



Fluensulfone on Potatoes and Sugar Beets

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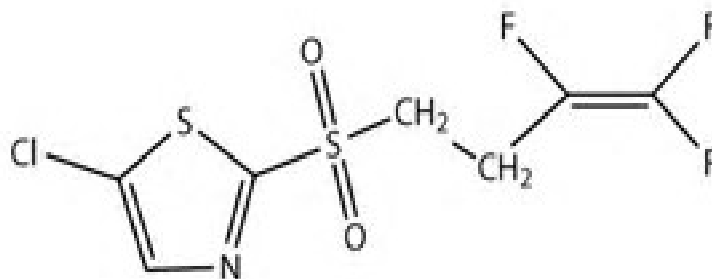
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Target Compounds

Fluensulfone



Metabolites

Thiazole Sulfonic Acid

Butene Sulfonic Acid

Fluensulfone on Potato



Potato Tubers
Wet Peel
Flakes
Chips

Potato
PR#10904 (2012)

Fluensulfone

1. Blend (5 minutes) then shake (5 minutes) in 50:50 acetonitrile : water
2. Decant and centrifuge
3. Filter aliquot
4. Analyze for fluensulfone by LC/MS/MS in positive mode with an acetonitrile/water gradient

Metabolites

1. Remove acetonitrile by evaporation from an aliquot equivalent to 1 g of matrix
2. Elute aqueous fraction through C18 spe cartridge, wash cartridge with water and combine fractions
3. Analyze for metabolites by LC/MS/MS in negative mode with an acetonitrile/water gradient

Initial Changes

To improve sensitivity, changed mobile phase to methanol/water from acetonitrile/water.

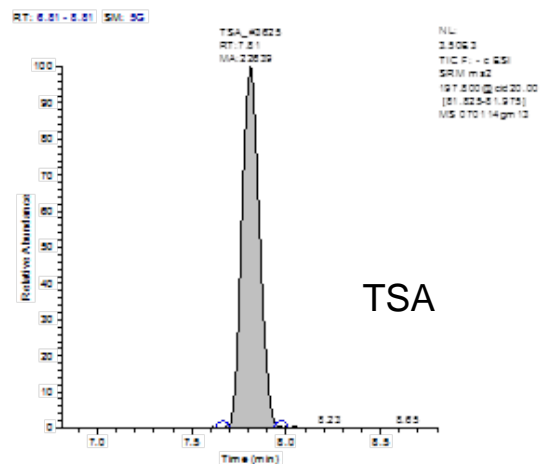
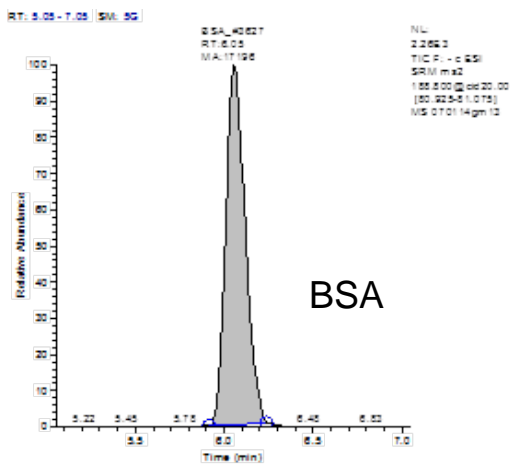
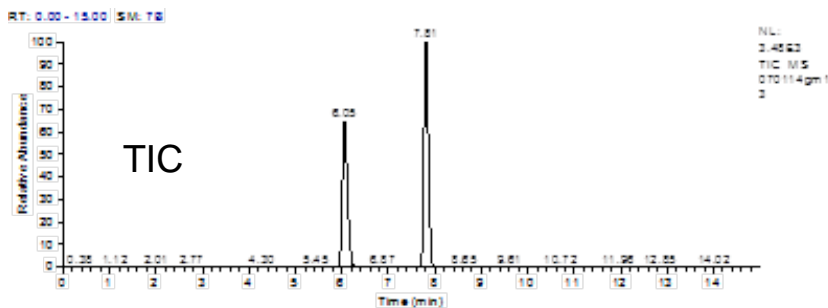
To improve peak shape, changed calibration standard solution organic/water composition.

Metabolites - Reference method worked relatively well

Fluensulfone - Recoveries were low likely due to matrix interference.

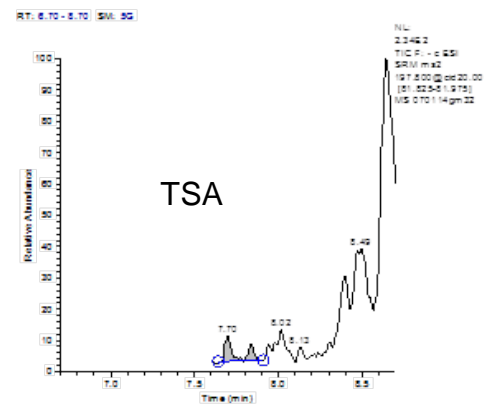
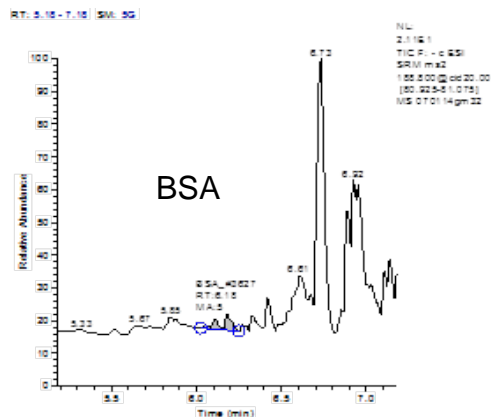
Modification: Used the C18 cartridge to clean-up the fluensulfone extract by adding a wash step after metabolite elution. Fluensulfone was eluted with acetonitrile.

Metabolite 1.6 ng/mL calibration standard

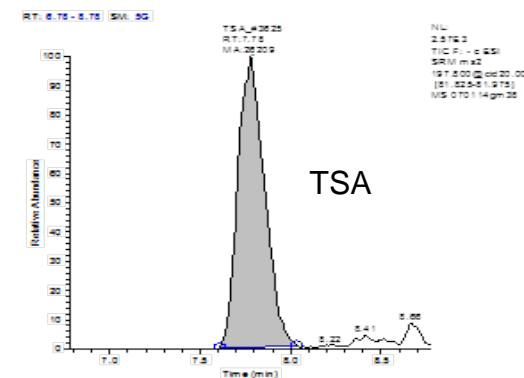
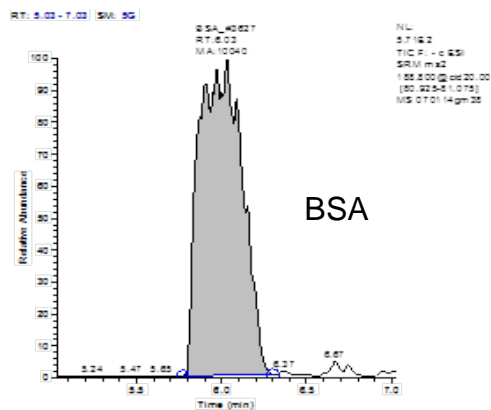


Metabolite – potato chips

Untreated Control



0.01 ppm fortification

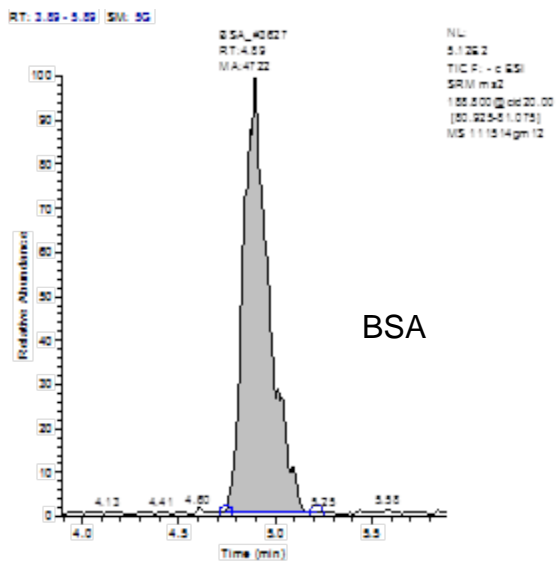


Potato Flakes and Chips

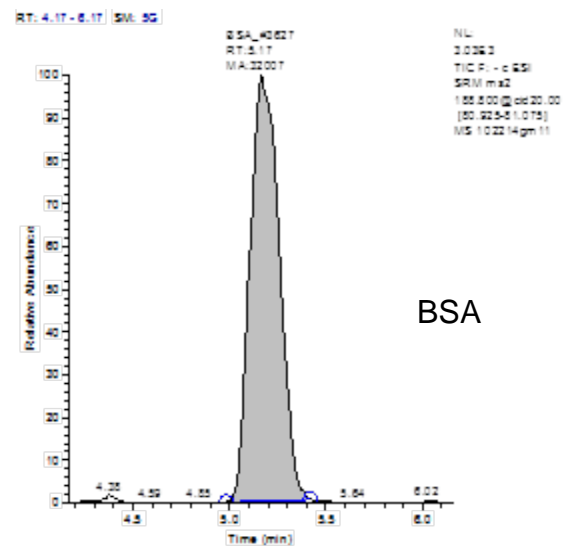
Interfering co-extractives were not effectively retained by C18.

- Metabolite - flakes and chips - substituted a 1 g polymeric hydrophilic-lipophilic balanced spe sorbent for C18
- Fluensulfone - flakes - substituted a 1 g C18 spe cartridge for 0.5 g cartridge
- Fluensulfone - chips - substituted a 1 g polymeric hydrophilic-lipophilic balanced spe sorbent for C18

Butene Sulfonic Acid after Modification



chips



flakes

Fluensulfone on Sugar Beet



Beet Roots
Beet Tops
Sugar
Molasses
Dried Pulp

Beet (Sugar)
PR#10908 (2013)

Sugar Beet – Roots and Tops

Roots

- Fluensulfone recoveries often <70%
- BSA recoveries were acceptable
- TSA recoveries near or below 70% at higher fortification levels

Tops

- Matrix interferences tended to increase recoveries at lower fortification levels



Modifications - Roots and Tops

To improve recoveries

- Additional shake
- Additional solvent
- Increased shaking time to 30 minutes

Modifications – Roots and Tops

To improve extract clean-up

- Weak anion exchange sorbents were used for metabolite extract clean-up.
 - Tops - polymeric weak anion exchange sorbent
 - Roots – NH₂ silica based sorbent
- Change in retention mechanism allowed the use of wash solvents containing organic solvents

Recoveries for Roots and Tops

Matrix	Level (ppm)	Number of Obs.	Fluensulfone	TSA	BSA
Roots	0.01	9	74 ± 7	90 ± 4	84 ± 4
	0.1	13	76 ± 6	80 ± 5	86 ± 4
	0.5	7	---	70 ± 2	85 ± 4
	1.0	5	---	70 ± 5	88 ± 10
Tops	0.01	12 (8)	75 ± 4	(109 ± 7)	86 ± 6
	0.1	11	76 ± 8	86 ± 7	87 ± 6
	5	7	---	75 ± 7	91 ± 5
	12	8	---	72 ± 4	94 ± 6
	20	5	---	66 ± 3	91 ± 4

Processed Fraction - Sugar

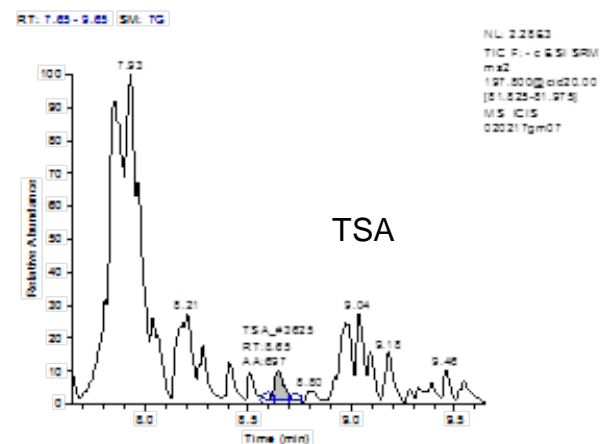
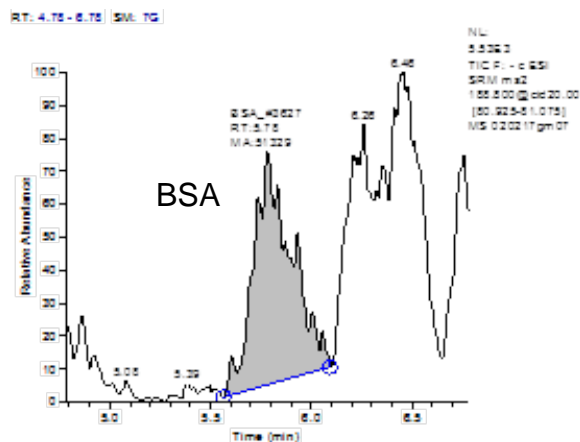
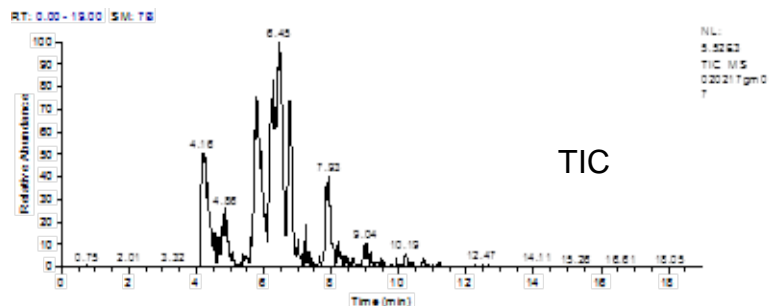
- Beet sugar was successfully extracted and analyzed using the working method for beet tops with slight modifications.
- One extract shaking step of 5 minutes
- Extract solution required stirring while aliquots were taken as phases began to separate after standing for a few minutes.

Processed Fraction - Molasses

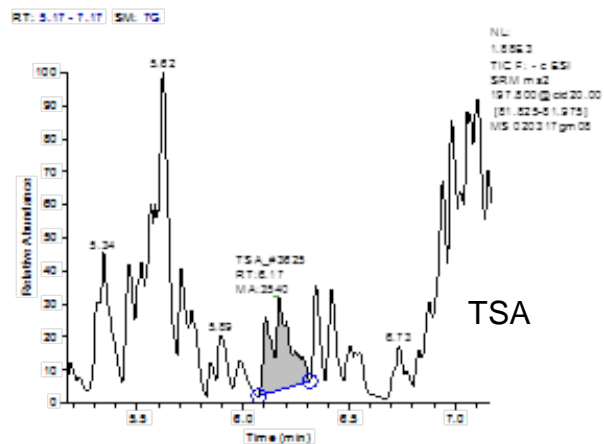
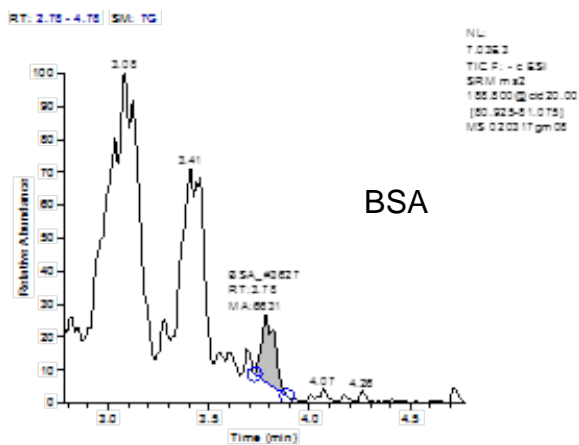
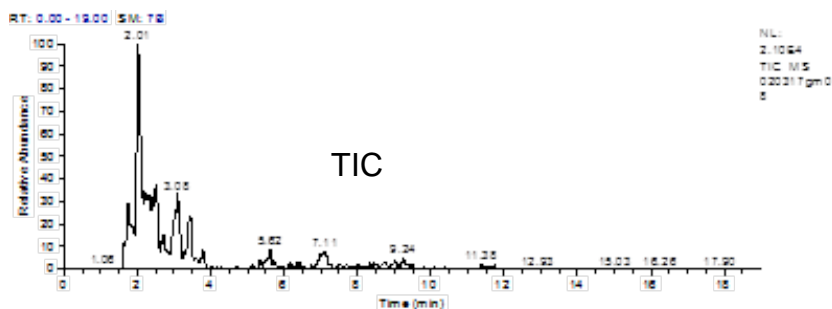


- Fluensulfone – The beet sugar method was used for extraction and analysis.
- Metabolites – The beet sugar method was used for extraction and clean-up, but the LC mobile phase was changed to deal with chromatographic interferences.

Molasses – untreated - methanol/water



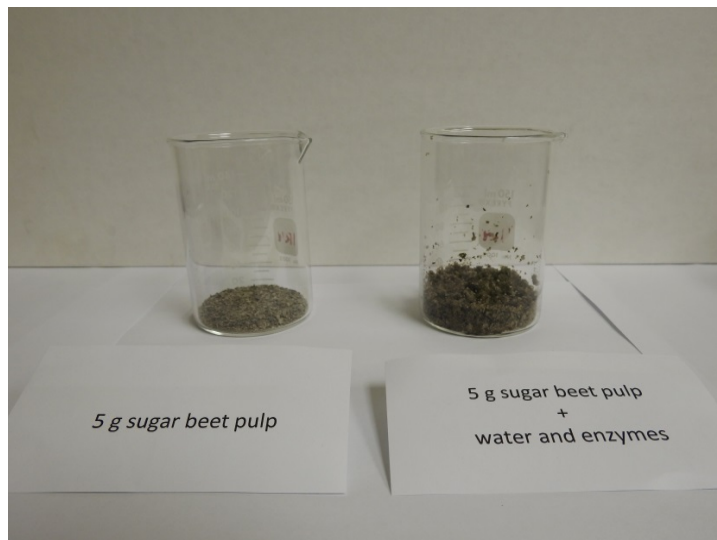
Molasses – untreated - acetonitrile/water



Recoveries for Molasses

Mobile Phase	Level (ppm)	Number of Obs.	Fluensulfone	TSA	BSA
Methanol & water	0.01	3	92 ± 10	115 ± 4	132 ± 6
	0.1	3	92 ± 15	87 ± 2	101 ± 1
Acetonitrile & water	0.01	3	---	92 ± 5	105 ± 6
	0.1	3	----	86 ± 3	100 ± 4

Sugar Beet - Dried Pulp



Sugar Beet - Dried Pulp

- Dried pulp rapidly expands with the addition of water. Pulp absorbs extraction solvent after rehydration.
- Cellulase and pectinase enzymes with water rehydrates matrix and less extraction solvent is absorbed.
- 5 g sample size
- Blend for 5 minutes and shake once for 30 minutes.
- Fluensulfone – clean-up with 0.5 g polymeric hydrophilic-lipophilic balanced spe sorbent
- Metabolites – clean-up with polymeric weak anion exchanger

Recoveries – Dried Pulp

Level (ppm)	Number of Obs.	Fluensulfone	TSA	BSA
0.01	3	70 ± 2	126 ± 1	104 ± 3
0.1	3	75 ± 2	93 ± 16	85 ± 3