Gas analysis in gasification of biomass and waste

Guideline report
Document 2 –
Factsheets on gas analysis techniques

IEA Bioenergy

IEA Bioenergy Task 33

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Document 2 – Factsheets on gas analysis techniques

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Introduction

Gasification is generally acknowledged as one of the technologies that will enable the large-scale production of biofuels and chemicals from biomass and waste. One of the main technical challenges associated to the deployment of biomass gasification as a commercial technology is the cleaning and upgrading of the product gas. The contaminants of product gas from biomass/waste gasification include dust, tars, alkali metals, BTX, sulphur-, nitrogen- and chlorine compounds, and heavy metals. Proper measurement of the components and contaminants of the product gas is essential for the monitoring of gasification-based plants (efficiency, product quality, by-products), as well as for the proper design of the downstream gas cleaning train (for example, scrubbers, sorbents, etc.). The deployment and implementation of inexpensive yet accurate gas analysis techniques to monitor the fate of gas contaminants might play an important role in the commercialization of biomass and waste gasification processes.

This special report commissioned by the IEA Bioenergy Task 33 group compiles a representative part of the extensive work developed in the last years by relevant actors in the field of gas analysis applied to (biomass and waste) gasification. The approach of this report has been based on the creation of a team of contributing partners who have supplied material to the report. This networking approach has been complemented with a literature review. This guideline report would like to become a platform for the reinforcement of the network of partners working on the development and application of gas analysis, thus fostering collaboration and exchange of knowledge. As such, this report should become a living document which incorporates in future coming progress and developments in the field.

HOW TO USE THIS MANUAL

This guideline report is composed of 2 different documents: Document 1 describes the available analysis techniques, both commercial and under development, for the detection of the different compounds of interest present in gasification gas. Document 2 (the present report) is an appendix to Document 1 which contains complementary information about the different analysis techniques mentioned in Document 1 in a list of factsheets. The analysis techniques have been classified in alphabetical order for the sake of convenience of use. Each item includes a brief description of the principle of measurement, advantages, limitations, and a list of contacts of partners that apply the technique in their institution or company. Document 2 also contains a final table with the contacts of the contributing partners of this collaborative guideline report.

IEA Bioenergy Task 33 Youtube channel:
https://www.youtube.com/channel/UCjZQMdEdmaDzNCScS6ckINw/featured

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Chalmers University of Technology

Energy research Centre of the Netherlands, part of The Netherlands Applied Research Organisation (ECN part of TNO)

Free University of Bolzano (UNIBZ)

French Alternative Energies and Atomic Energy Commission (CEA)

Gas Analysis Group (GAW)

German Aerospace Centre (DLR)

Göteborg Energy AB

Gothenburg University

Iowa State University (ISU)

Karlsruhe Institute of Technology (KIT)

Linnaeus University

Luleå Technical University (LTU)

National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA)

National Laboratory of Energy and Geology (LNEG)

National Renewable Energy Centre (CENER)

National Renewable Energy Laboratory (NREL)

Paul Scherrer Institute (PSI)

Research and Innovation Center in Gas and New Energies of ENGIE (ENGIE Lab CRIGEN)

RWE Essent

Scientific and Technological Research Council of Turkey (TÜBITAK Mam)

Stanford University

Swedish Gasification Centre (SFC)

Technical Research Centre of Finland (VTT)

Technical University Berlin (TU Berlin)

Technical University of Denmark (DTU)

Technical University Delft (TUD)

Technical University Graz (TUG)

Technical University of Munich (TUM)

Umeå University (UME)

University of California at San Diego (UCSD)

University of Castilla-La Mancha (UCLM)

University of Glasgow

University of Seville

Vienna University of Technology (TU Wien)

Abbreviations

AAS	Atomic Absorption Spectrometry
AFS	Atomic Fluorescence Spectroscopy
AMFIA	Ammonia Flow Injection Analysis
APS	Aerodynamic particle sizer
BFB	Bubbling fluidized bed
BTX	Benzene, toluene, xylenes
CFB	Circulating fluidized bed
CF-WMS	Calibration-free scanned wavelength-modulated spectroscopy
CVAAS	Cold vapor atomic absorption spectrometry
ELIF	Excimer laser-induced fragmentation fluorescence
ELPI	Electrical low-pressure impactor
ELS	Elastic light-scattering
EPA	United States Environmental Protection Agency
EPC	Electrostatic particle counter
FIA	Flow injection analysis
FID	Flame ionization detector
FTIR	Fourier-transform infrared spectroscopy
GC	Gas chromatography
GC-AED	Gas chromatography coupled to atomic emission detector
GC-BID	Gas chromatography coupled to barrier ionization discharge
GC-FID	Gas chromatography coupled to flame ionization detector
GC-FPD	Gas chromatography coupled to flame photometric detector
GC-MS	Gas chromatography/mass spectrometry
GC-NCD	Gas chromatography coupled to nitrogen chemiluminescence detector
GC-PDHID	Gas chromatography coupled to pulsed discharge helium ionization detector
GC-PFPD	Gas chromatography coupled to pulsed flame photometric detector
GC-SCD	Gas chromatography coupled to sulphur chemiluminescence detector
HPLC	High-performance liquid chromatography
IC	Ion chromatography
ICP-OES	Inductively coupled plasma atomic emission spectroscopy
IR	Infrared radiation
K-F	Karl-Fischer (titration)

LE	Laser extinction
LED	Light emitting diode
LIBS	Laser-induced breakdown spectroscopy
LIF	Laser-induced fluorescence
LII	Laser-induced incandescence
LPI	Low-pressure impactor
MBMS	Molecular beam mass spectrometry
NCD	Nitrogen chemiluminescence detector
NDIR	Non-dispersive infrared sensor
OF-CEAS	Optical feedback cavity enhanced absorption spectroscopy
PAH	Polycyclic aromatic hydrocarbons
PID	Photo-ionization detector
SEM/EDX	Scanning electron microscopy/Energy dispersive X-Ray
SID	Surface ionization detector
SMPS	Scanning mobility particle sizer
SCD	Sulphur chemiluminscence detector
SPA	Solid phase adsorption
TCD	Thermal conductivity detector
TEOM	Tapered element oscillating microbalance
TLDAS/TDLAS	Tunable laser diode (or diode laser) absorption spectroscopy
UV	Ultraviolet radiation
UV-VIS	Ultraviolet–visible radiation
VCSEL	Vertical-cavity surface-emitting lasers
VTDMA	Volatility tandem differential mobility analyser
WMS	Wavelength-scanned modulation spectroscopy

1. Absorption spectroscopy

This generic group includes a number of analysis techniques which are based on the measurement of the absorption of electromagnetic radiation from molecules.

ADVANTAGES

- Simple setup.
- Low operational cost.
- Possibility of real time, in situ measurement.

LIMITATIONS

- The large absorption by water and CO_2 makes challenging the measurement of other compounds present in product gas at lower concentrations.

EXAMPLES OF IMPLEMENTATION

University of Erlangen-Nuremberg and Free University of Bolzano

LED-induced absorption spectroscopy has been applied by University of Bolzano and University of Erlangen-Nuremberg for the online measurement of tar compounds from pyrolysis and gasification [1]. The implementation of the optical system can be seen in Figure 1. The measurement cell is composed of a heated pipe with 4 quartz windows placed at 90° of each other. The cell is kept at a fixed temperature of 350°C, in order to prevent tar condensation. The design of the system ensures laminar flow of the feed gas. The gas enters the measurement cell from the top, flows through the central quartz tube and leaves it at the bottom of the cell. Within the measurement cell, the gas flow is crossed by a UV-light beam produced by a LED light source. The LED is placed on one side of the measurement cell, while on the opposite side a photodiode detector equipped with electronic amplifiers and focus lenses collects the light beam. 4 different LED sources were tested: 265 nm (< 1 mW), 285 nm (< 1 mW), 300 nm (< 1 mW), and 365 nm (25 mW). The photodiode receives the light from the LED light source and it produces a voltage signal that is proportional to the light intensity that reaches its surface. In this work, the total tar yield was estimated by normalizing the content on a single tar component (naphthalene). This is because at the same wavelength, more than one tar species causes absorption, thus it is difficult to translate the absorbance signal into tar concentration. The 365 nm LED was found to be more sensitive for the detection of Polycyclic Aromatic Hydrocarbons (PAHs).

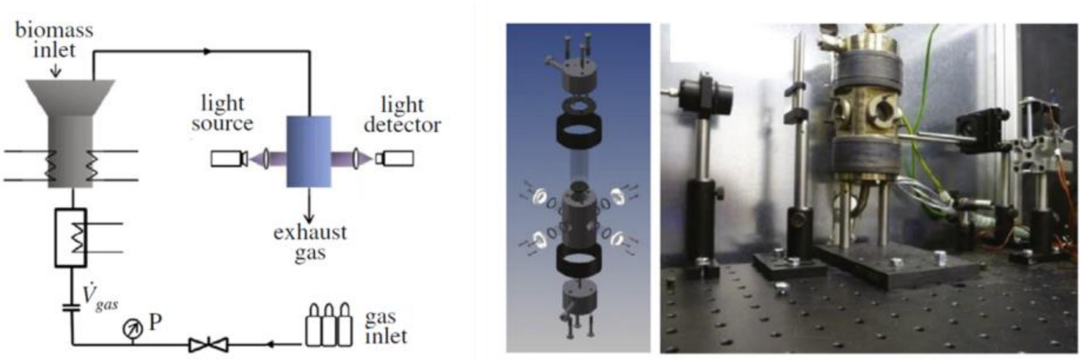

Figure 1. Implementation of LED-induced spectroscopy by Free University of Bolzano and University of Erlangen-Nuremberg: scheme of measurement cell implemented in gasifier setup (left); optical measurement cell (right) [1].

Paul Scherrer Institute

The Paul Scherrer Institute (PSI) has developed a system that combines a first step of liquid quench sampling and a second step of UV-Vis spectroscopy applied to the liquid phase. This approach is claimed to allow for easy calibration (and thus, less complex instrumentation is needed) [2]. The online UV-Vis spectra were recorded in a flow-through cell connected to a deuterium, tungsten-halogen light source and a single beam spectrometer (USB2000+XR1, Ocean Optics) by optical fibre. The spectra were recorded in the range 188-1032 nm.

RELATED TOPICS

The different spectroscopy techniques available for gasification applications are described in more detail in their respective section. The reader might refer to:

- Fluorescence spectroscopy (Factsheet 8).
- Fourier-transform infrared spectroscopy (FTIR) (Factsheet 10).
- Laser absorption spectroscopy (Factsheet 21).
- Raman spectroscopy (Factsheet 34).
- UV absorption spectroscopy (Factsheet 44).

CONTACTS

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2. Aerodynamic particle sizer (APS)

Aerodynamic particle sizers are used for the online determination of the number size distribution of particles with aerodynamic diameters in the range of 0.5 μm to 20 μm.

HOW IT WORKS

The aerodynamic diameter of a particle is defined as the physical diameter of a unit density sphere that settles through the air with a velocity equal to that of the particle in question. It is the most important aerosol size parameter because it determines the particle's behaviour while airborne [1]. Particles exhibiting the same airborne behaviour have the same aerodynamic diameter, regardless of their physical size, shape, density, or composition [4].

As the aerosol flow is drawn into the APS, it is divided into a sample flow and a sheath flow. The filtered sheath flow is used downstream to centre the sample flow and to accelerate the total flow through the nozzle. Due to the greater inertia of large particles, the resulting velocity of large particles is lower than the velocity of the gas, while small particles follow the gas. The particles pass through two laser beams and light is scattered, collected, and converted to an electrical pulse. The velocity of each particle is calculated by measuring the time between the two pulses and by using a calibration curve. Then the aerodynamic diameter can be calculated. The particle mass size distribution and concentration are calculated from the particle number size distribution, assuming spherical particles and standard density.

ADVANTAGES

- Online aerodynamic sizing and counting.
- Double-crest optics produce high-quality measurements.
- It measures light-scattering intensity from 0.37 to 20 μm.
- It can measure aerodynamic particle size from 0.5 to 20 μm.

LIMITATIONS

- The mass size distribution is estimated from assumed particles physical properties, which may have low accuracy (this can be compensated by comparing with results from LPI and TEOM measurements).

EXAMPLES OF IMPLEMENTATION

APS has been widely applied in various fields such as atmospheric studies, ambient air monitoring, indoor air-quality testing, filtering and air-cleaning testing. By combining with proper sampling and dilution systems, it can be also applied for aerosol particles characterization in hot product gas from gasification and hot flue gas from combustion. APS has been used for this application at Linnaeus University [5][6]. APS has also been applied for oxidation reactivity investigation of suspended fine char particles.

CONTACT

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3. Atomic Absorption Spectrometry (AAS)

(Cold vapour) atomic absorption spectroscopy (CVAAS) is a technique used for the determination of mercury.

HOW IT WORKS

A scheme of an AAS unit is shown in Figure 2. The UV-source (mercury lamp) emits light at a wavelength of approximately 254 nm, which is specifically absorbed by elemental mercury vapour. Depending on the concentration of mercury vapor, the light is proportionally absorbed, and the resulting intensity of light at the end of measurement cell is measured at the UV sample signal detector. Based on the difference between the reference and sample signal, the concentration of gaseous mercury is internally determined. The final output of the analyser is obtained as concentration of gaseous mercury in µg/m^3. The measurement range of specific equipment depends on the path length of the measurement cell. The path length can be increased up to a few meters by adding mirrors in the measurement cell [7].

The elemental mercury that enters in the measurement cell for analysis is been previously reduced from oxidized form in a reducing chemical solution (usually $SnCl_2$). The elemental mercury is then transported with a carrier gas through a dryer and then fed into the atomic absorption cell [8].

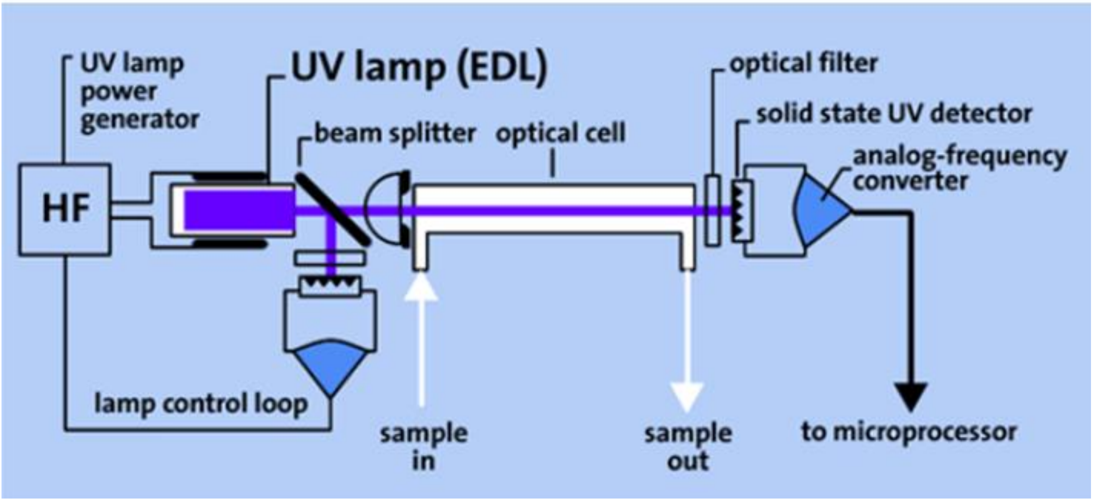

Figure 2. Schematic diagram of an AAS cell unit [9].

ADVANTAGES [8][9]

- Very low detection limits (in the order of ppt).
- Broad measurement range (2-3 orders of magnitude).
- Versatility of analytical methods for different sample matrices.
- Simple and robust.
- Relatively free from interferences related to quenching effect.
- Longer life and higher stability than conventional HG low pressure discharge lamps.
- Commercial status.
- Accuracy within 80-90% [7].

LIMITATIONS

- Some gas compounds, especially SO_2 present in flue gas from combustion, also absorb light in the same wavelength range of 253 nm. This results in interference, which affects the actual value of the mercury concentration. To avoid interferences with other gas components the analyser uses the method of differential absorption for background correction based on the Zeeman effect [7].

- Need for wet chemical reagents.

- The analyser should be kept in temperature-controlled or well ventilated cabinet for the optimal performance [7].

- The Teflon lines should be cleaned using demineralized water or changed during measurement to avoid any memory effect [7].

- It is important to avoid that fine particulate matter enters the reduction unit, since it can cause significant bias in the measurement [7].

4. Cold Vapour Atomic Absorption Spectrometry (CVAAS)

- Please refer to AAS (Factsheet 0).

5. Electrical low-pressure impactor (ELPI)

Electrical low-pressure impactors can provide real-time measurements on aerodynamic particle size distribution in the size range of 0.03–10 μm. ELPI has been widely applied in various fields such as atmospheric studies, ambient air monitoring, indoor air-quality testing, and air-cleaning testing. By combining with proper sampling and dilution systems it can be also applied for aerosol particles characterization for hot gases from gasification and combustion processes.

HOW IT WORKS

The instrument consists of a unipolar corona charger, a low-pressure cascade impactor (see Factsheet 26) and a multichannel electrometer. Initially, the sample is drawn into a positive corona charger and electrically charged to a known level of charge. After the charged aerosol enters the cascade impactor, particles are separated according to their aerodynamic diameter, in an analogous way as the size classification in a conventional LPI. The electric charges carried by the particles onto the electrically insulated impactor stages produce an electrical current which is measured in real time by a multichannel electrometer. Since the measured current of each stage is proportional to the number of particles, the number concentration of every stage is established. The particle mass size concentration and distribution are then calculated from the number concentration, assuming standard density and spherical particles.

ADVANTAGES

- ELPI can provide online aerodynamic sizing and counting with very fast response.
- It measures the current and calculates the number concentration based on the calibration using known aerosol particles.

LIMITATIONS

- Results usually have low accuracy, especially when applied to the case of biomass gasification or combustion, due to the complexity of particles in the hot gas. This can be compensated however by comparing with results from LPI and SMPS measurements.

EXAMPLES OF IMPLEMENTATION

ELPI been applied by Linnaeus University to online monitor particles from an indirect bubbling fluidized bed gasifier, and to measure charging and discharging behaviour while optimizing a small scale electrostatic precipitator (ESP) system. Its potential for online monitoring of heavy tar components was also proven.

CONTACT

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RELATED TOPICS

- ➢ Low-pressure cascade impactor (Factsheet 26).

6. Electromagnetic induction-based particle monitor

This technique measures the particle concentration from the currents induced by electrostatically-charged particles passing through an electromagnetic field.

HOW IT WORKS [10]

This inline system, schematically show in Figure 3, consists on a sensor inserted in the main pipe through a T-piece. The system generates a magnetic field inside the pipe. When electrostatically charged particles pass through this field, small currents are induced to the sensor rod. The electronics extract a specific frequency band of this signal and electronically filters out the dc current caused by particle collisions. This signal can be correlated to dust concentration by comparison to the results of an isokinetic sample. These instruments are typically used after bag filters and cyclones to monitor emissions, quantify particulate loadings in mg/m^3 and/or detect process upsets.

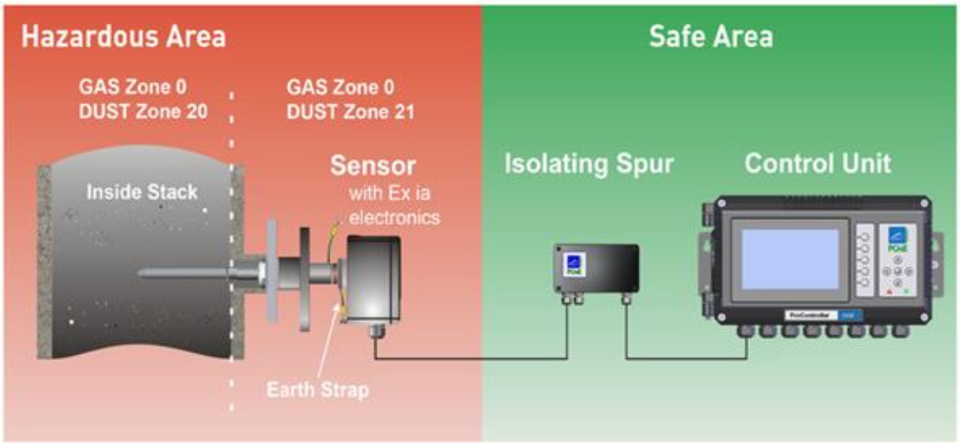


Figure 3. Schematic diagram of PCME Ex820 electromagnetic induction-based particle monitor [11].

ADVANTAGES

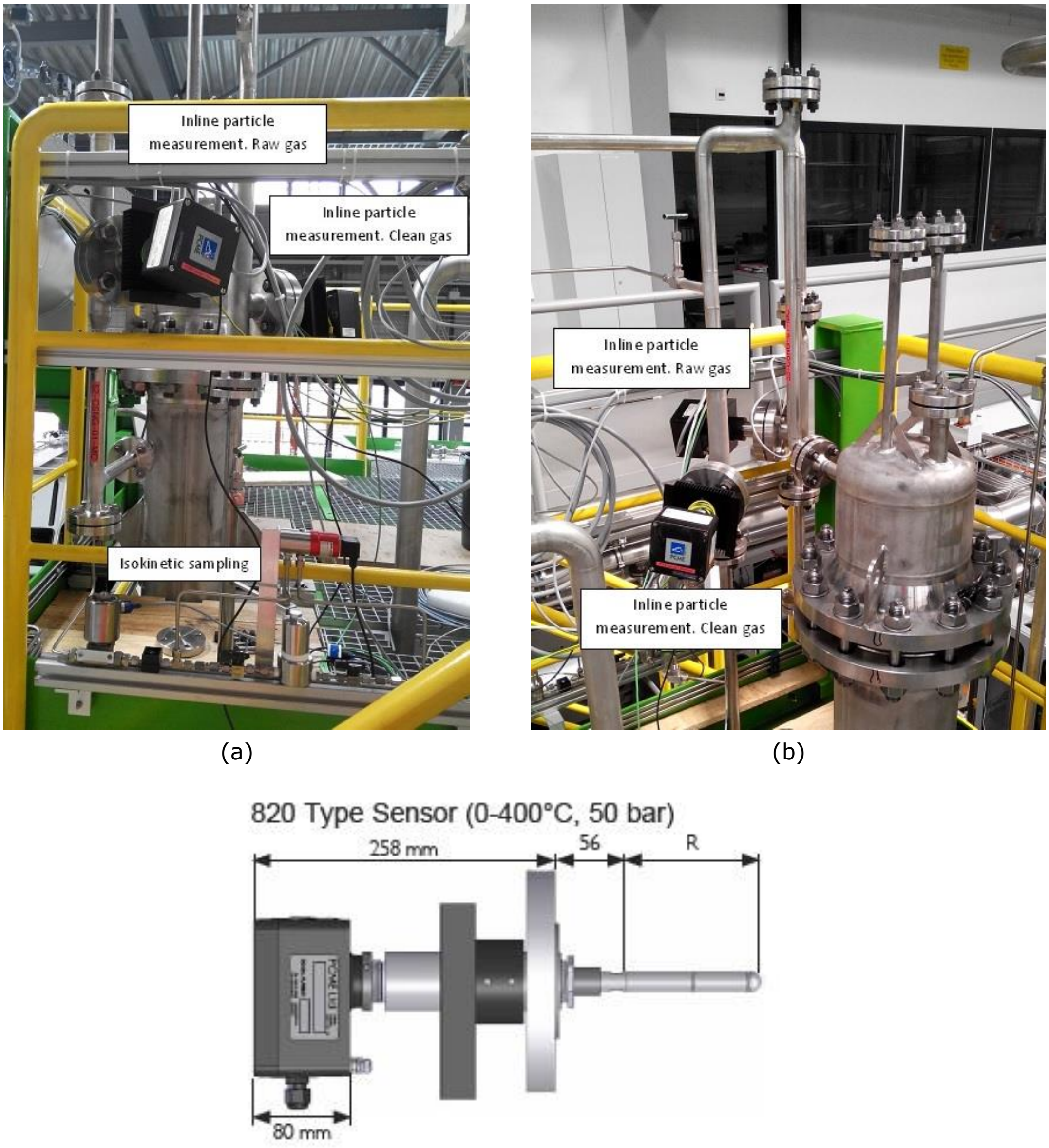
- Flexible in ranges of particle size (0.1 – 1000 μm) and particle concentration (0.1 – >1000 mg/m^3).
- Able to operate under high temperature and pressure conditions (up to 400°C and 40 bar), as well as under hazardous environments.
- No need for isokinetic sampling, once the sensor is calibrated.
- Commercially available (e.g. PMCE).

LIMITATIONS

- Need for external calibration with secondary method.
- Condensates interfere in the sensor signal and need therefore to be removed (heating).
- Electrical noise limits the detection level. Therefore, proper isolation of the probe from sources of noise and grounding is required.
- The flow field around the sensor is essential. Stokes numbers > 1 are required to ensure that the sensor rod does not interfere in the trajectories of the particles.

EXAMPLES OF IMPLEMENTATION

Paul Scherrer Institute is currently implementing an electromagnetic induction-based particle measurement system for the inline detection of particulate matter from fluidized-bed methanation processes. The sensors as installed in the setup are shown in Figure 4.



(a) (b)

(c)

Figure 4. Electromagnetic induction-based particle measurement system installed at PSI laboratories: (a) and (b) Two views of the setup; (c) Schematic of the sensor. Picture courtesy of PSI [10].

CONTACTS

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7. Excimer Laser-Induced Fragmentation Fluorescence (ELIF)

This laser-based technique is applied for the online measurement of alkali metals contained in product gas. UV light is used to photo-fragment alkali chloride and hydroxide molecules. The fluorescence from the excited atoms formed is used to determine total alkali concentration [12].

This technique has been applied by Erbel et al. ([13], cited by [12]).

8. Fluorescence spectroscopy

Fluorescence spectroscopy is an optical analysis technique which can be applied for the online quantification of tar compounds. The principle behind fluorescence spectroscopy for online tar measurement is that there is a linear correlation between a fluorescence signal and the tar concentration in a gas [14].

HOW IT WORKS [14]

When radiation of an appropriate wavelength and energy reaches an atom or molecule, it can absorb photons, thus raising its electronic state to an excited one. The number of energy states that the atom or molecule can reach is limited based on the quantum theory. Once excited, the atom or molecule can return to the original ground state (what is called relaxation) via different mechanisms: non-radiative or radiative transition. The mechanism of relaxation will be that which minimizes the lifetime of the excited state. Polycyclic aromatic hydrocarbons (PAH) can be excited by radiation with wavelength > 250 nm and tend to exhibit fluorescence (radiative emission) upon relaxation. The radiation needed for the excitation of the tar molecules can have different sources: it can be a laser or a Light Emitting Diode (LED). The differences will be explained later in this section.

EXAMPLES OF IMPLEMENTATION

Several groups have worked on this topic including Technical University of Munich, University of Erlangen-Nuremberg (in collaboration with Free University of Bolzano), TU Berlin, and University of Glasgow. Further extensive work applying LIF and similar techniques on tracing e.g. toluene or on PAH growth (soot formation) is performed in combustion science.

Technical University of Munich (TUM)

Figure 5 shows a schematic of the laser spectroscopy setup built at Technical University of Munich for online measurement of tars at the outlet of a gasifier [14]. The product gas fed to the optical setup can be either come from sampling line 1 (hot gas sampling) or from sampling line 2 (cold gas sampling, after tar guideline analysis). The optical setup is composed of a Nd:YAG laser, a spectrograph a CCD camera and a heated measurement cell.

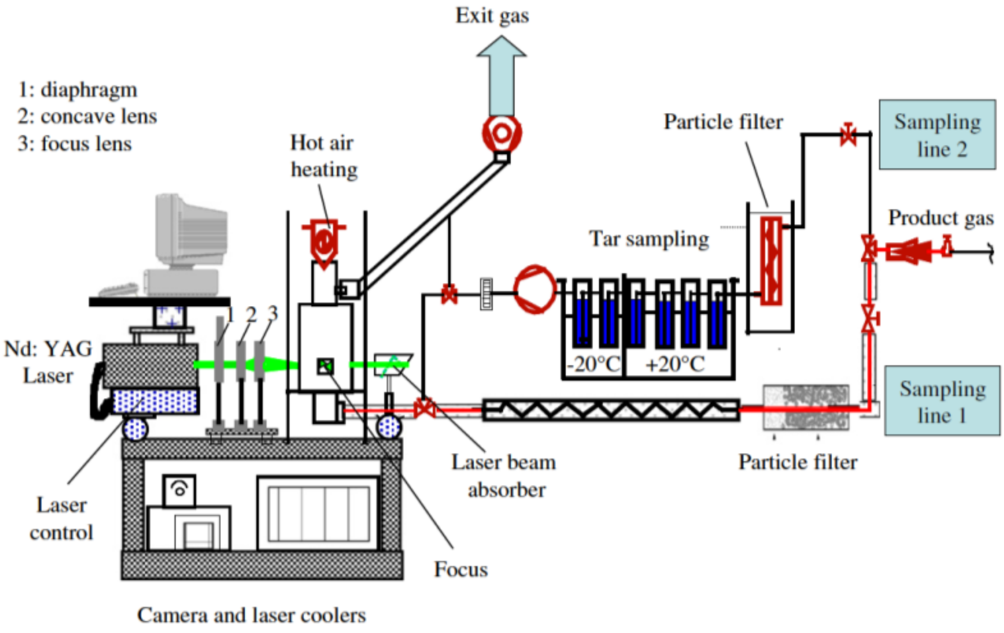

Figure 5. Schematic of implementation of laser-induced fluorescence for online tar analysis of product gas at Technical University of Munich [14].

However, due to the high cost of the laser setup components (laser, spectrograph and CCD camera), it was decided to continue the development of fluorescence spectroscopy by replacing the laser source with Light Emitting Diodes (LEDs). Figure 6 shows the implementation of the LED-induced fluorescence setup for online tar measurements [14]. The measurement cell was heated to 350°C to avoid tar condensation. A LED source is used for the excitation of fluorescence. Depending on the type and the beam angle of the LED, different lenses have to be used. A compact UV/vi spectrometer is used. Via a cylinder- and a convex-lens the fluorescence signal is focused on an optical fibre connected to the spectrometer. The whole measurement setup is mounted in a box to avoid influence of ambient light. Two different types of LEDs were investigated [14]:

- LEDs emitting in the range of 250-300 nm wavelength (deep UV radiation) were firstly selected for investigation, due to the fact the tar components such as toluene, phenol and naphthalene have one of their main absorption bands within this wavelength range. The tests revealed that the radiation of the LED was too weak to get strong fluorescence signals due to the low signal-to-noise ratio. Moreover, there was another issue related to the geometry of the measurement cell (a long absorption path length, which resulted in a large amount of absorption of the excitation light before the measurement area was reached). Modifications like shorter optical path lengths and more sensitive detectors can improve the fluorescence signals, and the optimization eventually led to strong fluorescence signals [14].

- LEDs emitting between 300 nm and 500 nm (near-UV radiation) were studied as an alternative. These radiation sources are available at the market at very low prices, although in this range only heavier PAH species (e.g. anthracene, pyrene) can be detected. This limitation can still be accepted in applications were high precision is not needed (for example, during process optimization, where qualitative information of tar content suffices).

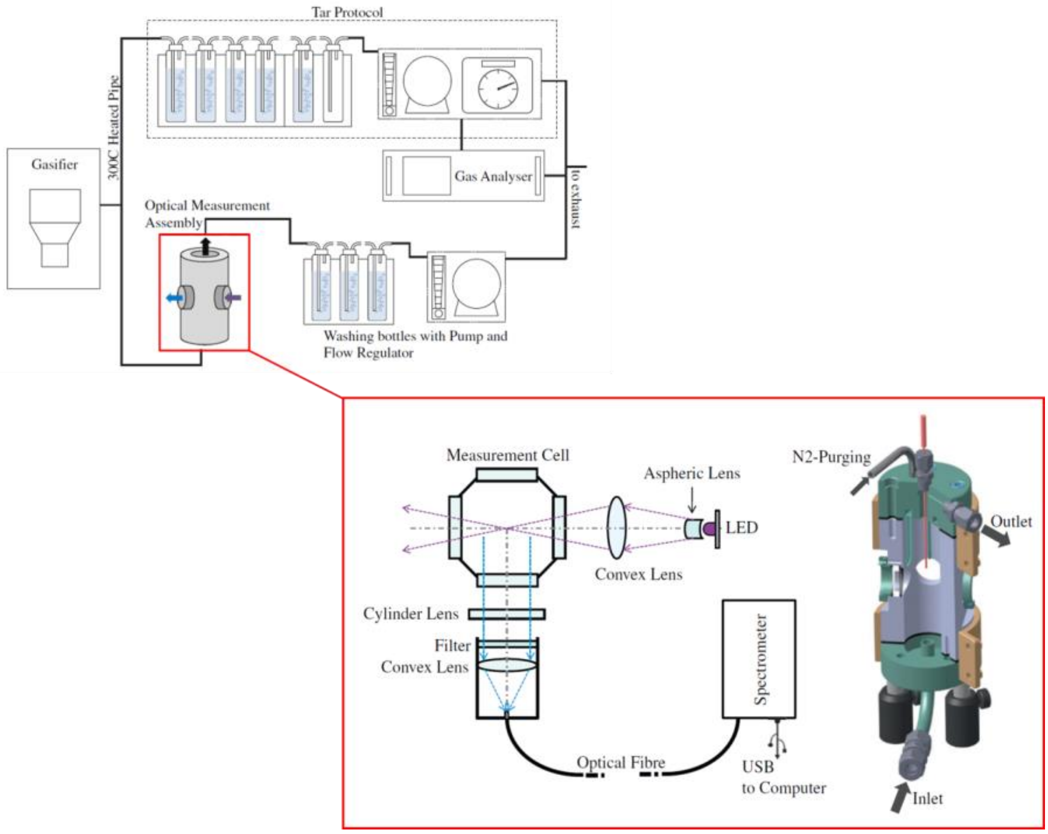

Figure 6. Implementation of LED-induced fluorescence spectroscopy at TUM in product gas line (top); detail of LED optical setup (bottom left) and 3D cross-section of the measurement cell (bottom right) [14].

University of Glasgow

In parallel, University of Glasgow is also developing low-cost, LED-induced spectroscopy. Figure 7 shows how the system is implemented. The detection system (optical cell) consists of a LED excitation source (1 mW, 280 nm wavelength), a 300 nm long-pass (LP) colour glass filter to isolate fluorescence radiation, and a photomultiplier tube to provide signal gain. The tar detection instrumentation is housed in a die-cast aluminium enclosure for electromagnetic and heat shielding during operation. An optical viewport including 4 optical entry ports was designed for multidirectional optical access from each side to the cell centre. The excitation by the LED is introduced through the top window. The system is attached via a mechanical coupling to the side of the optical cell wall [15].

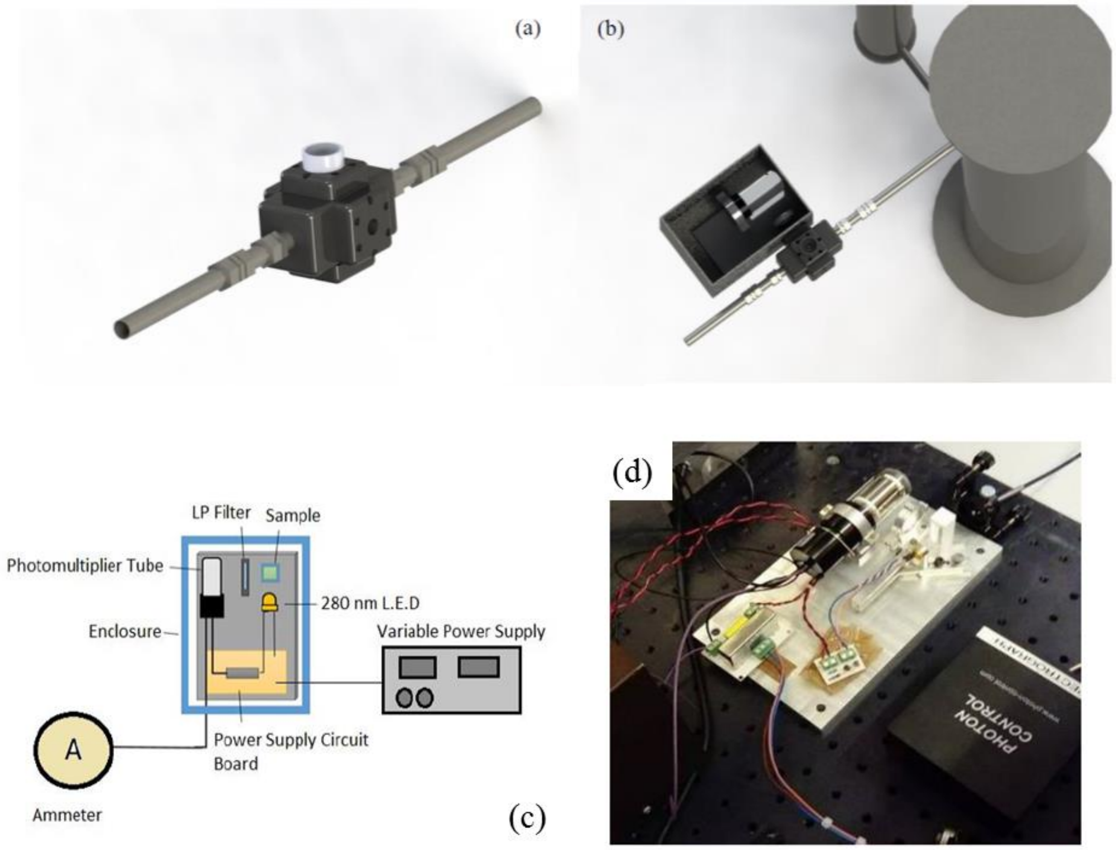

Figure 7. Implementation of online tar detection at University of Glasgow based on LED-induced spectroscopy: (a) design of optical cell; (b) integration of the cell in the gasification system; (c) schematic of the arrangement of optics in the cell; (d) system implementation for testing; Ammeter: electric current meter [15].

ADVANTAGES AND LIMITATIONS

	Advantages		Limitations
Laser-induced fluorescence	- Online tar measurement. - Linear correlation between fluorescence signal and tar content. - Non-invasive.	- High-precision. - High fluorescence signals due to higher power (compared to LED).	Very expensive (cost-to-benefit not suitable for industrial applications).
LED-induced fluorescence		- Low price: promising for industrial applications. - Stability of optical power.	Low optical power (0.1-1 mW). Limited number of tar components that can be excited at a single wavelength: loss of information (semi-quantitative results) Need external (offline) calibration. If the tar composition is not known it is difficult to translate the absorbance to tar concentration (more than one tar specie causes absorption at the same wavelength) [1] → it is necessary to express the content as one tar component to estimate the total yield of tars.

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9. Flow injection analysis (FIA)

Flow Injection Analysis is a widespread analysis technique which, under different configurations, can be used to detect a number of ion compounds, such as chlorides, ammonium, or cyanide.

HOW IT WORKS

A liquid sample (coming from wet chemical analysis sampling) is injected into a moving continuous liquid carrier which moves unidirectionally. The injected sample results in a change of the properties of the properties of the carrier and is transported toward a suitable detector located downstream. The type of detector, which can vary depending on the target analyte, monitors and records the changes in e.g. absorbance, electric potential, or colour, derived from the changes induced from the addition to the sample to the carrier. The signal from the detector reflects the gradient of the sample zone as it passes through the detector [16][17].

In the case of the detection of ammonia (AMFIA), the analysis sample is injected in a carrier stream consisting of water. The water carrier is continuously mixed with a basic solution and directed along a membrane. A fraction of the gas-phase ammonia diffuses through the membrane and is incorporated in a counterflow of pure water at the other side of the membrane. The conductivity of the receptor stream is a measure of the content of ammonium in the analysis sample.

ADVANTAGES

- Versatile technique.
- Easy to automate (only 2 mechanical components – pump and valve).
- Compatible with a very wide range of detection techniques [17].

LIMITATIONS

- Offline measurement (applied to liquid samples).

EXAMPLES OF APPLICATION

ECN part of TNO applies flow injection analysis for the measurement of nitrogen compounds contained in product gas. The sample injected in the equipment comes from wet chemical sampling of the gas (offline analysis). In the case of ammonia determination, a HNO_3 solution is used for the sampling, and NH_3 can be measured with a detection limit of 0.5 ppmv. In the case of measurement of HCN, a NaOH solution is applied for the sampling of gas, and HCN can be measured with a detection limit of 0.05 ppmv.

CONTACTS

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10. Fourier-transform Infrared Spectroscopy (FTIR)

FTIR is a specific type of absorption spectroscopy analysis in which infrared (IR) radiation is used as excitation source. FTIR offers a number of advantages with respect to (less advanced) dispersive IR spectrometers, which include a higher signal-to-noise ratio (thus, higher sensitivity), high wavenumber accuracy, shorter scanning time of frequencies, very high resolution, and a simpler mechanical design with only one moving part [18][19]. This technique has been used in a broad range of types of samples (solid, liquid, gas) and applications, including the food and pharmaceutical industry, agriculture, and environmental emissions (in soil, water and air) [20]. Within the scope of this report, FTIR has been applied for the online detection of a broad number compounds present in product gas, including CO, CO_2 ,CH_4, H_2O, NH_3, HCN, and HCl, among others.

HOW IT WORKS

The range of the infrared region covers from 10 – 12800 cm^{-1}, which is subdivided in near-infrared, mid-infrared and far-infrared regions [18][20]. However, the absorption radiation of most organic compounds and inorganic ions lies within the region between 400 cm^{-1} and 4000 cm^{-1}.

The basic principle of IR spectroscopy involves that when IR radiation passes through a sample (product gas in this case), the compounds selectively absorb part of the radiation corresponding to specific wavelengths, the rest being transmitted (going through the sample). The absorbed radiation results in the change of the dipole moment of the sample molecules, which leads to different effects such as vibration, rotation, stretching or shear. The number of absorption peaks is related to the number of vibrational freedom of the molecule, whereas the intensity of absorption peaks is related to the change of dipole moment and the possibility of the transition of energy levels [18]. Therefore, the resulting signal is a spectrum in the wavelength dimension which is the "molecular fingerprint" of the sample. In FTIR, a mathematical Fourier transform is used to convert the raw interferogram data to the dimension of wavenumber. The interferometer is the key component of the FTIR, and it produces a signal which encodes all the IR frequencies, thus reducing the scan time with respect to dispersive IR techniques [19][21].

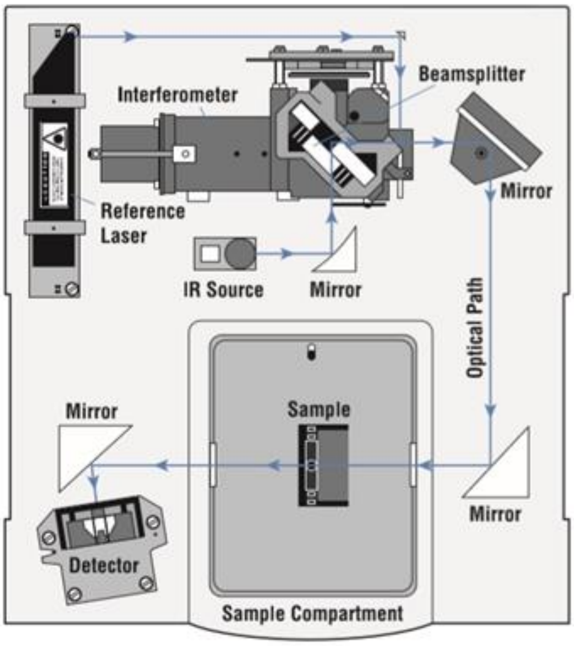


Figure 8. Simplified layout of FTIR spectrometer [19].

A FTIR unit is composed of the IR light source, the interferometer, a sample compartment, detector, amplifier, and A/D (analogic/digital) convertor, and software [18][19] (Figure 8). Radiation generated in the source passes the sample through the interferometer and reaches the detector. The beam splitter divides the incoming IR beam into 2 equal beams. One of them reflects in a fixed mirror, whereas the other beam reflects in a moving mirror. The 2 reflected beams are then recombined when meeting back at the beam splitter. The resulting signal is called interferogram, and every data point in it contains information about all the IR frequencies from the source [19]. The interferogram is amplified, digitized and transferred to a computer, where it is finally decoded by applying a Fourier transform to produce a frequency spectrum [18][19]. The process is illustrated in Figure 9.

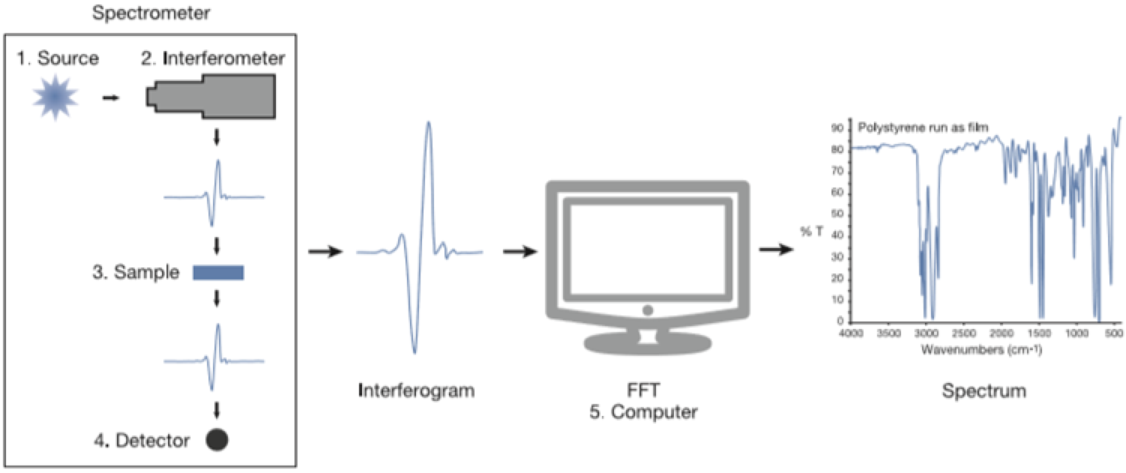


Figure 9. Analysis process in FTIR instrument: transformation from interferogram to spectrum [19].

ADVANTAGES

- Online, non-intrusive method.
- Fast analysis (in the order of seconds), faster than dispersive IR (in the order of minutes) [19].
- Higher sensitivity than dispersive IR (higher signal/noise ratio, possibility of signal averaging) [19].
- Allows online measurement of water, as well as other compounds which cannot be properly measured with micro-GC analysis (e.g. NH_3, HCl).
- Commercial status, also in portable applications.
- Suitable for industrial environment: equipment can handle wide humidity ranges and vibration.

LIMITATIONS

- Not suitable for dirty (tar-loaded) gases.
- Not able to detect diatomic molecules such as H_2, O_2, N_2 and Cl_2 (zero dipole change in the vibration and rotation).
- The large absorption spectrum of H_2O and CO_2 in the gas makes the detection of other compounds present in lower concentrations challenging. For example, it is claimed that H_2S cannot be quantified with FTIR due to the strong overlap with CO_2 [22]. Collisional broadening effects have also been reported

EXAMPLES OF IMPLEMENTATION

Application of FTIR in gasification processes resembles other applications of monitoring of industrial gases. In these cases, portable equipment units are used, although non-portable equipment has also been used for offline measurement of product gas [22]. Figure 10 shows an example of the FTIR spectrum obtained from product gas, with the different species indicated [22]. The spectral regions of detection of gasification compounds measured at TU Delft are summarized in Table 1.

Table 1. FTIR spectral regions and windows of some relevant gasification compounds [23].

	Regions (cm^{-1})		**Windows (cm^{-1})**	
	Start	End	Start	End
CO_2	2394.2	2395.3	2394.2	2395.3
CO	1978.3	1985.0	1978.3	1979.8
			1982.9	1985.0
CO low	2138.5	2148.0	2138.5	2140.3
			2146.0	2148.0
CH_4	2842.1	2846.0	2842.1	2846.0
HCN	3352.6	3359.3	3352.6	3353.9
			3357.6	3359.3
NH_3	918.0	919.5	918.0	919.5
C_2H_2	3347.4	3348.6	3347.4	3348.6
C_2H_4	3186.0	3189.0	3186.0	3189.0

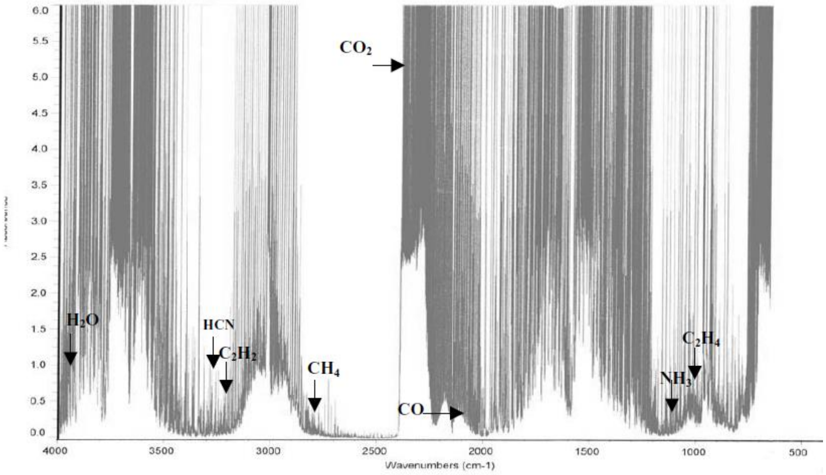


Figure 10. FTIR spectrum from biomass gasification product gas [22].

Figure 11 displays the measurement setup developed by DTU for the measurement of product gas components based on absorption spectroscopy (FTIR and UV spectroscopy) [24]. It is a portable unit which contains UV and FTIR spectrometers as well as two 50 cm long gas cells. Complementary, temperature, pressure and oxygen content are also measured (these data are necessary for an accurate quantification of the spectroscopy instruments). The setup includes 2 interconnected heated gas cells, UV/IR light sources and the spectrometry units. More details about the setup can be found in Grosch’s PhD Thesis [24]. Online gas extraction takes place at 150°C. More information about the Viking and LT-CFB gasifiers, and the Pyroneer pilot plant can be found in Section 3.2.6 of Document 1.

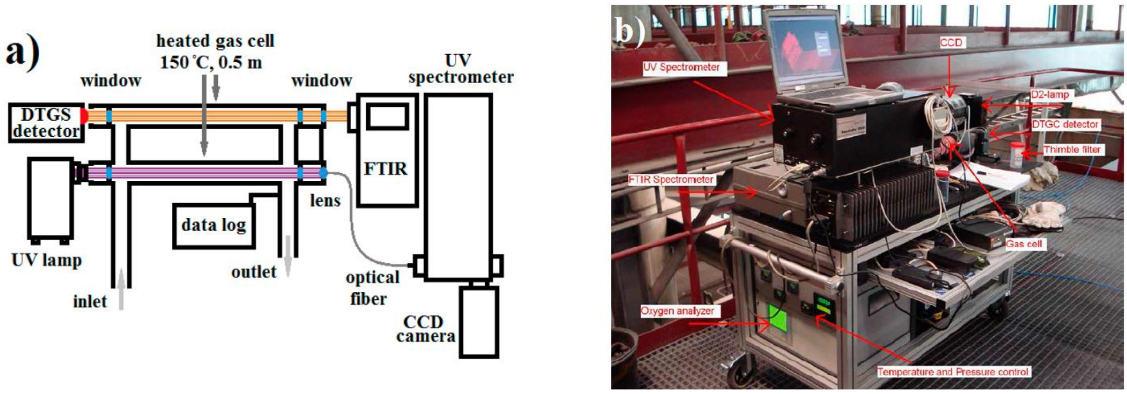


Figure 11. Absorption spectroscopy setup (FTIR + UV) developed by DTU: (a) schematic layout; (b) actual implementation [24].

Figure 12 shows some examples of in-situ FTIR spectra obtained by DTU with the FTIR spectroscopy setup. In-situ measurements were performed at the 6 MW Pyroneer pilot plant. Online gas extraction takes place at 150°C.

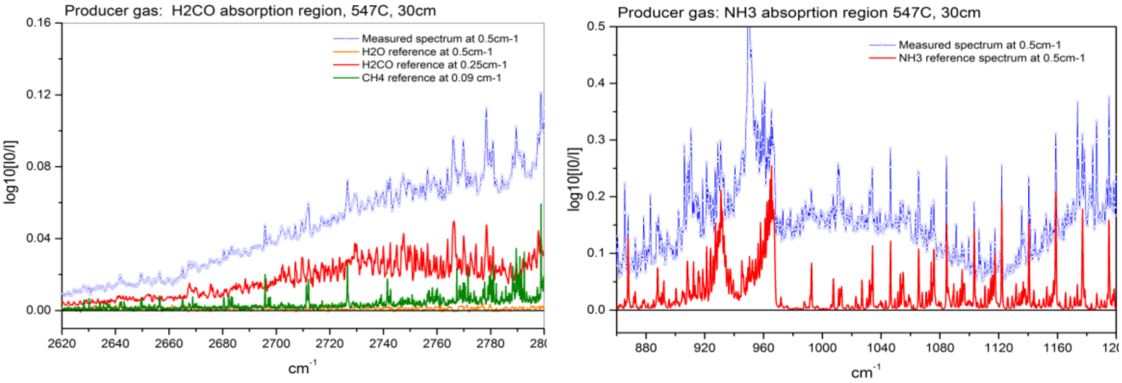


Figure 12. Examples of in-situ FTIR absorption spectra from the Pyroneer gasifier at 547°C obtained by DTU: H_2CO (left); NH_3 spectral ranges (right) [25].

FTIR has also been extensively applied at Technical University Delft (TUD) for the evaluation of the fate of nitrogen compounds in thermal conversion of coal and biomass. Among the different FTIR setups used at TUD, FTIR is part of the measurement equipment available at the pressurised fluidised bed setup (1.5 MW_{th} capacity), described in Section 3.2.13 of Document 1. The FTIR instrument used by De Jong [22] was a non-portable unit located at the control room near the pilot plant. The product gas was directed to the FTIR unit via Teflon lines. The FTIR unit used (400-4000 cm^{-1} spectral range, 0.125 cm^{-1} resolution, 15 scans per measurement, 2 m path length, 70 s measurement time) was able to quantify the content of CO, CO_2, CH_4, C_2H_4, NH_3, HCN, H_2O, HCl and COS (as well as other gases present in flue gas such as NO, NO_2, N_2O and SO_2). The same equipment was applied in another 50 kW_{th} pressurized fluidized bed gasifier located at University of Stuttgart [22].

Figure 13. FTIR equipment applied by Technical University Delft [22].

FTIR is acknowledged by VTT as a measurement method with high potential for online analysis of gas, and successful measurement has been achieved with their portable FTIR and sample dilution system (Figure 14). An important factor in the application to gasification processes is the need for sample dilution to get reliable results. Derived from this, other important points to consider is to ensure that the gas sample is representative and that the diluting gas is kept constant. HF_6 is added as marker gas. Despite the successful application, there is no solid data yet to prove that FTIR would provide more accurate results than wet chemistry analysis [26].

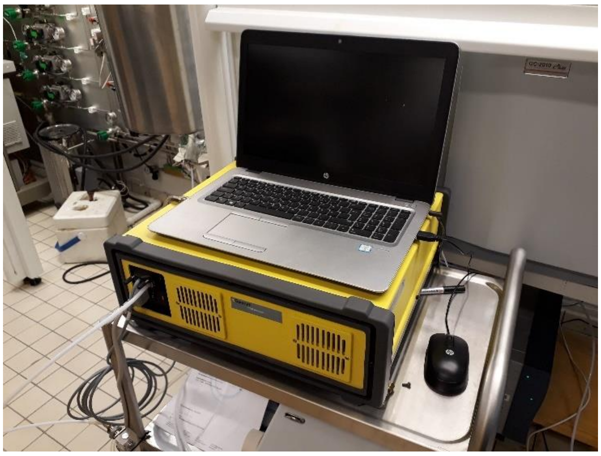
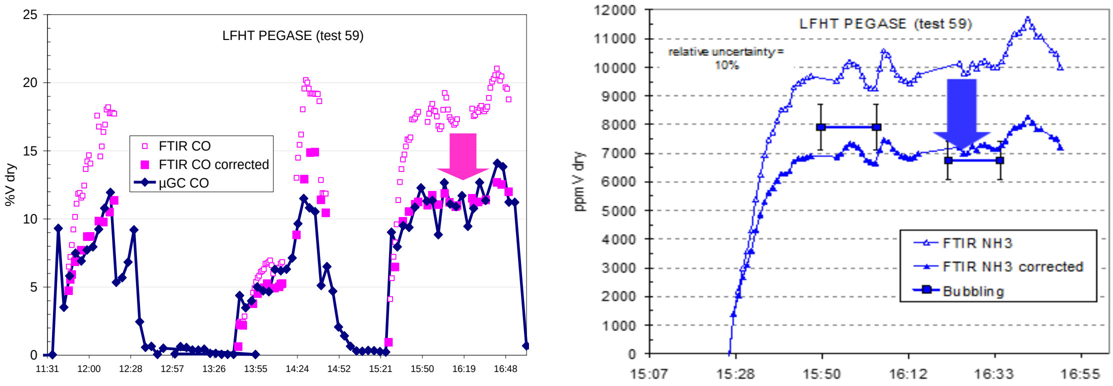


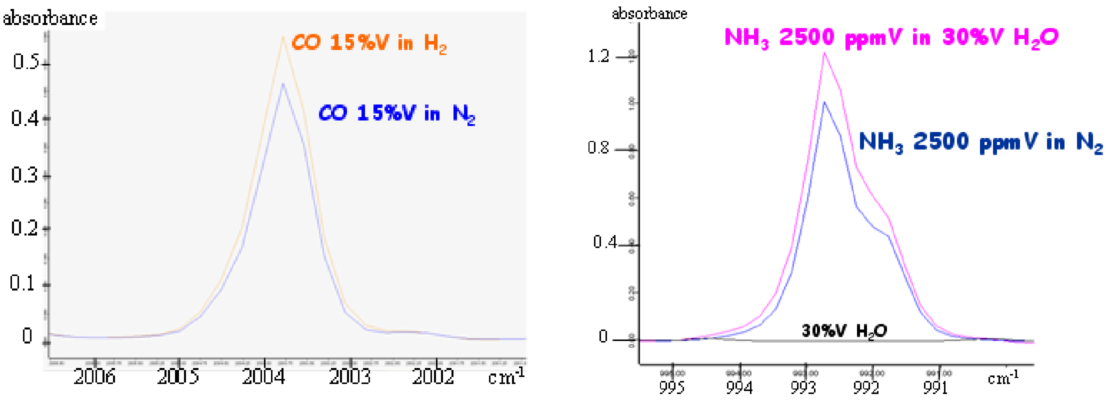
Figure 14. FTIR portable unit. Picture courtesy of VTT [26].

FTIR is also applied by the Alternative Energies and Atomic Energy Commission (CEA) for the measurement of permanent gases and ammonia. During a comparison between micro-GC and FTIR analysis, a matrix effect of H_2 on CO quantification in FTIR analysis was identified [27]. This discrepancy can be observed in Figure 15 (a). A similar matrix effect of H_2O on NH_3 quantification was also observed when comparing results of NH_3 concentration obtained from wet chemical analysis with FTIR (Figure 15 (b)). This effect, observed in Figure 16, is called collisional broadening and is due to gas/gas interactions when partial pressures are high (higher than a few vol.%). From the results of this study, it appears that H_2 and H_2O can induce an important error (close to 50%) on the CO and NH_3 quantification by FTIR, respectively, if they are not taken into account in the calibration method [28].



(a) (b)

Figure 15. (a) Comparison of micro-GC and FTIR for CO online measurement; (b) Comparison of wet chemical and FTIR for NH_3 online measurement [27].



(a) (b)

Figure 16. (a) Matrix effect of H_2 on 15 vol.% CO (2003 cm^{-1} wavelength); (b) Matrix effect of H_2O on 2500 ppmv NH_3 (992 cm^{-1} wavelength). Pictures courtesy of CEA.

In order to address the effect of collisional broadening, a mathematical model was developed and validated by CEA in gasification experiments. The model, is similar to the so-called coefficients of cross-correction applied in FTIR gas calibration software, and consists of applying the following equation:

$X_{corr.} = X + aY + bXY + cXZ$

being:

X: concentration of the specie having the matrix effect (in this case, CO or NH_3)
Y or Z: concentration of the species responsible for the matrix effect (in this case, H_2 and H_2O)
a = zero for CO and is k° for NH_3
b = k_{H2O} or k_{H2} for CO
c = k_{H2O} for NH_3

However, this equation cannot take into account a cross-correction by two species (for example, H_2 and H_2O for CO), because no Z is allowed in the cross-correction equation. The application of this correction allows for proper quantification using FTIR analysis.

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11. Gas chromatography (GC)

Gas chromatography (more correctly referred as gas-liquid partition chromatography, GLPC) is a form of chromatography analysis. It is one of the most widespread analysis methods used for the determination of (volatile) compounds present in gas produced in gasification.

HOW IT WORKS [29]

GC is based on the separation of compounds present in a complex gas sample. There are 2 main elements playing a role in GC: the mobile phase and the stationary phase. The mobile phase is a carrier gas (which can be e.g. helium, argon, nitrogen, hydrogen, etc.), helium being the most common type of gas used. The stationary phase is a substance (liquid or polymer) coated on an inert solid support, which is placed inside a glass or metal tubing (which is what is called the column). The column is located in an oven that can control the temperature.

During an analysis, the gas sample + carrier gas (mobile phase) flows through the column. The compounds present in the gas react in a specific way with the stationary phase, which causes the elution (separation) of the compounds present in the gas mixture, making them exit the column at a different time (called retention time). The order or time of retention can be modified by varying the carrier gas flow rate, the column length and the column temperature. The latter can be controlled by an oven which surrounds the column. A detector monitors the gas stream coming out of the column, thus allowing determining the time and amount of each component. The compounds are qualitatively identified by the order in which they elute from the column and their retention time.

Among other types, the most common detectors in GC in gasification applications are the flame ionization detector (FID) and thermal conductivity detector (TCD). Other detector types are further explained in individual Factsheets elsewhere in this document. The response of a TCD detector is based on the decrease of thermal conductivity of the eluted molecules. In a FID, hydrocarbons are pyrolyzed in a flame. The cations and electrons formed in the process can generate a current that is detected by adjacent electrodes. TCD can be used for any component provided that its thermal conductivity is different than that of the carrier gas, but FID is highly sensitive and linear, thus more suitable for detection of hydrocarbons (the FID signal is proportional to the amount of carbon in the sample). On the other hand, TCD detector is non-destructive, whereas FID is destructive (pyrolysis of carbon compounds). It is possible to operate both detectors in series (first TCD, then FID) for complementary detection.

GC analysis generates a chromatogram, which is a spectrum graph of the detector response (Y-axis) with respect to the retention time (X-axis). Each compound can be identified by its retention time. The integration of the peaks of the chromatogram can be used to quantitatively determine the concentration of each compound in the gas mixture. While desktop versions are most common, portable versions often called “micro-GC” or “portable-GC” allow easy field applications and quasi-online measurements due to their short (< 10 minutes) measurement times.

Figure 17. Micro-GC unit (GC-TCD) used for online analysis of H_2S and COS trace concentrations as well as bulk gases. Picture courtesy of PSI.

ADVANTAGES

- In micro-GC units, short measurement time (in the order of a few minutes) allowing quasi-online determination.
- Accurate measurement in complex gas mixtures.
- Widespread technique, commercial status.

LIMITATIONS

- Water can interact with the stationary phase and cause significant problems such as high baseline noise and column bleed in the output gas chromatogram, which reduces the sensitivity and decreases the column lifetime [30]. Therefore, dry, clean gas entering the GC is required in order to avoid deterioration of the column. As a consequence, a suitable pre-sampling system needs to be implemented in the gas sampling line to protect the equipment from particles and condensate (water and tars). This has in turn another consequence, namely the content of water present in the gas cannot be measured.
- The use of pre-sampling equipment can affect the accuracy of the measurement of light aromatics (BTX), as well as H_2S and COS.
- Relatively high lower detection limits.

EXAMPLES OF APPLICATION

Micro-GC analysis (GC-TCD) is extensively used by nearly all partners working with gasification. Just as an example, micro-GC is applied at ECN part of TNO for the measurement of CO, CO_2, H_2, CH_4, C_2H_2, C_2H_6, C_2H_4, benzene, toluene, H_2S, COS. In this case, the detection limit is 10 ppmv. PSI has also used a micro-GC for online analysis of biogas, where detection limits for H_2S of 1-2 ppmv were reached [31].

GC-FID can be broadly applied for the measurement of hydrocarbons, either permanent gases or condensables (e.g. PAHs in tars). In the case of applying GC-FID for the measurement of C_1-C_6 hydrocarbons (sampled for example in Tedlar gas bags), the detection limit is 1 ppmv. When applied to the measurement of tars (sampled with SPA or tar guideline), the detection limit is 0.1 ppmv (internal data from ECN part of TNO). Please refer to Factsheet 14 for further information about the application of GC-FID.

A special type of GC that has been applied to biogas and product gas is two-dimensional gas chromatography (2D-GC) [32]. In the case of gasification, 2D-GC is applied by ENGIE Gas CRIGEN for the analysis of tar and condensate samples. Target compounds include aromatics hydrocarbons such as benzene, naphthalene, etc.; oxygenated organic compounds such as phenol and phenol derivatives; and sulphur organic compounds such as thiophene and thiophene derivatives. 2D-GC is a very powerful technique when dealing with complex samples (that is, samples where many trace compounds are present at different concentration levels), such as raw product gas collected with tar protocol sampling or condensates. The use of 2D-GC can significantly improve the resolution, and thus the sensitivity of the analysis with respect to conventional GC, where some trace components cannot be identified because they are hidden behind other compounds. Two-dimensional gas chromatography is a valuable tool during R&D experiments (for example, for process optimization), because it can deliver a broad set of information in a one-shot analysis, as well as additional information with respect to conventional GC. An example of the application of 2D-GC to product gas can be found in Section 3.2.3 of Document 1.

RELATED TOPICS

- Gas chromatography coupled to Flame Ionization Detector (Factsheet 14).

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12. Gas Chromatography coupled to Atomic Emission Detector (GC-AED)

Gas Chromatography – Atomic Emission Detector or GC-AED is used in the analysis of gasoline, diesel, oil, environmental pollutants in soil, water and effluent, Volatile Organic Compounds (VOCs) in water [33][34], and sulphur compounds in jet fuels [35]. Within the scope of this report, GC-AED can be applied for the measurement of sulphur-containing compounds present in product gas.

HOW IT WORKS

The elements eluting from the GC capillary column enter into a microwave-powered plasma cavity (discharge cavity), where the compounds are destroyed, and their atoms are excited by the energy of the plasma. The light that is emitted by the excited particles is focused by a diffraction grating, and then separated into individual lines via a photodiode array. A computer then sorts out the individual emission lines and produce chromatograms from eluents that contain only a specific element [34]. The schematic of the instrument is depicted in Figure 18.

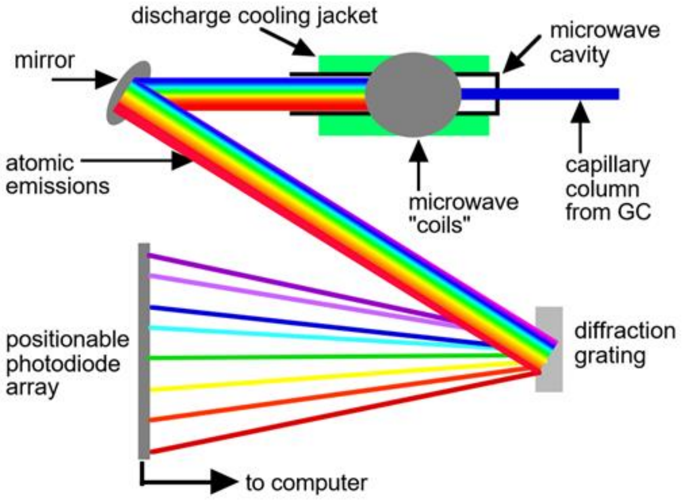

Figure 18. Schematic layout of GC-AED instrument [34].

ADVANTAGES

- Sensitive to low amounts of sulphur [35].
- Linear, equimolar response [40].
- Element specific without hydrocarbon compound interferences [35].
- Multi-element analysis can be run simultaneously [35].
- Commercially available [33][36].

LIMITATIONS

- Relative higher cost and more difficult maintenance than other sulphur-selective detectors (FPD, PFPD, SCD) [40].

13. Gas Chromatography coupled to Barrier Ionization Discharge (GC-BID)

HOW IT WORKS

Barrier Ionization Discharge is a specific type of detector applied to GC, in which a plasma is generated from helium by applying a high voltage. The compounds that elute from the GC column are ionized by the helium plasma and then captured by collection electrodes [33].

ADVANTAGES

Due to the extremely high photon energy of helium, it is possible to detect with a high sensitivity every compound except neon and helium itself [26][33]. The sensitivity of BID detectors is 2 times higher than FID and around 100 times higher than TCD. Thus, it is an analysis technique suitable for the detection of trace components at very low detection levels that cannot be reached by more conventional TCD and FID detectors [33].

LIMITATIONS

The high sensitivity and universal response of BID detectors entails a negative side: the easy saturation of the detector, which can make peak separation difficult [26].

EXAMPLES OF APPLICATION

VTT has applied GC-BID or PD-HID for the analysis of sulphur compounds as a supporting analysis method (thus, not regularly) to GC-FPD in special cases in which very low detection levels (ppb) are required [26].

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14. Gas chromatography coupled to Flame Ionization Detector (GC-FID)

GC-FID is a suitable technique for the analysis of hydrocarbons and volatile organic compounds. It is widely applied for a variety of applications. Within the scope of this report, GC-FID is used for the analysis of hydrocarbons and tar compounds contained in product gas.

HOW IT WORKS

The gas sample is combusted in a hydrogen/air flame, where ions and free electrons are formed. The charged particles produce a current flow in the gap between two electrodes located in the detector. The signal differential between the resulting current flow from the combustion of the sample and the signal from the carrier gas and the fuel gas flame provides information about the composition of the sample. Helium, nitrogen or hydrogen are normally used as carrier gas [41].

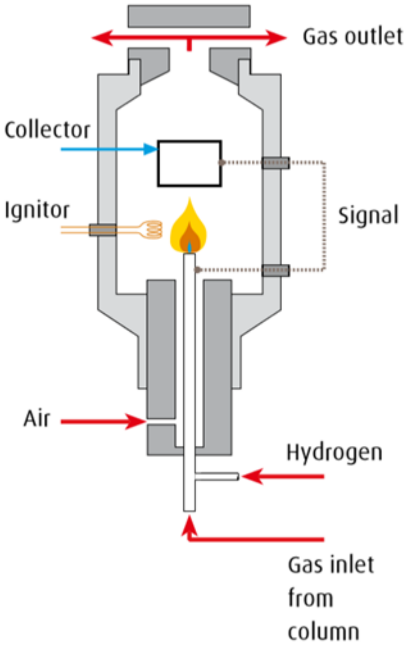

Figure 19. Schematic of FID detector [41].

ADVANTAGES

- High sensitivity.
- Wide range of linearity [41].

LIMITATIONS

- Destructive analysis (the gas sample is oxidized).

EXAMPLES OF IMPLEMENTATION

Within the scope of this report, GC-FID is widely used for the measurement of hydrocarbons contained in product gas. In this section we briefly mention a couple of examples of application:

- ECN part of TNO applies semi-offline GC-FID analysis (Figure 20) to gas bags for the measurement of C_1-C_5 hydrocarbons. The gas sampling in Tedlar bags takes 2 minutes, whereas the analysis takes 30 minutes. The GC-FID analyser quantifies the amount of H_2 and the following hydrocarbons:

CH_4
C_2H_6
C_2H_4
C_3H_8
C_3H_6
C_2H_2
Iso-C_4H_{10}
C_4H_{10}
C_4H_8 1-butene
C_4H_8 trans 2-butene
C_4H_8 isobutene
C_4H_8 cis 2-butene
C_5H_{10} cyclopentane
C_5H_{12} 2-methyl-butane
C_3H_4 propadiene or C_4H_6
C_5H_{12}
1,3-butadiene+propyn (as C4)
C_5H_8 cyclopentene
C_5H_{10} (sum 5 peaks)
C_6H_{12} me-cyclopentane
C_4H_6 1-butyne
C_6H_{14} 2,3-dimethylbutane
C_6H_{14} 2+3-methyl-pentane
C_5H_8 2-methyl-1,3-butadiene
C_6H_{14}
C_4H_6 2-butyne
C_5H_6 cyclo- or 1,3 and 1,4-pentadiene
C_6H_{10} cyclopentene (4 peaks)

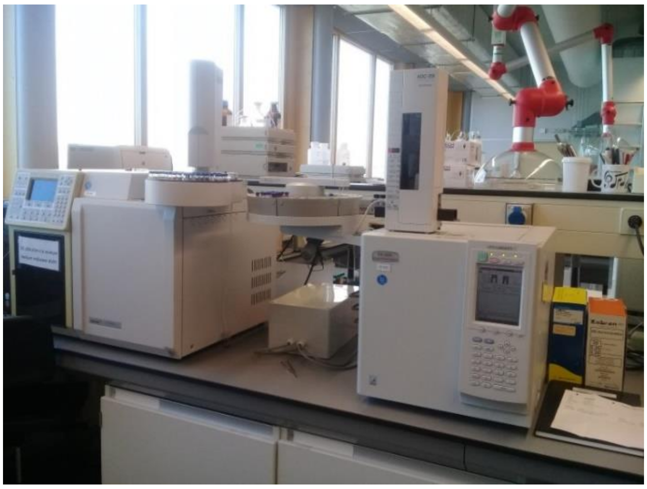

Figure 20. GC-FID unit used for tar analysis. Picture courtesy of ECN part of TNO.

- Technical University Delft (TUD) reports the application of GC-FID for the online measurement of tar compounds. For this, the GC unit was equipped with a heated gas injection loop set at 175°C connected to the gas sampling line, which enabled the injection of the product gas in a continuous mode. The developed analysis method was tested at the CFB gasifier located at TUD laboratories. During the gasification tests it was observed that the base line of the GC-FID chromatograms was not smooth and had a significant amount of noise, which was attributed to the large amount of water contained in the product gas. This noise negatively affected the quantification, which led to the need for manual correction, thus complicating the analysis procedure [42]. Moreover, the existence of non-heated lines in the setup led to difficulties in the calibration of naphthalene and other PAH compounds (not reproducible results). On the other hand, the temperature of the heated injection loop was too low to prevent condensation of tars, which resulted in the decrease of sample flow over time. This issue was overcome by increasing the temperature of the injection loop to 300°C [42].

CONTACTS

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15. Gas chromatography coupled to Flame Photometric Detector (GC-FPD) and Pulsed Flame Photometric Detector (PFPD)

This specific form of gas chromatography is used for the measurement of sulphur compounds (H_2S, COS, thiophene, methylthiophene, mercaptans, carbon disulphide, and dimethyl sulphide), P-containing compounds and metals such as Zn, B, As and Cr [30]. When applied to gasification applications

HOW IT WORKS

P- and S-containing hydrocarbons generate chemiluminescence at specific wavelengths. The resulting electrical signal (after a photo-multiplier) can be measured [30]. The working principle of a FPD detector is similar to that of FID, but with the addition of a photomultiplier tube and suitable filters for detection of S or P [38]. The inlet gas sample is mixed with air and burnt in a hydrogen-rich atmosphere, thus producing a flame. S- and P- containing sample molecules are decomposed into S_2 and HPO, respectively. The decomposed sample then enters into a second flame that supplies the energy for exciting these fragments. When returning to the initial energy state (relaxation), light is emitted (chemiluminescence) [38]. After the application of filters, this emission is converted into an electrical signal which is then amplified and measured.

ADVANTAGES

- GC-FPD can detect S-derived hydrocarbons that cannot be measured with micro-GC, and which are relevant for synthesis applications of product gas.
- Lower detection limits than micro-GC: suitable for trace determination of sulphur compounds, particularly when they are in the presence of much larger amounts of other types of compounds such as hydrocarbons [38].
- Relative lower cost and easier maintenance than other sulphur-selective detectors (PFPD, SCD and AED).

LIMITATIONS

- The detector output is proportional to the square of the S mass flow (related to the S_2 radical formed) [38]. As a consequence, there is a non-linear response for sulphur detection. This in turn results in difficult calibration and quantification. Thus, the GC-FPD signal is limited in terms of range and sensitivity.
- Higher detection limits than GC-MS, GC-PFPD, GC-SCD and GC-AED.
- The FPD detector is extremely sensitive to hydrocarbon impurities in the hydrogen and air supply for the flame. Hydrocarbon impurities can cause increased baseline noise and reduce the detector sensitivity [30].

EXAMPLES OF APPLICATION

As an example, at ECN part of TNO, the following sulphur compounds are semi-online analysed using GC-PFD:

Hydrogen sulphide, H_2S
Carbonyl sulphide, COS
DMS (Dimethyl sulphide) $(CH_3)_2S$
Carbon disulphide, CS_2
1-propanethiol (C_3H_8S)
Thiophene (C_4H_4S)
2-methylthiophene (C_5H_6S)
3-methylthiophene (C_5H_6S)
Methylmercaptan (CH_4S)
Ethylmercaptan (C_2H_6S)
Isopropyl mercaptan (C_3H_8S)

Figure 21. GC-FPD unit at ECN part of TNO for analysis of S-compounds.

Tedlar gas bags are used for gas sampling. The sampling takes approximately 5 minutes, whereas the subsequent analysis takes approximately 15 minutes. Figure 21 shows the GC-FPD equipment used at ECN part of TNO laboratories. GC-PFD is particularly useful to evaluate the performance of hydrodesulfurization catalyst (which must be able to convert organic S compounds into H_2S and COS) and sulphur sorbents. Both HDS and ZnO are reactors part of ESME, the methanation process developed at ECN part of TNO.

Due to the limited range and sensitivity of the FPD signal, the equipment has several ranges (10^0, 10^1, 10^3), which have different measurement ranges and detection limits. These different measurement ranges are separately calibrated with different methods:

- Method 10^0 range: calibrated for all compounds (except CS_2) in the range 0.5 – 6 ppmv. Detection limit: 0.02 ppmv.

- Method 10^1 range: calibrated in the range of 0.5 – 6 ppmv for DMS, ethylmercaptan, methylmercaptan, isopropyl mercaptan, 2-methylthiophene, 3-methylthiophene, and 1-propanethiol, and in the range of 2.6 – 20 ppmv for H_2S, COS and thiophene. Detection limit: 0.1 ppmv.

- Method 10^3 range: calibrated for H_2S, COS and thiophene in the range 2.6 – 100 ppmv. Detection limit: 2 ppmv.

Thus, measurements above 100 ppmv are not accurate. If the concentration of a sulphur compound is outside the measurement range, the peaks are capped. Thus, the sample needs to be injected again with a higher measurement range in the equipment. In case that the concentration is within the detector range but above the calibration line, a concentration number is calculated by the software from extrapolation but expressed in brackets. The value is not completely correct, but it can be used to compare with other measurements.

GC-FPD is also applied at CIEMAT, ENEA and VTT, whereas GC-PFPD is used at TU Delft, TU Graz and Tübitak Mam.

VARIATIONS – PULSED FLAME PHOTOMETRIC DETECTOR

Compared to conventional FPD, PFPD operates in a pulsed-flame instead of in a continuous-flame mode. This results in substantial improvements in sensitivity and selectivity by lowering the flow rates of the combustible mixtures (air + H_2) [39][40]. Its linear, equimolar response is another advantage with respect to GC-FPD, although it also suffers from hydrocarbon quenching problems and has a relatively higher cost.

CONTACTS

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16. Gas chromatography coupled to Sulphur Chemiluminescence Detector (GC-SCD)

This sampling and analysis method, described by the ASTM D5504 standard [43], allows the measurement of sulphur compounds (H_2S, COS, and organic S species such as thiophenes, mercaptans and organic sulphides).

HOW IT WORKS

Figure 22 shows schematically the GC-SCD instrument applied at University of California at San Diego for the measurement of sulphur compounds [44]. The gas sample is introduced in the lower part of the analyser. In a lower burner, the sample is oxidized at 800°C to produce SO_2. In a catalytic tube + burner, sulphur dioxide (SO_2) is converted to sulphur monoxide (SO). Afterwards, SO reacts with ozone in a reaction cell ($SO + O_3 \rightarrow SO_2^* + O_2$). As the high-energy SO_2^* returns to ground state through chemiluminescence, a photomultiplier measures the emitted light produced by the reaction.

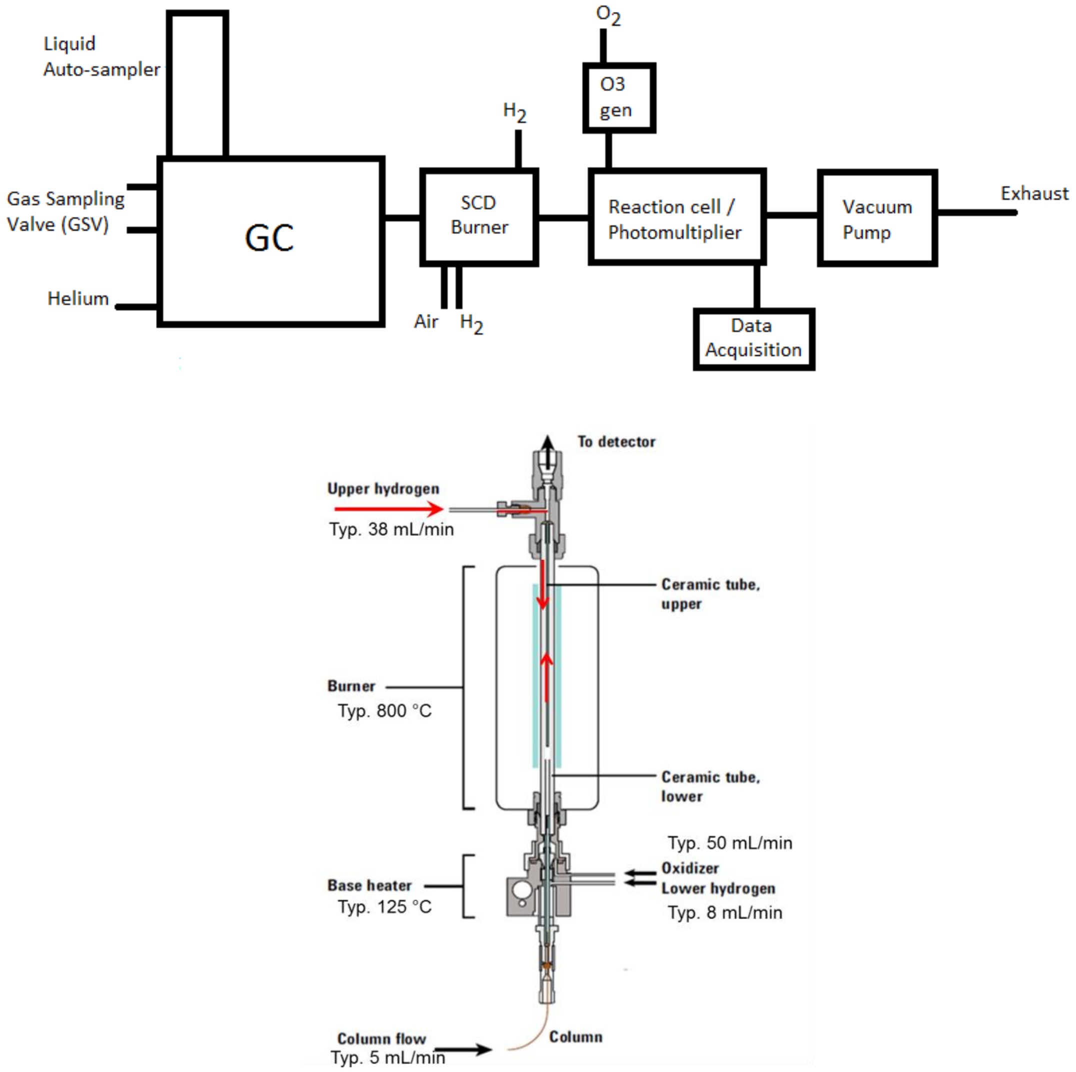

Figure 22. Schematic layout of GC-SCD analyser (top), with detail on the SCD burner (bottom) [44].

ADVANTAGES

- Good sensitivity and specific: detection of sulphur compounds down to ppb levels [44][45].
- Linear, equimolar response to sulphur compounds [40][46].

- No hydrocarbon quenching [40].
- Reproducible analysis.
- Commercial status [46].

LIMITATIONS

- Advanced technical knowledge required for troubleshooting and maintenance [40].
- There are some molecules that interfere with the measurement: benzene and thiophene (because of coke formation in the SCD reaction tube), H_2S (which is usually several orders of magnitude higher than other sulphur compounds), and H_2 (since it can deactivate the SCD reaction tube). For this reason a dilution of the sample might be recommended (e.g. via 10:1 split), increasing the level of quantification accordingly [44][47][48].

EXAMPLES OF APPLICATION

The University of California at San Diego has used a GC-SCD for the online measurement of sulphur compounds directly in the gas phase [44]. PSI uses a GC-SCD unit (Figure 23) to analyse sulphur compounds in liquid samples collected via liquid quench sampling to quantify sulphur tars from product gas [49] as well as sulphur compounds in biogas [31] (see Factsheet 25 for information about the liquid quench sampling system). Separately, PSI has also used a stand-alone SCD detector (that is, without a preceding chromatography column) to measure total-sulphur concentrations below 0.5 ppmv [50]. This unit is shown in Section 2.6.2 of Document 1. This is possible due to the equimolar, linear response of the detector, and is a useful breakthrough detection method for gas cleaning systems.

Figure 23. Stand-alone SCD (with no preceding chromatography column) used at PSI for total sulphur measurements. Images courtesy of PSI [10].

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17. Inductive Coupled Plasma- Optical Emission Spectrometry (ICP-OES)

This optical emission spectrometry technique is applied for the analysis of the elemental composition of a sample (liquid or solid). ICP-OES can determine the concentration (expressed in mg/kg) of the following elements:

Al As B Ba Ca Cd Co Cr Cu Fe K Li
Mg Mn Mo Na Ni P Pb S Sb Se Si
Sn Sr Ti V W Zn

HOW IT WORKS [51]

When plasma energy is externally supplied to an analysis sample, the atoms are excited. When the excited atoms return to the low energy level, they emit radiation. The emission rays that correspond to the photon wavelength are measured. The element type is determined based on the spectral position of the detected photon, and the content of each element is determined based on the radiation intensity.

To generate plasma, high-frequency current is applied at the tip of the torch tube. The electromagnetic field created in the torch tube ionizes argon gas and generates plasma. The high electron density and temperature (10000 K) of the plasma is used in the excitation-emission of the sample. The high temperature of the ionized argon can efficiently excite many elements compared to atomic absorption spectrophotometers (where the excitation temperature of the air-acetylene flames is 2000-3000 K).

ADVANTAGES

- Few chemical interference or ionization interference: analysis of high-matrix samples is possible.
- High sensitivity (lower detection limit ≤ 10 ppb for most compounds).
- Large number of measurable elements.
- Stable analysis.

LIMITATIONS

- Not applicable to online analysis of gases (either to liquid samples from wet chemical sampling or to solid samples e.g. particulate matter).

EXAMPLES OF APPLICATION

Bioenergy2020+ applies ICP-OES for the offline analysis of elemental contents of particulate matter in the product gas. The sample used in the analyser comes from wet chemical sampling (via impinger bottle with acid absorption solution) or particulate sampling (e.g. size-fractioned particulate matter sampling with a cascade impactor, followed by microwave assisted digestion of sampled solid particulate matter (see Section 2.12.3 in Document 1). Alternatively, particulate matter may be analysed by ICP-MS for lower detection limits or SEM-EDX.

CONTACTS

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18. Ion chromatography

This liquid chromatography technique is applied to measure concentrations of the following species:

- Anions such as fluoride, chloride, nitrate, nitrites and sulphates.

- Cations such as lithium, sodium, ammonium, potassium, calcium and magnesium in the ppb range.

- Organic acids.

When looking specifically at the application of gasification gas analysis (scope of this report), ion chromatography is used for the analysis of chlorine.

HOW IT WORKS

Sample solutions are injected into a pressurized chromatographic column (stationary phase), where ions are adsorbed by column constituents. An eluent (mobile phase) is constantly pumped through the column. As the eluent runs through the column, the ions previously adsorbed start to separate from the column [52][53][54]. This occurs because the eluent ions displace the anions bonded to the column. The difference in affinity between the various ions and the column are the basis for the separation of compounds. The higher the affinity for the column, the longer will be the elution time. After suppression of the background signal, the ions are detected with a conductivity detector (fluoride, chloride, nitrite, sulfate, bromide, nitrate and phosphate) and UV-detection (nitrite, bromide and nitrate).

There are different types of stationary phases available: modified organic polymer resins, modified silica gels, inorganic salts, glasses, zeolites, metal oxides and cellulose derivatives [54]. The most common types are silica gels and polymer resins.

ADVANTAGES

- Commercial status.

LIMITATIONS

- Offline gas analysis (samples can be solid or liquid, from wet chemical sampling).
- Issues related to large background signals due to solvent or to ions of co-absorbed compounds might lead to erroneous quantification [55][56] → please refer to the relevant issues in the 'Wet chemical analysis' factsheet (Factsheet 47).

EXAMPLES OF APPLICATION

At ECN part of TNO, ion chromatography is used for the (offline) analysis of HCl and total content of Cl in the product gas. The sample used in the analyser comes from wet chemical sampling (in this case using a HNO_3 solution or 2-propanol (in the latter case, Cl analysis can be applied on the same solution used in the tar guideline analysis). The column used in the ion chromatograph is a Dionex IonPac AS18. The detection limit is 0.5 ppmv.

CONTACTS

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19. Ion molecule reaction mass spectrometry (IMR-MS)

This method belongs to the group of mass spectrometry techniques, and within gasification applications it can be used for the online measurement of permanent gases, water content (if heated cell) and tars [57].

HOW IT WORKS

IMR-MS consists of a soft ionization (i.e. < 15 eV) mass spectrometry method. As a consequence of the mild ionization energy, it avoids the major drawback of conventional high ionization energy (70 eV) techniques, namely the fragmentation of molecules leading to complex mass spectra and multiple overlapping intensities in complex gas mixtures [58]. The soft ionization energy is achieved by a primary ion source from one of the three following gases: Hg (10.43 eV), Xe (12.12 eV), Kr (13.99 eV), previously ionized by electron impact.

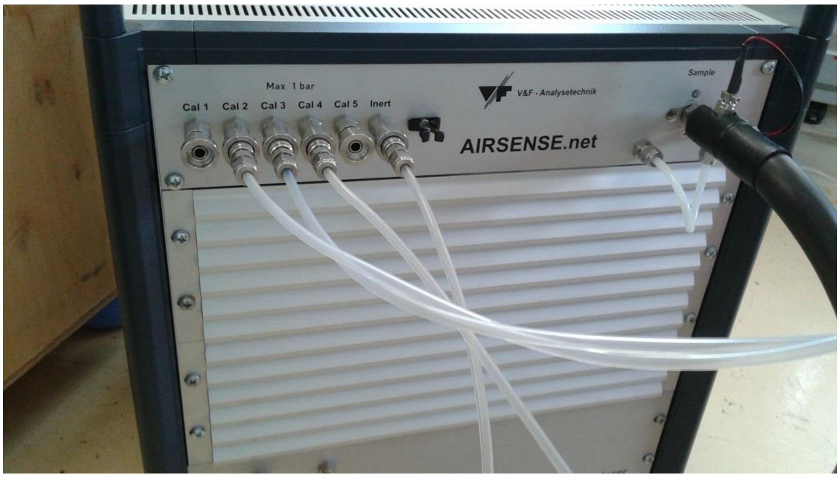

Figure 24. IMR-MS (Ion Molecule Reaction Mass Spectrometry). Picture courtesy of CEA.

EXAMPLES OF APPLICATION

The French Alternative Energies and Atomic Energy Commission (CEA) has implemented IMR-MS for online tar measurement. The IMR-MS apparatus was tested at a fluidized-bed gasifier in steam gasification tests [57]. A heated low-pressure capillary (operated at 180°C) was used to sample the gas. Measurements with both wet gas and dry gas from steam gasification were performed. In the case of wet gas, a prior dilution of the product gas with nitrogen was applied. The dilution is a disadvantage, since it leads to less consistent results (values close to detection limit of the apparatus). The masses corresponding to benzene, toluene, thiophene, phenol, indene, acenaphthylene, biphenyl + acenaphthene, fluorene, phenanthrene + anthracene are well defined. Other masses corresponding to some inorganic gaseous species such as H_2S, NH_3 C_2H_4 and thiophene could also be detected by the IMR-MS apparatus. Although the first validation tests were promising, this technique needs still some improvements. For example, the measurement of COS, H_2S, HCl and NH_3 is challenging when applied to wet gas due to overlapping in the signal.

ADVANTAGES

- it is a soft ionization (i.e. < 15 eV) mass spectrometry (MS) method, which avoids the fragmentation of molecules leading to complex mass spectra and multiple overlapping intensities in complex gas mixtures.

- Able to online measure BTX and PAHs (both at high concentration and trace levels).

LIMITATIONS

- Need for building a fragmentation database at such low ionization potential.
- Expensive equipment.

STATUS

The IMR-MS is commercially available [162]. The Airsense equipment commercialized by V & F is occasionally rented by CEA for several projects [57].

CONTACT

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20. Karl-Fischer titration

Karl-Fischer is an analytical method broadly applied for the measurement of water content in a sample. Within the scope of this report, KF is one of the available techniques for the (offline) determination of the water content of product gas.

This analysis technique is regulated by the standard ASTM E203 – 16 "Standard test method for water using volumetric Karl Fischer Titration" [59].

HOW IT WORKS

KF titration is based on a reaction in which water reacts with iodine (I_2). The process uses an organic base B (e.g. imidazole), SO_2, I_2 and an alcohol (e.g. ethanol). During the titration, I_2 is added to sample and the amount of iodine used to consume all the water contained in the sample is measured. The reaction that takes place is described as [60]:

$$SO_2 + CH_3OH + B \rightleftarrows CH_3SO^{3-} + HB^+$$

$$CH_3SO^{3-} + H_2O + I_2 + 2B \rightarrow CH_3SO_4- + 2HB^+ + 2I^-$$

During the reaction with water, iodine (brown color) is reduced to iodide (colorless). The endpoint of the titration is reached when all the water in the sample is consumed. Since it is difficult to visually determine the endpoint of the titration, this is usually determined with a double Pt wire electrode [60].

There are 2 types of KF titration depending on the way of adding I_2 to the sample [60]: volumetric KF and coulometric KF. In volumetric KF processes, a solution with an exactly known concentration of iodine is added to sample by means of an electric burette. In coulometric KF processes, iodine is generated by electrolysis, and the amount of I_2 added to the sample is determined by measuring the current needed for the electrolysis. There is an advanced hybrid KF process in which I_2 is produced by electrolysis, and if the moisture content of the sample exceeds a certain level, a solution with an exactly known concentration of iodine is added at the same time [60]. The coulometric method is more suitable for samples with a low water content (10 μg – 100 mg), whereas the volumetric method can be used for samples with a higher water content (0.1 mg – 500 mg) [60].

ADVANTAGES

- Standardized, widely used and commercially available.
- Accurate, fast and selective for water.
- Linear response: single-point calibration is sufficient.
- No costly preparation of sample is needed.
- The water needs to be in an alcohol solution: convenient combination of water determination with tar guideline analysis.

LIMITATIONS

- Offline method (requires lengthy gas sampling): not suitable to follow rapid changes in gasification process.
- Required used of reagents.

EXAMPLES OF IMPLEMENTATION

Karl-Fischer titration is often applied complementary to tar guideline analysis at ECN part of TNO for the determination of the water content of the gas sampled during the tar guideline. The 2-propanol solution resulting from the gas sampling in the impingers train is then subjected to KF titration for the determination of the water content of the gas.

CONTACT

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21. Laser absorption spectroscopy

Laser absorption belongs to the group of absorption spectroscopy techniques. This method has been applied for the measurement of permanent gases (including water content), and tar content.

Within this group, Tunable Diode Laser Absorption Spectroscopy (TDLAS) encompasses a number of techniques that use semiconductor lasers [61]. TDLAS has been applied to a wide variety of energy-related, harsh-environment applications (including internal combustion engines, and combustion and gasification processes) [62][63]. Within the scope of this report, TDLAS has been used for the online, in-situ determination of a number of compounds in the product gas, such as water, CO, CO_2, CH_4, HCl, soot and alkali metals.

HOW IT WORKS

A diode laser light is directed through the gas mixture. The laser light is tuned over a small frequency range around an atomic or molecular transition of the target species. As a result, the intensity is attenuated by absorption, and the intensity of the light transmitted through the sample is recorded [61]. In that way, the light absorbed by the atoms/molecules at the transition can be measured relative to the baseline further away from the transition, where no light is absorbed [61]. The variation in intensity is described by the Beer-Lambert Law, which is the basis for the theory of absorption spectroscopy. The Beer-Lambert law states that the absorbance (defined as the ratio between the transmitted and the incoming light intensities) is a function of the line strength and line shape of the transition, the gas pressure, the concentration of the gas present in the light's path, and the path length [24][61][64]. The absorption cross section (line strength) can be either obtained in available databases such as HITRAN [65], or determined in a laboratory under controlled environment [24][61]. From this, the species concentration can be derived. Uncertainties are often below 5%, depending on the individual uncertainties in the parameters [61]. Although this principle implies that no calibration is needed, validation with other techniques is recommended [61].

ADVANTAGES

- Online, in-situ measurement: fast response to changes in process.
- Non-intrusive method.
- Sensitive species-specific detection capabilities.
- Calibration-free: reliable quantitative measurements of absolute species concentrations (also gas temperature) can be obtained without having to compare to a reference [61][66].
- Allows measurement of both species concentration and gas temperature [67][68].
- Applied in other energy applications: power plants, incineration processes [68].
- Indirect estimation of soot content (e.g. in entrained-flow gasifiers) is possible.

LIMITATIONS

- Gasification is in general a challenging application for laser spectroscopy due to the strong light attenuation of product gas, the high temperature of application and the presence of a significant number of compounds, each of them with different cross sections [24].
- Negative effect of particulate matter in the gas (extinction of laser beam at longer path length). This limits the possible optical path length to get acceptable signal-to-noise ratios [67]. This influences the selection of the gas sampling point: the gas needs to be clean from particles.

- The absorption spectrum is broadened at high pressures (Figure 25). This poses a challenge in measurements in high-pressure reactors [66][69].

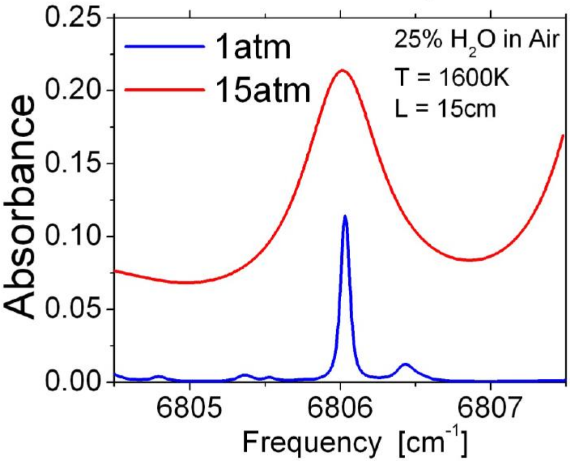


Figure 25. Effect of pressure on the absorption spectrum using TDLAS [62].

- H_2 cannot be measured (weak absorption spectrum): need for complementary detection methods.

- Although claimed to be calibration-free, TDLAS implementation still depends on good knowledge of absorption path length, molecular and atomic spectroscopic parameters (such as line strength), and averages over possible inhomogeneous conditions along the light path. Therefore, validation by comparison to other techniques might be still necessary [61]. This issue is further described in the "relevant aspects" section below.

RELEVANT ASPECTS

Selection of laser:

Whereas conventional tunable diode lasers are limited to the near infrared region, the application of quantum cascade lasers allows going to wavelengths above 4 μm, thus reaching the mid-infrared [66].

Selection of the absorption transitions:

Viveros Salazar et al. [64] make an excellent description of the procedure followed for the design of the laser sensor setup. In order to predict the absorption spectrum for a certain application, it is firstly necessary to compile a list of absorption transitions (including wavelength, line strength, and collision-broadening information) for each target compound in the gas mixture [64]. These data can be found in databases such as HITRAN [65] and HITEMP [70]. The right selection of the absorption transitions is an important part of the design of a laser absorption sensor [64][66][68]. For this, the first step is to determine or estimate the expected range of operating conditions (pressure, temperature, gas composition), an absorption spectrum of the gas can be calculated. Then, an estimate of the path length is required to determine the strength of the laser absorption signal. Once that the absorption spectrum for the target application is obtained, the next step is to identify and evaluate suitable wavelength transition candidates, which have to comply with the following requirements [64]:

- To have sufficient absorption signal for detection (i.e. to enable sensitive measurements of the target species). However, it has to be taken into account that if the absorbance is too high, the transition becomes optically thick, and sensitive measurements are not possible anymore. Thus, a design rule is to select transitions so the absorbance (defined as the ratio between the transmitted and the incoming intensity, I/I_0) is between 0.1 and 2 (that is, laser transmission between 90% and 10%).

- To ensure selective monitoring (that is, only one species absorbing at the target wavelength to avoid interference effects from other gas compounds).
- Another desirable criterion in the selection of wavelength is the availability of standard diode lasers in the market.

Sepman et al. [68] selected the transitions of the sensors (measurement of CO and H_2O) so as to have either small or linear dependence of the line strength with temperature.

Nau et al. [66] selected the transition lines according to the following criteria: the line pair must be within the scanning range of the laser diode, interference with other target molecules (namely CO_2 and water) should be minimized (which improves sensitivity and reliability), and the line strength needs to be high enough to ensure high signal-to-noise ratios. Other criteria for suitable lines include the possibility of simultaneous determination of temperature, and the suitability of materials for the optical ports (for example, at certain wavelengths the fundamental bands might be more difficult to access because quartz and sapphire, which are materials better suited for the typically harsh environment of a gasifier, are not transparent anymore) [66].

Sensor strategy - fixed- vs. scanned-wavelength and DA vs. WMS:

Another relevant aspect for the implementation of TDLAS in gasification applications is related to the sensor strategy, which in turn influences the performance of the sensor. Firstly, fixed-wavelength or scanned-wavelength approach needs to be selected. Fixed-wavelength approach requires the knowledge of the collision-broadened line shape, which is not known a priori in gasification applications. This difficulty can be overcome is wavelength-scanned approaches are selected, since they provide integrated absorption [64]. In turn, there are 2 sensor strategies for scanned-wavelength approaches which were evaluated by Viveros Salazar et al. [64]: wavelength-scanned direct absorption (DA), and wavelength-scanned modulation (WMS), see Figure 27 (c):

DA is performed by linearly scanning the laser wavelength up and down with a triangle wave. When the laser wavelength matches that of the absorption transition of the target species, the transmission is attenuated. The baseline I0 is determined by extrapolation across the absorption feature. The resulting absorbance is then fit to a Voigt line shape to enable accurate integration as a function of the wavelength. The integrated absorbance is then used together with the line strength, the temperature and pressure data to determine the mole fraction of the compound. The main disadvantage of DA is the difficulty to infer the zero absorbance value (which is sensitive to non-linearity of the laser intensity, other transmission variations such as etalons from windows, and intensity noise. The background of the DA signal is the non-absorbed laser intensity.

WMS adds a modulation waveform to the DA linear scan. The absorption information is thus found in the transmitted intensity data at harmonics of the laser modulation frequency. The harmonics can be then isolated to intensity vs. time data. By decoupling the measurement from the DA noise, the background of the WMS signal is almost zero.

Whereas DA is simpler to implement and interpret the resulting data, WMS allows improved noise rejection (measurement relatively immune to the noisy environment typical of field application), and fewer complications in measurements due to particle scattering and beam steering. In harsh measurement environments such as gasification applications, WMS offers an important advantage, namely that the signal can be normalized to account for non-absorption transmission losses such as window fouling, scattering due to particulate matter in the gas, or long-term drift in the laser intensity. The first harmonic of the WMS signal (1f) becomes the background (zero) absorption intensity, and it is used to normalize the second harmonic of the WMS signal, 2f. In the application to biomass gasification, there is a large absorbance at the wavelengths of CH_4 and H_2O transitions, thus the 1f is very small, and that results in large fluctuations of the 2f signal. The use of an average 1f signal over the scan range was applied to mitigate this issue [64]. Since the scanned-WMS is fit with 2 free parameters (the absorption linewidth and the integrating absorbance), it is not necessary anymore to know in detail about the collision broadening behaviour of the gas. This is crucial for the monitoring of gasification product gas, whose composition is not known a priori. Thus, WMS laser absorption shows improved performance (and is thus more suitable) for biomass gasification applications than DA [64].

Other relevant issues:

Modulation at high frequencies can lead to non-linear laser response and thus negatively affect the performance of the WMS sensor. That brings an undesired baseline to the 2f signal, which becomes larger at higher modulation frequencies. Therefore, diode lasers with linear response to injection current are best suited for WMS sensors. Additionally, the non-linear response to current sets an upper limit to the design modulation frequency of the sensor (despite the improvement in noise rejection associated to higher modulation frequencies).

The background signal tends to drift over time. This negative effect on the sensor performance can be reduced by calculating an equivalent mole fraction for a fixed modulation amplitude over a range of modulation frequencies. By doing so, then it is possible to select a modulation frequency with a correspondent equivalent mole fraction which is negligible for the design application of the sensor.

WMS laser sensors must be optimized to minimize any non-absorption background. In practice, this can be achieved by application of anti-reflection coated optics and careful beam alignment.

EXAMPLES OF IMPLEMENTATION

- TDLAS has been applied by University of Stanford and University of Utah at a pressurized, entrained-flow coal gasification process for in-situ measurement of CO, CO_2, CH_4 and H_2O (the rest of the gas assumed to be H_2). The gas composition allowed the online tracking of the heating value and Wobbe Index of the produced syngas [67]. Figure 26 shows as an example one of the TDLAS detectors implemented in the gasifier setup, located before in the quenching section of the gas, before particle removal in a filter. Another detector was placed after the filter (which showed improved results due to the negative effect of particulates in the measurement). In all cases, the optical access for the diode light consisted of sapphire windows sealed by Teflon gaskets. Sapphire was chosen as the window material due to its superior IR transmission capability and physical strength [67]. The window housing was heated to ~ 150°C to avoid water condensation.

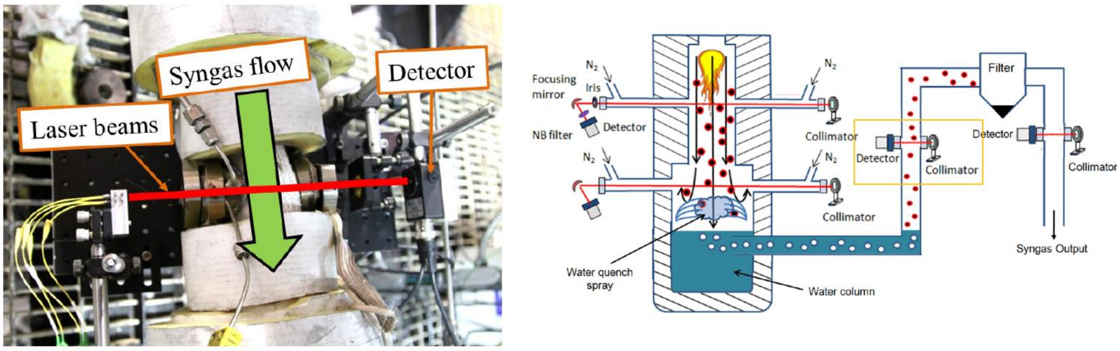
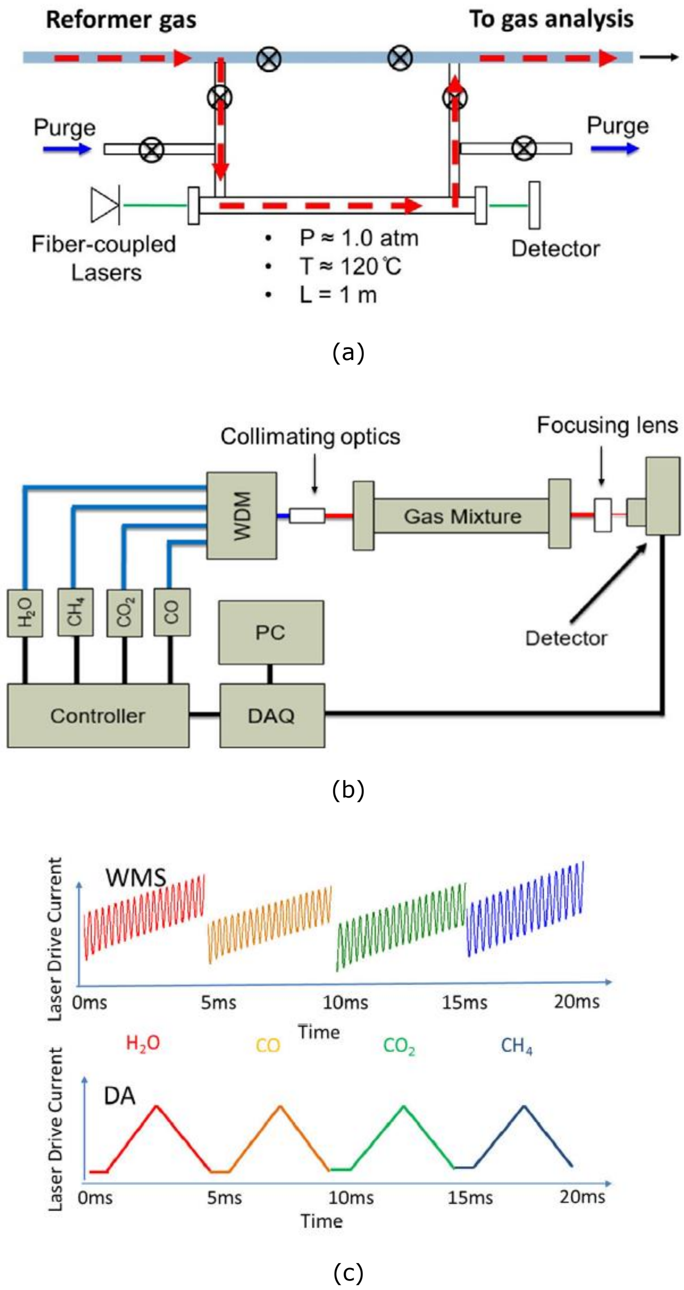


Figure 26. Implementation of TDLAS detector at University of Utah (left) and location of the detector at the entrained-flow gasifier setup (right). An additional TDLAS detector unit was implemented after the filter, as indicated in the right side of the diagram [67].

- Stanford University in collaboration with University of California at San Diego applied a TDLAS setup for the measurement of CO, CO_2, CH_4 and H_2O from biomass gasification [64]. After laboratory validation, the developed optical setup was tested at the West Biofuels pilot gasifier. The laser absorption laser was located downstream the gasifier before entering the tar reformer unit (Figure 27 and Figure 28). The gas lines and the optical sensor cell were traced to approximately 120°C to avoid fouling of the window optical access. The system configuration, which allowed the bypass of the optical setup, was intended to enable maintenance as well as to measure the background signal for sensor setup and testing [64]. Based on the design criteria described earlier in this section, the selected transitions for the diode lasers were 7203.9 cm^{-1} for H_2O, 6047 cm^{-1} for CH_4, 6243.8 cm^{-1} for CO_2, and 6383.1 cm^{-1} for CO. The 4 lasers were combined in an optical fibre (wavelength division multiplexer, see Figure 28 (b) and (c)), collimated into a free-space beam so that only one laser is operating at a time (sequential measurements at rate of 50 Hz), and directed through the gas. The transmitted light is collected and focused onto an InGaAs detector. The detector signal is then digitized and time resolved.

Figure 28 shows some pictures on the practical implementation of the optical cell setup developed by Stanford University at the West Biofuels pilot gasification plant. The TDLAS measurements (which showed good agreement with complementary GC and FTIR analysis) resulted in the improvement of the gasifier operation, since it allowed identification of transients in the fuel feeding system.

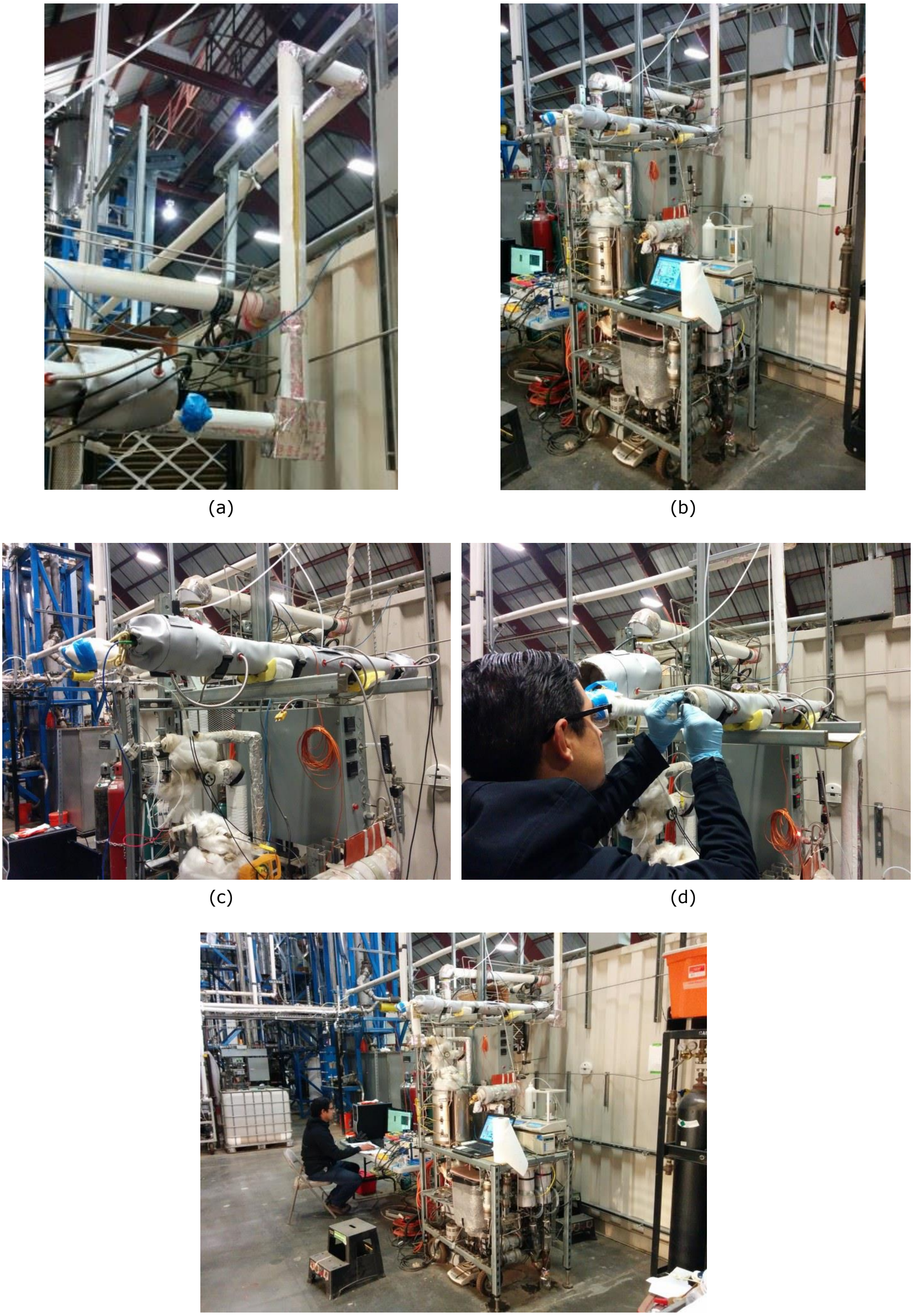


(a)

(b)

(c)

Figure 27. Schematics of implementation of TDLAS in West Biofuels gasifier (a); detail on the configuration of the laser (b); implementation of the time-multiplexation of the 4 laser signals (c) [64].



(a) (b)

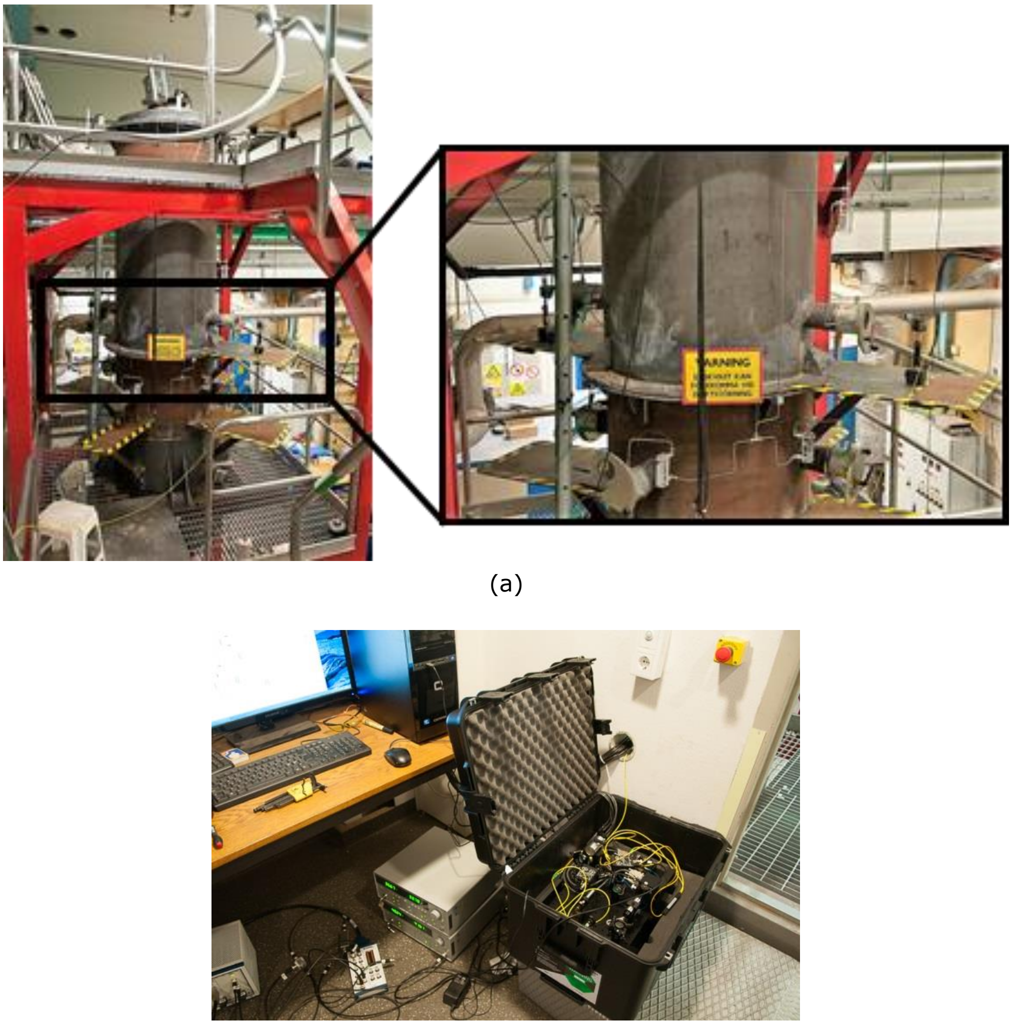
(c) (d)

(e)

Figure 28. Implementation of TDLAS at West Biofuels plant: (a) gas line from gasifier; (b) optical cell setup by tar reformer; (c) detail of optical cell with heaters; (d) alignment of windows of optical cell; (e) operation of optical cell setup. Pictures courtesy of Stanford University and University of California at San Diego (UCSD).

- A joint research group formed by KIT, ETB and Technical University of Darmstadt developed a method based on TDLAS for the online, non-intrusive measurement of HCl in biomass gasification processes in view of the application at pressurized entrained-flow gasification (Bioliq process). More details can be found in Section 3.2.5 of Document 1.

- Umeå University has developed a TDLAS system for the online measurement of CO, H_2O, potassium in the gaseous phase, and gas temperature. Figure 29 shows the practical implementation of the optical setup at a 100 kW_{th} air-blown gasifier located at Piteå [61].



(a)

(b)

Figure 29. Implementation of TDLAS setup developed at Umeå University at 100 kW_{th} biomass gasifier at Piteå: (a) view of the gasifier. The yellow optical fibre carrying the laser light can be seen in the forefront, and close-up of one of the optical ports for measurements. The light output from the optical fibre is in the foreground, and the receiver end with the photodetector is at the back of the reactor; (b) Portable, fibre-coupled optical setup in control room. Some of the other TDLAS sensors were placed near the gasifier at the optical ports. Pictures courtesy of Umeå University [61].

- The German Aerospace Centre (DLR) has developed a diode laser spectrometer for the online measurement of a number of gas compounds relevant in entrained flow gasification (CO, H_2O, CH_4 and C_2H_2), as well as temperature. For the design, 2 wavelength regions were selected so as to minimize interference of the target compounds with each other: CO and temperature were detected at 2.3 μm using a distributed feedback diode laser (DBL), whereas CH_4, C_2H_2 and H_2O were detected at 3.1 μm using an interband cascade laser (ICL). Wavelength division multiplexing was applied in order to enable simultaneous measurement of both wavelength regions [66]. The optical unit was tested at the REGA entrained flow gasification rig located at Karlsruhe Institute of Technology (KIT).

Figure 30 displays the schematic implementation of the laser spectrometer in the gasifier. The output of each laser beam is collimated with a lens and passes through an optical isolator. Then the laser beams are overlapped with a dichroic mirror and coupled with an off-axis parabolic mirror into a single mode ZrF_4 fibre. A small fraction of the overlapped laser beams is directed to a germanium etalon. After passing the reactor, the light is coupled into a second fibre and guided to the detection system. The signal beams are split with a second dichroic mirror and sent to separate detectors (InGaAs detector for the 2.3 μm beam, and MCT-IR detector for the 3.1 μm beam) equipped with narrow bandpass filters [66].

Water cooled probes are used for optical access to the reactor. The probes are purged with dry nitrogen. This ensures a defined optical path length, because absorption of the laser inside the probes is avoided. The nitrogen purge is also necessary to keep the windows free from deposition of particles and soot.

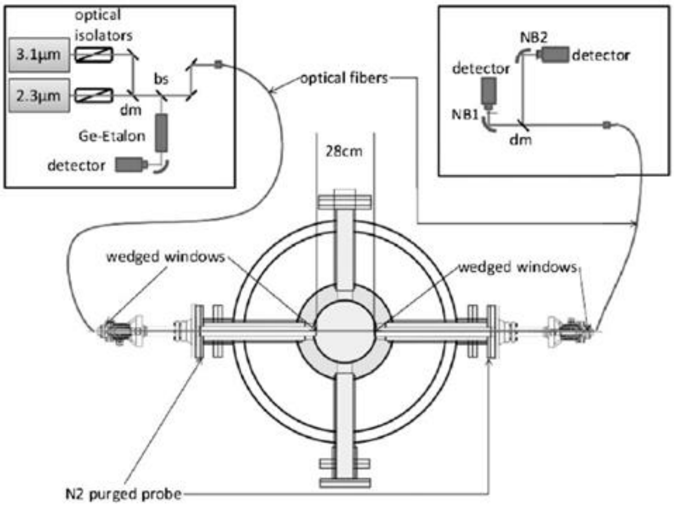


Figure 30. Schematic layout of implementation of laser absorption setup in an entrained flow gasifier [66].

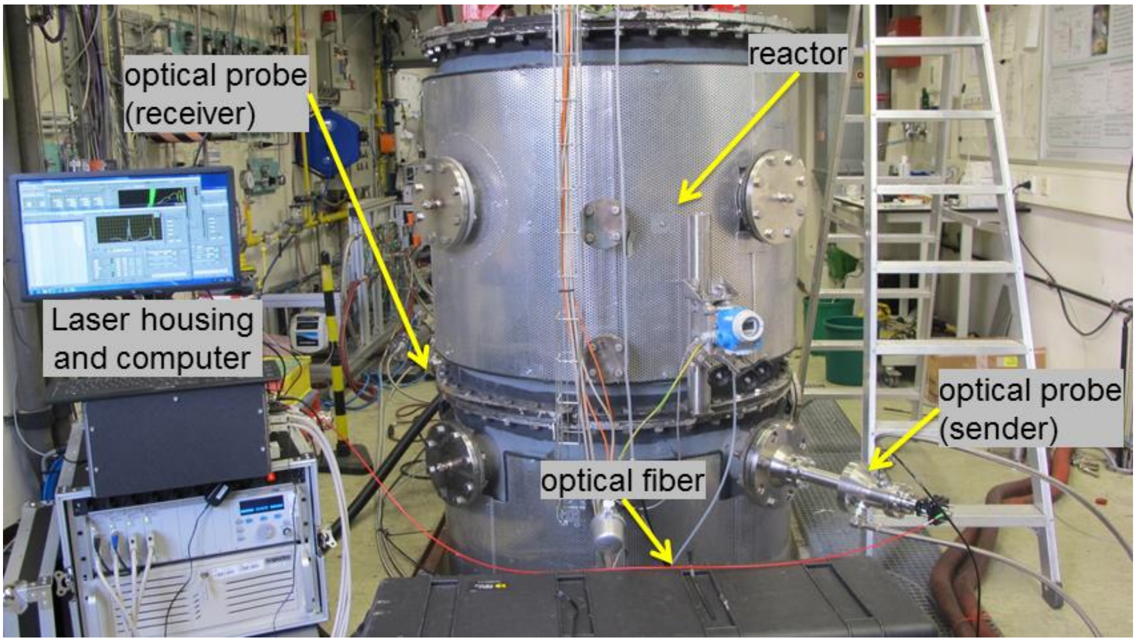


Figure 31. Implementation of TDLAS by DLR at the REGA gasifier at KIT. Housing for laser, electronics and computer is on the left. The red fibre delivers the laser to a probe for optical access. Signal is captured at the opposite of the reactor with a second fibre. Pictures courtesy of DLR and KIT [71].

CONTACTS

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RELATED TOPICS

- Raman spectroscopy (Factsheet 34).
- Tunable Diode Laser Absorption Spectroscopy (Factsheet 43).

22. Laser diffraction

This analysis technique is applied for the offline measurement of particle size of particulate matter contained in the gas.

HOW IT WORKS

Laser diffraction analysis can determine particle size distribution by measuring the angular variation in intensity of light scattered as a laser beam passes through a dispersed particulate sample. Large particles scatter light at small angles relative to the laser beam and small particles scatter light at large angles [72].

The analyzer measures the angle and intensity of light scattered from the particles in the gas sample. That information is then passed to an algorithm designed to use Mie scattering theory, which transforms the scattered light data into particle size information [73]. The Mie theory requires knowledge of the optical properties (refractive index and imaginary component) of the sample, as well as the refractive index of the dispersant (usually available in literature and included in in-built databases in instruments). For samples where the optical properties are not known, it is necessary to either measure or to estimate the properties. A simplified approach is to use the Fraunhofer theory, which does not require knowledge of the optical properties of the sample. This can provide accurate results for large particles, but it should be used with caution for particles < 50 μm [72].

ADVANTAGES

- Wide range of particle size can be measured (0.01 – 5000 μm).
- Calibration not necessary.
- Commercially available.

LIMITATIONS

- Offline analysis (can be applied to dust sampled e.g. in a filter).
- Cannot measure dust concentration.
- Small particles (< 10 μm) require knowledge of physical properties (refractive index).
- Particles in the nanometre scale cannot be detected.

CONTACT

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23. Laser-induced breakdown spectroscopy (LIBS)

This analysis method has been developed by the German Aerospace Centre (DLR) for the measurement of alkali compounds. LIBS can also be applied to determine the general elemental composition of the gas.

HOW IT WORKS [74]

A high energy laser pulse with a short pulse width (approximately 7 ns) is focused onto a sample. Photon absorption causes vaporization of the sample material (either gas or condensed phase) resulting in a plasma with a temperature of several thousands of Kelvins, which dissociates the material into atoms, electrons and ions. As the plasma temperature and the electron density decay, the species present in the plasma emit photons at characteristic atomic frequencies as they relax back to their ground state. Time-gated detection of the emitted photons using a spectrograph coupled with suitable calibration allows the identification and quantification of elemental concentrations of various species including nitrogen, oxygen, carbon, alkali and alkali earth metals. In principle, a differentiation between gaseous and condensed phase is possible based on the required laser pulse energies, differing by 1-2 orders of magnitude.

For application to gasification conditions, a water-cooled optical probe is mounted to the reactor, see Figure 32 left. It features a focusing lens at its tip which serves to focus the pulsed laser beam and also collects the emitted plasma emission. Outside the probe a dichroic mirror separates the outcoming signal from the incoming laser beam and transfers the plasma spectrum to the spectrograph.

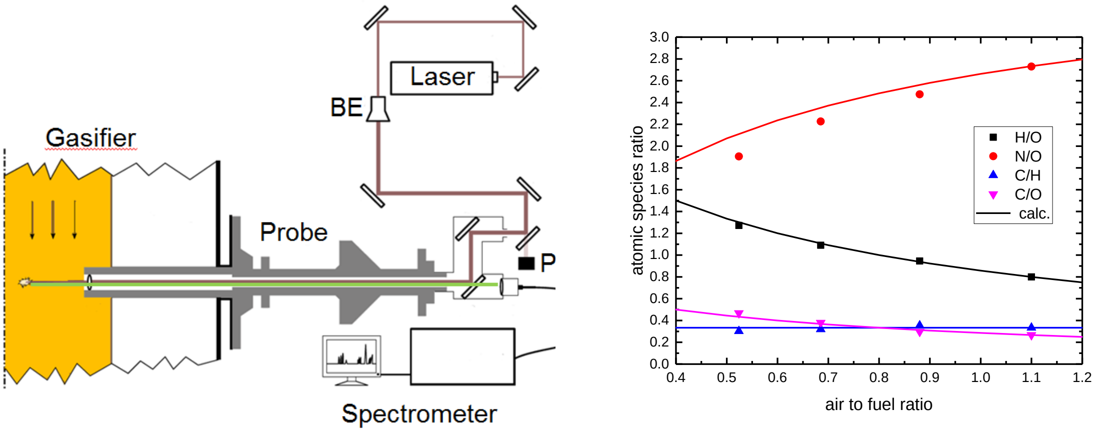

Figure 32. Optics setup and water-cooled optical probe for LIBS application at the Research Gasifier REGA at KIT (left);validation of setup at the gasifier in downstream location during ethylene glycol operation at different air to fuel ratios (right) [71][74].

ADVANTAGES [71]

- In-situ technique: no sample preparation necessary.
- High temporal resolution.
- Only minimal optical access is needed.

LIMITATIONS

- Optical access (one port) to the reactor is essential.
- Careful and extensive calibration measurements needed for quantitative results.

- Requires skilled operators for implementation, operation and data evaluation.
- Laser safety requirements.

EXAMPLES OF APPLICATION

The LIBS setup of the DLR Institute of Combustion Technology has been tested at the KIT Research Gasifier REGA for evaluation of the local equivalence ratio (Figure 32 right). In addition to that, application to pressurized conditions was proven at the Siemens entrained-flow coal gasifier in Freiberg at 26 bar behind the water quench. Latter application was in principle successful but revealed the essential need for efficient window purging to prevent blockage of the optical access [75].

STATUS

Further development at DLR is currently on hold.

CONTACT

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24. Laser-induced incandescence (LII)

Laser-induced incandescence is a laser-based diagnostic tool serving providing in-situ access to soot properties [76]. It can either be directly applied to the reactor (if optical access is available), or after sampling. In-situ application has gained maturity for characterization of combustion processes and even gas turbine combustion [77][78], soot particle mass characterization after sampling is frequently used for exhaust gases, and was selected as one of the standard tools for future aero-engine certification with respect to particles [79]. The suitability of the latter for gasification products, for example using a commercial LII300 apparatus still has to be proven [71].

HOW IT WORKS

A short and intense laser pulse is absorbed by black nanometre-scaled particles which thereby heat up to their vaporization temperature. The excess energy is then released via heat conduction to ambient gas, partially surface vaporization, black-body-like radiation and some other, less prominent phenomena (Figure 33). The intensity of the radiation can be related to soot concentration, whereas the decay behaviour is indicative of primary particle size [74]. For calibration of soot concentration measurements, either another independent diagnostics such as laser extinction is applied, or additional measurements in a calibration source of known soot concentration. Dependent on the studied quantity, either image intensified CCD cameras are employed or photomultiplier tubes. Preferably, the signal is recorded through a different optical port than that used for laser excitation, although backwards LII has been reported for other applications (carbon black production). Differentiation from other types of particles is based on the energy transfer process from the laser pulse to the particles: LII excitation for soot particles is significantly smaller than the laser wavelength (Rayleigh regime), and it is described as volumetric heat up by the electromagnetic wave, thus macroscopic particles are not heated to temperatures emitting significant LII radiation. Similarly, other types of particles can be heated up. But in the case of alkali particles or semi-transparent particles of different composition, those do not absorb the laser photons in a similarly effective wat, and have mostly lower vaporization temperatures, thus significantly higher laser power is required to yield detectable signal. Consequently, the application of LII should be accompanied by a measurement (or good estimation) of the local laser fluence in the measurement volume.

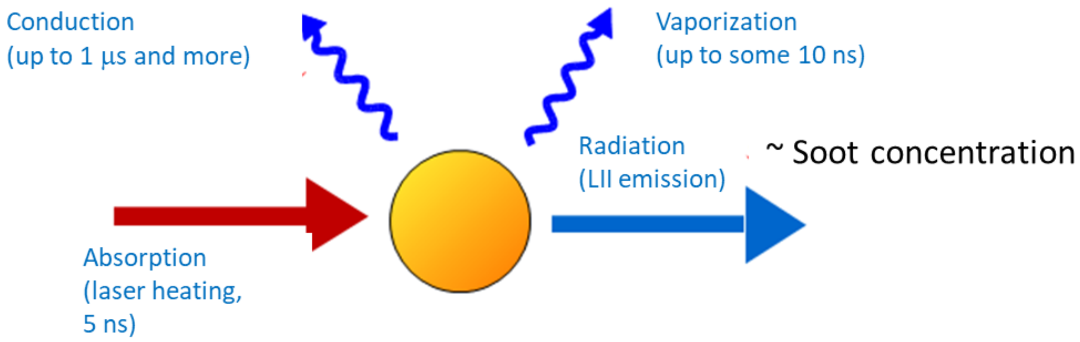

Figure 33. Major energy transfer processes occurring during LII – the emitted signal intensity is proportional to the local soot volume fraction; the signal decay behaviour indicates the primary particle size [71].

ADVANTAGES

- In-situ diagnostics.
- High time resolution which allows for studying transients.
- Low interferences with other species or size classes.

LIMITATIONS

- Requires optical access.
- Requires skilled operator and personnel for data evaluation.
- Laser safety requirements.

EXAMPLES OF IMPLEMENTATION

The LII setup of the DLR Institute of Combustion Technology has been tested at the KIT Research Gasifier REGA for particle characterization [80], see Figure 34. Operation of the reactor with ethylene glycol did not reveal any particles in the accessible measurement locations 300 and 680 mm downstream of the injector. On the contrary, operation with particle-laden slurry resulted in low and homogeneous signal, indicative of very low particle concentration at homogeneous spatial distribution. A draft signal decay analysis revealed particle sizes of about 20 nm. Due to window fouling issues the transmitted laser power could not be measured reliably such that the presence of alkali particles rather than soot cannot be ruled out. The potential of such particles to emit LII signal has still to be studied in more detail. The same set up was also successfully used to visualize clouds of hot (radiating) slurry particles intersecting with the camera field of view.

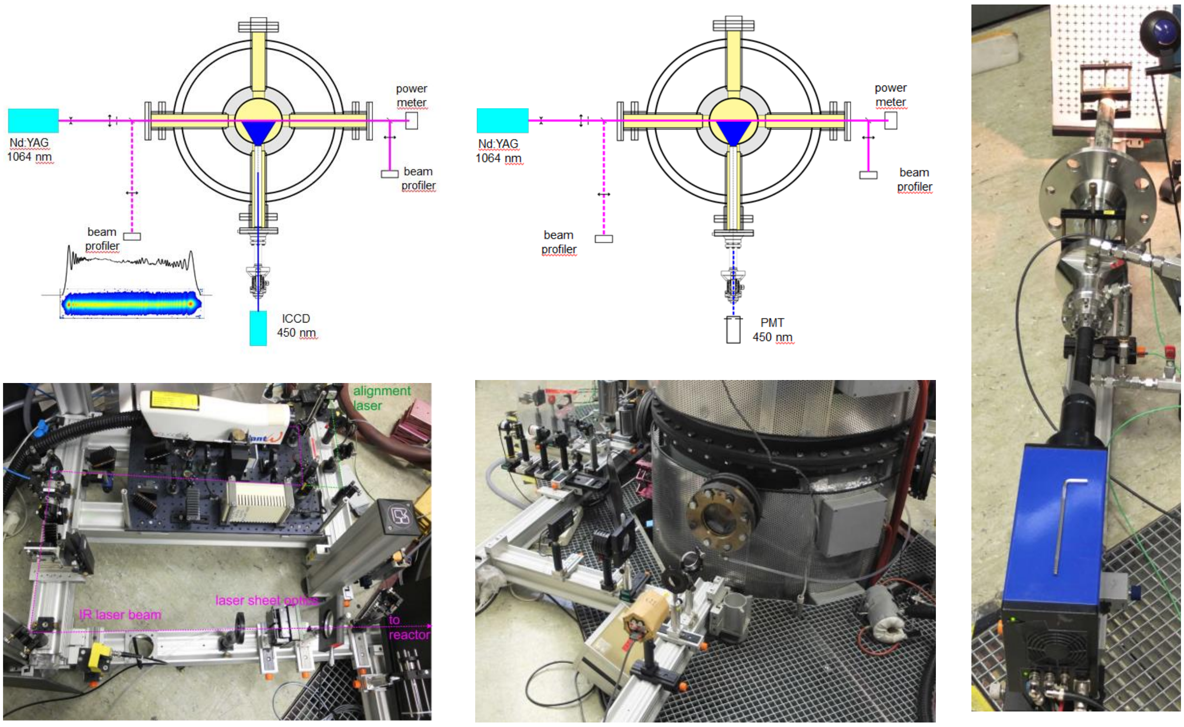

Figure 34. Implementation of DLR’s LII setup for application at the REGA gasifier at KIT for soot concentration measurements with CCD (top left) and particle size with PMT (top centre). Visual impression of the laser path (bottom left), the beam characterization equipment behind the reactor (bottom centre) and the used intensified CCD camera attached to the optical water cooled probe for insertion into the reactor (right) [71][78].

CONTACT

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25. Liquid quenching + UV-Vis spectroscopy, PSI

This sampling and analysis method has been developed by the Paul Scherrer Institute (PSI) for the online measurement of tars.

HOW IT WORKS

A liquid quench sampling system is implemented as a first step. The liquid quench system transfers condensable gas species, including tars, into an organic solvent flow whose absorbance is measured. In a second step, the liquid sample from the quench is analysed by UV-Vis spectroscopy [2].

ADVANTAGES

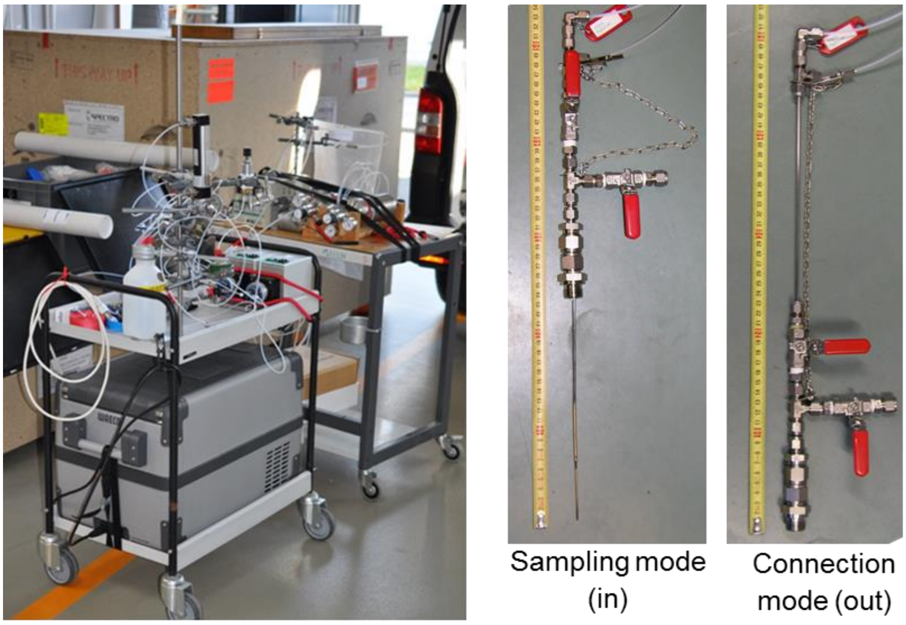
- Measurement in the liquid phase allows easy calibration compared with gas phase calibration → less complex instrumentation is required.
- Suitable for quantitative analysis of tar when the number of tar compounds is limited (clean gas after tar removal), or for qualitative analysis in complex tar mixtures (raw product gas).

LIMITATIONS

- In those cases in which a complex tar composition is expected (e.g. raw product gas), quantitative analysis is not possible due to the high number and spectral overlap (co-linearity) of tar compounds.
- Because the product of concentration and extinction coefficient of tar compounds can span over orders of magnitude, tar compounds with high absorbance might mask the presence of tar compounds with smaller ones.

STATUS

The UV-Vis analysis has been tested at PSI with model compounds and with real gas. The liquid quench is currently operational at PSI laboratories in 2 versions: the non-automated setup (Figure 35), and the automated setup (Figure 36).



Sampling mode (in)

Connection mode (out)

Figure 35. Non-automated version of the liquid quench sampling system (left) used at PSI to sample trace compounds in gasifier gas and syngas. Sampling lance (right) which is used in the liquid quench system to sample directly in the middle of gas flows. Picture courtesy of PSI [10].

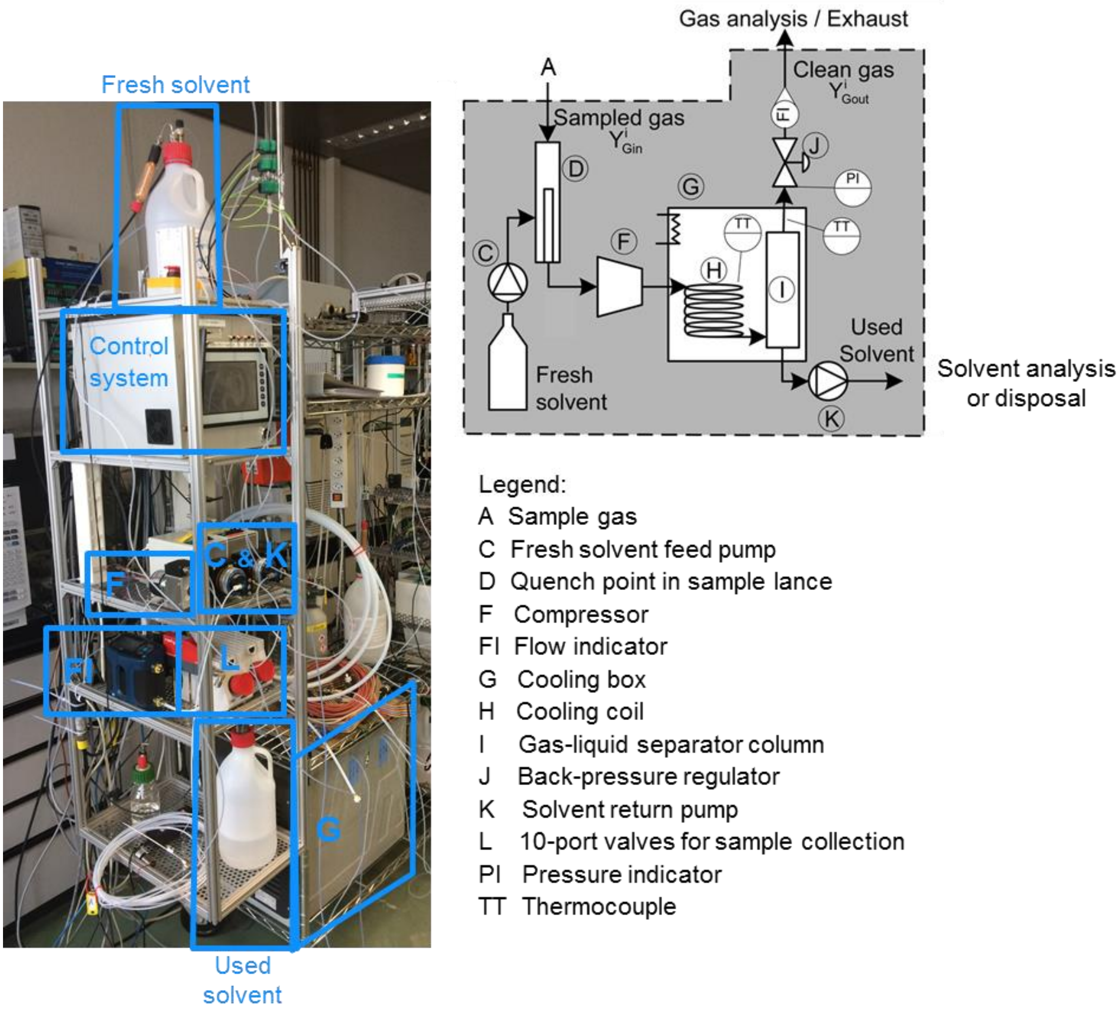


Figure 36. Automated version of the liquid quench sampling system used at PSI to sample trace compounds in gasifier gas and syngas. Image on left courtesy of PSI [10][49].

CONTACT

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26. Low-pressure cascade impactor

Cascade impactors can be used to sample particulate matter from raw syngas for the characterisation of aerodynamic fly ash properties of raw gasification ash in the product gas.

HOW IT WORKS

The sampling system consists of a heated inlet tube protruding into the product gas duct from the top to prevent settling of particles on- and into to the nozzle when no sampling flow is applied. The inlet nozzle is connected by a c-shaped transfer tube with a screw-on connector for the dust/gas sampling system, located under the duct, which should prevent the particles from settling at horizontal surfaces and at the same time provides the proper vertical position for the dust sampling train applied. The whole nozzle and transfer pipe assembly is trace heated and double insulated, ensuring proper isothermal conditions. The sampling gas flow has to be selected so as to ensure isokinetic sampling.

ADVANTAGES

- Determination of particle size distribution in hot gases.

LIMITATIONS

- Cumbersome sampling.
- Offline measurement.

EXAMPLES OF IMPLEMENTATION

Measurement campaigns for the comparison of the performance of particle measurement equipment was performed within the BRISK project [81]. As an example, in this section we describe the cascade impactor applied by ECN part of TNO [82]. The dust sampling consisted of a cascade impactor equipped with a cyclonic pre-cutter/primary deposition plate and 10 multi-jet-stages. The whole impactor and pre-cutter body was trace-heated at 400°C, and additionally insulated to prevent any cold spots and hence minimise the chance for tar condensation. Whole SS316 deposition substrates (inlays for the impactor stages where on the particulate is deposited) were used. The outlet of the impactor was connected via two impingers (for tar/condensate recovery) by Teflon tubing with a pumping unit, equipped with a silica-gel drier, membrane vacuum gas pump and a gas metering system (pressure/volume/temperature).

Firstly, gravimetric analyses were performed by weighing the deposition substrates, each of which is marked with a unique number, before and after the run on a dedicated micro-analytical balance, with an accuracy of 0.0001 g at dry, room temperature conditions. The difference in weight for each substrate was recorded and represents the mass of the particles in each size bin for the composite sample obtained. After the weighing, the material was mounted for SEM analyses. Then, based on the actual particle sizes observed (based on the largest diameter of irregularly formed particles) and wherever such distinction in sizes could be made, the particle density for each observed morphology per stage was derived extrapolating the observed dimensions into a spherical shaped particle of such diameter and comparing the actual volume of such particle to the ideal spherical particle with a unity volume (1 g/cm^3). Further information about the cascade impactor equipment applied at the BRISK project can be found in Section 2.12.3 of Document 1.

CONTACTS

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27. Mass spectrometry (MS)

Mass spectrometry is a measurement technique that is suitable for the analysis of components that are in the gas phase. With this technique, gas is drawn from a gas flow through a heated capillary. The molecules of the gas are then ionized by electrons from a filament and the fragments are analyzed by a detector. This forms an intensity spectrum where the intensity is plotted against the mass/charge ratio (m/z). This creates a characteristic peak pattern, usually containing one dominant peak. By following this peak (or a less dominant one) in time, the change in composition of the relevant gas flow can be measured. If necessary, this intensity can be calibrated to a concentration in the relevant gas flow [83].

In the field of gasification, online MS analysis can be applied to a variety of applications, including syngas composition (to keep track of the gasification conditions), monitoring of sulphur levels in the sulphur removal/recovery unit (gas upgrading for biofuel production), monitoring the extent of reactions in the upgrading section (e.g. degree of conversion of S/N/Cl compounds in HDS, extent of CO shift, purity of CO_2 stream in the acid gas removal unit).

HOW IT WORKS

The MS equipment (Figure 37) is composed of the gas inlet (for stream selection and sample introduction), the ionizer, the mass filter (quadrupole), the detector (Faraday and electron multiplier), and the data system (signal acquisition, processing and display).

The gas sample enters through an inlet to a vacuum system. Then, molecules are ionized in an ion source. The ions are separated by their molecular mass by several means [84]:

- By adjusting the electric field in a quadrupole, were only certain ions can pass at a time.

- In an ion trap where all ions are stored and then let out by varying radio frequencies.

- By acceleration of the ions in an electric field where lighter ions are faster than the heavier ones (time-of-flight, TOF).

The sample gas is firstly ionized by the use of fast electrons. Once the target analytes are ionized, they can be guided to a detector by applying an electrical field [84]. Each scan produces a set of peaks specific to the composition of the ionized gas.

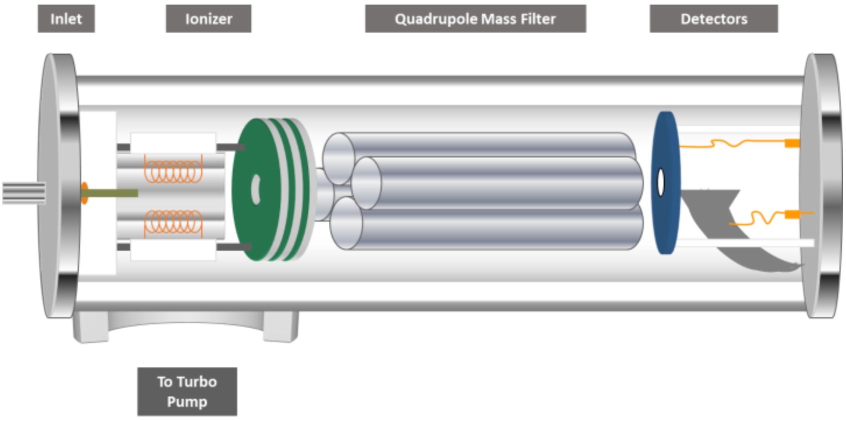


Figure 37. Traversal cut of MS vacuum chamber [85].

The sampling requirements are similar to other gas analysis methods: the gas sample (100 cm^3/min, 1.01-2.4 bar, max. 25°C) needs to be particle-free, and the compounds to analyse need to be in gas phase (non-condensing).

ADVANTAGES

- Online analysis.
- Applicable to all types of gasification processes.
- Versatile technique.
- Commercial status.
- Fully automation and integration in plant control systems.

LIMITATIONS

- Requires skilled operators for maintenance, operation and interpretation of results [84].
- Costly equipment.
- The gas sample needs to be free from particles and condensables to avoid plugging.
- Interference effects among gas compounds (Figure 38).

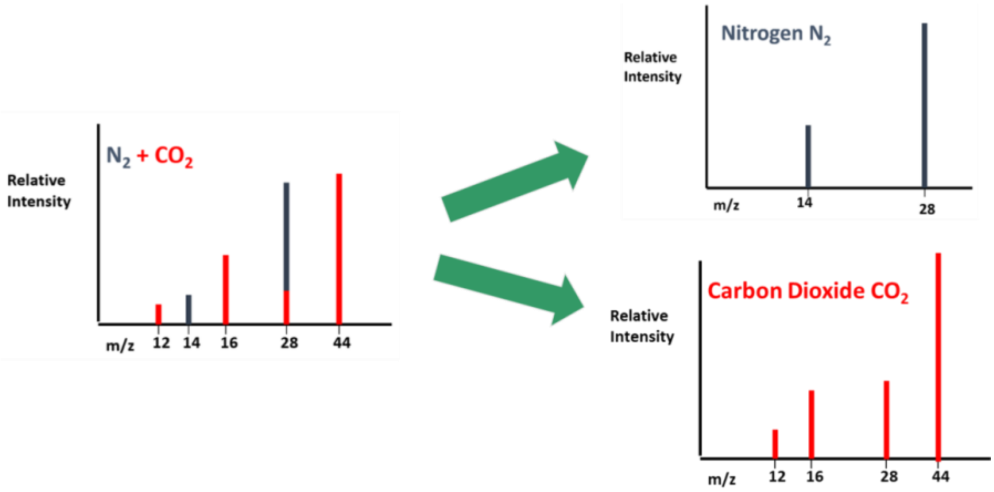
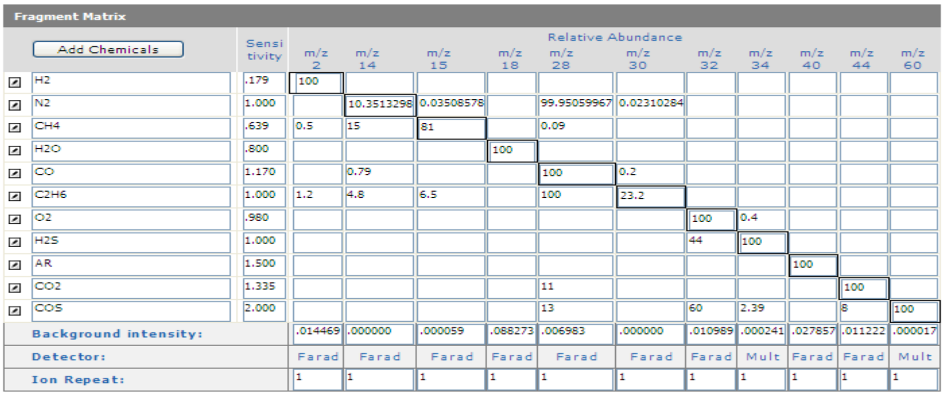


Figure 38. Overlapping of MS signals in gas mixtures: $N_2 + CO_2$ example [85].

EXAMPLES OF APPLICATION

- Mass spectrometry is applied by KIT at the Bioliq pilot plant for the online measurement of the syngas composition. Figure 39 shows the fragment matrix applied at Bioliq. More details about the gas analysis applied at the plant can be found in Section 3.2.5 of Document 1.



		Relative Abundance										
	Sensitivity	m/z 2	m/z 14	m/z 15	m/z 18	m/z 28	m/z 30	m/z 32	m/z 34	m/z 40	m/z 44	m/z 60
H2	.179	100										
N2	1.000		10.3513298	0.03508578		99.95059967	0.02310284					
CH4	.639	0.5	15	81		0.09						
H2O	.800				100							
CO	1.170		0.79			100	0.2					
C2H6	1.000	1.2	4.8	6.5		100	23.2					
O2	.980							100	0.4			
H2S	1.000							44	100			
AR	1.500									100		
CO2	1.335					11					100	
COS	2.000					13		60	2.39		8	100
Background intensity:		.014469	.000000	.000059	.088273	.006983	.000000	.010989	.000241	.027857	.011222	.000017
Detector:		Farad	Farad	Farad	Farad	Farad	Farad	Farad	Mult	Farad	Farad	Mult
Ion Repeat:		1	1	1	1	1	1	1	1	1	1	1

Figure 39. Fragment matrix in MS analysis of syngas applied by KIT [85][86].

- The application of MS for the online measurement of gas compounds (HCN, thiophene, HCl, phenol) in gasification product gas was evaluated at ECN part of TNO [83]. It was concluded that HCN, thiophene, HCl and phenol in principle can be measured and monitored with MS. However, one should be alert to any (minor) influences of other components. Benzene can be properly measured with MS, whereas toluene and p-xylene will always be measured together on mass 91. After an upgrade of the MS to a maximum m/z of 200 or 300, p-xylene and possibly higher aromatic compounds can also be measured. It should be noted that the identification of the relevant component becomes more difficult at higher masses. Measurement parameters in the MS (such as SEM voltage, measuring time, etc.) can be optimized (sometimes per component) for the best possible result. This often aims at maximizing the intensity and minimizing the influence of other components. MS analysis was applied at the Tondela waste gasification plant for the online measurement of tar compounds [87][88] (see Section 3.2.7 of Document 1).

CONTACTS

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RELATED TOPICS

- Molecular Beam Mass Spectrometry (MBMS) (Factsheet 28).

28. Molecular Beam Mass Spectrometry (MBMS)

This technique is a type of mass spectrometry method that can be used for the online measurement of inorganic compounds or tar content in the product gas.

HOW IT WORKS

The molecular beam is produced by line-of-sight extraction of vapor-phase sample at ambient temperature into the spectrometer. The pressure of the source is 10^4 times larger than the pressure at stage 1, which is in turn 10^4 higher than in stage 3. The resulting supersonic expansion leads to the rapid cooling of the sample, which preserves it from condensation or reaction. The subsequent mass spectrometry analysis produces instantaneously the chemical fingerprint of the sample [89].

ADVANTAGES [89]

- Real-time and robust monitoring of hot, raw product gas.
- Near-universal, reproducible and stable detection with sensitivity of approximately 1 ppmv.
- Good agreement with tar guideline.
- Commercially available.

LIMITATIONS

- Complex system [89].
- Quantification can be cumbersome, since it requires injection of standard for each target species and good measurement of wet gas volumetric flow [89].
- Difficult estimation of total gravimetric due to the problematic injection of heavy tar standards into the hot oven and capillary plugging [89].
- Expensive equipment (~ $300,000) [89].
- Interference with other gas compounds: in case that MBMS is applied for measurement of inorganic compounds, it is important to remove the organic compounds that can overlap with the target m/z peaks [90].

EXAMPLES OF APPLICATION

- MBMS has been applied at Jülich Research Centre for the study of the release of inorganic trace elements during gasification of wood, straw and Miscanthus [90]. As can be seen in Figure 40, the MBMS was located at the end of a pipe which was heated at very high temperature (max. 1480°C) to act as thermal cracker. This was done to destroy the organic compounds present in the gas that could potentially overlap with the target gases, thus interfering in the measurement. The presence of compounds from thermal decomposition was identified as one of the possible sources of inaccuracy. MBMS was applied to measure a number of inorganic species in the product gas. However, only qualitative measurements (measurement of peak area) was provided.

Species	Mass/charge (m/z)	Species	Mass/charge (m/z)
O_2^+/H_2S^+	34	PO_2^+	63
$^{13}CO^+$	29	Zn^+	64, 66, 67, 68
Cl^+	35, 37	KCl^+	74
HCl^+	36, 38	$NaKCl^+$	97
K^+	39	Pb	206, 207, 208
PO^+	47	$(P_2O_3)_2^+$	220
$NaCl^+$	58	$(P_2O_5)_2^+$	284

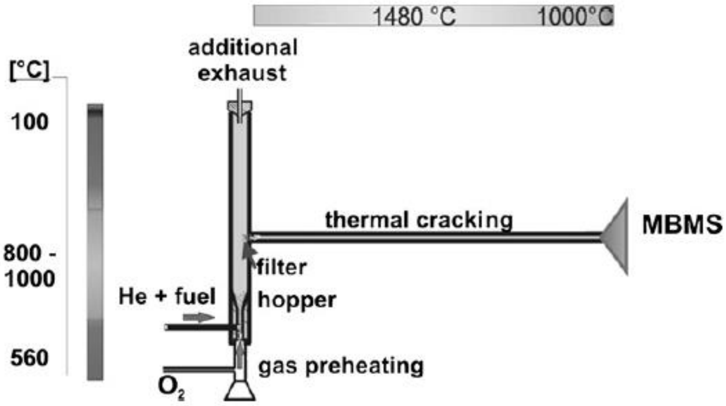

Figure 40. Schematic layout of the implementation of MBMS in lab-scale fluidized bed gasification at Jülich Forschungszentrum [90].

- The MBMS online analyser has also been extensively used by NREL for more than 30 years for online measurement of tars (quantified in terms of carbon partitioning to tar) and for measurement of alkali metals. Figure 41 shows the MBMS apparatus developed at NREL. This technique has been applied in different gasifiers, including the Battelle Columbus Laboratory indirect, circulating, fluidized-bed gasifier or the Gas Technology Institute (GTI) pressurized, fluidized-bed gasifier [91]. In 2011, MBMS was used at the Rentech's natural gas-to-liquids demonstration unit (Commerce City), which uses ClearFuels' High Efficiency Hydrothermal Reformer (HEHTR) gasification technology for more than 2200 hours of gasification operation and more than 1300 hours of integrated fuel production [91].

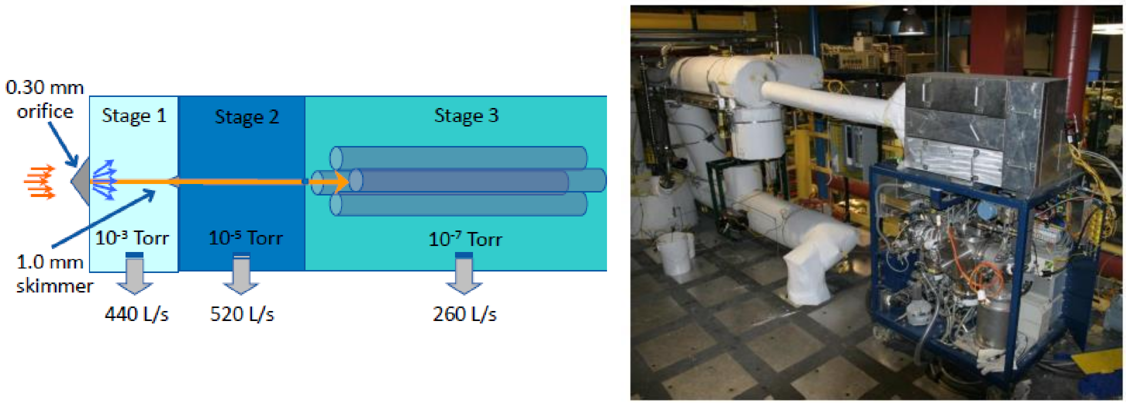

Figure 41. Molecular Beam Mass Spectrometer developed by NREL: formation of molecular beam (left), transportable MBMS apparatus (right) [89].

CONTACTS

Daniel Carpenter (NREL): daniel.carpenter@nrel.gov

Michael Müller (Jülich Forschungszentrum): mic.mueller@fz-juelich.de

29. Non-dispersive Infrared spectroscopy (NDIR)

This spectroscopic method is extensively applied in gasification for online gas detection (CO, CO_2, CH_4). Infrared spectrometers can be divided into 3 categories: dispersive, multiplex, and non-dispersive [93]:

- ○ Dispersive instruments use gratings or prisms to achieve wavelength selection and are typically used for qualitative measurement.

- ○ Multiplex instruments, or Fourier Transform Infrared (FTIR) Spectrometers, use a Michelson interferometer to modulate the intensity of the infrared radiation as a function of frequency, and then employ Fourier transform functions to convert the resulting time dependent spectrum into a standard wavenumber spectrum. FTIR is described separately in Factsheet 10 of this document.

- ○ Non-dispersive instruments have a much simpler design than both dispersive and multiplex instruments, since they do not use any gratings of prisms to achieve wavelength selection or use any an interferometer.

Non-dispersive instruments have been widely used for quantitative measurement of a variety of gaseous species by absorption, emission and reflectance spectroscopy. Non-dispersive infrared spectrometers work by measuring the intensity of light absorbed by a sample. Most NDIR instruments use 2 infrared sources and the difference in intensity between both is measured.

There are 3 main types of non-dispersive infrared spectrometers [93]:

- Total absorption analysers: they have no selectivity towards any gas and are based on total absorbance of infrared radiation.

- Negative filter analysers: improved selectivity by removal of a specific spectral region.

- Positive filter analysers: improved selectivity by implementing a detector containing the infrared absorbing gas of interest.

HOW IT WORKS

Spectroscopic methods are based on the principle that gases (with the exception of diatomic and noble gases) have a dipole moment and thus absorb radiation in the mid-infrared region of the electromagnetic spectrum [22]. In an NDIR analyser, the infrared radiation emitted by the source is divided and mechanically modulated. The sample gas is directed to a sample cell, whereas the reference chamber is filled with N_2 (which does not absorb IR radiation). The beams alternate between 4 chambers connected to each other: the analysis and reference chambers of both the sample cell and the detector. The changes in the absorbance of the beam produced by passing through the sample gas result in synchronous pressure fluctuations between the detector chambers (energy difference). The pressure difference is detected by a diaphragm capacitor and converted into an electrical signal which is proportional to the concentration of the target component [22].

ADVANTAGES

- Relatively low cost, ease of use and simple design.

- Allows online measurement of the main product gas compounds.

- Commercially available, widespread use.

LIMITATIONS

- Relatively high detection limits (200 ppmv).
- Cross-sensitivity between gas compounds (for example CO and CO_2), which affect the sensitivity and accuracy. This issue can be addressed by corrections, or by re-calibration of the instrument with gas composition as close as possible to the one expected in the application.

CONTACTS

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Arnold Toonen (ECN part of TNO): arnold.toonen@tno.nl

30. Online tar analyser, University of Stuttgart

HOW IT WORKS [94][95][96]

The device is composed of 3 sample loops, 2 tar filters, and a FID detector (Figure 42). Sample loops 1 and 2 are connected each to a tar filter, the temperature of which can be regulated independently from each other with an oven. The third sample loop is not connected to any tar filter (thus, corresponds to the raw gas).

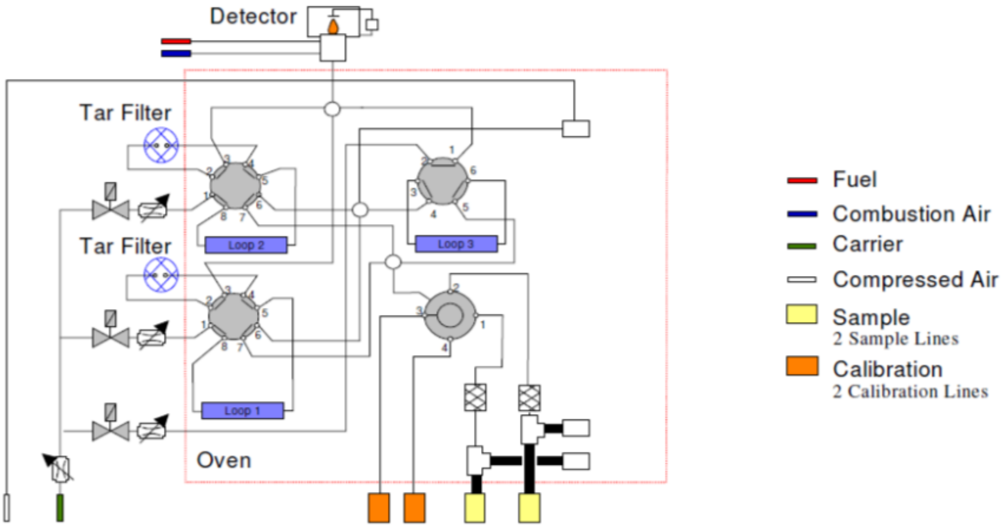
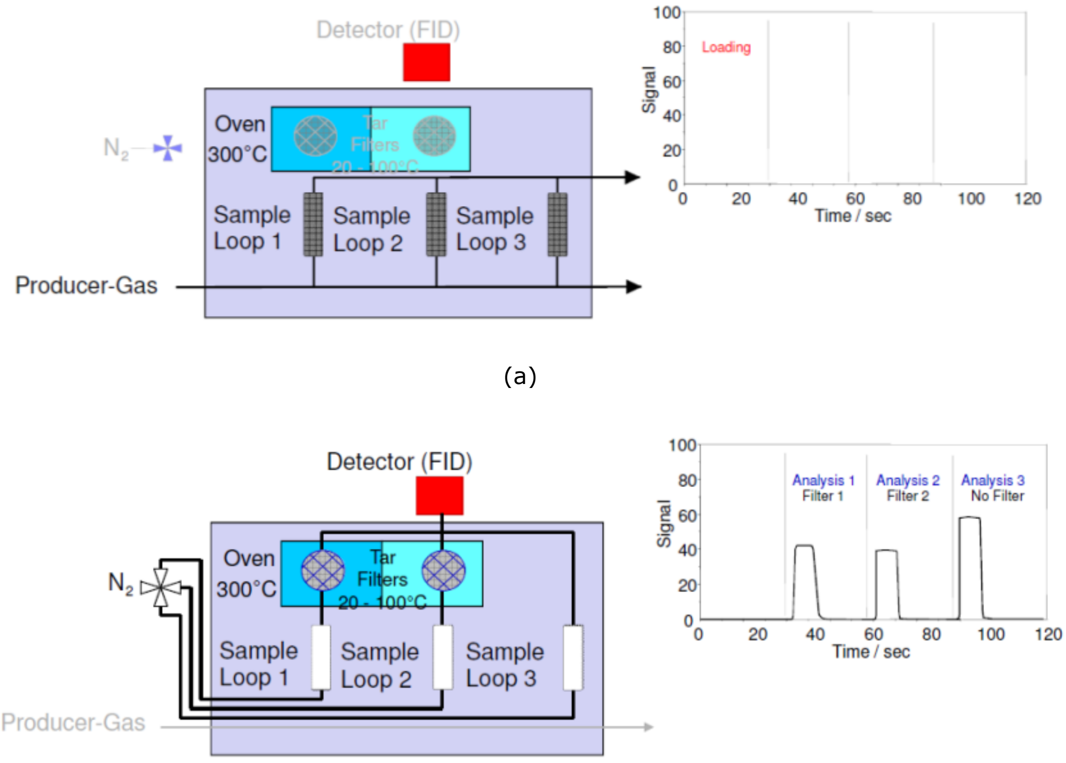


Figure 42. Schematic of the online tar analyser developed by University of Stuttgart [94].



(a)

(b)

Figure 43. Operating phases (including IFD signals) of the online tar analyser developed by University of Stuttgart: (a) Sampling phase; (b) Analysis phase [94].

The operation of the online tar analyser comprises 2 steps or phases, as depicted in Figure 43 [94]:

1. Sampling phase: Product gas is fed to the analyser by 3 injection pumps or Venturi nozzles, and the 3 sample loops are simultaneously loaded. The tar filters are back-flushed during the loading.

2. Analysis phase: the sample loops are flushed one after the other to the Flame Ionization Detector. The tar content is determined as the difference between loop 1 and loop 2 or 3.

SPECIFICATIONS [94][97]

Table 2. Technical specifications of the TA12-3 online tar analyser [97].

TA12-3 online tar analyser	
Detector	Flame Ionization Detector (FID)
Analysis temperature	Up to 300 °C
Filter temperature	4 - 80 °C (1°C increments)
Number of filters	2
Number of pumps	3, heated Venturi
Number of sample inputs	2
Measurement time	120 s (minimum 1 minute)
Measurement range	3 decades up to 120 g C/m^3.
Measurement limit	< 0.2 % of MRD < 0.02% of the total hydrocarbon content.
Reproducibility	± 1 % of MRD
Linearity	± 2 % of MRD
Sample Pressure	- 30 to 50 mbar
Sample Gas Flow Rate	100 - 300 L/h

TA12-3 online tar analyser	
Heating time	60 minutes
Ambient temperature	+5 to + 35 °C
Required gases	Fuel for FID: Hydrogen 5.0, 2 bar, 2 L/h Air for FID: Compressed air (HC-free), 3 bar, 20 L/h Carrier gas: Nitrogen 5.0 or Compressed air, 2 bar, 5 L/h Valve control: Compressed air, 6 bar, 50 L/h Calibration gas: 5 vol.-% CH_4 in N_2, max. 100 mbar
Gas connections	¼'' Swagelok
Main Power	230 VAC / 50 Hz / 900 VA
Weight and dimension	40 kg 6 HE x 19" x 480 mm (height x width x depth)

ADVANTAGES

- Fast, online and easy quantification of tar content.
- FID signal is almost linear to the amount of organically bound carbon in the sample.
- Minimal measurement time: approximately 1 minute.
- Comparison of results is possible.
- Able to determine total hydrocarbon content: total condensable hydrocarbons, and total of aliphatic/aromatic hydrocarbons.
- Proven and tested.
- Commercially available [97].

LIMITATIONS

- Maximum operating temperature: 300°C.
- Determination of tar composition (individual compounds) is not possible.

EXAMPLES OF APPLICATION

The online tar analyser was tested at Technical University Delft, complementary to SPA tar analysis [22].

IMPLEMENTATION AND STATUS

The online tar analyser is commercialized by Ratfisch (TA120-3) [97].

CONTACTS

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Norman Poboss (University of Stuttgart): norman.poboss@ifk.uni-stuttgart.de

31. Optical feedback cavity-enhanced absorption spectroscopy (OF-CEAS)

This method belongs to the group of laser spectroscopic technology based on absorption technique. Within the scope of gasification applications, OF-CEAS can be used for the online measurement of permanent gases, water content (if a heated cell is used), and inorganics.

HOW IT WORKS

OF-CEAS was developed and patented by University Joseph Fourier in Grenoble (France) [98], and commercialized since 2008. This is a laser spectroscopic technology based on absorption technique for quantitative assessments of species in gas phase. The radiation source is a continuous laser which provides to the system a high measurement stability. It is a low pressure (100 mbar), long optical path (1 to 10 km) and short response time (less than 1 second) technology allowing online measurement with very low detection limits (nmol/mol) and very few interference when simultaneous analysis of several gases is performed. These features make the difference with conventional infrared spectroscopy like Fourier transform Infrared Spectroscopy (FTIR).

ADVANTAGES

- Wide measurement range (from ppb to %).
- Low-pressure sampling (decrease problem with condensables, decrease interferences issues).
- Absolute measurement (no re-calibration required, no re-zero required, no instrumental response drift).
- Scanning speed / Co-addition (1 full spectrum = 200 equidistant discrete data points collected every 100 ms): fast response time.
- Low signal/noise.

LIMITATIONS

- Some molecules of interest need to have its own laser.
- Expensive equipment.

Figure 44. OF-CEAS equipment. Picture courtesy of CEA.

EXAMPLES OF APPLICATION

The OF-CEAS unit (Figure 44) has been applied at the bubbling fluidized bed pilot (LFHT) at CEA (described in Section 3.2.23 of Document 1). The apparatus has also been implemented in the

BioTfuel EFR pilot plant in Dunkirk [98]. As shown in Figure 45, the OF-CEAS equipment has a specific patented low-pressure gas sampling using sonic nozzle.

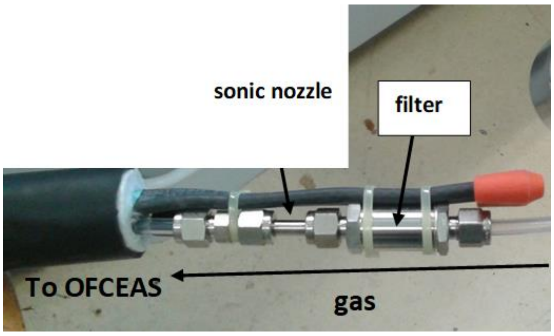

Figure 45. OF-CEAS sampling line. Picture courtesy of CEA.

At ENGIE's GAYA Platform (described in Section 3.2.3 of Document 1), a set of 4 laser spectroscopy OF-CEAS devices enables to measure permanent gases (CO, H_2, CO_2, CH_4, H_2O and O_2) and inorganic trace compounds (NH_3, H_2S and HCl), as shown in Figure 46. All along the process from the gasifier to bio-SNG production, these measurements allow to characterize the gas composition and assess the performance of gas treatments.

Figure 46. Set of 4 laser spectroscopy OF-CEAS in the shelter of the GAYA Platform. Picture courtesy of ENGIE Lab CRIGEN.

STATUS

The OF-CEAS analyser is commercially available [100].

CONTACT

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Etienne Basset (ENGIE Lab CRIGEN) : etienne.basset@engie.com

Françoise Defoort (CEA): francoise.defoort@cea.fr

32. Photo ionisation detector (PID)

This technique developed by BTG and KTH is used for the online qualitative measurement of tars.

HOW IT WORKS [101][102][103]

The main part of the detector is an ultraviolet (UV) lamp filled with a gas, which emits a monochromatic radiation. The selection of the gas filling the UV lamp determines the compounds that can be detected, since the emitted light has different wavelengths, and therefore a different energy content. If the energy of an incoming photon generated by the UV light is high enough (i.e., higher than the ionization potential of the target tar compounds), photo-excitation of the tar compounds can occur, which results in positively charged molecules that generate a current directly proportional to the concentration of the compound [102][103]. The energy required to remove an electron from a specific molecule is different for each compound, which determines the detector selectivity. The equations governing the number of arising ion pairs and the current in the electrodes of the ionization chamber can be found elsewhere [103].

Figure 47 shows a schematic layout of the PID detector. The sensor includes a light source (UV lamp), The product gas enters the ionization chamber, which contains a pair of electrodes (bias- and collector electrodes). An electromagnetic field is created in the ionization chamber when a positive potential is applied to the bias electrode. The ions resulting from the absorption of photons from the UV source are driven to the collector electrode. The ion current is then measured and computed [103].

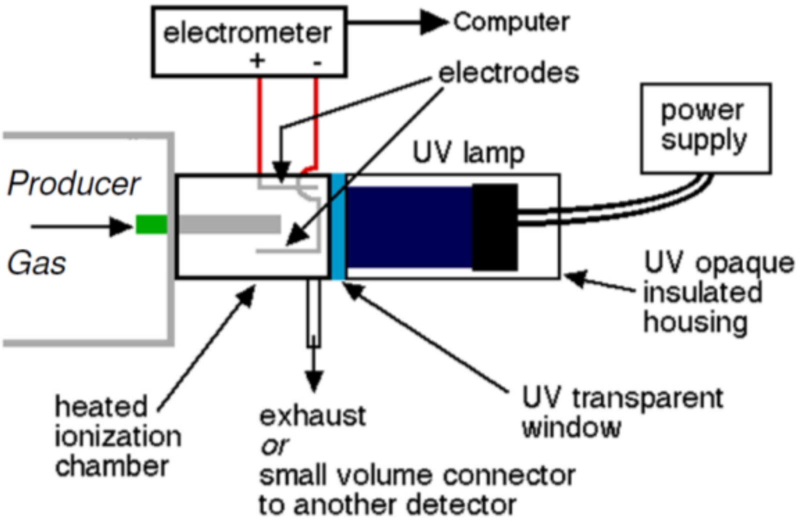

Figure 47. Schematic of PID detector [102].

The selection of the UV lamp (the type of gas filling the UV lamp) determines the compounds that can be detected, since the emitted light has different wavelengths, and therefore a different energy content. Figure 48 displays the PID signal (compounds detected) as a function of the ionization potential applied [102][103]. If the UV lamp used is filled with xenon (8.4 eV), tar compounds such as naphthalene, pyrene, acenaphthene, fluorene, biphenyl, anthracene, cresol, phenol and toluene can be detected [101].

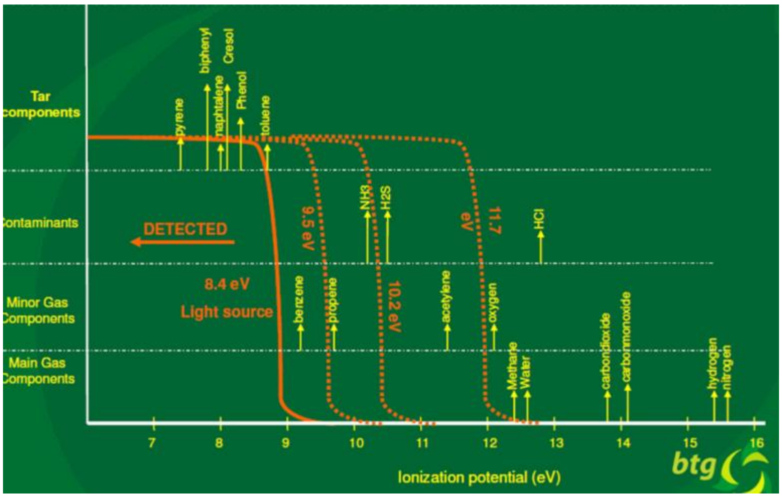

Figure 48. PID signal (compounds detected) as a function of the ionization potential applied [102][103].

ADVANTAGES

- Suitable for online qualitative monitoring of tars: short response time of a few seconds and stabilization of PID signal within a minute [101][103].
- Very sensitive to low concentrations (< 10 mg/Nm^3): sensitivity of PID detector is 10-50 times higher than that of FID [103].
- Linear response to tar compounds (see Figure 49).

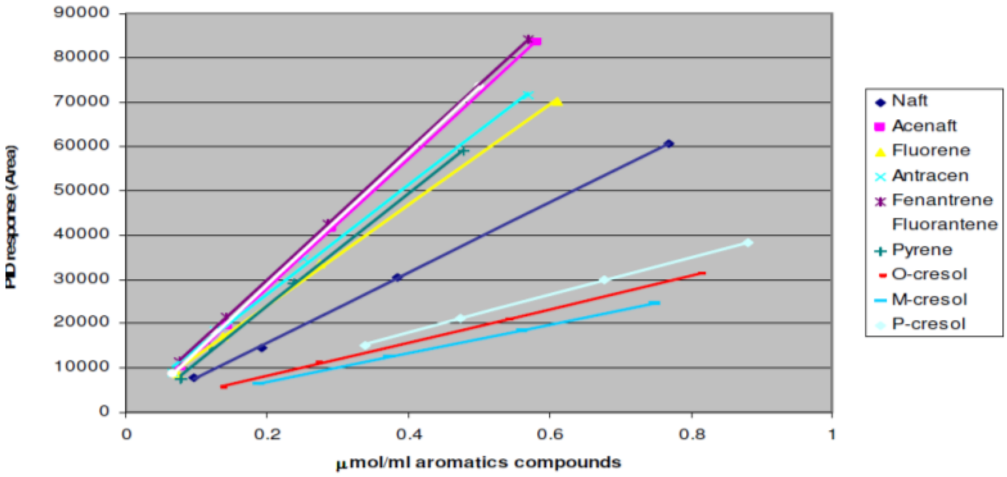

Figure 49. Response factor of PID for aromatic tar compounds [101][102][103].

- Non-destructive analysis (compared with FID) [103].
- No laborious sample treatment needed compared to offline tar analysis methods [103].
- Validated against SPA with individual tar compounds [103].

LIMITATIONS

- Not fully commercial: validation in different gasifiers and with different fuels still needed.
- Maximum operating temperature 300°C.
- Not possible to quantify individual tar compounds in the tar mixture.

- Lower detection response for real product gas than for individual naphthalene. This is not a problem if the composition of the tar compounds remains similar with varying total tar concentration, but changes in tar composition during the gasification process negatively affect the accuracy of the quantification [103].

- The lamp window of the excitation chamber needs periodic cleaning or protection due to fouling (tar polymerization), which decreases the PID response over time and interrupts the operation [101][102][103]. The fouling issue could be overcome by using more heat-stable materials for the lamp window or using several lamps in parallel [103].

RELEVANT ASPECTS

- The PID response depends on the ionization potential of the target molecule. A larger difference between the radiation energy and the ionization potential results in larger molar response. This influences in turn the selection of the UV source (for example, Zenon, krypton, argon) so as to ensure that the radiation energy results in a selective response of the detector [103]. A high radiation intensity will result in an increase of the detector response.

- The material of the source window which separates the discharge region from the ionization area determines defines the radiation energy entering the ionization chamber [103].

- In order to ensure detection selectivity, a suitable solvent which is not detected by the PID should be selected [103]. This is in turn depending on the choice of the UV lamp (the ionization potential of the solvent should be higher than the radiation energy of the UV source in order not to be detected).

- Unlike FID (where the response of the detector is proportional to the mass flow entering the detector), the response of the PID depends on the concentration of the compound, thus an increase of the flow rate due to the addition of a carrier gas (thus, lower concentration of the target compound) results in a decrease of the PID response [103].

- The response of the PID detector depends also on the chemical properties of the target compounds, being particularly sensitive to the functional groups of the tar compounds [101]. The sensitivity increases with the carbon number, and in this order [103]:

    - Alkanes < alkenes < aromatics.
    - Alkanes < alcohol < esters < aldehydes < ketones.
    - Cyclic compounds > non-cyclic compounds.
    - Branched compounds > non-branched compounds.

- The different response curves of the different tar compounds can make the quantification less accurate if the tar composition changes during operation [101].

EXAMPLES OF IMPLEMENTATION

The PID device was validated at the 5 kg/h 2-stage gasifier located at BTG, where the results of the PID were compared with SPA analysis [101].

CONTACTS

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Robbie Venderbosch (BTG): venderbosch@btgworld.com

33. Paramagnetic detector

This detector is implemented as part of gas monitors for the online measurement of O_2 in gases.

HOW IT WORKS

Two magnets produce an inhomogeneous magnetic field in a measuring compartment through which the sample gas flows. A dumb-bell (light displaceable body) is suspended in this magnetic field in such a way that it can rotate. The oxygen molecules (which have a paramagnetic behaviour) contained in the gas sample experience a force that draws them into the magnetic field. Since the magnetic field is non-homogeneous, a gradient in O_2 partial pressure takes place. A torque, which is proportional to the O_2 concentration, and as a result a rotary displacement is produced in the dumb-bell as a consequence of the gradient established. This torque is compensated by a current which is proportional to the dumb-bell position in order to produce an opposing torque that restores the dumb-bell to the original position. The compensation current (the output signal) is proportional to the oxygen concentration of the gas sample [22].

CONTACTS

Paramagnetic detectors are part of commercially available gas monitors, which are extensively applied for online analysis of the product gas composition. The contact list of contributing partners can be found in Appendix A of this document.

RELATED TOPICS

- Non-dispersive infrared detector (Factsheet 29).

34. Petersen column

This analytical method is included in the tar guideline CEN-TS 15439 [104] as one of the alternatives (together with the impinger train) for tar sampling.

HOW IT WORKS

An overview of the Petersen column is shown in Figure 50. The column requires connection to a cooling system and a pump to force the gas through the 2 stages. The outlet of the column ((4) in Figure 50) is connected to a gas pump and a gas meter in order to measure the volumetric flow through the column during sampling. At least 20-30 minutes before sampling the cooling of the column is started. The upper stage (opening (2) in Figure 50) is filled with 150 mL acetone, and the lower stage (opening (3) in Figure 50) is filled with 100 mL acetone. The gas line is then connected to the column inlet (4). Upon start of sampling, the outlet valve is opened, and the gas pump is started. During sampling, it is important to check that gas is bubbling through both stages. After 30 minutes, the gas pump is stopped. After sampling, it is advisable to flush the connection line to the inlet with solvent to recover any tars that might have condensed in the line. Then, the inlet is closed with a plug fitting.

An Erlenmeyer flask is placed below the column and connected to the column drain ((5) in Figure 50). Then, the drain valve is opened and both stages are emptied (with help of the gas pump). Once the column is emptied, both stages are rinsed with clean acetone, and the solvent is added to the rest of the solvent sample. The tar-loaded solvent is then transferred to a dark bottle and stored in a refrigerator until analysis with GC-MS.

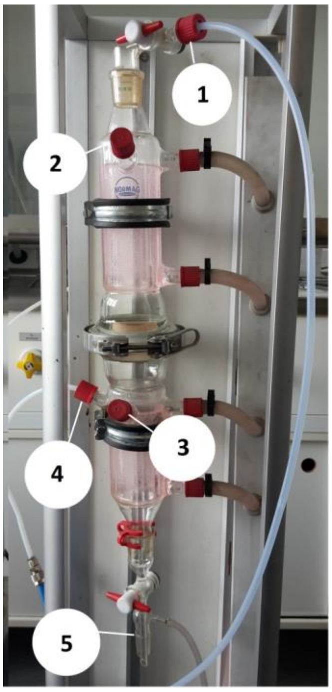

Figure 50. Petersen column for tar sampling: (1) column outlet (connection to gas pump); (2) and (3): openings for solvent filling; (4) column inlet; (5) column drain. Picture courtesy of DTU.

EXAMPLES OF IMPLEMENTATION

The Petersen column has been extensively applied by Technical University of Denmark (DTU) for tar sampling. A recent example of application is during a 2018 experimental campaign in the 100 kW_{th} LT-CFB gasifier, where SPA and Petersen column sampling were compared. The implementation of the Petersen column is shown in Figure 51. The sampling was performed simultaneously for proper comparison. The quantification results from both sampling techniques were found to be well in agreement for the quantified compounds. The main difference was observed for compounds with lower retention times such as furfurals and phenols, which were better detected using the Petersen column.

Figure 51. Petersen column applied during measurement campaign at the 100kW$_{th}$ LT-CFB gasifier. Picture courtesy of DTU.

ADVANTAGES

- Better detection of compounds with lower retention times such as furfurals and phenols with respect to SPA samples.

VARIATIONS – THE COMPACT TRAPPING SYSTEM

Inspired by the Petersen column, researchers at TU Graz started in 2002 an easy to handle, field deployable wet chemical sampling system [105]. The setup, displayed in Figure 52, consists of three jacket cooled flasks. Depending on the coolant flows cooling power of the first flask can be adjusted e.g. to avoid freezing collected water. The sample gas flow passes three impinger-like bottles. The sampled liquids can be emptied easily by opening a valve. Refilling is done from the top. This setup offers easier handling than the tar protocol impinger train, and more compactness and robustness than the Petersen column [105]. The Compact Trapping System has been applied by TU Graz, Bioenergy2020+ and the company Cleanstgas GmbH. Moreover, it has been used in two collaborative campaigns at the gasifier at PSI and at a test gas generator [106]. A later version was applied by TU Berlin.

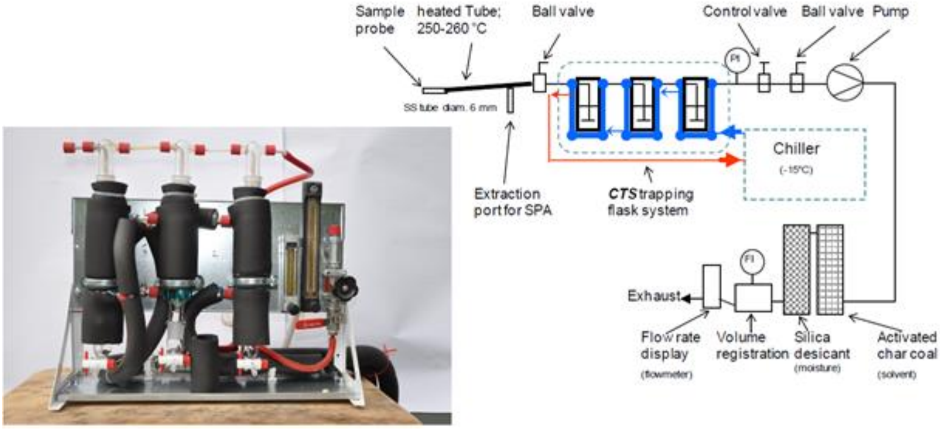

Figure 52. Compact Trapping System for tar sampling [105].

RELATED TOPICS

- Solid Phase Adsorption (SPA) (Factsheet 37).
- Tar guideline (CEN/TS 15439) (Factsheet 40).

MORE INFO

Video blog # 5 on tar sampling with Petersen Column at DTU:
https://www.youtube.com/watch?v=TVkVb5A2YOo&t=271s

CONTACTS

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Giulia Ravenni (DTU): grav@kt.dtu.dk

35. Raman spectroscopy

This optical method, based on the Raman effect, belongs to the group of laser absorption spectroscopy techniques, and within gasification applications, it can be used for the online measurement of permanent gases, water content and tar.

HOW IT WORKS

When an incident photon interacts with a molecule, it can be elastically scattered (Rayleigh scattering) or inelastically scattered (Raman scattering). In the latter case, the light can either lose part of its energy to the scattering system (Stokes scattering) or gain energy from it (anti-Stokes scattering) [109]. Raman scattering can be vibrational or rotational depending on the type of interaction between the light and the system.

EXAMPLES OF APPLICATION

Karellas and Karl [109] describe the development and testing of an optical Raman spectroscopy setup for the measurement of H_2, CH_4, CO, CO_2, H_2O ant tar content. After calibration, the setup was tested at the BioHPR (heat-pipe reformer), the gasifier developed at Technical University Munich (TUM).

The Raman spectroscopy setup is schematically shown in Figure 53. An industrial neodymium-doped yttrium aluminium garnet (Nd:YAG) laser was used as light source (532 nm wavelength). The product gas flows into the measurement cell via lines traced at 300°C to avoid tar condensation. A CCD camera gets a picture corresponding to the emission signal from the gas. In front of the objective of the spectrograph, a filter is applied to cut off the Rayleigh signal, which is more intense than the Raman signal [109]. A "black hole" is placed in front of the spectrograph-CCD in order to minimize the influence of reflections from objects and thus ensure a black background of the image taken with the CCD camera. There are 3 different gas sampling lines (the first one being the reference one; the second one allowing the measurement of the tar content by measuring clean gas, previously washed; and the third one being a spare line in case the first one is not operational).

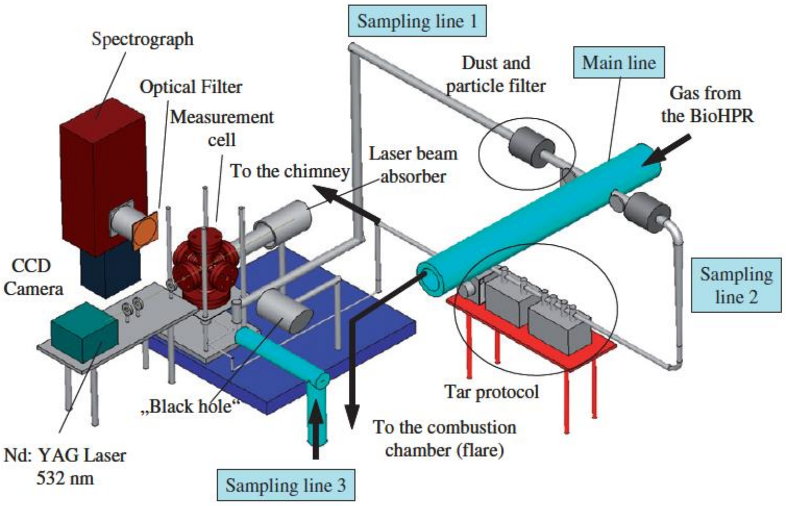
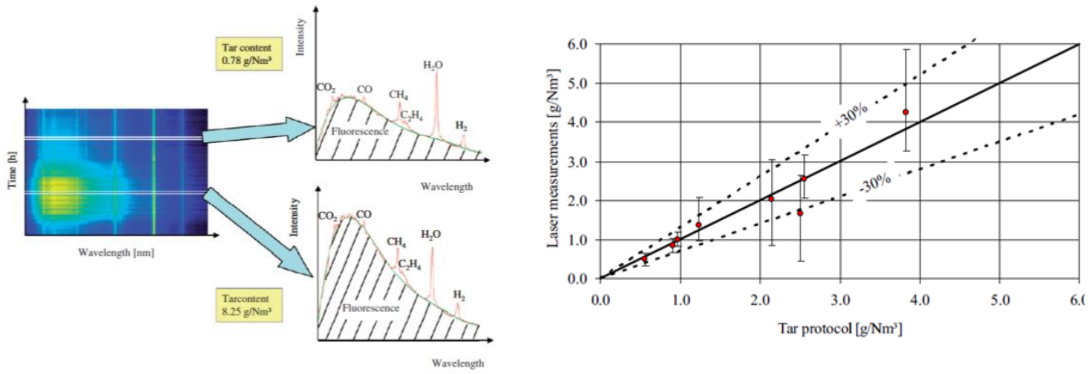


Figure 53. Schematic setup of Raman spectrometer developed for measurement of gasification product gas [109].

A numerical evaluation of the resulting signal detected by the CCD is applied to calculate the concentration of the different gas compounds. The integration of the area of the background in the signal corresponds to the total tar content in the gas (Figure 54 (a)). The results of tar content using Raman spectroscopy were compared with those obtained using tar guideline (Figure 54 (b)).



(a) (b)

Figure 54. Online tar measurement using Raman spectroscopy: (a) correlation of background Raman signal with tar content; (b) Comparison of results with tar guideline and Raman laser measurements [109].

ADVANTAGES

- Compared with conventional GC methods, the gas can be measured at high temperatures: water content and tars can be measured online (15 measurements/minute) [109].
- Non-intrusive method.

LIMITATIONS

- Total tar content is calculated: no information about tar composition. → complementary tar guideline or SPA sampling is necessary.
- If either the gas flow or the tar content in the gas are very high, the background of the signal is very intense, and the Raman peaks of the permanent gas compounds cannot be distinguished anymore [109].

RELEVANT ASPECTS

- It is important that the calibration is performed at the same operational temperature of the measurement cell (300°C in the work by Karellas and Karl [109]). This is due to the fact that temperature affects the spectral line of the gas, and thus, can influence the accuracy of the measurement.

- If online tar analysis is applied, it is necessary to perform in parallel a complementary tar measurement (e.g. with the tar guideline) in order to correlate the background signal with the total tar content. This has to be performed in each measurement, since the intensity of the background signal depends on the arrangement and performance of the equipment (laser, CCD camera, spectrograph) and can thus vary in every experiment [109].

36. Scanning Mobility Particle Sizer (SMPS)

The SMPS is a semi-online instrument that allows determining the number size distribution of particles with diameters between 10 nm and 700 nm. A scan of the particle number size distribution can be determined approximately every 2 to 3 minutes.

HOW IT WORKS

This method is based on the physical principle that the ability of a particle to traverse an electric field (electrical mobility) is fundamentally related to particle size. In a Differential Mobility Analyzer (DMA), an electric field is created and the particles drift in the DMA according to their electrical mobility. Particle size is then calculated from the mobility distribution [110].

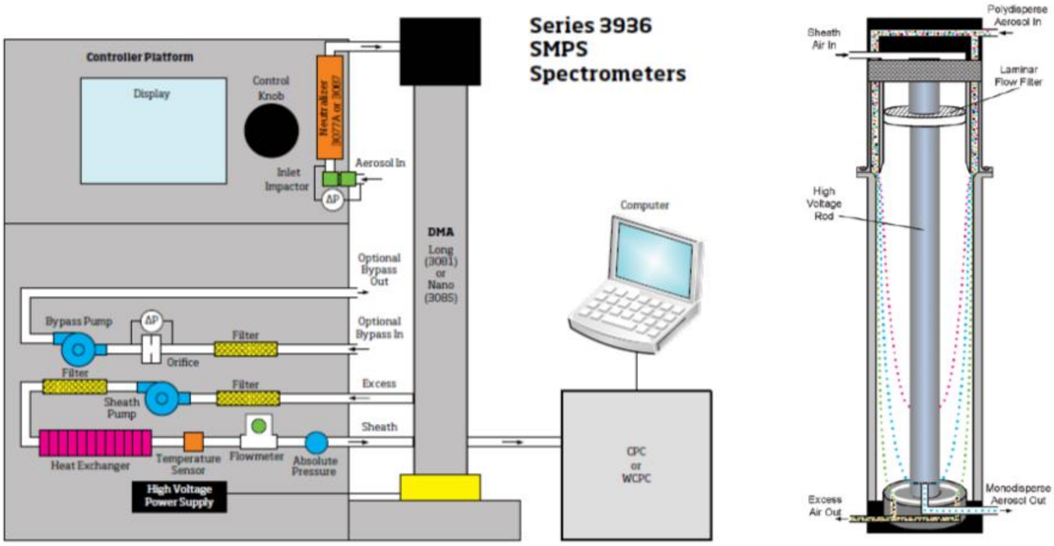


Figure 55. Schematic of SMPS unit (left); detail of differential mobility analyser (right) [110].

The SMPS uses the following measurement principle [81][110]: the aerosol is dried, led through a radioactive source where it gets into an equilibrium state with positive and negative charges (the so called Boltzmann-distribution). Then the charged aerosol enters the heart of the system, the differential mobility analyser (DMA), which consists of a cylinder and an inner centred rod. An electrical field is applied. Positively charged particles are attracted to the negatively charged collector rod in the centre of the DMA. During the travel of the aerosol through this section a sheath of air flows along the rod. The particles can penetrate through this layer of the clean air if the electrostatic force caused by the current applied to the rod is sufficient. This force is in general proportional to the voltage applied to the central rod and the charge of the particle. Assuming similar mass chargeability of all the particles, by varying the voltage particles of certain (minimum) size can be selectively made to penetrate towards the central rod. At the bottom of the central chamber, there is a slit-shaped opening in the inner rod, which carries the air and the particles into the CPC (Condensation Particle Counter). This part of the apparatus resembles a cloud chamber, where each particle – regardless the size – grows to a uniform diameter and charge. In the CPC the aerosol passes over heated 1-butanol and becomes saturated. During cooling, the particles grow by condensation of 1-butanol. Upon impaction the charge is freed and measured in the form of electric current, proportional to the total number of particles entering the CPC. The particles can also be counted optically. The exact time frame of the counted particles with respect to the applied voltage is matched by the on-board software and subsequent aerosol spectra are stored in the computer. A scan lasts about 2 minutes, and 30 seconds is needed for getting the system free of electrical load again where after the scan starts again from low to high voltage. The particle mass size distribution and concentration are then calculated from the particle number size distribution, assuming spherical particles and standard density [1].

ADVANTAGES [110]

- Broad size range: 2.5 - 1000 nm.
- Wide concentration up to 10^7 particles/cm^3.
- No calibration is required.
- Number concentrations are measured directly without assuming the shape of the particle size distribution.
- Method independent of the refractive index of the particle or fluid.
- High degree of absolute sizing accuracy and measurement repeatability.
- Commercially available.

LIMITATIONS [110]

- Low sample sizes (non-representative).
- Image edge definition problems.
- 3D to 2D image distortion.
- Operator bias.
- Sizing uncertainty: 3 - 3.5%.

37. Solid Phase Adsorption (SPA)

This analysis method, applied for the measurement of tar species and other organic compounds, was originally developed by KTH [111]. Since then, significant advances have been carried out by different partners. Currently SPA is, together with the tar guideline, the most commonly used method tar 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) consists of the extraction of tar compounds from the gas sample by adsorption on a solid-phase column, followed by offline desorption and analysis of the loaded solid cartridge. The schematic layout of gas sampling using SPA is shown in Figure 56. The tar-loaded gas sample goes through the sorbent (e.g. amino-based, activated carbon or combinations thereof), which captures the tar compounds. The loaded column is subsequently desorbed using a solvent, so that the tar compounds are finally analysed using gas chromatography (usually GC-FID or GC-MS).

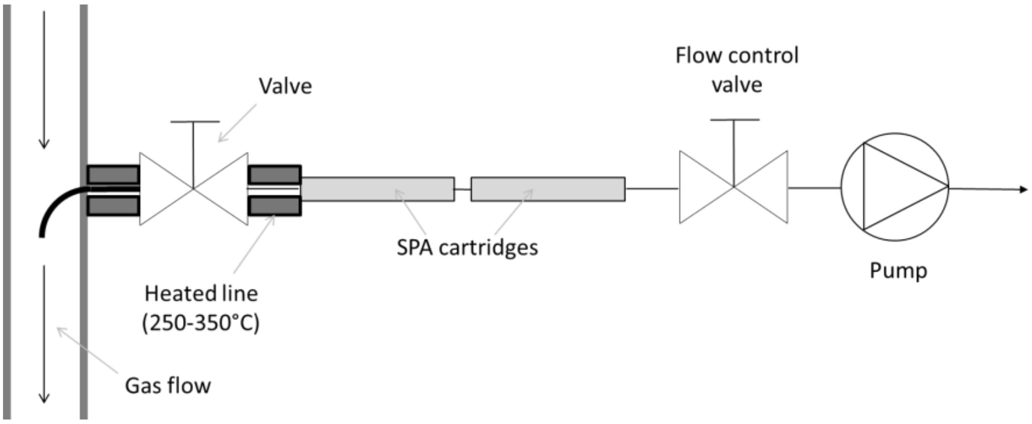


Figure 56. Schematic layout of sampling of gasification gas using SPA.

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 ECN part of TNO for SPA sampling (Figure 57) is described in detail below [118][120].

Sampling and storage:

A commercially available absorption column (LC-NH_2 100 mg)[116] is equipped with an injection needle. The needle is inserted into the hot, wet product gas duct by means of a sample port with graphite ferrule. An automatic syringe pump with 100 mL gastight 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 difference (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 (column + needle) is stored in a refrigerator at -18°C and taken to the analytical laboratory as soon as possible for analysis of tar components by GC-FID/MS. A blank column + needle is also added and analysed because the absorption column material can contain some small amounts of certain organic components.

Recovery of adsorbed compounds (desorption/extraction):

The next step is to extract the tars from the SPA samples. For this, the samples are firstly thawed. Then 50 µL of an internal standard solution (1 mg dodecane in 1 g isopropanol) is added. The addition of dodecane allows checking the efficiency of recovery. Then, 1 mL dichloromethane (DCM) is added via the needle (which is put on top of the column). The liquid which has passed through the needle and the SPA material is collected in a GV vial, which is then closed. When no more liquid is visible on top of the SPA material, extra 1 mL DCM is added to flush the remaining liquid.

Analysis:

The extract is quantitatively analysed by GC-FID for tar compounds and by GC-MS for screening of compounds or for the measurement of S and N compounds. SIM (Single Ion Monitoring) is used to increase the sensitivity level of the analysis. Samples of material not exposed to product gas are also extracted and analysed for background correction. For tar analysis, the GC is calibrated with certified PAH-mix standards. For organic sulphur analysis, the GC-MS is calibrated with a solution containing known amounts of (dibenzo)thiophene components.

ADVANTAGES

- Less complicated sampling compared to tar guideline.
- Several samples per hour are possible: better assessment of process variations compared to tar guideline.
- Lower analysis uncertainty than tar guideline [112].
- Reliable for compounds heavier than BTX, in particular for polycyclic aromatic hydrocarbons (PAHs) [113][114][115].
- No need for handling of organic solvents (safety regulations in industrial environments).
- The methodology can be easily adapted for measurement of S- and N tar compounds (see for example CIEMAT, ECN part of TNO and ENGIE Lab CRIGEN).

LIMITATIONS

- Despite faster sampling than guideline, it is still not an online method.
- Incomplete adsorption (capture) of light volatiles (BTEX, thiophene): not reliable quantification (see "Relevant aspects" in this factsheet for further details).
- Not suitable for quantification of heavy tar compounds [101].

RELEVANT ASPECTS

- Selection of SPA sorbent: there are different types of SPA columns, differing in composition and size. The amino-based LC-NH_2 100 mg [116] is the most widespread SPA material used for tar analysis. This standard material is reliable for tar compounds ranging from naphthalene to pyrene [101]. However, this column size is not sufficient to ensure complete adsorption of light aromatic compounds such as BTEX, particularly if the product gas is very hot or it contains a high water content [101]. In this case, the increase of the cartridge size can improve this issue by decreasing the breakthrough of light compounds to below detection limits [117]. Another possible option encompasses the addition of a second SPA column (active carbon) in series [101][118].

- Both the boiling point of the compounds (±80-140°C) and the polarity influence adsorption on the LC-NH_2 column. Given the high polarity of the LC-NH_2 material, a medium-polar column might work better for the capture of light aromatics.

- The gas sampling point should be kept at high temperature to avoid condensation of tars. However, the SPA cartridge warms up when sampling hot gas under real conditions due to the flow of hot gas and the condensation of the water contained in the gas. This increase in temperature can eventually result in a decrease of the adsorption of tar compounds in the sorbent column [101]. Therefore, controlling the temperature of the column during sampling may improve adsorption [118]. In this sense, several measures could be applied to enhance the capture of lighter compounds, for example keep the SPA material refrigerated until its use, active cooling of the syringe with SPA material, use of tandem SPAs, or use (combinations of) different sorbent materials [114][118]. An additional activated carbon adsorbent should be added in series to ensure complete adsorption [119]. If the focus is to measure low tar concentrations in a gas stream with low moisture content and temperature < 100°C, it is better to use the amine sorbent without additional activated carbon.

- For a proper determination of the sampled volume of gas, it is necessary to report the pressure and temperature during sampling [101][117]. Without proper reporting of pressure and temperature conditions, measurement uncertainty of 3-8% per 10°C can occur [117]. The sampled gas should also be corrected for moisture content [101].

- Volatile compounds are captured less effectively from very hot gas (≥ 300°C) or very wet gas (≥ 40 vol.%) [101]

- During sampling, it is important to ensure that there are no leakages in the septum or the extraction device [117].

- After sampling, it is recommended to wait approximately 30 seconds to wait for 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 (ensuring ambient temperature and pressure) will further influence the calculation of tar concentration [101]. If insufficient cooling time is allowed, the measurement error can increase [101].

- The use of an automated sampling system can significantly increase the repeatability of the method [117].

- Samples should be stored in the freezer immediately after sampling to minimize the desorption of volatile species. Losses of volatile tar compounds can occur within days of storage at room temperature [40]. Moreover, in order to ensure reliable samples, the elution step should be performed within 24 hours after sampling [117]. SPA samples can be stored in the freezer for several weeks, although it is reported that over 2 months storage, BTEX can be lost from the sorbent [101]. If the samples have to be transported over long distances (for example, in round robin tests), they need to be kept in a freezer box or packaged with freezer elements and thermal insulation in order to avoid loss of light compounds [40][101].

- 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 (T ≤ 730°C). The reason is the large amount of light and reactive tars which, due to their large polarity, are strongly adsorbed to the SPA material, and cannot completely eluate and thus cannot be analysed.

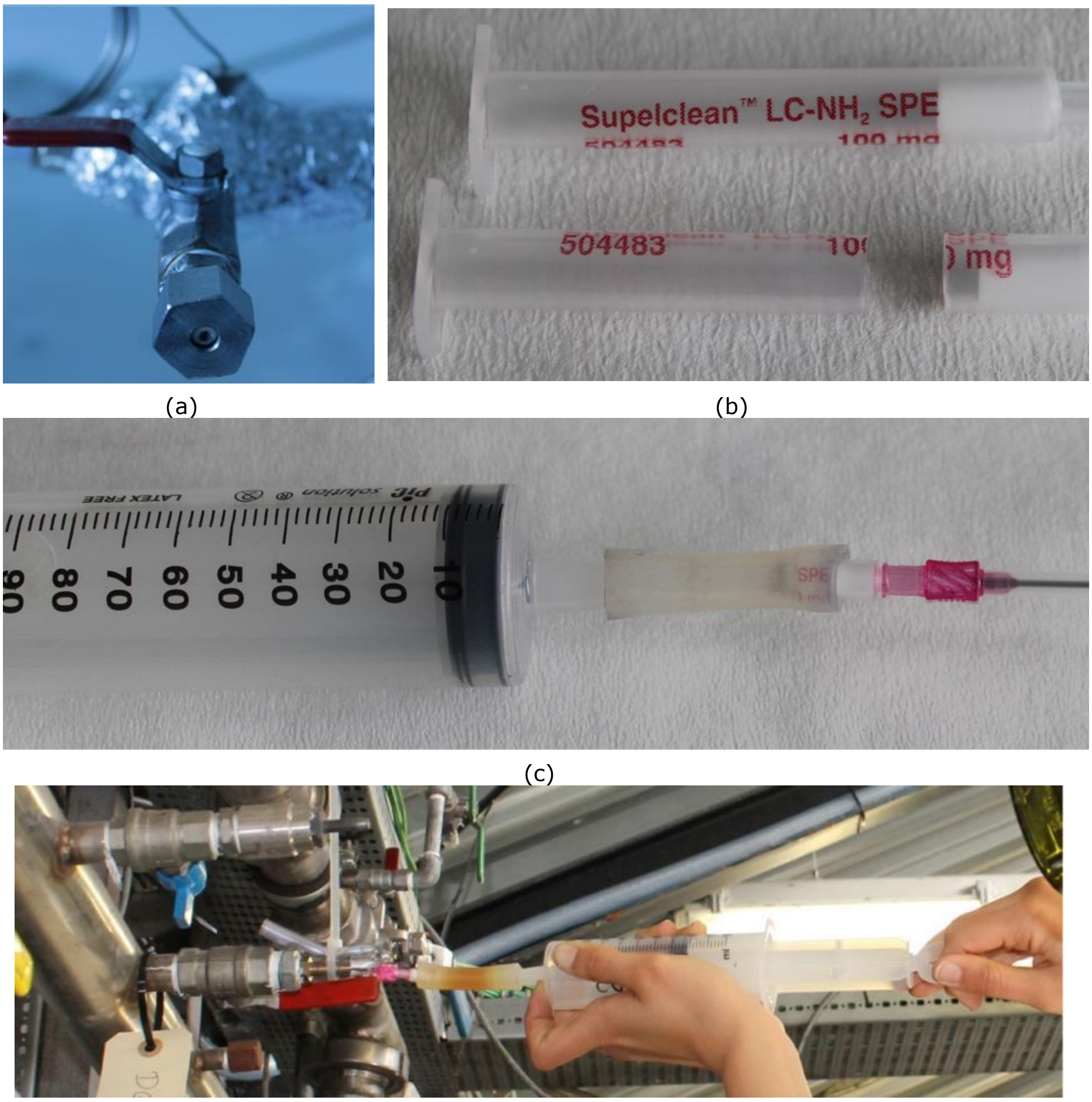
EXAMPLES OF IMPLEMENTATION

The implementation of SPA at ECN part of TNO (sampling point, equipment, storage of samples, extraction step) is depicted in Figure 57.


(a) (b) (c) (d) (e) (f) (g)

Figure 57. Implementation of SPA analysis at ECN part of TNO: (a) Sampling point; (b) Automated sampling system; (c) Column used, and labelled SPA sample (column + needle protected by plastic cap + rubber stopper) ready for storage after sampling; (d) SPA samples stored in freezer; (e) SPA sample port including lock graphite ferrule; (f) extraction of SPA cartridges with dichloromethane; (g) SPA samples taken along MILENA and OLGA columns. Pictures courtesy of ECN part of TNO.

The practical implementation of SPA at Technical University of Denmark (DTU) is shown in Figure 58. In this case, the excess part of the SPE tube is first cut, and then the syringe is assembled with the silicon connection, the SPE tube and the needle. The needle is then inserted in the sampling port through the septum. Once that the tip of the needle is placed in the centre of the gas flow, 100 mL of gas are slowly pumped by gradually pulling the syringe. The cartridge after sampling is removed, stored in an air-tight bag, and stored in a refrigerator until extraction and analysis. For the extraction step, the sorbent cartridge is removed from the tube. The sample is covered with 10 mL acetone, and 1 mL internal standard (for example, phenol d6 or naphthalene d8) is added. The sample is let to be desorbed overnight in the refrigerator. Then, the liquid sample is transferred to a flask, and the acetone is evaporated in a rotary evaporator. The sample is then re-dissolved in 1 mL acetone, and this liquid sampled is then GC-MS analysed [115].



(a) (b)

(c)

(d)

Figure 58. Implementation of SPA analysis at DTU [25][115]: (a) Sampling port for SPA with silicon septum; (b) cutting SPE tubes; (c) assembled SPA sampling syringe; (d) SPA sampling.

VARIATIONS

Just as with the guideline method, the basic methodology of SPA sampling has been adapted by various partners to better fit their analysis requirements. The variations include the type of sorbent column used for sampling, the sampling conditions, the storage of samples, and the procedure for the elution of tar compounds from the SPA column. Table 3 gives an overview of the specific features of SPA analysis as applied by different partners.

Table 3. Overview of SPA tar analysis methodology used by different institutes [101].

	Chalmers	**ECN part of TNO**	**KTH**
Sampling	Extraction of 100 mL of raw gas over a period of around 1 minute. Automated sampling (pneumatic robot)	Extraction of 100 mL of raw gas over a period of around 1 minute. Automated SPA sampling	Extraction of 100 mL of raw gas over a period of around 1 minute. Manual sampling
Sorbent column	LC-NH_2 500 mg	LC-NH_2 100 mg	LC-NH_2 100 mg
Storage	Sealing, labelling and storage in freezer (-20°C)	Sealing, labelling and storage in freezer (-18°C)	
Elution	2 liquid fractions: aromatic and phenolic. Flush with 1.8 mL of dichloromethane (DCM) to separate the aromatic fractions from the column, after which 1.5 mL of a mixture DCM/IPA/ACN is used to elute the phenolic compounds.	Elution with 1mL DCM Internal standard (50 µL): dodecane in iso-propanol. Extra flush with 1 mL DCM	2 liquid fractions: aromatic and phenolic. Elution with 400 µL DCM for aromatic extraction, and with 200 µL IPA-DCM for phenolic compounds
Analysis	GC-FID Internal standards: tert-butylcyclohexane and 4-ethoxyphenol	GC-FID (GC-MS for screening or for analysis of S- and N- tars) Use of response factors for adjoining unidentified peaks (“unknown tars”)	GC-FID Internal standards: tert-butylcyclohexane and p-ethoxyphenol

DCM/IPA/ACN: dichloromethane/isopropanol/acetonitrile.

The SPA analysis method has been adapted for the quantification of organic S- and N aromatic compounds. The methodology is described in Sections 2.6.5 and 2.7.4 of Document 1 [40][120].

The procedure is basically the same as described above in this factsheet. The main modifications with respect to tar analysis are [40][120]:

- Analysis using GC-MS (in SIM mode) instead of GC-FID. Splitless injection can be applied to lower the detection limits (useful for the detection of heavier compounds), but it should be only applied taking special precautions;

- Use of naphthalene-d8 and 4, 6 dimethyl dibenzothiophene (4,6-DMDBT) as internal standard;

- Calibration mixtures containing 13 sulphur compounds;

- Complementary identification of compounds (if needed) by GC-FPD.

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RELATED TOPICS

- Tar guideline (CEN/TS 15439) (Factsheet 40).

MORE INFO

Video blog # 2 on SPA sampling at ECN part of TNO:
https://www.youtube.com/watch?v=wTkkzhIEuGg

Video blog # 3 on preparation and analysis of SPA samples at ECN part of TNO:
https://www.youtube.com/watch?v=70bcpkxYQs0

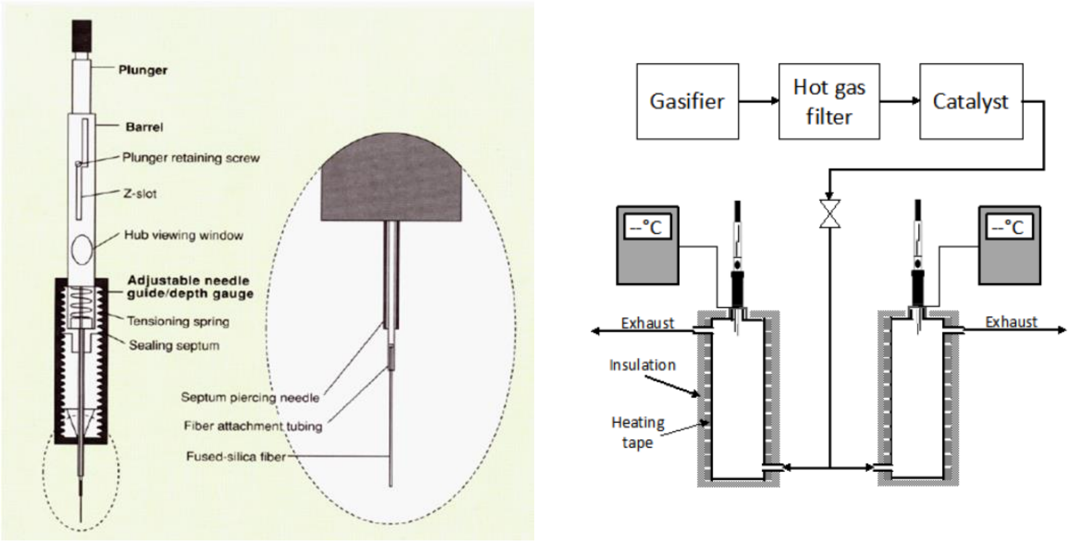
Video blog # 4 on SPA sampling at DTU:
https://www.youtube.com/watch?v=QV8gG-BoEKs

38. Solid Phase Micro-Extraction (SPME)

This technique, based on adsorption onto a solid stationary phase, is applied for the analysis of organic compounds in water, air and soil matrices [103][108]. Within the scope of this report, SPME is applied by KTH as an improvement over SPA for the analysis of tar compounds in product gas [101][104].

HOW IT WORKS

The general principle of SPME is similar to that already explained in Solid Phase Adsorption (see Factsheet 37). Figure 59 (a) depicts a schematic of the SPME sampling device. In the case of SPME for tar analysis, the stationary phase used is polydimethylsiloxane (PDMS) coated on a fused silica fibre [104]. The fibre is placed in a sampling vessel set at a certain temperature (Figure 59 (b)) [101][103]. Once the tar compounds are adsorbed onto the PDMS phase, the fibre is placed in the GC injector, where the analytes are directly desorbed (thus, no solvent extraction step is needed as in SPA analysis).



(a) (b)

Figure 59. SPME device (a) [103][108]; schematic implementation of SPME in gasification setup (b) [101][103][104].

ADVANTAGES

- Solvent-free sampling method.
- Suitable for analysis of trace amounts of tars (clean syngas) due to the lower detection limits compared to SPA analysis [101][103][104].
- The major compounds of product gas (CO, CO_2, H_2O, H_2, CH_4) are unlikely to compete with tar compounds for the adsorption sites [103]. Other compounds, such as H_2S, KNO_3 and KCl are not expected either to interfere in the adsorption dur to their polar nature [103].

LIMITATIONS

- Longer sampling times (10 minutes) compared to SPA (1 minute) [103].
- Application in raw product gas (relatively high amounts of tar) still uncertain [103].
- Long analysis time [101].
- Higher sampling temperatures are more favourable for the detection of heavier aromatic

compounds, but less favourable for detection of lighter compounds: need for several parallel analysis vessels at different temperatures to simultaneously cover all relevant tar compounds [101].

- Non-aromatic C_{5+} hydrocarbons might compete with the tar compounds for the adsorption sites (boiling point close to the sampling temperature) [103]. Although the concentration of C_{5+} hydrocarbons can be considered negligible in many wood gasification processes, gasification at low temperatures and/or using waste as feedstock (where the production of C_3-C_6 hydrocarbons in the gas is significantly higher) might pose a problem in the application of SPME.

- Condensation of heavier tar compounds during sampling is likely responsible for the significant deviation with respect to SPA results [103][104].

- No standard procedure available yet [101].

RELEVANT ASPECTS

- The adsorbed amount of tar compounds on the stationary phase is controlled by the affinity between the fibre and the compounds. The affinity is in turned determined by the polarity of the tar compounds and the solid phase. Since polydimethylsiloxane (PDMS) is a non-polar phase, the affinity is increased with decreasing polarity of the tar compounds [103].

- The sampling temperature has a strong impact on the adsorption on the SPME sorbent fibre. For each compound there is an optimal temperature for which sensitivity is maximized while avoiding condensation. For lighter and more polar compounds, this optimal temperature is achieved at 21°C, whereas for higher molecular weight tar compounds the maximum adsorption is shifted at higher temperatures, at which condensation of heavier compounds take place. This limits the concentration in the gas phase, and therefore also the amount adsorbed in the SPME fibre [103].

- Related to the point above, it is necessary to ensure that condensation does not occur in the runs used to determine the calibration points, since that will limit the adsorption of heavy tar compounds in the fibre. Therefore, high sampling temperatures are required for the measurement of heavier tar compounds, but it is harder to detect lighter compounds. Therefore, in order to cover both light and heavy tar compounds, several sampling vessels in parallel set at different temperatures should be necessary [101].

- The storage ability of the SPME fibre and the storage time are aspects that influence the stability of the adsorbed compounds (in order to avoid the loss of volatile compounds).

STATUS

Technique currently under development at KTH.

CONTACT

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RELATED TOPICS

- Solid Phase Adsorption (SPA) (Factsheet 37).

39. Surface Ionization Detector (SID)

This optical analysis method has been used for the measurement of alkali metal concentration in product gas [12][121][122].

HOW IT WORKS

Surface ionization is a natural phenomenon in which an atom adsorbed on a hot metal surface has a certain probability of being thermally desorbed in ionic form. The ionization probability is a function of (among others) the ionization potential and the surface temperature. The ion emission of a certain species is favoured when the ionization potential is lower than the surface work function. Although for more elements and compounds, the ion desorption is negligible, alkali metals have unusually low ionization potentials, which results in very high ionization probabilities (99% for K, and 94% for Na) on a hot platinum surface.

EXAMPLES OF IMPLEMENTATION

Figure 60 displays the schematics of a SI detector developed by University of Gothenburg [121]. It consists of a platinum filament heated at 1500 K which is subjected to a voltage of 350 V and placed parallel to an ion collector plate. Both filament and collector are housed in a cylindrical chamber which is equipped with a quartz window for optical measurement of the temperature with a pyrometer. Sample gas (1 L/min) is pumped through the detector. The alkali ions present in the gas are emitted from the hot platinum filament and diffuse to the ion collector. The ion current at the collector is fed to a current amplifier. The measurement principle of the detector is based on the linear relation between the ion current measured by the SID and the concentration of the alkali compound (KCl, KOH, K_2CO_3) in the gas [121].

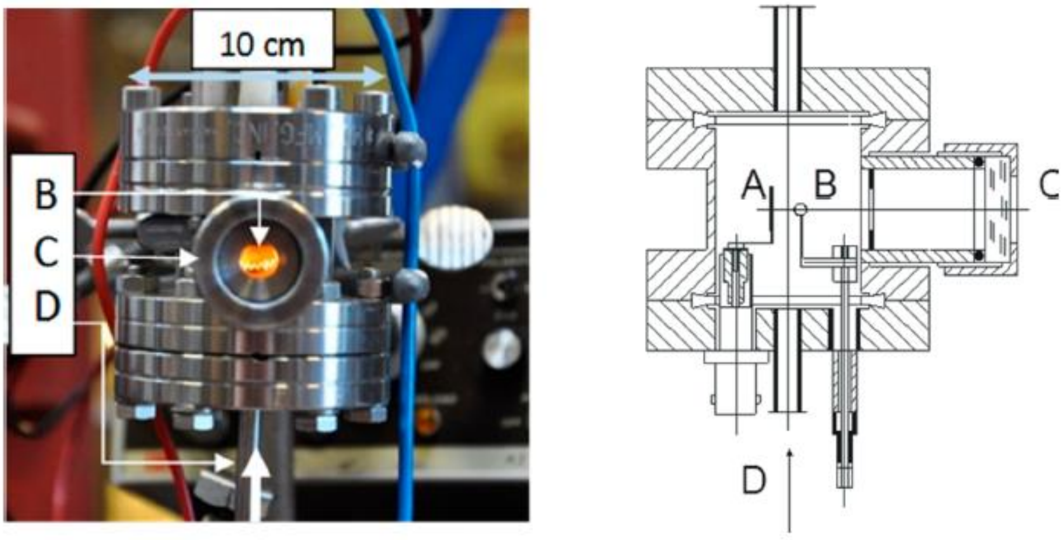

Figure 60. Surface Ionization Detector (SID) used by Gall et al. for the measurement of alkali metals in product gas [121]. A: ion collector; B: platinum filament; C: quartz window; D: sample gas flow direction.

While the detector exhibits a similar response factor to K chloride, carbonate and hydroxide, sodium salts have ~ 10% lower detection probability. If it is assumed that the Na/K ratio keeps constant in product gas, this results in an underestimation of the total alkali mass concentration by ~ 1%.

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40. Tapered element oscillating microbalance (TEOM)

Tapered element oscillating microbalance (TEOM) is an online true-mass measuring instrument of particulate matter. The measurement concentration ranges between 0-1 g/m^3, with a resolution as high as 0.1 μg/m^3.

HOW IT WORKS

It consists of three major components, the pre-conditioner (often a cyclone used as pre-cutter), the TEOM sensor unit, and the TEOM control unit. The control unit contains the data processing hardware, display, flow control components, and electronics controls for the system. The sensor unit contains the sample inlet and TEOM microbalance, which is the key part of the system. The microbalance performs a sensitive particulate mass measurement according to the inertial mass weighing principle. A TEOM microbalance consists of an exchangeable filter cartridge placed on the tip of a hollow, tapered tube (Figure 61). The wider end of the tube is fixed rigidly to a base. The tube with the filter on the free end is maintained in oscillation in a clamped-free mode at its resonant frequency. This frequency is determined by the physical characteristics of the tube and the mass on its free end. A particle-laden gas stream is drawn through the filter where the particles will be collected, and gas passes through the hollow tube to a flow controller. As particles deposit, the increase of the filter mass leads to a frequency decrease in the oscillation of the tube. The collected particle mass can be directly and inertially determined by accurately measuring the frequency change. Combining this mass change with the volume of gas drawn through the system during the sampling period yields an accurate measurement of the particulate mass concentration in real time.

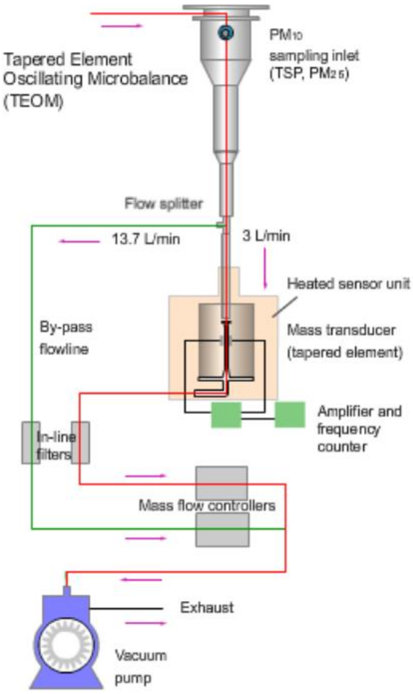

Figure 61. Schematic of a TEOM unit [123].

ADVANTAGES

- Direct mass measurement, not subject to measurement uncertainties found in other technologies [124].
- It can provide very accurate total particle mass measurements online according to its working mechanism.

LIMITATIONS

- Very sensitive to rather small change of pressure drop of the sampling line: it takes 15 to 20 minutes for TEOM to get stabilized after a pressure drop change in the sampling system [5].

EXAMPLES OF IMPLEMENTATION

Although initially developed for continuous ambient air monitoring for particulate matter concentration, the TEOM system can be applied for aerosol particles characterization in hot gases (product gas and flue gas) by combining with proper sampling and dilution systems. As an example, an aerosol-based method including APS and TEOM has been established at Linnaeus University to investigate the conversion of suspended fine char particles in the high temperature zone [5].

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41. Tar guideline (CEN/TS 15439)

The tar guideline is, strictly speaking, a specific type of wet analysis method (see Factsheet 47), in which tar is collected in a train of cold impinger bottles containing a solvent (2-propanol). This sampling and analysis method, developed by the European Committee for Standardization (CEN) with the assistance of a number of European research institutes, is described by the Technical Specification CEN/TS 15439 "Biomass gasification. Tar and particles in product gases. Sampling and analysis" [104]. This method also allows (optionally) the measurement of dust contained in the gas.

HOW IT WORKS

The layout of the guideline method is schematically shown in Figure 62. The method allows either the measurement of tars or the combined determination of dust and tars contained in the gas. If dust is also determined, the inlet gas needs to be directed into the sampling train under isokinetic conditions (that is, the gas flow in the sampling pump has to be selected so as to ensure similar gas velocity as the gas in the main gas line). The inlet of the sampling train is electrically traced to avoid condensation of tars before the capture in the impinger train. The particles are captured in a filter. Then, the gas goes through a series of impinger bottles filled with 2-propanol (solvent). The bottles are immersed in hot (40°C) and cold (-20°C) baths. The gas is bubbled in the solvent, whereby tars are absorbed in the solvent. Water is also condensed. The temperature difference between the bottles is intended to favour the capture of aerosols. The gas flow (needed for quantification of the sampled gas) is controlled with a flowmeter and a gas meter. The tar-loaded solution is finally offline analysed using GC-FID or GC-MS.

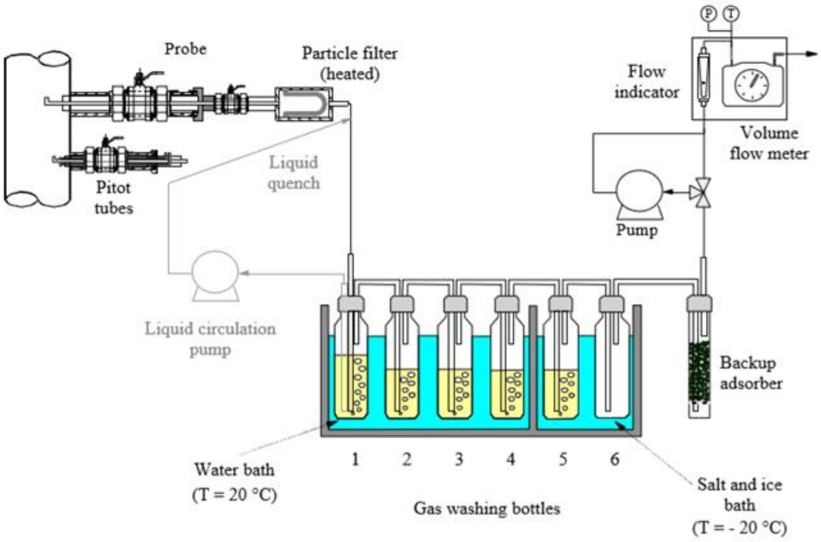


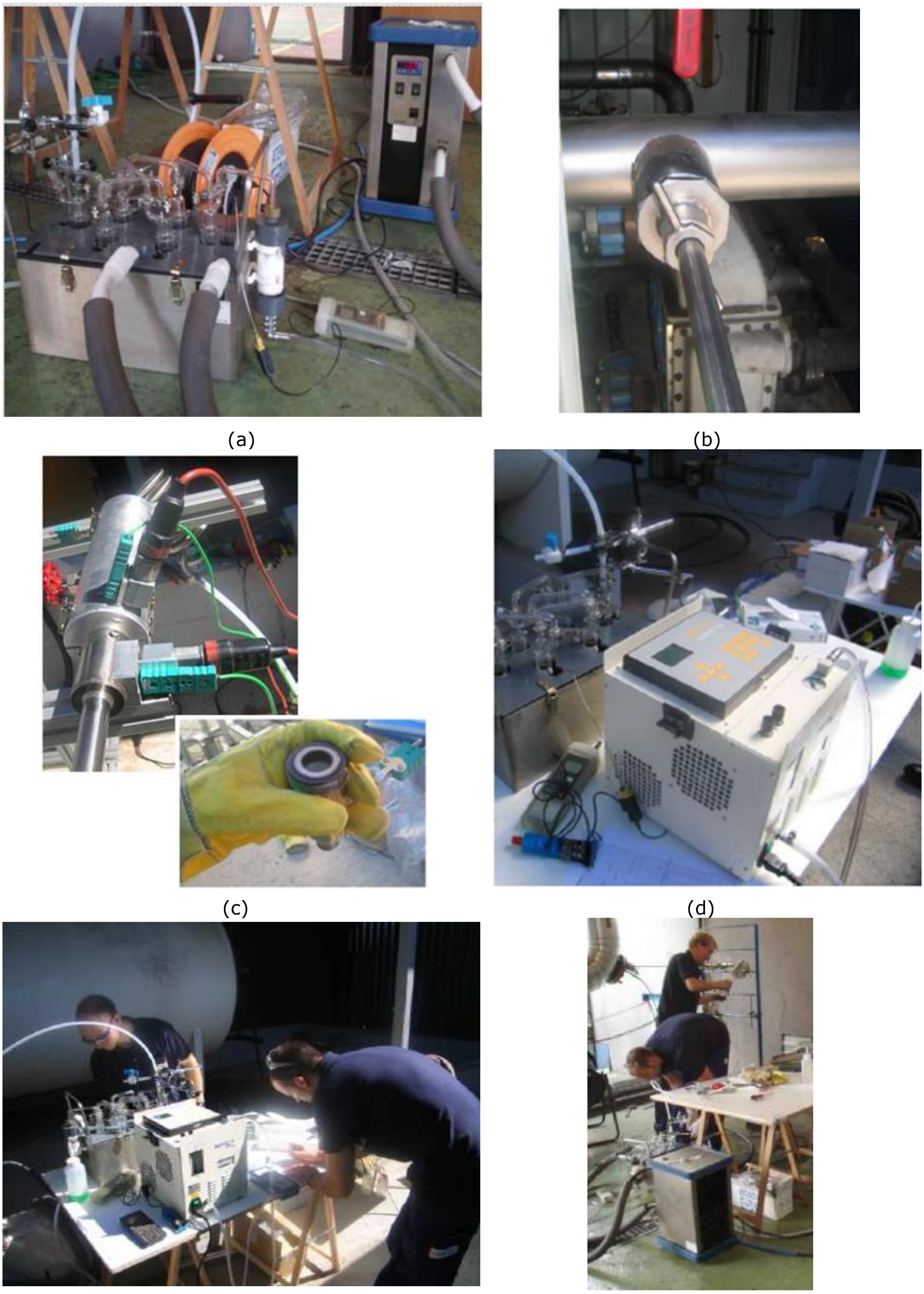
Figure 62. Schematic layout of the implementation of the "tar guideline" (CEN/TS 15439) for the measurement of dust and tars from biomass gasification gas [104][125].

EXAMPLES OF IMPLEMENTATION

The basic concept described above has been adapted by different institutions based on experience. The variations refer mainly to the configuration of the impinger train (temperature profile of the gas going through the bottles). Table 4 summarizes the how different partners have adapted the guideline method.

Table 4. Overview of variations of the tar guideline sample as used by different institutes.

Partner	Particle measurement	Configuration of impingers	Gas sampled	Reference
CENER	Glass-quartz fibre filter at 300-350°C	6 impingers: 3 impingers at ambient temperature; 3 impingers at -20/-15°C	0.1-0.6 Nm^3 Gas Flow depending on operating conditions	[129] Figure 63
CIEMAT	Quartz microfibre filter at 350°C	4 impingers at 35°C (100 mL 2-propanol each) 2 impingers at -20°C (one of them with 100 mL 2-propanol)	< 0.1 Nm^3 gas	Figure 64
ECN part of TNO	Quartz microfibre filter at 450°C	Impingers 1,2 and 4 at 40°C Impingers 3, 5 and 6 at -20°C All impingers filled with 2-propanol	100-500 L gas sampled 3-5 L/min gas flow	[126] Figure 65
UNIBZ	-	Impingers 1, 2 and 4 at 35-40°C Impingers 3, 5 and 6 at -15/-20°C All bottles filled with 2-propanol except the last one	> 0.7 m^3 gas in 1-2 hours	[127]
University of Seville	Glass fibre filter	Seven impingers: impingers 1-4 at 0°C; impingers 5-7 at -20°C. Final activated carbon bed	~100 L dry gas in 10 minutes	[128] Figure 66



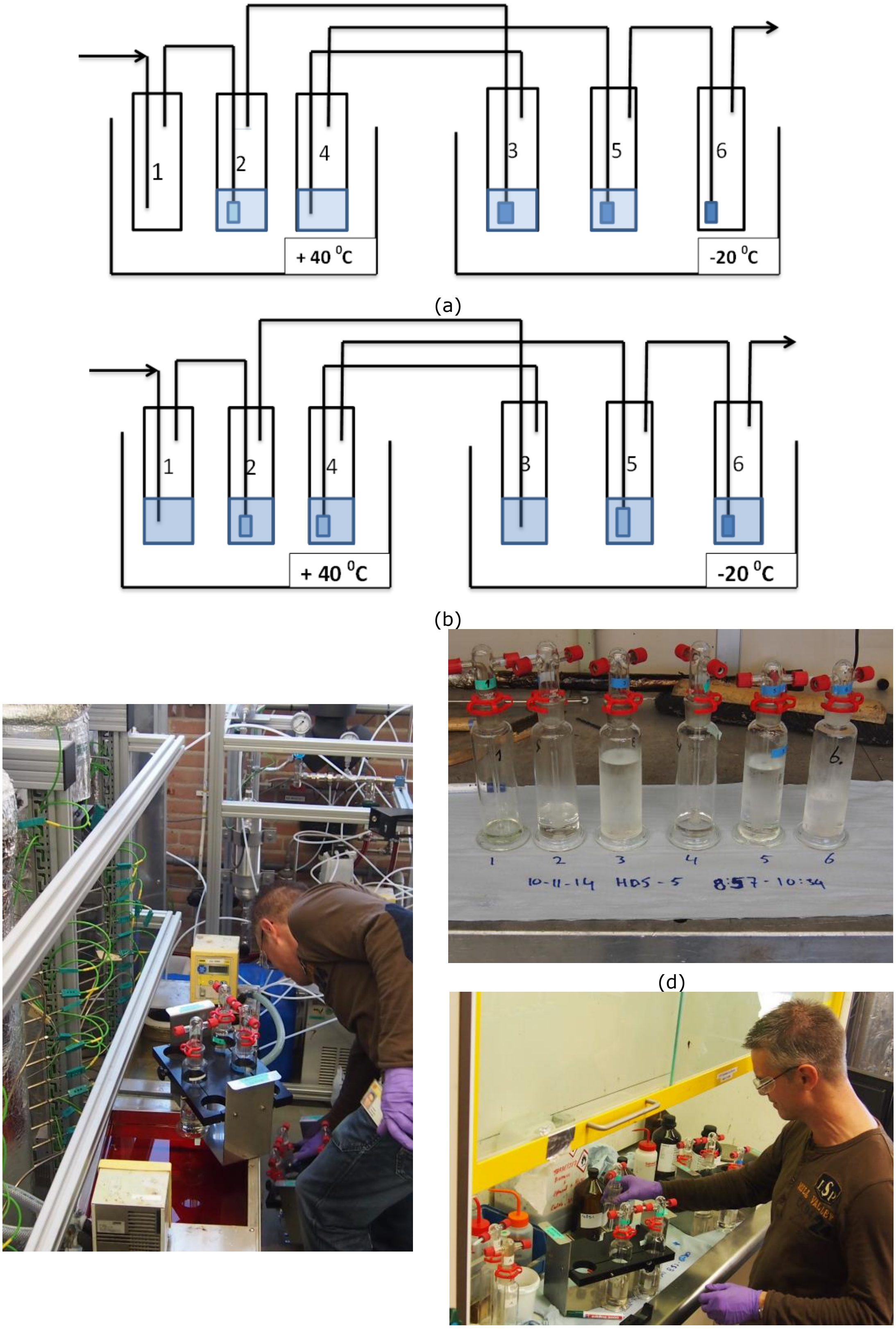
(a) (b) (c) (d) (e)

Figure 63. Implementation of CEN/TS 15439 tar guideline at CENER: (a) overview of tar sampling train; (b) isokinetic probe; (c) heated particle filter and particle filter extraction; (d) gas sampler; (e) mounting of tar sampling equipment at gasifier site [129].

Figure 64. Tar sampling system used at CIEMAT [130].

Figure 65 schematically plots the adaptation of the tar guideline implemented at ECN part of TNO [126], where slight modifications have been applied in the configuration of the impingers train, particularly in the amount of solvent and the type of frits used. This different setup of impingers/frits is intended to prevent the plugging of frits by fine particles or tar and plugging by ice crystals from the condensed water.

	CEN/TS 15439	**ECN part of TNO adapted configuration**	**TU Graz adapted configuration**
Impinger # 1	Empty impinger No frit	Filled with 2-propanol No frit	Filled with 2-propanol No frit
Impinger # 2	Filled with 2-propanol Coarse/fine frit	Filled with 2-propanol Coarse frit	Filled with 2-propanol No frit
Impinger # 3	Filled with 2-propanol Medium/fine frit	Filled with 2-propanol No frit	Filled with 2-propanol Coarse Frit
Impinger # 4	Filled with 2-propanol No frit	Filled with 2-propanol Coarse frit	Filled with 2-propanol No frit
Impinger # 5	Filled with 2-propanol Medium/fine frit	Filled with 2-propanol Coarse frit	Filled with 2-propanol Fine frit
Impinger # 6	Empty Medium/fine frit	Filled with 2-propanol Fine frit	Filled with 6 mm glass beads No frit



(a)

(b)

(d)

(c)

(e)

Figure 65. Adaptation of the configuration of the tar guideline train by ECN part of TNO (b) with respect to the standard (a) [126]; (c) placing the impingers in the baths; (d) impingers after tar sampling (location at HDS reactor inlet, that is, clean gas after tar and water removal); (e) taking the tar-loaded solvent from the impingers after gas sampling. Pictures courtesy of ECN part of TNO.

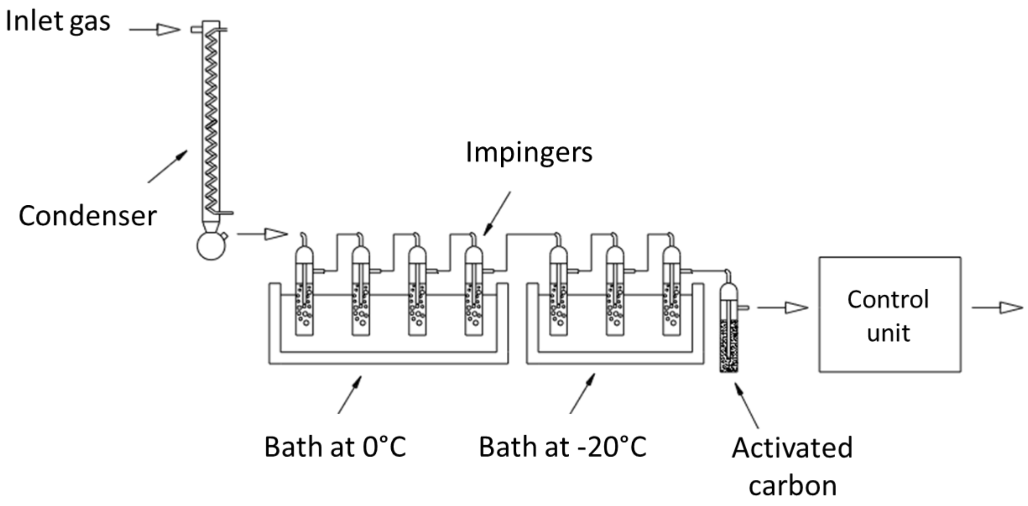


Figure 66. Configuration of tar sampling as applied in University of Seville [128].

ADVANTAGES

- Accurate quantification of individual tar compounds.
- Reliable quantification of light aromatic compounds (BTEX).

LIMITATIONS

- Difficult to implement.
- Offline method: only an average composition can be obtained. → not possible to track variations in the gasification process.
- Costly (need for solvent).
- Long sampling times (30-60 minutes).
- Safety issues (handling of organic solvents in industrial environments).
- Not adequate for very low concentrations (< 1 mg/Nm^3).

VARIATIONS OF THE TAR GUIDELINE – OTHER CONFIGURATIONS

- A version of the tar guideline which allows for faster determination has been developed at the Paul Scherrer Institute (PSI). However, this method still requires the use of a solvent on-site, as well as similar amounts of equipment [131][132]. An advantage of this modified guideline technique is that the tar spectrum can be analysed by online gas chromatography (GC), thus removing the need for sampling and storage of samples. However, it cannot be considered as an online method, since the GC run time (approximately 50 minutes) does not still allow a satisfactory resolution. As further described in Factsheet 25, the use of online UV-Vis analysis of the tar-containing solvent has been used to give a quantitative online measurement of certain tars in simple mixtures and qualitative monitoring of complex tar mixtures.
- Technical University of Denmark (DTU) applies a Petersen column for the sampling of tars instead of the impinger train. The structure of the Petersen column is shown in Figure 67. The two containers of the Petersen column are filled with acetone and kept at 0°C. All the tar is expected to dissolve in the two acetone layers, after which the gas goes through the pump. One tar sample includes the collected acetone from both layers. Then, the collected

samples from the Petersen column are filled up to a known volume (250 mL) [135]. More details about the Petersen column can be found in the dedicated Factsheet 34.

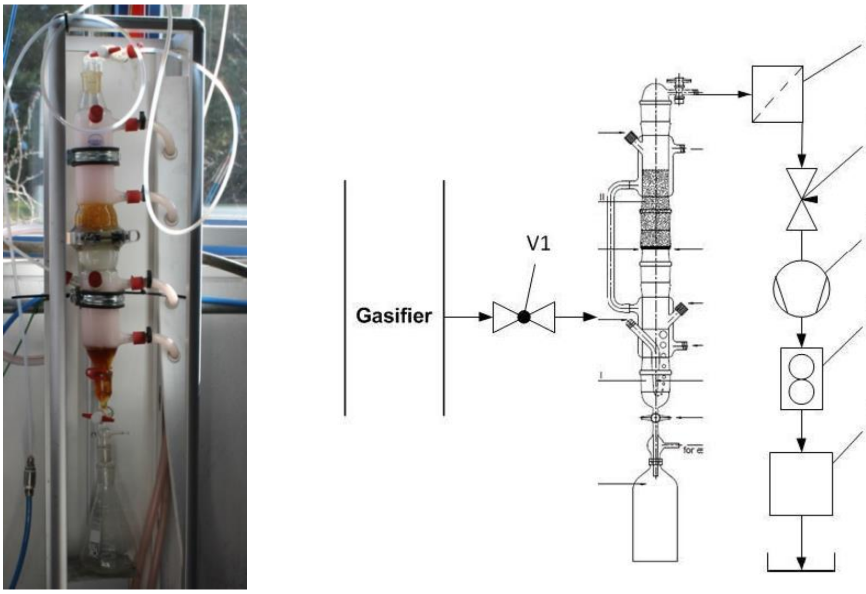
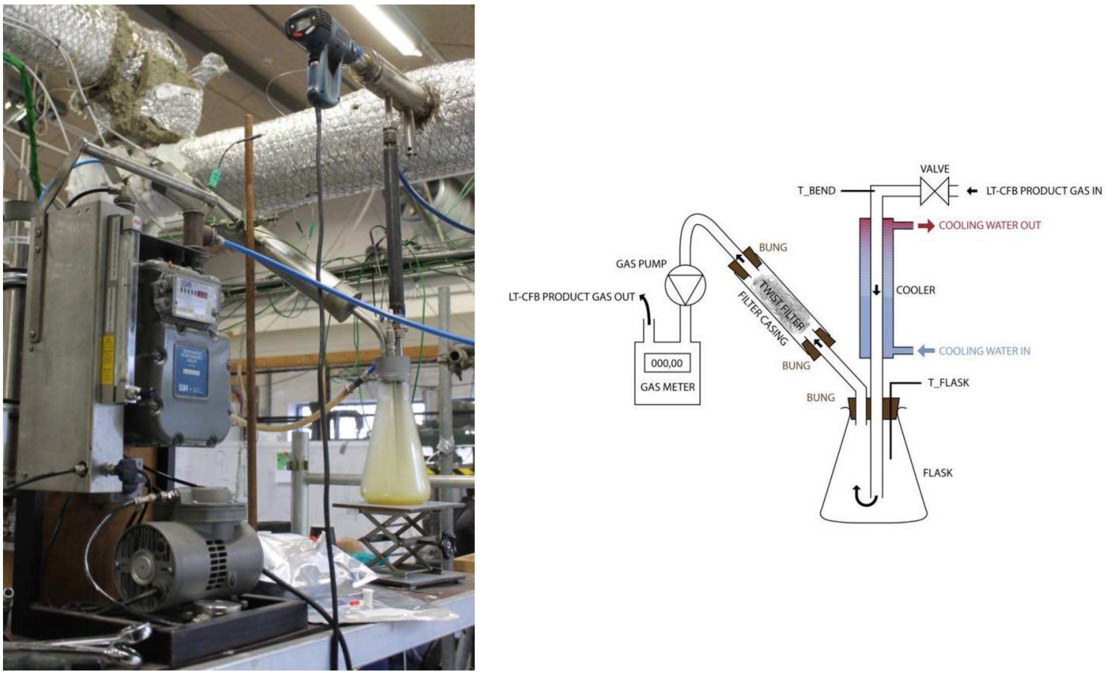


Figure 67. Petersen column for tar measurement applied at DTU (left); schematic layout of the Petersen column: V1 – sampling port valve; F- Filter before pump; V2 – needle valve for adjustment of gas flow, P1 – pump, FI – flow indicator – GA – gas analysis set [25][135][136].

Additionally, for gravimetric determination of tar and water content in product gas, DTU uses a self-designed tar capturing system (Figure 68) in which condensate is collected in a flask in 2 fractions - with and without water. The total volume of sampled gas is measured with gas meter. Then, calorimetry tests are run on the water and water-free phases. Assuming the heating value of gravimetric tar, the amount of water in the gas is derived [25]. This setup is a straightforward option to obtain useful information for mass- and energy balance calculations without making use of solvents and advanced sampling systems [115].



(a) (b)

Figure 68. Tar and water condensation setup designed by DTU for quantification of gravimetric tar and water [25][133][134].

- Iowa State University applies a dry condenser methodology which is designed to capture a heavy tar fraction comparable to that measured by the IEA tar protocol [137][138]. The dry condenser method consists of a heated thimble particulate filter, a dry condenser constructed from a household pressure cooker, a chilled bottle to condense water and some light hydrocarbons, a vacuum pump, and a dry gas meter. The dry condenser consists of a 6-m coil of Santoprene tubing (material selected because of its low cost and durability at elevated temperatures), and a fiberglass-filled stainless steel canister installed inside the pressure cooker. The removable lid of the pressure cooker is pierced by compression fittings to admit gas flow to and from the pressure cooker. Gas entering the pressure cooker flowed serially through the Santoprene tubing and the stainless steel canister before exiting the pressure cooker. Before sealing the pressure cooker, it was filled with sufficient distilled or deionized water to submerge the Santoprene tubing and most of the canister.

  The pressure cooker was placed on an electric hot plate adjusted to sufficient power to boil water within the pressure cooker. The pressure cock on the cooker was adjusted to boil water at 105 °C, which prevented water vapor in the sampled product gas from condensing inside the tubing and on the fiberglass. Gas exiting the pressure cooker flowed through an impinger bottle submerged in an ice bath for the purpose of removing water and some light hydrocarbons from the gas before it flowed through the vacuum pump. The pressure and temperature just ahead of the gas meter was recorded periodically during sampling [137].

- Hernández et al. [139] from University of Castilla-La Mancha describe the development of a HPLC analysis method for the quantification of tar compounds (BTEX, PAHs, phenol and pyridine). These authors report moreover the carcinogenic potential of the tars produced during biomass gasification.

- Technical University of Vienna applies a variation of the tar guideline method in which toluene replaces 2-propanol as solvent in order to take into account the high water content of product gas from steam gasification [140]. In addition, as can be seen in Figure 69, all the impinger bottles are placed in a cool bath at -8°C (thus, no temperature gradient is applied). The required sampling time depends on the gas sampling location (thus, on the tar loading of the gas). As an example, during measurement campaigns at the Oberwart CHP plant (Austria), the tar sampling time ranged between 8 minutes (after the gasifier, highest tar content), 15 minutes after the gas filter, and 45 minutes after the tar scrubber (lowest tar load) [140].

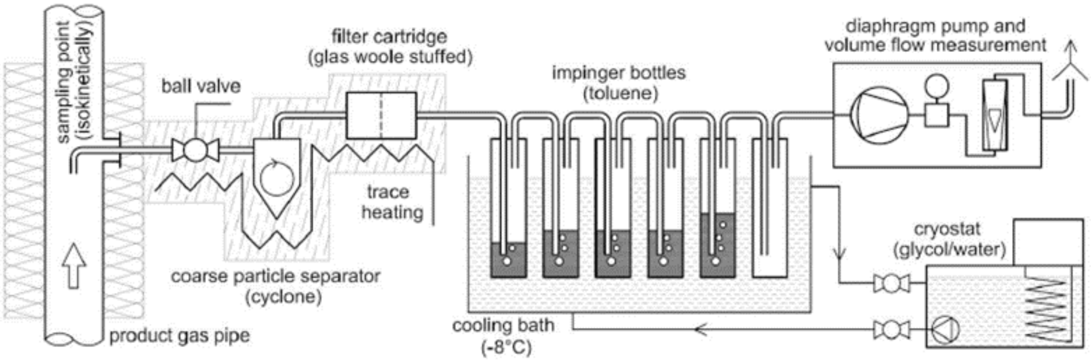


Figure 69. Schematic of the adapted tar sampling train applied at Technical University of Vienna [140].

- TU Graz applies the tar protocol to measure the tars of a lab-scale fluidized-bed gasifier. The setup follows the tar guideline with some adaptations (shown in Section 3.2.22 of Document 1). It consists of 6 impinger bottles with a volume of 250 mL. The first 5 impingers are filled with 100 mL 2-propanol and the last one is filled with 6 mm glass beads to capture evaporated 2-propanol which might otherwise damage the pump. According to the official setup of the tar-guideline, bottles 2, 3, 5 and 6 are equipped with a frit of porosity 3. However, with this setup the frits got blocked several times, so a different setup was chosen. Bottle 2 is used without any frit and bottle 3 has a frit of porosity 0. The last bottle has no frit either because it is easier to handle it with the glass beads in this way. The measurement time was selected to 40 minutes in order to capture enough tars for the gravimetric method. Afterwards, the liquid in the bottles is mixed and the tar content can be measured gravimetrically or measured with GC-FID. An important step to achieve consistent results is to clean the part of Teflon tubing (not heated externally) before the first bottle with acetone after the sampling and to add this liquid to the sample, in order to also capture the condensed tars in this section. To calculate the gravimetric grams of tars per Nm^3 gas, 100 mL of the liquid sample are evaporated in a rotary evaporator at a pressure of 0.1 bar and a temperature of 55°C and the remaining tars can be measured with a balance. Efforts were made in the past to measure gravimetrically the tars in a drying oven at 50°C and at atmospheric pressure, which would be simpler, but with this method no consistent results could be achieved.

CONTACTS

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RELATED TOPICS

- Petersen column (Factsheet 34).
- Liquid quenching + UV-Vis spectroscopy (Factsheet 25).
- Solid Phase Adsorption (SPA) (Factsheet 37).

MORE INFO

Video blog # 1 on tar guideline sampling at ECN part of TNO:
https://www.youtube.com/watch?v=e1r8ZlSDOkg

42. Tar dew point analyser

This device, developed within a collaborative project between ECN part of TNO and Mitchell Instruments, is the adaptation of an existing hydrocarbon dew point analyser used in natural gas applications. The upgrading consisted on the modification of the hardware of the sensor (e.g. high-temperature resistant fibre optics, use of ceramics in the sensor, increase of internal diameter of piping to prevent tar blockage, placement of the sensor cell within an oven to prevent cold spots), and the design of a gas conditioning section (dust filter, tar condenser, and water removal) to protect the sensor against fouling and corrosion, thus making it suitable for measurement in product gas from biomass gasification [141].

HOW IT WORKS

The tar dew point is defined as the temperature at which the gas gets saturated with tar. Thus, below the tar dew point temperature, tar is prone to condense if enough residence time and contact surface area are available. This is a relevant parameter in (biomass) gasification processes, since it indicates whether problems (fouling due to tar condensation) can be expected.

Figure 70. The tar dew point sensor located in the oven for testing [141] .

The sensor cell is the key element of the analyser. A beam of light is focused at the centre of an optical surface. The reflection of the light is measured. The difference between the intensity of the original light beam and its reflection is the signal used for the detection of the dew point of the hydrocarbons. As soon as the signal reaches a certain threshold value, the corresponding surface temperature of the optical surface is displayed as the dew point of the hydrocarbons contained in the gas.

A measurement cycle starts with flushing of the sensor cell with gas. When the cell is filled with gas, the flow is topped by means of valves, thus closing off the cell. The optical surface of the sensor is then slowly cooled down using compressed air or compressed natural gas. As soon as the hydrocarbons condense on the optical surface, the reflection of the light beam is changed by the condensate. The optical surface is recovered by increasing the temperature and flushing the sensor with natural gas. After recovery, the next measurement cycle can start. Every measurement cycle takes a few minutes [141].

During validation tests it was found that the shape of the dew point curve is similar to that of the dew point of hydrocarbons contained in natural gas. Thus, the analyser can be also applied in biomass gasification applications. However, the operating temperature of the analyser is restricted by the thermal resistance of the fibre optics.

ADVANTAGES

- Proper quantification of tar dew point at concentrations of tar between 150-500 mg/Nm^3.
- Accurate measurement of tar dew point in the range of 25-170°C.

LIMITATIONS

- Operating temperature limited by thermal resistance of fibre optics (thus, limited to 200°C) → equipment not suitable for raw product gas, but for gas after cleaning.
- Irreversible fouling of the sensor by tar polymerization is a potential risk for measurements at high temperature.

STATUS

The online tar dew point analyser is currently on hold.

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43. Tunable diode laser absorption spectroscopy (TDLAS)

- Please refer to Laser Absorption spectroscopy (Factsheet 21).

44. (Far-UV)/UV absorption spectroscopy

UV absorption belongs to the group of spectroscopy techniques. UV spectroscopy offers certain advantages with respect to (more conventional) IR spectroscopy, and thus has a good potential for in-situ/online measurement of gas compounds (e.g. NH_3, NO, O_2, N_2, SO_2, CH_3Cl, BTX), as well as tar compounds when a fast response time and high sensitivity are required.

Conventional UV absorption measurements (from 200 nm and upwards) can be performed with a mobile UV/IR system described in Factsheet 10 (FTIR), Figure 72 (left), whereas far-UV measurements (from 120 nm up to 250 nm), Figure 72 (right) can be performed with a much more compact system because of the strong absorption below 200 nm. It should be noted that UV measurements from 200 nm and upwards are not influenced by high CO_2/H_2O concentrations in the gas.

HOW IT WORKS

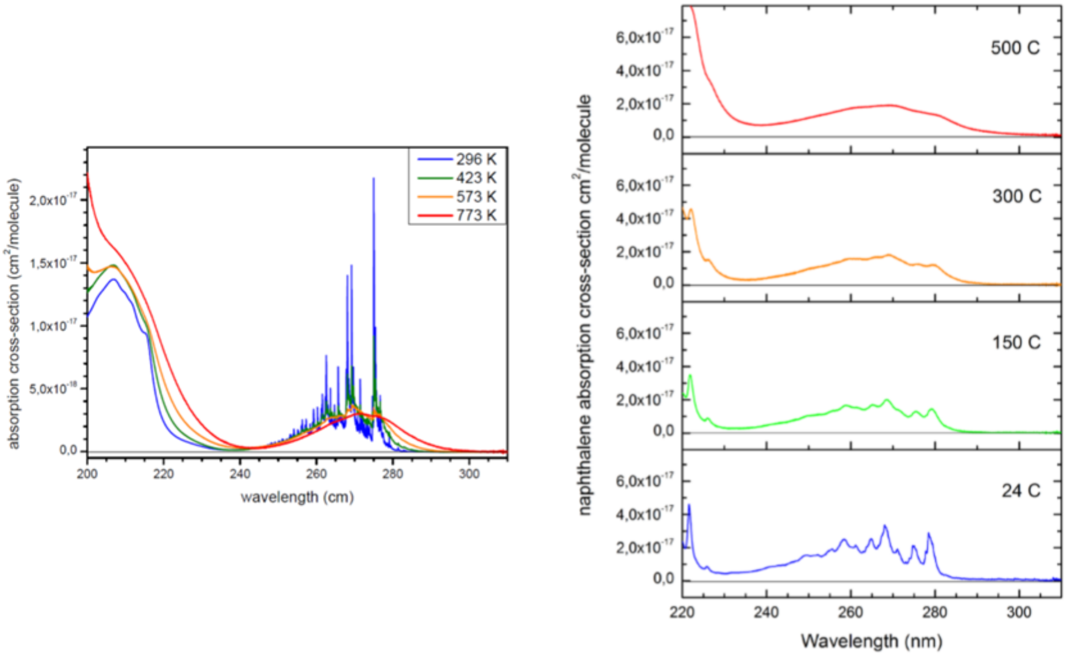
See Absorption spectroscopy (Factsheet 1).

ADVANTAGES

- The absorption path length for measurements can be as low as a few millimetres. This makes the system quite compact compared to IR absorption equipment [142].
- This system does not require any vacuum components (N_2/Ar purge is sufficient) and can be used for measurements of Cl-compounds, N_2, O_2, NH_3, various C_xH_y, BTX and tar.

LIMITATIONS / RELEVANT ASPECTS

- The absorption spectra of gases tend to become broader (and less defined) at higher temperatures. An example of this phenomenon can be seen in Figure 71 for phenol and naphthalene [163]. Thus, there is an optimal range of sampling temperatures (250-300°C) for UV absorption applied for online tar measurement at which there is a trade-off between avoiding tar condensation and preservation of the gas spectra [142].



Phenol Naphthalene

Figure 71. Effect of temperature on the UV absorption spectra of tar compounds [163].

EXAMPLES OF IMPLEMENTATION

UV absorption spectroscopy was developed and validated by Technical University of Denmark within a Forsk EL project [142]. The techniques were tested at different gasification setups: LT-CFB (100 kW_{th}), the Pyroneer plant (6 MW_{th}) and the Viking gasifier [142][163]. See more details in Section 3.2.6 of Document 1.

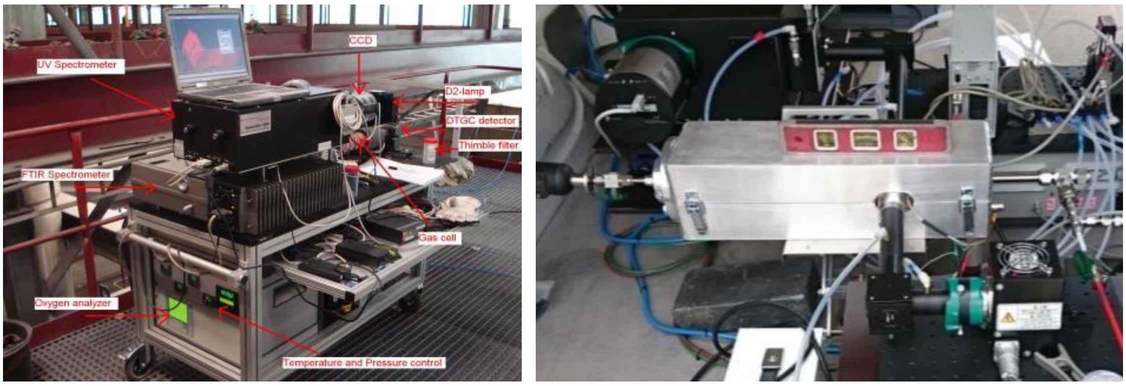


Figure 72. Gas sampling system for simultaneous UV/IR/O_2 measurement at 150°C (left); gas cell for far-UV absorption measurements up to 300°C (right) [25].

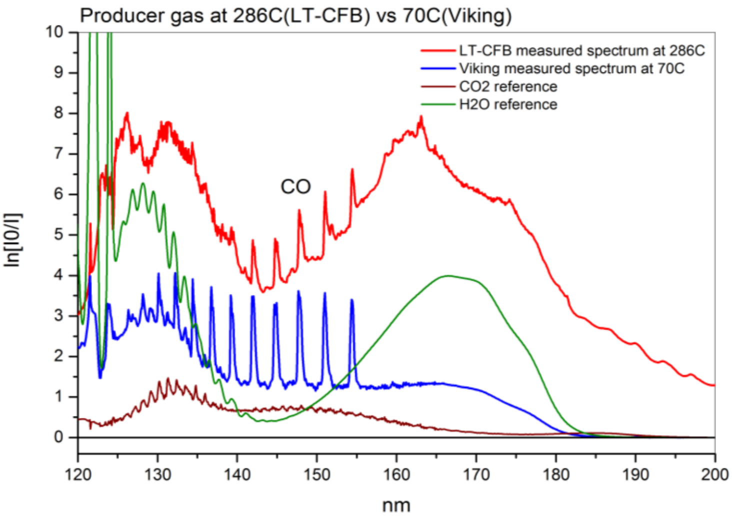


Figure 73. Representative far-UV absorption spectra measured by DTU at Viking (blue line, 70°C) and LT-CFB (red line, 286°C) gasifiers. Reference CO_2 (brown line) and H_2O (olive line) are shown for comparison.

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RELATED TOPICS

- Absorption spectroscopy (Factsheet 1).
- Laser absorption spectroscopy (Factsheet 21).

45. UV/UV-Vis fluorescence

HOW IT WORKS

Sulphur compounds can strongly absorb UV radiation. This property has been applied for the measurement of H_2S, COS, CS_2 and SO_2 (the latter being a broad application of UV analysers) [143].

The samples are decomposed in a vertical oven at 1000-1100°C in 2 stages, namely pyrolysis in an argon stream followed by thermal oxidation of the pyrolysis gases. All the organic S species are oxidized to SO_2, which in turn absorbs light in the UV region around 190-230 nm.

ADVANTAGES [143]

- Good option for the determination of trace sulphur content regardless of the nature of the sulphur compound.
- It does not require the use of expensive and short shelf-life gaseous calibration standards, but the instrument can easily be calibrated via liquid organic sulphur compounds, as prepared in house (the measurement principle stands for the total oxidation of organic sulphur compounds, regardless of liquid or gaseous form).
- Measurement cycle up to 3 minutes.
- The measurement can only be interfered with the presence of NO_x compounds, which are not formed at gasification processes.

LIMITATIONS [143]

- The results are expressed in total amount of sulphur: no speciation of sulphur compounds.
- UV-VIS needs a careful calibration for the quantitative analysis of thiophene since the bands of the wavelength for thiophene and H_2S detection may overlap.

EXAMPLES OF IMPLEMENTATION

Tübitak Mam has applied UV fluorescence for the measurement of thiophene and thiophene derivatives in product gas in the framework of the BRISK project. The analyser used is shown in Section 2.6.2 of Document 1. The results using UV fluorescence showed in general good agreement with GC-PFPD results [144].

CONTACT

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46. Volatility Tandem Differential Mobility Analyser (VTDMA)

VTDMA is a thermal-based analysis technique applied for the assessment of the thermal stability of aerosol particles.

HOW IT WORKS

VTDMA is based on the principle that different condensed components (tars, alkali compounds, soot) become volatile at characteristic temperature ranges. When the temperature of the particle (set in an oven) increases, a fraction of the particle volatilizes, which results in a reduction of the particle size. The temperature at which the volatilization takes place provides information about chemical composition of the aerosol particle [122].

VTDMA is practically implemented as follows: the system consists of 2 differential mobility analysers (DMA) in series separated by an oven. In the DMA, an aerosol with a well-defined charge distribution is produced. The particles are then separated based on their electric mobility. The first DMA is applied to select aerosol particles with a certain particle diameter. These particles are then sent to an oven set at a certain temperature. The particles coming from the oven are analysed (after cooling down to ambient temperature) in a second DMA to determine the size distribution after the heat treatment at the oven (which results on loss of particle mass and volume, thus reduction in particle diameter). The obtained evaporation profile (called thermogram) is then used for the chemical characterization of the sample aerosol, in an equivalent way as TGA is applied for solid samples [12]. A condensation particle counter is used to monitor the concentration of particles after the second DMA. Laminar gas flow is kept throughout the system. The typical total sampling time is approximately 1 hour in order to get a complete thermogram over an extended temperature range.

EXAMPLES OF IMPLEMENTATION

Gall et al. from University of Gothenburg [121][122] applied this measurement technique for the determination of the chemical composition of aerosol particles produced from gas sampling at the 4 MW_{th} dual fluidized bed gasifier located at Chalmers University of Technology [122]. The system was also tested at the GoBiGas bio-SNG plant [121]. An example of the thermograms produced by VTDMA during the GoBiGas campaign is displayed in Figure 74. As can be seen, the reduction of particle size at <350°C corresponds to heavy tars. No evaporation is visible in the temperature range where KCl and KOH would evaporate. The reduction in particle size at 600-700°C is due to the evaporation of K_2CO_3. A significant fraction of high thermal stability material (maybe soot) remains after 850°C.

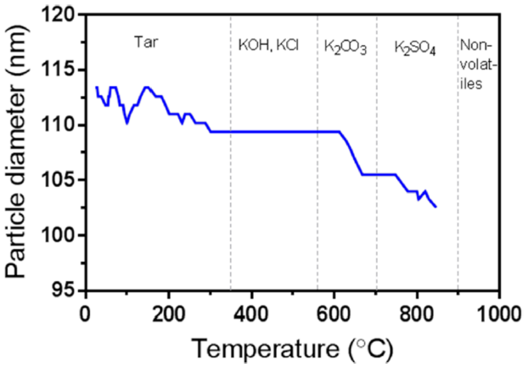

Figure 74. Thermogram generated by VTDMA for the determination of thermal stability (thus, chemical composition) of aerosol particles, produced at a measurement campaign at GoBiGas [121].

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47. Wet chemical analysis

The generic term "wet chemical analysis" includes a number of methods used for the (offline) measurement of different gas compounds present in product gas, including H_2S, NH_3, HCN, and HCl.

HOW IT WORKS

Wet chemical analysis includes 2 steps, firstly the sampling of product gas for the capture (accumulation) of target compounds in different chemical solutions; and offline analysis of the resulting solution using different techniques. During the sampling stage, the product gas is bubbled through a series of impinger bottles filled with a certain solution (see overview in Table 5), where the target gas compounds are absorbed via different physical-chemical processes (chemical solving, precipitation, solvation based on pH) [145].

Table 5. Overview of features of gas sampling in wet chemical analysis methods.

Target compound	Sampling solution	Train configuration	Analyte species	Analysis technique	References
H_2S (g)	$Zn(CH_3COO)_2$	2 impingers in series	S^{2-}	UV-Vis spectroscopy	[145]
	$CdSO_4$ (5 vol.%)	4 impingers in series, 30 mL solution each		Iodometry	[128]
	50 vol.% distilled water + 50 vol.% sulphide anti-oxidant buffer	N.R.		N.R.	[146]
NH_3 (g)	H_2SO_4 (5 vol.%/1 M)	pH stabilization 2 impingers in series, 150 mL solution each	NH_4^+	UV-Vis spectroscopy	[128]
	1 $MHNO_3$	2 impingers pH stabilization		AMFIA	[56][147]
	Distilled water	N.R.		Ion-selective electrode (ISE)	[146]
	HCl (5 vol.%)	3 impingers in series at 0°C: impingers 1		Titrimetric analysis	[55]

Target compound	Sampling solution	Train configuration	Analyte species	Analysis technique	References
	H_2SO_4	and 2 with HCl solution (200 mL each), impinger 3 with desiccant			
HCN (g)	$Hg(CH_3COO)_2$	2 impingers in series	CN^-	UV-Vis spectroscopy	[145]
	NaOH (5 vol.%)	2 impingers in series, 150 mL solution each		UV-Vis spectroscopy	[128]
	0.1 M NaOH	1 impinger		Ion-selective electrode (ISE)	[146]
	2.5 M NaOH	2 impingers pH stabilisation		FIA	[56]
HCl (g)	Na_2CO_3 HNO_3	2 impingers in series	Cl^-	UV-Vis spectroscopy	[145]
	Distilled water	4 impingers in series, 30 mL each		Ion chromatography	[128]
	Distilled water	1 impinger		Ion-selective electrode (ISE)	[146]

N.R.: not reported.

ADVANTAGES

- It allows the measurement of gas compounds which are difficult to measure with online techniques.

LIMITATIONS

- Labour- and time intensive: relatively long sampling times, and arduous preparation and handling of solvents and solutions.
- Offline method: only average values are obtained. Not possible to follow variations in the gasification process.

- Safety and health issues due to the handling of solvents.

- Interaction with other compounds can lead to inaccurate measurements: for example, it has been reported that abnormal HCN values might be due to interference with tar compounds (absorption of UV radiation in the same frequency range as CN^-) [128]. It has also been claimed that HCl and NH_3 measurement is challenging due to the reaction of HCl with NH_3 forming ammonia chloride at temperatures below 300°C [148]. Co-absorption of CO_2 is another issue during HCN sampling, which needs to be considered in the design of the sampling train in order to ensure that all the HCN in the gas is captured in the basic solution.

RELEVANT ASPECTS

Loss of analyte compounds – outlines for correct gas sampling:

A very important aspect to take into account when designing a gas sampling train is that sulphur compounds are very reactive and get selectively adsorbed on glass and metals surfaces, thus negatively affecting its quantification [149]. Loss of sulphur compounds in sampling lines depends mostly on three factors: materials, concentration levels, and flow rates [48]. Several recommendations to minimize the loss of sulphur compounds during sampling include [48][55][149]:

- Selection of materials: the use of glass or stainless steel in the analysis lines should be avoided whenever possible, and inert materials, e.g. ceramic (quartz, SiC filters) should be used instead. Teflon is permeable and can thus result in loss of sulphur compounds if used as tubing material [48]. Glass, Sulfinert®-coated stainless steel [150][151] and FEP sample bags [152] are recommended for low concentrations and long residence times. Stainless steel is acceptable for small fittings, since the surface will get passivated after a certain amount of time of constant flow.

- The gas flow rate should also be sufficiently high (2-3 NL/min) to reduce adsorption problems [149]. The reason is that since surfaces will adsorb a given amount of sulphur molecules, losses will be relatively smaller if a large flow rate of sulphur molecules is provided. For high sulphur levels (> 50 ppmv), stainless steel regulators and flow controllers are acceptable as well as aluminium gas cylinders. For sulphur levels below 1 ppmv, high flow rates are recommended relative to the surface area inside the lines and fittings that are in contact with the sample.

- The sampling lines should be reconditioned (e.g. back-flushing with nitrogen) when a feed gas with a different composition is sampled [149].

- Particles should be removed at a sufficiently high temperature so as to avoid sulphur adsorption in the char particles.

The outlines above can be also applied to the measurement of NH_3, HCN and HCl.

Several sources of uncertainty in the determination of HCN have been identified. On the one hand, HCN was found to be captured in acidic solutions and polar solvents like acetone if tar removal or NH_3 sampling are performed upstream the sampling with NaOH solution, thus leading to serious underestimation of the HCN content in the gas, as found by researchers at Iowa State University. Therefore, sampling in series of NH_3 or tar and HCN should be avoided and should be rather performed in parallel or in turns [153]. On the other hand, co-absorption of the CO_2 contained in the product gas can occur during HCN sampling in the alkaline solution ($2\ NaOH + H_2CO_3 \rightleftarrows Na_2CO_3 + 2\ H_2O$). Therefore, it is necessary to apply measures (such as the setting of several impingers in series, or the increase of the NaOH concentration in the sampling solution) in order to ensure that all the HCN contained in the gas is effectively captured in the solvent [56][154]. In order to address this issue, at ECN part of TNO it was calculated the minimum amount of NaOH necessary to be able to potentially absorb all the CO_2 contained in the product gas (upper limit, since an equilibrium takes place in practice) to ensure that sufficient NaOH was available to absorb also HCN. Tests were then performed using a train of 3 impingers in series (2 wash bottles filled with 200 mL of a 2.5 M NaOH solution followed by a guard impinger with 150 mL of the same solution) to assess whether complete capture of HCN could be performed. In order to assess the co-absorption, the CO_2 concentration was online measured during sampling before and after the impinger trains. For the processing of results, it was necessary to apply a correction to account for the reduction in the sampled gas volume caused by the significant capture of CO_2 in the impingers. The results of the experiment showed that, despite the fact that the pH of the solution decreased from 14 to 11-13 as a consequence of the acidification caused by the co-absorption of CO_2, the pH was still high enough to ensure the capture of HCN (even so, CO_2 was not completely captured in the impinger train, as shown by the non-zero CO_2 concentration in the outlet gas). From this test, it was concluded that the HCN contained in the gas could be fully absorbed in the first 2 impingers [154]. Underestimation of HCN can also occur if the gas sampling train is located downstream a gas cooler or other device that removes water from the gas, since a fraction of HCN will end up in the condensate. In this case, it would be recommended to quantify the amount of HCN contained in the condensate, or alternatively, select the gas sampling location upstream the removal of water.

HCl can be easily trapped in any aqueous solution regardless of its pH [149]. This implies that it is very easy for losses of HCl to occur, for example if tar removal below the water dew point temperature is applied, or if water condensation takes place upstream the sampling train. Moreover, HCl can easily react with surfaces and with other gas components. This issue was identified for example by researchers of University of Stuttgart during wet chemical measurement of ammonia in sewage sludge gasification [95][148]. Upon cooling down below 300°C, HCl reacts with NH_3 forming NH_4Cl. The ammonia chloride is dissolved together with other Cl containing compounds in the impinger bottles, thus leading to an underestimation of the ammonia concentration in the gas. In this sense, Ståhlberg et al. [149] report a sampling method used in coal gasification by Huston and Wachter, in which the sample gas is kept at 500°C to prevent NH_4Cl formation, and then tars and ammonia are decomposed in a cracker at 1000°C. The reaction of HCl with material surfaces leads in the practice to a 'memory effect' (that is, stable operation of several hours or days is required until equilibrium is reached in the HCl concentration) [149]. This aspect is particularly relevant if the gas composition is changed to lower Cl concentrations, since release to the gas phase of the adsorbed HCl in the walls will take place [149].

Storage of solution samples:

According to Ståhlberg et al. (VTT) [149], HCN solutions can be stored for a maximum of 24 hours, although analysis should preferably be performed immediately after gas sampling. The solutions need to be at pH levels of 11 – 12.5. Ammonia samples can be stored for longer time than HCN samples, at least for 1 month. In this case, the samples need to be stored at 2-5°C in a dark place at a pH of 2.

At ECN part of TNO, the NEN-EN-ISO 5667-3 standard [155] is applied for the storage of the solution samples. All liquid samples (either from NH_3, HVN or HCl sampling) are kept cooled. Samples from NH3 and HCl sampling are conserved at $pH < 2$ and are analysed within 1 month; samples from HCN sampling are conserved at $pH > 12$ and analysed within 5 days [56].

Analysis of solutions:

Norton and Brown (Iowa State University) [55] report erroneous results using ion chromatography (IC) for the detection of ammonia (NH_4^+ ions in the resulting solution from sampling). It is claimed that the large background associated to H_2SO_4 might be the cause for this problem. Instead, titrimetric analysis was applied with good results.

At ECN part of TNO, similar problems are experienced using IC for the detection of HCN. In this case, the background signal was due to the carbonate ions in the solution resulting from the co-absorption of CO_2 from the gas. Flow injection analysis was successfully applied instead [56].

Figure 75 and Figure 76 display the schematic layout of wet chemical analysis used by IFK-University of Stuttgart (Germany) and BE2020$^+$ (Austria). At the IFK group of University of Stuttgart, a number of measurement methods were adapted from standardized methods, tested and validated [95][96][148]: measurement of H_2S was based on the iodometric titration method (DIN 51855-4). NH_3 analysis was adapted from the indophenol method (DIN EN ISO 11732). Lastly, HCl was measured with coulometric analysis. At BE2020+, H_2S quantification is based on the DIN 38405 D26 standard; NH_3 measurement is based on DIN 38406-E5; and HCN measurement is based on DIN 38405-13 by photometric detection. HCl is routinely analysed by ion chromatography.

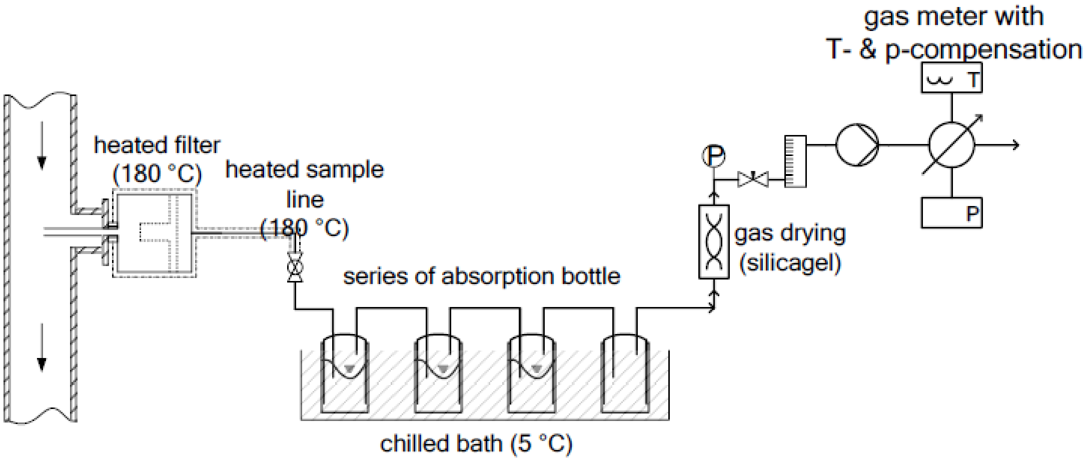

Figure 75. Layout for wet chemical analysis used at University of Stuttgart [95][96].

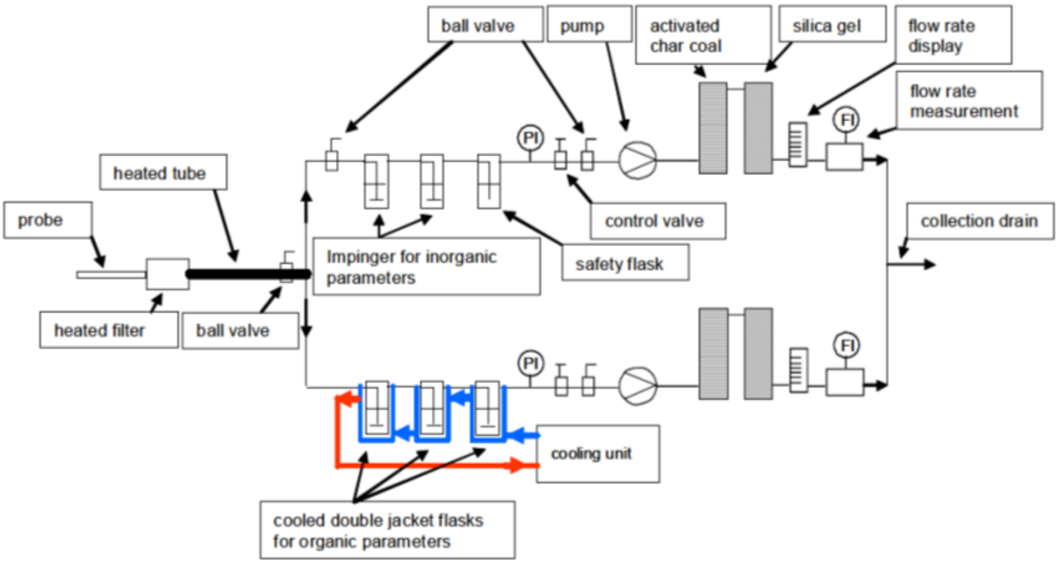

Figure 76. Layout of gas sampling train for analysis of organic and inorganic compounds used by Bioenergy 2020$^+$ [145].

Figure 77 displays the setup applied by DTU for the measurement of the nitrogen content of product gas from the gasifier. A small gas stream was extracted continuously from the large product gas pipe from the gasifier. The gas was bubbled through 3 impingers in series cooled by ice/water. The first 2 impingers contained 100 mL water and the third contained 100 mL of 0.5 M sulfuric acid solution. The ammonia condensates/dissolves in the impingers alongside some tar components and most of the water in the gas. Any remaining ammonia will be dissolved in the sulfuric acid. After the condensation process, the remaining gas volume and flow is measured, hereafter the gas entered a gas analyser that determined the NO-content by a UV measurement and the O_2 content with a chemical cell. O_2 was monitored to make sure the system did not take in air. During each measurement, 100 L gas was sampled through the system. The resulting solution of ammonia and organics in the water and sulfuric acid solution was analysed. For total nitrogen determination, the auto-analyser method G-086-93 was used. For the determination of ammonia in water, two standard methods were applied, DIN 38 406 Part 23, section 2 and ISO/DIS 11732 [135].

Figure 77. Impinger train used by DTU for determination of total nitrogen content in the gas [135].

Recari et al. [146] report the results of fluidized-bed gasification of solid recovered fuel (SRF). Wet chemical analysis was applied for the measurement of HCl, NH_3, HCN and H_2S. For this, the product gas was sampled in 25 L Tedlar bags, which were then sequentially pumped through a series of impingers. A gas flow of 1 NL/min was used, and the sampling time was 5 minutes per compound. After the sampling, the resulting liquid solutions were pH adjusted with 0.1 mL of a buffer solution. Then, the solutions were analysed with ion-selective electrodes (ISE).

Norton and Brown from Iowa State University [55] applied a series of 3 mL modified Greenburg-Smith impingers (easier to clean) for the sampling of NH_3 from product gas. The first 2 impingers contain 200 mL of 5 vol.% HCl solution, while the third impinger is filled with a desiccant. The samples are then titrimetric analysed. H_2SO_4 solutions have also been successfully applied for this purpose. Similarly, HCN can be measured using this setup with 100 mM sodium hydroxide in the impingers and then analysing the samples offline with an Ion Chromatograph (IC). The setup is schematically shown in Figure 78.

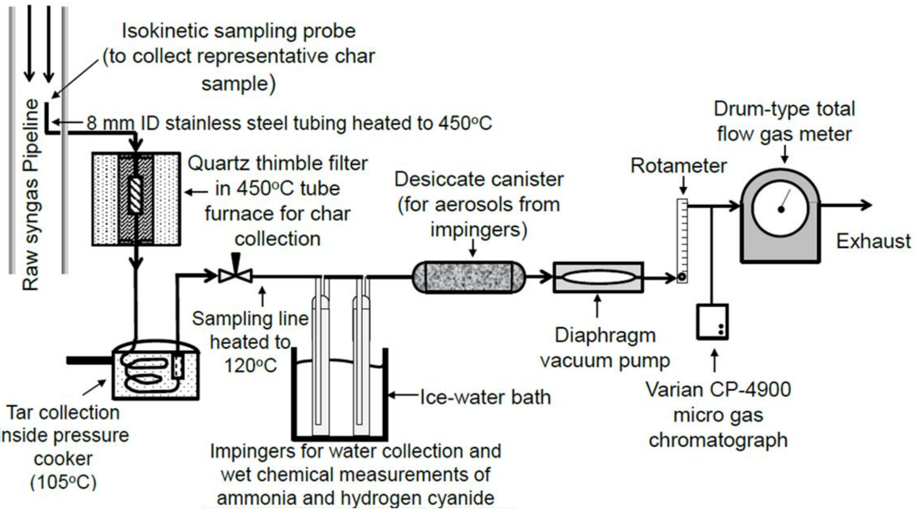

Figure 78. Diagram of train for sampling of tar, ammonia and wet chemical sampling of NH_3 and HCN at Iowa State University [45], adapted from [138].

Wolfesberger-Schwabl from Technical University of Vienna [140] describes the wet chemical analysis setup applied for the measurement of H_2S and NH_3 at several dual fluidized-bed gasification CHP plants. In both cases, a set of 6 impingers in series is applied, with the following configuration:

- H_2S sampling: the first impinger contains 50 mL toluene (used for tar removal); the second and third impingers contain 40 mL each of a 35 vol.% KOH solution; the fourth and sixth impingers are empty; and the fifth impinger contains 100 mL toluene.

- NH_3 sampling: the first 3 impingers contains a 0.05 M H_2SO_4 solution (50 mL in the first impinger, 100 mL in the second and third impingers). The fourth and sixth impingers are empty, and the fifth impinger contains 100 mL toluene. The resulting sample is then analysed with ion chromatography.

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