Mass Spectrometric Methods for Definitive Analysis of Perchlorate Compared to IC/Conductivity Method

October 2003

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MS Methods Used by STL

- LC/MS, single-stage mass spectrometry
  Method shown to work in 2001, but quickly dropped
- LC/MS/MS, triple-stage mass spec.
  Used as definitive method for 2 yrs, 2 instruments
- New IC/MS/MS
  Will show results from early tests

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Advantages of MS/MS Detection

- Used in preference to single MS
- With MS, only analyzing molecular ions
- MS/MS provides structural information from fragmentation
- Quiet background & better chromatography in difficult samples

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Natural Isotopes of Chlorine Provide Confirmation MS Methods

Molecular ions analyzed in first stage:

$ClO4^-$ = $Cl^{35}+4O^{16}$ = m/z 99, 75.5% abundance

= $Cl^{37}+4O^{16}$ = m/z 101, 24.5% abundance

Daughter ions analyzed in third stage:

$ClO3^-$ = $Cl^{35}+3O^{16}$ = m/z 83

= $Cl^{37}+3O^{16}$ = m/z 85

- **<u>QC Suggestion to EDQW</u>:**
  Require monitoring of ion ratios for all MS work

Characteristics Considered When Validating Methods

Linearity - predictable instrument response

Sensitivity - low concentration reliably detected

Precision - reproducibility of results

Accuracy - proximity of results to true value

Selectivity - ability to differentiate compound of interest from interferences

Ruggedness- ability of method to work properly in a variety of types of samples

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Groundwater Used for February 2003 Study

Groundwater from Missouri Landfill

General water quality parameters:

pH	= 8.0
Conductivity	= 1,600 uS
TDS	= 1,100 mg/L
Alkalinity	= 440 mg/L (as CaCO3)
Sulfate	= 460 mg/L
Chloride	= 75 mg/L

Groundwater Spikes Prepared for 2003 Study

	IC/Conductivity	LC/MS/MS
Blanks :	2 replicates	2 replicates
0.1 ug/L:	8 replicates	8 replicates
0.4 ug/L:	8 replicates	8 replicates
1.0 ug/L:	8 replicates	8 replicates
2.5 ug/L:	8 replicates	8 replicates
5.0 ug/L:	8 replicates	8 replicates

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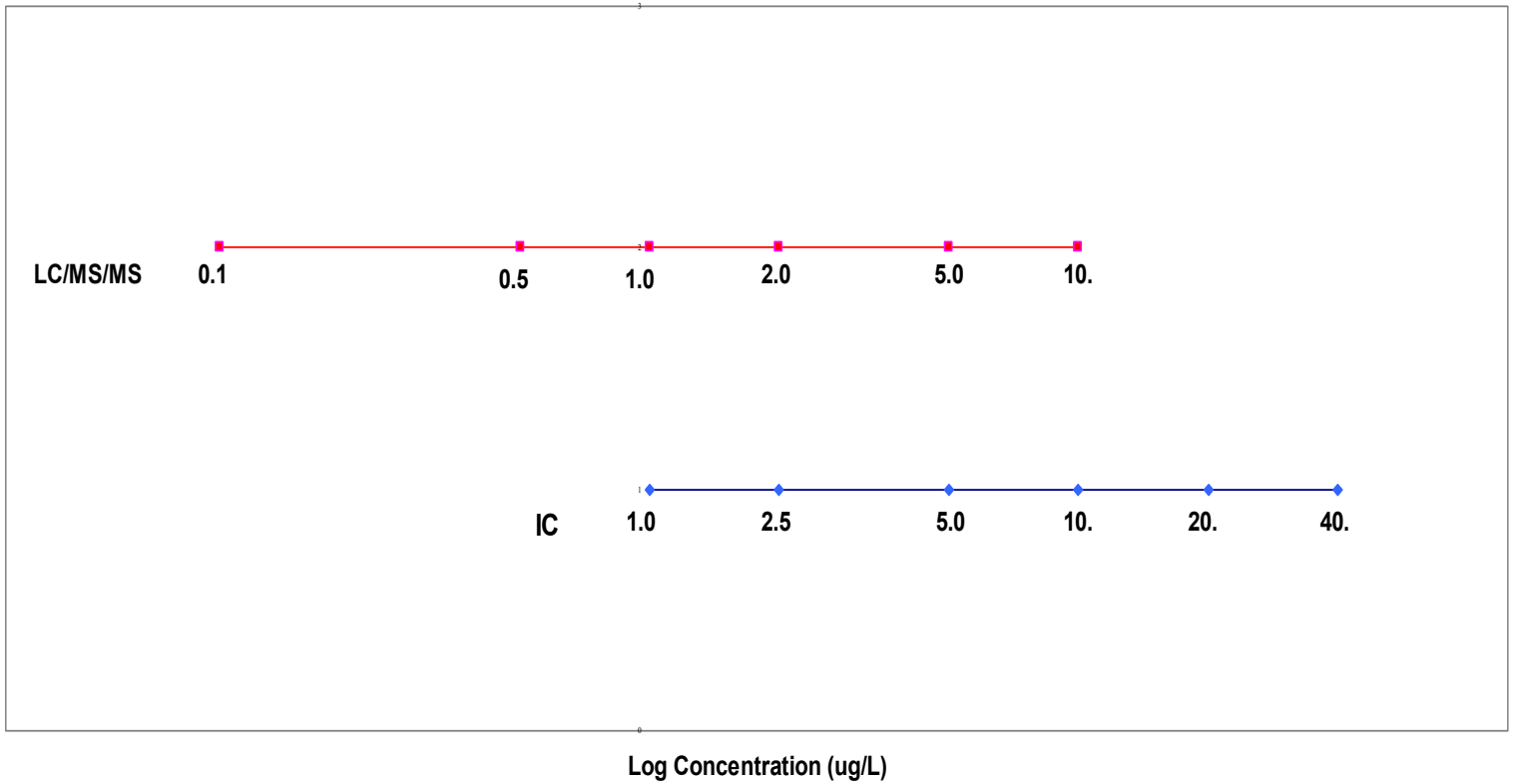
Calibration Range

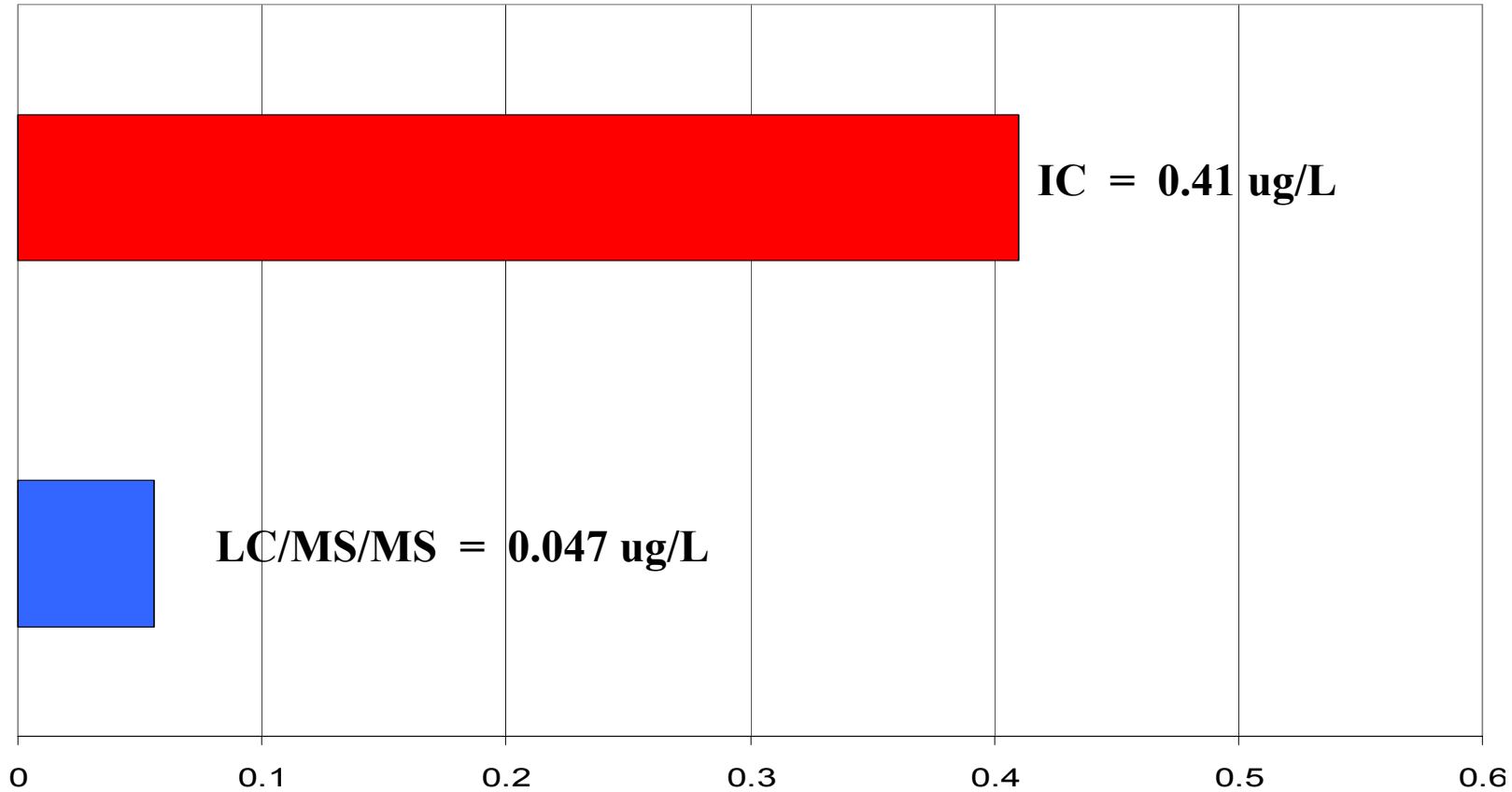


Performance Characteristics

1. Method Sensitivity

Method Detection Limits in Groundwater

(8 replicates: 1.0 ppb for IC, 0.1ppb for LC/MS/MS)



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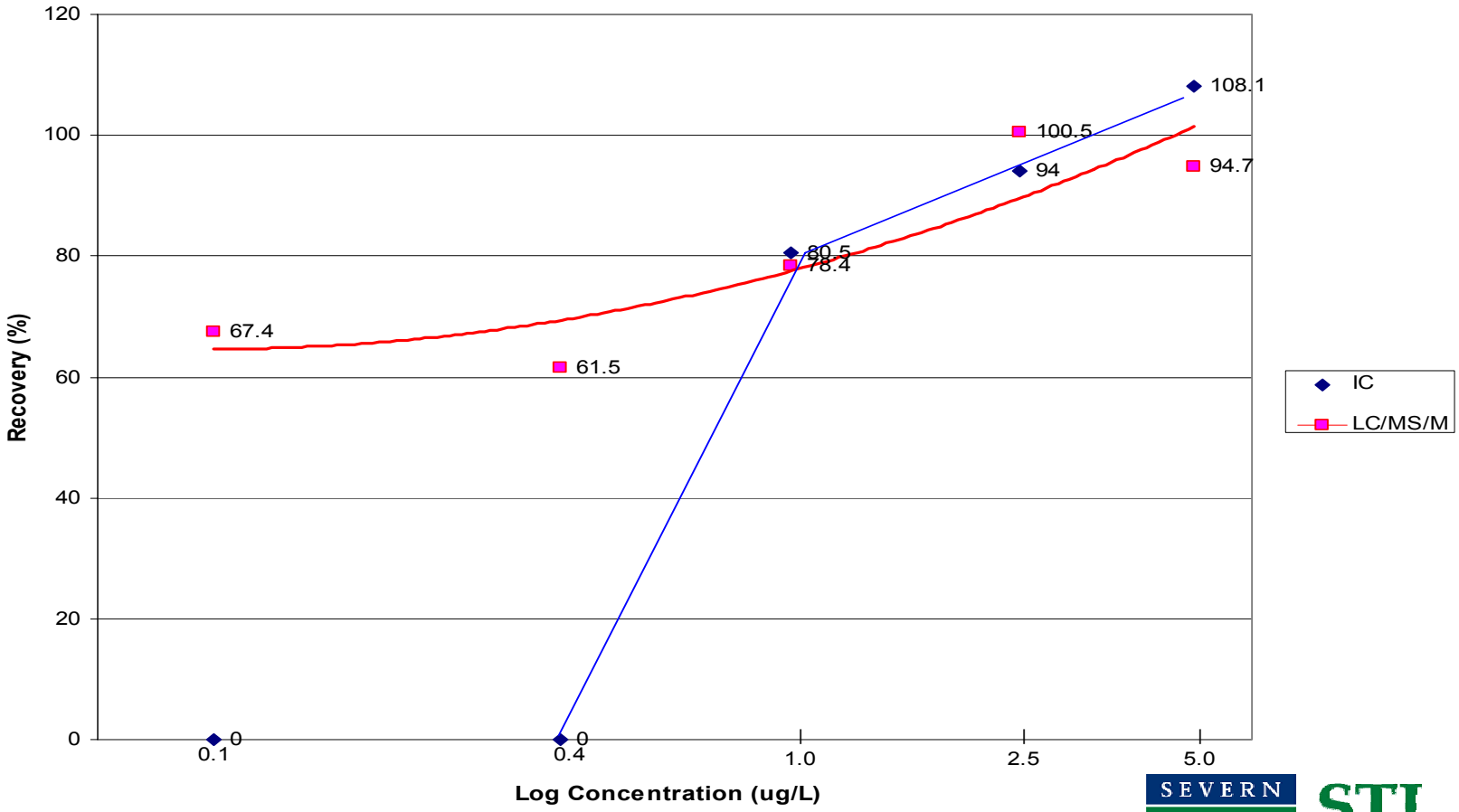
Sensitivity Issues

- LC/MS/MS is approximately 10 times more sensitive than IC/Conductivity
- Further conclusions about sensitivity made after accuracy data examined

Performance Characteristics

3. Method Accuracy

Recovery In Groundwater for Both Methods



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Quality Control Suggestion

- IC MDL does not verify, none of 8 replicates below 1.0 ug/L detected
- From graph estim. IC MDL = 0.7 ug/L

➢ **QC Suggestion to EDQW:**

Require MDL verification (spike at 2x MDL) in sample matrix for IC work

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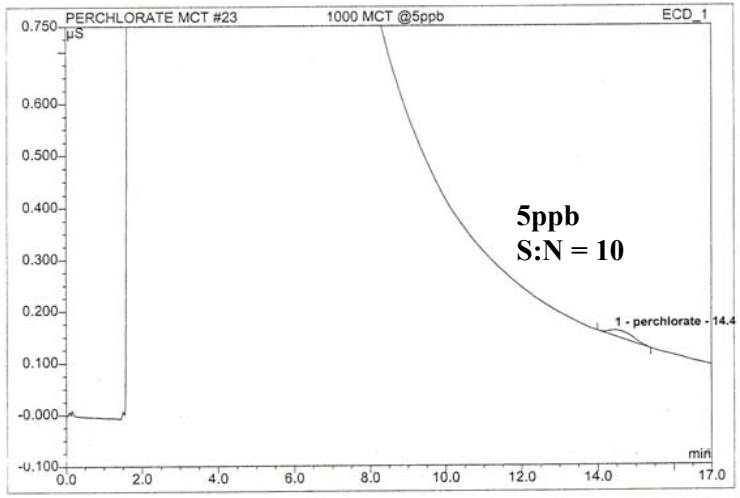
IC Detection Limit Near Maximum Conductivity Threshold (MCT)

23 1000 MCT @5ppb

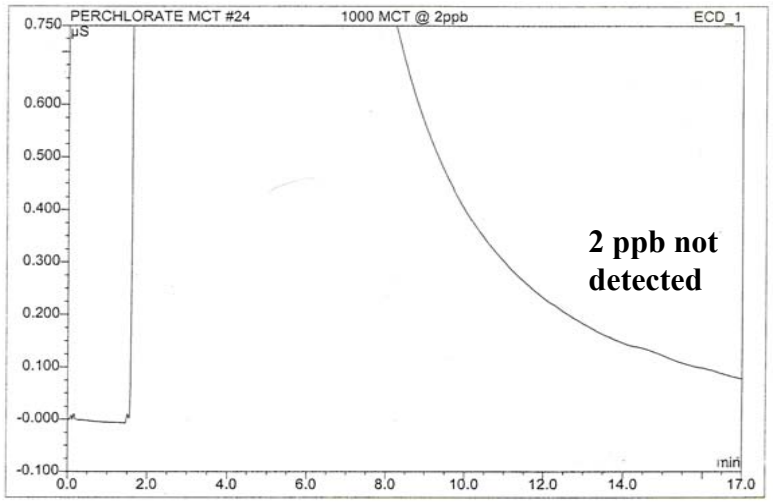
Sample Name:	1000 MCT @5ppb	Injection Volume:	1000.0
Vial Number:	23	Channel:	ECD_1
Sample Type:	unknown	Wavelength:	n.a.
Control Program:	Perchlorate Program 11-19-02	Bandwidth:	n.a.
Quantif. Method:	IC5 Perch Low Quant Method 12-16-02	Dilution Factor:	1.0000
Recording Time:	1/18/2003 3:36	Sample Weight:	1.0000
Run Time (min):	17.00	Sample Amount:	1.0000



No.	Ret.Time min	Peak Name	Height µS	Area µS*min	Rel.Area %	Amount ug/L	Type
1	14.45	perchlorate	0.011	0.010	100.00	3.979	BMB
Total:			0.011	0.010	100.00	3.979	

24 1000 MCT @ 2ppb

Sample Name:	1000 MCT @ 2ppb	Injection Volume:	1000.0
Vial Number:	24	Channel:	ECD_1
Sample Type:	unknown	Wavelength:	n.a.
Control Program:	Perchlorate Program 11-19-02	Bandwidth:	n.a.
Quantif. Method:	IC5 Perch Low Quant Method 12-16-02	Dilution Factor:	1.0000
Recording Time:	1/18/2003 3:56	Sample Weight:	1.0000
Run Time (min):	17.00	Sample Amount:	1.0000



No.	Ret.Time min	Peak Name	Height µS	Area µS*min	Rel.Area %	Amount ug/L	Type
Total:			0.000	0.000	0.00	0.000	

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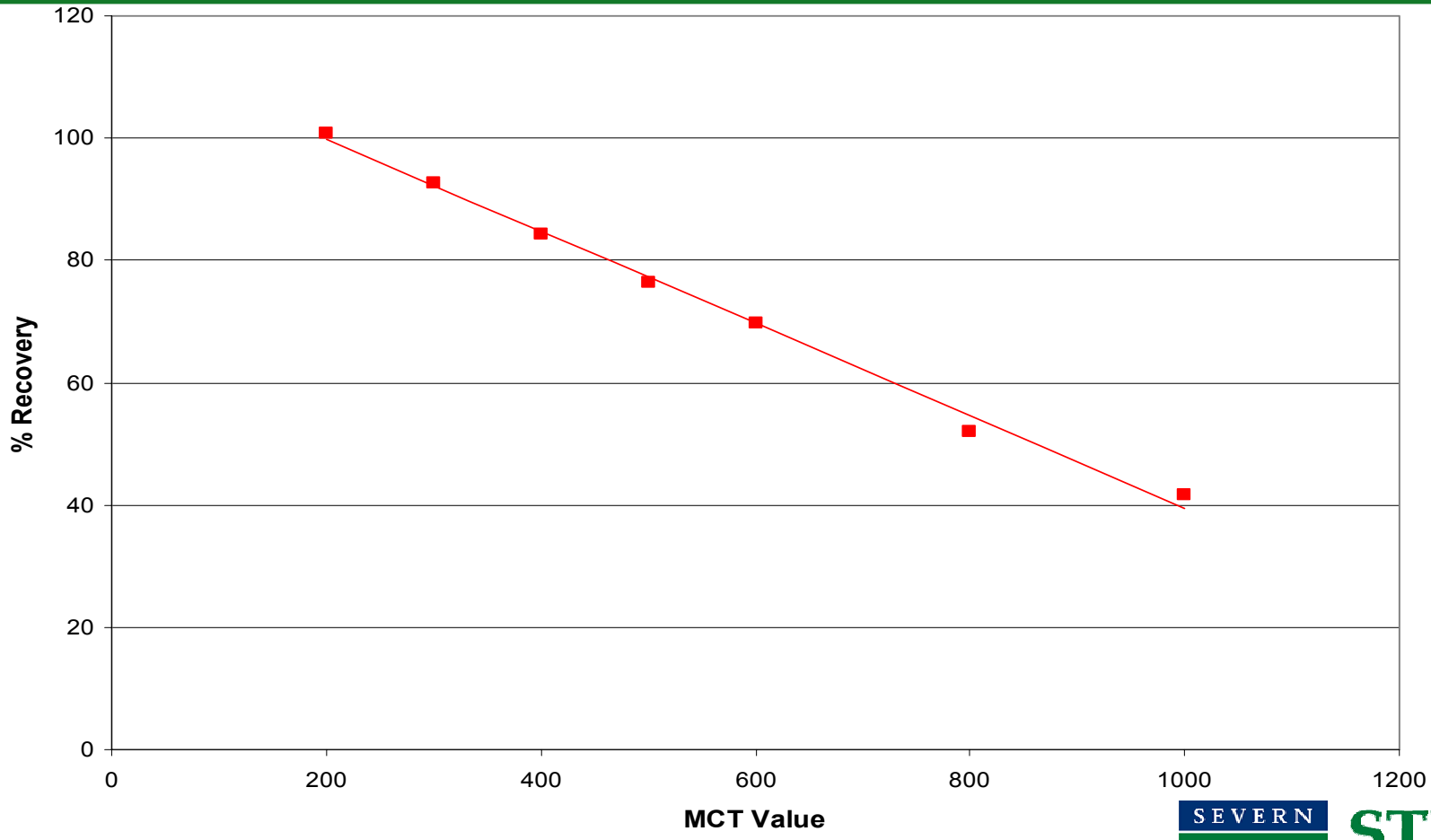
Ionization Suppression at ESI Interface
(5 ppb Perchlorate, uncorrected recovery)



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Techniques for Controlling Effect of Ionization Suppression – LC/MS/MS

1. Method of additions used for every sample

   Correction applied to 2003 groundwater data

2. More recently using O-18 labeled perchlorate added to all solutions, & calculation by isotope dilution technique

- **<u>QC Suggestion to EDQW</u>:**

  Accuracy <u>must</u> be measured and controlled in every sample

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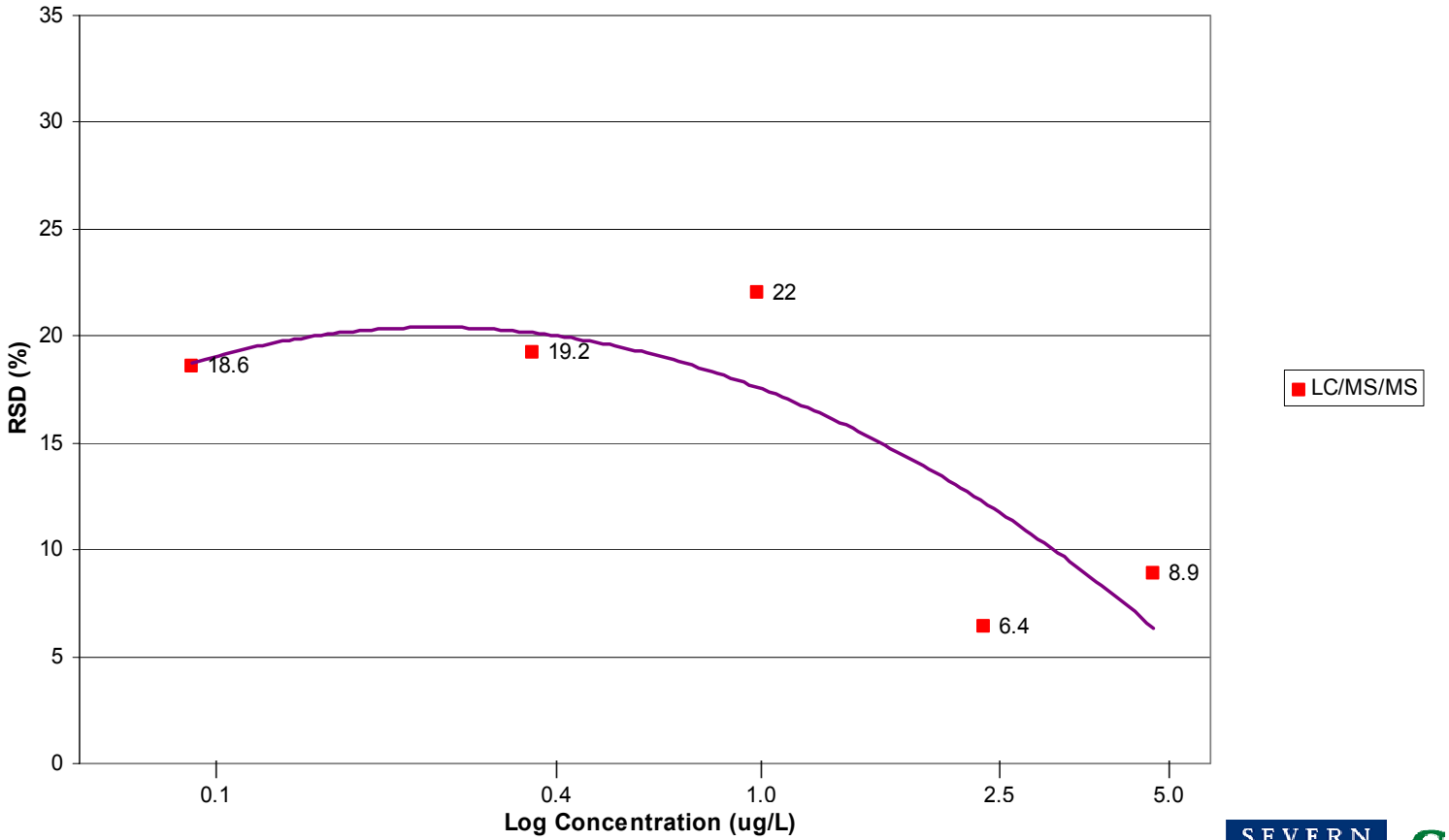
Performance Characteristics

2. Method Precision

2003 Groundwater Study
Precision for LC/MS/MS



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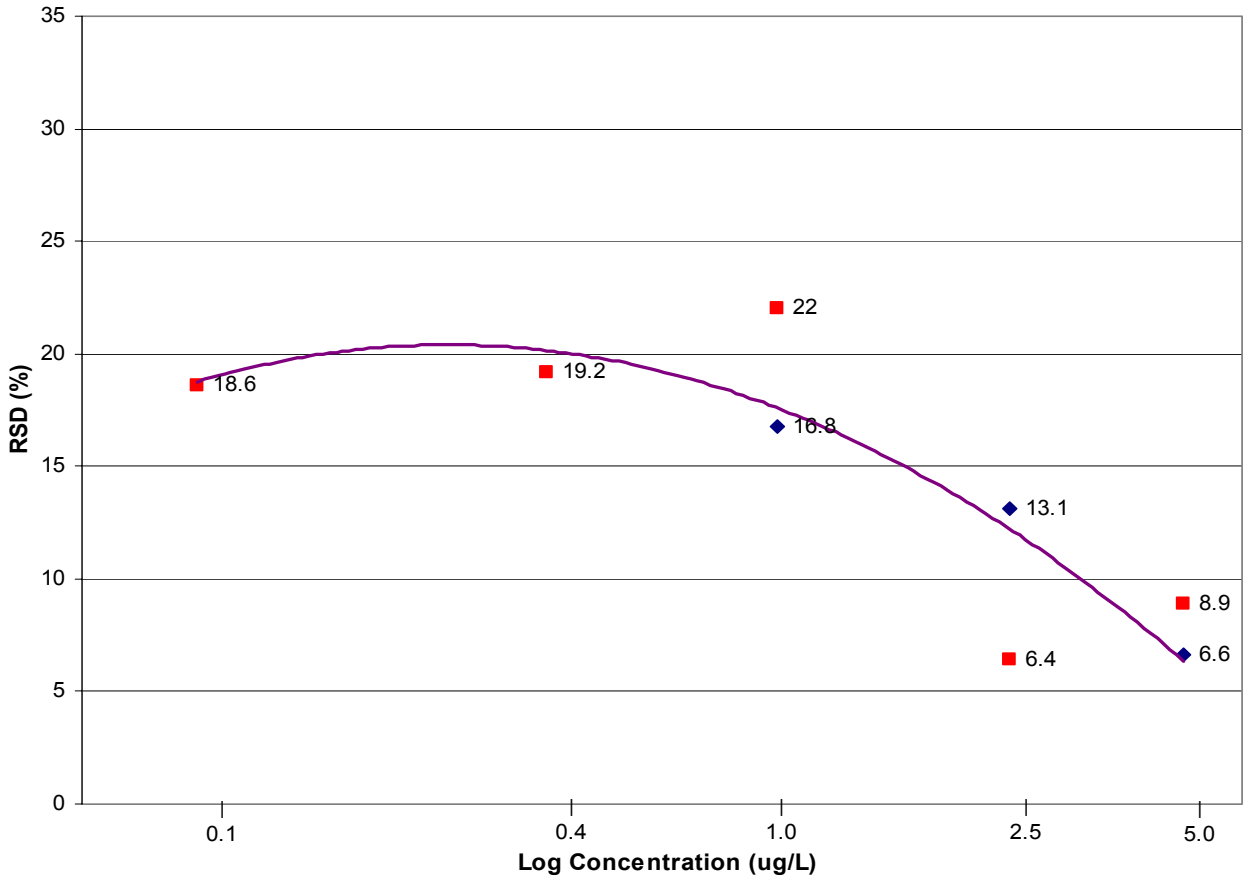
Precision in Groundwater is Equivalent for Both Methods



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Method Performance Characteristics
2003 Groundwater Study

	IC	LC/MS/MS
Linear Range:	1-40 ug/L	0.1-10 ug/L
Precision (RSD):	7-17%	6-22%
Accuracy:	0-108%	62-101%
MDL in GW:	~0.7 ug/L	0.047 ug/L

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Performance Characteristics

4. Method Selectivity

Selectivity Concerns

- Qualitative reliability/selectivity was not a problem in our groundwater study, but
- Tests continue to show serious IC/Conductivity problems due to:
  - Perchlorate RT shifts of up to 1.2 minutes
  - Co-elutions with unidentified interfering substances

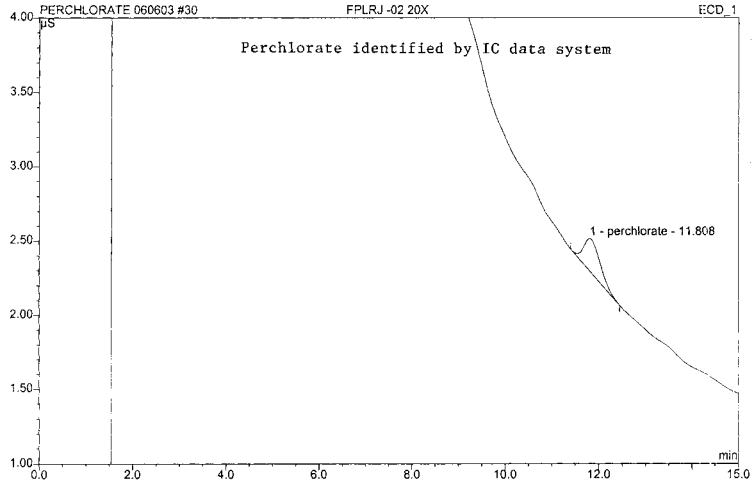
Treated Wastewater from Rocket Motor Manufacturer by 314.0

- Sample diluted 20x because of high conductivity
- Calculated result 670 ug/L perchlorate
- Similar to result reported by another laboratory

30 FPLRJ -02 20X

Sample D3E290330-02 20x dilution

Sample Name:	**FPLRJ -02 20X**	*Injection Volume:*	**1000.0**
Vial Number:	**19**	*Channel:*	**ECD_1**
Sample Type:	**unknown**	*Wavelength:*	**n.a.**
Control Program:	**Perchlorate Program 11-19-02**	*Bandwidth:*	**n.a.**
Quantif. Method:	**IC5 Perch Low Quant Method 12-16-02**	*Dilution Factor:*	**20.0000**
Recording Time:	**6/8/2003 3:46**	*Sample Weight:*	**1.0000**
Run Time (min):	**15.00**	*Sample Amount:*	**1.0000**



No.	Ret.Time min	Peak Name	Height µS	Area µS*min	Rel.Area %	Amount ug/L	Type
1	11.81	perchlorate	0.217	0.091	100.00	670.546	BMB
Total:			0.217	0.091	100.00	670.546	

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Treated Wastewater from Rocket Motor Manufacturer by 314.0
(Continued)

- Sample tested by LC/MS/MS
- Perchlorate was not detected, < 0.2 ug/L
- Which is correct?

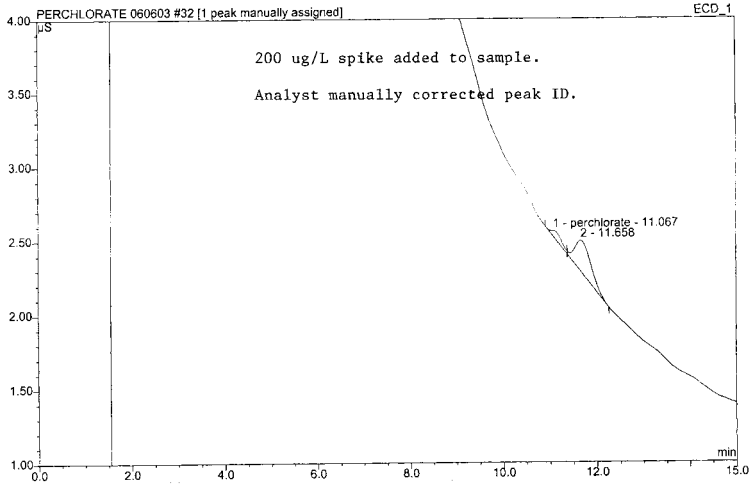
Treated Wastewater from Rocket Motor Manufacturer by 314.0 (Continued)

- 200 ug/L perchlorate addition produces 2nd peak, original peak cannot be perchlorate
- 0.6 minute RT shift
- Every sample from site had false positive

32 FPLRJ -02 20X MS

Sample D3E290330-02 matrix spike, 20x dilution

Sample Name:	**FPLRJ -02 20X MS**	*Injection Volume:*	**1000.0**
Vial Number:	**21**	*Channel:*	**ECD_1**
Sample Type:	**unknown**	*Wavelength:*	**n.a.**
Control Program:	**Perchlorate Program 11-19-02**	*Bandwidth:*	**n.a.**
Quantif. Method:	**IC5 Perch Low Quant Method 12-16-02**	*Dilution Factor:*	**20.0000**
Recording Time:	**6/8/2003 4:21**	*Sample Weight:*	**1.0000**
Run Time (min):	**15.00**	*Sample Amount:*	**1.0000**



No.	Ret.Time min	Peak Name	Height µS	Area µS*min	Rel.Area %	Amount ug/L	Type
1	11.07	perchlorate	0.035	0.014	14.03	102.412	BM ^
2	11.66	n.a.	0.208	0.086	85.97	n.a.	MB
Total:			0.243	0.100	100.00	102.412	

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Example from Last 2 Weeks Sanitary Landfill Leachate

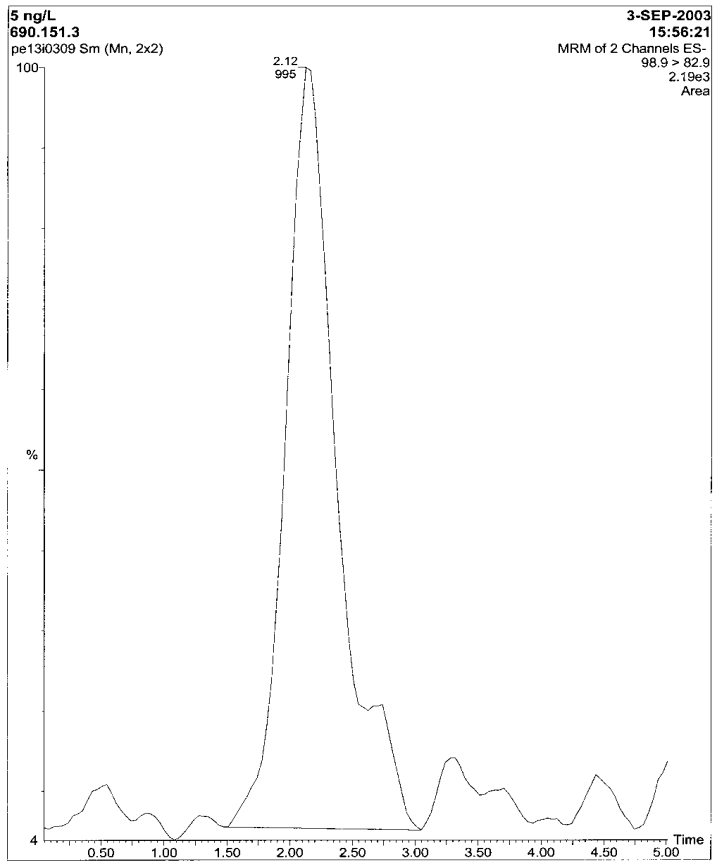
- Landfill had no history of disposal of munitions, fireworks, air bags, etc.
  - 314.0 Perchlorate Results = 7,200 ug/L
  - LC/MS/MS Perchlorate < 5 ug/L

Unique IC/MS/MS Configuration

- Quieter background
- Better separation
- Conductivity/MS/MS detection

Unique IC/MS/MS (cont.)

5 ppt Calibration Standard



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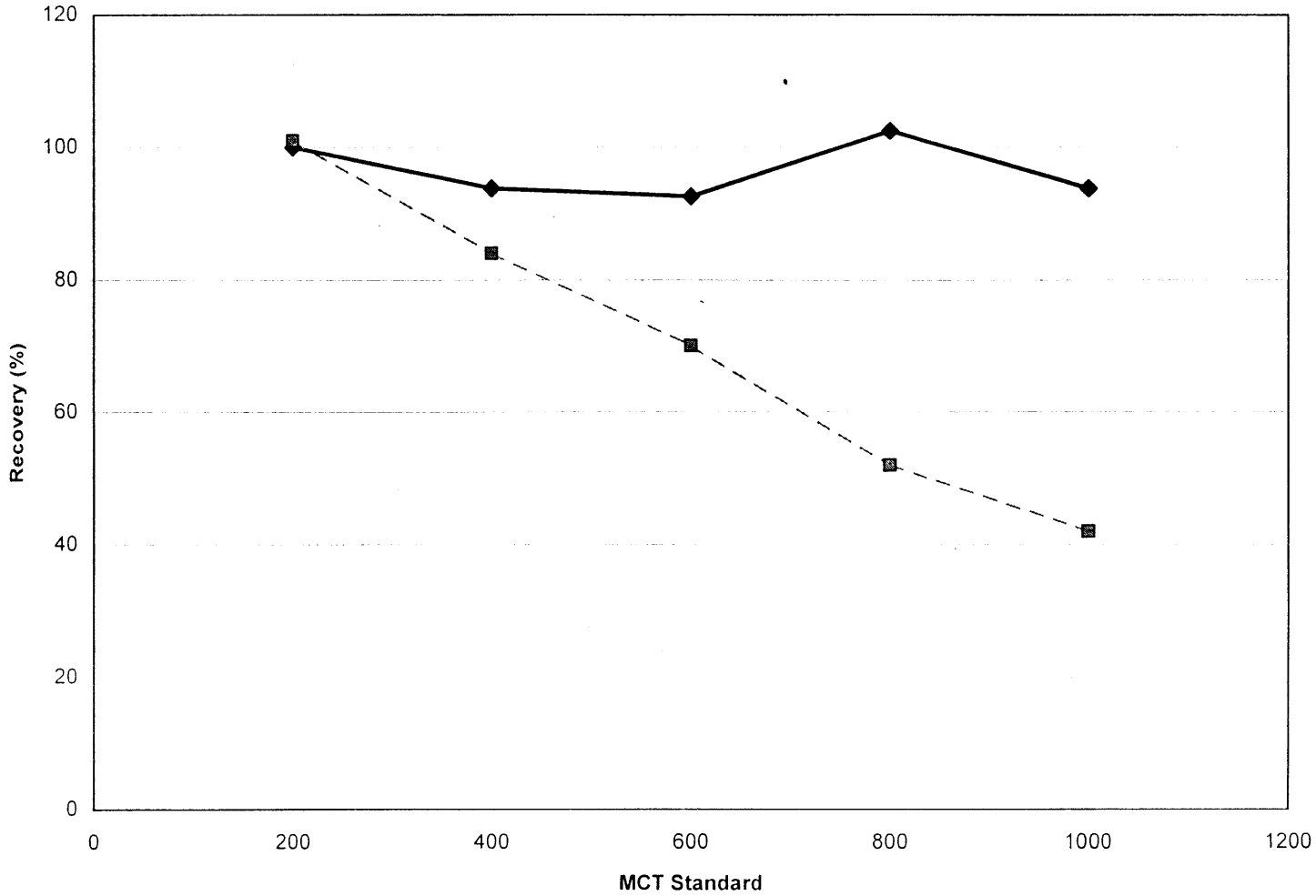
Unique IC/MS/MS (cont.)

- Working range 5 – 100 ng/L
- Minimal ESI ionization suppression

Change in Perchlorate Recovery Versus Anion Concentration

5 ppb Perchlorate for LC/MS/MS 0.05 ppb Perchlorate for IC/MS/MS

Without Isotope Dilution or Standard Addition Correction



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Unique IC/MS/MS (cont.)

- **IC/MS/MS Research Samples at STL:**
  - **Analysis of ancient brines for naturally occurring perchlorate in continental US**
  - **Analysis of leaves from deep-rooted desert plants to use as indicator of subterranean perchlorate**
- **These tests, plus controlled method performance study are underway**
- **May replace LC/MS/MS**

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