

A Product Defense Story:

Perchlorate in Fertilizers

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Presented by

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- ☛ Dr. Wayne P. Robarge, NCSU, data on fertilizers samples & technical assistance
- ☛ Dr. Edward T. Urbansky, publications cited throughout
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Perchlorate Contamination: A Public Health Issue?

- ☛ Disrupts production of thyroid hormones
- ☛ Safe concentration yet to be determined
 - California has established an action level of 18 ppb in drinking water supplies
 - primary route of exposure: oral uptake
- ☛ Added to the EPA's drinking water candidate contaminate list in 1998
- ☛ Perchlorate added to UCMR List 1 for assessment monitoring.

Past & Current Activities

- ☛ **Ongoing Characterization in Water Sources**
- ☛ **Methodology Investigations for Materials High Dissolved Solids (Fertilizers)**
- ☛ **Remediation Mechanisms Being Studied**
- ☛ **EPA is Gathering Information for Risk Characterization**
- ☛ **Sources of Contamination Being Researched**

Common Sources:

- ☛ Rockets
- ☛ Missiles
- ☛ Fireworks
- ☛ Match production
- ☛ Medicinal
- ☛ *Fertilizers?*

Methodology Investigations

- ☛ Various Analytical Techniques
 - IC, capillary electrophoresis, Electrospray Mass Spec., Raman Spectroscopy
- ☛ Issues - Sampling, Extraction Techniques, Detection Limits, Anion Interference
- ☛ These and Other Methodology Issues have been addressed through a Coordinated Effort.
- ☛ Developing a Robust Set of Data for Fertilizer Materials and Products

Concentrations in Fertilizer Components?

Table 1

Table 1. Perchlorate Concentrations in Fertilizer Compounds

component	perchlorate %
phosphate rock (western)*	0.10 +/- 0.01
phosphate rock (Florida)*	0.11 +/- 0.02
potash (commercial)	0.29 +/- 0.03
potash (muriate)	0.36 +/- 0.04
dihydrogen ammonium phosphate*	0.46 +/- 0.05
urea	0.25 +/- 0.02
langbenite	1.86 +/- 0.21
Chilean nitrate	3.64 +/- 0.34

*Samples purchased from NIST

Source: Sursala, S. et al, Perchlorate Identification in Fertilizers, *Environmental Science & Tech*

Table 2. Perchlorate Concentrations in Commercial Fertilizers

values not duplicated using EPA/600/R-01/026

brand/description (N-P-K)	manufacturer	perchlorate %
ammonium nitrate 34-0-0	Gold Kist Commerce, GA	0.22 +/- 0.04
Lesco 17-3-11	Lesco Rocky River, OH	0.57 +/- 0.03
Procare 10-10-10	Gro Tech Inc.,GA	0.20 +/- 0.08
fallfeed winterizer 18-6-12	Purcell Industries, AL	0.15 +/- 0.08
STA-Green 12-6-6	Purcell Industries, AL	0.84 +/- 0.18
Scotts Winterizer 22-4-14	The Scotts Co., OH	0.51 +/- 0.05
Vigaro 10-10-10	Gro Tech Inc.,GA	0.55 +/- 0.06
premium lawn 27-2-5	Vigoro Industries, Fl.	0.33 +/- 0.08
Pennington 34-0-0	Gro Tech Inc.,GA	0.61 +/- 0.04

Source: Sursala, S. et al, Perchlorate Identification in Fertilizers, *Environmental Science & Technology*, 1999, 33, 3469-3472.

Table 1-reported corrections

Table 1. Perchlorate Concentrations in Fertilizer Compounds

component	perchlorate %
phosphate rock (western)*	ND
phosphate rock (Florida)*	ND
potash (commercial)	0.004
potash (muriate)	ND
dihydrogen ammonium phosphate*	ND
urea	ND

*Samples purchased from NIST

Source: Sursala, S. et al, Perchlorate Identification in Fertilizers, *Environmental Science & Technology*, 1999, 33, 3469-3472.

Determination of Perchlorate in Fertilizer Matrices at IMC

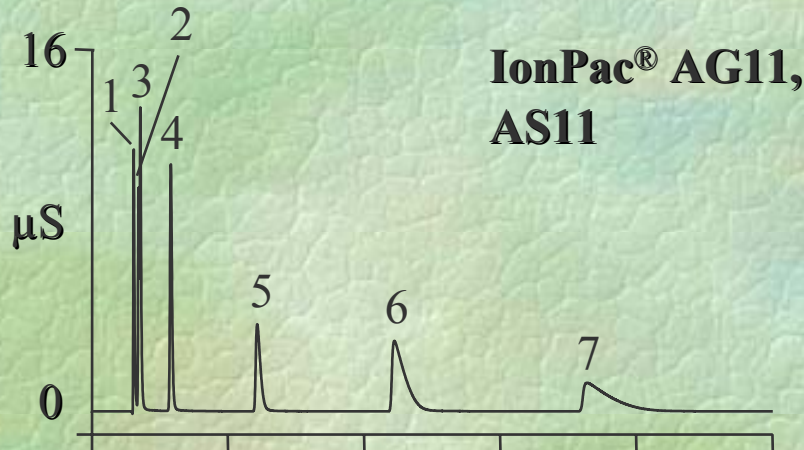
Analysis by Ion Chromatography

Dionex[®] DX-600

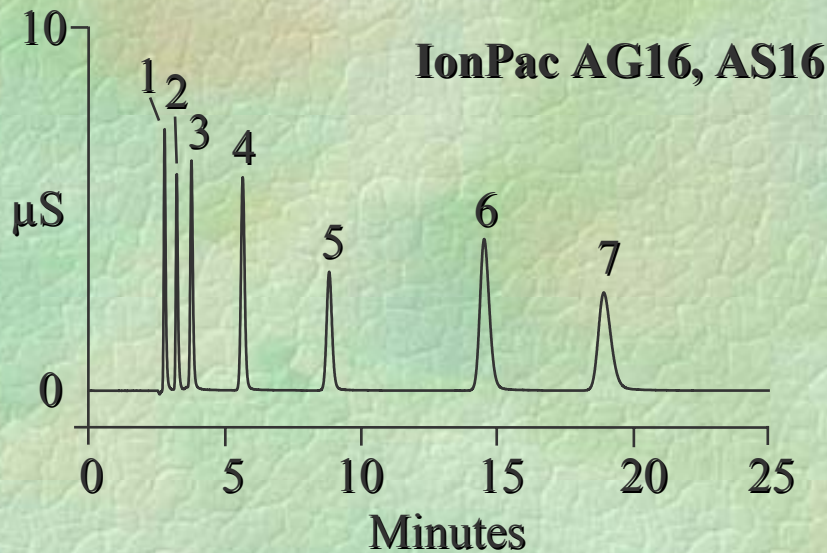
- ☛ Peaknet[®] 6.11 Software
- ☛ LC-25 chromatography oven
- ☛ CD-25 conductivity detector
- ☛ AS-40 autosampler
- ☛ AS/AG-16 Analytical & guard column
- ☛ ASRS-Ultra Suppressor at 300 mA
 - external water mode
- ☛ 50 mM OH Eluent (EG-40 generator)
- ☛ 18 megaohm water
- ☛ 1000 microliter loop

Comparison of AS11 and AS16 for Polarizable Anions

source: [Environmental Analysis of Inorganic Anions and Perchlorate by Ion Chromatography](#), P.E.Jackson et. al.



Column: IonPac AS11 or AS16
Eluent: 35 mM Sodium hydroxide
Temperature: 30 °C
Flow Rate: 1 mL/min
Inj. Volume: 10 μL



Peaks: 1. Fluoride 2 mg/L
2. Chloride 3
3. Sulfate 5
4. Thiosulfate 10
5. Iodide 20
6. Thiocyanate 20
7. Perchlorate 30

Beware Of...

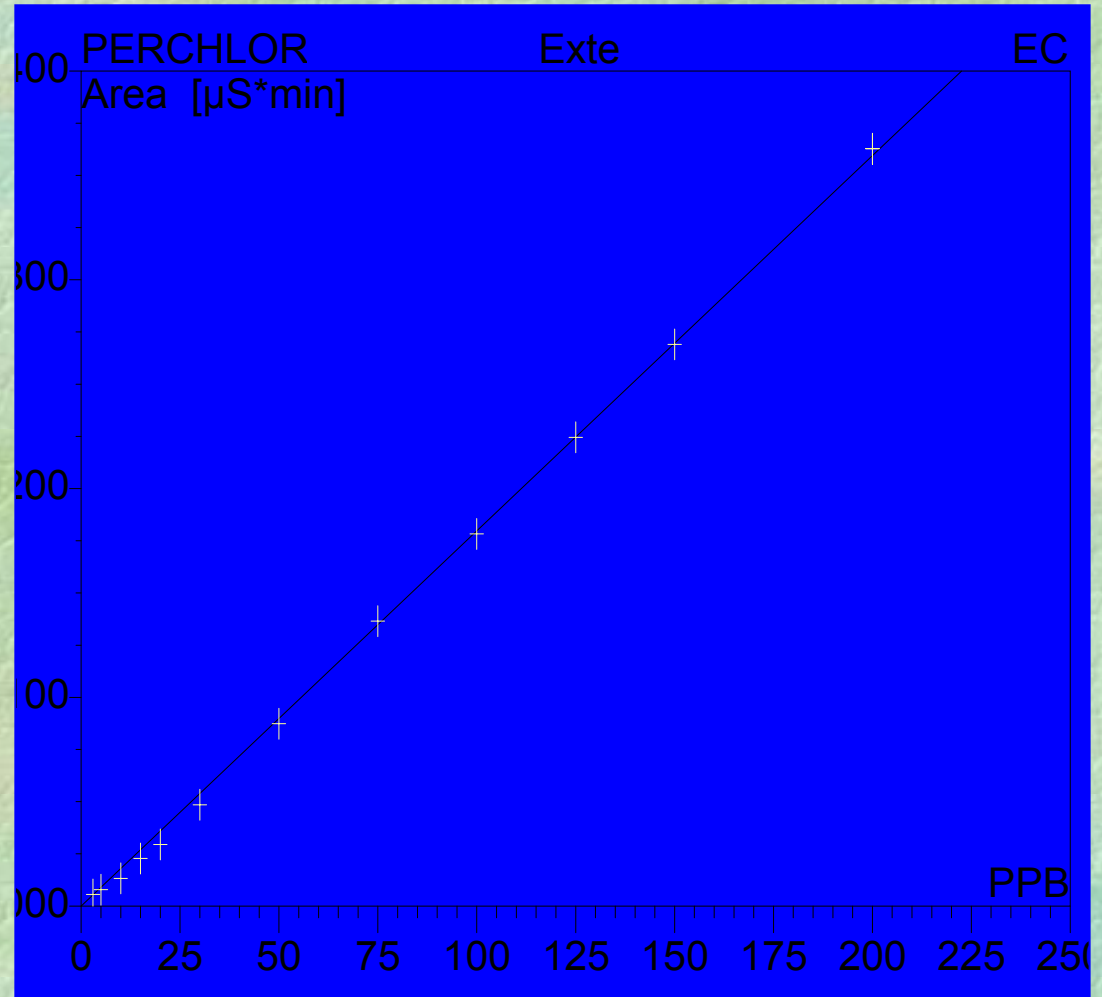
☛ Interferences:

- High TDS
- DI water quality
- Suppressor/column efficiency
- overloading the column
- Carbonate peaks
- Peak shifting
- Sensitivity setting

SPIKE ALL SAMPLES!

Calibration

- Twelve point calibration ranging from 3 - 200 ppb & verified w/ spex
- Correlation coefficient LR = 0.9998

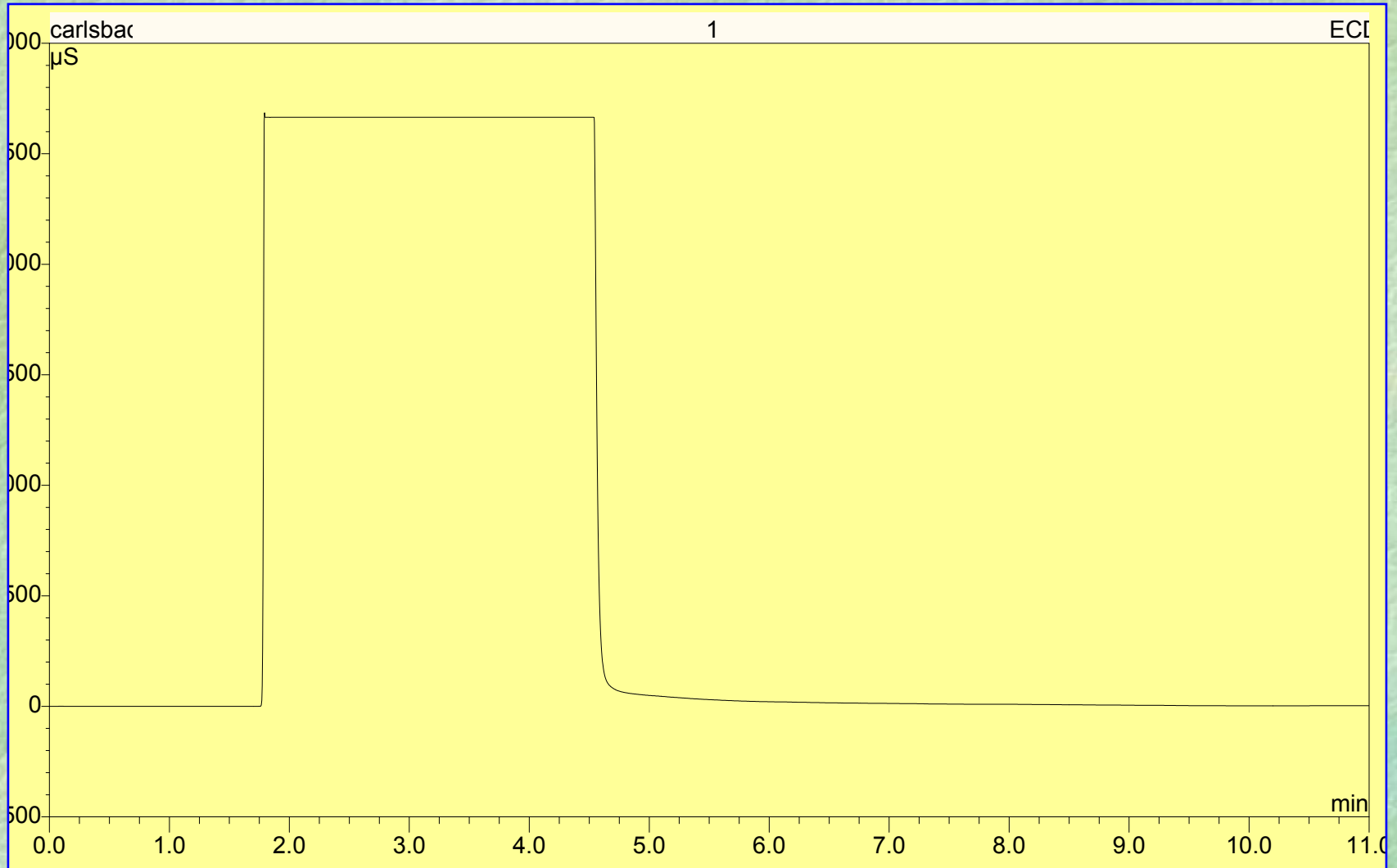


Extraction

from Collaborative study by Collette, Robarge, & Urbansky
EPA/600/R-01/026 (modification of EPA 314.0)

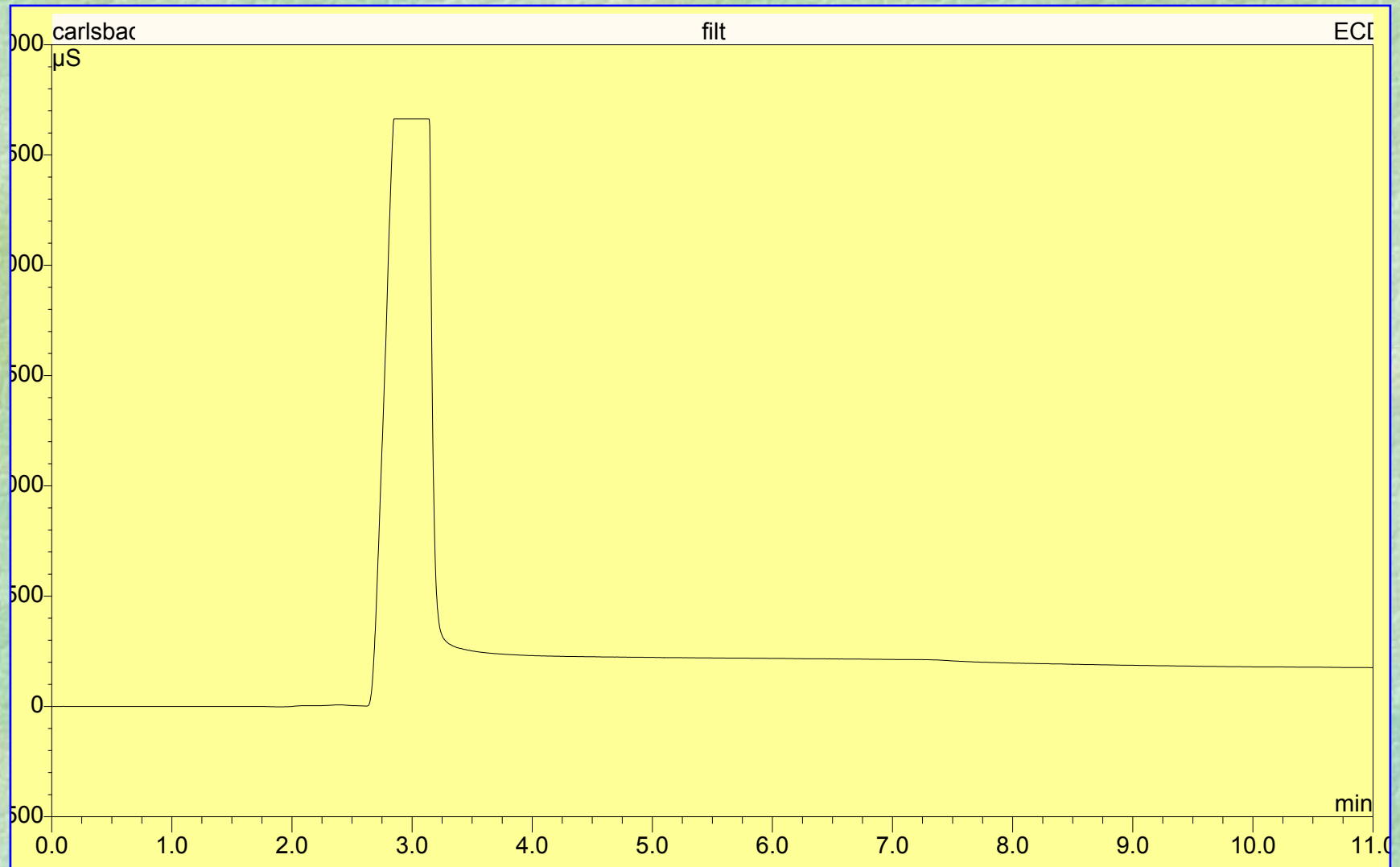
- ☞ 0.100 g solid/ mL liquid “ratio” (study: weigh 4 g of material, add 40 mL DI water)
- ☞ Shake, overnight (typically 8-14 hrs.)
- ☞ Begin run with 1/1000 dilutions
- ☞ Adjust dilutions as needed & spike
- ☞ Centrifuge/Filter if necessary
- ☞ May be able to remove some interferences

Langbeinite (1/10) interference peak- blocks signal of interest?

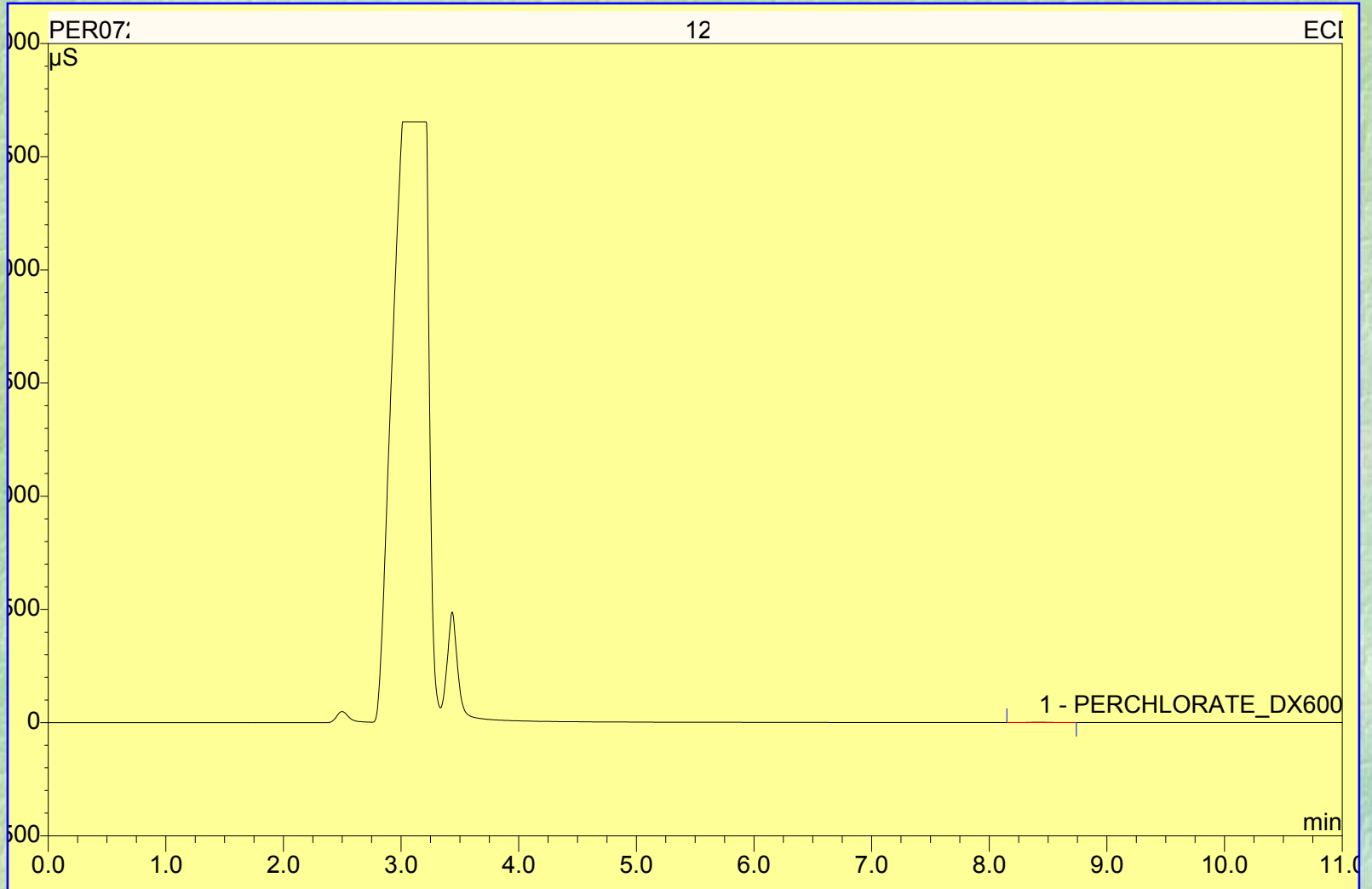


Langbeinite 1/10- cleanup

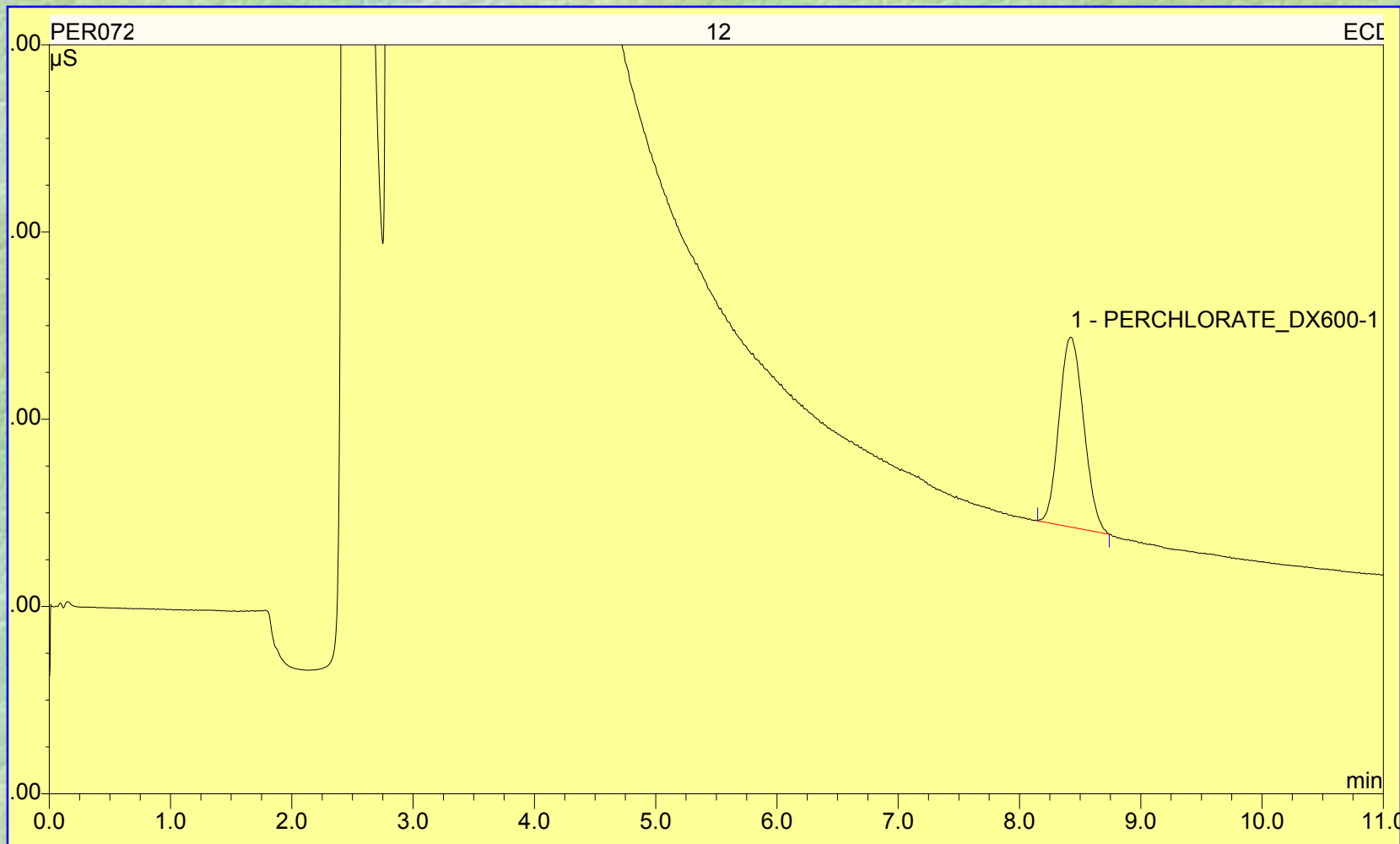
filtered with Ba & Ag discs



Scales to largest peak

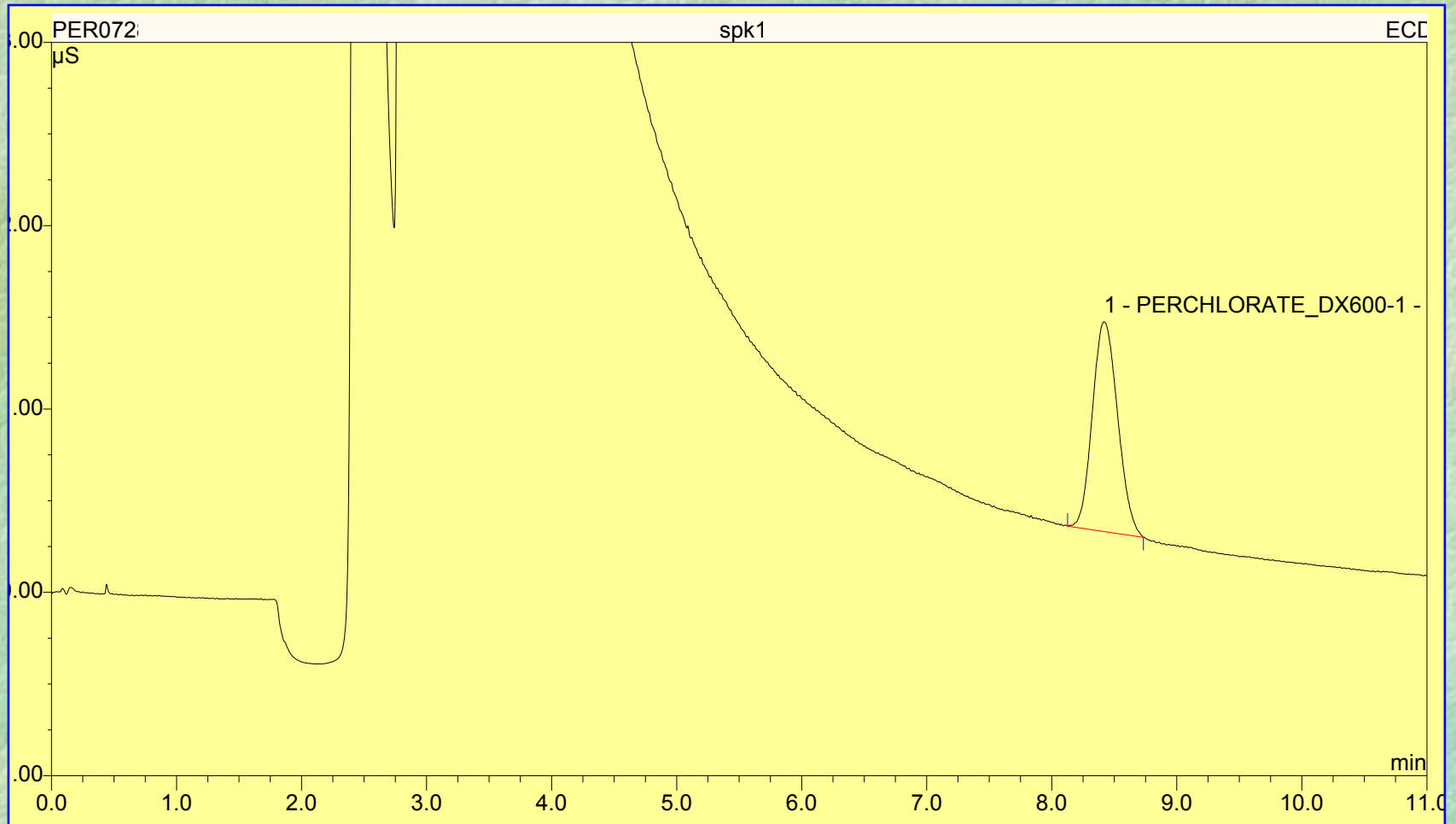


Magnified

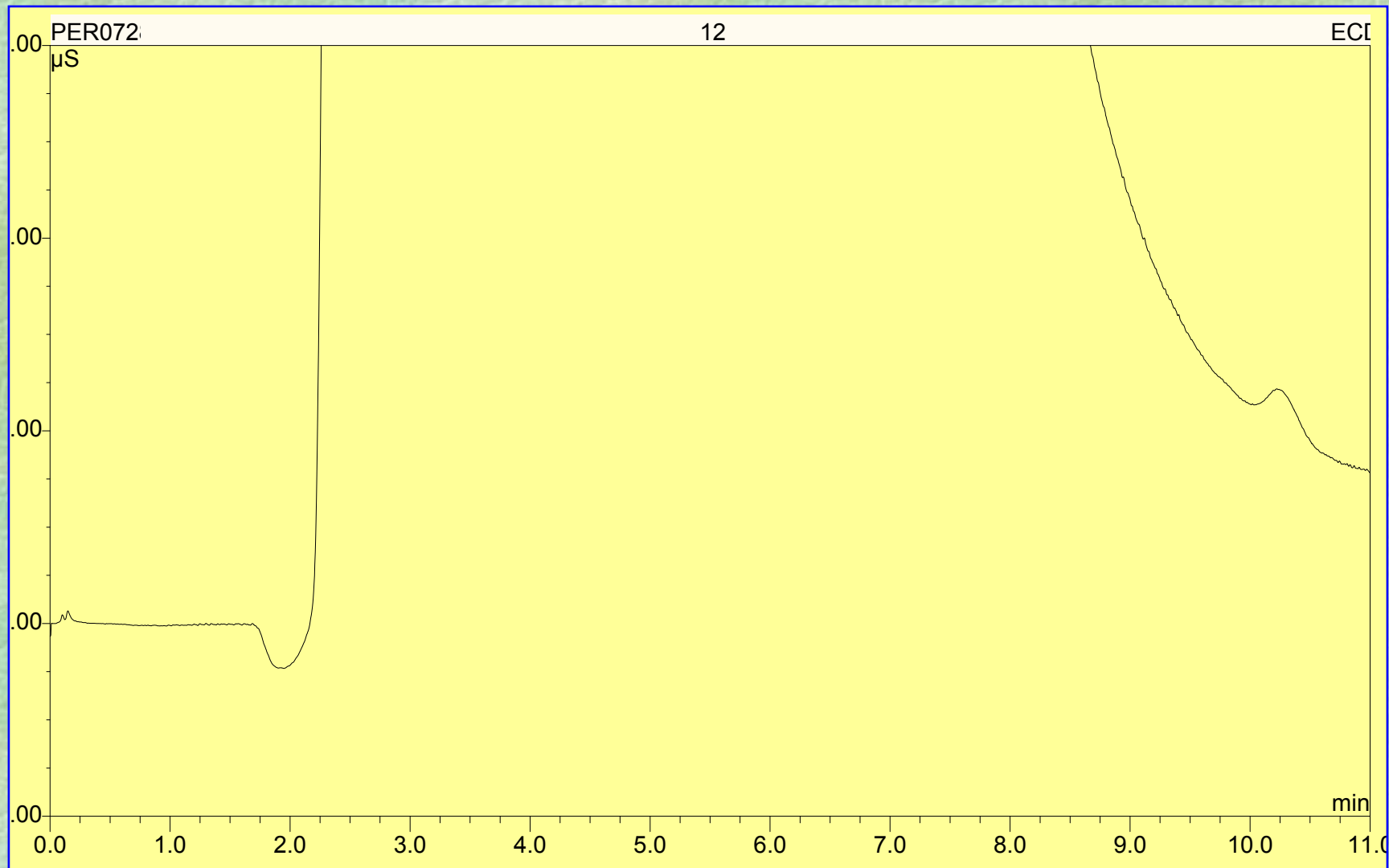


Spike sample

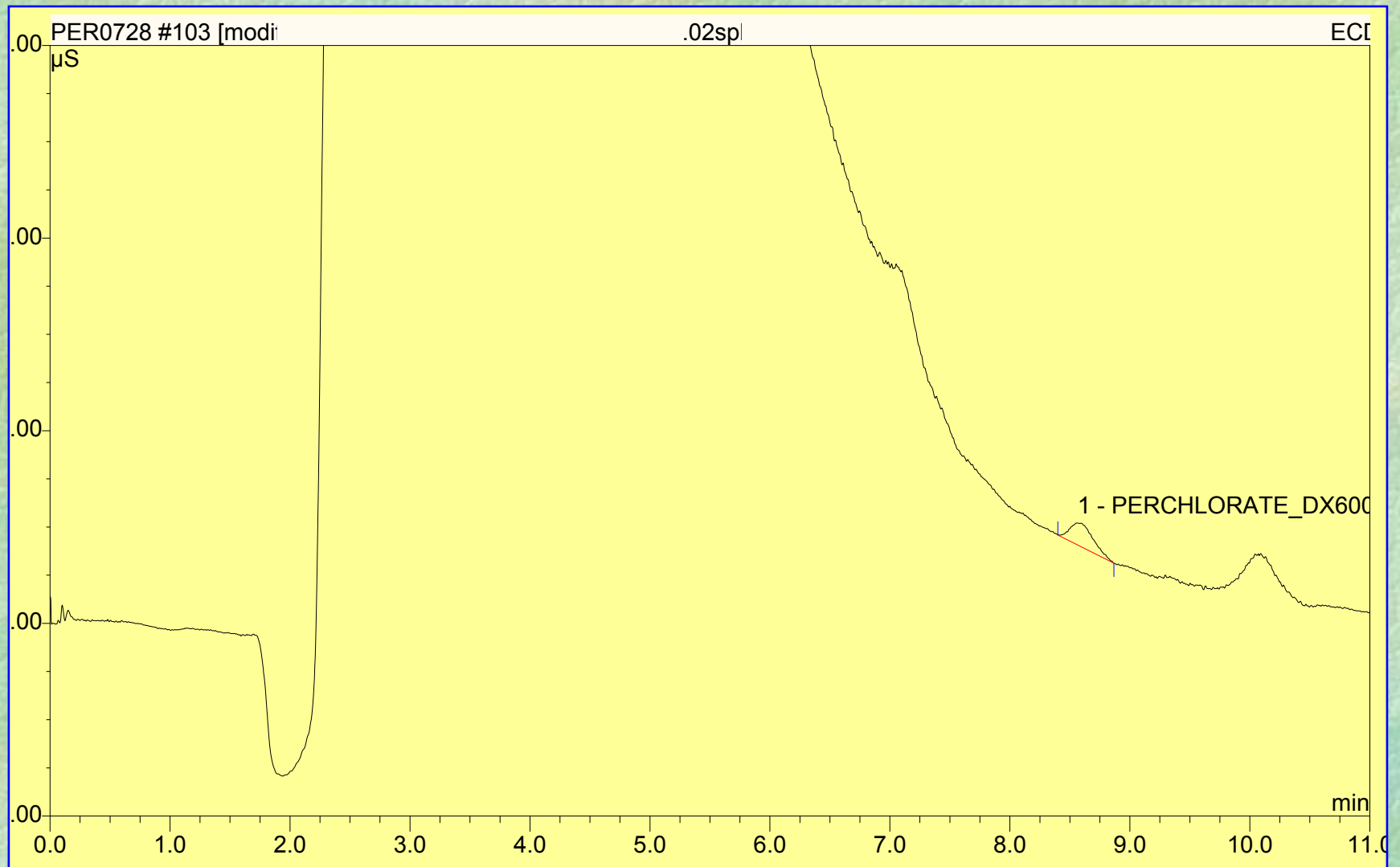
Look for increase in peak area



To name or not to name?



Not to name!



Sample Base (2001-IMC)

Fertilizer Source Materials:

No Detectable Peaks:

- **Granular & Premium K-Mag (Carlsbad)**
- **Granular SOP (Carlsbad)**
- **Esterhazy red course MOP**
- **Carlsbad sylvite**
- **Carlsbad Langbeinite ore, blasting & mechanical methods**
- **Carlsbad SMOP & GMOP**
- **Muriate of Potash (Colonsay)**
- **Granular KCl (Belle Plain)**
- **Magruder check samples**

One Fertilizer sample (1999)

- **Vigoro 15-30-15 contained 450 mg ClO₄/kg (contained chilean nitrate)**

Specific sites-2000 (IMC)

Also no detectable peaks

- ☛ Langbeinite Ore, IMC Kalium Carlsbad area 7, Drill and Blast Mining method, August 2000
- ☛ Langbeinite Ore, IMC Kalium Carlsbad area 9, continuous mining method, August 2000
- ☛ Carlsbad KMAG Process Dryer Feed
- ☛ IMC Potash Colonsay, ore sample, July 2000
- ☛ Langbeinite ore sample-mechanical mining method, 2000
- ☛ Langbeinite finished product, 2000

2001 Magruder results

Magruder Study - Perchlorate						
Sample #	ID	N-P-K Analysis	mg ClO ₄ ⁻ /kg			History
			IMC	NCSU	Avg	
1	9311-B	0-0-61 Pot. Chloride	ND	ND	ND	Bill Hall, Vigoro Industries
2	9406-B	0-0-22 SPM	ND	ND	ND	Jim Smith, Sul Po Mag (Langbernite), IMC
3	9509	2-5-20 + minor elem.	ND	ND	ND	Bill Hall, Vigoro Industries, Ag. Blend
4	9804	10-10-10 All Purpose	ND	ND	ND	Sandy Simon, Pursell Ind.
5	9805	20-5-15 Vig. Lawn Fert.	ND	ND	ND	Bill Hall, IMC Vigoro
6	9806	6-24-24 Ag Granulated	ND	ND	ND	Pat Peterson, CF Industries
7	9812	5-10-15 Garden Fertilizer	ND	ND	ND	Don Day, PCS Sales
8	9901	18-4-10 Lawn Fertilizer	ND	ND	ND	Greg Haberkost, Lebanon Fert.
9	9902	20-20-20 All Purpose W/S	ND	ND	ND	Bill Hall, IMC Vigoro
10	9905	20-4-4 Lawn Fertilizer	ND	ND	ND	Greg Haberkost, Lebanon Fert.
11	9907-A	Phosphate Rock	ND	ND	ND	CF Ind, Harold Falls
12	9907-B	40-0-0 Methylene Urea	ND	ND	ND	Dick Harrell, NuGro
13	9908	19-19-19 All Purpose	ND	ND	ND	Bob Beine, U of Ky
14	9909	27-3-5 Scotts Turfbuilder	ND	ND	ND	V. Snyder, Scotts Co.
15	9911	10-20-20 Garden Fert.	ND	ND	ND	Greg Haberkost, Lebanon Fert.
16	9912	13-13-13 Gran. All Purp.	ND	ND	ND	B. Avant, IMC/Royster Clark

IMC participation in EPA Perchlorate Round Robin Study

- ☛ EPA: Survey of Fertilizers and Related Materials for Perchlorate, Urbansky et. al., EPA/600/R-01/049, May 2001.
- ☛ Also Calif. Dept. of Food & Agric., NCSU Dept. of Soil Science, American Pacific Corp., Dionex Corp.
- ☛ Nitrogen sources, potassium (potash) sources, and phosphate sources from many manufacturers, and diverse geological sources tested.

Table 2.2 (excerpt) Phase II

Source: EPA Survey of Fertilizers and Related Materials for Perchlorate
EPA/600/R-01/049 May 2001

(Names of the 5 participating labs are listed in the report)

Item #	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5
33	4066	3700	4020	4200	3860
33 dup	4136	3925	4270	3700	3850
34	u	u	u	0.9	u
34d	u	u	u	u	u
KCl+ 6.8 mg ClO ₄ /g	6377	5720	5960	6200	6140
Urea + 1.8 mg ClO ₄ /g	1511	1540	1790	1430	1810

Phase II results

slide quotes taken from Survey of fertilizers and related materials for perchlorate, ET Urbansky, ACS national conference in Chicago, IL. August ,2001

- ☛ Perchlorate identified only in Chilean nitrate products: NaNO_3 , KNO_3 , or blends
- ☛ Satisfactory interlaboratory agreement
- ☛ Satisfactory duplicate agreement
- ☛ 80-120% spike recovery
- ☛ 7 QC samples accurately analyzed (+/- 10%)
- ☛ Small negative bias in QCS results

Implications

Courtesy of Bill Hall, IMC-Global

60,120,212	Total Tons
17,405,269	Containing K
5,872,529	K Materials
5,251,655	KCl (0-0-60)
1,800,000	All Lawn & Garden
144,618	Langbeinite (0-0-22)
~50,000	All SQM(Chilean) Imports

0.0833%

SQM (Chilean) Nitrates in USA

source: SQM: Reduction of Perchlorate Levels of Sodium and Potassium Nitrates (Derived from Caliche Ore); A. Lauterbach, SQM, 2001 ACS national meeting, Chicago IL.

- ☞ “Although SQM has no reason to believe fertilizer use has contributed to perchlorate in the environment, the company has developed methods to produce limited amounts of fertilizers with perchlorate levels below 0.01% w/w”
- ☞ “SQM is continuing its research into perchlorate reduction processes to develop cost-effective methods to reduce perchlorate in its products.”
- ☞ “For the above reasons SQM is investing heavily in developing processes for reducing perchlorate in its various fertilizer production lines. Corresponding research is being performed in both Chile, and in the US.”

Comment on ES& T Article...

On: Perchlorate Identification in Fertilizers, Susarla et. al., Table 2; by ET Urbansky, USEPA, Subsequent Addition/Correction

“...that phenomenon appears to have constituted a sporadic-if not singular-event rather than reflecting a recurring problem. In fact, 17 additional products analyzed by the same investigators contained no detectable perchlorate.”

Conclusions

- ☞ IC can be a viable method for the determination of perchlorate ion in a fertilizer matrix, though a confirmatory method may be necessary.
- ☞ The vast majority of crop nutrients do not contain perchlorate. Less than 0.1% of fertilizers used in the US contain Chilean nitrate, currently the only known potential source of perchlorate in fertilizer products.
- ☞ SQM, supplier of Chilean nitrate, is currently eliminating or reducing perchlorate levels in its product.
- ☞ Further study does not seem to be warranted, some occasional monitoring may be recommended to prevent further controversy.

References & Acknowledgements

- Edward T. Urbansky :Perchlorate in the Environment; Environmental Science Research, vol 57
- USEPA: Ion Chromatographic Determination of Perchlorate in the Analysis of Fertilizers and related materials, Feb. 2000
- EPA Survey of Fertilizers and Related Materials for Perchlorate, Final Report, EPA/600/R-01/049. May 2001.
- Evaluation of the Composition of Fertilizer Source Materials:Perchlorates Wayne P. Robarge, NCSU (2000 ACS national meeting, Washington DC)
- Perchlorate Identification in Fertilizers, S. Susarla et.al.; also Additions & Corrections ES&T vol. 34, No.1,2000; and: Comment on “Perchlorate Identification in Fertilizers” and the Subsequent Addition/Correction-ET Urbansky
- Environmental Analysis of Inorganic Anions and Perchlorate by Ion Chromatography; PE Jackson, K. Chassaniol, D. Thomas, Dionex Co. Sunnyvale, Ca. (2001 ACS national meeting Chicago, IL.)
- Reduction of Perchlorate Levels of Sodium and Potassium Nitrates (derived from Caliche Ore), A. Lauterbach- SQM, 2001 ACS national meeting, Chicago, IL.
- The Fertilizer Institute; Jim Skillen, Bill Hertz
- Bill Hall, Annette Revet, Steve Gamble, David Gadsby, IMC-Global
- Wayne P. Robarge, NCSU
- Bill McBride, Dr. A. Lauterbach, SQM