

RemTech 2013

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ANALYSIS OF ELEMENTAL SULPHUR IN SURFICIAL ALBERTA SOIL SAMPLES BY HPLC

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Maxxam

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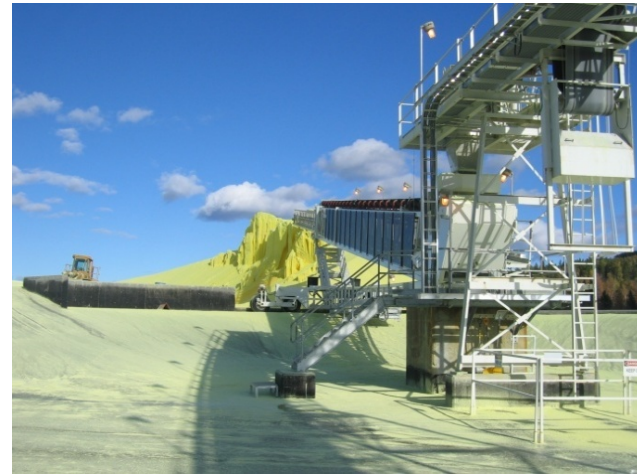
1. Maxxam Analytics International Corporation
2. Environment and Sustainable Resource Development (ESRD), Government of Alberta

Background

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Elemental Sulphur (S₈): major by-product in Oil & Gas industry

- **4.37 million tonnes produced in Alberta, 2012 (ERCB, 2013)**



The environmental problems associated:

- **On-site – Strong acidification in soils, groundwater, S-containing waste, S-contaminated soils**
- **Off-site – Vegetation damage, soil acidification with airborne S dust**

Land and Forestry Policy Branch, Environment and Sustainable Resource Development (ESRD)

ESRD regulates elemental S largely through:

- Alberta Tier 1 Soil and Groundwater Remediation Guidelines
- Guidelines for landfill disposal of sulphur waste and remediation of sulphur containing soils
- Directive for monitoring the impact of sulphur dust on soils
<http://environment.gov.ab.ca/info/library/8433.pdf>

Available Analysis Method has Limitations

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Colorimetric method

- based on Can. J. Soil Science, 1985, 65, 811-813:
- Acetone extraction
- Reaction of S8 with sodium cyanide
- Lack of sensitivity
 - Regulatory criterion @ 500 mg/kg; RDL @ 300 mg/kg
 - Insufficient at low levels – problematic for baseline monitoring
- High method uncertainty at criterion level: 500 mg/kg
- Lack of specificity/selectivity
 - Interferences from organics
 - 70% of elemental S handling/processing plants in Alberta are located in forested areas.

New Method Development Project Initiated

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Supported by ESRD's Land Monitoring Funding

Analytical challenge: need suitable methods for elemental sulphur

- High selectivity, good sensitivity
- Compatible with commercial laboratory requirements
- Forest litter samples - reduce/eliminate interference

Input from a network of commercial laboratories:

- Need for standard operating procedures (SOP)
- LC method desired due to required selectivity/sensitivity

Maxxam Analytics was contracted to refine existing or develop new methods

Existing LC Methods

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- Watkins et al. 1987, LC/UV method for S8 analysis from soil
 - Aust. J. Soil Res. 1987, 25, 167-78
 - Method had proven valuable in Australia/NZ for mineral soils
 - Employed older LC technology
 - Chloroform extraction
 - Polymeric column, large particle size, solid-liquid partitioning
 - Chloroform mobile phase – toxic
 - UV detection, 254 nm
- Goal: newer column technology and less toxic mobile phase
 - Azarova et al. J. Anal. Chem., 2001, 56, 1062-66 (sediment analysis)
 - Acetone extraction
 - C18 column, methanol mobile phase, UV detection, 200 nm

Sulphur-Solvent Solubility Studies

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- Acetone - following Maynard and Addison (1985) and Azarova (2001)
- Chloroform - following Watkinson et al (1987)
- Dichloromethane (DCM) - common laboratory solvent for soil extractions
- Methanol - target mobile phase

Sulphur-Solvent Solubility Studies

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Excess solid S added to solvent, sonicated 1 hr,
centrifuged, decanted, analyzed colorimetrically

Acetone	612 mg/L (n=3)	Incomplete, very small amount of dusty sediment
DCM	6330 mg/L (n=3)	Incomplete, visible amount of sediment
Chloroform	6670 mg/L (n=1)	Incomplete, visible amount of sediment
Methanol	257 mg/L (n=3)	Incomplete, visible amount of dusty sediment

Azarova (2001) reported acetonitrile solubility @ 75 µg/mL

Extraction Efficiency Study

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Samples used:

- Mineral soils:
 - High organic clay (9% o.c.), Low organic clay (2% o.c.)
- Leaf litters
 - White spruce, Lodgepole pine, Aspen
- Samples dried at 60 °C, ground to <2 mm.

Extraction Solvents:

- Chloroform, DCM, Acetone

Extraction Efficiency Study

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- Solvent / Soil ratios targeted – 2:1 5:1 10:1 20:1
 - Insufficient solvent recovery from leaf litter soils at 2:1
 - Excessive solvent use, loss of sensitivity at 20:1
- Soil aliquots spiked with S8 in DCM, mixed, allowed to evaporate overnight
- Extraction:
 - Solvent added at the desired ratio
 - solvent/soil mixed,
 - sonicated 30 min, tumbled 1 hr., centrifuged,
 - Analysed by both colorimetry and LC
 - DCM interfered with colorimetric method unless diluted with acetone

Extraction Efficiency Study Results

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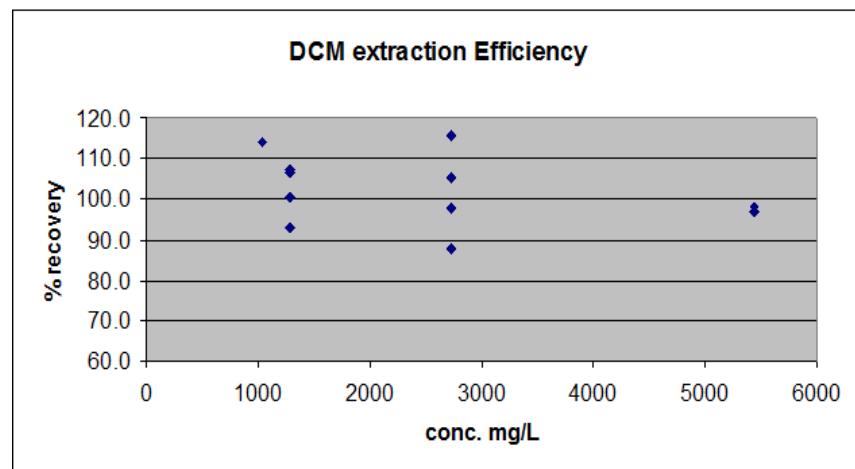
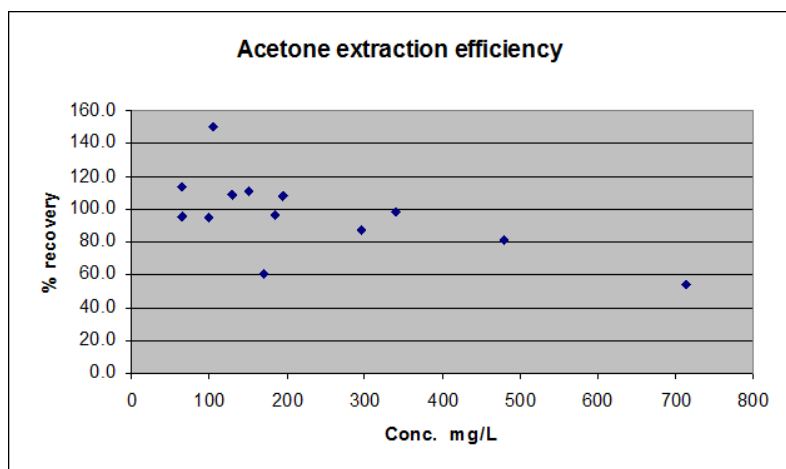
Observations:

- Acetone is sufficient up to 400 mg/L
- DCM & chloroform sufficient to 6,000 mg/L

Implementation:

- Solvent/soil ratio 10:1
- Acetone to be used as routine up to solubility limit
- If soils have higher S8 amounts, re-extract with DCM

Extract Ratio (Solvent to Soil)	Design µg/mL	Average Recovery	Standard Deviation
10 to 1	2	130% (106%)	26%
5 to 1	4	104%	23%
10 to 1	10	88%	11%
5 to 1	20	87%	12%



Recoveries from High Organic Soil

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Sample	Spike level (µg/g)	Average Recovery	RSD	Sample Size (n)
Acetone Extract				
Lodgepole Pine	20	118%	9.2%	8
High Organic Clay	20	113%	11.5%	8
Lodgepole Pine	200	101%	9.5%	8
High Organic Clay	200	105%	3.2%	8
Lodgepole Pine	1,000	84%	1.4%	6
High Organic Clay	1,000	90%	0.8%	6
Lodgepole Pine	3,600	98%	3.4%	6
High Organic Clay	3600	106%	3.6%	6
DCM Extract				
Lodgepole Pine	200	94%	4.5%	8
High Organic Clay	200	89%	4.1%	9
Lodgepole Pine	10,000	101%	6.6%	6
High Organic Clay	10,000	98%	7.1%	6
Lodgepole Pine	36,000	98%	4.3%	5
High Organic Clay	36,000	93%	5.5%	6
Overall Average		99.1%	5.3%	

LC Method Development Goals

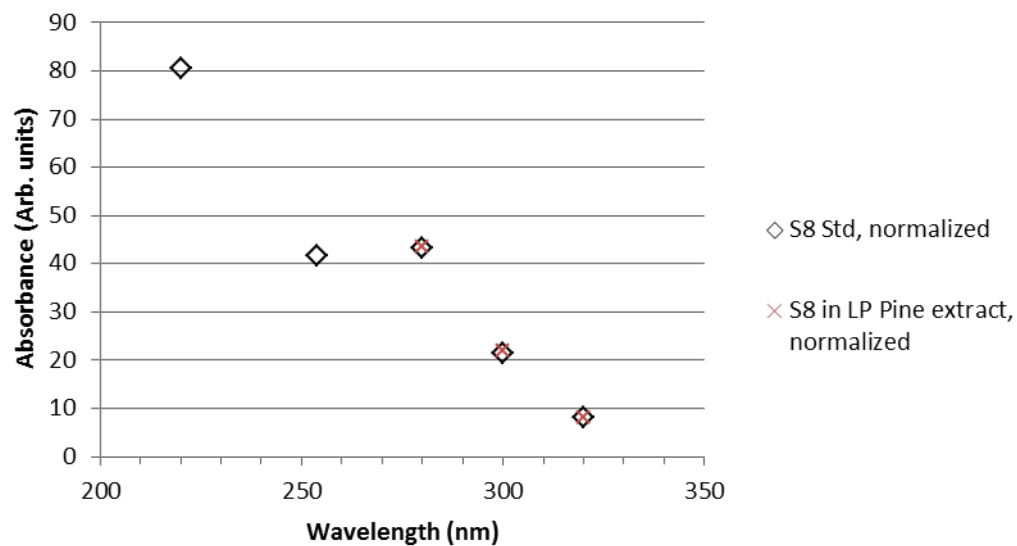
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- C18 stationary phase:
 - AkzoNobel Kromasil® C18 column (100 mm x 4.6 mm, 3.5 μ m particle size)
 - Guard Column, C18 (10 mm x 4.6 mm, 5 μ m particle size)
- Lower UV wavelengths for better detection sensitivity
 - Chloroform has a high UV cut-off
- Determine selectivity/sensitivity
- Determine column capacity and resolution
 - primary drivers in method development

UV Cut-offs:

- Chloroform: 245 nm
- Methanol: 205 nm
- Acetone: 330 nm

UV Absorbance Profile for S8 in Methanol mobile phase
from chromatographic peak areas



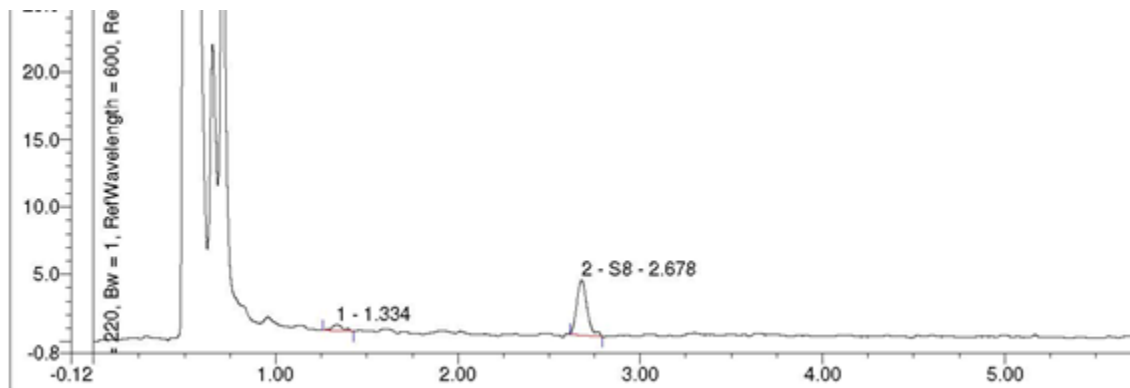
LC Method Comparison

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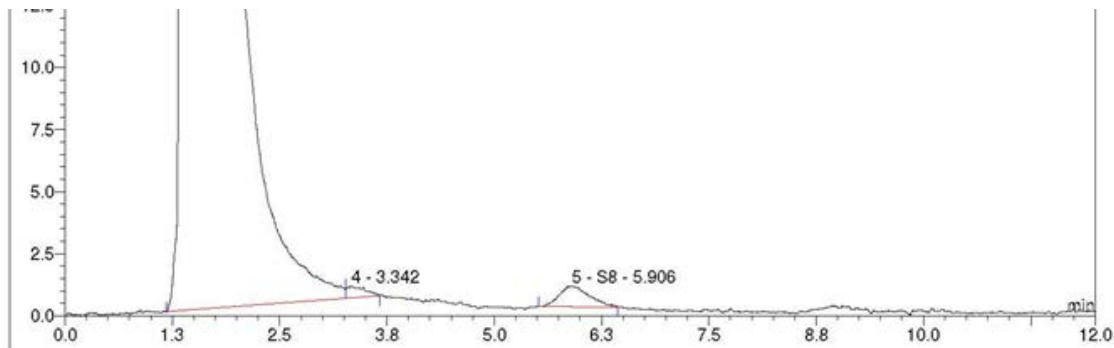
Selected C18/methanol method over CHCl₃/chloroform

- Mainstream technology
- Better S8 peak shape and resolution
- Low toxicity of methanol vs. chloroform
- Chloroform mobile phase requires normal phase (Teflon) pump seals

C18/methanol - High Organic Clay in Acetone (2 µg/mL)



PRP/chloroform - High Organic Clay in Acetone (2 µg/mL)



Method Development Decisions

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The following consensus was reached for validation:

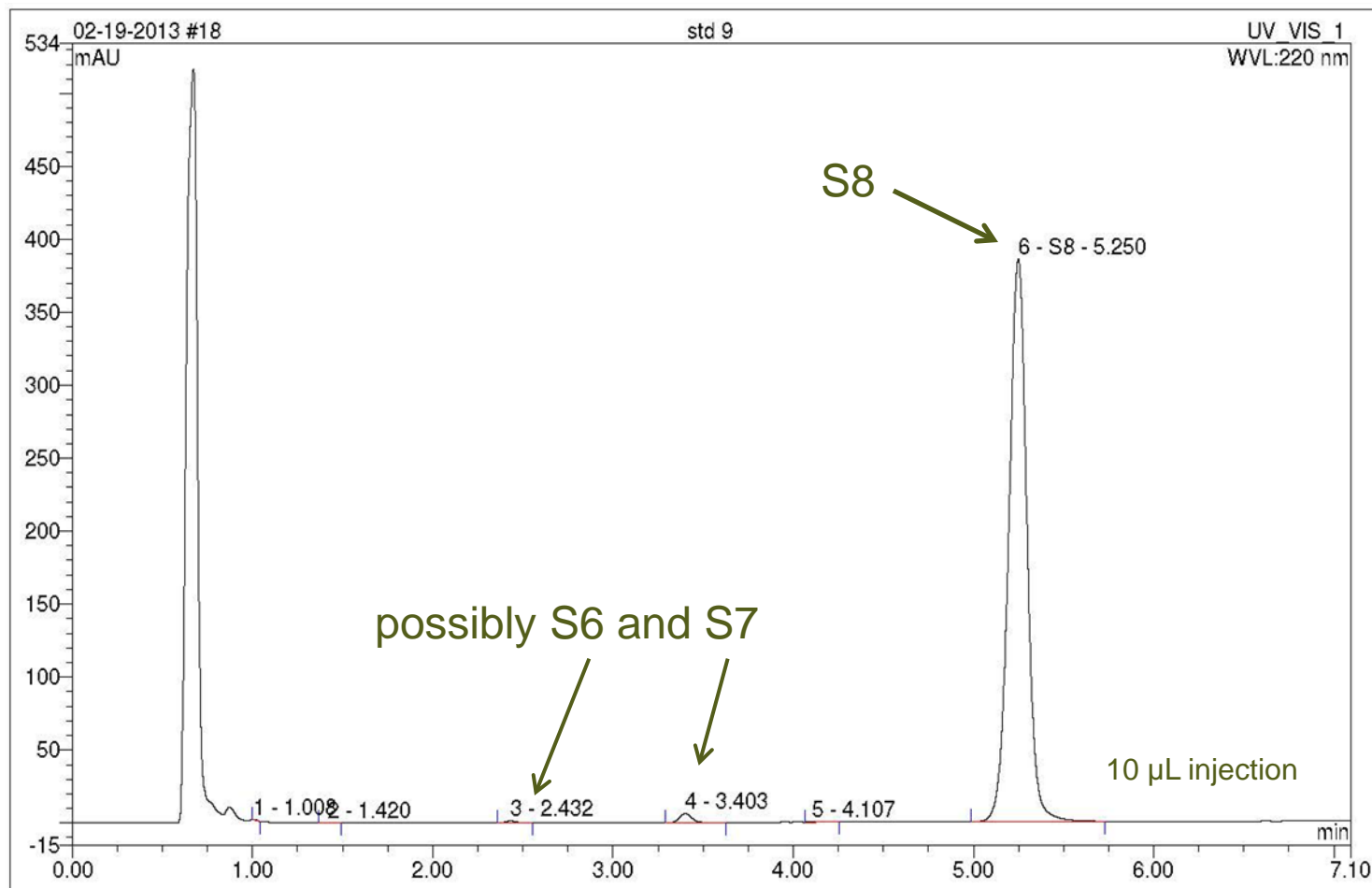
- Solvent/soil extraction ratio: 10/1
- Validate both methods: acetone-HPLC & DCM-HPLC.
- HPLC using detection wavelength 220nm, C18 column, methanol-water isocratic mobile phase
 - DCM extracts diluted 10x with acetone
 - Acetone extracts run undiluted

Methods to be optimized using difficult samples

- High organic clay (HOC) (most difficult to extract)
- Lodgepole pine litter (most interferences)

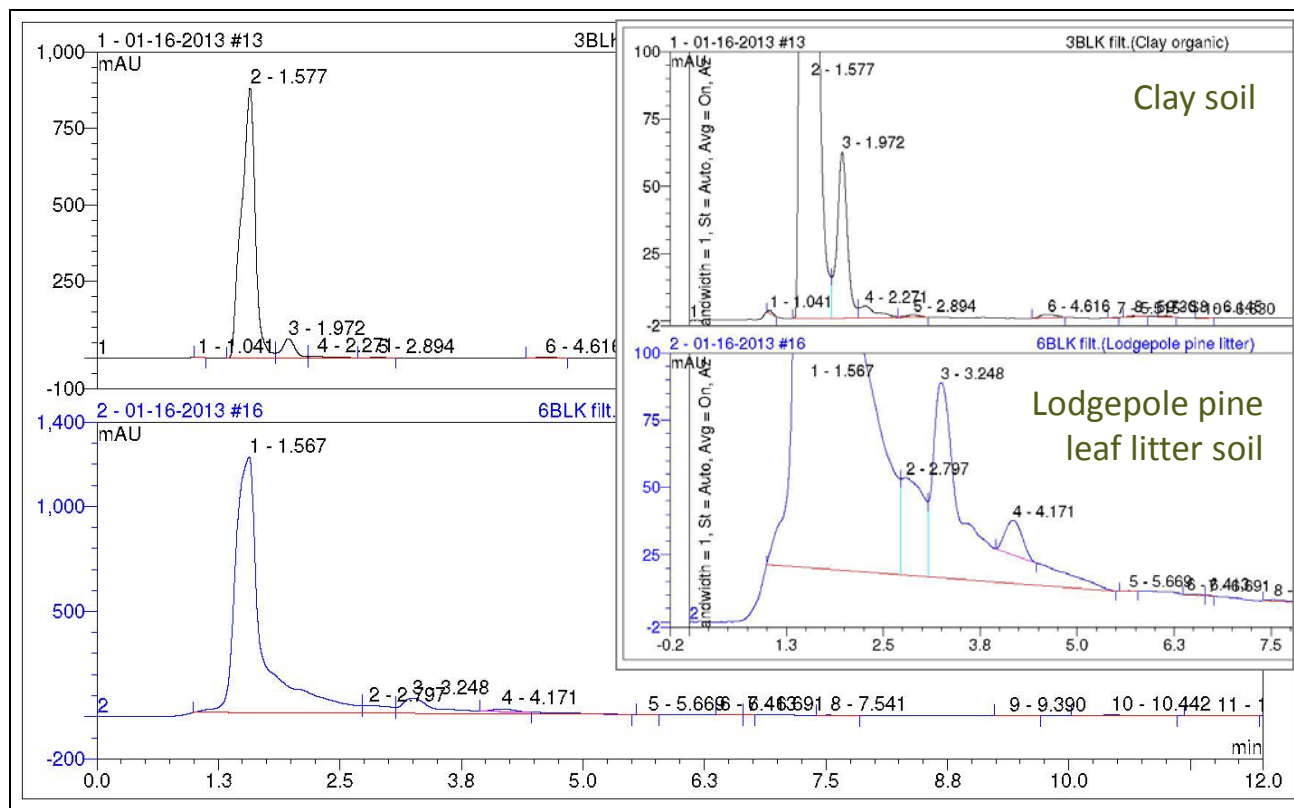
S8 Standard Injection (20 µg/mL)

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Soil Extraction Results - Interferences

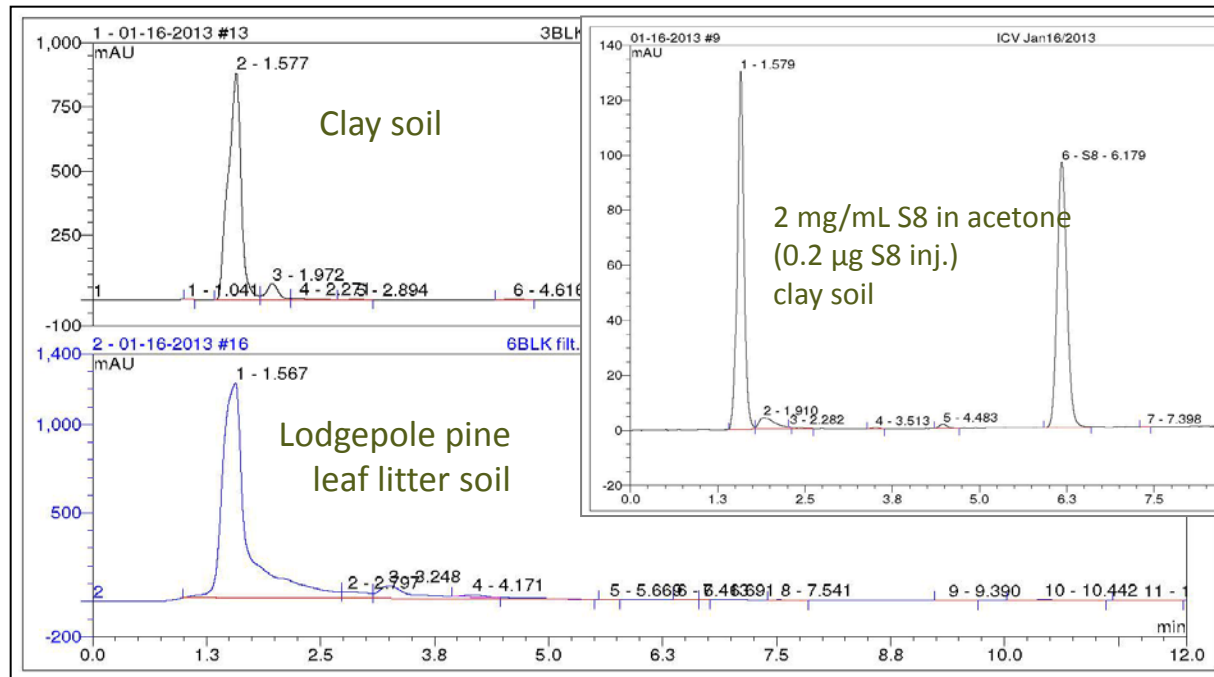
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- High levels of co-extracted polar materials in Alberta leaf-litter soils
- Must be removed to avoid high bias

Elemental Sulphur: Soil Extraction Results

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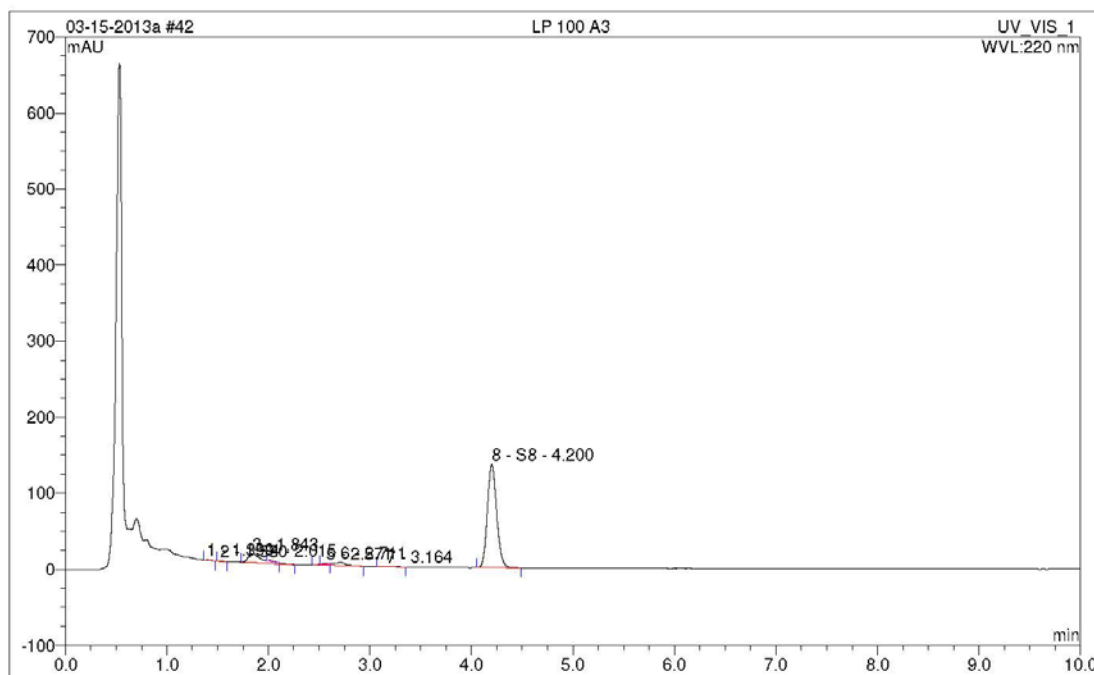


Chromatographic method separates S8 from interferences

Final Chromatographic Conditions

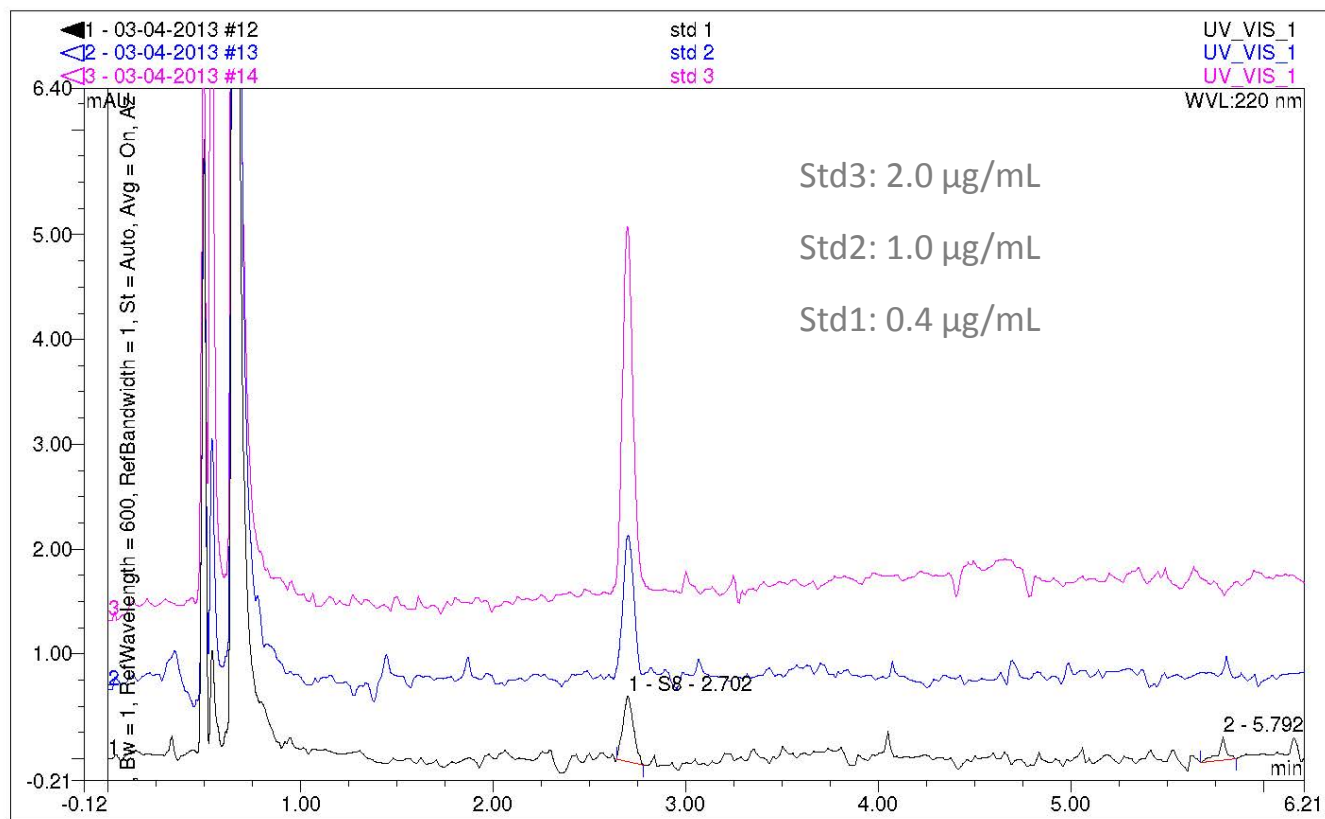
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Lodgepole pine litter, S8 spiked at a concentration of 1,000 µg/g,. acetone extract concentration 100 µg/mL mobile phase 90:10 MeOH:H₂O.



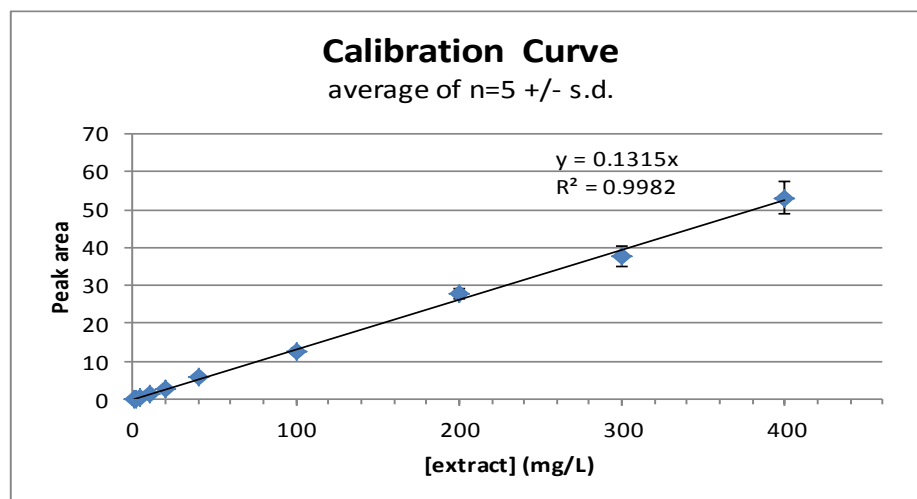
Standards at 0.4, 1.0, 2.0 $\mu\text{g/mL}$

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Optimized Method – Calibration and MDL

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Method Detection Limits

µg/g Elemental Sulphur			
Acetone Extract	Day 1	Day 2	Average
Lodgepole Pine	6.4	5.4	6.8
High Organic Clay	6.2	9.3	
DCM Extract	Day 1	Day 2	Average
Lodgepole Pine	19	44	33.5
High Organic Clay	35	36	

- Full SOP developed as part of the project
- Freely available to interested laboratories
- Contact either Maxxam or ESRD for a copy

Standard Operating Procedure for the Analysis of Elemental Sulfur in Alberta Soils by High Performance Liquid Chromatography

1.0 Introduction:

1.1 Scientific Principle

Sulfur is the only non-metal that is cheaply available in the elemental form. It is an odourless, brittle yellow solid, which can be easily oxidized or reduced, depending on the environment to which it is subjected. Sulfur is used directly in the elemental form in the manufacture of paper and pulp, carbon disulfide, for crop dusting, rubber and other elastomers. It is used in industry in the form of sulphuric acid. Sulfur occurs naturally in the vicinity of volcanoes and hot springs as well as in natural gas and petroleum crudes. Elemental sulfur is slowly converted to sulfate in soil by the action of autotrophic bacteria. Elemental sulfur leaches in soil as sulfate at a slow rate.

Elemental sulfur is insoluble in water and only slightly soluble in solvents, such as ether, petroleum ether, toluene, chloroform, and alcohol.

In this method, after drying and grinding to < 2 mm, soil samples are extracted with either acetone or dichloromethane. These solvents effectively extract all forms of elemental sulphur from soil matrix up to concentrations limited by the solubility of S8 in these solvents. The extract is separated from the soil residue and analyzed by High Performance Liquid Chromatography using a methanol : water mobile phase and UV

Round-Robin Study

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- Six Canadian labs participated in the study
- Samples selected as some of the more challenging Alberta soils
- Duplicate samples provided to all participants
- Participants selected their method of choice
 - Two HPLC methods (described method and one other)
 - Two colorimetric methods
 - Two ICP methods

Sample Type	Spike Level	Spike Level
Lodgepole Pine	Low spike	High Spike
High Organic Clay	Low spike	High Spike
Peat	Low spike	High Spike
Natural Sample	No Spike	-
CRM	As per CRM	-

Quantitative Results ($\mu\text{g/g}$)

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	CRM	ESRD	LPP	LPP	LPP	HOC	HOC	Peat	Peat	Peat
Technique	5000		30	500	0	80	2000	30	300	0
HPLC Ref	3515	1423	33	478	<10	80	1965	262	621	252
	3464	1423	37	492	<10	80	2077	295	596	194
Colour 1	4524	1808	44**	465	47*	92	1864	300	543	290
			46**	473	50*	105		270	568	
HPLC2	2720	1360	27	425	<1	63	1460	226	460	199
Colour 2	3830	1920	69	585	124	93	2181	373	610	389
ICP 1	2970	1050	20	293	<10	45	1590	176	388	192
ICP 2	3100	1110	<10	177	<10	52	1680	233	512	277

mean	3439	1445	34	424		76	1831	267	537	256
stdev	661	356	21	129		21	265	59	81	71
RSD	19%	25%	62%	30%		28%	14%	22%	15%	28%

* uncorrected for background

** background corrected

Recovery Results

Recovery	CRM	LPP 30	LPP500	HOC80	HOC2000	Peat30	Peat300
HPLC Ref	70%	117%	97%	100%	101%	185%	129%
Colour 1	90%	150%	94%	123%	93%	<	89%
HPLC2	54%	90%	85%	79%	73%	90%	87%
Colour 2	77%	230%	117%	116%	109%	<	74%
ICP 1	59%	65%	59%	56%	80%	<	65%
ICP 2	62%	<33%	35%	64%	84%	<	78%

Average Recovery of Spiked Samples (exc. LPP30 and Peat 30)				
	Recovery	Stdev	Min	Max
HPLC Ref	105%	15%	97%	129%
Colour 1	104%	16%	123%	89%
HPLC2	81%	6%	73%	90%
Colour 2	106%	21%	74%	117%
ICP 1	63%	11%	56%	80%
ICP 2	65%	22%	<33%	84%

Round Robin Summary

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- There were no outliers for any of samples as determined by the Grubb's test ($P = 0.05$).
- The HPLC method developed for ESRD performed well for a variety of different and difficult matrices, typical of Alberta soils.
- The colorimetric procedure, when background correction is applied, also performed well.
- The low bias for the ICP and HPLC2 procedures was likely due to incomplete extraction.

Questions?

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