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Biomass Gasification — Tar and Particles in Product Gases — Sampling and Analysis

Thermischer Biomassevergasung — Teer und Staub aus dem Produktgas — Probenahme und analytische Bestimmung

Gazéification de Biomasse — Goudron et Particules dans le Gaz Combustible — Échantillonnage et analyse

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Contents

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Foreword

This document TC BT/TF 143 WI CSC 03002.4 has been prepared by Technical Committee CEN/TC BT/TF 143 “Measurement of organic contaminants (tar) in biomass producer gases”, the secretariat of which is held by NEN.

This document is a working document.

Introduction

The main contaminants in the product gases of biomass gasification are dust and soot particles, tars, alkali metals, acid gases and alkaline gases. Measuring techniques for these contaminants allow determination of the functioning of the gasifier itself, of the efficiency of the gas cleaning process and of the quality of the cleaned gas to be used in a gas engine or gas turbine.

For most contaminants, well-developed measurement techniques exist which are similar to techniques used for related technologies, such as coal combustion and coal gasification. For tars, however, no well-developed and widely used measurement techniques exist in these related technology fields. As some of the tars are seen as the major problem causing contaminants in biomass gasification, manufacturers and other workers in this field use a number of different sampling and analysis methods to determine the level tars. As a result, comparison of data and definition of clear maximum allowable concentrations for tars is problematic. This forms an obstacle for market introduction of the biomass gasification systems as tars can cause damage or an unacceptable level of maintenance.

This Technical Specification gives methods for sampling and analysis of tars and particles in product gases from biomass gasifiers operating under atmospheric or pressurised conditions. The sampling and analysis methods in this Technical Specification differ from most of the methods used for sampling organic compounds present in the gaseous emissions from various industrial processes such as flue gases or automobile exhaust gases. The differences are related to the fact that the concentration level of the organic compounds present in the gasification product gases exceed the concentrations found in flue gases generally by more than 3 orders of magnitude. Hence the methods described in this Technical Specification are not intended to be applicable for sampling organic compounds in trace concentrations (sub-ppm range).

The tar-containing biomass gasification product gas is formed by thermal decomposition of biomass at sub stoichiometric conditions (pyrolysis, gasification) and is typically used to produce electricity, heat, or gaseous or liquid biofuels. As tars from pyrolysis or gasification of coal are similar in nature compared to (high temperature) biomass gasification tars, also coal tars can be sampled and analysed with this Technical Specification.

Biomass in this Technical Specification is defined as material of biological origin excluding material embedded in geological formations and transformed to fossil[1]. The Technical Specification is developed for uncontaminated biomass, a term being defined in Chapter 3 "Terms and definitions". Tests on accuracy and repeatability of the Technical Specification have been performed with uncontaminated biomass. The Technical Specification may also be used for tars produced from gasification of contaminated biomass and for tars produced from gasification of fossil fuels, however, in this case it is up to the user to assess to which extent the concentration and composition of the tars differ from gasification of uncontaminated biomass. Biomass gasifiers as referred to in this Technical Specification can be updraft fixed bed gasifiers, downdraft fixed bed gasifiers, stage divided gasifiers, fluidised bed gasifiers, entrained flow gasifiers and other types of gasifiers. Updraft and downdraft fixed bed, fluidised bed and entrained flow gasifiers are described in more detail in [TECHNICAL REPORT = GUIDELINE].

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[1] This definition is the same as the definition of biomass in CEN TC 335 Solid Biofuels

1 Scope

This European Technical Specification gives methods for sampling and analysis of organic tars and particles in biomass gasification product gases The Technical Specification applies for sampling and analysis of tars and particles in the concentration range typically from 1 mg/m$_n^3$ to 300 g/m$_n^3$ at all relevant sampling point conditions (0 - 900°C and 0,6 - 60 bar)[2, 3].

Application of this Technical Specification allows determining four different numbers:
A. The concentration of gravimetric tar in mg/m$_n^3$;
B. The sum of the concentrations of GC-detectable tar in mg/m$_n^3$;
C. The concentration of individual organic compounds in mg/m$_n^3$. This Technical Specification data on repeatability and reproducibility for the compounds listed in Annex B. The Technical Specification is applicable also for other organic compounds (*eg* those mentioned in Annex A.2), however, it is not evaluated for compounds other than those in Annex B;
D. The concentration of particles in mg/m$_n^3$.

2 Normative references

This Technical Specification incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this Technical Specification only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

(number)	(date)	(title)
ISO 5725-1:1994 Technical Corrigendum:1998	1998-02	Accuracy (trueness and precision) of measurement methods and results - Part 1: General principles and definitions
ISO 5725-2:1994 Technical Corrigendum:2002	1994-12	Accuracy (trueness and precision) of measurement methods and results - Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method
ISO 9096:2003	2003-02	Stationary source emissions – Manual determination of mass concentration of particulate matter

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[2] In fact it is not correct to give a concentration or to give concentration ranges for “tar” (see also its definition in Chapter 3). This Standard is designed and is evaluated to measure tar and particles in the following concentration ranges:

Gravimetric tar	50 mg/m$_n^3$ to 300 g/m$_n^3$
Sum of GC-detectable tars	1 mg/m$_n^3$ to 300 g/m$_n^3$
Particles	5 mg/m$_n^3$ to 30 g/m$_n^3$

[3] The performance characteristics in Chapter 14 are determined under atmospheric conditions. Under pressurised conditions, the Standard as a whole is not evaluated. However, sampling under pressurised conditions is based on relevant experience (relevant construction details of probes are mentioned in a Technical report [TECHNICAL REPORT]) and the analysis of the liquid samples is identical for atmospheric and pressurised gasification. Therefore, pressurised conditions are included in this Standard.

3 Terms and definitions

For the purposes of this Technical Specification, the following definitions apply:

3.1
Aerosols
A suspension of solid or liquid particles in a gas. The term aerosol includes both the particles and the suspending gas. The particle size may range from about 0,002 to more than 100 µm

3.2
Biomass
Material of biological origin excluding material embedded in geological formations and transformed to fossil.

Note: This definition is the same as the definition of biomass in CEN TC 335 Solid Biofuels

3.3
Contaminated biomass
Biomass not being uncontaminated biomass (see uncontaminated biomass)

3.4
Downdraft gasification
A gasification process in which a bed of solid carbon-based material moves slowly downward under gravity as it is gasified, whilst the gasification agent (e.g., air or oxygen) passes through the bed co-currently. The product gas leaves the gasifier at the bottom

3.5
Entrained flow gasification
A gasification process in which carbon-based material is fed co-currently with the gasification agent (e.g., air or oxygen), where the velocity of the gasification agent is sufficiently high to maintain entrainment of the carbon-based material

3.6
Fluidised bed gasification
A gasification process in which carbon-based material is fed into a suspended (bubbling) or circulating hot bed of inert particles (e.g., sand or ash), the suspension or circulation being created by the gasification agent (e.g., air or oxygen)

3.7
Gasification
Thermal conversion of carbon-based materials into a product gas composed primarily of CO, H_2, methane and lighter hydrocarbons in association with CO_2, H_2O and N_2 depending on the specific gasification process considered.
Gasification can be accomplished by direct internal heating provided by partial oxidation using substoichiometric air or oxygen. Alternatively, concepts using either indirect heating methods or autothermal methods using exothermic reduction reactions may be applied

3.8
GC detection limit
text of the definition

3.9
Gravimetric tar
Evaporation/distillation residue from particle free sampling solution(s) determined by gravimetric analysis.

3.10
Isokinetic sampling
text of the definition

3.11
Organic compounds
Generic term for individual organic compounds listed in Annex A.1

3.12
Particles
Solid residue from particle filter after solvent extraction or solid residue from filtration of sampling solution(s). Solid residue may contain a small amount of insoluble polymerised tar

3.13
Product gas
Gas resulting from gasification. The product gas from biomass gasification can be used as a fuel (then also named fuel gas or producer gas) in internal and external combustion engines, fuel cells, and other prime movers for heat and mechanical or electrical power. Alternatively, the product gas may be used as a feedstock (then also named synthesis gas or syngas) for the petrochemical and refining industries, e.g. for the production of fuel liquids or chemicals

3.14
Pyrolysis
Thermal decomposition in the absence of an oxygen source such as air, oxygen, H_2O or CO_2

3.15
Sampling train
The equipment used for sampling particles and tars, which are the particle filter, the impinger bottles, the pump and flow measuring equipment and all connecting tubes

3.16
Soxhlet extraction
Batch extraction method at the boiling point of the used solvent and atmospheric pressure

3.17
Standard conditions
273,15 K, 101325 Pa = 1,01325 bar, dry

3.18
Tar
Generic (unspecific) term for entity of all organic compounds present in the gasification product gas excluding gaseous hydrocarbons (C1 through C6)

3.19
Uncontaminated biomass
Biomass from the following sources:

- Products from agriculture and forestry;
- Vegetable waste from agriculture and forestry;
- Vegetable waste from the food processing industry;
- Wood waste, with the exception of wood waste which may contain halogenated organic compounds or heavy metals as a result of treatment with wood preservatives or coating, and which includes in particular such wood waste from construction- and demolition waste

Note: This definition reflects the biomass that falls - as solid biofuels - under the scope of CEN TC 335 Solid Biofuels

3.20
Updraft gasification

A gasification process in which a bed of solid carbon-based material moves slowly downward under gravity as it is gasified, whilst the gasification agent (e.g., air or oxygen) passes through the bed counter-currently. The product gas leaves the gasifier at the top

4 Symbols and abbreviations

BTX	:	Benzene, Toluene and Xylenes
GC-FID	:	Gas Chromatography – Flame Ionisation Detector
GC-MS	:	Gas Chromatography – Mass Spectrometer
ID	:	Internal diameter
m_n^3	:	cubic metre at Normal conditions
m/z	:	Molar mass-to-charge ratio
MW_{th}	:	Mega Watt based on the thermal input of the biomass
PAH	:	Polycyclic Aromatic Hydrocarbons
PTFE	:	Polytetrafluoroethene
ppm	:	parts per million

NOTE The designation of the variables RF, M and A is explained just below the equations in which they are used.

5 Principle of the test method

5.1 Introduction

The principle of the test method is based on the discontinuous sampling of a gas stream containing particles and organic compounds (tar) under isokinetic conditions. The determination of particles and tars in biomass gasification product gases is carried out in two steps: sampling and analysis.

Please note that not all of the tar constituents are amenable to GC analysis, because of the presence of high molecular weight material, thermal labile or extreme polar compounds. GC analysis will usually determine more than 80% of the tar, the remainder being e.g. high-molecular weight material of >350 g/mol. Only for updraft gasifier tars, this fraction may be considerably lower.

5.2 Sampling

5.3 Analysis

The samples are analysed in a laboratory. The particle filter containing the particle sample is Soxhlet extracted in order to remove adsorbed tars. Subsequently the amount of particles is determined gravimetrically. The tars from the Soxhlet extraction are added to the liquid tar samples. If required, the liquid tar samples are filtrated for removal of solid matter.

For tars two analysis methods are given in this Technical Specification, analysing respectively gravimetric tar and gas chromatographable tar. The user is free to choose either one or both methods, depending on the kind of information needed. The users attention is drawn to the fact that the two values are not supplementary, but that there is an overlap between the two tar values.

5.3.1 Gravimetrical determination

Part of the homogeneous liquid sample is evaporated under well-defined conditions, the evaporation residue is weighed. The result is then recalculated to the amount of gravimetric tar in mg per m_n^3.

5.3.2 Gas chromatography

Part of the liquid sample is injected on a gas chromatograph (GC). This analysis results in concentrations of individual tar compounds and of the sum of GC-detectable tars, both in mg per m_n^3.

Positive identification of the condensed material as biomass tar is performed using GC-MS. The presence of tar is indicated typically by the presence of the US-EPA suite of PAH compounds, phenols and BTX. Quantitative determination of each compound is performed either by GC-MS or GC-FID analysis using internal standards.

6 Reagents

6.1 Solvent for tar collection and Soxhlet extraction

Isopropanol (2-propanol or isopropylalcohol) is the solvent used in this Technical Specification for tar collection, for Soxhlet extraction and for sample preparation and analysis. The minimum purity of the isopropanol is 99%. Verify with a blank GC determination that the solvent does not contain GC detectable amounts of relevant tar compounds.

Ethanol is used in gravimetric analysis procedure to remove trace water from evaporation residue (gravimetric tar). The required minimum purity is 99%.

Other solvents like ethanol, acetone or dichloromethane (DCM) are only used for cleaning of the glass and PFTE equipment.

6.2 Carrier gas in gas chromatography

Helium or other suitable gas as specified by the instrument manufacturer.

6.3 Calibration standards

Insert a description of pureness of the standards ***analytical grade, > 99% ???****
The tar compounds are named in Annex A.2 and Annex B.

7 Equipment

7.1 Equipment for sampling

7.1.1 Description of sampling principle

The equipment for sampling consists of a heated probe, a heated particle filter, a condenser, a series of impinger bottles containing a solvent for tar absorption, and equipment for pressure and flow rate adjustment and measurement. Upstream of the condenser the tubes connecting these parts are heated in order to prevent tar condensation. Temperatures for heating the probe, filter and tubes were properly selected to avoid both condensation of tars and thermal decomposition of tars. Temperatures of the condenser and the impingers were properly selected to ensure quantitative collection of the tars. Tar collection occurs both by condensation and absorption in the condenser and in the impingers and by capturing of aerosols in glass frits.

The sampling equipment consists of 4 main modules and respective submodules. The main modules are gas preconditioning, particle collection, tar collection and volume measurement. These modules are shown in Figure 7-1. The basic equipment of these modules is mentioned in the next paragraph in Table 1. A more detailed description of each module is found elsewhere [TECHNICAL REPORT = GUIDELINE].

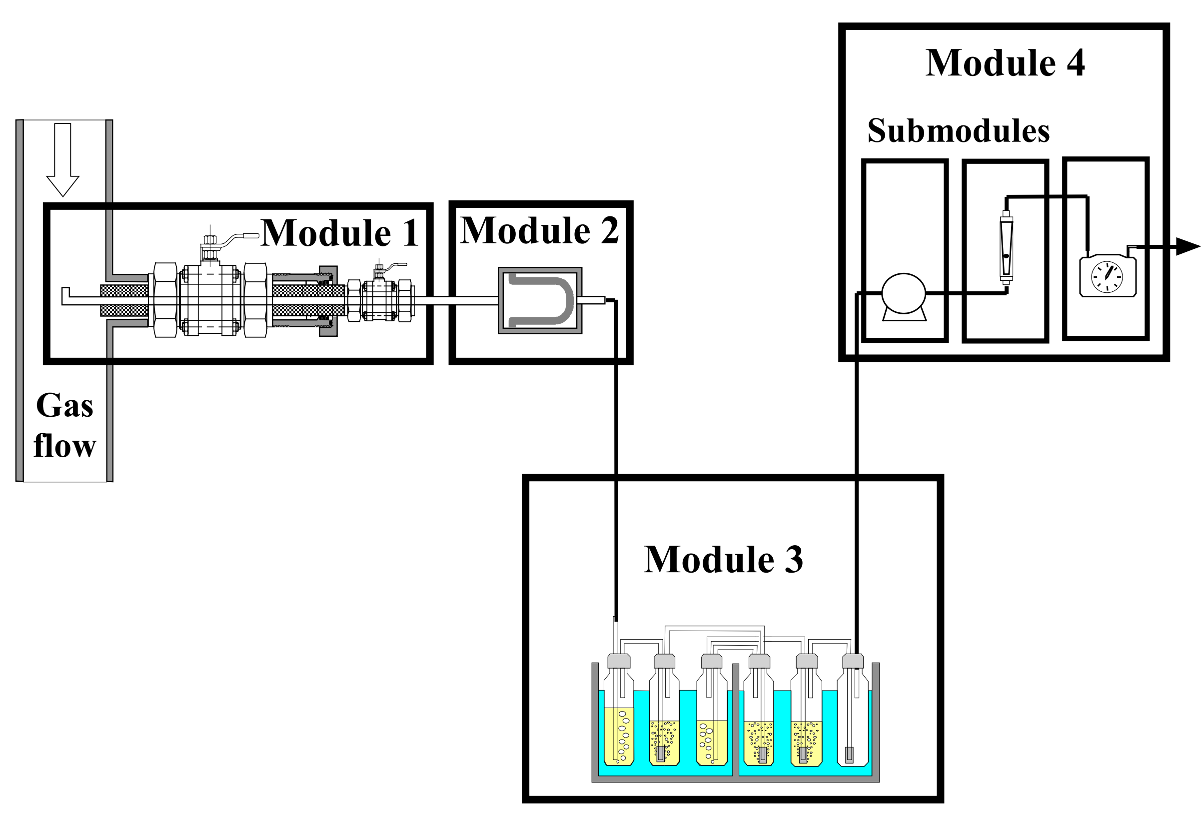

Figure 7-1 Concept of the modular sampling train.

7.1.2 Equipment for sampling

The equipment needed for sampling is mentioned in Table 1. Examples and details on construction are described elsewhere [TECHNICAL REPORT = GUIDELINE], including the adaptations needed for module 1 if tars and particles have to be sampled from pressurised gasifiers.

Table 1 - General description of modules and submodules with purpose and equipment used

	Function	**Main equipment**
Module 1 (Gas preconditioning)	Gas cooling, pressure letdown	Nozzle, valves, sampling lines
Module 2 (Particle collection)	Separation and collection of solids	Heated filter (high temperature)
Module 3 (Tar collection)	Moisture collection and partial tar condensation	Condenser with solvent (1 impinger bottle)
	Tar collection	Impingers with solvent (4 impinger bottles, some with glass frits)
	Drop collection	Empty impinger (1 bottle with a glass frit)
Module 4 (Volume sampling)		
SubModule 4.1	Gas suction	Pump
SubModule 4.2	Gas volume integration	Gas meter, needle valve (adjustment and control of flow rate), rotameter (flow indication), pressure gradient and temperature indicators, barometer
SubModule 4.3	Vent/exhaust gas handling	Outdoor ventilation

NOTE: After ECN has performed a comparison of impinger bottles and Petterson column, then:
- these are evaluated and discussed in group (Rome or at forehand by e-mail)
- if comparison proves to be good: we decide that Petterson column can be alternative in Technical Specification;
- then, DTI + VTT + ECN write report with (1) description Petterson column and (2) results comparisons at DTI, VTT and ECN. This report will later be issued as a Technical Report under this Task Force;
- finally, the Technical Specification will be updated (to leave choice for either impinger bottles or Petterson column), making reference to the Technical Report.

7.1.3 Requirements for sampling equipment

The sampling equipment shall meet the following functional requirements:

- The equipment including the solvent impingers is designed for flow rates between 0,1 and 0,6 m_n^3/h.
- The sampling equipment allows isokinetic sampling according to ISO 9096. If only tars are analysed, isokinetic sampling is required in all cases except for pressurised gasifiers, large-scale gasifiers with large pipe diameters (for example in ISO 9096 duct diameter must be < 0,35 m for only 1 sampling point) and if only tar is sampled while the temperature of the gasification product gas at the sampling site exceeds 350°C. Isokinetic sampling demands an undisturbed gas flow. Recommendations on how to measure isokinetically according to ISO 9096 are given elsewhere [TECHNICAL REPORT = GUIDELINE].
- The equipment is gas tight.
- The minimal nozzle diameter is 4 mm according to ISO 9096. For isokinetic sampling, the nozzle is designed according to ISO 9096.
- Temperatures of the sampling line and the particle filter are:
  - between 100 and 125°C for updraft gasification;

  - between 300 and 350°C for downdraft and fluidised-bed gasification.

- Gas flow rates in the sampling lines are higher than 25 m/s to avoid particle deposition.

- The material of the filters (absolute filters) shall be quartz. Retention capacity of the filters is at least 99,998 % of the particles of size 0,3 μm (DOP standard[4]).

- The type of filter depends on the particle concentration:
  - below 20 mg/m_n^3 plate filters are used with a minimum diameter of 90 mm;
  - above 20 mg/m_n^3 thimble filters are used.

  If the particle concentration cannot be estimated at forehand, use a thimble filter or take a test sample and estimate the particle concentration.

  Select the dimensions of filter thimbles to be suitable for subsequent Soxhlet extraction. The recommended dimensions for the filter thimble are a diameter of 30 mm and a length of 77 or 100 mm. As a general indication, a filter surface area of 100 cm^2 allows the collection of several grams of particles without significant increase in pressure drop over the filter. This is valid for sample flows of 0,6 m^3_n/h and for gasification product gases containing high temperature tar.

- The material of the probe and filter holder shall not affect the composition of tar compounds and shall endure 50°C higher temperature than the operating temperature is (e.g. AISI 310, AISI 316).

- A thermocouple is placed inside the filter holder to measure the gas temperature at the filter.

- Tar collection is performed with 6 impinger bottles of which the first acts as a condenser for water. Standard impinger bottles of 100 or 250 ml are used. Use impinger bottles of 250 ml for gas flow rates. > 0,3 m^3_n/h. Impinger bottles 1, 2, 3, 4 and 5 contain approximately 50 ml of solvent, impinger bottle 6 is empty. With high moist gas, a large amount of condensate will be generated thus requiring a large condenser.

- The solvent in the liquid impingers is isopropanol.

- Choose one of the two setups for the 6 impinger bottles. The alternative setup is only used when the pressure drop over the impinger bottles is too high or when, for safety reasons, it may never become high. When using the alternative setup, the user shall verify the collection efficiency over the impinger bottles.

  Standard setup

  - Impinger bottles 2, 3, 5 and 6 contain glass frits. These frits are placed either as a filter at the end of the inner tube, or are placed around the inner tube covering the rest of the diameter of the impinger bottle. G3 frits shall be used, if this results in a too high pressure drop over module 3, use G2 frits.

  - The temperature of impinger bottles 1, 2, and 4 is between 35 and 40°C, the temperature of impinger bottles 3, 5 and 6 is between -15 and -20°C.

  Alternative setup

  - The impinger bottles do not contain glass frits.

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[4]:The test method was developed in USA during World War II. DOP is Bis(2-ethylhexyl) Phthalate and is (like other Phthalates) an undesirable compound according to National and EU environmental rules. The most common test aerosols nowadays are Latex particles or DEHS Di (2-ethylhexyl) Sebacate or DOS Dioctyl Sebacate. The term ‘DOP test’ is used in everyday language, but DOP is not used any more.

  - The temperature of impinger bottles 1, 2, 3 and 4 is between 35 and 40°C, the temperature of impinger bottles 5 and 6 is between -15 and -20°C.

- The gas suction pump is oil-free and air-tight with minimal pulsation. It is able to displace at least 1 m^3_n/h at an absolute pressure of 50000 Pa.

- The dry gas meter with thermocouple is calibrated. The pressure drop over the volume-measuring device does not exceed 250 Pa.

7.2 Equipment for sample pretreatment and analysis

7.2.1 Equipment for gravimetric analysis

- Soxhlet apparatus
- Standard rotary evaporator with pressure indicator
- Desiccator
- Calibrated analytical balance with a resolution of at least 0,1 mg, 0,01 mg is preferable
- General laboratory equipment as volumetric flasks and measuring cylinders

7.2.2 Equipment for gas chromatography

- Soxhlet apparatus
- Gas Chromatograph-Mass Spectrometer (GC-MS) or Gas Chromatograph – Flame Ionisation Detector (GC-FID) High resolution gas chromatographs. MS: Bench top mass spectrometer with mass range of 20-400 m/z.
- Integration software package (usually included with GC)
- Column – non-polar capillary GC column, for example DPDM-siloxane (5%diphenyl + 95% dimethyl) copolymer phase. Dimensions are typically 30 to 60 m length, 0,25 mm id., film thickness 0,25 µm
- Calibrated analytical balance with a resolution of at least 0,1 mg, 0,01 mg is preferable
- General laboratory equipment as volumetric flasks, measuring cylinders, syringes and pipettes, all calibrated according to relevant National Standards
- Ferrules made up of no more than 49% graphite (e.g. 60% polyimide/40% gragphite) shall be used at teh GC column injection inlet to avoid possible adsorption of tar compounds.

8 Preparation of sampling equipment

8.1 Preconditioning of filter thimbles or plates

- Dry the quartz thimble or plate filter in an oven at 110°C at atmospheric pressure overnight (according to ISO 9096).
- Remove the filter from the oven and wrap it directly in aluminium foil.
- Allow to acclimatise in a desiccator at room temperature. Weigh the filter plus aluminium foil using an analytical balance with an accuracy of ± 0,1 mg.
- Weigh the aluminium foil on the same analytical balance and calculate the weight of the filter.
- Mount the filter and heat the filter holder to its set value.

8.2 Cleaning of equipment

IS THIS CHAPTER NOT TOO DETAILED? CAN WE NOT JUST REFER TO GOOD LABORATORY PRAXIS?

Before using the equipment in connection with a site measurement, all glass equipment shall be cleaned according to an internal laboratory instruction. Oil or tar contaminated glass equipment shall be put to soak in an alkaline bath (pH 11-12) for 24 hours. After this the glass parts shall be washed in a laboratory dishwasher with the following program:

- Primary rinse with soften water
- Wash at 85°C for 45 minutes.
- Rinse 4 times with demineralised water.

After this, the glass parts shall be heated in an oven to 500°C for 2 hours in order to remove possible organic residue on the glass.

After cooling, the glass parts shall be sealed with plastic wrap (parafilm).

PTFE hosing and impinger bottles are rinsed with isopropanol (or with another solvent like DCM and/or acetone to remove yellow-coloured tar residues) under safe laboratory conditions until the tubes appear clean. From time to time, the cleaning procedure is checked by analysis of rinsing liquid. OR DO WE HAVE TO RUN A BLANK DETERMINATION? After washing, the tubes are sealed with plastic wrap (parafilm).

8.3 Preparation of impinger bottles

- Add approximately 50 ml of solvent in each impinger.
- Place the drop-collecting bottle after the impingers and heat or cool the impingers to the appropriate temperature.

Cooling shall be performed by a mixture of ice/salt/water, by a mixture of isopropanol/dry ice or by cryostatic cooling of isopropanol. When using an ice/salt/water cooling mixture, make sure that the mixture is wet. Allow 30 minutes for cooling of the impinger bottles from room temperature to the sampling temperature of -20°C.

8.4 Sampling train leak test

8.4.1 Introduction

Prior to sampling a leak test shall be performed. Choose one of the two ways to perform this test: pressurising or underpressurising the entire sampling train:

8.4.2 Pressurising the entire sampling train

- Gently feed nitrogen or compressed air from a cylinder into the particle filter inlet and the rest of the sampling train, up 0,2 bar above the maximum sampling over pressure during sampling. The exit of the gas pump shall be locked by a ball valve.
- Monitor the pressure in the sampling line by a pressure indicator. The pressure shall stay constant.
- Possible leaks are detected as gas bubbles in the impingers or by leak indicators.
- Stop the gas supply from the cylinder and carefully open the shutoff valves after the pump. This pressure release procedure shall be undertaken with utmost care and generally lasts for at least one minute.

8.4.3 Underpressurising the entire sampling train

- Place a shut-off valve in a closed position at the inlet of the particle filter.
- Turn the gas pump on and reduce the pressure gently to a pressure of 0,2 bar below the minimum sampling under pressure.
- Possible leaks are detected as gas bubbles in the impingers or by monitoring the gas meter reading.
- Terminate the leakage test by carefully opening of the ball valve at the particle filter inlet while the pump is still displacing. When gas bubbles penetrate the condenser and the impingers, reduce the gas flow rate by gently opening the bypass valve over the pump. The pressure release procedure shall be performed with utmost care and generally lasts for at least one minute.

9 Procedure for sampling

9.1 Introduction

WARNING – The gas is harmful for your health and it may be explosive. The sample port and the sample equipment shall be gas tight. The exhaust gas from sampling shall be burned or conducted to the open air in a way so that no inconvenience arises.

Measurements are performed during stable and known operating conditions of the gasifier. The characteristic operating conditions (such as heat rate, gas production rate, fuel type) during the sampling are recorded, examples of sampling logs are given elsewhere [TECHNICAL REPORT = GUIDELINE]. The volume, temperature, pressure, and gas flow rate through the equipment are measured after the impinger bottles. It is preferred that these are measured and recorded continuously.

In general, sampling of tar and particles is performed simultaneously except for pressurised and/or large-scale gasifiers (>20 MW_{th}) where a sampling strategy based on separate sampling of tar and particles is applied. In pressurised processes, isokinetic operating conditions would require much higher sampling flow rates than 0,6 m_n^3/h when using the minimal nozzle diameter of 4 mm. Hence tar sampling is performed non-isokinetically for pressurised gases.

Isokinetic sampling is also not necessary when only tar is sampled and when the gas temperature under study at the sampling site exceeds 350°C. Such temperatures generally safely avoid tar condensation in the form of aerosols and/or droplets and also minimises adsorption of organic compounds on particles.

9.2 Sampling procedure

1. Record the gas meter reading and record the starting time. Turn the probe tube until the nozzle faces directly upstream, open the stop valve, start the vacuum pump and start the timing device. Then adjust the control valve to give the required flow reading as calculated according to nozzle size, gas velocity, etc.
2. Monitor the rotameter, which is used as an indicator of the gas flow and the static pressure measurement at the gas volume meter. Adjust the control valve as necessary throughout the sampling period to maintain isokinetic sampling. Record the temperature and static pressure at the gas volume meter (calculated from the pressure gradient over the gas volume meter and from atmospheric pressure) at regular intervals. During sampling check the temperature of the impinger cooling bath and the temperature of the filter housing.
3. Occasionally agitate the condenser cooling liquid and the impingers to ensure even temperature distribution in the cooling media.
4. When an adequate quantity of tar and particles is collected or if the pressure drop in the sampling train prevents isokinetic sampling, the sampling is terminated (see next paragraph).
5. Stop the vacuum pump, close the stop valve in the sample line, stop the timing device and turn the probe tube through 90°. Dismantle the particle filter.
6. Record the time for stopping and the gas volume meter; as soon as possible remove the filter cartridge from the filter housing and store it in solvent in a tightly closed bottle, to avoid polymerisation of tar during cooling.

7. Clean the sample line (see paragraph 8.2): Wash all surfaces (including metal surfaces) contacting the gas, at temperatures lower than the process temperature, with the solvent. Combine the washes with the actual sample. This is easy to arrange in atmospheric processes, but very difficult in pressurised systems. Prepare the impinger bottles for subsequent analysis (see paragraph 8.3).
8. Immediately after sampling, decant the content of the impinger bottles into a storage bottle. Rinse the impinger bottles with solvent and pour rinsing solvent into the storage bottle.
9. Flush the probe with N_2 if the probe is not removed. A procedure for removal of the probe is given elsewhere [TECHNICAL REPORT = GUIDELINE].

9.3 Duration of sampling

The actual gas volume to be collected for a good sample depends on the concentration of tar in gasification product gas. The recommended minimal sampling volume is 0,1 m_n^3 for all gasification product gas types. The total content of tar in the solution shallbe at least 100 mg/ (kg of solution) for gravimetric analysis and about 10 mg/(kg of solution) (10 ppm) for each compound analysed by GC (although the GC detection limit is significantly lower for single compounds). It is recommended to aim for concentrations in the sample that are higher by a factor of 10-100.

With high concentration measurements (tar concentration above 1 g/m^3_n) the calculated minimum sampling time for collection of an adequate quantity of tars can be < 30 minutes. In this case it is recommended to sample more than the minimum amount of tars required. For isokinetic sampling it is generally recommended to select the largest possible nozzle and highest flow rate. If the particle filter clogs up within 30 minutes however, the sampling should be stopped and a new sample should be started with smaller nozzle and lower sample flow rate, but still in accordance with isokinetic sampling.

In connection with low concentration measurements it is recommended to use the largest nozzle possible and the highest allowed sampling flow rate, also in accordance with isokinetic sampling. If possible, extend the sampling period so that at least the minimum recommended concentrations of tar in the solution are obtained.

10 Storage of samples

The sampling solution shall be stored in a sealed, dark bottle, which shall be marked with a clear identification label and kept at a temperature < 5 °C until analysis. When oxygenated tars are expected (e.g. in raw gases of updraft gasifiers) store the solution in a sealed, dark bottle under nitrogen atmosphere. Perform and complete the analysis as soon as possible and within a month of sampling. A glass bottle may be used in place of a dark bottle, provided it is kept in the dark.

Handle the particle filter with great care. When removing the filter from the housing it is imperative that no particles are added to or dropped from the filter. It is also imperative that no filter material is lost during handling.

Store the filter cartridge in isopropanol in a jar with a sealed screw cap. Mark the storage jar with a clear identification label and keep it at a temperature < 5 °C until analysis.

Store plate filters in a sealed petri dish of a suitable diameter.

11 Preparation of analysis

11.1 Introduction

Tars are analysed by standard gas chromatographic (GC) analysis methods that are used for the detection of aromatic hydrocarbons. The fundamentals of GC analysis is described in VDI 2457 Part 1.

The analyst chooses the operating conditions of the GC analysis to accommodate the requirements of the GC-MS or GC-FID and the type of column fitted. Typical operating conditions for analysis of tar are:

GC column conditioning	Temperature at heating rate of 8°C min^{-1} up to 325°C Total run time 45 minutes
Injector temperature:	275°C programme of 30°C up to 300°C at a rate of 3°C min^{-1} with a final hold temperature of 1 hour
Carrier gas:	Helium
Pressure:	Depends on the detector and column length
Flow rate of carrier gas:	1-2 cm^3/min
Split ratio:	typically 75:1 (ratio depends on sensitivity of instrumentation and sample concentration)
Injection volume:	typically around 1 μl, depending on the injection port, temperature and pressure
Oven programming:	Initial isothermal at 50°C for 5 minutes Temperature programme at heating rate of 8°C min^{-1} up to 325°C Total run time 45 minutes
Injector temperature:	275°C
Detector temperature	Depends on the detector (FID: the same temperature as the highest temperature in oven programme, MS: the temperature is specified by the manufacturer)

The analyst chooses the compounds that are used for external and internal calibration. Compounds that have been used successfully as calibration compounds for analysis of biomass tar compounds are:

	GC-FID	GC-MS
Internal Calibration	n-decane, n-dodecane, o-Terphenyl	phenanthrene-d$_{10}$, benzene-d$_8$, phenol-d$_6$, or benzopyrene-d$_{12}$
External Calibration	Compounds listed in Annex B1	Compounds listed in Annex B1

Examples of how to prepare calibration standards can be founds elsewhere [Technical Report]. This Technical Specification only gives the requirements for the calibration standards and leaves the procedures to the analyst who will use own experience and/or the examples mentioned.

11.2 Requirements for calibration standards of GC-FID and GC-MS

The calibration standards of GC-FID and GC-MS shall meet the following functional requirements:

- Internal calibration standard solutions shall be prepared from pure or – if available – certified standard materials and shall be prepared in isopropanol;
- If the calibration standard compound is a suspected carcinogen, primary dilutions of this material shall be undertaken in a fume cupboard;
- All internal calibration standards shall be stored in amber teflon-sealed screw-cap bottles in a refrigerator;
- All internal calibration standards shall be replaced after six months or if comparison with check standards indicates a problem;

- External calibration standards shall be made up from pure or – if available – certified compounds listed in Annex B1 and shall be prepared in isopropanol;
- External calibration standards shall be prepared at between three and five concentration levels for each compound of interest. The lowest concentration level shall be near the detection limit;
- Unless the manufacturer's information or stability trails indicate otherwise, the calibration standards solutions shall be stored in the dark between 0 and +4°C.

12 Analysis procedures

12.1 Soxhlet extraction procedure

Prior to the particle and tar analysis, the particle filters are Soxhlet extracted in order to remove tars from the particles and in order to add these tars to the tar samples.

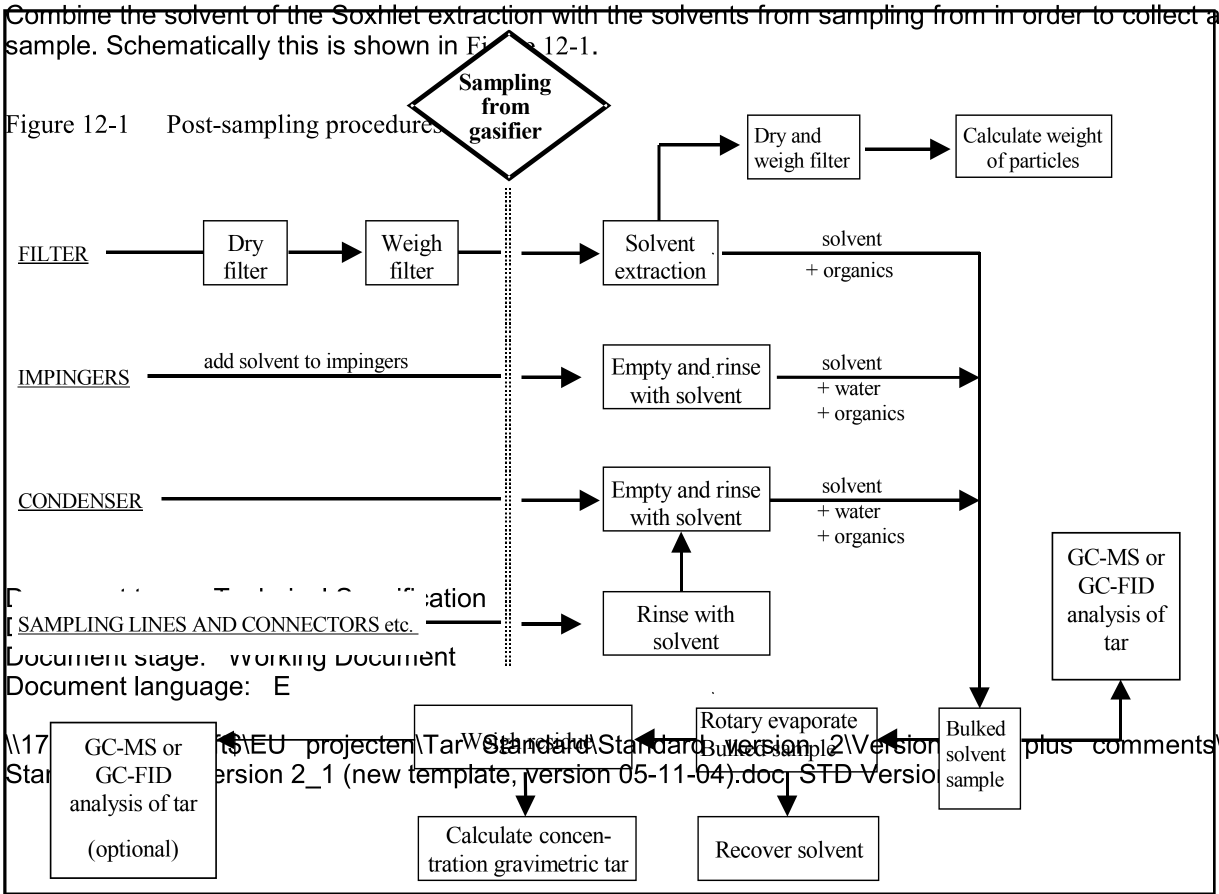
- Transfer the thimble or plate filter to the Soxhlet apparatus. Keep it in the vertical position to avoid loss of particles. Carefully add the appropriate amount (250-500 ml) of isopropanol to the Soxhlet apparatus. Extract the filter until the drops of isopropanol are clear, but at least 6-8 hours. Note that at low tar concentrations salts dissolving from the filter might influence the concentration of graphimetric tar. Therefore, when low tar concentrations are to be expected, limit the extraction to 8 hours maximum.
- Remove the filter from the Soxhlet and keep in the vertical position. To determine the particle concentration of the gas, follow the procedure described in paragraph 12.3.
- Add the isopropanol solution from the Soxhlet extraction procedure to the sample collected from impinger bottles. Record the volume/weight of this bulk sample.

Run a blank sample (i.e. a fully prepared filter which has not been used) in parallel to the used filter for quality control purposes. This ensures that there are no contributing error factors from the Soxhlet procedure. **QUESTION OF JOHN TO R&D group: DE WE DO THIS IN PRACTICE ?**

12.2 Combination of solvents

Combine the solvent of the Soxhlet extraction with the solvents from sampling from in order to collect all tars in one sample. Schematically this is shown in Figure 12-1.

Figure 12-1 Post-sampling procedure



12.3 Determination of particle mass

- The same drying and weighing procedure is used for sample analysis as the one used for the initial preparation of the filters, described in paragraph 8.1.
- After Soxhlet extraction, dry the quartz thimble or plate filter in an oven at 110°C at atmospheric pressure overnight (according to ISO 9096).
- Remove the filter from the oven and wrap it directly in aluminium foil.
- Allow to acclimatise in a desiccator at room temperature. Weigh the filter plus aluminium foil using an analytical balance with an accuracy of ± 0,1 mg.
- Weigh the aluminium foil on the same analytical balance and calculate the weight of the filter plus particulate material.
- Calculate the mass of particulate matter collected by subtracting the initial filter weight from the sampled filter weight. Calculate the concentration of particles in the gasification product gas in g/m_n^3 by using the volume of gas sampled and the temperature & pressure readings.

12.4 Determination of gravimetric tar mass

The mass of gravimetric tar is determined by means of solvent distillation and evaporation, as follows:

- Use the combined tar solution from Paragraph 12.2.
- Use a standard rotary evaporator with a pressure indicator. Adjust the flow rate of water to reach a vacuum of 100 mbar (absolute pressure) with an empty flask.
- Use a 200 or 250 ml flask, dry it and acclimatise it in a dissicator for at least 1 hour. Then, weigh it with an accuracy of 1 mg or preferably 0,1 mg. Pour exactly 100 ml of the tar solution in the flask.
- Connect the flask to the rotary evaporator and start the evaporation with the water bath at 55°C. The vacuum will be higher than 100 mbar (absolute pressure) at the start and will gradually fall to 100 mbar (absolute pressure). Drops should fall from the cold finger at a rate of 1-2 drops per second. Once almost all solvent is evaporated, the rate of drops falling will decrease. With a stopwatch observe the time between two drops falling. Continue until there are at least four (4) seconds between two consecutive drops falling.
- After the latter of these two drops, continue the evaporation for a further fifteen (15) more minutes. If at this point traces of water are observed, remove the flask from the rotary evaporator, add 20 ml of ethanol and restart at the previous step (Connect the flask to the rotary evaporator and … etc). If no traces of water are observed, continue the evaporation for a further thirty (30) minutes while the sample is flushed with nitrogen. Adjust the nitrogen flow so that the vacuum does not exceed 350 mbar (absolute pressure).
- Remove the vacuum by letting in air and shutting off the nitrogen purge, then stop the rotation of the flask. Remove the flask from the heated water bath, dry it and acclimatise the flask in a dissicator for at least 2 hours. Weigh the flask accurately and calculate the amount of gravimetric tar as described in Section 9.

To determine the GC-detectable components in the gravimetric tars (optional) re-dissolve the tars as described in Paragraph 12.5.4 and perform a GC analysis.

12.5 Determination of individual tar compounds by GC–MS or GC-FID

12.5.1 Introduction

Tars are analysed by standard gas chromatographic (GC) analysis methods that are used for the detection of aromatic hydrocarbons. Examples of the procedures for sample preparation and GC-detection can be founds elsewhere [Technical Report]. This Technical Specification only gives the requirements for sample preparation and for analysis and leaves the procedures to the analyst who will use own experience and/or the examples mentioned.

WE HAVE TO DESCRIVE WHAT KIND OF CALIBRATION SHALL BE PERFORMED.
FOR INSTANCE THE WAY PAUL HAS DECRIBED: EITHER INTERNAL + EXTERNAL CALIBRATION OR EXTERNAL CALIBRATION ONLY (IS THIS VALID FOR GC-FID AS WELL AS FOR GC-MS?)

THE SECOND REQUIREMENT OF 12.5.3 INDATES THAT INTERNAL CALIBRATION IS OBLIGATORY !

12.5.2 Requirements for sample preparation using internal calibration standards

The sample preparation using internal standards shall meet the following functional requirements:

- Internal calibration shall not be performed when analysing a sample containing significant amounts of oxygenates or nitrogen containing compounds with GC-FID;

SHOULD THE ABOVE SENTENCE BE REMOVED (COMMENT VTT)?

- The concentration of the internal standard in the samples shall be exactly the same as in the external calibration standards, or a correction factor is required when calculating quantitative results;

12.5.3 Requirements for sample storage, analysis, identification of compounds, and reporting

- Until required for laboratory preparation, samples shall be stored in sealed containers protected from the light at temperature below 5^{o}C. Samples shall be extracted within one month after sampling has been completed. When oxygenated tars are expected (e.g. in raw gases of updraft gasifiers) the solution shall be stored in a sealed, dark bottle under nitrogen atmosphere;
- Prior to analysis, the sample shall be at room temperature and the sample shall be mixed thoroughly to insure homogeneity;
- No quantification of compounds shall be undertaken if no internal standard is used;
- The identification of compounds in a GC-FID quantitative analysis is based on retention times of the compounds. The retention times shall be determined by qualitative GC-MS analysis and shall be confirmed by internal standard;
- In case of uncertain identification in GC-FID analysis the identification of compounds shall be confirmed by GC-MS or the compound shall not be reported;
- Organic compounds that are not included in the external calibration may be reported semi-quantitatively by assuming a response factor of unity or taking an average response factor for type of compound;

12.5.4 Preparation of sample for GC-MS and GC-FID analysis

TO MY OPINION, THE PARAGRAPHS 12.5.4. AND 12.5.5 (WHICH WERE THE OLD 12.5.1 - 12.5.3) CAN BE REMOVED (apart from the fourth paragraph from here starting with GC-FID…) BECAUSE THIS IS STANDARD GC PRACTICE AND SHOULD BE DESCRIBED IN THE EXAMPLE IN THE TECHNICAL REPORT.

- Take 10 ml of the bulk sample solution (Paragraph 12.2) and add 10 µl of ISTD.
- Depending on the concentration of tar, dilute the sample with isopropanol to ensure that the concentration of organic compounds fall within the operation limits of the instrument. Always dilute *after* having added the ISTD.
- Shake the contents of volumetric flask. Transfer the sample into an amber teflon-sealed screw-cap bottle and store in a refrigerator until ready to use.

GC-FID or GC-MS analysis may also be performed with the tar residue from paragraph 12.4 to evaluate the overlap between gravimetric analysis and GC analysis. Note that part of tar has been evaporated during gravimetric evaporation procedure so the analysis of gravimetric tar residue cannot replace the analysis of the original solution. The sample shall be prepared as follows:

- Accurately weigh about 0,1 g of the tar residue into a 10 ml ground glass stoppered volumetric flask.
- Add 10 µl of ISTD, make up to the 10 ml mark with isopropanol and shake contents of volumetric flask.
- Depending on the concentration of tar, the sample shall be diluted to ensure that the concentration of organic components fall within the operation limits of the instrument. Always dilute after having added the ISTD.
- Transfer the sample into an amber teflon-sealed screw-cap bottle and store in a refrigerator until ready to use.

12.5.5 Analysis by GC-MS or GC-FID

- Prior to analysis allow the sample to reach room temperature.
- Inject approximately 1 µl of the bulk sample solution (see Figure 12-1) onto the GC column using a syringe.

12.5.6 Identification of compounds

This is based upon retention times in combination with mass spectra. **For GC-FID there has to be decided on the compounds used for identification.**

1. **Identification by retention time.** The width of the retention time window entered in the software program and used to make identifications shall be based upon measurement of actual retention time variation of standards. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

2. **Identification by mass spectrometry.** Set up the calibration software to search for the specified components based on their retention time and their mass spectrum. Identification of the compounds present in the total ion chromatogram is performed by comparison of the unknown spectra with the mass spectral library.

13 Calculation of results

13.1 Calculation of GC results

The results are calculated using the following equations.

The system software can be set up and used to automatically quantify the compounds analysed. Response factors can also be calculated manually using the following equation:

$$RF_c = \frac{A_c / A_{is}}{M_c / M_{is}}$$

where RF_c = Response factor for compound
A_c = Area of compound
A_{is} = Area of internal standard
M_c = Mass of compound
M_{is} = Mass of internal standard

The mass of each compound can be calculated using one of several methods:

i Automatically using the system software if an appropriate calibration file has been set up
ii Using a spreadsheet with response factors and manual input of peak areas
iii Manual calculations using response factors and peak areas:

$$M_c = \frac{A_c M_{is}}{A_{is} RF_c}$$

What about external calibration procedure?

Write a small paragraph on how to calculate concentration in mg/mn3 from Mc. Make a note: Generally, also the moisture content of the gas is determined thus a certain amount of condensate is required to accurately determine the gas moisture.

14 Performance characteristics

14.1 Introduction

This Standard gives methods for (1) sampling of organic compounds and particles from gasification product gases, and (2) analysis of organic compounds and particles in the samples taken. As the sampling is a critical part of the overall method, it is included in the evaluation of the performance characteristics. This cannot be done at several locations due to the fact that different biomass gasifiers yield different (and variable with time, biomass input etc) concentrations of tars. Therefore, the characterisation of the performance of this Technical Specification has been done in two steps:

A. Characterisation of the performance of the analysis procedures with Round Robin tests;
B. Characterisation of the performance of the whole Technical Specification by having several users sample tars with the Technical Specification at the same location and at the same time. The analysis results have been compared afterwards. This evaluation is referred to as “parallel tests with the whole Technical Specification”.

The remainder of this Chapter is subdivided into a paragraph 14.2 on the performance of the analysis methods (Round Robin tests) and a paragraph 14.3on the performance of the whole Technical Specification (parallel tests).

Different biomass gasifiers yield different set of tar compounds in varying concentrations, depending among other things on type of gasification process, gasification temperature, residence time and biomass input. However, gasification tars can be divided roughly into two categories based on tar formation temperature (gasification temperature), high temperature tar and low temperature tar.

High temperature tar is formed in processes like downdraft or fluidised bed gasification and it contains mainly non-polar aromatic compounds. Low temperature tar is formed in low process temperature which occurs for example in updraft gasification process. The matrix of low temperature tar is highly complex, meaning that the number of individual tar compounds present in gasification product gas is extremely high. The nature of low temperature tar is also different compared to high temperature tar as significant part of low temperature tar consists of polar compounds whereas high temperature tar contains remarkable amount of nonpolar aromatic compounds.

14.2 Performance of the analysis methods (Round Robin tests)

14.2.1 Introduction

Data on precision of the analysis methods were obtained by two series of Round Robin tests. The first series of Round Robin tests considered the analysis of individual organic compounds, the second series of Round Robin tests considered the analysis of gravimetric tar.

14.2.2 Round Robin tests on the analysis of individual organic compounds

Two series of Round Robin test for GC analysis were performed, the first with synthetic tar samples and the second with real tar samples taken from the product gas of a biomass gasifier.

Synthetic tar samples contained typical concentrations of 8 - 9 organic compounds which are often present in gasification product gas. Results from Round Robin tests with synthetic tar samples were used to make preliminary estimation of the precision for analysis method.

Real tar samples were collected from fluidised bed gasifier (high temperature tar) and from updraft gasifier (low temperature tar), in both cases from raw gasification product gas and from cleaned gasification product gas. 11 individual compounds listed in Annex B were to be analysed from the real tar samples. When the concentration of an individual compound was near or below detection limit it was not possible to determine its reproducibility and repeatability values. In addition, all organic matter detected by GC was to be determined (called total GC detectable tar) and calculated as naphthalene.

All analyses were performed by 6 laboratories, each laboratory making 3 or 6 determinations. These determinations were carried out under repeatability conditions as defined in ISO 5725-1; *i.e.* one operator, same apparatus, identical operation conditions, same calibration and a minimum period of time. From the values obtained, the repeatability and reproducibility were calculated according to the procedure specified in ISO 5725-2. The repeatability and reproducibility values for high temperature tar and low temperature tar are presented in Table 2. Repeatability and reproducibility values of low temperature tar are significantly higher than values of high temperature tar due to the complexity of the matrix of low temperature tar.

The reproducibility and repeatability limits presented in this standard are valid provided that following factors which affect to the accuracy of the method are satisfied:
- A professional GC-analyst shall be responsible of the implementation of analysis;
- The GC-program shall be selected to suit for the type of tar sample;
- Carefully performed calibration and correct identification of single compounds are crucial.

Data on which repeatability and reproducibility values are based is presented in more detail in

and Table 9 in of Annex C.1. The repeatability and reproducibility values of synthetic tar samples are given as additional information in Table 10 of Annex C.1although the data was not included in determination of repeatability and reproducibility of the analysis method.

Table 2 - Repeatability and reproducibility for the analysis of individual organic compounds and total GC-detectable tar.

Tar type	**Concentration range**	**Repeatability standard deviation**	**Repeatability limit**[2]	**Reproducibility standard deviation**	**Reproducibility limit**[3]
		s_r	**r**	s_R	**R**
	mg/dm^3	**%**	**%**	**%**	**%**
HIGH TEMPERATURE TAR					
Individual compounds	20 – 140	2.5	7.1	7.3	20
Individual compounds	1– 10	4.8	13	13	35
Individual compounds	0.2 – 0.3	17	47	28	78
LOW TEMPERATURE TAR					
Individual compounds	30 – 560	4.8	13	19	54
Individual compounds	2 – 8	8.2	23	28	80
TOTAL GC-DETECTABLE TAR[1]	300 – 6000	2.9	8.2	13	37
	5 – 50	10	28	74	210

[1] Calculated as naphthalene

[2] The difference between two test results found on the same sample by one operator using the same apparatus within the shortest feasible time interval will exceed the repeatability limit on average not more than once in 20 cases in the normal and correct operation of the method.

[3] Test results on the same sample reported by two laboratories will differ by more than the reproducibility limit on average no more than once in 20 cases in the normal and correct operation of the method.

14.2.3 Round Robin tests on the gravimetric analysis

Two series of Round Robin test were performed for the analysis method of gravimetric tar. All samples contained real tar from the product gas of a biomass gasifier. In the first test series the samples were same as the real tar samples in Round Robin test for GC method. However, the results were discarded due to differences in used evaporation procedures.

Samples of the second test series represented only tars from updraft gasifier. Samples were mixtures of heavy tar and aqueous tar in different ratios, dissolved in iso-propanol. Also the water content of the samples varied.

All analyses were performed by 6 laboratories, each laboratory making 3 or 6 determinations. These determinations were carried out under repeatability conditions as defined in ISO 5725-1; *i.e.* one operator, same apparatus, identical operation conditions, same calibration and a minimum period of time. From the values obtained, the repeatability and reproducibility were calculated according to the procedure specified in ISO 5725-2. The repeatability and reproducibility values for high temperature tar and low temperature tar are presented in Table 3.

Data on which repeatability and reproducibility values are based is presented in more detail in Table 11 of Annex C.2.

Table 3. Repeatability and reproducibility for the gravimetric analysis of tar.

Tar type	Concentration range g/dm^3	Repeatability standard deviation s_r %	Repeatability limit[1] r %	Reproducibility standard deviation s_R %	Reproducibility limit[2] R %
GRAVIMETRIC TAR	5 – 60	6.5	18	26	71

[1] The difference between two test results found on the same sample by one operator using the same apparatus within the shortest feasible time interval will exceed the repeatability limit on average not more than once in 20 cases in the normal and correct operation of the method.

[2] Test results on the same sample reported by two laboratories will differ by more than the reproducibility limit on average no more than once in 20 cases in the normal and correct operation of the method.

NOTE: No explanation has been found so far to explain what causes the differences between the laboratories.

It seems that the when the concentration decreases the standard deviation increases (see table in appendix). The concentration of gravimetric tar in RRT 2 samples were in 3 cases lower than any of the samples in round 3

. (REALTAR 1: 10–15 g/dm^3, REALTAR 2: 1–2 g/dm^3, REALTAR 3: 0.1–0.2 g/dm^3, REALTAR 4: 0-0.05 g/dm^3)

14.3 Performance of the whole Technical Specification (parallel tests)

WE HAVE TO DEFINE REPEATABILITY AND REPRODUCABILITY LIMILS FOR BOTH THE GRAVIMETRIC ANALYSIS AND THE GC ANALYSIS

15 Test report

The test report shall include at least the following information:

a) all information necessary for the identification of the sample, including:
  - date and time of sampling
  - the gasification conditions during sampling;
  - the sampling parameters (duration, flow rate, atmospheric pressure, any unusual features during sampling);
  - the sample preparation procedures and any unusual features during sampling preparation;
  - the laboratory performing the analysis and the date of the analysis;

b) a reference to this European Technical Specification (EN/TS …..:20**);

c) the results, and the form in which they are expressed;

d) any unusual features noted during the determination

e) any operation not included in this European Technical Specification, or any optional operation which may have influenced the results.

Document type: Technical Specification
Document subtype:
Document stage: Working Document
Document language: E

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Bibliography

[1] VDI 2457 – Part 1 - Gaseous emission measurement. Chromatographic determination of organic compounds. Fundamentals, 1997-11

[2] CEN/TS 14588: 2004 Solid biofuels. Terminology, definitions and descriptions

Document type: Technical Specification
Document subtype:
Document stage: Working Document
Document language: E

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Annex A
(informative)

Individual organic compounds in biomass gasification product gases

A.1 List of individual organic compounds

The next table gives the names, CAS-registry numbers and boiling points of individual organic compounds that are determined in biomass gasification product gases. The list of compounds as given by this table is not exhaustive. The list is given to specify the definition for “organic compounds” (see Chapter 3). The list is explicitly not a list of compounds to be determined by this Technical Specification, see also the leading text under Annex A.2.

Table 5 - List of individual organic compounds to be found in biomass gasification product gases

Group / common name	Other / (more) trivial name	Chemical Abstract Service (CAS) Registry Number	Boiling point (°C) (Handbook of Chemistry and Physics, vol. 77)
Acids			
Formic acid	Methanoic acid	64-18-6	101
Acetic acid	Ethanoic acid	64-19-7	117,9
Propionic acid	Propanoic acid	79-09-4	141,1
Butyric acid	Butanoic acid	107-92-6	163,7
Sugars			
Levoglucosan	1,6-amhydro-beta-D-Glucopyranose		
Alpha-D-Glucose	Alpha-D-Glucopyranose	604-68-2	Sub[1]
Beta-D-Fructose	Beta-Levulose	53188-23-1	
Cellobiosan			
Alcohols			
Methanol	Methyl alcohol	67-56-1	64,6
Ethanol	Ethyl alcohol	64-17-5	78,2
Aldehydes and ketones			
Formaldehyde	Methanal	50-00-0	-19,1
Acetaldehyde	Ethanal	75-07-0	20,1
Acetone	2-Propanone	67-64-1	56,0
2-Cyclopenten-1-one	Cyclopenten-3-one	930-30-3	136
(Methyl)- 2-Cyclopenten-1-one	(2- 3- 5-) methyl-2-cyclopenten-1-one	1120-73-6, 2758-18-1, 14963-40-7	157; 157,5; 140
Phenols			
Phenol	Hydroxybenzene	108-95-2	181,8
Cresols (o, m or p)	(2-, 3- or 4-)methyl-phenol	95-48-7, 108-39-4, 106-44-5	191,0; 202,2; 201,9
Xylenols	(2,3- 2,4- 2,5- 2,6- 3,4- or 3,5-) dimethylphenol	526-75-0, 105-67-9, 95-87-4, 576-26-1, 95-65-8, 108-68-9	216,9; 210,9; 211,1; 201,0; 227;, 221,7
Butylphenols	(2-, 3- or 4-)butyl-phenol	3180-09-4, 4074-43-5, 1638-22-8	235; 248; 248
Methylbutylphenols	2-butyl-4-methyl-phenol	6891-45-8	228

Naphthols	(1- 2-) Naphthol or -Naphthalenol	90-15-3, 135-19-3	288; 285
Methylnaphthols	4-methyl-1-naphthol, 1-methyl-2-naphthol	10240-08-1, 1076-26-2	166; 160
Guaiacols			
Guaiacol	2-methoxy-phenol	90-05-1	205
Creosol = 4-methyl-guaiacol	2-methoxy-4-methyl-phenol	93-51-6	221
Ethylguaiacol	2-methoxy-4-ethyl-phenol	2785-89-9	236,5
Eugenol	2-methoxy-4-(2-propenyl)-phenol	97-53-0	253,2
Isoeugenol	2-methoxy-4-(1-propenyl)-phenol	97-54-1	266
Furans			
Dimethylfuran	(2,4- 2,5-)dimethylfuran	3710-43-8, 625-86-5	94; 93,5
Furfural (2-furaldehyde)	2-Furancarboxaldehyde	98-01-1	161,7
Methyl Furfural	5-Methyl-2-furancarboxaldehyde	620-02-0	187
Furfuryl alcohol	2-Furanmethanol	98-00-0	171
Benzofuran	Coumarone	271-89-6	174
Methylbenzofurans	(2- 3- 5- 7-) methylbenzofuran	4265-25-2, 21535-97-7, 18441-43-5, 17059-52-8	197,5; 197; 198; 190,5
Dimethylbenzofurans	(2,5- 2,6- 2,7- 3,5- 3,6- 4,6- 4,7- 5,6- 5,7- 6,7-) dimethylbenzofuran	29040-46-8, 24410-51-3, 59020-74-5, 10410-35-2, 24410-50-2, 116668-34-9, 28715-26-6, 24410-52-4, 64965-91-9, 35355-36-3	220; 217,5; 216; 220,5; 222; 219; 216; 221; 222; 218
Dibenzofuran	2,2'-biphenylene oxide	132-64-9	287
Methyldibenzofurans			
Mixed oxygenates			
Glyoxal	Ethandial	107-22-2	50,4
Hydroxyacetaldehyde	(Hydroxyethanal, glycolaldehyde)	141-46-6	
Propanal-2-one	(methyl glyoxal, 2-oxopropanal, pyruvaldehyde)	78-98-8	72
Acetol	1-hydroxy-2-propanone	116-09-6	145,5
2-hydroxy-3-methyl-2-cyclopentene-1-one			
Methoxybenzene	Anisol	100-66-3	153,7
Dimethoxybenzenes	(1,2- 1,3- 1,4-) dimethoxybenzene	91-16-7, 151-10-0, 150-78-7	206; 217,5; 212,6
Trimethoxybenzenes	(1,2,3- 1,3,5-) trimethoxybenzene	634-36-6, 621-23-8	235; 255,5
Trimethoxyphenols			
Vanillin	4-hydroxy-3-methoxybenzaldehyde	121-33-5	285
Aromatic compounds			
Benzene		71-43-2	80,0
Toluene	Methylbenzene	108-88-3	110,6
Xylenes (o, m and p)	(1,2- 1,3- and 1,4-)dimethylbenzene	95-47-6, 108-38-3, 106-42-3	144,5; 139,1; 138,3
Ethynylbenzene		536-74-3	143
Styrene	Ethenylbenzene	100-42-5	145
4-Methylstyrene	1-ethenyl-4-methyl-benzene	622-97-9	172,8

Document type: Technical Specification
Document subtype:
Document stage: Working Document
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\\172.22.17.9\neeft$\EU projecten\Tar Standard\Standard version 2\Version 2_1 plus comments\CEN - Tar Standard - draft version 2_1 (new template, version 05-11-04).doc STD Version 2.1c

Indene (1H-Indene)	Indonaphthene	95-13-6	182
Methylindene	(1- 2- 3- 4- 6- 7-)methyl-1H-indene	767-59-9, 2177-47-1, 767-60-2, 7344-34-5, 20232-11-5, 7372-92-1	199; 206; 198; 209; 207; 209
PAHs (* indicate EPA list of 16 PAHs)			
Naphthalene*		91-20-3	217,9
(1- or 2-) Methylnaphthalene		90-12-0, 91-57-6	244,7; 241,1
Diphenyl	1,1-Biphenyl	92-52-4	256,1
Acenaphthylene*	Acenaphthalene	208-96-8	280; 150[2]
Acenaphtene*	1,2-dihydro-Acenaphthylene	83-32-9	279
Fluorene* (9H-Fluorene)	2,2'-Methylenebiphenyl	86-73-7	295
Phenanthrene*		85-01-8	340
Anthracene*		120-12-7	339,9
Fluoranthene*	1,2-(1,8-Naphthylene)benzene	206-44-0	384
Pyrene*	Benzo(def)phenanthrene	129-00-0	404
Benzo(a,b,c) fluorene	11H-Benzo(a)fluorene, ?, ?	238-84-6, ?, ?	405
Benzo(a)anthracene*	1,2-Benzanthracene	56-55-3	-
Chrysene*	1,2-Benzophenanthrene	218-01-9	448
Benzo(b*, j or k*) fluoranthene	B.(b)fl.=Benz(e)acephenanthrylene B.(j)fl.=Dibenzo(a,jk)fluorene B.(k)fl.=2,3,1',8'-Binaphthalene	205-99-2, 205-82-3, 207-08-9	-; -; 480
Benzo(a* or e)pyrene	(2,3- 1,2-)Benzopyrene	50-32-8, 85-02-9	-; 352
Dibenzo(a,h)anthracene*	1,2,5,6-dibenzanthracene	53-70-3	-
Perylene	Dibenzo(de,kl)anthracene	198-55-0	-
Indeno(1,2,3-cd)pyrene*			
Benzo(g,h,i)perylene*	1,12-Benzperylene	191-24-2	-
Dibenzopyrenes			
Anthanthrene			
Coronene		191-07-1	525
Nitrogen containing aromatics			
Pyridine	Azine	110-86-1	115,2
Methylpyridines, Picolines	(2- 3- 4-)Methylpyridine (2- 3- 4-)Picoline	109-06-08, 108-99-6, 108-89-4	129,3; 144,1; 145,3
Quinoline	1-Azanaphthalene	91-22-5	237,1
Isoquinoline	Benzopyridine	119-65-3	243,2

[1]: sublimates

A.2 List of most abundant individual organic compounds

The next table gives the names of individual organic compounds that are frequently reported in biomass gasification product gases. This list is more specific than Annex A and is mentioned to enable analysts being inexperienced with the composition of biomass gasification product gases, to identify the most abundant compounds. Please not that the Technical Specification is evaluated for this list of compounds (hence this is an informative list), Chapter 1 "Scope". In this table, compounds that are commonly measured are printed in standard style. Compounds that are analysed less frequently or occur in lower concentrations are printed in *italics.*

Table 6 - List of most abundant individual organic compounds.

Downdraft / Fluidised bed gasification	Pyrolysis and Updraft gasification
Phenols Phenol _Cresols (o, m or p)_ _Xylenols_ _(Methyl)Naphthols_ **Furans** **_Benzofuran_** _Methylbenzofurans_ _Dimethylbenzofurans_ _Dibenzofuran_ **Aromatic compounds** Benzene Toluene Xylenes (o, m and p) _Ethynylbenzene_ _Styrene_ Indene (1H-Indene) Methylindene **PAHs** (* indicate EPA list of 16 PAHs) Naphthalene* (1- or 2-) Methylnaphthalene Diphenyl Acenaphthylene* Acenaphtene* Fluorene* (9H-Fluorene) Phenanthrene* Anthracene* Fluoranthene* Pyrene* Benzo(a,b,c) fluorene _Benzo(a)anthracene*_ Chrysene* _Benzo(b*, j or k*)fluoranthene_ _Benzo(a* or e)pyrene_ _Dibenzo(a,h)anthracene*_ _Perylene_ _Indeno(1,2,3-cd)pyrene*_ _Benzo(g,h,i)perylene*_ _Dibenzopyrenes_ _Anthanthrene_ _Coronene_	**Acids** Formic acid, Propionic acid, Butyric acid Acetic acid **Sugars** Levoglucosan _Alpha-D-Glucose, Beta-D-Fructose, Cellobiosan_ **Alcohols and phenols** _Methanol, Ethanol_ Phenols, Cresols (o, m or p), Xylenols **Aldehydes and ketones** _Formaldehyde, Acetaldehyde_ _Acetone_ _2-Cyclopenten-1-one, (Methyl)- 2-Cyclopenten-1-one_ **Guaiacols** Guaiacol, Creosol (= 4-methyl-guaiacol) Ethylguaiacol, Eugenol, Isoeugenol **Furans** Dimethylfuran, Furfural (2-furaldehyde) Methyl Furfural, Furfuryl alcohol _(Methyl- or dimethyl-)benzofurans and dibenzofurans_ **Mixed oxygenates** Hydroxyacetaldehyde, Acetol, Vanillin Propanal-2-one, Glyoxal _2-hydroxy-3-methyl-2-cyclopentene-1-one_ _(di-, tri-)Methoxybenzenes, Trimethoxyphenols_ **Aromatic compounds** Benzene, Toluene, Xylenes (o, m and p) Ethynylbenzene Styrene Indene (1H-Indene), Methylindene **PAHs** (* indicate EPA list of 16 PAHs) Naphthalene* (1- or 2-) Methylnaphthalene _Diphenyl_ Acenaphthylene* _Acenaphtene*_ Fluorene* (9H-Fluorene) _Phenanthrene*, Anthracene*, Fluoranthene*, Pyrene*_

Nitrogen containing aromatics Pyridine Methylpyridines, Picolines (Iso)Quinonoline	**Nitrogen containing aromatics** (Methyl)pyridines, Picolines, *(Iso)Quinoline*

Annex B
(normative)

List of organic compounds for which precision data have been collected

The next table gives the names of individual organic compounds for which precision data (accuracy and reproducibility tests) are collected.

Table 7 - List of organic compounds for which precision data have been collected.

Organic compound
Pyridine
Toluene
Phenol
Indene
Guaiacol
Naphthalene
Acenaphthylene
4-methylguaiacol (Creosol)
Phenanthrene
Fluoranthene
Pyrene

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Annex C
(Informative)

Additional information on Round Robin analysis

C.1 Round Robin tests on the analysis of individual organic compounds

The Round Robin tests were performed in 2003. In each Round Robin test, 6 laboratories from different countries participated. Full details of the results were reported in report **************** in 200******.

The results of the Round Robin tests on analysis of individual compounds from real tar samples (biomass gasification tar) are presented in Table 8 and the results from synthetic tar samples in Table 10. The concentration of those organic compounds which are listed in annex B but are not reported at above mentioned tables has been either so near or below the detection limit that it was not possible to determine reproducibility and repeatability values. The results of the Round Robin tests on analysis of total GC-detectable tar are presented in Table 9.

Table 8 - Results obtained in Round Robin tests on analysis of individual compounds from real tar samples (low temperature tar).

Organic Compound	Concentration		Repeatability conditions				Reproducibility conditions			
	Range	Mean value	Repeatability standard deviation (s_r)		Repeatability[1] (r)		Reproducibility standard deviation (s_R)		Reproducilbility[2] (R)	
	mg/dm^3	mg/dm^3	mg/dm^3	%	mg/dm^3	%	mg/dm^3	%	mg/dm^3	%
TAR 01 (low temperature tar)										
Guaiacol	260 – 320	290	8.3	2.9	23	8.0	19	6.6	54	18
Creosol	130 – 380	280	13	4.7	37	13	94	33	260	93
Phenol	100 – 130	110	6.0	5.4	17	15	7.8	6.9	22	19
Toluene	22 – 73	50	2.1	4.1	5.9	12	17	33	46	92
Naphthalene	4.6 – 9.9	7.5	0.79	10	2.2	29	1.7	23	4.9	65
Phenanthrene	1.0 – 2.5	1.8	0.11	5.9	0.29	17	0.60	34	1.7	94
Pyrene	0.40 – 0.46	0.43	0.008	1.9	0.022	5.2	0.030	7.1	0.084	20
TAR 02 (low temperature tar)										
Toluene	460 – 640	560	23	4.2	65	12	42	7.6	120	21
Guaiacol	100 – 150	130	5.0	3.7	14	10	16	12	44	32
Phenol	34 – 71	47	3.6	7.7	10	21	12	25	33	70
Indene	36 – 62	46	2.3	5.0	6.4	14	12	26	33	72
Creosol	43 – 64	54	4.0	7.4	11	21	6.8	13	19	35
Naphthalene	25 – 49	33	1.0	3.1	2.8	8.6	10	31	28	86
TAR 03 (high temperature tar)										
Naphthalene	110 – 140	120	2.4	2.0	6.8	5.7	13	11	37	31
Toluene	27 – 31	29	0.99	3.4	2.8	9.5	1.4	4.9	4.0	14
Phenanthrene	19 – 23	21	0.47	2.2	1.3	6.3	1.4	6.4	3.8	18
Acenaphthylene	17 – 20	18	0.47	2.5	1.3	7.1	1.3	6.8	3.5	19
Indene	11 – 14	12	0.50	4.3	1.4	12	1.0	8.9	2.9	25

Fluoranthene	5.3 – 7.4	6.5	0.33	5.1	0.93	14	0.73	11	2.1	31
Pyrene	5.1 – 8.2	6.9	0.322	4.7	0.91	13	1.0	15	2.8	41
Pyridine	0.75 – 1.2	1.0	0.031	3.2	0.087	8.9	0.19	19	0.53	54
TAR 04 (high temperature tar)										
Naphthalene	1.4 – 2.0	1.6	0.10	6.6	0.29	18	0.14	9.1	0.40	26
Phenanthrene	0.20 – 0.41	0.28	0.031	11	0.087	30	0.080	28	0.23	78
Toluene	0.18 – 0.41	0.25	0.055	22	0.15	63	-	-	-	-

[1] The difference between two test results found on the same sample by one operator using the same apparatus within the shortest feasible time interval will exceed the repeatability limit on average not more than once in 20 cases in the normal and correct operation of the method.

[2] Test results on the same sample reported by two laboratories will differ by more than the reproducibility limit on average no more than once in 20 cases in the normal and correct operation of the method.

Table 9. Results obtained in Round Robin tests on analysis of total GC-detectable tar (calculated as naphthalene) from real tar samples.

	Concentration		**Repeatability conditions**				**Reproducibility conditions**			
	Range	**Mean value**	**Repeatability standard deviation (s_r)**		**Repeatability[1] (r)**		**Reproducibility standard deviation (s_R)**		**Reproducilbility[2] (R)**	
	mg/dm^3	**mg/dm^3**	**mg/dm^3**	%	**mg/dm^3**	%	**mg/dm^3**	%	**mg/dm^3**	%
TAR 02	5000 - 7000	6400	74	1.2	210	3.2	730	11	2000	32
TAR 01	3400 - 6100	4500	270	5.9	750	17	770	17	2200	48
TAR 03	230 - 310	260	4.3	1.7	12	4.6	30	11	83	32
TAR 04	5 - 52	23	2.3	10	6.5	28	17	74	47	210

[1] The difference between two test results found on the same sample by one operator using the same apparatus within the shortest feasible time interval will exceed the repeatability limit on average not more than once in 20 cases in the normal and correct operation of the method.

[2] Test results on the same sample reported by two laboratories will differ by more than the reproducibility limit on average no more than once in 20 cases in the normal and correct operation of the method.

Table 10 - Results obtained in Round Robin tests on analysis of individual compounds from synthetic tar samples.

Organic Compound	**Concentration**		**Repeatability conditions**				**Reproducibility conditions**			
	Range	**Mean value**	**Repeatability standard deviation (s_r)**		**Repeatability[1] (r)**		**Reproducibility standard deviation (s_R)**		**Reproducilbility[2] (R)**	
	mg/dm^3	**mg/dm^3**	**mg/dm^3**	%	**mg/dm^3**	%	**mg/dm^3**	%	**mg/dm^3**	%
SYNTAR1										
Creosol	130 – 170	160	7.8	4.9	22	14	11	6.7	30	19
Guaiacol	81 – 100	92	4.4	4.8	12	13	7.3	8.0	21	22
Phenol	45 – 66	57	2.2	3.9	6.2	11	5.6	10	16	27
Indene	4.4 – 8.6	6.7	0.24	3.5	0.66	10	1.4	21	4.0	59
Naphthalene	5.7 – 9.0	6.5	0.38	5.9	1.1	17	0.70	11	1.9	30
Toluene	2.5 – 5.5	4.3	0.27	6.3	0.75	18	1.0	24	2.9	67
Phenanthrene	3.2 – 4.2	3.7	0.17	4.7	0.49	13	0.33	8.9	0.92	25
Fluoranthene	0.39 –0.72	0.52	0.045	8.7	0.13	24	0.11	20	0.30	57
Pyrene	0.20 –0.45	0.31	0.043	14	0.12	39	0.090	29	0.25	81
SYNTAR2										
Naphthalene	79 – 140	120	9.0	7.5	25	21	17	14	46	39
Phenanthrene	25 – 31	27	0.31	1.2	0.88	3.2	2.6	9	7.1	26
Fluoranthene	5.2 – 9.8	7.7	0.49	6.4	1.4	18	1.2	16	3.4	44
Indene	4.0 – 6.0	4.7	0.34	7.1	0.94	20	0.44	9	1.2	26
Phenol	3.6 – 5.8	4.7	0.12	2.5	0.33	6.9	0.71	15	2.0	42
Pyrene	1.8 – 2.8	2.2	0.11	5.0	0.31	14	0.38	17	1.1	48
Toluene	1.4 – 2.3	1.9	0.15	7.9	0.42	22	0.20	11	0.57	30

[1] The difference between two test results found on the same sample by one operator using the same apparatus within the shortest feasible time interval will exceed the repeatability limit on average not more than once in 20 cases in the normal and correct operation of the method.

[2] Test results on the same sample reported by two laboratories will differ by more than the reproducibility limit on average no more than once in 20 cases in the normal and correct operation of the method.

C.2 Round Robin tests on the analysis of individual organic compounds

The Round Robin test on the gravimetric analysis was performed in the year 2004. 6 laboratories from 6 different countries participated the test. The obtained results are presented in Table 11. Results in full details were presented in report **************** in 200******.

Table 11. Results obtained in Round Robin tests on analysis of gravimetric tar.

	Concentration		Repeatability conditions				Reproducibility conditions			
	Range	Mean value	Repeatability standard deviation (s_r)		Repeatability[1] (r)		Reproducibility standard deviation (s_R)		Reproducilbility[2] (R)	
	g/dm^3	g/dm^3	g/dm^3	%	g/dm^3	%	g/dm^3	%	g/dm^3	%
GRAVTAR 01	55 – 79	62	2.3	3.7	6.5	10	7.6	12	21	34
GRAVTAR 05	20 – 36	26	1.4	5.3	3.8	15	4.7	18	13	51
GRAVTAR 03	11 – 26	16	1.2	8.0	3.5	22	4.6	30	13	83
GRAVTAR 04	7.4 – 17	11	0.72	6.7	2.0	19	3.1	29	8.7	81
GRAVTAR 02	2.9 – 8.1	4.7	0.42	9.0	1.2	25	1.8	39	5.1	110

[1] The difference between two test results found on the same sample by one operator using the same apparatus within the shortest feasible time interval will exceed the repeatability limit on average not more than once in 20 cases in the normal and correct operation of the method.

[2] Test results on the same sample reported by two laboratories will differ by more than the reproducibility limit on average no more than once in 20 cases in the normal and correct operation of the method.

Annex D
(Informative)

Additional information on parallel tests

The parallel tests were performed in 2004. In each Round Robin test, ***** laboratories from ***** different countries participated. Full details of the results were reported in report **************** in 200******.

Table ********** lists the results of the two parallel tests on the sampling and analysis of organic compounds from updraft gasification (test 1) and from fluidised bed gasification (test 2).