Solid Phase Adsorption (SPA) method for tar and sulphur compounds

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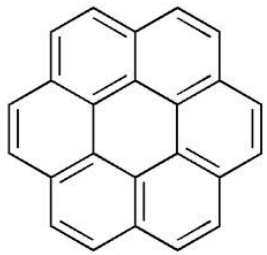
Introduction

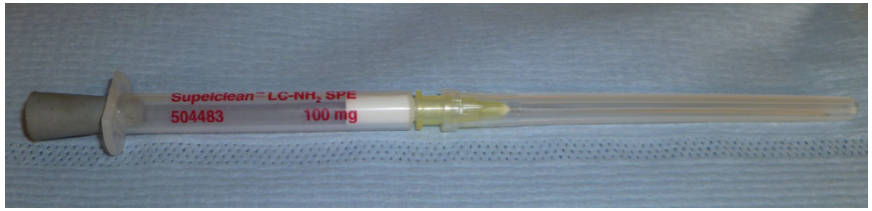
- Our desire: measurement of biomass tars after gasifier/gas clean-up, easy to use, low cost up to analysis
- Guideline method too cumbersome, only used by gasification <700°C @ ECN
- Since 1998 ECN used & improved the SPA method (originally developed by KTH, Sweden)
- SPA measures Polycyclic Aromatic Hydrocarbons (PAHs) with MW 104 (styrene) to 300 (coronene)
- SPA reproducibility within 10% for most tar components



SPA method for tars: sampling

- 100 ml gas at constant flow rate (50 ml/min) by automated syringe pump
- Type of SPA: LC-NH2 (aminopropyl), 100mg

- Volatile compounds (BTEX) are not 100% adsorbed (pass through adsorbent, we use micro-GC for Benzene & Toluene)
- All other measured compounds (oxygenated compounds , N PAHs & PAHs without hetero atoms) adsorb & desorb well
- Heavy compounds (MW>300) do not evaporate sufficiently in a GC-FID and are not measured



SPA method for tars: analysis

- 33 compounds identified, other peaks labelled as ‘Unknowns’ & classified in 5 groups according to elution on the GC column
- Tar clasification system by ECN:

Class 1	GC undetectable tars. This class includes the heaviest tars that condense at high temperature even at very low concentrations.
Class 2	Heterocyclic components (like phenol, pyridine, cresol). These are components that generally exhibit high water solubility, due to their polarity.
Class 3	Aromatic components. Light hydrocarbons that are not important in condensation and water solubility issues.
Class 4	Light polyaromatic hydrocarbons (2-3 rings PAH’s). These components condense at relatively high concentrations and intermediate temperatures.
Class 5	Heavy polyaromatic hydrocarbons (4-5 rings PAH’s). These components condense at relatively high temperature at low concentrations.

Experiments with tandem SPA column: tars

- SPA sampling of hot gas leads to warming of SPA column
- Experiment with two SPAs in series, 1st results (ratio component in SPAs) :

	Benzene	Toluene	Ethyl - Benzene	m/p - Xylene	O-Xylene + Styrene	Phenol	Naphtalene
1st SPA	16%	14%	16%	26%	28%	100%	100%
2nd SPA	84%	86%	84%	74%	72%	0%	0%

- Light compounds (< phenol) adsorb more in 2nd column
- Benzene & toluene not completely adsorbed after 2 SPAs: according to µGC only 20% and 66% of amount in gas adsorbed
- SPA method not perfect for measurement of light tars from hot gas

Conclusion tandem SPAs: tars

- BTEX not well adsorbed on 1st SPA
- 1st SPA warms up when sampling from hot gas
- Boiling point (±80 - 140 °C) & polarity influence adsorption on LC-NH2 column
- Tandem SPAs improve capture of lighter compounds
- LC-NH2 is high polar, perhaps medium polar columns work better
- Controlling the temperature of the column during sampling may improve adsorption

- So far, ECN is satisfied with the SPA method, but there is room for improvement or adaptation to other compounds than tars

‘Heavy’ tar measurements: first results

‘Heavy tars matter most’

Fluoranthene (202 g/mol)	Benzo(a)pyrene (252 g/mol)	Coronene (300 g/mol)	Dew Point (calculated)
-	-	100 mg/Nm^3	236°C
-	1 000 mg/Nm^3	100 mg/Nm^3	237°C
10 000 mg/Nm^3	1 000 mg/Nm^3	100 mg/Nm^3	239°C

- 50 g/mol heavier tars dominate tar dew point, even at 1/10th the concentration
- Fouling by tar occurs at surfaces with temperature of 300 and even above 400°C
- ´Coronene is not the problem´
- SPA does not quantify the tars that matter

‘Heavy’ tar measurement

- GC-FID tar analysis limited to coronene (MW300)
- Quantify ‘heavy’ tars by measurement with microfiber extraction (Soxhlet) thimbles
- Tar condensation at thimble temperature of 350, 450, 550 °C
- Extraction with DCM
- Sample point after MILENA gasifier

‘Heavy’ tar measurement

- 1st and 2nd experiment: extracts with DCM
- GC-FID indicate majority Coronene and peaks beyond Coronene
- Tar and dust collected in the same thimble
- Conclusion: probably not all tars are extracted with DCM or are irreversibly condensed on dust or filter material

- 3rd experiment: 1st thimble @ 550 °C (dust filter), 2nd @ 350 °C (tar condensation), extraction with DCM and NMP

- HT GC-FID method under development to analyse tars MW>300
- Extracts send to JRC for SEC (Size Exclusion Chromatography)

Final remarks

- ECN can analyse SPA samples for 3rd parties
- Perhaps implementing improvements of the SPA method, developed by different groups, into one document, resulting in a united improved SPA method?


Thank you for your attention!
Questions?

Acknowledgement

Part of the work was funded by the EDGaR program and the BRISK project:

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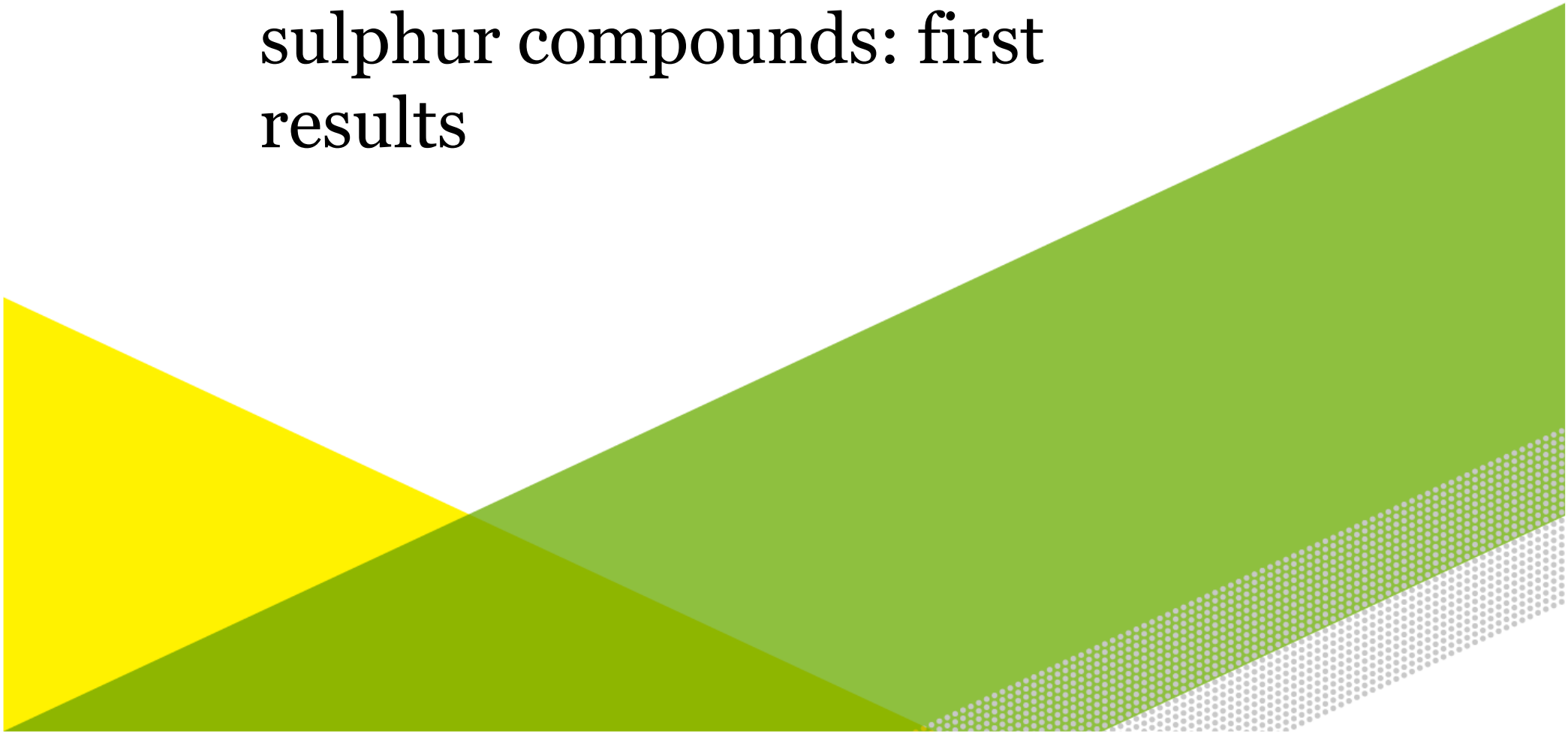
SPA measurement for sulphur compounds: first results



Experiments with tandem SPA column: sulphur compounds

- Heavy (Di)methyl DBTs below detection limit
- Experiment with two SPAs in series, 1st results:

	Thiophene	2-Methyl thiophene	3-Methyl thiophene	1-benzo thiophene	Dibenzo thiophene
1st SPA	14%	<35%	<25%	>99%	>95%
2nd SPA	86%	>65%	>75%	<1%	<5%

- Single ring compounds not adsorbed on one column
- (D)BT adsorbs well on one column
- Thiophene not completely adsorbed after 2 SPAs: according to GC-FPD 20% adsorbed
- SPA method not perfect for measurement of single ring S compounds from hot gas, similar to BTEX

Conclusion tandem SPAs: tars and S-compounds

- 1-ring S compounds not well adsorbed on 1st SPA
- 1st SPA warms up when sampling from hot gas
- Boiling point (±80 - 140 °C) & polarity influence adsorption on LC-NH2 column
- Tandem SPAs improve capture of lighter compounds
- LC-NH2 is high polar, perhaps medium polar columns work better
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