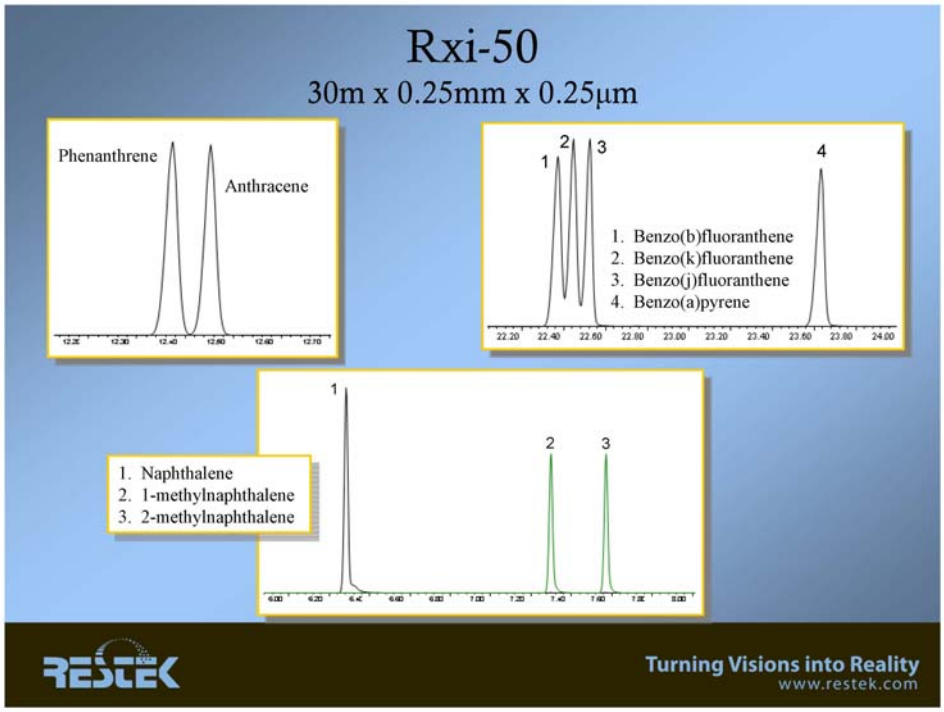
Rxi-50
30m x 0.25mm x 0.25µm
Phenanthrene
Anthracene
1. Benzo(b)fluoranthene
2. Benzo(k)fluoranthene
3. Benzo(j)fluoranthene
4. Benzo(a)pyrene
1. Naphthalene
2. 1-methylnaphthalene
3. 2-methylnaphthalene
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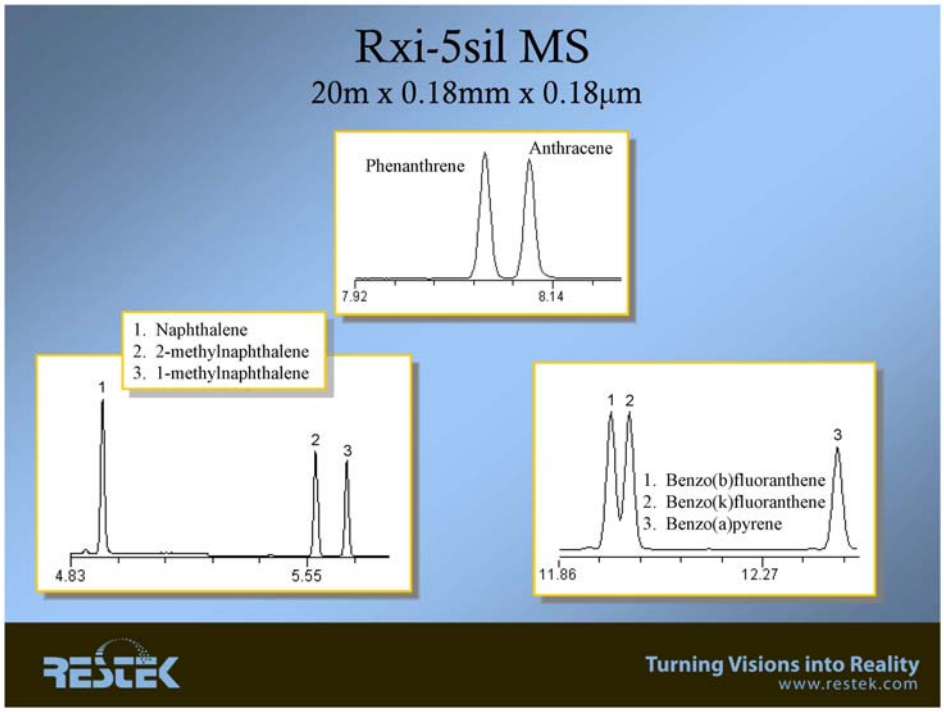
Rxi-5sil MS
20m x 0.18mm x 0.18µm
Phenanthrene
Anthracene
7.92
8.14
1. Naphthalene
2. 2-methylnaphthalene
3. 1-methylnaphthalene
4.83
5.55
1. Benzo(b)fluoranthene
2. Benzo(k)fluoranthene
3. Benzo(a)pyrene
11.86
12.27
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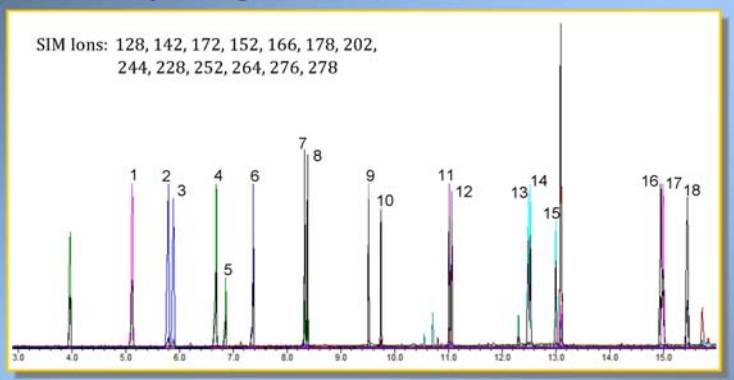
Analyzing PAHs out of Olive Oil



1. Naphthalene
2. 2-methylnaphthalene
3. 1-methylnaphthalene
4. Acenaphthylene
5. Acenaphthene
6. Fluorene

7. Phenanthrene
8. Anthracene
9. Fluoranthene
10. Pyrene
11. Benzo(a)anthracene
12. Chrysene

13. Benzo(b)fluoranthene
14. Benzo(k)fluoranthene
15. Benzo(a)pyrene
16. Indeno(1,2,3-cd)pyrene
17. Dibenzo(a,h)anthracene
18. Benzo(ghi)perylene

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Closing Remarks

- PAHs are a topic of concern
  - Targeted analytes being added
  - Investigation of potential health effects
- Both GC and LC can be utilized
  - Analysis can be performed either way
  - Many column choices

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The Development of EPA Method 524.3 for the Determination of Volatile Organic Compounds in Drinking Water

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David J. Munch; USEPA, Office of Ground Water and Drinking Water Technical Support Center, 26 W. Martin Luther King Drive, Cincinnati, Ohio, 45219

ABSTRACT

Research is now complete on the US Environmental Protection Agency's effort to revise the method for volatile organic contaminants in drinking water. The new method, Method 524.3, achieves several significant goals. It has a revised list of analytes that now includes the iodinated trihalomethanes (ITHMs), fuel oxygenates, and Contaminant Candidate List 3 (CCL3) volatile organic compounds amenable to purge-and-trap. It employs Maleic acid, a common food preservative, to preserve samples thereby no longer requiring the shipment of hazardous preservations reagents (HCl) to the field. The new method also allows selected ion monitoring for the detection of four analytes that have historically challenged the laboratory community.

Three purge-and-trap concentrators and several traps were evaluated under a large range of purge volumes, purge rates and dry purge times to determine acceptable limits for these parameters in order to allow method flexibility without jeopardizing performance. The performance characteristics of the new method promise to make this an attractive choice for compliance monitoring once approved by EPA for this purpose. Method flexibility, which was aimed at allowing analysts and manufacturers to take advantage of future technological developments, should make Method 524.3 a versatile method for years to come.

Development of a Gas Chromatography/Mass Spectrometry Method for the Analysis of the Solvent Stabilizer 1,4-Dioxane in Drinking Water

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Cincinnati, OH 45268
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grimmett.paul@epa.gov

ABSTRACT

The solvent stabilizer 1,4-dioxane was named to the latest draft Drinking Water Contaminant Candidate List (CCL3) in February 2008 by the United States Environmental Protection Agency (USEPA). To collect occurrence data under the Unregulated Contaminant Monitoring Regulation (UCMR) program, a standardized method that exhibits ruggedness, accuracy, and precision is needed. Analysis of 1,4-dioxane has proved challenging because its volatility and miscibility with water make the compound a poor candidate for traditional extraction and concentration techniques. USEPA's National Exposure Research Laboratory (NERL) has developed a new method, employing an activated carbon solid phase extraction, with quantitation performed by gas chromatography/mass spectrometry (GC/MS) in selected ion mode (SIM). Using the method parameters, 1,4-dioxane (1.0 µg/L) was recovered from groundwater, surface water, and surface water high in total organic carbon (TOC) at efficiencies of 96%, 99%, and 102%, respectively, using 500-mL drinking water samples. Relative standard deviations (RSD) were less than 6% for all drinking water sources (n = 7). Small-scale extractions using 100-mL water samples yielded comparable results. Method detection limits (MDL) calculated from fortified water samples analyzed at three laboratories were 0.012 µg/L, 0.020 µg/L, and 0.021 µg/L, with lowest concentra-tion minimum reporting level (LCMRL) values of 0.013 µg/L, 0.036 µg/L, and 0.080 µg/L. Drinking water samples preserved with sodium bisulfate, dechlorinated with sodium sulfite, and stored under refrigeration were stable for 28 days.

EPA United States Environmental Protection Agency

Development of a Gas Chromatography/Mass Spectrometry Method for the Analysis of the Solvent Stabilizer 1,4-Dioxane in Drinking Water

Paul E. Grimmett
Jean W. Munch

Office of Research and Development
National Exposure Research Laboratory, 26 W. Martin Luther King Dr., Cincinnati, OH 45268

July 30, 2008

EPA United States Environmental Protection Agency

Molecular formula	$C_4H_8O_2$
Molar mass	88.11 g/mol
Density	1.033 g/cm³
Melting point	11.8°C
Boiling point	101.1°C

1,4-Dioxane Background

- Primarily used commercially as a solvent stabilizer for degreasing agents
- Chlorinated solvents, such as 1,1,1-Trichloroethane (TCA), used as degreasing agents require stabilization compounds to prevent breakdown and to extend the solvent lifespan.
- 6.75 million pounds – U.S. production (1982); 10-18 million pounds by 1990
- Estimated 90% of 1,4-dioxane produced was used for chlorinated solvent stabilization.
- Improper disposal from degreasing operations is the major source of 1,4-dioxane's environmental presence.

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Molecular formula	$C_4H_8O_2$
Molar mass	88.11 g/mol
Density	1.033 g/cm³
Melting point	11.8°C
Boiling point	101.1°C

1,4-Dioxane Background (continued)

- By-product of ethoxylated detergents and surfactants found in many personal care products
- Non-biodegradable, persists in the environment
- USEPA's Toxic Chemical Release Inventory - nearly 1 million pounds of 1,4-dioxane were released into the environment in the U.S. in 1996
- Concentrations as high as 200,000 µg/L - reported in contaminated groundwaters (2100 µg/L in drinking water)

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Risk Data and Notification Levels for 1,4-Dioxane

- USEPA has established a concentration in drinking water for a 1 in 10^6 lifetime cancer risk of 3 µg/L*
- Some states have set Notification Levels and maximum Standard Levels: 3-85 µg/L
- World Health Organization drinking water guideline of 50 µg/L

* currently under review and may be revised

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1,4-Dioxane and the UCMR

- 1,4-dioxane was one of 93 chemical contaminants listed on the USEPA's Feb. 2008 draft Drinking Water Contaminant Candidate List (CCL3).
- Nationwide occurrence data is required for USEPA to make a regulatory determination.
- USEPA has collected occurrence data for CCL chemicals through its Unregulated Contaminant Monitoring Regulation (UCMR) program.
- A standardized method for 1,4-dioxane measurement in drinking water must be available in order for it to be included in the UCMR.
- Method must meet/exceed sensitivity, specificity, accuracy, and precision requirements, while keeping cost in mind.

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Problems with Previous Techniques

1. Direct Injection (DI) – no extraction
   a. high detection limits (mg/L)
   b. limitations – UCMR will require µg/L (possibly sub-) detection limits
2. Purge and trap
   a. recoveries of < 1% using USEPA's standard purge and trap technology
   b. limitations - heating and salt-addition improve efficiency, but potentially expose the instrumentation to salt and water vapor, affecting precision and accuracy, as well as instrument down-time

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Potential Extraction Techniques (continued)

3. Solid-phase microextraction (SPME)
   a. limit of quantitation (LOQ) reported at 2.5 µg/L without background subtraction
   b. limitations - requires specialized equipment, expensive to automate, and still may not provide enough sensitivity. Background subtraction not allowed for drinking water analysis

4. Liquid-liquid extraction (LLE)
   a. recoveries ranging from 5-80%, depending on sample size, extracting solvent, and salt concentration added
   b. limitations - accuracy, time-consuming, large amounts of solvent consumed

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Why Solid Phase Extraction (SPE)?

- SPE - normally used for hydrophobic non-polar compounds (reverse-phase), e.g. C_8, C_{18}, PSDVB
- Recent carbon-based sorbent applications for hydrophilic, volatile compounds, such as *N*-nitrosamines, have been successful.
- Japanese researchers report 1,4-dioxane at 100% extraction efficiency from 500-mL water samples using 0.5 g of carbon fiber felt and similar results from a commercially available Sep-Pak® cartridge.
- Next step ➡ research efficiency of activated coconut-based carbon sorbents

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1,4-Dioxane Analysis - Instrumentation

- Traditional GC detectors (FID, PID) lack sufficient specificity and sensitivity.
- 1,4-dioxane lacks a specific heteroatom or functional group that would respond to specific GC detectors (ECD, NPD).
- MS detection, in either full-scan and selected ion monitoring (SIM), is used almost exclusively for the detection of 1,4-dioxane because of its relatively low MW and boiling point.
- GC/MS, with a thick film column and used at low initial oven temperatures, has been demonstrated to be effective for 1,4-dioxane analysis.

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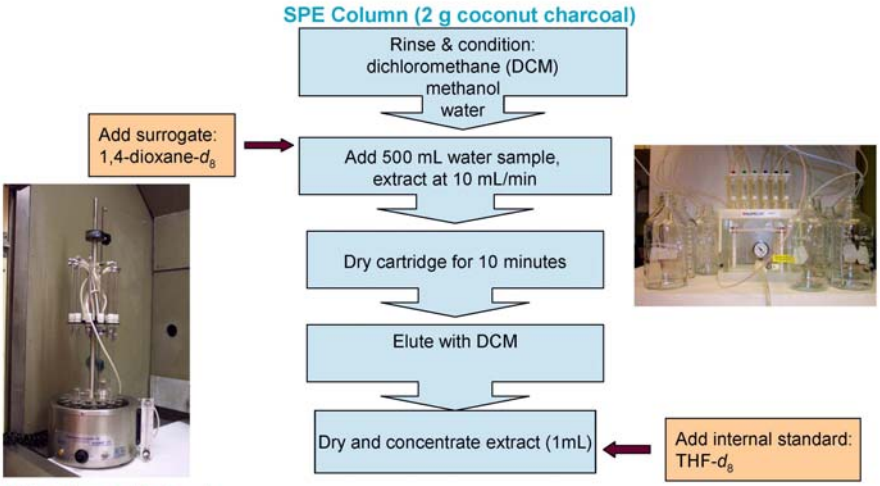
Initial SPE Approach for Full-Scan GC/MS Analysis



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Full Scan GC/MS Analysis

Parameters

Column: Varian CP-Select 624 CB
(6% cyanopropyl phenyl, 94% PDMS phase)
30 m x 0.25 mm x 1.4 µm column

Injector: 200 °C (splitless mode)

Inj. vol: 1 µL

Flow: 1 mL/min

Oven: 30 °C for 1 min, 90 °C at 8 °C/min, 200 °C at 20 °C/min, 200 °C for 4 min

MS: ion-trap MS
full scan *m/z* 40-200 (0.61 s/scan)
emission current : 25 µA
pre-scan ionization time:100 µs

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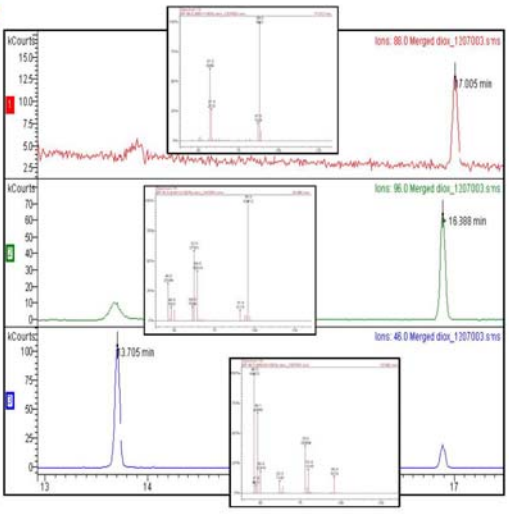
Results from Full Scan Data

- Results were inconsistent **(> 15% RSD)** and resulted in analyte loss up to 30%.
- Loss traced to evaporation/concentration of extract (due to the volatility of 1,4-dioxane)
- Concentration was necessary to achieve adequate sensitivity levels in full scan MS mode



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Options for Overcoming 1,4-dioxane Evaporation Losses

1. Isotope Dilution using a labeled surrogate: "correction factor"
   - increases accuracy and precision
   - past researchers have had success using this technique

   Problems: Adds additional QC criteria (recovery standard monitoring); Minimum Reporting Limit (MRL) varies with absolute recovery, which creates a problem setting the MRL for UCMR.

2. Eliminate Evaporation Step
   Problem: target not concentrated enough to meet sensitivity requirements in full scan MS mode.

   Solution: SIM (Selected Ion Monitoring) mode
   - MS only scans for ions of selected interest (as opposed to an entire range)
   - Improves sensitivity (> S/N ratio) = lower limit of detection (LOD)

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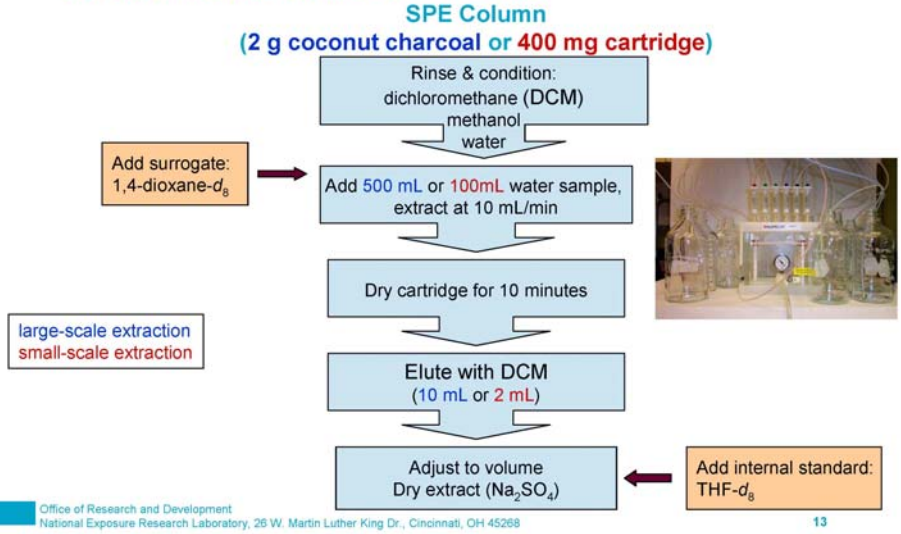
SPE Approach for GC/MS-SIM Analysis



EPA United States Environmental Protection Agency

GC/MS-SIM Analysis

Parameters

Column: Varian CP-Select 624 CB
(6% cyanopropyl phenyl, 94% PDMS phase)
30 m x 0.25 mm x 1.4 µm column

Injector: 200 °C (splitless mode)

Inj. vol: 1 µL

Flow: 1 mL/min

Oven: 30 °C for 1 min, 90 °C at 7 °C/min, 200 °C at 20 °C/min, 200 °C for 3 min

MS: quadrupole MS
SIM mode
Segment 1: m/z 46*, 78, 80
Segment 2: m/z 58, 62, 64, 88*, 96*
dwell time: 100 µs
emission current: 100 µA

*quantitation ions for internal std., surrogate, and target

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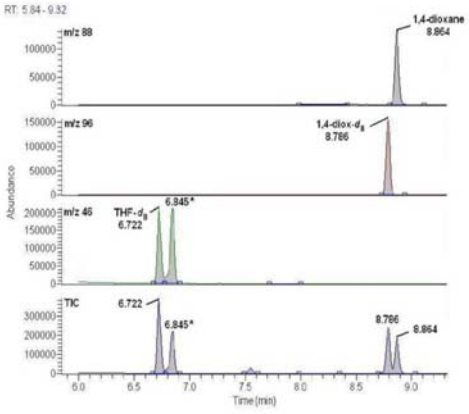
Results from GC/MS-SIM Data: Lab-Fortified Blanks

- Mean recoveries of 1,4-dioxane for two separate brands of 2-g activated carbon columns were **87%** and **92%**, respectively, with RSD values **< 3%** (*n* = 7)
- Mean recovery of 1,4-dioxane was **104%**, with an RSD of **4%** (*n* = 4) using 400mg small-scale cartridges
- Linear calibration range of 0.040 - 20.0 µg/L 1,4-dioxane (qualifier ion ratios were consistent)



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Initial Sample Preservation and Dechlorination Trials

- Copper sulfate – microbial inhibitor
  a. used in other USEPA drinking water methods
  b. requires a buffer to keep in solution (prevent precipitation)
  c. ammonium chloride and Trizma® were used as buffers
  d. sodium sulfite as a dechlorinating agent

Problem: Trizma® buffer + copper sulfate successful in keeping precipitate from forming, but when added to a surface water with a high total organic carbon (TOC) content 1,4-dioxane extraction recoveries dropped to **80%** (3% RSD, $n = 7$).

Problem: Ammonium chloride was substituted for the Trizma®, but caused precipitate formation in some samples, restricting flow during the extraction. Recoveries exhibited a **10-20% loss** when precipitate was formed.

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Final Preservation and Dechlorination

- Sodium bisulfate – microbial inhibitor
  a. acidifying agent, solid
  b. 1 g/L of sodium bisulfate reduced drinking water matrices to pH <3
  c. microbial viability is limited to a pH range of 4.5 to 9.0
  d. sodium sulfite as a dechlorinating agent

NOTE: dechlorinating agent (sodium sulfite) must be added prior to the acidifying agent (sodium bisulfate)

A holding time experiment was performed to test the chemical stability of 1,4-dioxane in the presence of the preservation agents during simulated shipping and a 28-day+ holding time.

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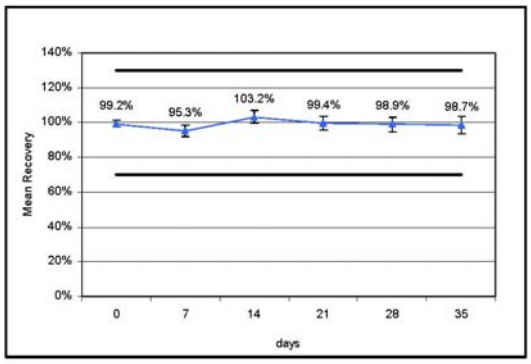
1,4-Dioxane Holding Time Study

- Stability of 1,4-dioxane in preserved drinking water stored at 10 °C for 48 hours (simulated shipping), then stored at 6 °C over a 35-day time period.
- Replicate samples (n = 7) were fortified at 1 µg/L 1,4-dioxane.
- Matrix blank data was used to correct for native analyte concentrations.
- Lower and upper control limit bars set at 70% and 130%, respectively.



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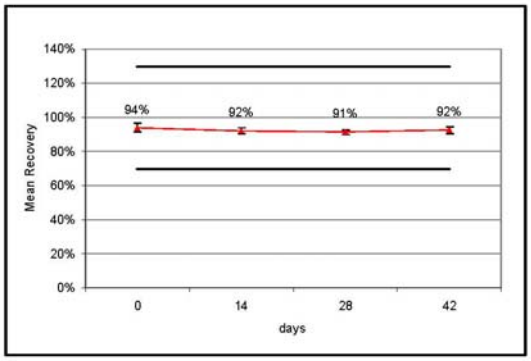
Stability of 1,4-Dioxane in Sample Extracts

- Stability of 1,4-dioxane in sample extracts stored at -5 °C over a 42-day time period.
- Replicate samples (n = 7) were fortified to a concentration of 10 µg/L 1,4-dioxane.
- Lower and upper control limit bars set at 70% and 130%, respectively.



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Method Performance in Drinking Water Matrices: Large- and Small-Scale SPE Options

- Matrix Samples Fortified at 1.0 µg/L (n = 7 for each matrix)
- Large-scale option: 500 mL extracted w/ 2 g activated carbon
- Small-scale option: 100 mL extracted w/ Waters Sep-Pak® cartridge

Compound/ Extraction Option	Surface Water	
	Mean % recovery	RSD (%)
1,4-dioxane (500 mL w/ 2g activated carbon)	99.0 [a]	4.9
1,4-dioxane-d_8 (SUR) (500 mL w/2 g activated carbon)	100	2.5
1,4-dioxane (100 mL w/ Waters Sep-Pak® cartridge)	97.0 [a]	4.6
1,4-dioxane-d_8 (SUR) (100 mL w/ Waters Sep-Pak® cartridge)	98.5	2.5
	Surface Water (high in TOC) [b]	
	Mean % recovery	RSD (%)
1,4-dioxane (500 mL w/2 g activated carbon)	102	3.5
1,4-dioxane-d_8 (SUR) (500 mL w/2 g activated carbon)	99.8	2.4
1,4-dioxane (100 mL w/ Waters Sep-Pak® cartridge)	98.5	5.6
1,4-dioxane-d_8 (SUR) (100 mL w/ Waters Sep-Pak® cartridge)	101	4.2
	Groundwater (high in mineral content) [c]	
	Mean % recovery	RSD (%)
1,4-dioxane (500 mL w/2 g activated carbon)	95.9 [a]	2.1
1,4-dioxane-d_8 (SUR) (500 mL w/2 g activated carbon)	98.2	2.5
1,4-dioxane (100 mL w/ Waters Sep-Pak® cartridge)	101 [a]	3.3
1,4-dioxane-d_8 (SUR) (100 mL w/ Waters Sep-Pak® cartridge)	104	5.9

a. Correction of matrix background from 0.42-0.77 µg/L.
b. Total organic carbon measured at 4.950 mg/L.
c. Hardness measured at 289 mg/L as calcium carbonate.

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20

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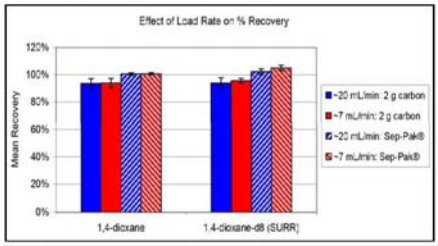
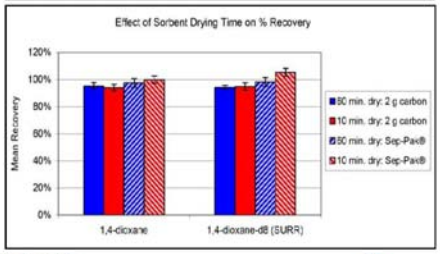
Robustness Testing – Can We Make the Extraction Fail?

- Mean recoveries of 1,4-dioxane and surrogate analyte 1,4-dioxane-d_8 at ~20 mL/min and ~7 mL/min load rates.
- The samples were LRW replicates (n = 3) fortified at 1 µg/L.
- Error bars represent ± 1 standard deviation from the mean recovery.



- Mean recoveries of 1,4-dioxane and surrogate analyte 1,4-dioxane-d_8 at 10 min and 60 min sorbent drying times.
- The samples were LRW replicates (n = 3) fortified at 1 µg/L.
- Error bars represent ± 1 standard deviation from the mean recovery.



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21

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Interlaboratory ruggedness

- Method sensitivity, accuracy, and precision in three laboratories
- Lowest concentration minimum reporting level (LCMRL) - lowest true concentration for which the future recovery is predicted to fall between 50 and 150 percent recovery (99% confidence).
- LCMRL values are well below the EPA one in 10^6 lifetime cancer risk concentration and the WHO drinking water guideline of 50 µg/L.

	LCMRL, µg/L	MDL, µg/L	% Recovery (RSD) Tap Water[a]	% Recovery (RSD) Reagent Water[b]
Lab 1	0.036	0.020	97 (4.6)	110 (20.0)
Lab 2	0.013	0.012	101 (2.3)	100 (10.1)
Lab 3	0.080	0.021	88 (6.0)	99 (7.0)

a. Fortified drinking water: 0.2-1.0 µg/L
b. Fortified reagent water: 0.03-0.10 µg/L

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Conclusions

- 1,4-Dioxane can be accurately extracted and analyzed in drinking water to sub-µg/L levels using SPE techniques coupled with GC/MS-SIM technology
- No need for specialized extraction equipment (e.g. purge-and-trap and SPME)
- Multiple vendor sources for the activated carbon SPE sorbent
- Proven rugged across a wide analytical range
- Detection limits are well below current EPA cancer risk levels

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Acknowledgements

- Alan Zaffiro and Barry V. Pepich of Shaw Environmental & Infrastructure, Inc., under contract to USEPA OGWDW Technical Support Center

- Peggy Knight and Megan Pickett of USEPA Region 10 Laboratory, Port Orchard, WA

Risk-Based Characterization and Assessment of Extractable Petroleum Hydrocarbon Contamination Using Comprehensive Two-Dimensional Gas Chromatography with Dean's Switch Modulation

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ABSTRACT

Approximately ten years have passed since the first generation of risk-based petroleum methods was developed and put into production in the environmental laboratory. However, the precise amounts of the several different solvents needed, in addition to variables affecting the fractionation media, often result in "breakthrough" of target compounds into the wrong fraction(s) and/or contamination of the final extract(s). Advances in gas chromatographic and flow control technologies can now be used to replace the tedious sample preparation techniques previously required to obtain the separate sample extracts ("fractions") used for site characterization/assessment.

Soil/wastewater samples are extracted using methylene chloride. Extracts are dried with sodium sulfate, concentrated and treated with silica gel to remove polar, non-petroleum related compounds. The final extract is then analyzed using a two-dimensional gas chromatograph (2-D GC; GC x GC) designed to separate the aliphatic and aromatic species present in the extract using flame ionization detection (FID). This new approach meets the original intent of the Massachusetts state and TPH Working Group methods to measure and quantitate collective aliphatic and aromatic hydrocarbon concentrations, as well as target polynuclear aromatic hydrocarbons (PAHs).

Risk-Based Characterization and Assessment of Extractable Petroleum Hydrocarbon Contamination Using Comprehensive Two-Dimensional Gas Chromatography with Dean's-Switch Modulation

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Approximately ten years have passed since the first generation of risk-based petroleum methods was developed and put into production in the environmental laboratory. However, the precise amounts of the several different solvents needed, in addition to variables affecting the fractionation medium often result in "breakthrough" of target compounds into the wrong fraction(s) and/or contamination of the final extract(s). Advances in gas chromatographic and flow control technologies can now be used to replace the tedious sample preparation techniques previously required to obtain the separate sample extracts ("fractions") used for site characterization/assessment.

Soil/wastewater samples are extracted using methylene chloride. Extracts are dried with sodium sulfate, concentrated and treated with silica gel to remove polar, non-petroleum related compounds. The final extract is then analyzed using a two-dimensional gas chromatograph (2-D GC; GC x GC) designed to separate the aliphatic and aromatic species present in the extract using flame ionization detection (FID).

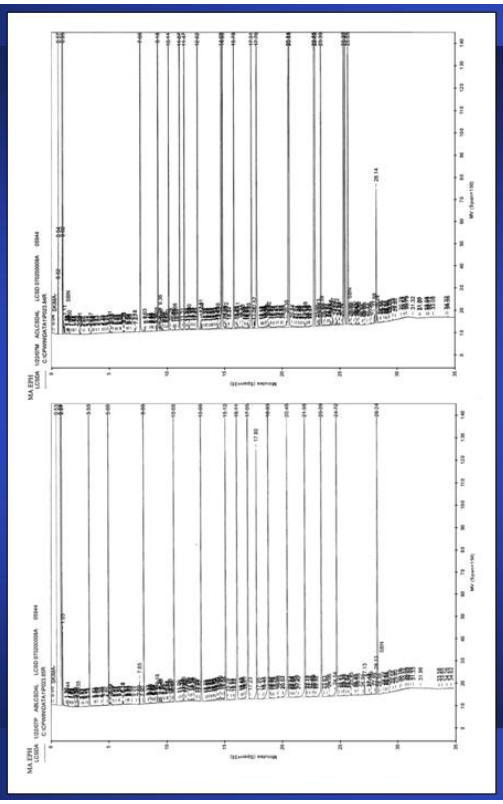
This new approach meets the original intent of the Massachusetts state and TPH Working Group methods to measure and quantitate collective aliphatic and aromatic hydrocarbon concentrations, as well as target polynuclear aromatic hydrocarbons (PAHs).

Challenges of "Classic" Fractionation Method

- Invasive prep procedure
- High consumables cost
- Highly technique-dependent
- Variability in reagents/media, etc.
- Long analysis time
- Lenient acceptance criteria

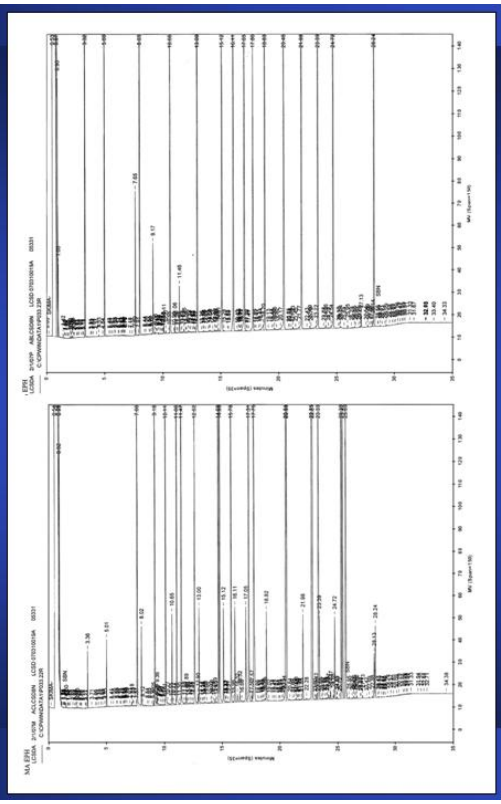
Scenario A:

Successful Fractionation



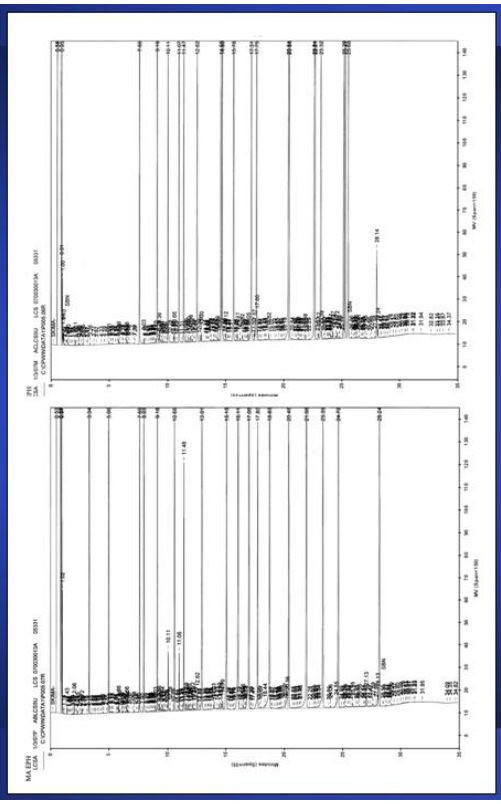
Scenario B:

Poor Fractionation; unacceptable breakthrough of naphthalene and 2-methylnaphthalene into aliphatic fraction (13% and 9%, respectively). Retention of aliphatics on silica gel column. Aliphatics end up in Aromatic fraction.



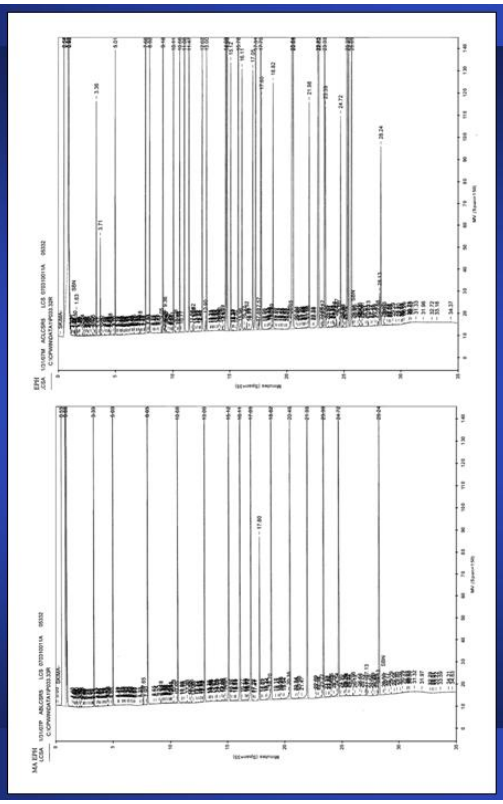
Scenario C:

Poor Fractionation; unacceptable breakthrough of naphthalene and 2-methylnaphthalene into aliphatic fraction (34% and 33%, respectively).



Scenario D:

Poor Fractionation; Retention of aliphatics on silica gel column and into aromatic fraction (31% C9-C18%; 28% C19-C36). This results in "acceptable" recoveries for all target ranges (C11-C22 aromatics = 81% vs. 61% w/out aliphatics; C9-C18 = 52%; C19-C36 = 56%).



Blind Field Duplicate Samples (MT EPH)

Sample #	EPH Screen Total (ppb)	EPH Fractionated Total (ppb)	C11-C22 Aromatics (ppb)	C9-<C19 Aliphatics (ppb	C19-C36 Aliphatics (ppb)
1111111	5,100	1600 (31%)	670 (42%)	560 (35%)	<100 (<24%)
2222222	4,900	2700 (55%)	330 (12%)	2,200 (81%)	<500 (<8%)
RPD	4%	51%	68%	119%	NA

Challenges Addressed

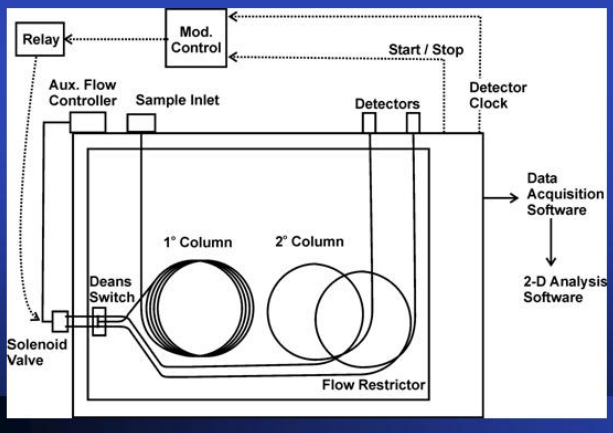
- No loss in sensitivity, accuracy or precision.
- Easy to implement in lab production environment with minimal capital investment.
- Exploit differences between two dimensions (boiling point and polarity) to separate target species chromatographically using opposing GC column phases instead of relying on tedious prep.
- Reagent volume and cost will drop.
- Time saver / money saver.

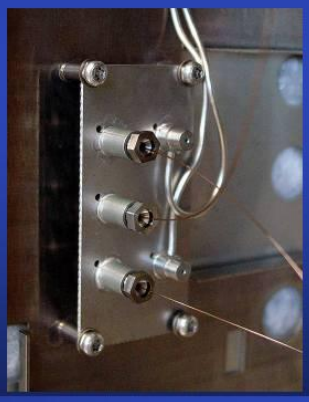
A Microfluidic Deans Switch As A GC x GC Modulator

Agilent Deans switch etched onto a metal plate.

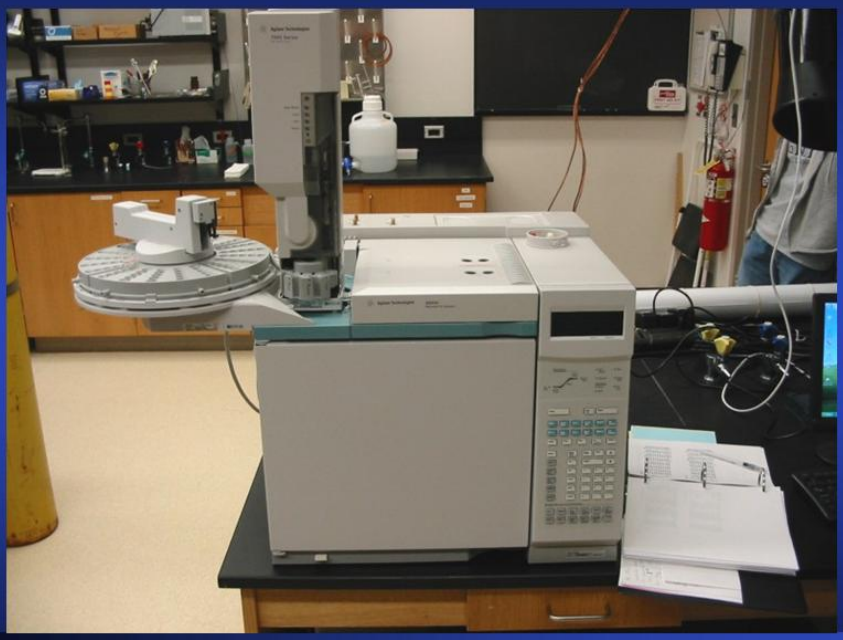
Rugged device with a very wide temperature range and inert surfaces.

Direct diversion modulation with no temperature restrictions.





Agilent 6890N Fitted With A Deans Switch Modulator



Development of GC x GC Separation

- Screen column combinations.
- Established the optimal run conditions.
- Did several SPE fractionations of Diesel Fuel and Gas-Oil to show that the aliphatic and aromatic regions were well separated.

Key Conclusions:

- The aliphatic and aromatic regions are essentially separated with the column set employed.
- This should allow silica gel fraction step to be eliminated.

Analysis Conditions/Parameters

Agilent 6890 fitted with Agilent Dean's switch flow modulator set to 1 sec modulation period. 0.07 duty cycle.

Cool on column injection of 1ul. Inlet temp tracked ~ 3C above oven temp.
1 m x 0.32 mm fused silica retention gap ("guard column")
Primary column: DB-17ht (45M x 0.25mm x 0.15um)
Secondary column: DB-1ht (2.5M x 0.25mm x 0.1um)

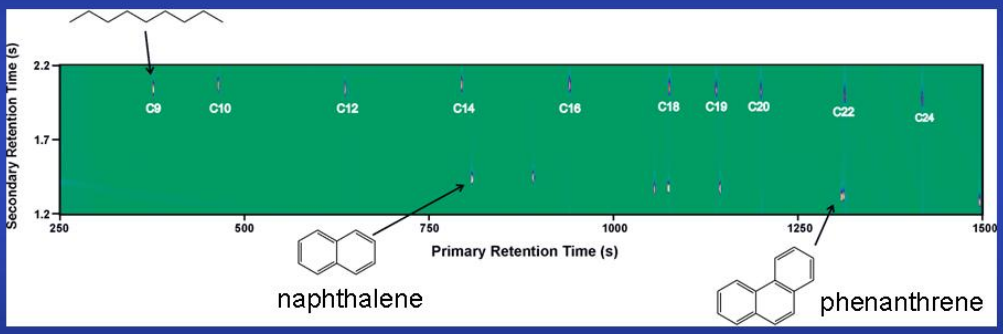
FIDs @ 340C

Carrier gas: Hydrogen
Primary flow: 1 ml/min
Secondary flow: 10 ml/min split between the 2o column and flow restrictor.
Oven Program: 40C for 3.25 min; 13C/min to 70C; 10.5 C/min to 120C; 9.5C/min to 340C; hold @ 340C 5 min.

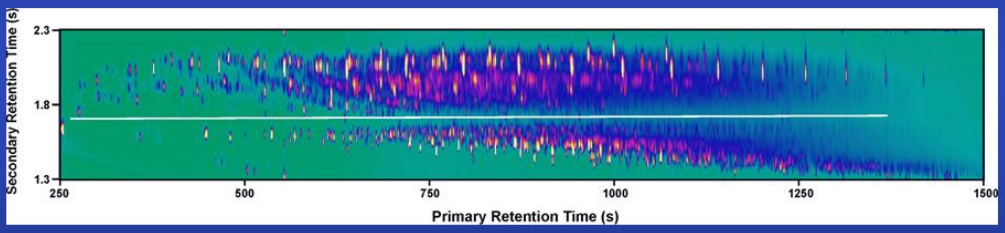
Run time: 35 minutes

FIDs were set at 340 oC

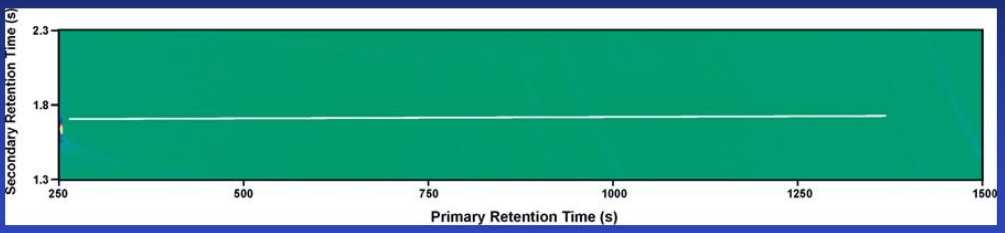
Examples of Two-Dimensional Chromatograms



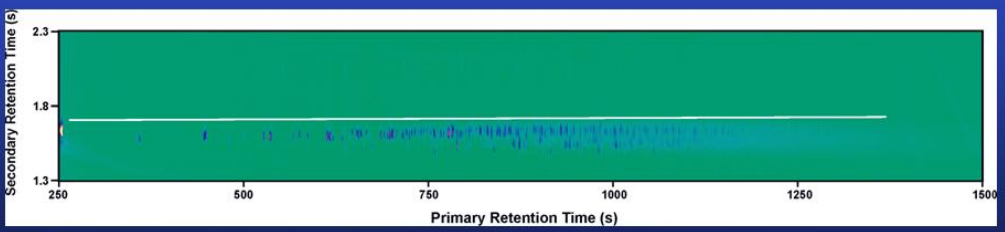
0.2% Diesel Fuel in Hexane (Dividing Line)



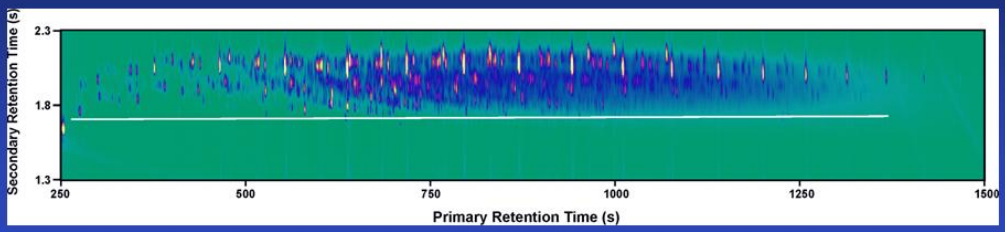
0 to 5 ml Hexane Fraction



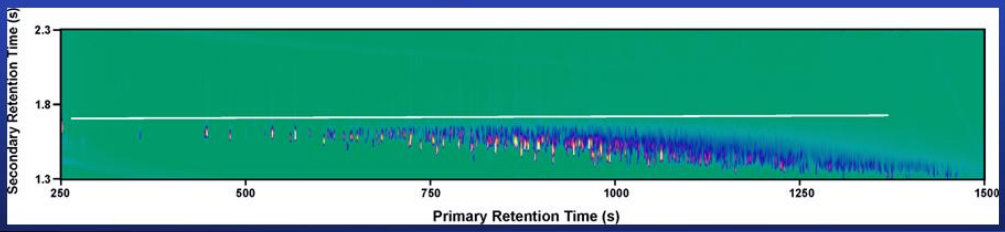
0 to 5 ml Methylene Chloride Fraction



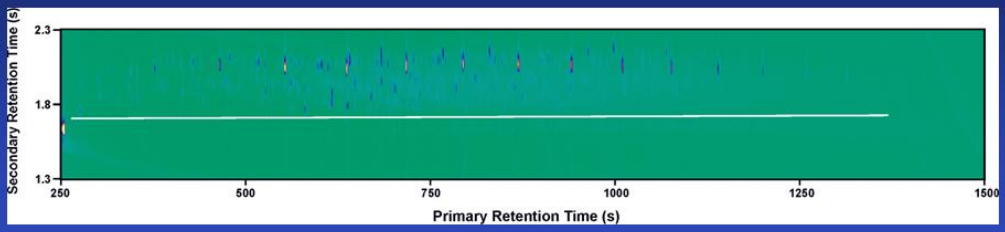
5 to 10 ml Hexane Fraction



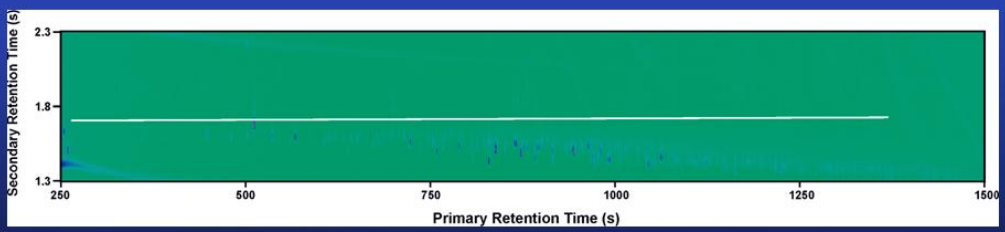
5 to 10 ml Methylene Chloride Fraction



10 to 15 ml Hexane Fraction



10 to 15 ml Methylene Chloride Fraction



Testing Water Samples That Have Been Analyzed With Standard Methods

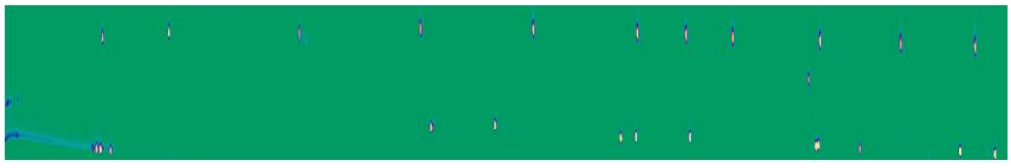
Calibrated system.

Checked calibration with LCS and LCSD. Excellent Agreement. (95% certainty)

Checked calibration with known mixtures of diesel fuel. Excellent Agreement. (95% certainty)

Analyzed water extracts and measured much higher aromatic content than determined with conventional methods.

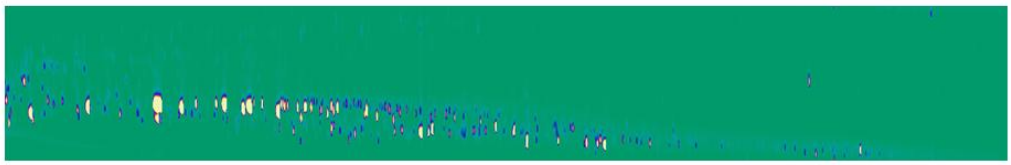
LCSD for water sample.
Components are 40 ppm in CH2Cl2.
Calibration results correctly predict concentrations to within 5%
This picture shows the spatial ranges of the n-alkanes and PAHs.
File Name: 1218LCD2



Sample #: 4912819
GC File Name: 121819

Reported Concentrations
Alkanes C9-C18: 350 ppb
Alkanes C19-C36: N.D.
Aromatics C11-C22: 100 ppb

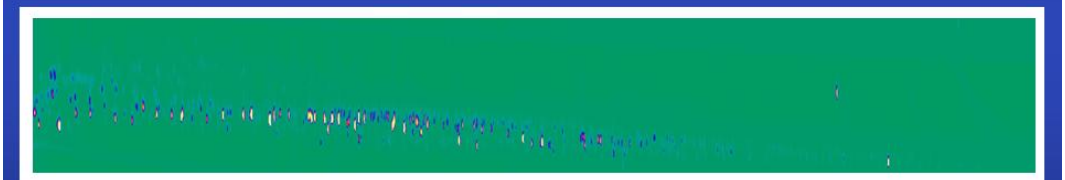
GCxGC Measured Concentrations
Alkanes C9-C18: 25 ppb
Alkanes C19-C36: N.D.
Aromatics C11-C22: 1,500 ppb



Sample #: 4912821
GC File Name: 1218121

Reported Concentrations
Alkanes C9-C18: 260 ppb
Alkanes C19-C36: N.D.
Aromatics C11-C22: 220 ppb

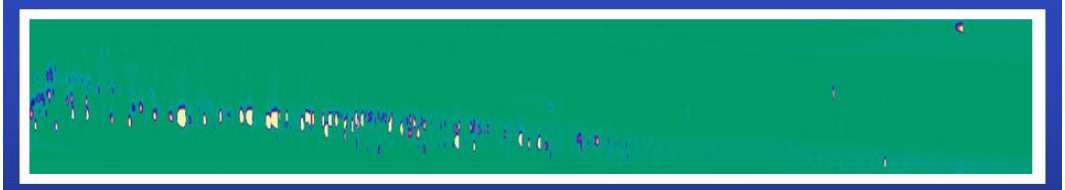
GCxGC Measured Concentrations
Alkanes C9-C18: 16 ppb
Alkanes C19-C36: N.D.
Aromatics C11-C22: 790 ppb



Sample #: 4912822
GC File Name: 121822

Reported Concentrations
Alkanes C9-C18: 1200 ppb
Alkanes C19-C36: N.D.
Aromatics C11-C22: 210 ppb

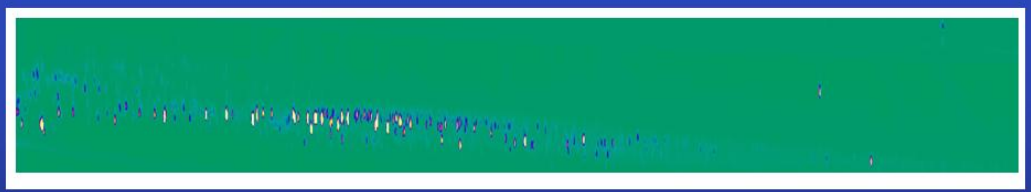
GCxGC Measured Concentrations
Alkanes C9-C18: 15 ppb
Alkanes C19-C36: N.D.
Aromatics C11-C22: 1,600 ppb



Sample #: 4912827
GC File Name: 121827

Reported Concentrations
Alkanes C9-C18: 380 ppb
Alkanes C19-C36: N.D.
Aromatics C11-C22: 300 ppb

GCxGC Measured Concentrations
Alkanes C9-C18: 15 ppb
Alkanes C19-C36: N.D.
Aromatics C11-C22: 1,100 ppb



Analysis of Soil Samples

Switched to ZB-50 Primary column and DB-1 secondary column.

Same tailing issues as DB-17ht x DB-1ht combination.

Recalibrated system.

Checked calibration with LCS and LCSD mixtures and got excellent agreement. (95% certainty)

Analyzed soil samples.

Analysis Conditions/Parameters

Agilent 6890 fitted with Agilent Dean's switch flow modulator set to 1 sec modulation period. 0.07 duty cycle.

Cool on column injection of 1ul. Inlet temp tracked ~ 3C above oven temp.
1 m x 0.32 mm fused silica retention gap ("guard column")
Primary column: ZB-50 (30M x 0.25mm x 0.25um)
Secondary column: DB-1 (2.5M x 0.25mm x 0.1um)

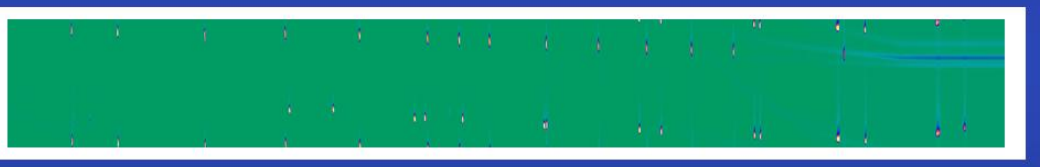
FIDs @ 340C

Carrier gas: Hydrogen
Primary flow: 1 ml/min
Secondary flow: 10 ml/min split between the 2o column and flow restrictor.
Oven Program: 40C for 2.5 min; 12C/min to 110C; 10.5C/min to 340C; hold @ 340C 5 min.

Run time: 35 minutes

FIDs were set at 340 oC

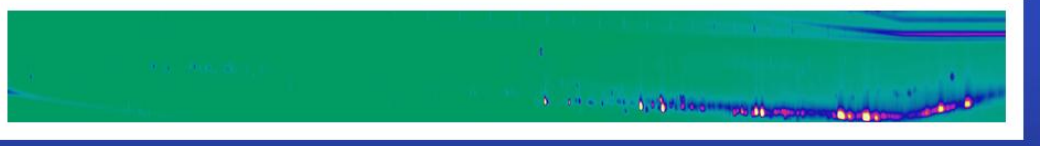
Sample #: Level 4 Std (20 ppm of each compound)
GC File Name: 0214CS4



Sample #: 4957951 (5X dilution)
GC File Name: 021551_5

Reported Concentrations
Total Aliphatic: 70 ppm
Total Aromatic: 260 ppm

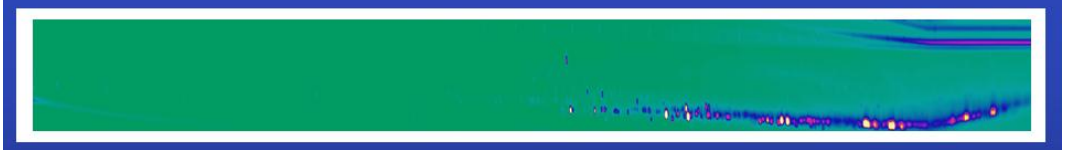
GCxGC Measured Concentrations
Total Aliphatic: N.D.
Total Aromatic: 650 ppm



Sample #: 4957952 (5X dilution)
GC File Name: 021552_5

Reported Concentrations
Total Aliphatic: 13 ppm
Total Aromatic: 300 ppm

GCxGC Measured Concentrations
Total Aliphatic: N.D.
Total Aromatic: 580 ppm



Sample #: 4957955 (20X dilution)
GC File Name: 0215520

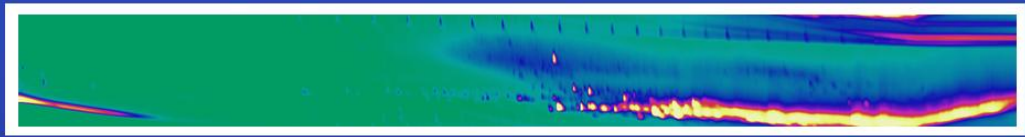
Reported Concentrations
Total Aliphatic: 130 ppm
Total Aromatic: 680 ppm

GCxGC Measured Concentrations
Total Aliphatic: ND
Total Aromatic: 870 ppm

Sample #: 4957954
GC File Name: 02167954

Reported Concentrations
Total Aliphatic: 400 ppm
Total Aromatic: 830 ppm

GCxGC Measured Concentrations
Total Aliphatic: N.D.
Total Aromatic: 730 ppm



Challenges Met

- More accurate/precise data.
- Perform “routine” TPH extraction.
  No need for solvent exchange, multiple concentrations or fractionation steps.
- Minimal hardware/software upgrades.
- Simplified prep procedure results in only one sample extract for analysis, cutting run time in half.
- Easy to implement without sacrificing extra lab space.

AUTHOR INDEX

NATIONAL ENVIRONMENTAL MONITORING CONFERENCE PROCEEDINGS 2008

AUTHOR INDEX