

Measurement of organic sulphur and nitrogen compounds in biomass producer gas by SPA sampling

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July 2014
ECN-M--14-038



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Solid phase adsorption (SPA), commonly used for tar measurements, can also be used for similar compounds containing sulphur or nitrogen.

Sub-ppm levels can be detected, a level required for protection of catalysts.

Sampling Method

- Small volume of gas (e.g. 100 ml) is drawn slowly through SPA material (LC-NH₂).
- Gas and SPA material are allowed to cool to room temperature (or lower), which reduces gas moisture content to a few percent.
- Temperature and pressure are recorded for correction to standard conditions (0°C, 1 bar).



Automated SPA sampling system

SPA material + protective cap

Sample treatment

- Samples are stored in freezer until extraction for analysis.
- Small amount of reference standard is added to SPA material.
- SPA material + container + needle are flushed with small volume of DCM to extract tar, including heavy organic S and N compounds.
- Quantitative analysis by GC-FID for tar, GC-MS for organic S and N compounds. (Identification organic S by GC-PFPD).

Conclusion

- Benzothiophene and heavier organic S compounds are captured, thiophene and methylthiophenes do not bind well.
- GC-MS SIM analysis can detect organic S compounds to about 10 ppb.
- Pyridine and heavier organic N compounds are captured.
- More polar nature of N compounds leads to higher detection level.

Recovery test of organic S compounds

- Small volumes of a solution with organic S compounds were applied to standard SPA material (LC-NH₂).
- SPA samples were left to dry at room temperature for 1 hour.
- Samples were extracted and analysed (see **Sample treatment**).
- Recovery ~100% for DBT and heavier compounds, 90% for BT, lower for more volatile compounds

Compound	Test amount 0.13 µg	Test amount 13 µg
Thiophene	82%	73%
2-Methyl thiophene	81%	78%
3-Methyl thiophene	84%	78%
Benzothiophene (BT)	91%	87%
Dibenzothiophene (DBT)	108%	99%
4-Methyl DBT	113%	97%
4,6-Dimethyl DBT	110%	97%

SPA capture of tar, organic S and N from hot gas

- Two SPA columns in tandem to investigate whether capture is complete in first one (i.e. in normal conditions).
- Tandem samples (6 pairs) extracted and analysed separately.
- Volatile tar and S compounds lower in 1st than in 2nd SPA => standard SPA not reliable at all, tandem SPA to be doubted.
- Standard SPA >95% reliable for naphthalene, BT and heavier compounds, and for polar compounds such as phenol and pyridine.

Compound	1 st SPA	Compound	1 st SPA	Compound	1 st SPA
Benzene	<15%	Thiophene	<15%	Pyridine	95%
Toluene	<15%	2-Methyl thiophene	<35%	2-Methylpyridine	>95%
Ethylbenzene	<15%	3-Methyl thiophene	<35%	3-Methylpyridine	>95%
Xylene	<25%	Benzothiophene	100%	4-Methylpyridine	>95%
Styrene	<25%	Dibenzothiophene	>95%	Quinoline	100%
Phenol	100%			Isoquinoline	100%
Indene	~70%	<i>Accuracy for Methylthiophene, Methylpyridine and Dibenzothiophene limited by low concentrations</i>			
Naphtalene	100%				

Possible improvement: LC-NH₂/active carbon

- Captures 50-100% benzene and ~100% toluene
- Significantly higher background peaks, especially near toluene
- Captures ~25% thiophene

Acknowledgement

This research is co-funded by



BRISK is funded by the European Commission Seventh Framework Programme (Capacities)



Investing in your future. The research program EDGaR acknowledges the contribution of the funding agencies: The Northern Netherlands Provinces (SNN). This project is co-financed by the European Union, European Fund for Regional Development and the Ministry of Economic Affairs. Also the Province of Groningen is co-financing the project.

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