Instrument for Solvent Extraction and Analysis (ISEE) of Organics from Regolith Simulant Using Supercritical Fluid Extraction and Chromatography

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July 20th, 2017

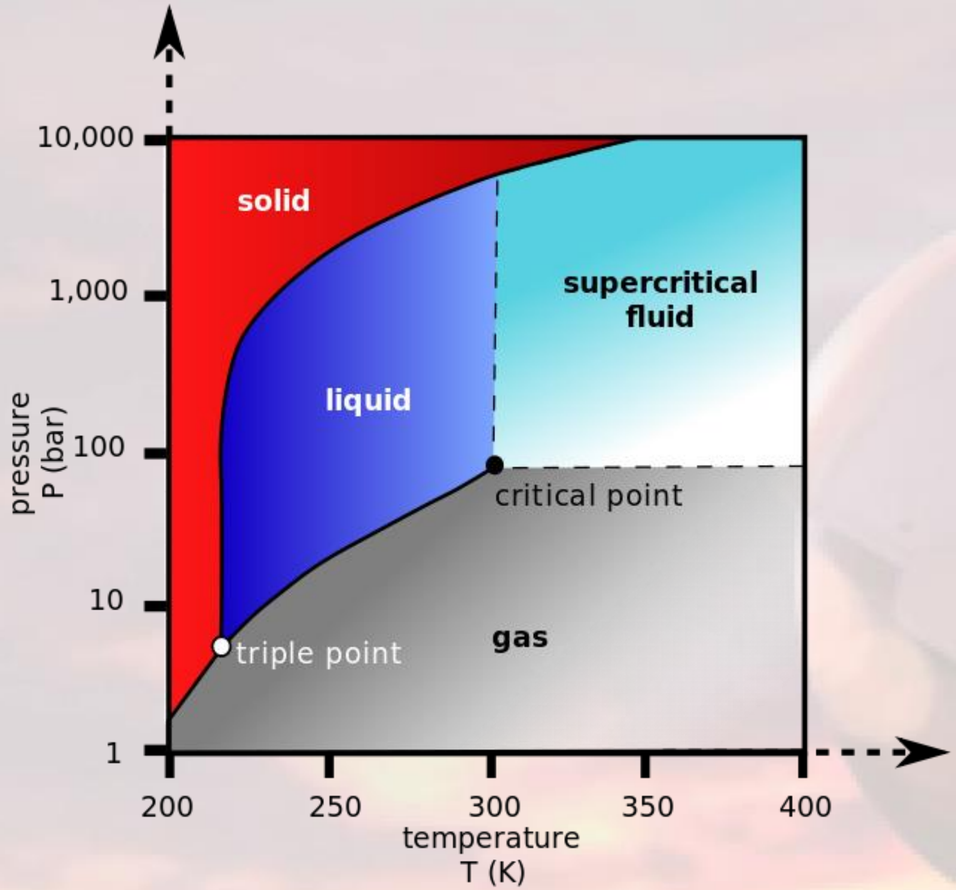
Background

- Best method for characterizing organic material found in a solid matrix is solvent extraction followed by chemical analysis
- ISEE will use supercritical fluid extraction (SFE) and supercritical fluid chromatography (SFC)
- SFE has found terrestrial applications ranging from extracting pollutants in soils to decaffeinating coffee beans
- SFC uses supercritical carbon dioxide to dissolve many nonpolar compounds and with the use of a polar modifier can dissolve polar compounds

Background

- Instrument for Solvent Extraction and Analysis of Extraterrestrial Bodies (ISEE)
  - Proposed novel, miniature system that enables solid extraction and chemical analysis at extraterrestrial locations
  - ISEE's desired capabilities
    - Rapid extraction and characterization of organic compounds
    - Determination of chirality
    - Solvent reuse
    - Solvent capture from in situ resources

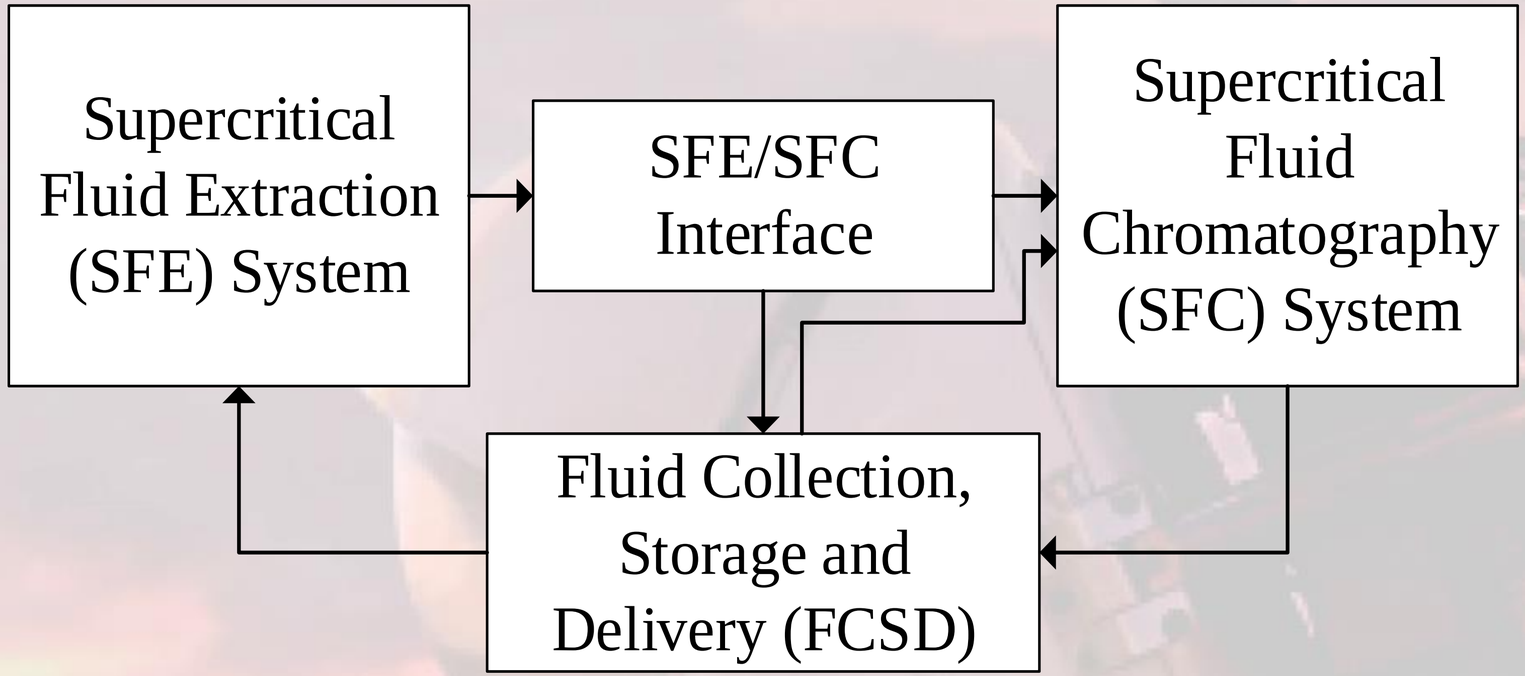
Supercritical Fluids



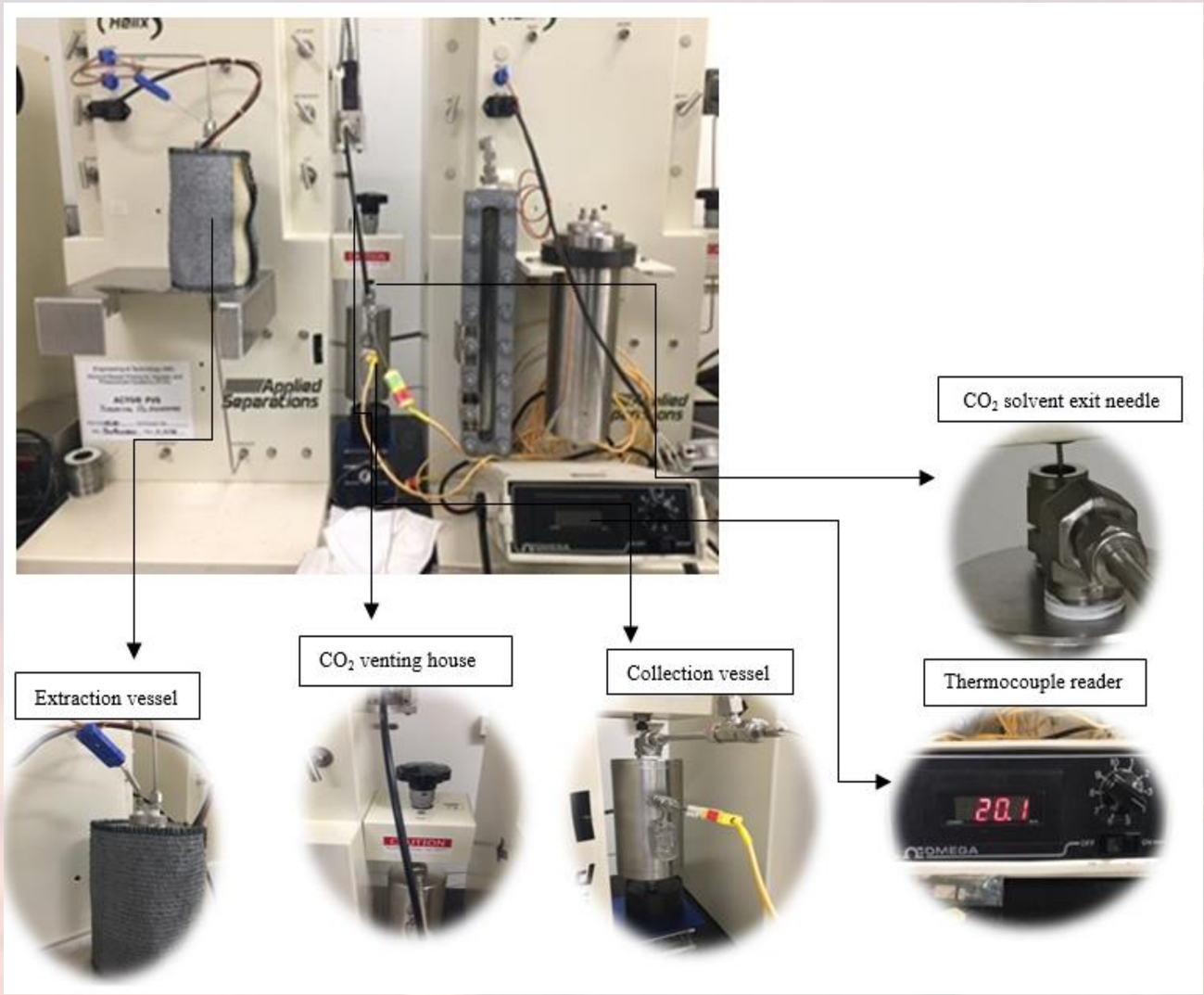
https://commons.wikimedia.org/wiki/File:Carbon_dioxide_pressure-temperature_phase_diagram.svg

- Substance at a temperature and pressure above its critical point
  - Critical point = end point of a phase equilibrium curve
- A supercritical fluid has both properties of liquids and gases
  - Good solvents
  - Selective solvents
  - Suitable replacements for organic solvents

ISEE Scheme


Supercritical Fluid Extraction (SFE) System
SFE/SFC Interface
Supercritical Fluid Chromatography (SFC) System
Fluid Collection, Storage and Delivery (FCSD)

Helix Applied Separations SFE System



Supercritical Fluid Extraction Method Development

- Organics chosen for extraction and analysis:
  - Naphthalene
  - Stearic acid
  - L-tryptophan
  - Polystyrene

Extraction vessel volume (mL)	Temp. (˚C)	Pressure (psi)	CO_2 exit flow (SLPM)	Modifier flow rate (mL/min)	Extraction Time (min)
1000	35 – 80	1740 – 2000	2 – 5	0 – 8.5	Variations among steady for as long as 30 min or dynamic with modifier flow for 40 min, followed by a short period of time steady time
50	40 – 120	1160 – 2000	2	2.2 – 5.7	Variations of short periods steady, followed by 40 dynamic w/ mod. and an extra short period without modifier

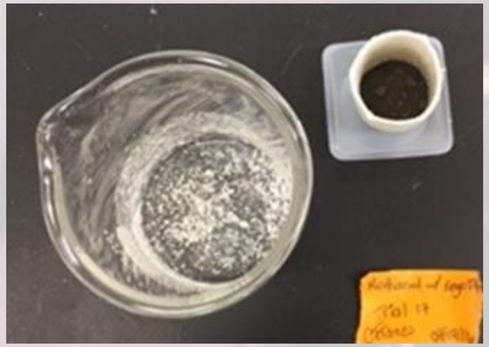
Extraction Experiments

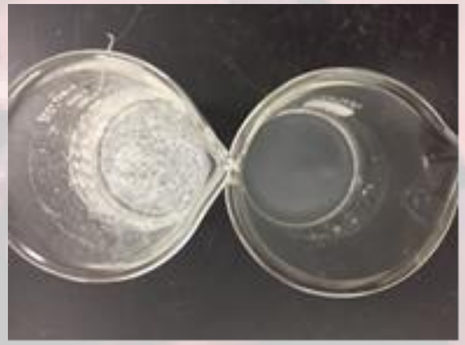
- For initial tests all contaminants were added to a 60 mm diameter circular aluminum plate inside 1000 mL extraction vessel
    - 2000 psi
    - 35 ˚C
    - no modifier flow static for 30 min

- Low decrease in the contaminant was observed
    - Polystyrene changed its physical appearance, from small white crystal to white lumps
    - Naphthalene was extracted easily
    - Stearic acid and L-tryptophan did not show any reduction in mass, nor any physical change
- Other pressures and temperatures were tried for stearic acid and L-tryptophan as well as the addition of methanol as modifier

Extraction Experiments

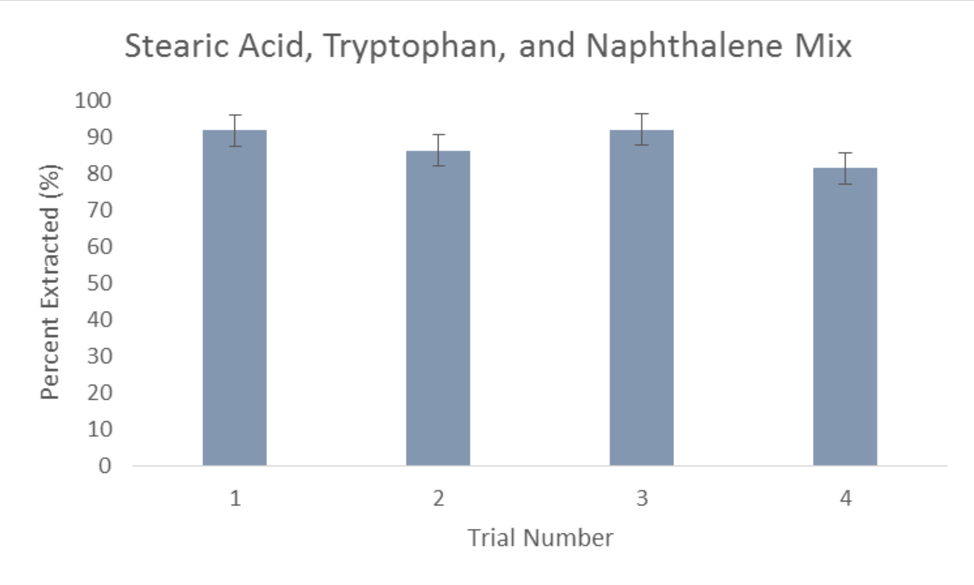
- Conditions that successfully extracted three of the substances
  - 2000 psi
  - 40 ˚C
  - 5 min batch extraction
  - 40 min dynamic extraction with methanol flow at 2.2 mL/min





- Aluminum plates were changed to smaller rectangular ones and later to 25 x 35 mm cylindrical cellulose thimbles for convenience
- New experimental tests were performed with the spiked regolith simulant
- Simulant was spiked with 1% by weight of each compound, resulting in a total of 4% by weight of the organic compounds

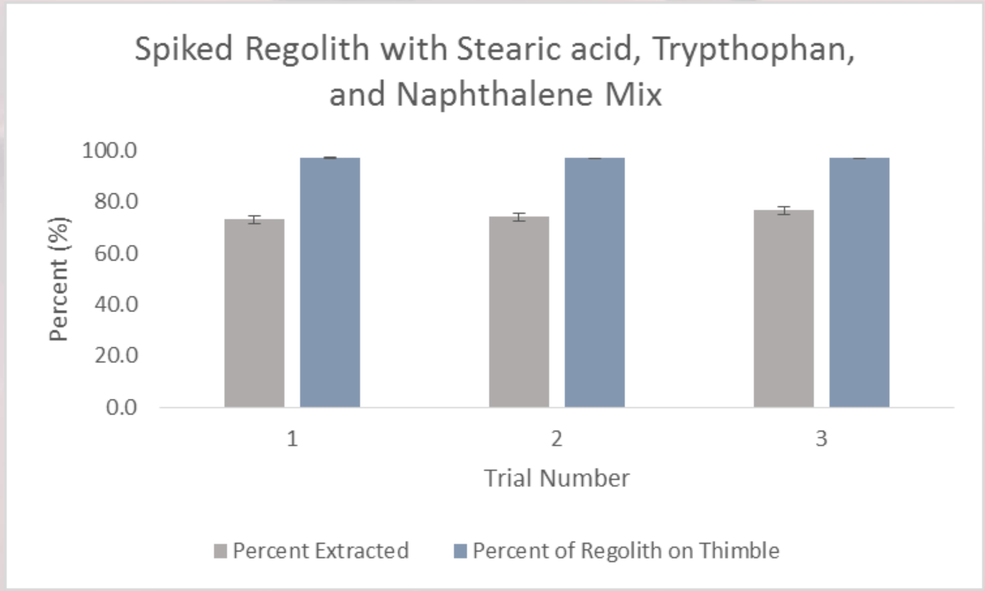
Extraction Experiments



- Extraction performed in 50 mL vessel at conditions previously described
- Extraction of mixture of stearic acid, L-tryptophan, and naphthalene
- Average extracted percentage was 86.4 ± 4.3%

Extraction Experiments

- Extraction of spiked JSC-1A lunar simulant
- Simulant was spiked with1% by weight of each of the four compounds
- Average extracted percentage was 74.6 ± 1.6%
- Percent of original regolith in thimble after extractions 97.7 ± 0.08%

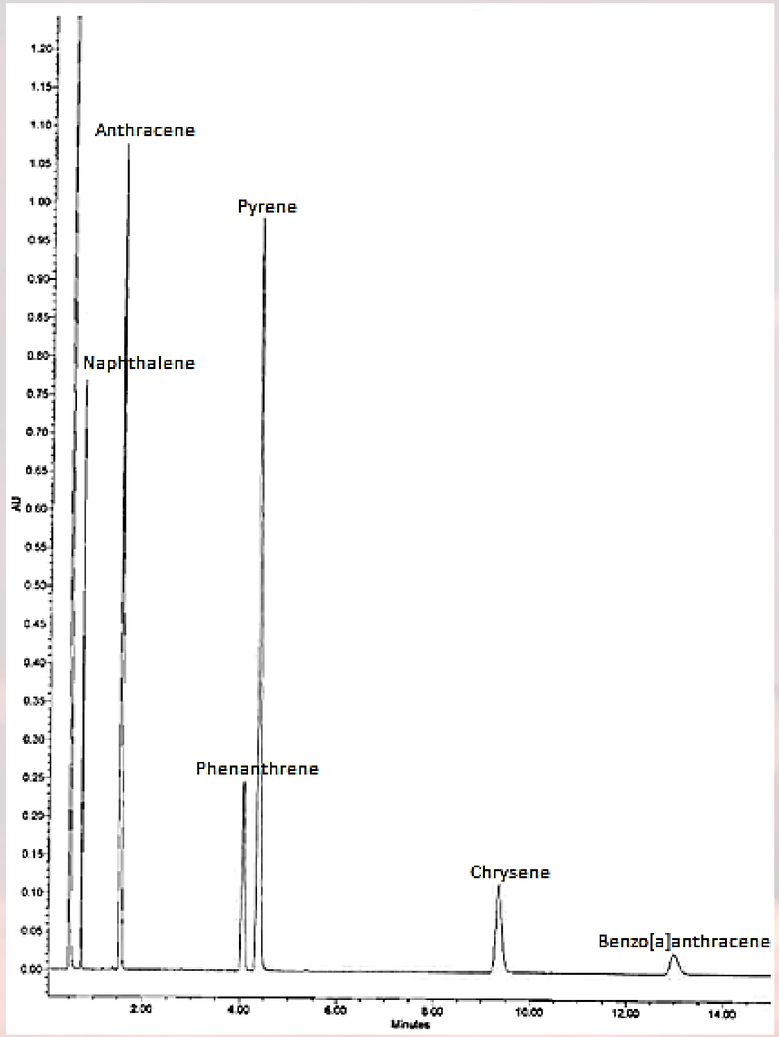


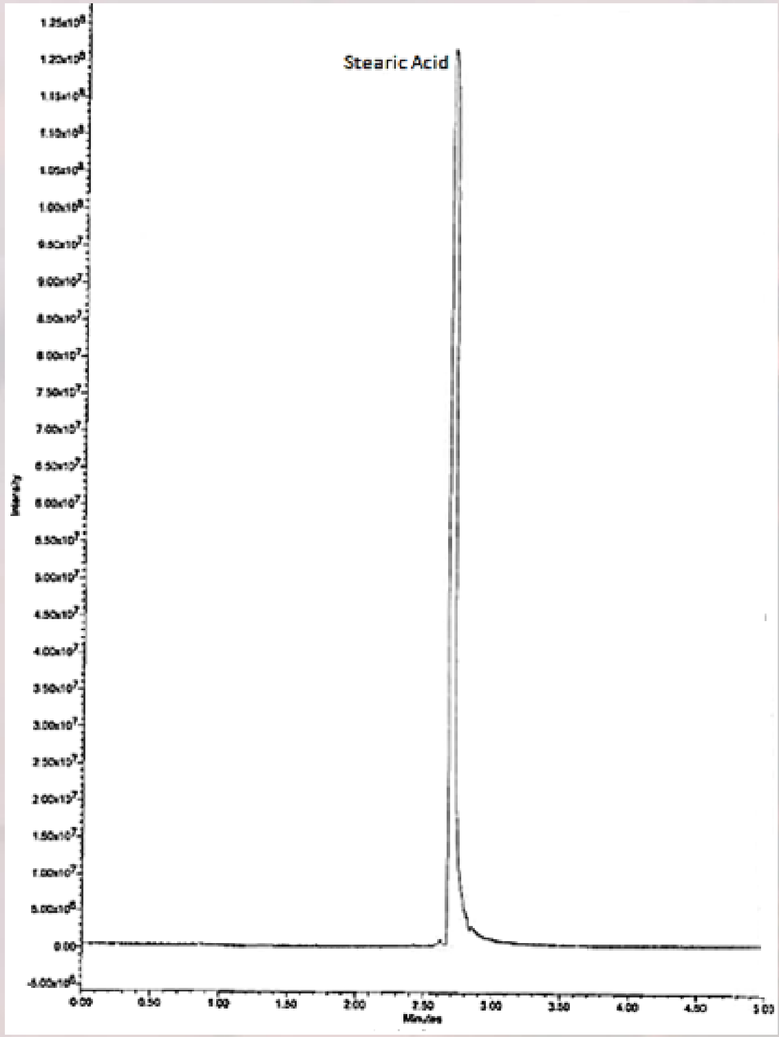
Supercritical Fluid Chromatography Method Development

- All solutions (naphthalene, stearic acid, L-tryptophan, and polystyrene) were between 6000 and 1500 ppm concentration and amino acids were diluted down to 40 and 4 ppm
- Four chromatographic columns were tested: Torus-2PIC (a-picolylamine), Torus-DIOL high density DIOL), BEH 2-EP (2-ethylpyridine), and HSS C18 SB
- Four modifiers were used:

B1	100% Methanol
B2	100% Methanol and 0.2% Ammonium hydroxide
B3	95% Methanol, 5% H_2O, 0.1% Trifluoroacetic acid
B4	79% Tetrahydrofuran, 20% Methanol, 1% Water, 0.1% Trifluoroacetic acid

Standards Chromatogram





Conclusions

- A series of proof of concept experiments were carried out to identify extraction conditions and columns for separation of extracted compounds
- Optimization of variables for the extraction of organics from spiked regolith simulant samples was successfully developed
- Best conditions chosen for extraction were 2000 psi pressure, 40 ˚C temperature, and 2.2 mL/min modifier flow for 40 min
- Extraction efficiency was comparable to traditional wet chemistry extraction methods; however, the collection efficiency was poor
- Visit to Waters facilitated narrowing of column selection as several methods were run and optimized for each set of organic compounds
- Columns selected were a HSS C18 SB 1.8 µL packed column and a Torus DIOL 1.7 µm

Conclusions

- Selection of the third column still has to be determined but it must have the ability to separate chiral compounds
- Waters visit enabled the creation and optimization of methods to successfully separate a wide range of poly-aromatic compounds as well as long chained carboxylic acids
- A method for detection of amino acids was also optimized; however, no method was created for separation of amino acid enantiomers yet

Acknowledgements

- This work was funded by NASA's Science Innovation Fund
- The authors would like to acknowledge Dr. Michael Fogwill, Principle Research Scientist in the Core Research organization of Waters Technologies Corporation for help and hosting Dr. Franco during initial SFC tests
- This work was greatly helped by two outstanding interns, Riley Daulton from The Ohio State University and Sarah Sheffield from Duquesne University

THANKS