



Status of IEA Task 33 gas analysis special report

B.J. Vreugdenhil, C. Mourao Vilela, G. Aranda Almansa
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Project background

- Proposal accepted in May 2017.
- Agreed deadline: 30/06/2018 → **extended during last IEA meeting.**
- Scope: gas analysis techniques applied to biomass- and waste gasification.
- Objectives: dissemination of current work in gas analysis, reinforcement of research network and collaboration in the field by exchanging expertise and experience.

Project approach

- Creation of team of contributing partners.
 - Close collaboration with Gas Analysis Group:
Regular contact/meetings with S. Biollaz (PSI) and Y. Neubauer (TUB)
 - Call for participation among:
 - Gas Analysis Group network.
 - Other institutes not associated to the GA Group.
 - Gasification plants.
 - Regular contact with project partners.
- Complementary literature review in parallel to material from project team.

Report structure

2 parts:

1. Gas analysis report: available techniques per target gas compound, practical implementation, new developments.
2. Complementary factsheets of gas analysis techniques.

Table of contents

1.	Introduction	12
1.1	Motivation of this work	12
1.2	How to use this manual	14
1.3	Scope of this report	14
2.	Measurement of target compounds of gasification product gas	15
2.1	Measurement of permanent gases	15
2.1.1	Main gas compounds – CO, CO ₂ , H ₂ , CH ₄	15
2.1.2	C1-C5 hydrocarbons	18
2.1.3	Gas conditioning for analysis	20
a)	Pre-sampling system at ECN-TNO	20
b)	Dilution system at VTT	21
c)	Gas conditioning at TU Delft	22
2.2	Measurement of water content of product gas	23
2.3	BTX (Benzene, Toluene, xylenes)	24
2.3.1	General considerations	24
2.3.2	Measurement of BTX	25
2.4	Tar measurement	27
2.4.1	Offline tar analysis methods	28
2.4.2	Online tar analysis methods	30
2.5	Sulphur compounds	33
2.5.1	General considerations	33
2.5.2	Analysis of sulphur compounds	34
2.5.3	Sampling of sulphur compounds	36
2.5.4	Organic S compounds	36
2.6	Nitrogen compounds	41
2.6.1	General considerations	41
2.6.2	Online measurement of NH ₃ and HCN	41
2.6.3	Offline measurement of NH ₃ and HCN	42
2.6.4	Organic N compounds	44
2.6.5	Application of SPA for organic S- and N- compounds	45
2.7	Chlorine and halogenated compounds	48
2.7.1	General considerations	48
2.7.2	Measurement of HCl	48
2.7.3	Measurement of other Cl compounds	50
2.7.4	Application of diode laser-based spectroscopy (TDLAS) for online HCl detection	50
2.8	Alkali compounds	51
2.8.1	General considerations	51
2.8.2	Online measurement of alkali compounds based on SID and VTDMA	53
2.8.3	Online measurement of K using TDLAS	55
2.9	Trace elements	57
2.9.1	General considerations	57
2.9.2	Measurement of trace compounds	57
2.9.3	Measurement of mercury	57
2.10	Silica compounds – siloxanes	59
2.10.1	General considerations	59
2.10.2	Measurement of siloxanes in biogas	60
2.11	Particulate matter measurement	61
2.11.1	General considerations	61
2.11.2	Low-pressure cascade impactors (LPI)	65
2.11.3	Scanning Mobility Particle Sizer (SMPS)	71
3.	Practical implementation of gas analysis at pilot- and industrial gasification plants	73
3.1	Introduction	73
3.2	Implementation of gas analysis – practical cases	73
3.2.1	General considerations	73
3.2.2	Gasification for heat production – the Amer 9 plant, The Netherlands	73
3.2.3	Small-scale gasification for combined heat and power (CHP)	76
3.2.4	Gas analysis at CENER gasification pilot plant	76
3.2.5	Gas analysis at BFB pilot plant at University of Seville	77
3.2.6	Gas analysis at the Güssing plant – CHP production + research on synthesis	78
3.2.7	Gas analysis at measurement campaigns by VTT	79
3.2.8	Gas analysis at pressurized fluidized bed gasifier at Technical University Delft	80
3.2.9	Gas analysis at biokip pilot plant	80
3.2.10	Gasification for production of Synthetic Natural Gas – the GoBiGas plant, Sweden	82
3.2.11	Low-temperature gasification - 100 kW LY-CFB and 6 MW Pyroener gasifier (DTU)	85
3.2.12	Waste gasification – the Lahti Energia plant	86
3.2.13	Waste gasification – the Tondela plant	87

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Task 33

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Appendix A.

Factsheets of gas analysis techniques applied to biomass/waste gasification

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- Elution of the sorbents in a single fraction instead of different liquid samples can lead to lower measurement errors as well as shorter analysis time.
- SPA is not completely reliable for measurement of low temperature tars ($< 270^{\circ}\text{C}$). The reason is the large amount of light and near-IR rays which, due to their large polarity, are strongly adsorbed to the SPA material, and cannot completely elute and thus cannot be detected.

Examples of implementation



Figure 108. SPA sampling in (a) 100 mL sampling vials or (b) sealed sampling vials (c) 100 mL and (d) 100 mL sample bottles + sample protected by plastic cap + rubber septum ready for storage after sampling (e) SPA samples stored in frozen (200 mL) sample bottles (ready for gasification).

188

Appendix A. Factsheets of gas analysis techniques applied to biomass/waste gasification

- High degree of accuracy using accuracy and measurement repeatability.
- Commercially available.

Limitations [66]

- Low sample sizes (less than 100 mg).
- Image edge detection problems.
- 30 to 20 image distortion.
- Operator bias.
- Sample consistency of ~ 1 –3.5%.

Contacts

Dr. Chaper (ICM-THY) chaper@icm-thy.de

3.52 Solid Phase Adsorption (SPA)

This column method, applied for the measurement of tars and other organic compounds, was originally developed by PFA (2002). Currently SPA is, together with the tar guidelines, the most commonly used method for measurement. The convenience of this technique has led to the exploration of its application to other compounds beyond tars, such as organic sulphur and nitrogen compounds.

How it works

Solid Phase Adsorption (SPA) is based on the adsorption of volatile compounds on a solid-phase sorbent. The tar-laden gas sample flows through a sorbent (e.g. amino-based, activated carbon) which captures the tar components. The loaded column is subsequently desorbed using a solvent, so that the tar components are finally analysed using gas chromatography (GC-MS). The schematic layout of gas sampling using SPA is shown in Figure 106.

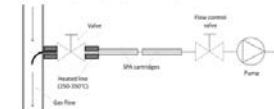


Figure 107. Schematic layout of sampling using SPA in shown in Figure 106.

189



Figure 109. SPA sampling in (a) 100 mL.

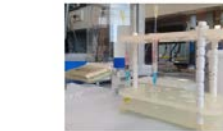


Figure 110. Extraction of SPA cartridges with a solvent.

The SPA sampling is composed of a number of stages: sampling and storage, recovery of the adsorbed compounds by means of a solvent, and analysis of the extract for the quantification of the compounds. As an example, the experimental procedure followed at ICM-THY for SPA sampling (Figure 109) is described below:

at sampling and storage

A commercially available adsorption column (ICM-THY 100 mg) is equipped with an injection needle. The needle is inserted into the hot, wet producer gas flow by means of a sample port with graphite ferrule. An automatic syringe pump with 100 mL graphite syringe is used to draw gas through the column at a constant flow rate of 50 mL/min. Once the gas pump has filled with gas the 100 mL glass syringe, the sampling is stopped. The column with the needle is removed as soon as the pressure differential (as indicated by the pressure indicator) has dropped to zero. The outside part of the needle is cleaned with a tissue. The column is sealed with a rubber stopper and the attached needle with a cap. The gas volume has to be corrected for pressure and temperature conditions in order to calculate the dry gas sampled.

The sample (Extrakt) is needed to be stored in a refrigerator at -20°C , and later to the analytical laboratory as soon as possible for analysis of tar components by GC-MS/MS. It

179

Advantages

- Less complicated sampling compared to tar guidelines.
- Several samples per hour are possible: allows better assessment of process variations.
- Reliable for compounds heavier than BTEX.
- No need for handling of organic solvents (safety regulations in industrial environments).

Limitations

- Despite faster sampling than guidelines, it is still not an online method.
- Incomplete adsorption (leakage) of light volatiles (BTEX, thiophenes) (see "Relevant aspects" for further details).

Relevant aspects

- Selection of SPA sorbent: there are different types of SPA columns, differing in composition and size. The amino-based (ICM-THY 100 mg) is the most widespread sorbent used for tar analysis. However, this column size is not sufficient to ensure complete adsorption of light aromatic compounds such as BTEX. In this case, the increase of the cartridge size can improve this issue by decreasing the breakthrough of light compounds to below detection limits [34]. Another possible option involves the addition of a second SPA column (before or after) in series [37].
- Sampling: the sampling point should be kept at high temperature to avoid condensation of tars.
- For a precise determination of the sampled volume of gas, it is necessary to report the pressure and temperature during sampling. Without proper reporting of pressure and temperature conditions, measurement uncertainty of 8.8% per 1°C can occur [34].
- After sampling, it is recommended to seal aseptically 10 seconds to seal the gas to completely cool down to ambient temperature, in order to ensure that the actual gas volume is equal to the target value (usually 100 mL). An accurate measurement of the gas volume (assuming ambient T and P) will further influence the calculation of the concentration.
- The use of an automated sampling system can significantly increase the repeatability of the method [34].
- During sampling, it is important to ensure that there are no bubbles in the syringe or the injection device [34].
- During sampling, the temperature of the SPA column increases due to the flow of hot gas and the condensation of the water contained in the gas. The increase in temperature can eventually result in a decrease of the adsorption of tar components in the sorbent column. Active cooling of the sorbent during sampling might improve the accuracy of measurement of the more volatile compounds, which are more likely to desorb from the cartridge [34]. Alternatively, an additional activated carbon adsorbent should be added in series to ensure constant adsorption [34]. If the focus is to measure the tar concentrations in a gas stream with low moisture content and temperature $< 100^{\circ}\text{C}$, it is better to use the amino sorbent without additional activated carbon.
- Samples should be stored in the freezer immediately after sampling to minimize the desorption of volatile species. Moreover, in order to ensure reliable samples, the elution step should be performed within 24 hours after sampling [34].

Project status

- So far, 32 partners on board 😊
- Draft submitted to IEA Task 33 members and contributing partners for feedback and submission of further material.
- Remaining gaps:
 - Video blogs (candidates, but no input yet).
 - Experiences from measurement campaigns and gasification plants: **coal to liquids**, host site measurement at Stuttgart.



Project status

- Project on track.
- Latest draft sent around to report contributors and members – waiting for feedback.
- Latest contributions still to be received, e.g. etc.
- IEA Task 33 board meeting in progress.
- Request for funding granted:
 - Material from joint measurement campaign at University of ...
 - extra time for delivery of videos and material from partners.

→ **Material from partners still welcome!**

Thanks to you all for your contribution!!!



Thanks for your attention!

Contact: carlos.mouraovilela@tno.nl
guadalupe.aranda@tno.nl
berend.vreugdenhil@tno.nl



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