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Tar measurement in biomass gasification, standardisation and supporting R&D

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Acknowledgement/Preface

The work described in this report has been conducted in the framework of EU-project ENK5-CT-2002-80648 and SenterNovem project 2020-03-11-14-007. Both projects have been co-ordinated by ECN. However, the final result of a CEN accredited and approved Technical Specification could not have been obtained without the skilful and enthusiastic participation of a range of European organisations as well as of one organisation in the United States of America. Firstly, SenterNovem and NEN are gratefully acknowledged for their efforts as chairman and secretary of the CEN Task Force 143. Secondly, the following organisations made valuable contributions ranging from participation in measurement campaigns and round robin analyses to scientific discussions: ECN, BTG, SenterNovem and NEN (The Netherlands) VTT (Finland), KTH (Sweden), DTI (Denmark), Fraunhofer - Umsicht (Germany), Verenum (Switzerland), TU-Graz (Austria), Casella (United Kingdom), Enea (Italy), CIRAD (France) and NREL (United States of America). Finally, the authors acknowledge the contributions of Ineti (Portugal) and Cener (Spain) in the discussions on the drafting and optimisation of the TS.

Abstract

This report describes the CEN accredited and approved Technical Specification (TS) for the measurement of tar in biomass gasification and supporting R&D which has been developed in this SenterNovem project in combination with a European project during the last years. The final voting was executed until February 2006 and the TS was fully approved by the CEN representatives (25 countries) and no against votes were given.

The procedures are designed to cover the tar measurements for different types of air or oxygen blown gasifiers. Although several institutes have sometimes used these procedures, they did not have the status of an international standard yet. The overall objective of the projects was therefore to remove this obstacle by standardisation and optimisation. The development and standardisation of the procedures was via extensive in-house tests at ECN, round robin tests and parallel measurement campaigns of several specialised laboratories in Europe and the US. The measurement principle is based on the discontinuous sampling of a gas stream containing particles and condensable organic compounds.

The TS method extensively covers the determination of a broad range of organic compounds which can occur in biomass gasification and that can generally be named 'tar'. The tar compounds are divided into gravimetric tar and a number of individual organic compounds (GC-detectable tars). These tars are in detail described in the CEN TS.

The parallel measurement campaigns at a commercial scale updraft gasifier in Denmark and at a CFB gasifier in Germany have provided information on the accuracy and reproducibility of the sampling method and of the analysis techniques. With the aid of this Technical Specification the performance of different types of gasifiers and subsequent gas cleaning equipment and engine or turbine generators can be monitored accurately and will allow manufacturers and legislative organisations to have a reliable determination of tar emissions.

The CEN Technical Specification is available at the national standardisation institutes. Information is also available at the websites www.tarweb.net and www.gasnet.uk.net.

Keywords

Biomass gasification, tar emissions, tar measurements, product gas sampling, tar analysis, European tar measurement standard

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Summary

This report describes the CEN accredited and approved Technical Specification (TS) for the measurement of tar in biomass gasification and supporting R&D which has been developed in this SenterNovem project in combination with a European project during the last years. The final voting was executed until February 2006 and the TS was fully approved by the CEN representatives (25 countries) and no against votes were given. The development of the TS dates back from the late 1990's and focussed on the standardisation at both a national and European level (CEN) of the measurement of organic contaminants (called 'tar').

The procedures are designed to cover the tar measurements for different air or oxygen blown gasifier types (updraft or downdraft/fixed bed or fluidised bed gasifiers), operating conditions (0 - 900°C and 0.6 - 60 bars), and tar concentration ranges from 1 mg/m_n^3 to 300 g/m_n^3. Although several institutes have sometimes used these procedures, they did not have the status of an international standard yet. The overall objective of the projects was therefore to remove this obstacle by standardisation and optimisation. The development and standardisation of the procedures was via extensive in-house tests at ECN, round robin tests and parallel measurement campaigns of eight specialised laboratories in Europe and one in the United States. The measurement principle is based on the discontinuous sampling of a gas stream containing particles and condensable organic compounds. The sampling train is shown schematically in Figure 1.

The TS method extensively covers the determination of a broad range of organic compounds which can occur in biomass gasification. The TS is capable of determining organic compounds that can generally be named 'tar'. Tar that is formed at low temperature in the updraft gasifier consists mainly of polar compounds while high temperature tars from downdraft and fluidised bed gasifiers mainly contain non-polar compounds. The tar compounds are divided into two different groups - the gravimetric tar and a number of individual organic compounds (GC-detectable tars). These tars are in detail described in the CEN TS descriptions.

The parallel measurement campaigns have provided information on the accuracy and reproducibility of the sampling method and the analysis techniques. The measurement campaigns were carried out at the commercial scale updraft gasifier of Harboøre (Denmark) and at a CFB gasifier of Umsicht in Germany. The results indicated a good reproducibility of the TS as illustrated in Figures S.2 and S.3. The first measurement campaign has been attended by three partners (ECN, DTI, Umsicht). In the second measurement campaign at Umsicht 6 institutes participated (Umsicht, ECN, BTG, VTT, TU-Graz, DTI).

With the aid of this TS the performance of different types of gasifiers and subsequent gas cleaning equipment and engine or turbine generators can be monitored accurately and will allow manufacturers and legislative organisations to have a reliable determination of tar emissions.

The CEN Technical Specification is available at the national standardisation institutes. Information is also available at the websites www.tarweb.net and www.gasnet.uk.net.

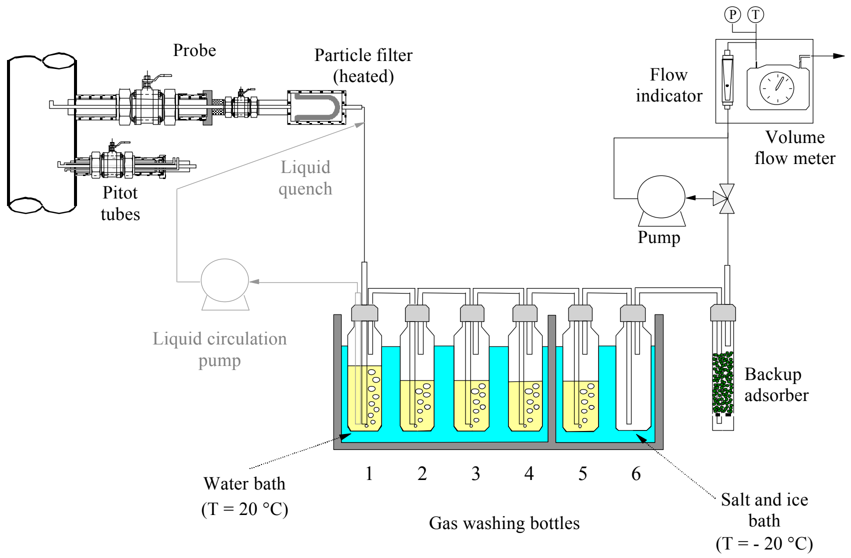

Figure S.1 *The CEN TS sampling set-up: atmospheric and isokinetic sampling train for tar and particles with removable probe and Pitot tubes for flow measurement. Set-up CEN TS: (1) +40 °C,(2) +40 °C (F),(3) -20 °C (F),(4) +40 °C (F),(5) -20 °C (F), (6) -20 °C (F). F designates a glass frit to capture aerosols*

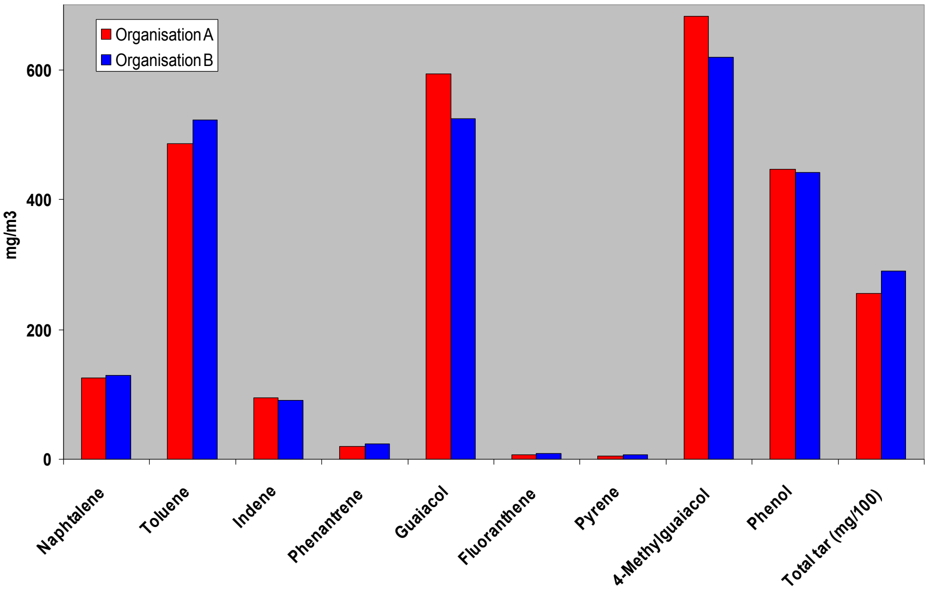

Figure S.2 *Tar sampling and analysis results of the first parallel measurement campaign in Denmark at an updraft gasifier*

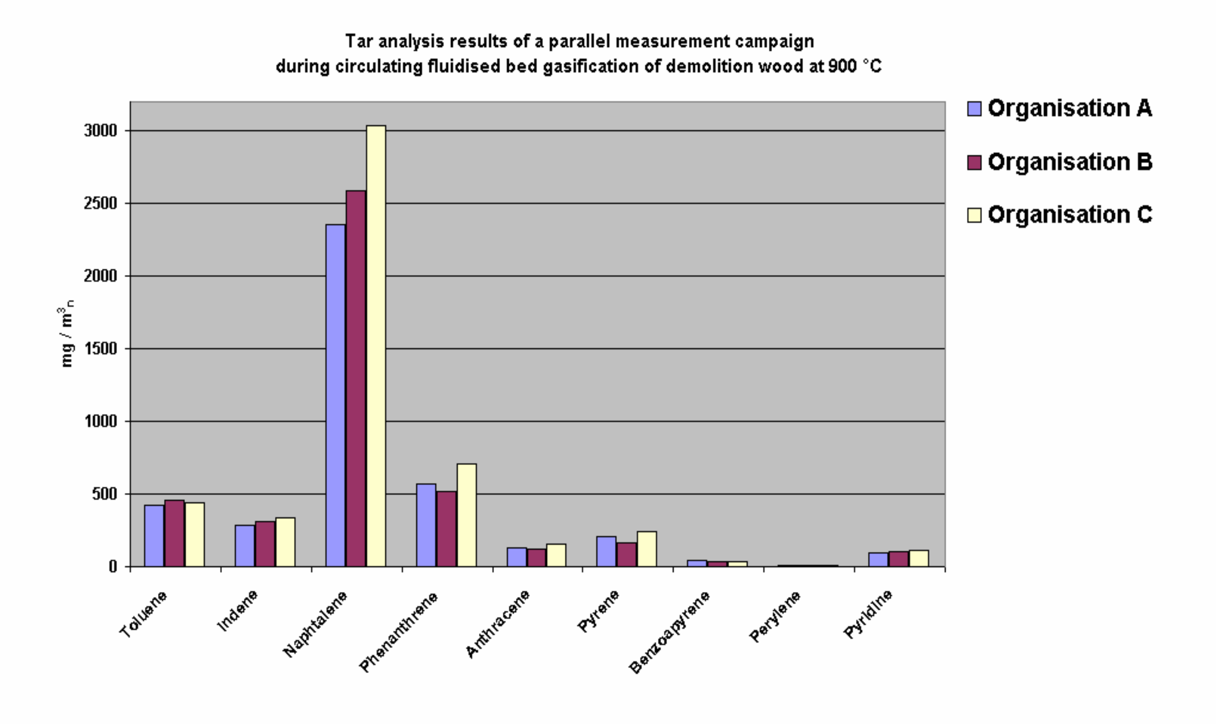

Figure S.3 *Comparison of tar measurement results from the second parallel measurement campaign in Germany at a CFB gasifier.*

1. Project Overview

1.1 Objectives

This project focuses on the standardisation of a Technical Specification (TS) for the measurement of organic contaminants (called ‘tar’). This TS provides a set of procedures for the measurement of organic contaminants and particles in producer gases from biomass gasifiers. The procedures are designed to cover different gasifier types (updraft or downdraft fixed bed or fluidised bed gasifiers), operating conditions (0 - 900°C and 0.6 - 60 bars) and concentration ranges (1 mg/m_n^3 to 300 g/m_n^3).

Although several institutes have used this Technical Specification, it did not have the status of an international standard yet. The overall objective of the project has been to remove this obstacle by standardising the TS, resulting in a CEN (Comité Européen de Normalisation) Technical Specification (CEN TS). As acceptance and use by others is considered to be essential, dissemination and internalisation of the CEN TS formed part of this project.

1.2 Work performed

The work in this project has been subdivided into three activities:

(i) Development / definition of the CEN Technical Specification for the measurement of tar in biomass gasification,
(ii) Supporting R&D,
(iii) Dissemination of the results.

In the first activity, standardisation has been performed in a task force installed directly under the European Committee for Standardisation (Comité Européen de Normalisation, CEN). The technical experts of the projects were actively involved in the work of the European task force, bringing in their expertise into the standardisation work. Via different national projects the experts of the European projects acted as national representatives in the task force. Due to a co-ordinated joint effort of dissemination of the activities, technical experts of other European countries were participating in the work of the CEN task force. The standardisation trajectory has been defined in terms of type of European Technical Specification to be produced, and in March 2006 this TS has obtained a full CEN TS accreditation.

For the Technical Specification to obtain this status, technical specifications such as accuracy and reproducibility of the method needed to be assessed. These fundamental aspects have been assessed in several R&D activities within this specific Dutch focused project. They are also of importance in the international context.

One extensive round robin test (RRT) and two parallel measurement campaigns were successfully performed in March and November 2004/2005. One campaign was performed at Harboøre in Denmark on a fluidised bed downdraft gasifier and one at Umsicht in Germany on an updraft gasifier. In the experimental programmes 9 laboratories participated and substantial amounts of data were collected. The CEN activities take advantage of the R&D activity performed, with input from the RRT being already implemented in the draft TS.

Dissemination activities were a fundamental, intrinsic part of the project, as the aim is to ensure a widespread acquaintance with the TS. Dissemination is aimed at companies, institutes and universities working in the field of biomass gasification. The Internet site www.tarweb.net is the main source of dissemination of the work. The “tarweb site” has been fully updated with all information on the project and with an invitation for technical experts to join the activities of the task force. During the project a number of organisations have joined the task force. Papers were published and presented at conferences in Rome, Budapest, Lisbon and Paris. Also, an article has been written for the Gasnet newsletter.

1.3 Results and possible exploitation

The primary result of this project is a standardised Technical Specification for tar measurements, aimed to reduce the technical and non-technical risks for implementation of biomass based CHP-systems in the future.

With the aid of this reliable and standardised measurement technique, the performance of the gasifier, gas cleaning equipment and engine or turbine generator set can be monitored to learn about and suppress the technical risks. The TS is fully adapted for both updraft and downdraft fluidised-bed gasifiers. With this knowledge, consensus about tolerances (maximum allowable concentrations of tars) for trouble free operation of gas engines, gas turbines and gas cleaning equipment can be better defined. The result is that manufacturers of gas cleaning equipment and gas engines/turbines can give more reliable guarantees, which can improve the realisation of biomass CHP (Combined Heat and Power) systems. These guarantees decrease the non-technical risks of implementation of CHP-systems.

2. Technical Background, Objectives and Strategic Aspects

2.1 Techno-Socio-Economic objectives and strategic aspects

Despite remarkable efforts at research, development, and demonstration of biomass technologies in the last two decades, commercial implementation on the Dutch and European energy market has remained modest. Only small-scale biomass combustion up to several MW significantly contributes to the energy (i.e. heat) demand in some European countries (Austria, Finland, Sweden). Additional efforts should mainly focus on CHP (combined heat and power) systems.

According to the White Paper, the contribution of biomass for CHP production will have to increase to 10.000 MW (thermal capacity) by 2010. When it is estimated that the contribution of small-scale CHP systems to the total capacity of 10.000 MW mentioned above is 10 %, then there is a need for at least 200 small-scale systems (5 MW_{th} and 1 MW_e) and 100 large-scale systems (on average 90 MW_{th} and 30 MW_e).

The present project aims at reducing the technical and non-technical risks when implementing biomass based CHP systems. It does so by development and dissemination of a standard for tar measurement in biomass fuel gases. Tars are among the major contaminants that have to be removed from fuel gases as they cause damage to the engine or turbine or incur an unacceptable level of maintenance. Currently, measurement of tars is performed with diverse, non-uniform and often poorly documented techniques. An overview of different tars and associated components is given in Appendix C and D. The diversity of techniques causes that the performance of gasifiers and gas cleaning cannot properly be compared with respect to their technical performance. As a result, end-users wanting to implement biomass based CHP systems cannot minimise technical risks associated with the occurrence of tars.

A standard measurement technique would allow manufacturers of gasifiers, gas cleaning systems and engine or turbine generator sets to convince potential end users on the technical performance of the sub-systems. Besides, it would allow them to define tolerances from which guarantees on performance, system lifetime etc. can be derived. These guarantees decrease non-technical risks of implementation of CHP-systems. In this way, the present project contributes to implementation of biomass based CHP systems.

The development of a standard for measurement of organic contaminants can have a positive effect on health and safety of the European citizens by better detection of health-hazardous compounds that occur in biomass producer gases and possibly are emitted from gas engines. The combustion of product gas in gas engines is not complete; it is well known that a small part of a few per cent of the product gas can leave the engine not combusted. It is also well-known that the product gas contains carcinogenic compounds such as benzo(a)pyrene, which can be present at concentration levels in the order of mg's per m^3. The flue gases of engines running on product gas can, therefore, be a health risk to citizens. With a good and standardised measurement technique for organic contaminants these hazardous organic compounds can be detected.

Implementation of (small-scale) biomass technology is labour intensive compared to (large-scale) energy production using fossil or nuclear power. Thus, the realisation of biomass using energy plants also creates employment. Most of the jobs will be related to fuel handling and plant operation. Assuming that 5 skilled workers are needed to operate a 1 MW_e biomass CHP plant in 5 shifts, and similarly 15 skilled workers are needed to operate a 30 MW_e biomass CHP plant, at least 2.500 jobs can be created by implementing this technology in Europe through the 300 CHP-based systems mentioned above. Additionally, jobs can be created in agriculture and horticulture as well as in the energy sector. Besides the creation of new jobs, exploitation of biomass as an energy source can have a positive impact on rural development. The implementation of small-scale biomass plants opens a route for the use and valorisation of agricultural and forestry by-products thereby increasing the profitability of the main agricultural and forestry activity. On the longer term energy crops can be incorporated.

The implementation of biomass based CHP-systems contributes to the reduction of greenhouse gas emissions, which has a long-term beneficial effect on the quality of life. The overall EU objective has been quantified in the White Paper: In the year 2010 a 15% emission reduction of green house gases (base level 1990) should be accomplished. The above-mentioned number of 300 biomass CHP installations corresponds to a CO_2-emission reduction of approx. 10 million tons per year. This implies that each of the member states should aim to reach this goal.

An important policy strategy of the EU is to decrease the dependence of energy imports. At present about 50% of the EU energy is imported and without change in policy this number will increase in the coming decades. By using indigenous biofuel the increase in amount of energy imports can be lowered or even reduced. The above-mentioned number of 300 biomass CHP installations corresponds to a saving of 5000 million litres of oil per year.

2.2 Scientific objectives

A number of companies have developed, and are developing, CHP (combined heat and power) systems based on the gasification of biomass. These technologies have three process steps, the gasification reactor, cleaning of the producer gas, and an engine or turbine generator set. The producer gas from a gasification reactor always contains contaminants that, if not removed, would damage the engine or turbine or incur an unacceptable level of maintenance. The efficiency and reliability of the gas-cleaning step is therefore fundamental for successful operation of this technology.

The main contaminants are dust and soot particulates, organic contaminants (often being referred to as "tars"[1]), alkali metals, acid gases and alkaline gases. For most contaminants, well-developed and standardised measurement techniques exist, which allow to determine the gas cleaning performance and to assess the clean gas quality. For tars this is not the case and different sampling and analysis methods are currently being used.

Therefore, in previous national and international projects with acronym "Tar Guideline", a method for tar measurement ("the guideline") was developed. Although several institutes have used this guideline, it does not have the status of an international standard and it is not yet applied on a routine basis as no detailed data on accuracy and reproducibility of the guideline have been collected and compared.

The objective of the project has been to remove this obstacle by performing specific focused measurements on different (semi-) industrial installations including standardising the guideline, collection of, comparison of, and discussion on data on accuracy and reproducibility. The result will be a CEN Technical Specification. As acceptance and use by others is considered to be essential, dissemination and internalisation of the Technical Specification forms part of this project.

This objective has a broad support in the community of biomass gasification. An initiative to come to one standard method for tar measurement was already taken in March 1998 when

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[1]: The word "tar" is not defined in detail; it is a generic and unspecific term for the entity of all organic compounds present in the product gas excluding gaseous hydrocarbons (C_1 through C_6). Benzene is not included in tar. The numbers that are determined in the guideline and in the future standard are accurately defined. These numbers are the concentration of gravimetric tars and the concentrations of individual, GC-detectable tar compounds.

members of the gasification task of the IEA Bioenergy Agreement, the US DoE and DGXVII of the European Commission organised a meeting in Brussels on this subject. Since then, the subject has had constant attention at national and international levels. Details on previous R&D results can be found at http://www.tarweb.net/results/index.html .

The output of this project is a CEN Technical Specification for the measurement of tars from biomass product gases, which is accepted and used by the companies, institutes and universities working on biomass gasification.

3. Scientific and Technical Activities

3.1 Background

The international state-of-the-art

The present measurement of tars from biomass fired systems by institutions and companies is still performed via diverse, non-uniform and often poorly documented methods. This diversity of methods and definitions does not allow comparison of concentrations of tars that are determined at different locations (different companies, institutes, universities). This has resulted in major technical problems for the further development and market introduction of CHP-based systems, which are:

1. It is impossible to compare the exact performance of different biomass gasification technologies, as there is no consensus on how to measure and compare tar concentrations.
2. It is impossible to compare the performance of different cleaning techniques for organic contaminants, because the performances of the different techniques have been determined using different definitions and measurement methods.
3. Because of this lack of consensus, tolerances (maximum allowable concentrations of tars) for trouble free operation of gas engines, gas turbines and gas cleaning equipment cannot be defined. The result is that manufacturers of gas cleaning equipment and gas engines/turbines are not willing to give guarantees, which increases the risks of realisation of biomass CHP systems.

This project focused on the design and development of a standard for tar measurement which has the possibility of giving two types of concentrations for tar - a GC, compound analysis and a gravimetric compound analysis. No other methodology presently available has this comprehensive and powerful characteristic.

The work in this project has been subdivided into three activities:

(i) Development / definition of the CEN Technical Specification (CEN TS) for the measurement of tar in biomass gasification,
(ii) Supporting R&D,
(iii) Dissemination of the results.

In the first two activities, standardisation has been performed in a task force installed directly under the European Committee for Standardisation (Comité Européen de Normalisation, CEN). This task force had been applied for at CEN in a previous EU project and was installed at the start of this project. Its activities were threefold:

(a) Communicate with CEN on progress of standardisation, following the CEN rules and procedures, document versions of the Technical Specification (including formal enquiry stage and formal vote stage) and plan plus organise meetings of the task force including the technical experts. Activities include holding the secretary and the chair of the CEN task force. These activities were co-ordinated by SenterNovem, ECN and the Dutch branch of CEN.
(b) Perform experimental campaigns on tar measurements under controlled and well defined laboratory conditions, round robin tests in order to evaluate the laboratory performances, and extensive (semi-)industrial scale tests in order to compare the results from the different measurement apparatus. It is this part where substantial effort and financial resources were included from different national governments. In this manner specific focused tasks could be executed. The Netherlands played a prominent role in this since the chairmanship of the CEN taskforce was via SenterNovem and the project-management of the overall project was conducted by ECN.
(c) Ensure technical input to the task force from technical experts. They bring in their expertise on tar measurement and use of the TS and define the specifications the standard

has to fulfil. This group of technical experts discusses existing data on the standard in preparation and takes action to ensure collection of missing data. In particular, data on accuracy and reproducibility of the draft standard are essential in the process of standardisation.

In the third activity, the results from this project have been disseminated to ensure widespread acquaintance with the Technical Specification. Dissemination was aimed at the companies, institutes and universities working in the field of biomass gasification. Dissemination has been performed by means of an internet site, by using internet mailing lists/discussion groups and by means of papers and presentations at biomass conferences. The main website for dissemination is Tarweb which is hosted by BTG and ECN and profiles The Netherlands on the frontiers of technology concerned with tar measurements.

Relevant user groups and main innovation by this standardisation project

Relevant user groups are the major European and North American companies, institutes and universities that develop or commercialise biomass gasification technology. The expected advance of the current state of the art is the following:

1. The CEN TS will enable the comparison of tar numbers in RTD by companies, institutes and universities. Some will use the TS for tar analysis; other might use it to demonstrate that concentrations of tars from biomass gasifiers can be compared. The TS will not replace the use of other methods. However, it is foreseen that all existing methods will be compared against the CEN Technical Specification so that their relative performance will be known. In this way, the CEN TS will act as a “mother method” to which others methods can be compared and calibrated. It has already been shown that this is feasible; in a previous work the Technical Specification has been compared with a method called “solid phase adsorption” and it was shown that in a range of tars – which are relevant for a certain range of applications of biomass producer gas – the methods give the same results.
2. It will allow manufacturers of gasifiers, gas cleaning systems and engine or turbine generator sets to definite tolerances for tar concentrations from which guarantees on performance, system life time etc. can be derived. These tolerances and guarantees are essential for these manufacturers to convince potential end users on the technical performance of the sub-systems. These guarantees decrease the non-technical risks of implementation of CHP-systems.

3.2 Summary of the specific experimental activities

Looking at the work plan it can be seen that the second and third year of the project were devoted to perform the experimental activities. According to the original work plan the most relevant experimental project tasks have been:

a. round robin tests and analysis for a set of specially prepared samples on gravimetric and gas chromatographic method in order to identify possible deviations at different laboratories,
b. parallel measurement campaigns with the Technical Specification and the Petersen method. These were executed in Harboøre (Denmark) and Umsicht (Germany),
c. detailed measurements at ECN on two fluidised bed gasifiers for comparison of the different versions of the Technical Specification,
d. further development of the standardisation activities and descriptions under the CEN umbrella and the production of an official CEN Technical Specification,
e. dissemination work via publications of the results on the websites and official publications.

Laboratories involved in the round robin test are listed below in alphabetical order:

BTG-Biomass Technology Group B.V. - Enschede, The Netherlands
CIRAD Forêt - Montpellier, France
DTI-Danish Technological Institute - Aarhus, Denmark
ECN Biomass - Energy Research Centre of the Netherlands - Petten, The Netherlands
Fraunhofer UMSICHT - Oberhausen, Germany
NREL-National Renewable Energy Laboratory - Golden, CO, USA
Technical University of Graz - Graz, Austria
University of Zaragoza - Zaragoza, Spain
VTT Energy - Espoo, Finland

Six of these laboratories participated in both rounds and two participated in just in one round.

The final results of the RRT exercise have been evaluated and an extensive report is available on the data. This report is not included into this report due to size constraints. In Annex 2-3-4 a full technical motivation and description of the Technical Specification is given.

The parallel measurement campaigns have been executed in April and November 2004 and evaluated in detail during 2005. Also sets of additional tests have been executed at ECN in 2004 and 2005 on the WOB and BIVKIN fluidised bed installations which are specifically designed for controlled measurements under biomass gasification conditions.

In these campaigns the following companies participated:

BTG-Biomass Technology Group B.V. - Enschede, The Netherlands
DTI-Danish Technological Institute - Aarhus, Denmark
ECN Biomass - Energy Research Centre of the Netherlands - Petten, The Netherlands
Fraunhofer UMSICHT - Oberhausen, Germany
TU-Graz - Austria
VTT Energy - Espoo, Finland

The following tar measurement methods have been used:

- Technical specification: +40,+40F,-20F,+40,-20F,-20F (numbers are °C, F is for glass Frit)
- Alternative TS: +40,+40, +40, +40, -20, -20
- Other TS option: Petersen Column

In summary, the following experimental activities have been conducted:

<u>round robin tests (DTI)</u>
- BTG, Cirad, DTI, ECN, NREL, VTT
-- Focus on laboratory analysis method with prepared samples
-- Reports RRT 01,02,03 are prepared

<u>1st parallel measurement campaign</u>
- Harboøre, Denmark, April 2004, Updraft gasifier
-- DTI, ECN, Umsicht, (KTH)
-- Detailed analysis of the results (DTI, ECN)

<u>2nd parallel measurement campaign</u>
- Weeks 47/48 at Umsicht in Germany
- Standard Guideline: BTG, ECN, Umsicht
- Alternative Guideline: VTT
- Petersen Column: DTI, TU-Graz
- Similarity in measurement procedure

The parallel measurement campaigns (PMC) were set up such that all partners measured at the same time under the same conditions. The PMC in April was performed on the updraft gasifier in Denmark and the PMC in November on the Umsicht CFB gasifier. This allowed the partners to measure over the full range of low and high tar concentrations.
Also substantial information on the accuracy and reproducibility of the sampling methods i.e. Technical Specification, Petersen column and collection methods have been collected.

Additional comparative measurements were performed at ECN during WOB and BIVKIN tests under controlled conditions.

3.3 Procedure for Standardisation

There are different types of standard (see Annex-1):

- TS (Technical Specification)
- TR (Technical Report)- not normative
- EN (European Standard) – highest degree of standard.

For each standard type a different procedure applies in terms of drafting process and in terms of voting/ administrative procedure at CEN. For the standardisation of the measurement of tar in biomass product gas, the Technical Specification type of standard has been chosen instead of the originally foreseen EN type of standard. The main reason is because the EN standard implies two stages of voting procedure that would make it impossible to finalise the standard in the framework of the project lifetime. However, it has to be pointed out that both EN and TS type of standard have the same normative value[2]. This means that changing to a TS type of standard does neither modify the standardisation trajectory with respect to the project lifetime nor does it modify the normative value of the final deliverables.
The 2nd iteration and the 3rd iteration on the draft standard have been extensively discussed in the CEN 143 meetings held in Oberhausen and in Zurich. In these meetings the combination of experimental information and description of the standard were combined by a team of international experts. The chairmanship of these meetings was via SenterNovem and the technical project co-ordination via ECN.

In Annexes 2, 3 and 4 the full technical description and the CEN standard description are given.

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[2] Both EN and TS type of standards have the same normative value; a CEN TS is a normative document; CEN member countries are not obliged to implement that as national standard, but are obliged to announce the publication of the TS and to make the TS available. National standards on the subject can continue to exist alongside the TS. After a maximum of three years, the TS is reviewed by the CEN member countries with the purpose to achieve agreement to change the status to EN (or else confirmation or withdrawal). Currently there are no national standards on the subject, neither in development, so it is reasonable to expect the TS to be upgraded in a few years time to an EN standard.

4. Management and Co-ordination

Voting for the CEN Technical Specification took place in February/March 2006 and the standard was accepted without any against-votes. The milestones during the set-up of the standard are shown below.

Milestone No	Milestone title	Delivery date
M1[*]	Go/No Go: The results of the R&D work in WP2 must meet the CEN requirements for Standardisation	Month 26 (was 24)
M2	Final draft Standard developed by the CEN Working Group	Month 28 (was 26)
M3	First formal (CEN-PREN) version of the Standard for public enquiry (6 months ballot period)	Month 29 (was 26)
M4	Second formal (CEN-PREN) version of the Standard for formal voting (2 months ballot)	Month 36 (was 32)

The CEN TF 143 has established official liaisons with other CEN task forces or task force like the CEN task force of standardisation of solid Biofuels, (CEN BT 335), as well as with ASTM (the American Standardisation Institute), and ISO, as to initiate activities aiming at the later internationalisation of the standard and acceptance as a measurement method at a broad international level. Currently, at international level there are no other similar activities on tar measurement like the current European initiative. In the US, contacts have been established with NREL (National Renewable Energy Laboratories) which is going to initiate a similar standardisation procedure in the US, as soon as the European standardisation activity will be about to deliver its final results.

In May 2005 an extensive 2 days meeting (CEN and technical) was held at Verenum in Zurich for the evaluation of the measurement results and the determination of the technical requirements for the final Technical Specification for the measurement of tar in biomass gasification.

4.1 Dissemination Activities

Dissemination is an intrinsic part of the project, as the aim is that the method reaches widespread acceptance among end-users, research institutes, and equipment manufacturers.

The activities of the project have been presented at an international brokerage event on Bioenergy organised by the European Commission in Budapest in October 2003, at a conference in May 2004 in Rome,2nd World Biomass Conference for Energy and Industry (refereed paper), and at Vancouver, Conference in Science and Thermal Biomass Conversion, in August 2004 (refereed paper). In addition, one article has been published on the Gasnet newsletter, which has a large number of members among experts in biomass conversion techniques (in research and applications), and follow-up news related to participation to the

CEN TF 143 activities have been also sent out on the same newsletter. Furthermore a presentation on the results and on the Technical Specification has been held at the Clean Air Conference in July 2005 in Lisbon.

The " tar site" www.tarweb.net, has been set up and further updated during the project. During the project but also afterwards requests for information and measurement campaigns on industrial sites were received. ECN is the main co-ordinator/measurement organisation for these activities (http://www.tarweb.net/).

4.2 Comparison of planned activities and actual work accomplished

Basically in terms of technical content no major deviations have occurred in relation to the original work plan.

The main task in the first year was a set-up of the organisational structure, the detailed determination of the partners tasks, set-up of the required experiments, and a time-plan.

The main tasks for the 2nd years were the execution and analysis of the round robin results, the execution of the Harboøre parallel measurement campaign and the execution of the Umsicht parallel measurement campaign. This has all been performed.

In the 3rd year all experimental results were analysed and evaluated. The final CEN TS and the technical descriptions were prepared.

The dissemination has occurred throughout the project, several publications at international conferences were made and two websites were set-up.

An overview of all tasks and workpackages is given below in Table 4.1

Table 4.1 *List of work packages*

WP	Work package title	WP leader	Start month	End month	Deliverable No
WP0	Project co-ordination and document control	ECN	1	36	1
WP1	CEN Task Force-Management	NEN	1	36	2
WP2	CEN Task Force- Availability of R&D data on draft Standard	VTT	1	24	3,4,5,6,7
WP3	Dissemination of results	BTG	1	36	8,9,10
WP4	Reporting	ECN	34	36	11

In the following Table 4.2, the total list of deliverables of the tar measurement standard project is shown.

Table 4.2 *List of deliverables*

Deliverable No	Deliverable title	Responsible partner	Delivery date	Type of deliverable	Dissemination level
D1	Updated and numbered versions of the draft standard	ECN	Month 6-36	Draft standard	PU
D2	Minutes of the six Task Force Meetings and the (at least) four National meetings between Project Co-ordinator and Chairman and Secretary of the Task Force.	NEN	Month 6, 12, 18, 24, 30, 36	Minutes	RE
D3	CEN-EN standard	NEN	Month 35 (was 34)	Standard	PU
D4	Updated inventory of R&D requirements for optimisation & evaluation of the draft standard.	VTT	Month 6	Inventory list	PU
D5	Evaluation of Gas Chromatographic methods.	DTI	Month 13	Report part of D8	PU
D6	Comparison of draft standard with other potential tar sampling methods.	VTT	Month 26 (was 24)	Report part of D8	PU
D7	Parallel testing results of the draft standard	DTI	Month 26 (was 24)	Report part of D8	PU
D8	R&D report describing the accuracy and reproducibility of the draft Standard or critical parts of the draft standard	DTI	Month 26 (was 24)	Report	PU
D9	Input to and discussions on the BioEnergy and the Gasification mailing list /discussion groups	ECN	Month 4-29	Presentation, Publication	PU
D10	A website presenting the draft standard and the "Updated inventory of R&D requirements"	BTG	Month 0-36 (12)	Updated website	PU
D11	Presentations (oral or poster) at two or more European Biomass conferences	ECN, BTG	Month 0-36	Presentation	PU
D12	The final draft report of the project to be send to the European Commission	ECN	Month 35 (was 34)	Report	PU

Deliverable No	Deliverable title	Responsible partner	Delivery date	Type of deliverable	Dissemination level
D13	A final report in month 35 of the project. This report includes the final CEN-EN standard that meets the criteria set in objective 1.	ECN	Month 35	Report	PU
D14[*]	Mid-term report	ECN	Month 18	Report	PU
D15	Management reports	ECN	Month 6,18,30	Report	PU

Additional comments on the deliverables:

1) D1: 4 versions of the draft standard have been produced- those have been discussed respectively at the four CEN TF 143 meetings held in 2003, 2004 and 2005.

2) D2: Four meetings of the National Task Force (gathering the project co-ordinator, ECN, the chairman and the secretary of the task force) were held during the project.

3) D9: Input has been put on the gasification mailing list concerning the commencement of the project and a request for technical experts working in the field to join the activities. In addition, 5 articles were published which already completes this deliverable.

4) D10: The " tar site" www.tarweb.net has been fully updated and can act as a question base for tar measurements.

5) D11: The activities of the project have been presented at an international brokerage event on Bioenergy organised by the European Commission in Budapest in October 2003, at a conference in May 2004 in Rome,2nd World Biomass Conference for Energy and Industry, (here also a publication (refereed) was prepared), and at Vancouver, Conference in Science and Thermal Biomass Conversion, in August 2004 (also a refereed paper). Furthermore a paper plus oral presentation was presented at the Clean Air Conference in Lisbon in July 2005. In addition, one article has been published on the Gasnet newsletter, which has a large number of members among experts in biomass conversion techniques (in research and applications), and follow-up news related to participation to the CEN TF 143 activities have been also sent out on the same newsletter.

Dissemination and use of the results

The major aim of the project was to deliver an national and EU standard for measurement of organic contaminants (tars) in biomass producer gases. The standard enables the comparison of tar numbers in RTD by companies, institutes and universities. Many national and EU experts in the biomass field are already applying the Technical Specification method (Cirad-Foret, France; NREL, US; TU-Munich and University of Stuttgart, Germany; DTU, Denmark; Ineti, Portugal, CENER, Spain, ENEA Italy and all partners involved in this project.)

At present the actual standard applies to clean biomass. It is expected that in the future the standard can be modified for contaminated biomass too (like sewage sludge, chicken litter, etc.) for which also a large potential in CHP based on gasification at a national and European levels is foreseen. The method needs to be changed to be adapted to high sulphur and/or high chlorine content of the fuels.

The activities of the project have been presented at an international brokerage event on Bioenergy organised by the European Commission in Budapest in October 2003, at a conference in May 2004 in Rome, at the 2nd World Biomass Conference for Energy and

Industry, (refereed publication), at the Vancouver Conference in Science and Thermal Biomass Conversion, in August 2004 (also a refereed paper) and a paper has been presented at the Clean Air Conference in Lisbon in July 2005 (refereed paper). In addition, one article has been published on the Gasnet newsletter, which has a large number of members among experts in biomass conversion techniques (in research and applications), and follow-up news related to participation to the CEN TF 143 activities have been also sent out on the same newsletter.

Actual practical applications and fallout's of project results
The method allows manufacturers of gasifiers, gas cleaning systems and engine or turbine generator sets to definite tolerances for tar concentrations from which guarantees on tar emission performance can be derived.

Extensive tests have been performed on gasifiers in Denmark and Germany. Detailed laboratory experiments have been performed at ECN.

However, no measurements could be performed on the biomass CFB gasifier of Essent in the Netherlands. The reason for this was the fact that the installation was not actively running during the whole project duration. These planned measurements have been replaced by the experiments in Germany on a CFB installation which has provided a large database and comparison between methods when applied by several partners.

Additionally, during the project industrial measurements have been performed by ECN in The UK and in South America on industrial gasifiers in order to demonstrate the potential of the Tar Measurement Standard.

Patentable results, including a list of patents applied for, if appropriate

(No patentable results are applicable to the project, resulting overall in general knowledge production).

4.3 Management and co-ordination aspects

The technical project has been co-ordinated by ECN while the standardisation trajectory has been taken care of by SenterNovem and CEN.

ECN was the overall co-ordinator of the project and has been responsible for the project management and has functioned as intermediary and interface between the project and the EC. ECN has consolidated the project planning, progress reports, cost statements and budgetary overviews etc. using the inputs from the other partners. Besides, ECN has coordinated the communication between the partners and has documented changes and additions to the standard next to the registration of version numbers.

NEN and SenterNovem held respectively the secretary and the chair of the CEN Task Force 143. The Secretary NEN has been responsible for communication with CEN on progress of standardisation, for following the CEN rules and procedures, for document versions of the standard (including formal vote stage) and for planning and organising meetings of the task force. NEN has a broad experience in holding the secretary of CEN task forces.

SenterNovem has been responsible for chairing the meetings of the task force and for ensuring a proper communication on technical matters between the technical experts, the project co-ordinator and the CEN and the CEN Task Force. SenterNovem as an organisation has not performed this task before, however, the former project co-ordinator from the EU project "tar guideline" has moved to SenterNovem. In the previous project, he and NEN have worked together on the proposal to CEN to get a task force installed. As the former project co-ordinator, he has a broad

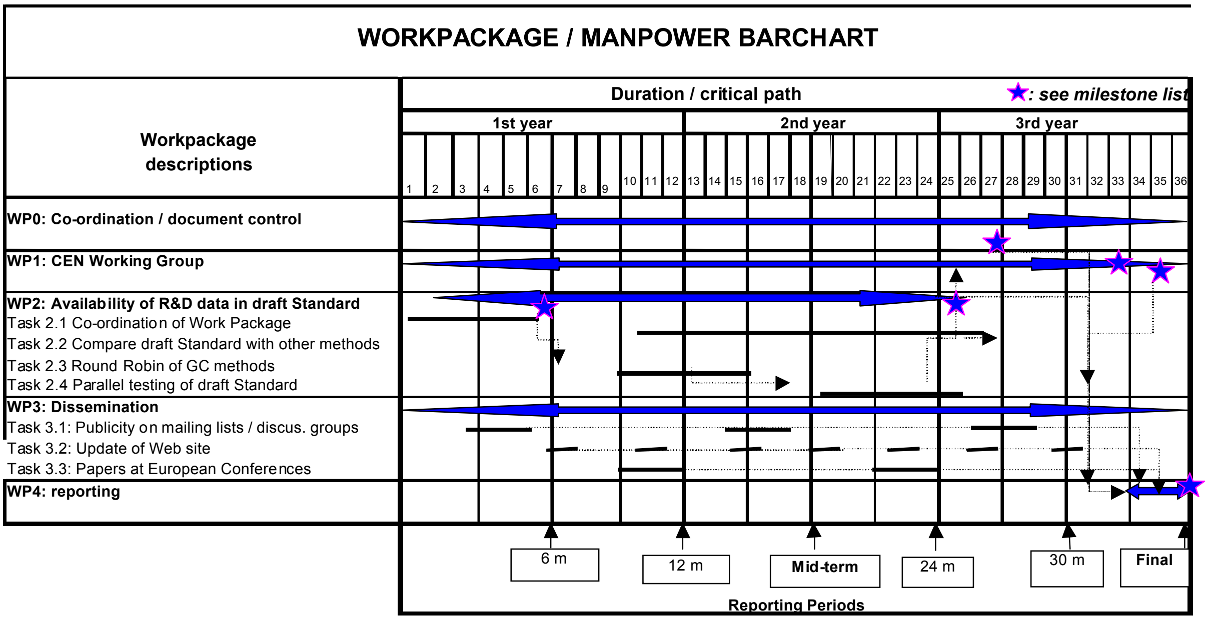
experience with the development of the guideline and he has extensively communicated with all project partners.
VTT and DTI have managed the group of technical experts. VTT has been responsible for co-ordination of the work package WP2 on “Availability of R&D data on draft standard”. DTI has managed sub-tasks in this WP2. VTT has a broad experience in R&D on biomass gasification and tar measurement, and VTT has co-ordinated many EU project. Besides, both VTT and DTI have a very well managed analytical lab to support in this co-ordinating task.

The technical experts have brought in their expertise on tar measurement and use of the draft standard and have defined the specifications the standard has to fulfil. This group of technical experts has discussed existing data and has taken action to ensure collection of data that were still missing. In particular, data on accuracy and reproducibility of the guideline are essential in the process of standardisation. Besides DTI and VTT, also BTG, ECN, EMC, KTH and Verenum have extensive experience with tar measurement and field-testing. BTG, DTI, KTH, Verenum and VTT did develop own tar measurement methods in the past, and all seven partners have experience with testing tar measurement methods “on location”.

There has been a strong communication between the project co-ordinator ECN and the secretary and the chair of the task force NEN and SenterNovem. The project co-ordinator ECN and the chairmen SenterNovem have strong communication lines with partner VTT who co-ordinates input of technical data together with DTI and both have strong communication lines with the other technical experts.
As far as publications and conference attendance are concerned, these have been reported in previous sections.

Manpower and budget

- No major deviations from the original planning have occurred and more than the planned experimental work has been executed. One omission has been the experiment at the biomass fired Amer-CFB installation. This experiment could not be performed due to operational problems with the CFB-plant during the project. These measurements have been compensated via extensive measurements in Germany, Denmark and the UK.



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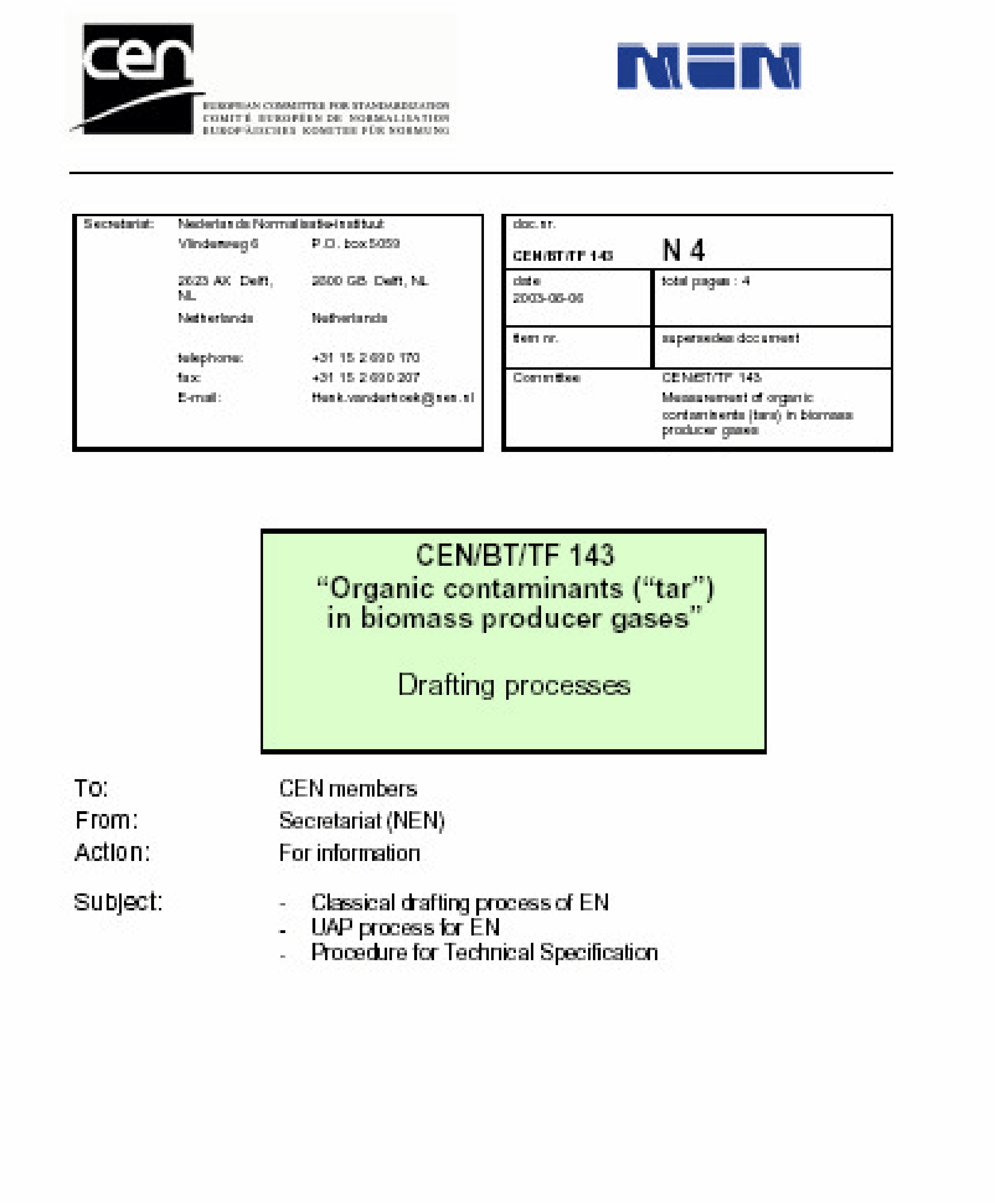
Glossary of Abbreviations

TF	Task Force
CEN	European Committee for Standardisation
Tar	Generic (unspecific) term for entity of all organic compounds present in the producer gas excluding gaseous hydrocarbons (C1 through C6). Benzene is not included in tar.
RRT	Round robin test
GC	Gas chromatography
FID	Flame Ionisation Detection
MS	Mass Spectrometry
CHP	Combined Heat and Power
CFB	Circulating fluidised Bed
Gravimetric tar	Evaporation/distillation residue from particle free sampling solution(s), determined by gravimetric analysis
Product gas	Gas produced from thermal biomass conversion reactor (gasifier). May also include pyrolysis gas
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

Appendix A Drafting procedure for Technical Specification type of standard



EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

NEN

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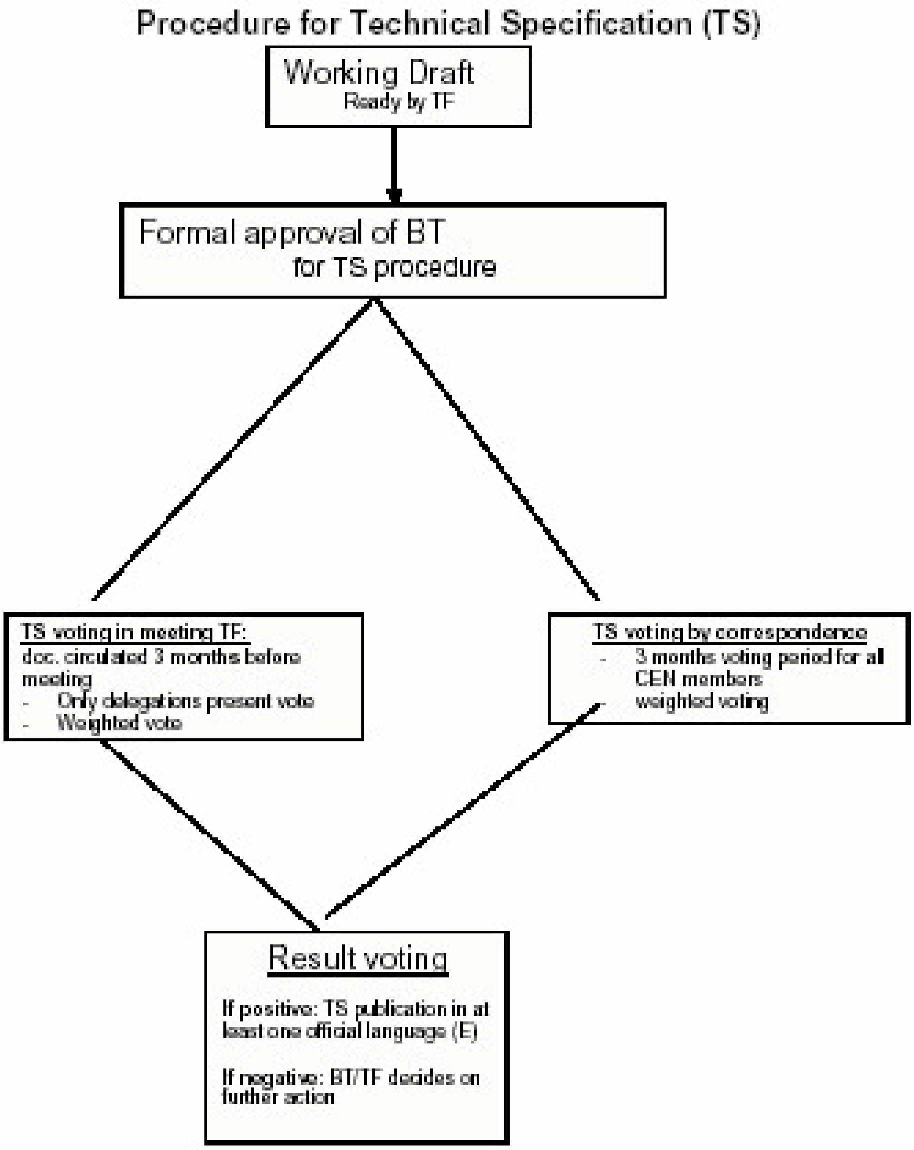
doc. nr. CEN/BT/TF 143	N 4
date 2003-06-06	total pages : 4
item nr.	supersedes document
Committee	CEN/BT/TF 143 Measurement of organic contaminants (tars) in biomass producer gases

CEN/BT/TF 143
"Organic contaminants ("tar") in biomass producer gases"

Drafting processes

To: CEN members
From: Secretariat (NEN)
Action: For information

Subject:
- Classical drafting process of EN
- UAP process for EN
- Procedure for Technical Specification



Procedure for Technical Specification (TS)

TS voting in meeting TF:
doc. circulated 3 months before meeting
- Only delegations present vote
- Weighted vote

TS voting by correspondence
- 3 months voting period for all CEN members
- weighted voting

Result voting

If positive: TS publication in at least one official language (E)

If negative: BT/TF decides on further action

Appendix B Rationale for Set-up of the TMS system

Rationale for setup of impinger train

as used in the Technical Specification of Sampling and Analysis of Tar and Particles in the Product Gases of Biomass Gasification.

Technical background document

Prepared under

CEN BT/TF 143 "Organic contaminants ("tar") in biomass producer gases"

by J.P.A. Neeft, SenterNovem (The Netherlands),
convenor of CEN BT/TF 143

January 2005

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5. Introduction

This document is a background document to the development of a method for sampling and analysis of tar and particles in the product gases of biomass gasification. This method was developed in two subsequent EU projects under the EU fifth framework programme. The first project was aimed at the development of the "Tar Guideline", the second project was aimed at standardisation of this Guideline into a CEN Technical Specification. The second project was performed under the umbrella of a Technical Committee under CEN, called CEN/TC BT/TF 143 “Measurement of organic contaminants (tar) in biomass producer gases”.

In the method, the tars are sampled from biomass gasification product gases by impinger bottles containing isopropanol. The sum of the six individual impinger bottles is referred to as the "impinger train". During the development of the Guideline and the Technical Standard, the actual conditions of the impinger train proved to be of large importance for the efficiency of collection of tars. In the project group, long discussions were held in order to optimise these conditions. In a meeting in Rome, June 2004, the final conditions were agreed upon. This document describes the rationale behind the choice for these final conditions.

This report focuses on the temperature of the impinger bottles and the use of glass frits and glass beads. Other topics that were researched as part of the development of a method for sampling and analyses of tars, are described in an R&D report that was made at the end of the first EU project [Brage, 2002]. In this 2002 report, for instance, the rationale for the choice of isopropanol as a solvent is given. As the discussion on the collection efficiency has continued after issuing the 2002 report, this part is updated by the current document.

In the current document, the following topics are covered:

- The R&D that has been performed on the efficiency of collection of tars in the impinger train is presented in Chapter 2;
- The arguments that were used in discussions on the optimised sampling conditions are given in Chapter 3;
- The final conditions of the Technical specification are given in Chapter 4;
- Finally, chapter 5 gives reference to the full R&D reports.

6. Main results on R&D towards the efficiency of tar collection

6.1 Available data

To the author's knowledge, so far only two institutions have performed R&D work on the efficiency of tar collection in which the collection efficiency of tar compounds was quantitatively determined. The results of this R&D work by ECN and VTT will be described in this chapter. Other institutes, like BTG, DTI, TU-Graz, Umsicht and Verenum, have used the Guideline or the draft Technical Specification[2] over the last years. They did not, however, check the concentrations of tars after the impinger train to determine the collection efficiency. BTG did report on the collection efficiency [Gansekoele, 2002], however, the collection efficiency was determined qualitatively by the colour of a back-up filter. Therefore, these BTG results will not be considered here.

The discussion in this chapter is focused on the efficiency of tar collection by the impinger train. Other R&D topics are not covered. For instance, BTG and ECN have performed a joint R&D programme in which R&D topics like the temperature of the particle filter, the solvent in the impinger bottles and the method for analysis of gravimetric tars were evaluated. The overall report [Gansekoele, 2002] contains R&D results on these topics, which are summarised in [Brage, 2002].

6.2 Results of ECN

The results given in this paragraph are copied from [Neeft, 2001], unless otherwise stated. At ECN, in 2001 three series of tests with the Guideline were performed:

Samples taken:	Gasifier conditions	Aim of sampling
March 16, 2001	CFB, 850°C	Check methoxypropanol as a solvent, compare Guideline with SPA
July 20, 2001	BFB, 825°C	Compare ethanol and isopropanol as solvents, compare Guideline with SPA
September 26, 2001	CFB, 880°C	Parallel testing BTG and ECN, compare Guideline and SPA

The March 2001 samples will not be considered as their main aim was to compare the Guideline with the SPA method. The September 2001 samples are only considered qualitatively as the collection efficiency in these tests was not determined (SPA samples were only taken upstream from the impinger train). Results from the July tests are described in detail. In the July and September tests two types of frits were used: a standard G1 frit and a denser G3 frit. Conditions in the impinger bottles and the type of frits are shown in the table below.

---

[2]: During the first EU project (2000-2002) the method for sampling and analysis of particles and tars from biomass producer gases was named the "Tar Guideline". During the start of the second project (2002-2005) the name was changed into "draft Tar Standard" which was changed again into "draft Technical Specification (on sampling and analysis of particles and tars)" once it became clear that the CEN standardisation will result in a CEN Technical Specification (CEN TS) and, for the moment being, not in a CEN standard. This CEN TS will later (after 1 or 2 years) be changed into a CEN EN Standard. All these names refer to the same method for sampling and analysis of tars. Of course, the method was improved by small changes over the years 2000 – 2004. At the end of 2004, the final method was established.

		Liquid Quench	**Solvent**	**Impingers (temperature, type of frit)**					
				1	2	3	4	5	6
Date	**Test**			(150 ml)	(75 ml)	(75 ml)	(75 ml)	(75 ml)	Empty
July 2001	1	Yes	Isopropanol	0°C, no frit	0°C, G1	-20°C, G1	-20°C, G3	-20°C, G1	-20°C, G3
July 2001	2	Yes	Isopropanol	**40°C, no frit**	**40°C, G1**	**-20°C, G3**	-20°C, G3	-20°C, G1	-20°C, G3
July 2001	3	Yes	Isopropanol	40°C, no frit	40°C, G1	-20°C, G3	**40°C, G3**	-20°C, G1	-20°C, G3
July 2001	4	Yes	**Ethanol**	40°C, no frit	40°C, G1	-20°C, G3	40°C, G3	-20°C, G1	-20°C, G3
July 2001	5	**No**	Ethanol	40°C, no frit	40°C, G1	-20°C, G3	40°C, G3	-20°C, G1	-20°C, G3
September 2001	1	Yes	Isopropanol	40°C, G1	40°C, G3	-20°C, G1	-20°C, G3	-20°C, G3	-20°C, G3
September 2001	2	Yes	Isopropanol	40°C, G1	**-20°C, G3**	**40°C, G1**	-20°C, G3	-20°C, G3	-20°C, G3

In these tests, the sample flow rate was set to 150 l/h, sampling was performed for about 30 min. Downstream of impinger 6, a µm-filter was placed in all five tests. The pressure drop over the sampling train incl. µm-filter was about 50-100 mbar. During the first test, the pressure difference increased to about 400 mbar. In all other tests, the pressure difference rose slowly to 150-200 mbar pressure difference. Before and after the sampling train (and after the µm-filter), tars were also sampled with the SPA method. SPA is an abbreviation for "Solid Phase Adsorption", the method was developed by KTH, details can be found in [Brage, 1997].

The last test (September 2001, test 2) was performed for only 24 minutes and was then stopped because of a problem with the gasifier (fuel feed was temporarily stopped). During the last four minutes of this test the tar concentration was probably strongly reduced due to an increased air-to-fuel ratio.

During sampling, some qualitative observations were made:

Mist and/or tar aerosols are visible during sampling

1. A thick white mist appears in the first impinger trains. The first impinger with a G3 frit catches most of the mist, however, a close look learns that a fraction of the mist escapes from the impinger and is only removed in subsequent impingers.

Solvent in impingers and filters after impingers obtain a yellow to orange colour

2. The solvent colours yellow to orange-brown. The colour of the first impinger bottle seems to be more orange/brown than the colour of the 4 subsequent impingers filled with liquid which also have a lighter colour.
3. The µm-filters after the sampling train (samples July) get a similar yellow colour. Also BTG observed this yellow colour in a backup-filter after their sampling train during the September tests. This yellow colour is, in the eyes of ECN, a good indicator of the performance of the sampling train. When the filter after the sampling train colours yellow, then also the frit in the last (empty) impinger bottle turns yellow. Apparently, still a small part of the aerosols pass the sampling train, which will further be denoted to as “aerosol slip”.

A temperature gradient in the impinger train reduces the “aerosol slip”

4. It was observed that when the temperature of the first impinger is increased (from 0°C to 40°C) or when two temperature gradients are used (in tests 3, 4, and 5 in July and in test 2 in September), then the aerosol slip is decreased. This is most obviously visible from the colours of the five µm-filters from the July tests, see Figure 1. This shows that a temperature increase from 0 to 40°C of the first impingers results in a lighter yellow colour of the µm filter. The filter remains colourless when also impinger bottle 4 is kept at 40°C so that a second temperature gradient is introduced. In the September tests the two filters stayed colourless independent of the use of one or two temperature gradients. The colour of the isopropanol in impinger 5 was, however, very lightly yellow in test 1 which had only one temperature gradient from +40 to -20°C whereas this colour was almost transparent (very, very lightly yellow) in test 2 with two such temperature gradients. The µm-filters in the September tests remained colourless.

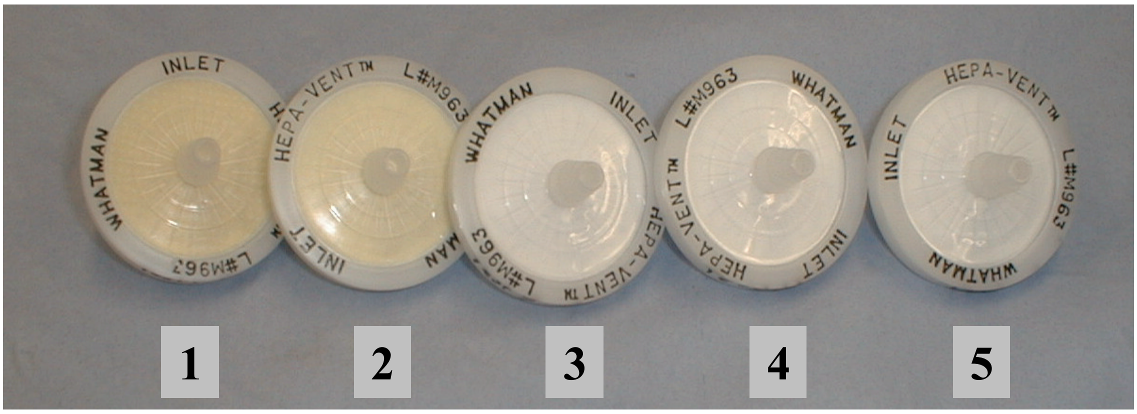

Figure 1 *The five µm-filters for tests 1 to 5 performed July 20, 2001. For black-white prints: the filters 1 and 2 have a clear yellow colour whereas filters 3, 4 and 5 are white*

The collection efficiency in the impinger trains was calculated from the SPA samples before and after the impinger trains: collection efficiency = 100%*(1 – [SPA,after]/[SPA,before]). These data were not published before (*i.e.* they are not part of the [Neeft, 2001] report). For all compounds reported except for the lightest compounds (benzene, toluene, xylenes) the concentrations as measured by SPA correspond very well to the concentrations measured by the Guideline. The collection efficiency for the July tests are shown in the table below.

	Removal efficiency in July tests				
Compound	**Test 1**	**Test 2**	**Test 3**	**Test 4**	**Test 5**
Benzene	**75,5%**	**95,6%**	**97,1%**	**98,9%**	**99,1%**
Pyridine	100,0%	100,0%	100,0%	100,0%	100,0%
Toluene	**89,8%**	**93,5%**	**94,8%**	**98,0%**	**97,9%**
m/p-Xylene	100,0%	100,0%	100,0%	100,0%	100,0%
o-Xylene + Styrene	100,0%	100,0%	100,0%	100,0%	100,0%
Phenol	**99,0%**	**99,2%**	**99,5%**	**97,1%**	100,0%
Indene	100,0%	100,0%	**99,8%**	100,0%	100,0%
Naphthalene	100,0%	100,0%	100,0%	100,0%	100,0%
2-methylnaphthalene	100,0%	100,0%	100,0%	100,0%	100,0%
1-methylnaphthalene	100,0%	100,0%	100,0%	100,0%	100,0%
Biphenyl	100,0%	100,0%	100,0%	100,0%	100,0%
Ethenylnaphthalene	100,0%	100,0%	100,0%	100,0%	100,0%
Acenaphthylene	100,0%	100,0%	100,0%	100,0%	100,0%
Fluorene	100,0%	100,0%	100,0%	100,0%	100,0%
Phenanthrene	100,0%	100,0%	100,0%	100,0%	100,0%
Anthracene	100,0%	100,0%	100,0%	100,0%	100,0%
Fluoranthene	100,0%	100,0%	100,0%	100,0%	100,0%
Pyrene	100,0%	100,0%	100,0%	100,0%	100,0%
Chrysene	100,0%	100,0%	100,0%	100,0%	100,0%
Benzo(b)fluoranthene	100,0%	100,0%	100,0%	100,0%	100,0%
Benzo(k)fluoranthene	100,0%	100,0%	100,0%	100,0%	100,0%
Benzo(a)pyrene	100,0%	100,0%	100,0%	100,0%	100,0%
Perylene	100,0%	100,0%	100,0%	100,0%	100,0%
Total GC tars (excl. Benzene)	**99,3%**	**99,4%**	**99,6%**	**99,7%**	**99,8%**
Tars from acenaphthylene to pyrene	**100,0%**	**100,0%**	**100,0%**	**100,0%**	**100,0%**

6.3 Results of VTT

VTT has performed several tests after bubbling and circulating fluidised bed gasifiers. A number of different solvents were used in the impinger trains (DCM, ethanol, isopropanol, methoxypropanol) as part of the work was aimed at choosing the solvent and optimising the impinger train design. In this report, only the isopropanol results of VTT will be reported. In the VTT tests with isopropanol, the temperature of the impinger bottles was varied (see table beneath). In order to determine the collection efficiency, a second impinger train was added. VTT did not use glass frits, but used glass beads (outer diameter 6 mm) in impinger bottles 1, 5 and 6. More details on these tests can be found in the Appendix.

The results are shown in the two tables below. Tests were performed at three temperature levels of the impingers, for each level two tests were performed and an average removal efficiency was calculated. The removal efficiency was calculated as the percentage of the tar found in the first sampling train, compared to the total amount of tar found (first and second sampling trains). For the 6 tests, the removal efficiency is shown in the first table:

Sample	**Cooling**	**Removal efficiency**			
		Total GC tars	**Average**	**Tars from acenaphtylene to pyrene**	**Average**
		%	**%**	**%**	**%**
1	4 x +40°C / 2 x –20°C	99		95	
2	Idem	100	100	98	97
3	4 x +20°C / 2 x –20°C	98		87	
4	Idem	100	99	96	92
5	2 x +20°C / 4 x –20°C	97		82	
6	Idem	98	98	87	85

Compounds specific removal efficiencies for tests 1, 2, 5 and 6 are listed in the following table:

	Compound specific removal efficiency in VTT tests			
Compound	**Test 1**	**Test 2**	**Test 5**	**Test 6**
Benzene	**99,4 %**	100 %	100 %	100 %
Toluene	100,0 %	100 %	100 %	100 %
Ethynylbenzene	100,0 %	100 %	100 %	100 %
Styrene	100,0 %	100 %	100 %	100 %
4-Methylstyrene	100,0 %	100 %	100 %	100 %
Indene	100,0 %	100 %	100 %	100 %
Naphthalene	100,0 %	100 %	100 %	100 %
2-Methylnaphthalene	100,0 %	100 %	100 %	100 %
1-Methylnaphthalene	100,0 %	100 %	100 %	100 %
Biphenyl	100,0 %	100 %	100 %	100 %
2-Ethylnaphthalene	100,0 %	100 %	100 %	100 %
Acenaphthylene	100,0 %	100 %	100 %	100 %
Acenaphthene	100,0 %	100 %	100 %	100 %
Fluorene	100,0 %	100 %	**92 %**	**94 %**
Phenanthrene	100,0 %	100 %	**73 %**	**77 %**
Anthracene	100,0 %	100 %	**70 %**	**74 %**
4H-Cyclopenta[def]phenanthrene	100,0 %	100 %	**65 %**	**71 %**
Fluoranthene	100,0 %	100 %	**70 %**	**77 %**
Benz[e]acenaphthylene	100,0 %	100 %	**67 %**	**71 %**
Pyrene	**72,7 %**	**86 %**	**63 %**	**72 %**
Total GC tars (excl. Benzene)	**99,1 %**	**99,6 %**	**96,8 %**	**97,8 %**
Tars from acenaphthylene to pyrene	**95,9 %**	**97,7 %**	**82,4 %**	**86,8 %**

7. Arguments used in the discussion on optimised sampling conditions

7.1 General arguments

The number of parameters, that have an influence on the collection efficiency of the impinger train, is large. At least the following parameters were discussed:

- Solvent in the impinger bottles;
- Temperatures of the impinger bottles;
- Flow rate of the producer gas through the impinger bottles;
- Actual design of the impinger bottles
  (specifically the height and the diameter of the bottle and the standpipe);
- Presence of glass frits or glass beads in the impinger bottles;
- Pressure drop over the sampling train as a result of the presence of glass frits.
- Safety of the use of the method "on-site" (industrial plant facility, north-European weather conditions)
- Actual composition of the tar
  (optimised conditions could be different for low temperature tar compared to high temperature tar);

It was acknowledged that much R&D work could be performed in order to optimise these parameters towards high collection efficiency of the tars. It was decided to follow a practical approach, basically because of the following two arguments:

1. Limited time and budget to perform R&D
2. Focus on the development of a practical method, which should be **good enough,** and not necessarily be the **best one possible**.

Therefore, it was decided to use the information that was available and to choose for the best method **on the basis of this information**. This method should be good enough to give satisfactory repeatability and reproducibility date in Round Robin analysis and parallel tests.[3]

7.2 Specific arguments

The following specific arguments led to the set-up in the current Technical Specification on sampling and analysis of particles and tars in biomass producer gases:

7.2.1 Poor tar sampling is (partly) a result of formation of tar aerosols

A number of observations led to the conclusion that the formation of aerosols is at least partly responsible for the fact that a collection efficiency of 100% is difficult to reach with the impinger train. These observations are:

1. At the entrance of the impinger train, almost in all tests a white fog can be seen. This white fog disappears in downstream impinger bottles (observation 1 of paragraph 2.2).
2. In some tests, both glass frits in the empty 6th impinger bottle and backup μm-filters coloured yellow. This colour is ascribed to the collection of yellow coloured tar aerosols.
3. When analysing the tar content in the 6 individual impinger bottles (in a test without frits), tars were found in all bottles and the tar concentrations in impingers 2 – 6 were more or

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[3]: As sampling is part of the method, it is not possible to obtain full data on repeatability and reproducibility by sending round samples for Round Robin analysis. Apart from Round Robin analysis on the analysis part of the method, also two parallel tests were performed. In a parallel test, several institutions are present at a running gasifier to sample the product gases simultaneously in order to obtain data on repeatability and reproducibility of the overall method.

less constant (figure 3 in [Brage 2002]). This observation was ascribed to aerosols passing the impingers [Brage, 2002].

It was tried to analyse the tar compounds in the yellow deposit on the backup μm-filters. No tar compounds could be detected by GC-FID or GC-MS. Apparently, the deposit contains other (high molecular) compounds. The same observations had earlier been made for the extracts of the 325°C particle filter, which was yellow but which did not or hardly contain GC-FID or GC-MS detectable tar compounds (see [Neeft, 2001]). After discussion, the members of the CEN BT/TF 143 still believe that the yellow deposit is likely to be tar as the colour is the colour of high temperature biomass gasification tar and the colour of the isopropanol after collection of tars.

7.2.2 A temperature of 40°C in the first impingers gives a better performance than 20°C

The results of VTT tests 1-4 indicate that the method performs better when the temperature of the first impinger bottles is 40°C instead of 20°C. A plausible explanation is that the dissolution of tars at higher temperature is faster than at lower temperature. A second possible advantage of a higher temperature is that at a higher temperature more isopropanol will evaporate, leading to a higher concentration of aerosols and/or to larger aerosol droplets when the gas is cooled to -20°C and, therefore, to a more efficient collection of the tars which are part of the aerosols.

A temperature of 40°C is the highest temperature possible for sampling with isopropanol, as at higher temperatures the evaporation of isopropanol is that high that the isopropanol might be totally evaporated before the sampling is completed, in particular when sampling times have to be long due to low tar concentrations. At long sampling times (longer than one hour), it is recommended to have a first impinger bottle of 250 ml with 150 ml of solvent in order to avoid evaporation of all solvent during sampling.

7.2.3 Fine glass frits improve the efficiency of sampling of tar aerosols

When comparing the results of the VTT tests with the ECN tests, it can be concluded that the collection efficiency of the ECN tests is higher (100% for tars from acenaphthylene to pyrene) compared to the VTT tests (up to 97% for tars from acenaphthylene to pyrene). The major difference between the ECN and the VTT set-up was the use of glass beads in the VTT set-up and the use of glass frits in the ECN set-up.

After discussion, the hypothesis is that G3 frits capture part of the aerosols and, therefore, increase the collection efficiency. This hypothesis is supported by the visual observations when performing a test with and without a G3 frit. Without a frit a white fog is witnessed in three, four or even five impinger bottles whereas a G3 frit in the second impinger bottle removed all or virtually all visible droplets [Brage, 2002]. Visually, there is a large difference between G1 frits / glass beads and G3 frits. The G1 frits and the glass beads cause relatively large gas bubbles, the frits / beads might therefore not be capable of removing small aerosols. They do, however, have a function in the tar collection as the gas bubbles in the impingers are smaller than bubbles without frit or glass beads. The smaller bubbles enhance the dissolution of tars in the isopropanol (they increase the mass transfer rate by decreasing the transfer distance). It was concluded, therefore, that G3 frits are preferred.

The above hypothesis was also supported by the more detailed analysis on a compound basis. In the ECN tests, the only compounds that were not collected with an efficiency of 100% were the small compounds (benzene, toluene, xylene, phenol and in one test indene). In the VTT test, on the contrary, the smaller compounds were collected quantitatively (on behalf of one number for benzene of 99,4 %) whereas the higher tar compounds were not collected quantitatively. This indicates that in the VTT test, slip of aerosols does occur whereas the dissolution of smaller compounds is somewhat more efficient which is possibly due to the four impinger bottles at +40°C in comparison with three such bottles in the ECN tests. The most logical explanation that was found in the discussions in the CEN BT/TF 143, was that G3 frits enhance the capturing of aerosols.

7.2.4 A second temperature drop (+40 to -20°C) improves the efficiency of sampling of aerosols

It was also concluded to be likely that the temperature gradient (from +20 or +40°C to -20°C) enhances the formation of aerosols and, therefore, the capturing of tars in combination with G3 frits. The rationale for this is that at 40°C isopropanol evaporates and the gas becomes saturated or almost saturated with isopropanol. When the temperature of the gas is decreased to -20°C, the isopropanol vapour will partly condense forming more or larger aerosols compared to the amount or size of aerosols in a gas that stays at one temperature.

In ECN tests 3, 4 and 5 a second temperature gradient was introduced (*i.e.* impingers 1 and 2 at +40°C, impinger 3 at -20°C, impinger 4 at +40°C and impingers 5 and 6 at -20°C). In these tests the μm backup filters did not colour yellow whereas they did in the tests with only one temperature gradient. Although it could not be shown that this yellow colour is indeed caused by tar aerosols (tar compounds could not be detected in the yellow deposit), is seems likely that the yellow colour is caused by high-molecular tar compounds and that the yellow colour, therefore, is a marker for the presence of tar aerosols after the impinger train.

The final conclusion was that G3 frits are preferred, in combination with a temperature of +40°C and two temperature gradients from +40°C to -20°C. As the G3 frits remove the aerosols after a temperature decrease (including the one after the particle filter to the impinger train), and as the first impinger should preferably not contain a frit due to former experiences with blockage of this impinger, it was decided to place G3 frits in impinger bottles 2, 3 and 5. Besides, a G3 frit is placed in impinger bottle 6 as an indicator for passing aerosols (when it turns yellow, this means that some aerosols pass the impinger train).

7.2.5 Fine glass frits cause a risk of high pressure drops over the sampling train

Using fine G3 frits introduces the risk that the pressure drop over the sampling train increases during the tar sampling. The pressure drop can become that high that a good tar sampling is no longer guaranteed. When this happens, it is advised to use courser G2 frits. So far (among others: ECN tests reported here, parallel tests in Oberhausen in November 2004), too high pressure drops have not occurred.

At some sampling locations, the risk of higher pressure drops over the sampling trains should be avoided at any time. This is for instance the case when tars are to be sampled at a commercial gasifier where the risk of a gas leakage should be kept to an absolute minimum. For these circumstances, an alternative set-up of the impinger train is given in the Technical Specification. This set-up is similar to the set-up that VTT did use in the tests that are described in this document: 4 impinger bottles at +40°C, two impinger bottles at –20°C, no frits but glass beads with outer diameter of 6 mm in impinger bottles 1, 5 and 6. When using this alternative set-up, the user should check the collection efficiency of the impinger train as it can be low for the high molecular tar compounds, especially when compounds with a larger molecular weight than pyrene will be reported (see VTT results).

7.2.6 A liquid quench does not seem to have an effect on collection efficiency

In older versions of the Tar Guideline, a liquid quench was part of the set-up. The rationale behind this liquid quench was that the introduction of the solvent isopropanol directly after the hot particle filter would lead to an improved collection efficiency due to:

(a) dissolving tars into the isopropanol already before the impinger train; and
(b) evaporation of isopropanol at increased temperatures directly after the particle filter, resulting in more aerosols in the first impinger bottles and a better collection of tars.

As a better collection efficiency was not found (e.g. compare ECN July 2001 tests 4 and 5), it was decided that a liquid quench is not a required part of the method. A liquid quench can be installed, it still has the advantage that the tubes from the particle filter up to and including the standpipe of the first impinger are washed with isopropanol, avoiding the deposition of tars. Without a liquid quench, washing of these tubings and of the first impinger after the sampling takes more time.

8. Final conditions of Technical Specification

The arguments that were given in the previous chapter have led to the next two requirements for the impinger train in the Technical Specification:

1. Tar collection shall be performed with 6 impinger bottles of which the first acts as a condenser for water. Standard impinger bottles (NS 29/32) of 100 or 250 ml can be 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.
2. One of the following two setups for the 6 impinger bottles shall be chosen. The alternative setup shall only be 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.

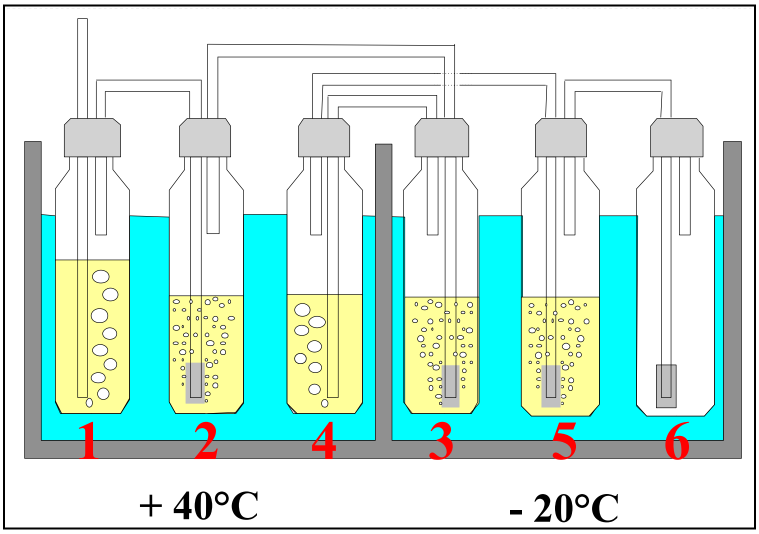
Standard setup

- 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, G2 frits shall be used.
- The temperature of impinger bottles 1, 2, and 4 shall be between 35 and 40°C, the temperature of impinger bottles 3, 5 and 6 shall be between -15 and -20°C.

Alternative setup

- Impinger bottles 1, 5, and 6 contain glass beads. The outside diameter of the glass bead is 6 mm.
- The temperature of impinger bottles 1, 2, 3 and 4 shall be between 35 and 40°C, the temperature of impinger bottles 5 and 6 shall be between -15 and -20°C.

The next figure gives a schematic representation of the impinger train in the Standard Setup.



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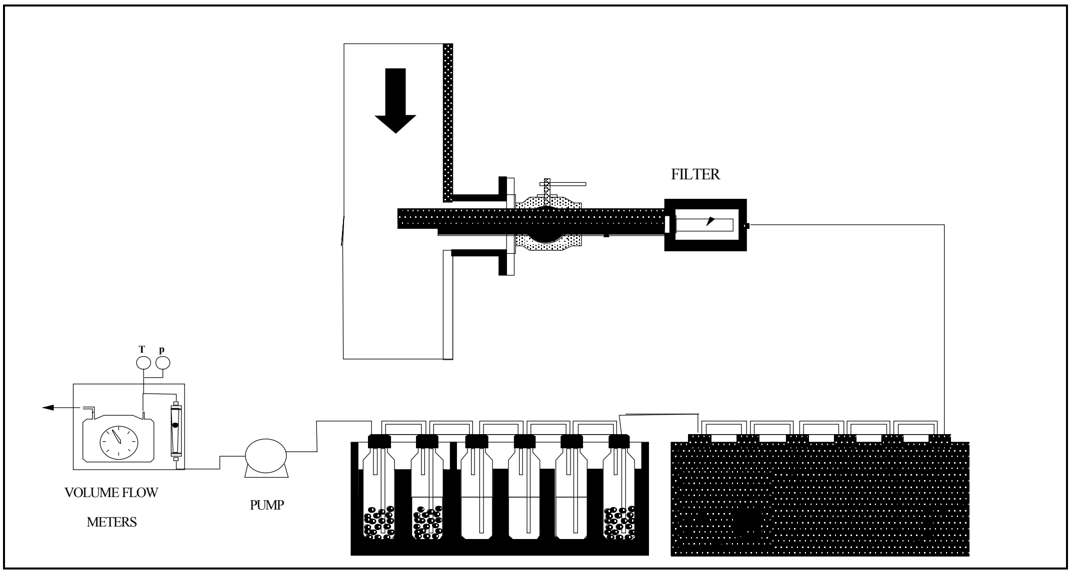
[Neeft, 2001]	J.P.A. Neeft, E. Zuiver and B.F. van Egmond, "ECN contribution to R&D work supporting the development of a Guideline for sampling and analysis of tars in biomass producer gases. Sub-report to a joint BTG-ECN report to Novem". ECN-CX-001-048, October 2001

Appendix B Results of VTT

Data reported by Marjut Suomalainen to the project partners, april 2004.

Set-up

A **check-up** sampling train (a VTT method sampling train, 6 impinger bottles, solvent DCM) was connected between the **actual** sampling train and the pump (picture 1) in order to determine the amount of tar passing through the actual sampling train.



Picture 1 *The set-up*

The cooling of impinger bottles in different experiments are given in the table 1. No frits were used.

Table 1 *The cooling of impinger bottles*

Measurement	**1,2**	**3,4**	**5,6**	**Check-up**
Solvent	IP	IP	IP	DCM
Filling of the impinger bottles:				
Bottle 1	100 ml + glass beads	100 ml + glass beads	100 ml + glass beads	0 ml + glass beads
Bottle 2	100 ml	100 ml	100 ml	70 ml
Bottle 3	100 ml	100 ml	100 ml	70 ml
Bottle 4	100 ml	100 ml	100 ml	70 ml
Bottle 5	100 ml + glass beads	100 ml + glass beads	100 ml + glass beads	30 ml + glass beads
Bottle 6	50 ml + glass beads	50 ml + glass beads	50 ml + glass beads	0 ml + glass beads
Cooling of the impinger bottles:				
Bottle 1	+40 °C [1]	+20 °C	+20 °C	0 °C
Bottle 2	+40 °C	+20 °C	+20 °C	0 °C
Bottle 3	+40 °C	+20 °C	-20 °C	0 °C
Bottle 4	+40 °C	+20 °C	-20 °C	0 °C
Bottle 5	-20 °C	-20 °C	-20 °C	-70 °C
Bottle 6	-20 °C	-20 °C	-20 °C	-70 °C

Results

Results are in the table 2. Removal efficiency is calculated as follows: tar concentration of actual sampling train, per cent of total tar concentration (actual + check-up sampling trains).

Table 2 *Results*

Sample	Cooling	Removal efficiency			
		Total GC tars %	Average %	Tars from acenaphtylene to pyrene %	Average %
1	4 x +40C / 2 x -20C	99		95	
2	4 x +40C / 2 x -20C	100	100	98	**97**
3	4 x +20C / 2 x -20C	98		87	
4	4 x +20C / 2 x -20C	100	99	96	**92**
5	2 x +20C / 4 x -20C	97		82	
6	2 x +20C / 4 x -20C	98	98	87	**85**

Appendix C Description of the full CEN Tar Measurement Standard

CEN/BT/TF 143

Date: 2005-07

TC 143 WI CSC 03002

Pr CEN/TS 15439

CEN/TC 143

Secretariat: NEN

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

Thermische Biomassevergasung — Teer und Staub aus dem Produktgas — Probenahme und analytische Bestimmung
Gazéification de Biomasse — Goudron et Particules dans les Gaz produits — Échantillonnage et analyse

ICS: 75.160.30
Descriptors: Biofuels - Biomass - Determination of content - Mathematical calculations - Organic compounds - Particles - Product gases - Sampling - Specimen preparation - Tar - Testing

Foreword

This document TC 143 WI CSC 03002 has been prepared by Technical Committee CEN/TC 143 “Measurement of organic contaminants (tar) in biomass producer gases”, the secretariat of which is held by NEN.

This document has been fully accepted by the official CEN voting commissions.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association.

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9. 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, for instance, a gas engine or gas turbine.

The development of this Technical Specification started out of the need for a reliable method for the measurement of tars. For most contaminants in product gases of biomass gasification, well-developed measurement techniques exist that 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 existed in these related technology fields. As some of the tars were (and are) seen as the major problem causing contaminants in biomass gasification, manufacturers and other workers in this field used a number of different sampling and analysis methods to determine the level of tars. As a result, comparison of data and definition of clear maximum allowable concentrations for tars was problematic. This formed an obstacle for market introduction of biomass gasification systems, as tars can cause damage or require 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 levels of the organic compounds present in the gasification product gases exceed the levels found in flue gases generally by more than three 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, coal tars can also 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[4]. 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 what 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 a background Technical Report [1].

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

10. Scope

This European Technical Specification gives methods for sampling and analysis of tars and particles in order to determine the load of these contaminants in flowing biomass gasification product gases. The Technical Specification is applicable to sampling and analysis of tars and particles in the concentration range typically from 1 mg/m_n^3 to 300 g/m_n^3 (tars) and from 20 mg/m_n^3 to 30 g/m_n^3 (particles) at all relevant sampling point conditions (0 °C to 900°C and 60 kPa to 6000 kPa (0,6 bar to 60 bar))[5), 6)]. Particle concentrations lower than 20 mg/m_n^3 are outside the scope of this Technical Specification and can be measured according to EN 13284-1.

Application of this Technical Specification allows determination of five different parameters:

A. The concentration of gravimetric tar in mg/m_n^3;
B. The concentration of individual organic compounds in mg/m_n^3. This Technical Specification gives data on repeatability and reproducibility for the compounds listed in Annex B. The Technical Specification is also applicable for other organic compounds (e.g. those mentioned in Annex A), but repeatability and reproducibility have not been assessed for compounds other than those in Annex B;
C. The sum of concentrations of identified GC-detectable compounds listed in Annex B;
D. The sum of concentrations of all GC-detectable compounds with retention times in the range of benzene to coronene calculated as naphthalene (benzene excluded), given that this sum of concentrations can be determined.
E. The concentration of particles in mg/m_n^3.

[5)] In fact it is not correct to give a concentration or to give concentration ranges for "tar" (see also its definition in chapter 0). This Technical Specification is designed and has been evaluated for measurement of tar and particles in the following concentration ranges:

Gravimetric tar	500 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	20 mg/m_n^3 to 30 g/m_n^3

The concentration range mentioned for gravimetric tar is a range based on a sampling time of 2 hours. Lower concentration limits can be attained with proportionally longer sampling times (*e.g.* 100 mg/m_n^3 with a sampling time of 10 hours). Due to the determination method, it is recommended not to determine gravimetric tar below the concentration limit.

[6)] The performance characteristics in chapter 23 are determined under atmospheric conditions. Under pressurised conditions, the Technical Specification as a whole has bot been evaluated. However, sampling under pressurised conditions is based on relevant experience (relevant construction details of probes are mentioned in a background document [1]) and the analysis of the liquid samples is identical for atmospheric and pressurised gasification. Therefore, pressurised conditions are included in this Technical Specification.

11. 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).

EN 13284-1:2001	*Stationary source emissions – Determination of low range mass concentration of dust – Part 1: Manual gravimetric method*
ISO 5725-1:1994 Technical Corrigendum 1:1998	*Accuracy (trueness and precision) of measurement methods and results – Part 1: General principles and definitions*
ISO 5725-2:1994 Technical Corrigendum 1:2002	*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	*Stationary source emissions – Manual determination of mass concentration of particulate matter*

12. Terms and definitions

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

3.1

aerosol

suspension of solid or liquid particles in a gas.

NOTE The term aerosol includes both the particles and the suspending gas. The particle size may range from about 0,002 µm 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 [7]

3.3

contaminated biomass

biomass not being uncontaminated biomass

NOTE See 3.20

3.4

downdraft gasification

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) passes through the bed co-currently[7]. The product gas leaves the gasifier at the base

3.5

entrained flow gasification

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

3.6

fluidised bed gasification

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, oxygen or steam)

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

NOTE Gasification can be accomplished by direct internal heating provided by partial oxidation using e.g. substoichiometric air or oxygen. Alternatively, concepts based on either indirect heating methods or autothermal methods using exothermic reduction reactions may be applied

3.8

GC detection limit

lowest concentration that can be detected by the GC equipment.

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[7] Co-current does not automatically mean downdraft but can also mean updraft, although co-current updraft designs are uncommon

NOTE This concentration depends on the quality of the equipment and is defined as twice the noise level in the GC chromatogram.

3.9
GC-detectable tar
tar that can be measured as a gaseous mixture of individual components according to standard (or state of the art) gas chromatographic practice

3.10
gravimetric tar
evaporation/distillation residue from particle free sampling solution(s) determined by gravimetric analysis

3.11
isokinetic sampling
sampling at a flow rate such that the velocity and direction of the gas entering the sample nozzle are the same as they are in the gas in the duct at the sampling point

3.12
normal conditions
conditions with a temperature of 273,15 K, pressure of 101 325 Pa (1,013 25 bar) and on a dry basis

3.13
particles
solid residue collected by a particle filter after solvent extraction or solid residue from filtration of sampling solution(s)

NOTE Solid residue may contain a small amount of insoluble polymerised tar

3.14
Petersen column
alternative to impinger bottles in the sampling train. The Petersen column is a piece of glass equipment with two containers for liquid, which act as washing stages to remove soluble compounds from a gas. The two containers are separated by a glass frit. A description of the Petersen column is given in Annex C

3.15
product gas
gas resulting from gasification

NOTE The product gas from biomass gasification can be used as a fuel (then also named fuel gas, producer gas or water 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 liquid fuels or chemicals

3.16
pyrolysis
thermal decomposition in the absence of an oxygen source such as air, oxygen, H_2O or CO_2

3.17
sampling train
equipment used for sampling particles and tars, consisting of the particle filter, the impinger bottles or Petersen column, the pump and flow measuring equipment and all connecting tubes

3.18
soxhlet extraction
batch extraction method at the boiling point of the used solvent and atmospheric pressure

3.19
tar

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

3.20
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 that may contain halogenated organic compounds or heavy metals as a result of treatment with wood preservatives or coatings, and including in particular wood derived from construction and demolition waste

NOTE This definition reflects the biomass categorised as “solid biofuels“ under the scope of CEN TC 335 Solid Biofuels [7]

3.21
updraft gasification

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-currently8), where the product gas leaves the gasifier at the top

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8) Counter-current does not automatically mean updraft but can also mean downdraft, although counter-current downdraft designs hardly exist

13. Symbols and abbreviations

BTX : Benzene, Toluene and Xylenes

GC-FID : Gas Chromatography – Flame Ionisation Detector

GC-MS : Gas Chromatography – Mass Spectrometer

id : Internal diameter

ISTD : Internal Standard
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 (lower heating value)

Pa : Pascal
PAH : Polycyclic Aromatic Hydrocarbons

PTFE : Polytetrafluoroethene

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

14. Principle of the measurement method

14.1 Introduction

The principle of the measurement method is based on the discontinuous extractive sampling of a representative part 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.

14.2 Sampling

Samples of tars and particles are taken at a gasifier sample port, which is gas tight so that neither can gas escape from the system nor can oxygen enter it. The sampling train is configured as a heated probe with a heated particle filter to remove solid matter. The volatile tars are trapped in heated or chilled impinger bottles containing an organic liquid absorbent. The sampled gas volume is measured under dry conditions by means of a gas meter. The samples are prepared on-site and are stored until they can be analysed.

14.3 Analysis

14.3.1 Introduction

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 filtered for removal of solid matter.

For the analysis of tars two 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 resulting values are not supplementary, but that there is an overlap between the two tar values. The users attention is also drawn to the fact that the gravimetric method is not suitable for clean gases with low tar concentrations and that its reproducibility is significantly poorer than the GC analysis method.

14.3.2 Gravimetric determination

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

14.3.3 Gas chromatography

Part of the liquid sample is injected into 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 of product gas.

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.

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. However, for updraft gasifier tars the fraction determined may be considerably lower.

15. Reagents

15.1 Solvent for tar collection and Soxhlet extraction

Isopropanol (2-propanol) shall be used as the solvent for tar collection, for Soxhlet extraction and for sample preparation and analysis. The minimum purity of the isopropanol is 99%. It shall be verified with a blank GC determination that the solvent does not contain GC detectable amounts of relevant tar compounds.

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

Other solvents like ethanol or dichloromethane shall only be used for rinsing of the glass and PTFE equipment when cleaning with isopropanol leaves tar residues that can be visually observed.

15.2 Carrier gas in gas chromatography

The carrier gas shall be helium of acceptable purity or a suitable alternative as specified by the GC manufacturer.

15.3 Calibration standards

All reagents shall be of recognised analytical reagent quality, preferably analytical or "pro analysis" grade. The tar compounds are named in Annex A and Annex B.

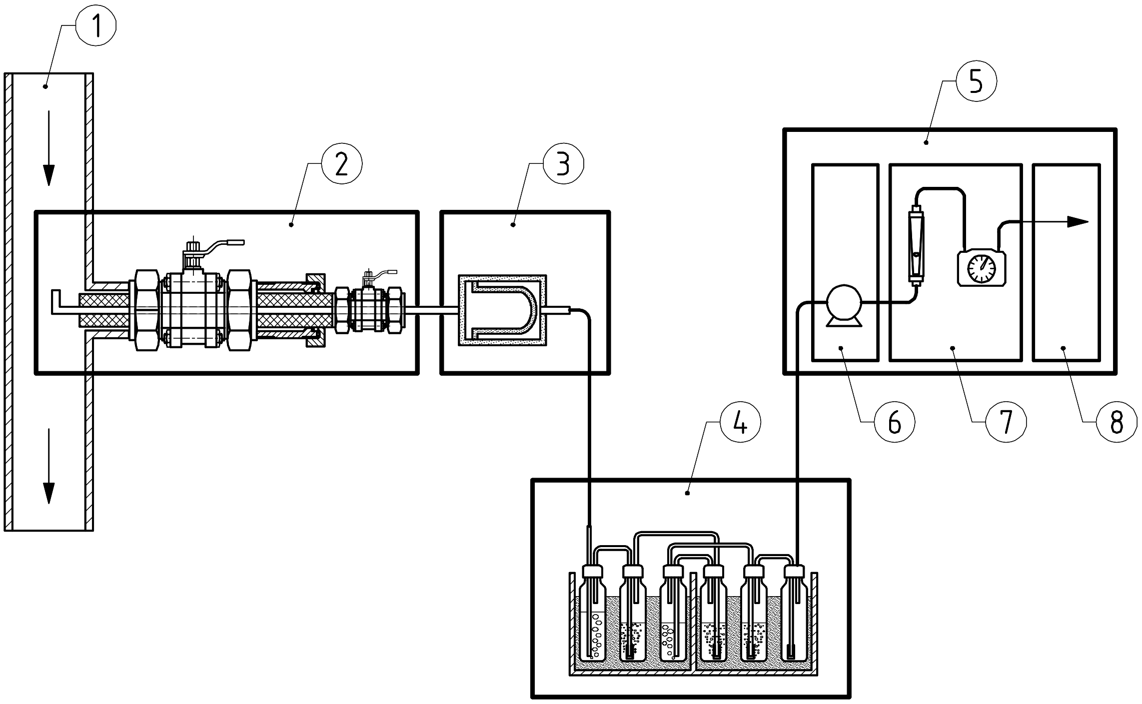
16. Equipment

16.1 Equipment for sampling

16.1.1 Description of the sampling equipment

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 are specified to avoid both condensation of tars and thermal decomposition of tars. Temperatures for the condenser and the impingers are specified to ensure quantitative collection of the tars. An explanation for the choice of equipment and conditions is given in a separate document entitled “Rationale for setup” [2].

The sampling equipment consists of four main modules and respective sub-modules. The main modules are gas preconditioning, particle collection, tar collection and volume measurement. These modules are shown in Figure 1. The basic equipment of these modules is mentioned in the next paragraph in Table 16.1. A more detailed description of each module is found in a background Technical Report [1].



Key

1	Gasflow
2	Module 1
3	Module 2
4	Module 3
5	Module 4
6	Sub-module 4.1
7	Sub-module 4.2
8	Sub-module 4.3

Figure 1 — Concept of the modular sampling train

The equipment needed for sampling is mentioned in Table 16.1. Examples and details on construction are described in a background Technical Report [1], including the adaptations needed for module 1 if tars and particles have to be sampled from pressurised gasifiers.

Table 16.1 — General description of modules and sub-modules with purpose and equipment used

	Function	Main equipment	
Module 1 (Gas preconditioning)	Gas cooling, pressure reduction	Nozzle, valves, sampling lines	
Module 2 (Particle collection)	Separation and collection of solids	Heated filter (high temperature)	
Module 3		Option 1	Option 2
(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)	Petersen column (see Annex C)
	Drop collection	Empty impinger (1 bottle with a glass frit)	
Module 4 (Volume registration)			
Sub-module 4.1	Gas suction	Gas drying, pump	
Sub-module 4.2	Gas volume integration	Gas meter, needle valve (adjustment and control of flow rate), rotameter (flow indication), indicators for temperature and differential pressure, barometer	
Sub-module 4.3	Off-gas handling	Outdoor ventilation	

16.1.2 Requirements for sampling equipment

The sampling equipment shall meet the following functional requirements:

- When using impinger bottles of standard design (NS 29/32-250), flow rates through the impinger bottles shall be between 0,1 and 0,6 m_n^3/h. For high gas velocities, requiring a flow rate through the nozzle higher than 0,6 m_n^3/h to meet isokinetic conditions, this requirement plus the requirements on the minimum nozzle diameter and on isokinetic sampling shall be met by splitting the gas flow between the nozzle and the impinger bottles.
- The sampling equipment allows isokinetic sampling according to ISO 9096. If only tars are analysed, isokinetic sampling is still required in all cases with the following exceptions: (1) for pressurised gasifiers; (2) for large-scale gasifiers with large pipe diameters (for example in ISO 9096 duct diameter shall be < 0,35 m for only one sampling point); and (3) if only tar is sampled and 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 in a background Technical Report [1].

- For pressurised gasifiers, the product gas temperature at the location of sampling shall exceed 350°C.
- The equipment shall be gas tight.
- The minimum nozzle diameter shall be 4 mm according to ISO 9096. For isokinetic sampling, the nozzle shall be designed according to ISO 9096.
- Temperatures of the sampling line and the particle filter shall be:
  - between 100 °C and 125°C for updraft gasification;
  - between 300 °C and 350°C for downdraft, fluidised bed and entrained flow gasification.
- Gas velocities from the nozzle to the particle filter shall be higher than 25 m/s to avoid particle deposition.
- The filters (absolute filters) shall be manufactured from quartz and shall have a retention capacity of at least 99,998 % for particles of size 0,3 μm (DOP standard[9]).
- Thimble filters shall be used. The dimensions of filter thimbles shall be selected 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 mm 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 probe and filter holder shall be manufactured from 310 or 316 grade stainless steel or, when using another material, the user shall verify that the material does not affect the composition of tar compounds. Any material used shall endure a temperature 50°C higher than the operating temperature.
- A thermocouple shall be placed either on the surface of, or inside, the filter holder to measure the gas temperature at the filter.
- Tar collection shall be performed either with six impinger bottles (A) or with a Petersen column (B). The user shall decide to use either a Petersen column (B) or one of the setups with impinger bottles (A1 or A2).

  (A) Impinger bottles
  Standard impinger bottles (NS 29/32) of 100 ml or 250 ml can be used. Standard dimensions are a length of 200 mm and an outer diameter of 40 mm (100 ml impinger bottle) or 55 mm (250 ml impinger bottle). For gas flow rates higher than 0,3 m^3_n/h, impinger bottles of 250 ml shall be used. The first impinger bottle acts as a condenser for water. For high moisture gas or for sampling times longer than 1 hour, the first impinger bottle shall have a size of 250 ml as a large amount of condensate will be generated. Impinger bottles 1, 2, 3, 4 and 5 shall contain solvent, impinger bottle 6 shall be empty.

  One of the following two setups for the 6 impinger bottles shall be chosen. The alternative setup shall only be used when the pressure drop over the impinger bottles is too high or when, for safety reasons, the pressure drop must be kept low. When using the alternative setup, the user shall verify the collection efficiency over the impinger bottles.

  (A1) Standard setup with impinger bottles

  - Impinger bottles 2, 3, 5 and 6 shall be fitted with glass frits located either as a filter at the end of the inner tube or 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, G2 frits may be substituted and/or the frit in impinger bottle 2 may be replaced by a G1 frit.

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[9] 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 the reagent DOP is no longer used.

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

<u>(A2) Alternative setup with impinger bottles</u>

- Impinger bottles 1, 5, and 6 contain glass beads. The outside diameter of the glass bead is 6 mm.
- The temperature of impinger bottles 1, 2, 3 and 4 shall be between 35 °C and 40°C, the temperature of impinger bottles 5 and 6 shall be between –15 °C and –20°C.

(B) Petersen column

- The Petersen column shall be constructed according to the dimensions given in Annex C.
- The temperature in the cooling jacket of the Petersen column shall be between –3 °C and +3°C, preferable 0 °C.

- The solvent in the liquid impingers shall be isopropanol.
- The gas suction pump shall be oil-free and air-tight with minimal pulsation. It shall be able to displace at least 1 m^3_n/h at an absolute pressure of 50 000 Pa.
- A calibrated dry-gas meter fitted with a thermocouple shall be used. The pressure drop over the volume-measuring device shall not exceed 250 Pa. An absolute pressure indicator is required at the outlet of the dry gas meter covering the range of 0 kPa to 120 kPa (1,2 bar). Alternatively a differential pressure indicator that can measure ± 20 kPa (± 0,2 bar) may be used in combination with an accurate measurement of local atmospheric pressure.

16.2 Equipment for sample pretreatment and analysis

16.2.1 Equipment for gravimetric analysis

The following equipment is required for gravimetric analysis:

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

16.2.2 Equipment for gas chromatography

The following equipment is required for gas chromatographic analysis:

- Soxhlet apparatus
- A high resolution Gas Chromatograph – Mass Spectrometer (GC-MS), incorporating a mass spectrometer with a mass range of 20 M/z to 400 M/z, or a high resolution Gas Chromatograph – Flame Ionisation Detector (GC-FID).
- Integration software package (usually included with GC)
- Non-polar capillary GC column packed with, for example, DPDM-siloxane (5 % diphenyl + 95 % dimethyl) copolymer phase. Dimensions are typically 30 m to 60 m length, 0,25 mm id. and a film thickness of 0,25 µm
- Calibrated analytical balance with a resolution of at least 0,1 mg, 0,01 mg being preferable
- General laboratory equipment, such as volumetric flasks, measuring cylinders, syringes and pipettes, all calibrated according to relevant National Standards
- If there is any risk that ferrules may be in contact with the sample gas, ferrules made up of no more than 49 % graphite (e.g. 60 % polyimide/40 % graphite) shall be used at the GC column injection inlet to avoid possible adsorption of tar compounds.

17. Preparation of sampling equipment

17.1 Preconditioning of filter thimbles

Filter thimbles shall be pre-calibrated as follows:

1. The quartz thimble filter shall be dried in an oven at 110 °C at atmospheric pressure overnight (according to ISO 9096).
2. An aluminium foil shall be weighed using an analytical balance with an accuracy of ± 0,1 mg.
3. The filter shall be removed from the oven and shall be wrapped directly in the aluminium foil.
4. The filter shall be allowed to acclimatise in a desiccator at room temperature.
5. The filter plus aluminium foil shall be weighed on the same analytical balance and the weight of the filter shall be calculated.
6. The aluminium foil shall be removed from the filter, the filter shall be mounted and the filter holder shall be heated to its set value.

17.2 Cleaning of equipment

Laboratory glassware shall be cleaned according to good laboratory practice, for example by using a cleaning agent (laboratory detergent) followed by an annealing treatment at 500°C for 2 hours. An example of such a cleaning method is given in a background Technical Report [1].

The efficiency of the treatment shall be randomly verified experimentally using blank determinations to ensure that no interfering contamination has occurred.

17.3 Preparation of impinger bottles or Petersen column

17.3.1 Impinger bottles

Impinger bottles shall be prepared as follows:

1. An amount of 50 ml of isopropanol shall be added to 100 ml impinger bottles and an amount of 100 ml of isopropanol shall be added to 250 ml impinger bottles. For sampling times longer than 1 hour only, a 250 ml bottle shall be used for the first impinger bottle and this shall be filled with 150 ml isopropanol to avoid the evaporation of all isopropanol during the sampling.

2. The drop-collecting bottle shall be placed after the impingers.

3. The impinger bottles shall be cooled or heated 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. At least 30 minutes shall be allowed for cooling of the impinger bottles from room temperature to the sampling temperature of –20°C.

17.3.2 Petersen column

Approximately 200 ml isopropanol shall be added through the filling stubs to both washing stages of the Petersen column, above and below the glass frit. In total, approximately 400 ml of isopropanol shall be used.

The isopropanol shall be circulated in the same direction as the gas flow (co-currently) through the cooling jacket of the column and the liquid cooling unit until the isopropanol has reached a temperature of approximately 0°C.

After sampling, the first washing stage shall be emptied by opening the lower valve of the column. The second washing stage above the glass frit shall then be emptied by applying suction below the frit (achieved by use of the sampling train vacuum pump). The flash back of solvent through the frit will keep the frit clean. The solvent from both washing stages shall be collected in the same storage bottle.

17.4 Sampling train leak test

17.4.1 Introduction

Prior to sampling a leak test shall be performed. This can be carried out by either pressurising or evacuating the entire sampling train. The user shall select which of these procedures to follow.

17.4.2 Pressurising the entire sampling train

The method for leak testing by pressurisation of the sampling chain is as follows:

1. Nitrogen or compressed air from a cylinder shall be gently fed into the particle filter inlet and the rest of the sampling train, up to 20 kPa (0,2 bar) above the maximum sampling pressure achieved during sampling. The exit of the gas pump shall be isolated by a ball valve adjusted to a closed position. When the excess pressure has reached 20 kPa (0,2 bar), the gas supply from the cylinder shall be stopped.
2. The pressure in the sampling line shall be monitored by a pressure indicator. The pressure shall stay constant. Possible leaks are detected as gas bubbles in the impingers, by a decreasing pressure or by leak indicators.
3. The shutoff valves after the pump shall be carefully opened. This pressure release procedure shall be undertaken with utmost care and over a period of at least one minute.

17.4.3 Evacuating the entire sampling train

The method for leak testing by evacuation of the sampling chain is as follows:

1. A shut-off valve shall be placed at the inlet of the particle filter and adjusted to a closed position.
2. The gas pump shall be turned on and the pressure shall be gently reduced to a pressure of 20 kPa (0,2 bar) below the minimum pressure achieved during the sampling.
3. Possible leaks are detected as gas bubbles in the impingers or by monitoring the gas meter reading.
4. The leakage test shall be terminated by carefully opening the ball valve at the particle filter inlet while the pump is still displacing. When gas bubbles penetrate the condenser and the impingers, the gas flow rate shall be reduced by gently opening the bypass valve over the pump. The pressure release procedure shall be performed with utmost care and over a period of at least one minute.

18. Procedure for sampling

18.1 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 such 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 in a background Technical Report

[1]. 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 specified minimal nozzle diameter of 4 mm. Hence tar sampling is performed non-isokinetically for pressurised gases. The sampling has to be performed at temperatures of at least 350°C.

Non-isokinetic sampling may also be used when only tar is sampled and when the gas temperature under study at the sampling site exceeds 350°C. Such temperatures generally avoid the risk of tar condensation in the form of aerosols and/or droplets and also minimise adsorption of organic compounds on particles.

For product gasses that contain a high concentration of condensables or steam, it is recommended that the outlet flow rate to the dry test meter be adjusted so the inlet flow to the sampling train is limited to 0,6 m_n^3/h .

18.2 Duration of sampling

The actual gas volume to be collected to provide an adequate sample depends on the concentration of tar in the 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 shall be at least 5000 mg/kg of solution for gravimetric analysis and about 10 mg/kg of solution 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 to 100.

With high concentration measurements (tar concentrations 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 that the largest possible nozzle and highest flow rate be selected. If the particle filter clogs up within 30 minutes however, the sampling shall be stopped and a new sample shall be collected using a smaller nozzle and lower sample flow rate, but still in accordance with isokinetic sampling.

In connection with low concentration measurements the use of the largest nozzle diameter and the highest allowed sampling flow rate possible is recommended. If possible, the sampling period should be extended so that at least the minimum recommended concentration of tar in the solution is obtained.

18.3 Sampling procedure

The following sampling procedure shall be followed:

1. The gas meter reading and the starting time shall be recorded. The probe tube shall be turned until the nozzle faces directly upstream. The stop valve shall be opened. The vacuum pump and the timing device shall be started. Then the control valve shall be adjusted to give the required flow reading as calculated according to nozzle size, gas velocity, condensable (steam) volume percent, etc.

2. The rotameter shall be monitored to provide an indication of the gas flow and the static pressure measurement at the gas volume meter. The control valve shall be adjusted as necessary throughout the sampling period to maintain isokinetic sampling. The temperature and static pressure at the gas volume meter (calculated from the pressure gradient over the gas volume meter and from atmospheric pressure) shall be recorded at regular intervals. During sampling the temperature of the impinger cooling bath and the temperature of the filter housing shall be checked.

3. Occasionally the condenser cooling liquid and the impingers shall be agitated 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 shall be terminated (see next paragraph).
5. The vacuum pump shall be stopped, the stop valve in the sample line shall be closed, the timing device shall be stopped and the probe tube shall be turned through 90°. The particle filter shall be dismantled.
6. The time for stopping and the gas volume meter shall be recorded. As soon as possible the filter cartridge shall be removed from the filter housing. It shall be stored in solvent in a tightly closed bottle, to avoid polymerisation of tar during cooling.
7. The sample line shall be cleaned: all surfaces (including metal surfaces) contacting the gas at temperatures lower than the process temperature, shall be washed with the solvent. The washing solutions shall be combined with the actual sample.
8. Immediately after sampling, the content of the impinger bottles or Petersen column shall be decanted into a storage bottle. The impinger bottles or Petersen column shall be rinsed with solvent. The rinsing solvent shall be poured into the storage bottle.
9. If solid tar residue is observed in the impinger after several rinsings with isopropanol, it shall be washed with a more efficient solvent, for example dichloromethane. The amount of solvent shall be as small as possible and the rinse shall be combined with the sample solution. Before using any other solvent than isopropanol the suitability of the other solvent for use with the GC program shall be checked. No ketonic solvent shall be used for rinsing the sampling train due to detected reactions between acetone and ammonia from the producer gas.
10. When the water concentration in the product gas is high (e.g. when using steam or steam/oxygen as gasification agent or when gasifying very moist biomass), the combined sample can be heterogeneous (i.e. the sample separates into two or more phases). If it is heterogeneous, isopropanol shall be added to the combined sample until it remains homogeneous after stirring 10).
11. The probe shall be flushed with N_2 if the probe is not removed. This is intentionally not according to ISO 9096. A procedure for removal of the probe is given in a background Technical Report [1].

---

10) For very moist product gases, excess isopropanol should be added to the combined sample until the solution becomes homogeneous. This will result in a rather diluted sample. Another solution, instead of diluting the combined sample with isopropanol, is to analyse the contents of the moisture collector separately. Eventual rinsings of the moisture collector with apolar solvents should be added to the combined sample. This solution would result in a slight modification of Figure 2 (see page 83) and doubles the number of (GC or gravimetrical) analyses to be made.

19. 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) the solution shall be stored in a sealed, dark bottle under a nitrogen atmosphere. The analysis shall be performed and completed as soon as possible and within one month of sampling. A clear glass bottle may be used in place of a dark bottle, provided it is kept in the dark.

The particle filter shall be handled 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.

The filter cartridge shall be stored in isopropanol in a jar with a sealed screw cap. The storage jar shall be marked with a clear identification label and shall be kept at a temperature < 5°C until analysis.

20. Preparation for analysis

20.1 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 are described in VDI 2457 Part 1 [3].
The analyst shall select the operating conditions of the GC analyser to accommodate the requirements of the MS or FID detector 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 port temperature:	275°C
Carrier gas:	Helium
Pressure:	Depends on the detector and column length
Velocity of carrier gas:	(20 – 40) cm s^{-1}
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
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 shall select the compounds for external calibration (calibration standards) and for internal calibration (internal standards). Compounds that have been used successfully as calibration compounds for analysis of biomass tar compounds are listed in Table 20.1.

Table 20.1 — Calibration compounds for analysis of biomass tar compounds

---	GC-FID	GC-MS
Internal Standards	n-decane, n-dodecane, o-terphenyl	phenanthrene-d_{10}, benzene-d_6, phenol-d_6, or benzopyrene-d_{12}
Calibration Standards	Compounds listed in Annex B	Compounds listed in Annex B

Examples of how to prepare calibration standards can be found in a background Technical Report [1]. This Technical Specification only gives the requirements for the calibration standards. The procedures shall be selected by the analyst based on experience and/or the examples quoted.

20.2 Requirements for GC calibration standards and internal standards (ISTD)

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

- If the compound to be used for external calibration or an ISTD is a suspected carcinogen, primary dilutions of this material shall be undertaken in a fume cupboard;
- All solutions with ISTD and calibration standards shall be stored in amber PTFE-sealed screw-cap bottles in a refrigerator;
- ISTD solutions shall be prepared from pure or, if available, certified standard materials and shall be prepared in isopropanol;
- ISTD solutions shall be replaced after six months or if comparison with check standards indicates a problem;
- Calibration standards shall be made up from pure or, if available, certified compounds listed in Annex B and shall be prepared in isopropanol;
- Calibration standards shall be prepared with at least five concentration levels for each compound of interest. The lowest concentration level shall be near the detection limit;
- The linearity of the calibration function, as determined from linear regression, shall be at least 0,995.
- Unless the manufacturer's information or stability trails indicate otherwise, the calibration standard solutions shall be stored in the dark between 0 °C and +4°C.

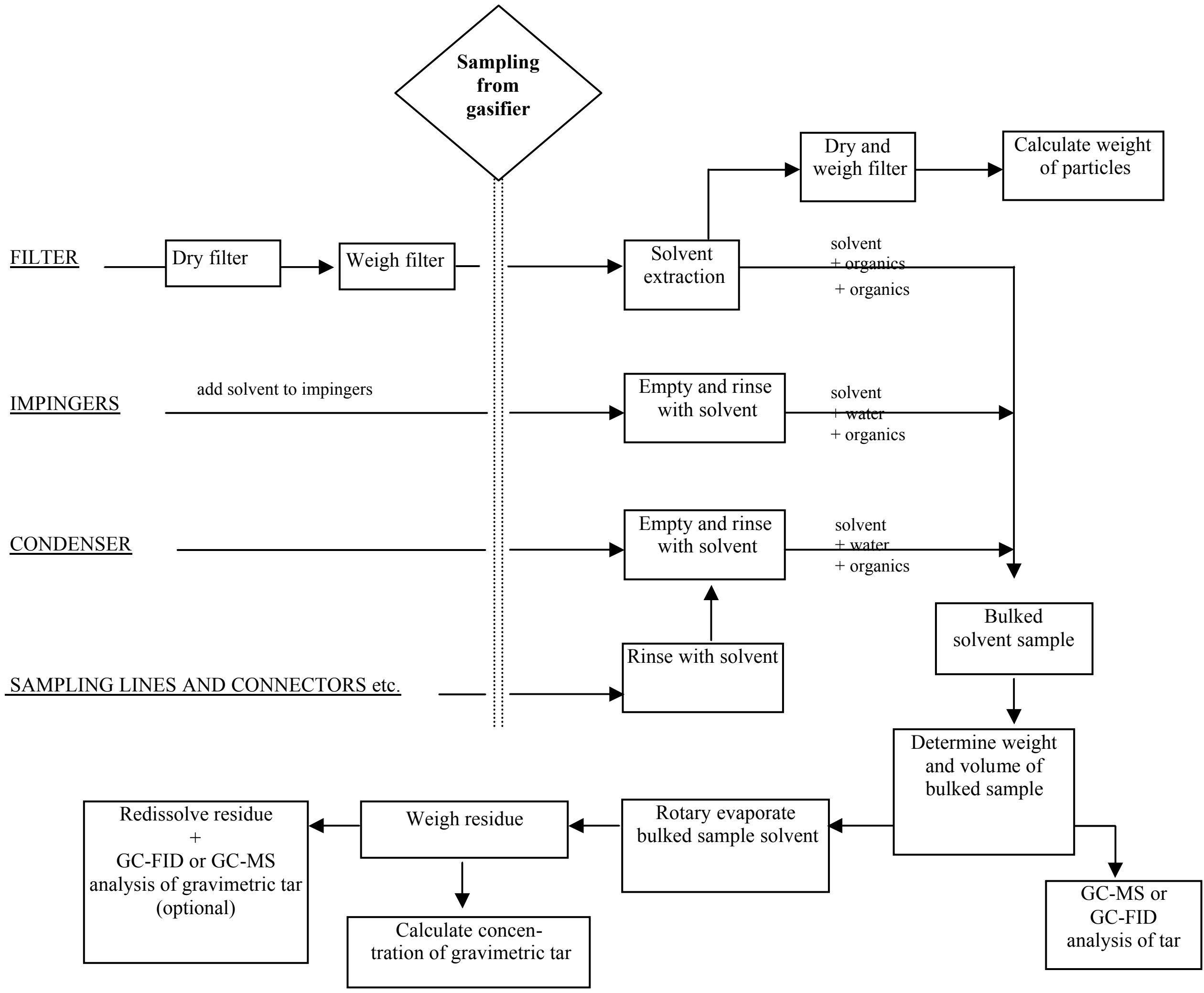

Figure 2 — Post-sampling procedures

21. Analysis procedures

21.1 Soxhlet extraction procedure

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

1. The thimble filter shall be transferred to the Soxhlet apparatus. It shall be kept in the vertical position to avoid loss of particles. The appropriate amount (250-500 ml) of isopropanol shall carefully be added to the Soxhlet apparatus. The filter shall be extracted until the drops of isopropanol coming out of the filter are clear or for at least six to eight (6-8) hours, whichever is the greater. Note that at low tar concentrations, salts dissolving from the filter might influence the concentration of gravimetric tar. Therefore, when low tar concentrations are to be expected, the extraction shall be limited to eight (8) hours maximum.
2. The filter shall be removed from the Soxhlet and shall be kept in the vertical position. To determine the particle concentration of the gas, follow the procedure described in paragraph 21.3 shall be followed.

A blank sample (i.e. a fully prepared filter which has not been used) shall be run in parallel to the used filter for quality control purposes. This ensures that there are no contributing error factors from the Soxhlet procedure.

21.2 Combination of solvents

The isopropanol solution from the Soxhlet extraction procedure in paragraph 21.1 shall be added to the sample collected from the impinger bottles. Schematically this is shown in Figure 2.

The resulting sample might contain solids, rather than appearing as a clear, transparent liquid. In this case, the solids shall be removed from the sample by, for instance, filtration, centrifugation or precipitation.

Both the volume and weight of the resulting bulk sample shall be determined and recorded.

21.3 Determination of particle mass

The same drying and weighing procedure is used for sample analysis as that adopted for the initial preparation of the filters, described in paragraph 17.1. The procedure is as follows:

1. After Soxhlet extraction, the quartz thimble shall be dried in an oven at 110 °C at atmospheric pressure overnight (according to ISO 9096).
2. An aluminium foil shall be weighed using an analytical balance with an accuracy of ± 0,1 mg.
3. The filter shall be removed from the oven and shall be wrapped directly in the aluminium foil.
4. The filter shall be allowed to acclimatise in a desiccator at room temperature.
5. The filter plus aluminium foil shall be weighed on the same analytical balance and the weight of the filter plus particulate material shall be calculated.

The mass of particulate matter collected shall be calculated by subtracting the initial filter weight from the sampled filter weight. If the sample was collected isokinetically, the concentration of particles in the gasification product gas in g/m_n^3 shall be calculated by using the volume of gas sampled and the temperature and pressure readings recorded.

21.4 Determination of gravimetric tar mass

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

1. A standard rotary evaporator with a pressure indicator shall be used. The pressure shall be 10 kPa (100 mbar) (absolute) with an empty flask.
2. A 200 or 250 ml flask shall be used. It shall be dried and acclimatised in a dissicator for at least one (1) hour. Then, it shall be weighed with an accuracy of 1 mg or preferably 0,1 mg. Exactly 100 ml of the combined tar solution from paragraph 21.2 shall be poured into the flask.
3. The flask shall be connected to the rotary evaporator and the evaporation shall be started with the water bath at 55°C. The pressure will be higher than 10 kPa (100 mbar) (absolute) at the start and will gradually fall to 10 kPa (100 mbar) (absolute). Drops should fall from the cold finger at a rate of 1-2 drops per second.
4. Once almost all solvent is evaporated, the rate of drops falling will decrease. With a stopwatch the time between two drops falling shall be observed. Evacuation shall be continued until there are at least four (4) seconds between two consecutive drops falling. Then, the flask shall be removed from the rotary evaporator and 20 ml of ethanol shall be added.
5. The flask shall be connected again to the rotary evaporator and the evaporation shall be started with the same conditions as before (drops falling at a rate of 1-2 drops per second). Once almost all solvent is evaporated, the rate of drops falling will decrease. The observation of drops falling shall be continued until there are at least four (4) seconds between two consecutive drops falling.
6. After the rate of one drop per four (4) seconds has been achieved, the evaporation shall be continued for a further fifteen (15) minutes. If at this point traces of water are observed, the flask shall be removed from the rotary evaporator, 20 ml of ethanol shall be added and the procedure shall be restarted at the previous step. If no traces of water are observed, the evaporation shall be continued for a further thirty (30) minutes 21.2 with the sample being simultaneously flushed with nitrogen. The pressure during flushing shall not exceed 35 kPa (350 mbar) (absolute).
7. The vacuum shall be removed by letting in air and shutting off the nitrogen purge. Then the rotation of the flask shall be stopped. The flask shall be removed from the heated water bath, it shall be dried and it shall be acclimatised in a dissicator for exactly two (2) hours. The flask shall be weighed accurately and the amount of gravimetric tar shall be calculated.
8. If the weight of evaporation residue is lower than the minimum reportable weight of 0,5 g, a comment shall be made to the reported value stating that the measured weight of tar falls below the minimum specified in the scope of the Technical Specification and, therefore, the reported value is only semi-quantitative.

To determine the GC-detectable components in the gravimetric tars (optional) the evaporation residue shall be re-dissolved and a GC analysis shall be performed.

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

21.5.1 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 found in a background Technical Report [1]. This Technical Specification

only gives the requirements for sample preparation and for analysis. The procedures shall be selected by the analyst based on experience and/or the examples quoted.
Identification of compounds is based upon retention times (for GC-FID) or mass spectra (GC-MS).

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.** The calibration software shall be set up 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.

GC-FID or GC-MS analysis may also be performed with the tar residue from paragraph 21.4 to evaluate the overlap between gravimetric analysis and GC analysis. Note that part of the tar will have been evaporated during the gravimetric evaporation procedure so the analysis of gravimetric tar residue cannot replace the analysis of the original solution.

21.5.2 Requirements for sample preparation using internal standards (ISTD)

The sample preparation using ISTD shall meet the following functional requirement:

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

21.5.3 Requirements for analysis, identification of compounds, and reporting

The analysis, identification of compounds and reporting shall meet the following functional requirements:

- Prior to analysis, the sample shall be at room temperature and the sample shall be mixed thoroughly to ensure homogeneity;
- No quantification of compounds shall be undertaken if a calibration standard is not used;
- ISTD shall be used for samples containing tars from downdraft, fluidised bed or entrained flow gasification in order to obtain the numbers for repeatability and reproducibility as mentioned in chapter 23 of this Technical Specification. Failure to use an ISTD will likely result in a performance that is poorer than the performance described in chapter 23;
- ISTD shall not be used when analysing a sample containing updraft gasification tars with GC-FID;
- Failure to use an ISTD shall be reported;
- The identification of compounds in a GC-FID quantitative analysis is based on retention times of the compounds. Each respective retention time 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 be reported as not determined;
- Organic compounds that are not included in the calibration standard solution may be reported semi-quantitatively by assuming a response factor of unity or taking an average response factor for a similar, quantitatively characterised compound.

22. Calculation of results

22.1 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:

$$RF_c = \frac{A_c / A_{is}}{M_c / M_{is}} \qquad (1)$$

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.

For each compound the mass is given by the following expression:

$$M_c = \frac{A_c M_{is}}{A_{is} RF_c} \qquad (2)$$

23. Performance characteristics

23.1 Introduction

This Technical Specification 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 concentrations of tars that are variable with time, biomass input etc. Therefore, the validation of the performance of this Technical Specification has been carried out 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 in accordance 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 23.2 on the performance of the analysis methods (Round Robin tests) and a paragraph 23.3 on 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 the 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), namely high temperature tar and low temperature tar.

High temperature tar is formed in processes like downdraft, fluidised bed or entrained flow gasification and it contains mainly non-polar aromatic compounds. Low temperature tar is formed at low process temperatures which occur, for example, in updraft gasification processes. 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 a significant part of low temperature tar consists of polar compounds.

23.2 Performance of the analysis methods (Round Robin tests)

23.2.1 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 and the second series of Round Robin tests considered the analysis of gravimetric tar.

23.2.2 Round Robin tests on the analysis of individual organic compounds

The repeatability and reproducibility values from the Round Robin tests are presented in Table 23.1.

These reproducibility and repeatability limits are valid provided that following conditions are satisfied:

- A professional GC-analyst shall be responsible of the implementation of analysis;
- The GC program shall be selected to suit the type of tar sample being analysed;
- Calibration shall be performed carefully and identification of single compounds shall be correct.

The data on which repeatability and reproducibility values are based, are presented in more detail in Tables D.1 and D.2. The repeatability and reproducibility values of synthetic tar samples are given as additional information in Table D.3, although this data was not included in determination of repeatability and reproducibility of the analysis method.

Table 23.1 — Repeatability and reproducibility for the analysis of individual organic compounds and total GC-detectable tar

Tar type	Concentration range mg / l (of solution)	Repeatability standard deviation s_r %	Repeatability[b] r %	Reproducibility standard deviation s_R %	Reproducibility[c] R %
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[a]	300 – 6 000	2,9	8,2	13	37
	5 – 50	10	28	74	210

[a] Calculated as naphthalene

[b] The difference between two test results obtained for 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.

[c] 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.

23.2.3 Round Robin tests on the gravimetric analysis

The repeatability and reproducibility values from the Round Robin test on the gravimetric analysis are presented in Table 23.2. The data on which repeatability and reproducibility values are based are presented in more detail in Table D.4.

Table 23.2 — Repeatability and reproducibility for the gravimetric analysis of tar

Tar type	Concentration range g / l (of solution)	Repeatability standard deviation s_r %	Repeatability[a] r %	Reproducibility standard deviation s_R %	Reproducibility[b] R %
GRAVIMETRIC TAR	5 – 60	6,5	18	26	71

[a] The difference between two test results obtained for 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.

[b] 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.

23.3 Performance of the whole Technical Specification (parallel tests)

This Technical Specification has been validated during a parallel measurement test campaign at a circulating fluidised bed gasifier (high temperature tar). The repeatability and reproducibility values obtained represent only high temperature tar.

The repeatability and reproducibility values for the gravimetric method are based only on three measurements, meaning that the reliability of the values is limited and that the values shall be considered only as suggested values. It is assumed that the true repeatability and reproducibility values for gravimetric analysis will be markedly higher.

The data on which repeatability and reproducibility values are based, are presented in more detail in Tables E.1, E.2 and E.3.

The determination of particle concentration was carried out during the test campaign. However, repeatability and reproducibility values could not be determined due to missing repeatability measurements. Only one sample was taken per operator per measurement point and single sample results in only one value (contrary to GC analysis where several GC values can be obtained from one sample). The range, mean, standard deviation and 95 % confidence intervals of the measurements are presented in Table E.4.

Table 23.3 — Repeatability and reproducibility for sampling and analysis of individual organic compounds and total GC-detectable tar from product gas containing high temperature tar

Tar type	**Concentration range** mg / m^3_n (of product gas)	**Repeatability standard deviation** s_r %	**Repeatability**[b)] r %	**Reproducibility standard deviation** s_R %	**Reproducibility**[c)] R %
GC-DETECTABLE TAR					
Individual compounds	1 700 – 4 000	4,5	13	24	66
Individual compounds	11-1 300	3,6	10	31	86
Individual compounds	0,40-18	3,4	9	48	134
Total GC-detectable tar[a)]	500-2 500	7,4	21	23	63
	3 000 – 20 000	10	29	26	72
GRAVIMETRIC TAR	2000 – 12 000	27	76	47	133

NOTE 1: Repeatability values represent only analysis, not the whole method

[a)] Calculated as naphthalene

[b)] The difference between two test results obtained for 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.

[c)] 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.

24. 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 (CEN/TS …..:2005);

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.

(informative)

Appendix A List of most abundant individual organic compounds in biomass gasification product gases

The next table gives the names of individual organic compounds that are frequently reported in biomass gasification product gases. This list is included to enable analysts inexperienced with the composition of biomass gasification product gases, to identify the most abundant compounds. Please note that the Technical Specification is not evaluated for this list of compounds, hence this is an informative list (see chapter 10 "Scope"). In this table, compounds that are commonly measured in relatively high concentrations are printed in standard font. Compounds that are analysed less frequently or occur in lower concentrations are printed in *italics.*

Table A.1 — List of most abundant individual organic compounds

Downdraft / fluidised bed / entrained flow 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* **Nitrogen containing aromatics** Pyridine Methylpyridines, Picolines (Iso)Quinonoline	**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** (Methyl)pyridines, Picolines, *(Iso)Quinoline*

(normative)

Appendix B 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 on repeatability and reproducibility are collected and reported.

Table B.1 — List of organic compounds for which precision data have been collected and reported

Organic compound
Pyridine
Toluene
Phenol
Indene
Fluorene[11)]
Guaiacol
Naphthalene
Acenaphthylene
4-methylguaiacol (Creosol)
Anthracene[11)]
Phenanthrene
Fluoranthene
Pyrene
Benz(a)pyrene[11)]

[11)] : These compounds have only been measured in the parallel tests (see Table E.1), not in the Round Robin tests (see Tables D.1 and D.3)

(normative)

Appendix C Dimensions of the Petersen column

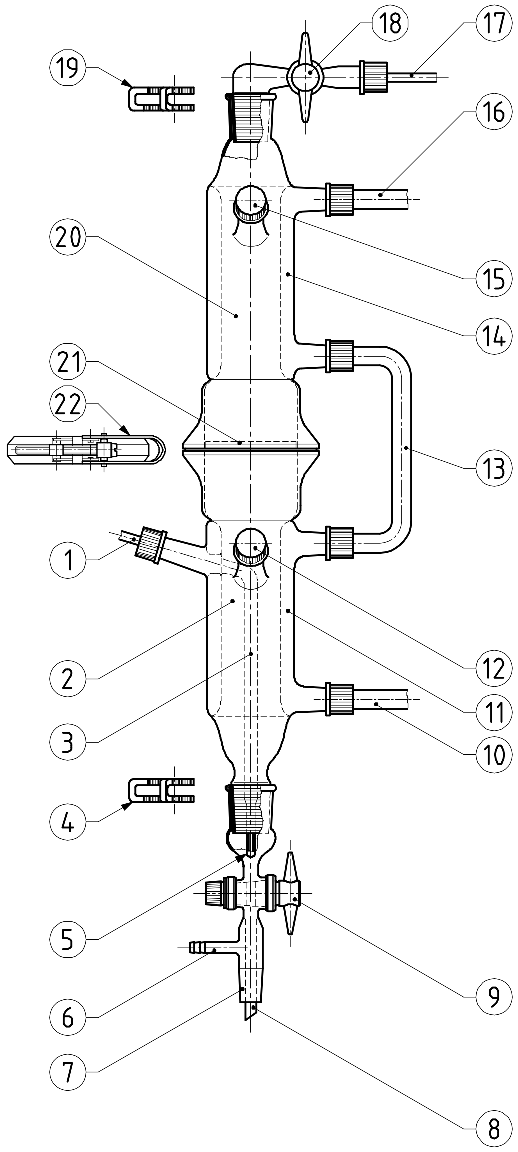

Figure C.1 – Petersen Column

Key

1	Gas admission
2	First washing stage (diameter 45 mm)
3	Impinger tube (diameter 45 mm)
4	Clamp for ground joint
5	Gas outlet into solvent
6	Pipe stub for connection to vacuum pump
7	Ground joint with PTFE seal
8	Solvent outlet to transport flask
9	Stopcock with PTFE key
10	Cooling liquid admission (from cooling unit)
11	Cooling jacket for first washing stage
12	Solvent admission for first washing stage
13	Connection hose for cooling liquid
14	Cooling jacket for second washing stage
15	Solvent admission to second washing stage
16	Cooling liquid outlet (to cooling unit)
17	Stopcock with PTFE key
18	Gas outlet (to vacuum pump and volume meter)
19	Clamp for ground joint
20	Second washing stage
21	Glass filter disc assembled with PTFE gasket (G3, diameter 60 mm)
22	Conic clamp for connection of the two washing stages

(informative)

Appendix D Additional information on Round Robin analysis

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

Two Round Robin tests for GC analysis were performed, the first with synthetic tar samples and the second with gasifier sampled tars taken from the product gas of two biomass gasifiers. 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 two separate reports on the Round Robin tests [4] and [5].

Synthetic tar samples contained typical concentrations of 8 - 9 of the organic compounds listed in Annex B. Results from Round Robin tests with synthetic tar samples were used to make preliminary estimates of the precision of the analysis method.

The gasifier sampled tars were collected from a fluidised bed gasifier (high temperature tar) and from an updraft gasifier (low temperature tar). In each case, both raw gasification product gas and cleaned gasification product gas were sampled. The eleven individual compounds listed in Annex B were analysed from the tar samples. In addition, all organic matter detected by GC was determined (called total GC detectable tar) and calculated as naphthalene.

All analyses were performed by six laboratories, each laboratory making three or six 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 overall repeatability and reproducibility values for high temperature tar and low temperature tar are presented in Table 23.1. The poorer repeatability and reproducibility values (higher values for r and R) for low temperature tar compared to high temperature tar are ascribed to the complexity of the matrix of low temperature tar.

More detailed results of the Round Robin tests on analysis of individual compounds in tar samples collected from the gasifiers (biomass gasification tars) are presented in Table D.1 and the results from synthetic tar samples in Table D.3. The concentration of those organic compounds listed in Annex B but are not reported was near or below the detection limit, so 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 D.2.

Table D.1 — 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[a] (r)**		**Reproducibility standard deviation (s_R)**		**Reproducilbility[b] (R)**	
	mg / l (of solution)	mg / l (of solution)	mg / l (of solution)	%	mg / l (of solution)	%	mg / l (of solution)	%	mg / l (of solution)	%
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	-	-	-	-

[a] The difference between two test results obtained for 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.

[b] 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 D.2 — Results obtained in Round Robin tests on analysis of total GC-detectable tar (calculated as naphthalene) from gasifier collected tar samples

	Concentration		**Repeatability conditions**				**Reproducibility conditions**			
	Range	**Mean value**	**Repeatability standard deviation (s_r)**		**Repeatability[a] (r)**		**Reproducibility standard deviation (s_R)**		**Reproducilbility[b] (R)**	
	mg / l (of solution)	mg / l (of solution)	mg / l (of solution)	%	mg / l (of solution)	%	mg / l (of solution)	%	mg / l (of solution)	%
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

[a] The difference between two test results obtained for 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.

[b] 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 D.3 — 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[a] (r)**		**Reproducibility standard deviation (s_R)**		**Reproducilbility[b] (R)**	
	mg / l (of solution)	mg / l (of solution)	mg / l (of solution)	%	mg / l (of solution)	%	mg / l (of solution)	%	mg / l (of solution)	%
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

[a] The difference between two test results obtained for 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.

[b] 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.

D.2 Round Robin tests on the analysis of gravimetric tar

One Round Robin test was performed for the analysis method of gravimetric tar. The Round Robin test was performed in 2004. All samples contained real tar from the product gas of a biomass gasifier.

The samples of the test represented only tars from an updraft gasifier. Samples were mixtures of heavy tar and aqueous tar in different ratios, dissolved in isopropanol. Also the water content of the samples varied.

All analyses were performed by six laboratories, each laboratory making three or six 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 results obtained are presented in Table D.4. Full details of the results are presented in two separate reports [4] and [5].

Table D.4 — 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[a] (r)**		**Reproducibility standard deviation (s_R)**		**Reproducilbility[b] (R)**	
	g / l (of solution)	g / l (of solution)	g / l (of solution)	%	g / l (of solution)	%	g / l (of solution)	%	g / l (of solution)	%
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

[a] The difference between two test results obtained for 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.

[b] 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.

(informative)

Appendix E Additional information on parallel tests

In the parallel measurement test campaign, which was performed in 2004 on a circulating fluidised bed gasifier, six laboratories from different European countries performed simultaneous measurements according to this Technical Specification. In each individual measurement, at least three of the laboratories participated. Tar was sampled both from raw product gas and from cleaned product gas. One team used an alternative setup with impinger bottles (A2) and one team used the Petersen column (B), other teams used a standard setup with impinger bottles (A1). Samples were analysed (one to three analyses per sample) both gravimetrically and by GC. Some samples were analysed also by other laboratories.

Repeatability and reproducibility values were calculated according to the procedure specified in ISO 5725-2 and are presented in Table 23.3. However, the measurements to determine the repeatability value for the whole method could not be performed during the test campaign as one operator took only one sample per measurement point. Several analyses of each sample were carried out. The repeatability values are based on all the available analysis results and so the repeatability values in Table 23.3 and the Tables E.1 to E.4 in this Annex represent only the analysis procedure. Thus the reproducibility values of the whole method are somewhat biased and can only be considered as indicative.

Table E.1 lists the results of the individual compounds determined by GC from parallel measurement tests. Samples were taken from the raw gasifier product gas and from gas that was cleaned in a gas cleaning section including a catalytic tar reformer. Samples CLEAN2 to CLEAN4 were measured from cleaned gas and samples RAW2 to RAW5 were measured from raw product gas. The results of total GC-detectable tar (calculated as naphthalene) are presented in Table E.2 and the results of gravimetric tar are presented in Table E.3.

Table E.4 lists the results of the sampling and analysis of particles, although the repeatability and reproducibility values could not be determined. Samples CLEAN2 to CLEAN3 were measured from cleaned gas and samples RAW2 to RAW5 were measured from raw product gas.

Full details of the results were given in a separate report published in 2005 [6].

Table E.1 — Results obtained in parallel measurement tests on individual organic compounds determined by GC

Organic Compound	**Concentration**		**Repeatability conditions**				**Reproducibility conditions**			
	Range	**Mean value**	**Repeatability standard deviation (s_r)**		**Repeatability[a)] (r)**		**Reproducibility standard deviation (s_R)**		**Reproducilbility[b)] (R)**	
	mg / m^3_n (of product gas)	mg / m^3_n (of product gas)	mg / m^3_n (of product gas)	%	mg / m^3_n (of product gas)	%	mg / m^3_n (of product gas)	%	mg / m^3_n (of product gas)	%
CLEAN2										
Naphthalene	400-440	390	16,2	4,1	45,4	11,6	62,7	16	180	44,9
Toluene	28-39	33,5	0,8	2,4	2,2	6,7	4,7	13,9	13,1	39
Phenanthrene	17-49	28,8	0,4	1,4	1,1	3,9	17,2	59,7	48,2	170
Indene	11-17	13,3	0,2	1,5	0,6	4,2	2,8	21,1	7,9	59,1
Pyridine	7,0-14	10,4	1,1	10,6	3,1	29,6	4,1	39,9	11,6	110
Pyrene	3,0-18	8.0	0,2	2,5	0,6	7.0	8.0	100	22,4	280,1
Fluorene	3,0-6,0	4,2	0,1	2,4	0,3	6,7	1,6	38,2	4,5	110
Anthracene	0,4-3,7	1,7	0,1	5,9	0,3	16,5	1,7	100,2	4,8	280
CLEAN3										
Naphthalene	710-1300	950	37,5	4.0	110	11,1	250	26	690	72,7
Phenanthrene	82-150	120	11,2	9.0	31,4	25,3	30,2	24,4	84,7	68,4
Toluene	68-180	100	4.0	3,9	11,2	10,9	49,8	48,4	140	140
Fluoranthene	20-46	35,3	0,8	2,3	2,2	6,3	13,2	37,5	37	110
Pyrene	21-49	34,2	0,4	1,2	1,1	3,3	13,3	38,9	37,3	110
Pyridine	24-45	33,1	2,4	7,3	6,7	20,3	7,7	23,2	21,5	65
Indene	23-41	29,2	0,7	2,4	2.0	6,7	7.0	24,1	19,7	67,5
Fluorene	11-17	13,9	0,2	1,4	0,6	4.0	2,9	20,9	8,1	58,6
Anthracene	5,0-12	8,2	0,1	1,2	0,3	3,4	3,8	46,4	10,6	129,8
CLEAN4										
Naphthalene	550-600	570	27,9	4,9	78,1	13,8	36,8	6,5	100	18,1
Phenanthrene	55-81	65,9	0,9	1,4	2,5	3,8	12,5	19	35,1	53,2
Toluene	43-53	50,1	0,8	1,6	2,2	4,5	5,1	10,1	14,2	28,3
Pyridine	16-29	21,5	1,4	6,5	3,9	18,2	6,2	28,7	17,3	80,2
Fluoranthene	14-25	19	0,6	3,2	1,7	8,8	5,2	27,6	14,7	77,1
Pyrene	13-25	18,9	0,7	3,7	2.0	10,4	5,2	27,8	14,7	77,7
Indene	14-19	17	0,3	1,8	0,8	4,9	2,6	15,4	7,3	43,1
Fluorene	7,0-8,4	7,7	0,2	2,6	0,6	7,3	0,6	8,2	1,8	23
Anthracene	2,2-7,3	4,5	0,1	2,2	0,3	6,2	2,5	55,6	7,0	156
RAW2 (6)										
Naphthalene	1900-4000	2600	125,6	4,7	350	13,2	890	33,6	2500	94
Phenanthrene	410-1000	720	31,2	4,3	87,4	12,1	290	40,2	820	110

Organic Compound	**Concentration**		**Repeatability conditions**				**Reproducibility conditions**			
	Range	**Mean value**	**Repeatability standard deviation (s_r)**		**Repeatability[a)] (r)**		**Reproducibility standard deviation (s_R)**		**Reproducilbility[b)] (R)**	
	mg / m^3_n (of product gas)	mg / m^3_n (of product gas)	mg / m^3_n (of product gas)	%	mg / m^3_n (of product gas)	%	mg / m^3_n (of product gas)	%	mg / m^3_n (of product gas)	%
Toluene	340-870	530	41,3	7,8	120	21,7	230	42,8	640	119,8
Indene	240-480	320	12,1	3,8	33,9	10,7	99,6	31,6	280	88,4
Fluoranthene	140-420	270	7,7	2,8	21,6	7,9	120	43,4	330	120
Pyrene	120-380	260	9.0	3,5	25,2	9,7	120,3	46,4	340	129,9
Anthracene	95-200	150,1	6,3	4,2	17,6	11,8	49	32,6	140	91,4
Fluorene	90-190	130	2.0	1,6	5,6	4,4	51,1	40,5	140	110
Pyridine	87-160	120	7,4	6.0	20,7	16,8	36,6	29,6	100	83
RAW3 (7)										
Naphthalene	1900-3200	2500	160	6,3	430	17,7	370	15	1000	42
Phenanthrene	420-1000	590	14,1	2,4	39,5	6,7	200	34,3	570,3	96,2
Toluene	310-360	470	48,3	10,4	140	29,1	110	22,5	290	62,9
Indene	240-410	310	10,4	3,3	29,1	9,3	51,2	16,4	140	46
Fluoranthene	150-410	230	5,6	2,4	15,7	6,7	110	45,8	300	130
Pyrene	130-370	210	5,8	2,7	16,2	7,7	94,1	44,5	260	130
Fluorene	110-190	140	0,7	0,5	2.0	1,4	41,4	30,1	120	84,2
Anthracene	100-200	140	2,9	2,1	8,1	5,9	42,8	31,3	119,8	87,7
Pyridine	83-180	120	5,3	4,5	14,8	12,5	36,1	30,5	100	85,3
Benz(a)pyrene	28-59	41,2	3,8	9,2	10,6	25,8	11,9	28,9	33,4	81
RAW4 (8)										
Naphthalene	1700-2400	2100	57,6	2,7	160	7,6	220	10,1	610	28,4
Phenanthrene	360-860	570,4	16,3	2,9	45,6	8.0	190	33,7	540	94,2
Toluene	250-490	370	5,7	1,6	16	4,4	81,3	22,2	230	62,2
Indene	250-280	270	9,8	3,6	27,4	10,1	11,2	4,1	31,3	11,6
Fluoranthene	140-400	240	2,8	1,2	7,8	3,3	110	46,1	310	130
Pyrene	120-350	210	4,7	2,2	13,2	6,2	98,2	46,5	280	130,1
Anthracene	110-190	140	1,5	1,1	4,2	3.0	37,6	26,4	110	74
Fluorene	110-170	130	2,4	1,9	6,7	5,4	33,2	26,4	92,9	74
Pyridine	73-180	110	12,2	11,7	34,2	32,7	38,1	36,5	110	100
RAW5 (9)										
Naphthalene	2200-2500	2800	120	4,4	350	12,3	1000	36	2900	100
Phenanthrene	490-1200	730	22,2	3.0	62,2	8,5	270	37,1	760	100
Toluene	250-460	360	6,6	1,9	18,5	5,2	68,1	19,1	190	53,6
Indene	250-300	320	13,8	4,4	38,6	12,2	110	35,1	310	98,3
Fluoranthene	170-540	310	6,1	2.0	17,1	5,6	150	48,1	410	140

Organic Compound	**Concentration**		**Repeatability conditions**				**Reproducibility conditions**			
	Range	**Mean value**	**Repeatability standard deviation (s_r)**		**Repeatability[a] (r)**		**Reproducibility standard deviation (s_R)**		**Reproducilbility[b] (R)**	
	mg / m^3_n (of product gas)	mg / m^3_n (of product gas)	mg / m^3_n (of product gas)	%	mg / m^3_n (of product gas)	%	mg / m^3_n (of product gas)	%	mg / m^3_n (of product gas)	%
Pyrene	140-550	289,8	5,5	1,9	15,4	5,3	160	56,2	460	160
Anthracene	120-240	170	3,6	2,2	10,1	6,1	49,7	29,9	140	83,7
Fluorene	110-160	130	1,8	1,4	5.0	4.0	29,3	23,3	81,9	65,1
Pyridine	90-170	120	10,3	8,5	28,8	23,9	33,6	27,9	94,1	78
Benz(a)pyrene	30-58	43,7	1,3	3.0	3,6	8,3	12,2	27,8	34,1	78

NOTE 1: Repeatability values represent only analysis, not the whole method

[a] The difference between two test results obtained for 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.

[b] 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 E.2 — Results obtained in parallel measurement tests on total GC-detectable tar calculated as naphthalene

Organic Compound	**Concentration**		**Repeatability conditions**				**Reproducibility conditions**			
	Range	**Mean value**	**Repeatability standard deviation (s_r)**		**Repeatability[a] (r)**		**Reproducibility standard deviation (s_R)**		**Reproducilbility[b] (R)**	
	mg / m^3_n (of product gas)	mg / m^3_n (of product gas)	mg / m^3_n (of product gas)	%	mg / m^3_n (of product gas)	%	mg / m^3_n (of product gas)	%	mg / m^3_n (of product gas)	%
CLEAN2	514 - 1060	712	20	2,8	56	7,9	230	32,3	644	90,4
CLEAN3	1000 - 2328	1585	206	13,0	577	36,4	439	27,7	1230	77,6
CLEAN4	787 - 995	920	59	6,4	165	18,0	71,8	7,8	201	21,9
RAW2	4846 - 9325	7480	195	2,6	546	7,3	1788	23,9	5006	66,9
RAW3	3476 - 10160	6458	1221	18,9	3419	52,9	1990	30,8	5571	86,3
RAW4	5539 - 7007	6415	100	1,6	280	4,4	699	10,9	1958	30,5
RAW5	5402 - 15889	7690	1463	19,0	4096	53,3	2886	37,5	8082	105

NOTE 1: Repeatability values represent only analysis, not the whole method

[a] The difference between two test results obtained for 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.

[b] 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 E.3 — Results obtained in parallel measurement tests on gravimetric analysis

Organic Compound	**Concentration**		**Repeatability conditions**				**Reproducibility conditions**			
	Range	**Mean value**	**Repeatability standard deviation (s_r)**		**Repeatability[a] (r)**		**Reproducibility standard deviation (s_R)**		**Reproducilbility[b] (R)**	
	mg / m^3_n (of product gas)	mg / m^3_n (of product gas)	mg / m^3_n (of product gas)	%	mg / m^3_n (of product gas)	%	mg / m^3_n (of product gas)	%	mg / m^3_n (of product gas)	%
RAW3	1948 - 11198	6330	1719	27,2	4813	76,0	2998	47,4	8394	133

NOTE 1: Repeatability values represent only analysis, not the whole method

[a] The difference between two test results obtained for 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.

[b] 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 E.4 — Results obtained in parallel measurement tests on particle determination

	Concentration		**Standard deviation**	**95 % Confidence Interval**	**-95 % Confidence Interval**	**+95 % Confidence Interval**
	Range mg / m^3_n (of product gas)	**Mean value** mg / m^3_n (of product gas)	mg / m^3_n (of product gas)	%	mg / m^3_n (of product gas)	mg / m^3_n (of product gas)
CLEAN2	4100-7500	5800	1400	24	4100	7600
CLEAN3	8200-10600	9400	1300	13	7400	11500
RAW2 (6)	10600-16100	13700	2600	19	9700	17800
RAW3 (7)	7300-17800	13200	3800	29	8500	17900
RAW5 (9)	9000-13700	11500	2500	22	7500	15500

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Appendix D Technical Report on the Tar measurement Standard

Sampling and analysis of tar and particles in biomass producer gases

-

Technical Report

Prepared under

CEN BT/TF 143 "Organic contaminants ("tar") in biomass producer gases"

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25. Aim of the Technical Report

The Technical Report aims to provide background information in support of the CEN Technical Specification "*Biomass Gasification – Tar and Particles in Producer Gases – Sampling and Analysis*" which is being prepared by CEN task force BT/TF 143 WI CSC 03002.4TC. The report is not part of the Technical Specification itself, and the information contained herein is provided for guidance only.

The content of this report is based on the "Tar Guideline", which is a method for sampling and analysis of tars and particles from biomass producer gases, developed in a project under the EU fifth framework programme from 2000 to 2002. When this Guideline was transferred to a CEN Technical Specification between 2003 - 2005, some parts of the technical descriptions were removed as they were examples and not mandatory procedures.

It is the aim of this report to ensure that these technical descriptions remain available as background information for those who work with the Technical Specification.

Definitions, for instance for "tar" and "gravimetric tar" are given in the Technical Specification.

26. Measuring Principle

26.1 Overview

The required level of information about the gasification products often depends on the end use of the gas. In some applications a very rough estimate of the gas heating value is sufficient for successful operation while very detailed chemical characterisation of the effluents may be needed in another application.

The measurement principle is described in this chapter. The principle is based on the discontinuous sampling of a gas stream containing particles and organic compounds (tar) under isokinetic conditions. The instructions for isokinetic sampling of flue gases are given in the standards ISO 9096 or VDI 2066.

The aim has been to keep the principle as simple as possible. This is because the measuring conditions can vary from 'comfortable' laboratory situations to a fullscale operating plant gasifier where there is no customised area for measurements or measurement apparatus. The weather conditions can also be challenging, for instance in northern Europe measurements may have to be performed at temperatures below 0°C.

The tar and particle sampling system consists of a heated probe, a heated particle filter, a condenser and a series of impinger bottles or alternative equipment[12] containing a solvent for tar absorption. The impinger bottles or alternative equipment[12] collecting tar are placed in a temperature controlled bath so that staged warming and cooling of the sampled gas takes place. The gas is sampled for a specified period through the sampling line and filter. The flow rate is maintained with the aid of either process pressure or a pump.

The sampling lines including the filter are heated to prevent tar condensation. However, to avoid thermal decomposition of organic compounds, these temperatures must be properly selected. The actual temperatures are given in the Technical Specification.

The tar collection occurs both by condensation and absorption in isopropanol, which was found to be the most suitable solvent. The volume, temperature, pressure, and gas flow rate through the equipment are measured. The gases from by-pass lines and sample gas are vented safely to atmosphere.

Immediately after sampling the content of the impinger bottles or alternative equipment[12] is decanted into a dark storage bottle, (if a dark bottle is not available, the bottled sample must therefore be stored in a dark place). All surfaces (including metal surfaces) contacting the gas, at temperatures lower than the process temperature, are washed with the solvent. The washes are combined with the actual sample. This is easy to arrange in atmospheric processes, but very difficult in pressurised systems. The storage bottle is stored, tightly closed at a cool (< 5°C) temperature for later analysis.

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 when using the minimal nozzle diameter of 4mm. Hence tar sampling is performed non-isokinetically for pressurised gases. Non-isokinetic tar sampling is also practical in large-scale atmospheric gasifiers where the pipe diameter is large.

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[12]: The alternative equipment is called the "Petersen column". It is described in paragraph 26.4.2.

Isokinetic sampling is also not required when only tar (and not particles) is sampled and the gas temperature under study at the sampling site exceeds 350°C. Such temperatures generally avoid tar condensation in the form of aerosols and/or droplets and also minimise adsorption of organic species onto particles.

The measuring principle is based upon a modular sample train consisting of a heated probe, a heated particle filter, a condenser, a series of impinger bottles or alternative equipment[12] containing a solvent for tar absorption, and equipment for pressure and flow rate adjustment and measurement. More details on the sampling train can be found in the Technical Specification. A detailed description of each of the modules is given on the following pages.

26.2 Description of sampling module 1 (gas preconditioning)

26.2.1 General

The sampling line consists of a sampling probe, a sampling port (through which the probe is mounted) and additional heated tubes and valves. The line should be short, small in volume and as simple as possible. Additional joints, valves, filters, etc. should be avoided to minimise the risk of leaks. When designing the sampling line consideration should be given to cleaning of the line, sufficient cleaning of sample gas and prevention of condensation.

26.2.2 Isokinetic or non-isokinetic sampling?

For high-temperature (>350°C) sampling, where the tar is completely in gas phase, non-isokinetic sampling is sufficient for measuring tar. In non-isokinetic sampling the alignment of the probe in relation to the gas flow as well as the shape of the probe nozzle can be designed more freely to prevent the nozzle from blocking. This is important especially during pressurised operation since the probe cannot be removed from the gas line. The end of the probe must point against the direction of the gas stream. The tip of the nozzle can be straight-ended or at 45° angled.

Isokinetic sampling requires a special probe. The design of such a probe is described in Paragraph 27.3.

26.2.3 Gas preconditioning for atmospheric gasifiers

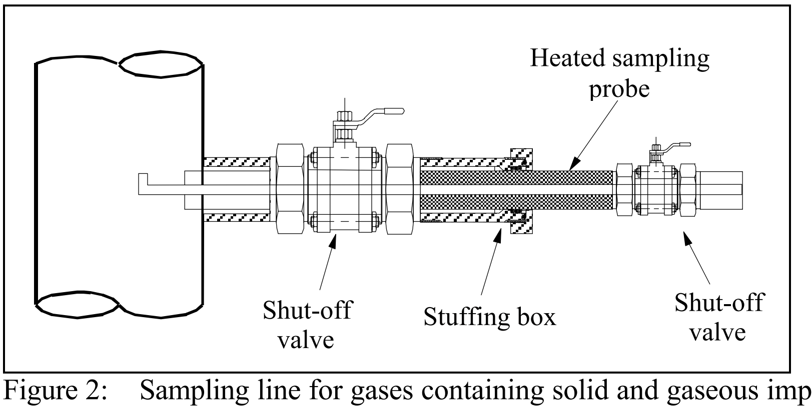

Figure 2: Sampling line for gases containing solid and gaseous impurities at atmospheric pressure.

The sampling line under atmospheric conditions is designed in such a way that the probe can be removed through the shut-off valve (ball valve) during operation of the gasifier. The design of the stuffing box is described in more detail in Paragraph 29.2 and Figure 12. A second shut-off valve (ball valve) is mounted between the probe and the particle filter for shutting off the sampling line at any time (also in case of leaks). The valve should be resistant to process temperature (high temperature shut-off valve). External heating of the sampling line (for example electrical or hot N_2 circulation in a jacket) prevents condensation of water vapour and condensable gases (clogging of the sampling line). The insulating material should completely cover the sampling line and particle filter to sustain the minimum necessary temperature level and to avoid the formation of cold spots (possible tar condensation) in the line or in the filter.

When only tar is measured, the particle removal from the sample gas can be carried out at the process temperature with a ceramic filter positioned at the tip of the probe (SiC is a suitable material, since it has very little or no catalytic effects on tar decomposition).

The pressure and temperature of gas is measured at the sampling point.

The sampling line for an atmospheric process is shown in Figure 2 above.

26.2.4 Gas preconditioning for pressurised gasifiers

For pressurised gases a sampling strategy with separate sampling of tar and particles is required. The gas preconditioning is composed of an inline ceramic filter for the particle collection followed by a pressure relief device (Figure 3). The whole sampling line is heated and tar is sampled at ambient pressure.

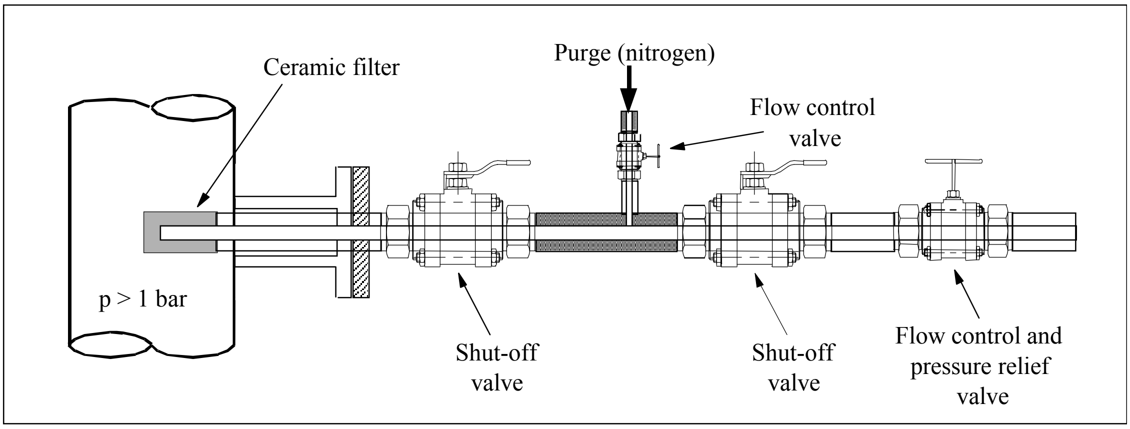

Figure 3: An example of a sampling line for a pressurised process for tar measurement only

A shut-off valve is positioned first in the sampling line enabling shut off at any time (also in case of leaks). The shut-off valves must endure the gas temperature at the process pressure. The material of the valves must be carefully selected for each process.

Pressure relief is carried out in stages with three manual control valves. It can also be performed with one valve only (flow control), but steadier pressure relief and increased reliability (leaks due to contamination of valves) are achieved by installing several valves. Pressure relief and clogging in the sampling line are monitored by pressure measurements.

The last valve (flow control and pressure relief valve) in the line, from which the gas is led through a PTFE hose or glass pipe into the condenser, regulates the flow of sample gas. The length of this line should be kept to a minimum.

Condensation of water vapour and condensable gases before the condenser is prevented by heating the sampling line (for example electrically or by hot N_2 circulation). This prevents blocking of the sampling line. Blocking problems can also be minimised by using two parallel sampling lines equipped with facilities for purging and solvent washing. The type and number of particle separators in the sampling line is chosen on the basis of solids contents in the sample gas. Both quartz and fibreglass filters can be used as hot filters while, when measuring tar only, ceramic filters can be employed.

As it is not possible to remove the probe from the sample port under pressurised conditions, the sampling probe and the filters can be cleaned by nitrogen purge. Nitrogen flush lines are positioned to ensure that the most important valves and gas lines are cleaned in both directions. The nitrogen flush of the probe tip has to be continuous except during the sampling.

26.3 Description of sampling module 2 (particle filter)

Particles are collected in an external heated filter system. Quartz filters (absolute filters) should be used as filter material. Retention capacity of the filters should be at least 99,998 % of the particles of size 0,3 µm (DOP standard[13]).

For particle concentrations above 20 mg/m_n^3, thimble filters are used. Dimensions of thimble filters are selected for subsequent Soxhlet extraction procedures. The recommended dimensions for the thimble filter 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.
The filter holder must be gas tight. An example of a possible way to mount the filter is shown in Figure 4.

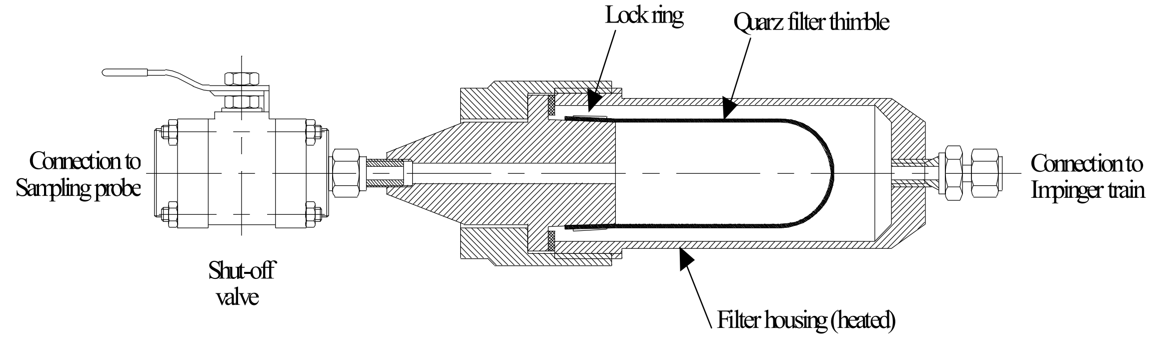

Figure 4: Module 2: the heated particle filter. This figure shows one of the possible ways to mount the thimble filter in the housing.

The material of the filter holder should not affect the composition of tar compounds and must endure 50°C higher temperature than the operating temperature (e.g. AISI 310, AISI 316). A thermocouple is placed inside the filter holder to measure the gas temperature at the filter.
The temperature of the filter is critical. It must be sufficiently high in order to prevent filter plugging, caused by the tar build-up, but low enough to prevent further reactions of tar on the filter surface. Temperatures are given in the Technical Specification.
In case of non-isokinetic tar sampling applications, the particle removal from the sample gas can be undertaken with a ceramic filter at the process temperature, which is positioned at the tip of the probe. SiC is a suitable material for this filter as SiC has very little or no catalytic effects on tar decomposition. Reverse flow, high-pressure nitrogen purge should be available to clean the particles from the SiC filter.

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[13]: 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.

26.4 Description of sampling module 3 (tar collection)

The connection between the hot metal tubing and the glassware must be carefully designed to assure the tightness of the joint. One possible design principle is as follows: The end of the metal tubing is formed to be identical to the male glass ball ground joint so that it fits the female ground joint of the impinger bottle. The radius of the metal ground joint should be the same, or slightly smaller, than the glass joint. The smaller radius makes the cracking of the female glass joint due to different thermal expansion less likely, however special attention then needs to be given to the sealing of the joint.

Collection of moisture and tar is performed in a series of 6 impinger bottles or in a specially designed equipment referred to as "Petersen column". The sampling principle and equipment of these two equipments (6 impinger bottles and Petersen column) are described in paragraph 26.4.1 and paragraph 26.4.2, respectively.

26.4.1 Series of impinger bottles

A schematic drawing of the impinger bottles is shown in Figure 5.

In the series of impinger bottles, the first impinger bottle acts as a moisture collector, in which water and tar are condensed from the process gas by absorption in isopropanol. The heat released by gas cooling and condensation is removed either in an external water bath or by an additional heat exchanger before the condenser. The heat exchanger may be necessary for high moisture producer gases (e.g. from steam gasification) and should be designed to meet the demands of the gasifier.

The condenser is a standard impinger bottle (reference arrangement) or can optionally be equipped with an internal liquid quench system which is especially suitable for producer gases containing higher tar levels. When using a liquid quench, isopropanol is the circulating liquid. The working principle of the liquid quench is described in Appendix A.

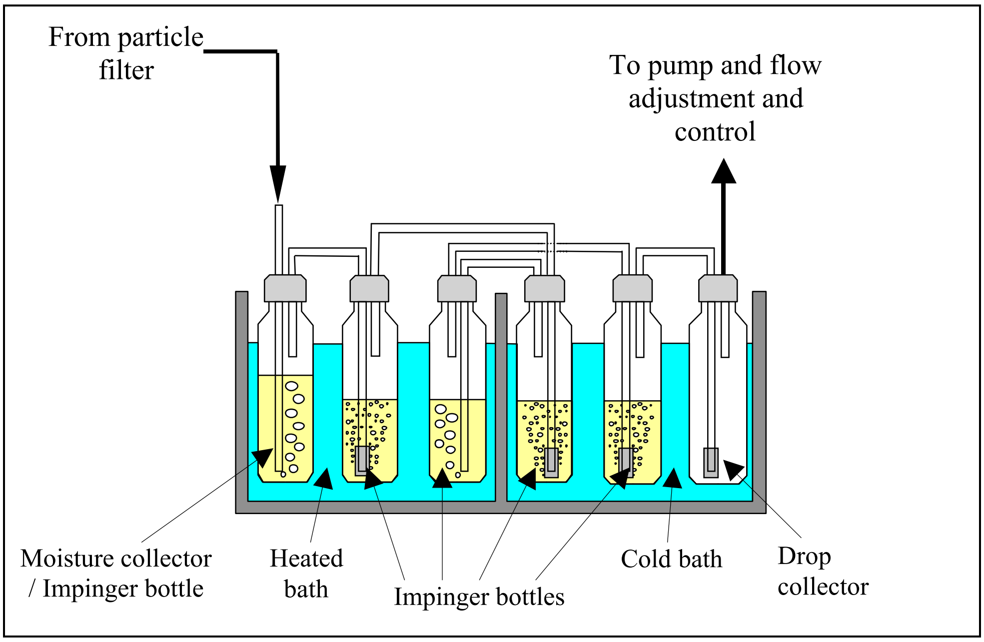

Figure 5: Example of module 3 of the sampling train: Impinger bottles

There are two possible impinger set-ups, which are described in more detail in the Technical Specification. A brief description of the sampling principle and equipment is given here.

After the moisture collector the gas is passed through a series of 4 impingers with solvent and 1 final impinger which is empty. Direct condensation of the liquid effluent without diluting media, e.g., with cold trapping, can result in further reactions of the trapped compounds.

Fine-meshed frits give better results than coarse-meshed frits; G3 frits should be installed in the impinger train. If G3 frits give a too high a pressure drop (e.g. 0,5 bar), G2 frits should be used.

Standard glass impingers (100 ml or 250 ml volume) with an inner tube diameter of 4 mm are recommended. An alternative modified impinger design is shown in Appendix F.1.

Cooling liquid can be either made of a mixture of salt/ice/water or a mixture of dry ice with isopropanol or by a mechanical cooling device. The bath should be insulated.

26.4.2 Petersen column

DTI has developed an alternative equipment for the 6 impinger bottles in module 3. The name of this alternative equipment is ”Petersen column” after the inventor Finn Petersen. The "Petersen column" consists of two washing stages filled with isopropanol. Stage 1 is a traditional washing stage with an impinger. The bottom of stage 2 consists of a G3 glass frit with two functions: a) it retains tar droplets (aerosol) and b) it generates a large number of very small gas bubbles in washing stage 2 which results in an improved washing efficiency. The two washing stages are filled with the washing medium (solvent, isopropanol) through two nozzles. During normal pressure (atmospheric pressure), the solvent is kept back in stage 2 by the glass frit, as the liquid runs very slowly through the frit. If there is a little vacuum in washing stage 2, no liquid runs through the frit.

Figure 6 shows the "Petersen column". A more detailed description plus the requirements for the essential dimensions are given in the Technical Specification.

The "Petersen column" is jacket cooled. The cooling fluid and cooling temperature can be selected as required e.g. in relation to the gas temperature. The column is constructed in such a way so it is easy to replace the glass frit if it is polluted by particles that cannot immediately be rinsed out with solvent.

When sampling has ended, the tube which is connected to the vacuum pump is moved to the connecting stub at the drain cock at the bottom of the "Petersen column". By creating a little vacuum in washing stage 1, the solvent is sucked from washing stage 2 through the frit. That results in washing stage 2 being emptied at the same time as the frit is cleaned by the solvent. Solvent from both washing stages is collected in a storage bottle which is kept sealed against the cone of the drain cock.

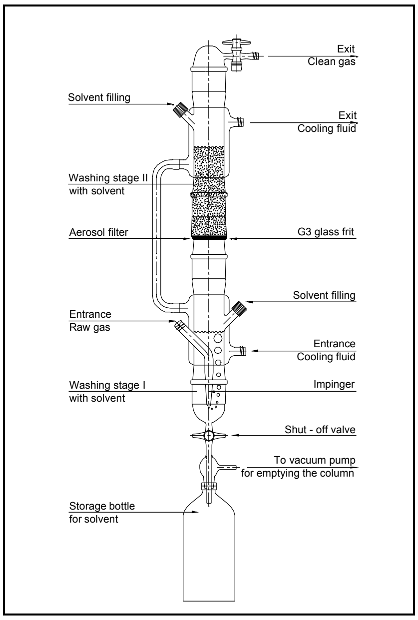

Figure 6: The "Petersen column"

Tests have shown that the "Petersen column" has a high sampling efficiency. During measurements in heavily polluted countercurrent gas, less than 1% of the chromatographable tar is found in a backup system. 85% of this material consists of benzene.

26.5 Description of sampling Module 4 (volume metering)

Figure 7 displays the Module 4 equipment: a pump, a flow control valve, a flow indicator, pressure and temperature measurement and a volume flow meter.

26.5.1 Sample gas suction device

The gas suction pump (vacuum pump) must be oil free, airtight and pulsation must be minimal. Membrane pumps are recommended because of easy clean up and maintenance. The gas pump must be able to displace at least $1m^3_n/h$ at an absolute pressure of 50000Pa. A flow control valve is recommended to adjust the sample flow rate.

There is no need for a pump when sampling pressurised gasification systems at pressures much larger than 10^5Pa. However, for gasification systems which are only slightly over-pressurised, (up to 150kPa), a pump may still be needed.

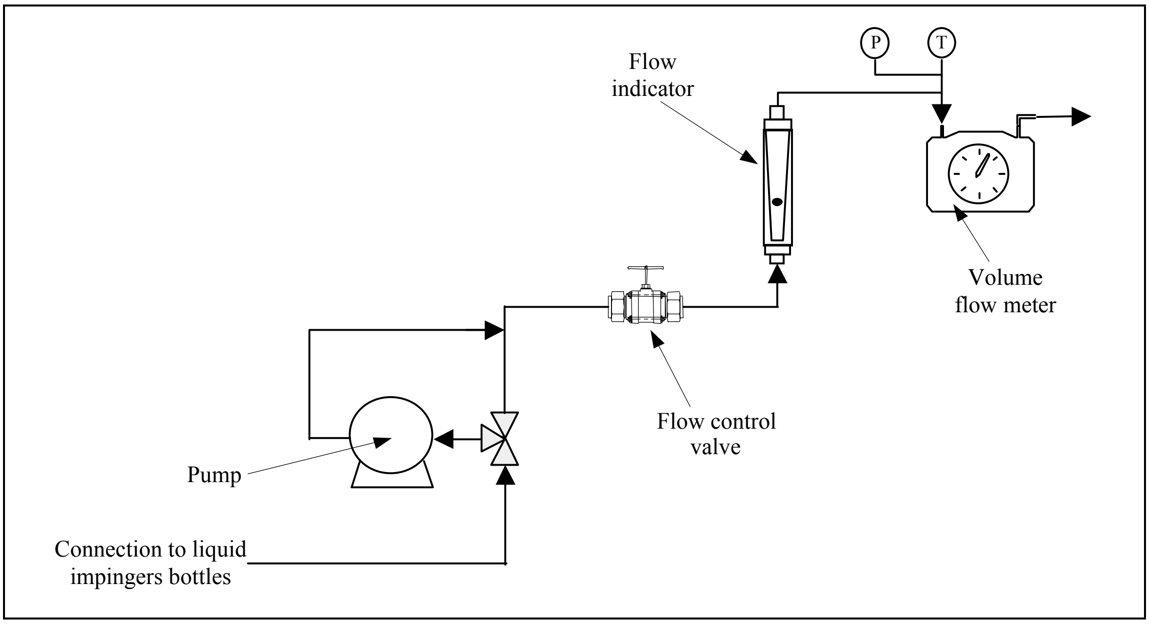

Figure 7: Pump and flow measuring equipment in Module 4.

26.5.2 Sample gas meter

To determine the volume of sampled gas, a barometer and a calibrated dry gas meter with thermocouple and indicator for pressure difference are used. The pressure drop over the volume-measuring device should not exceed a few hundred Pa.

The gas flow during the removal of flushing gases and essential sampling is monitored with a rotameter. The rotameter should be located between the pump and the volume-measuring device, which is used to adjust and compensate the sample flow. A temperature indicator, differential pressure indicator and a barometer are used to correct for temperature and ambient pressure to normal conditions.

The exhaust gases from by-pass lines and sample gas must be safely vented to atmosphere.

26.6 Equipment and materials

For sampling line temperatures below 200°C, PTFE or glass tubing is used. For higher temperatures up to 700°C, stainless steel tube (AISI 316 or AISI 310) is a suitable material.

When the temperature exceeds 700°C the accumulation of the catalytically active matter (for example limestone or dolomite) to the tip and bends of the probe may prove problematic.

The equipment and materials required for the construction of sampling system are presented in Table 26.1. All materials and equipment used in sampling should be compatible with national safety regulations. In case the sampling environment is classified as potential explosion area (e.g. standard EN 60079-10) electrical equipment used in sampling should fullfill the required national safety regulation for potentially explosive atmospheres (e.g. standard EN-50014).

Table 26.1: Materials and equipment for sampling system.

Probe :	Acid-proof stainless steel, AISI 316 or Fire-proof stainless steel, AISI 310
Condenser:	Acid-proof steel, AISI 316, glass
Filter:	Quartz fibre filter, size 30 x 77mm
	Max. temperature 950°C
	Retention capacity 99.998% (0.3 μm), DOP-stand.
Filtration:	Filter holder: Acid-proof steel, AISI 316
Ceramic filter:	Silicon carbide, 50 x 30 x 135 mm
	Silicon carbide, o.d. 12.7 mm, i.d. 20.5 mm, length 100 - 300 mm
Liquid quench:	Peristaltic pump (3 l/h; 3 m riser level) with Tygon tube, PTFE and stainless steel tubing
Pumps (e.g.):	Membrane pump
Rotameters (e.g.):	Standard rotameter for gas flow rates 1 - 20 l/min
Gas meter:	Dry gas meter
Impinger bottles:	Material is standard laboratory glass (100 ml or 250 ml)
Glass beads:	o.d. 6 mm
Solvent:	Isopropanol, minimum purity 99%. The solvent should not include GC detectable amounts of relevant tar compounds (blank determination by GC essential).
Cold bath:	Acid-proof steel, AISI 316
	Ice bath with salt, ice
	Compression cooler
Sample bottles:	500 ml glass storage bottle with PTFE coated screw plug (GL45) and pouring ring
Gaskets in the filter holder etc.	PTFE or graphite or copper or Viton

27. Isokinetic sampling

27.1 Introduction

Isokinetic sampling means that the velocity entering the sample probe (nozzle) must equal the free stream velocity of the gas being sampled:

$$v'_a \;=\; v'_N \qquad \text{(Eq. 3-1)}$$

When the sample gas velocity v'_N is higher than the gas velocity in the duct v'_a, the sampling is designated as over isokinetic. Since over isokinetic sampling implies lower sampling errors in particle concentrations and exact isokinetic sampling is not always possible in practice, the sampling should be conducted within the following limits:

$$0.95 < \frac{v'_N}{v'_a} < 1.15 \qquad \text{(Eq. 3-2)}$$

Within this Technical Report, two isokinetic sampling principles and one quasi-isokinetic principle based on a mass balance are described. The principles are:

a) Measurement of dynamic pressure with a pitot tube followed by determination of actual gas velocity and isokinetic flow rates

b) Measurement of static pressure difference with an O-type probe and adjustment of isokinetic sampling conditions

c) Estimation of the producer gas generation rate by applying a mass balance

27.2 Adjustment of isokinetic sampling based on pitot tube measurement

Pitot tubes measure the pressure difference between the total pressure and the static pressure = the dynamic pressure in the sampling line. When using a standard pitot tube, the gas velocity v'_a at a sampling point is expressed as

$$v'_a \;=\; \sqrt{\frac{2 \cdot \Delta\, p_{Pt}}{\rho'_a}} \;=\; \frac{q'_{Va}}{A \cdot 3600} \qquad \text{(Eq. 3-3)}$$

In connection with this Technical Report the dried gas sample flow rate q_{Vg} is measured by a gas volume meter. The velocity in the nozzle opening amounts to

$$v'_N \;=\; \frac{q'_{VN}}{a \cdot 3600} \;=\; \frac{q_{Vg}}{a \cdot 3600} \cdot \frac{p_{am} + p_g}{p_{am} + p_a} \cdot \frac{273.15 + \Theta_a}{273.15 + \Theta_g} \cdot \left(1 + \frac{f_n}{0.804}\right) \qquad \text{(Eq. 3-4)}$$

From equations 4-1, 4-3 and 4-4 it follows that the volumetric gas flow rate through the gas meter becomes

$$q_{Vg} \;=\; \sqrt{\Delta p_{Pt}} \;\cdot\; 3600\; a \;\cdot \sqrt{\frac{2}{\rho'_a}} \;\cdot\; \frac{p_{am} + p_a}{p_{am} + p_g} \;\cdot\; \frac{273.15 + \Theta_g}{273.15 + \Theta_a} \;\cdot\; \frac{1}{(1 + \frac{f_n}{0.804})} \qquad \text{(Eq. 3-5)}$$

A list of symbols is given at the end of this chapter.

27.3 Adjustment of isokinetic sampling conditions using O-type probe

Isokinetic sampling is best performed using an O-type probe, which incorporates separated hollow chambers surrounding the nozzle. The hollow chambers (measurement chambers) are provided with a number of holes internally and externally, which connect the chambers with the interior and the exterior of the nozzle through which the main stream of gases pass. The static pressure in the chambers is monitored via pipe connections to the pressure gauge. Figure 9 shows an O-type nozzle of this design, however, it has the disadvantage that special fabrication is required. A simpler O-type probe is illustrated in Figure 8.

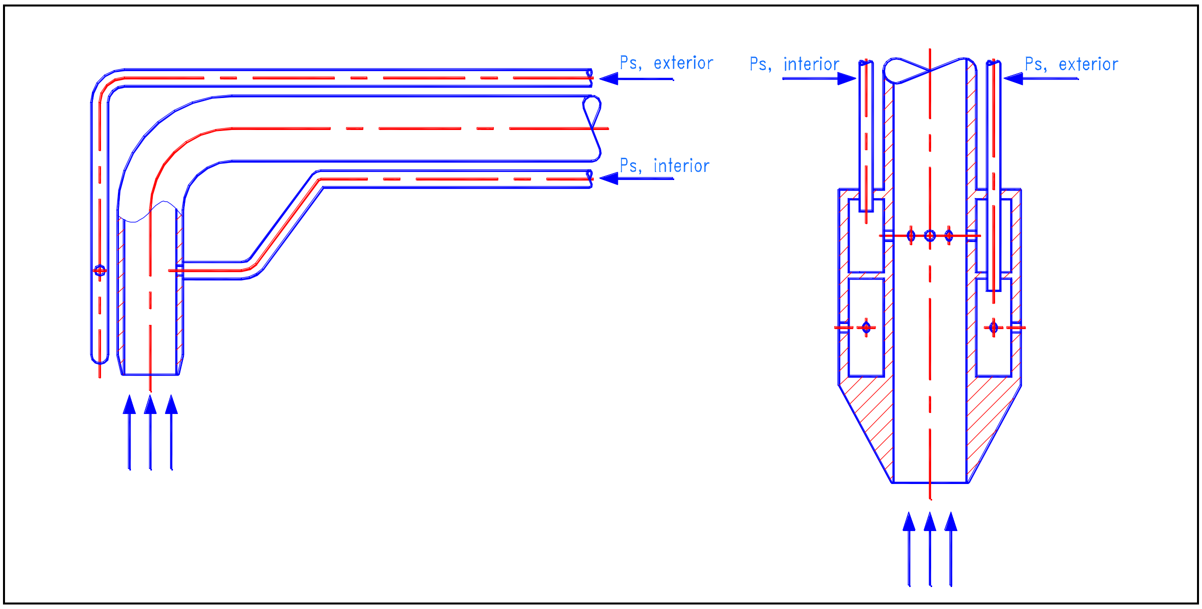

Figure 8 Simple O-type probe

Figure 9 O-type probe

An O-type probe configuration for isokinetic sampling can be used both for sampling atmospheric pressure gas and pressurised gases. For sampling from pressurised systems an O-type probe configuration is the preferred choice; this type of probe has been found to operate relatively well under pressure.

Isokinetic sampling conditions are achieved by equalising the interior and exterior static pressure signal. Figure 10 shows how the pressure difference is measured. When the difference between the two signals is zero, the gas velocity in the nozzle is deemed to be the same as outside the nozzle. Continuous equalisation is established by means of the bypass valve on the vacuum pump.

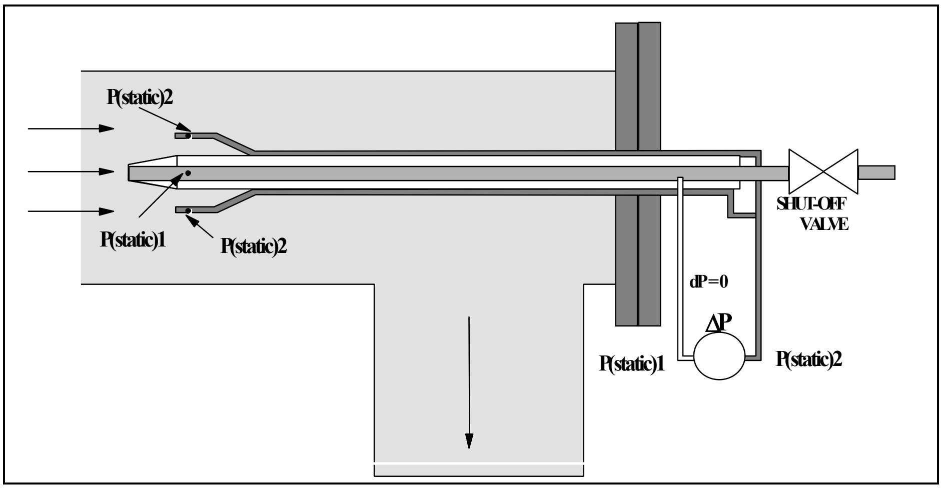

Figure 10 The configuration of the O-type probe

A series of tests have been carried out in order to determine the magnitude of errors resulting from deviations from the zero pressure. The tests show that in low velocity streams significant sampling errors may result from small deviations from zero pressure. For example, in a duct with a gas velocity of 5m/s, a 40% sampling error may result from a 12 Pa deviation from zero. For a gas velocity of 15m/s, the same deviation from zero would result in only a 3% sampling error. In sites where steady flow conditions frequently do not exist and in low velocity streams the use of O-type probe is not reliable and it is useful only as a rough means of adjustment to approximate isokinetic conditions.

Isokinetic sampling is required for particles and low-temperature tar sampling points (temperatures under 350°C), where a proportion of the tar can be present as aerosols in the gas. In the case of isokinetic measurements the number of measuring points is defined by the diameter of the gas pipe. Details are found in ISO 9096 or VDI 2066. For non-isokinetic sampling one measurement point is sufficient.

27.4 Calculation of isokinetic sampling conditions

Where pitot tubes or O-type probes cannot be used or are not available, the producer gas flow rate and the isokinetic sampling flow rate can be calculated from a nitrogen based or carbon based mass balance. The nitrogen based mass balance can be applied to air-blown gasifiers, the carbon based mass balance can be applied to all types of gasifiers (air-blown, oxygen- and oxygen/steam gasifiers. In case of gasification systems with two resulting gas streams (like the Güssing gasifier or the Ferco Silva Gas gasifier), two mass balances are needed to calculate the producer and the exhaust gas yields.

The nitrogen based method provides the actual producer gas flow rate (m^3_n: normal conditions, 273,15 K, 101325 Pa = 1,01325 bar, dry basis). As the sampled gas volume is also measured as dry gas, the target isokinetic sampling flow can be controlled during sampling by monitoring and adjusting the gas meter.
The nitrogen content in the producer gas can be measured directely (GC based measurement) or as the difference of 100% of all other main producer gas components (CO, CO_2, CH_4, H_2, H_2O).

$$q_{V,producergas} = q_{V,air} \cdot \frac{N_{2,air}}{N_{2,producergas}} \qquad \text{(Eq. 3-6)}$$

where $q_{V,producergas}$ = Producer gas flow rate [m^3_n/h]
$q_{V,air}$ = Primary air flow rate (gasification agent flow rate) [m^3_n/h]
$N_{2,air}$ = N_2 content of primary air (gasification agent) [Vol.-%]
$N_{2,producergas}$ = N_2 content of primary air (gasification agent) [Vol.-%]

The carbon based method presented here is based on a total carbon balance and can be applied when the following requirements are satisfied:

a) Gasifier operation is stable;
b) Main gas composition (CO, CO_2, CH_4) is known;
c) Fuel feeding rate (in kg/h), fuel moisture and carbon content are known;
d) Solid or liquid carbonaceous effluent streams (bottom ashes, particles, tar) and their carbon content are known.

The general calculation of the producer gas flow rate based on an elemental carbon balance can be written as

$$q_{m,fuel} cc_{fuel} + \sum q_{V,agent} cc_{agent} = q_{V,gas} \cdot \left(cc_{gas} + c_{tar} cc_{tar} + c_{particles} cc_{particles} \right) + q_{m,ash} cc_{ash} \qquad \text{(Eq. 3-7)}$$

where $q_{m,fuel}$ = Fuel feeding rate [kg dry biomass / h]
cc_{fuel} = Carbon content of fuel [kg C / kg dry biomass] (= 0.47 for woody biomass)

$q_{V,agent}$ = Gasification agent feeding rate [$\mathrm{m^3_n/h}$]

cc_{agent} = Carbon content of gasification agent [kg C / $\mathrm{m^3_n}$]

$q_{V,gas}$ = Producer gas generation rate [$\mathrm{m^3_n/h}$]

cc_{gas} = Carbon content of non-condensable gases (CO, CO_2, CH_4) in producer gas [kg C / $\mathrm{m^3_n}$]

c_{tar} = Tar concentration in producer gas [$\mathrm{kg/m^3_n}$]

cc_{tar} = Carbon content of tar [kg C / kg tar]

$c_{particles}$ = Particle concentration in producer gas [$\mathrm{kg/m^3_n}$]

$cc_{particles}$ = Carbon content of particles [kg C / kg dry biomass]

$q_{m,ash}$ = Bottom ash rate [kg dry ash / h]

cc_{ash} = Carbon content of bottom ash [kg C / kg dry ash]

Generally, the gasification agent does not contain carbonaceous gas components, hence $cc_{agent} = 0$ except, for example, when the bed material contains carbon containing additives like limestone. Dividing equation (Eq. 3-7) by the fuel feeding rate and rearrangement gives the specific producer gas yield

$$Y_{gas} = \frac{q_{V,gas}}{q_{m,fuel}} = \frac{cc_{fuel} - c_{ash,fuel}\ cc_{ash}}{cc_{gas} + c_{tar}\ cc_{tar} + c_{particles}\ cc_{particles}} \qquad \text{(Eq. 3-8)}$$

where Y_{gas} = Producer gas yield [$\mathrm{m^3_n}$/kg dry biomass]

$c_{ash,fuel}$ = Ash content of fuel [kg / kg dry biomass]

The carbon based method determines the producer gas yield on dry basis and does not require any information on the moisture content of the producer gas. Multiplication of the gas yield by the fuel feeding rate (dry basis) provides the actual producer gas flow rate. As the sampled gas volume is also measured as dry gas, the target isokinetic sampling flow can be controlled during sampling by monitoring and adjusting the gas meter.

Analogous to the pitot tube velocity measurement, the calculation of the effective isokinetic sampling conditions from equation (Eq. 3-8) can also be performed after the sampling.

The producer gas yield is a characteristic feature of the chosen gasification reactor under the given operating conditions (load, fuel moisture, fuel type etc.). Examples of producer gas yields are given in Table 27.1.

For a typical co-current gasifier, the fraction of carbon found in the bottom ash, particles and tar typically amounts to 1% of the total carbon in the gas. Hence, the carbon in the carbonaceous effluent streams has no significance for the producer gas yield calculation for such type of gasifiers. For counter-current and fluidised-bed gasifiers, the amount of carbon in particles and tar ranges from 10% to 15% of the total carbon in the gas. In these cases, some prior information regarding the tar and particle levels is required to determine gas yields accurately.

Another method for estimation of the producer gas flow rate which can be used, e.g. for co-current gasifiers coupled to IC engines, is based on the determination of the displaced gas volumes within the engine cylinders [Ramackers et al., 1985]. This method requires the cylinder volume, the engine speed and air supply and the oxygen content in the exhaust gas.

		Countercurrent fixed bed gasifier	Cocurrent fixed bed gasifier	CFB gasifier
Fuel moisture	wt% (daf)	50	16	15
Ash content	wt% (daf)	1	1	1
C in bottom ash	wt%	1	50	10
H_2	%	18.0	14.2	14.8
CO_2	%	7.0	12.9	15.0
CO	%	32.0	18.0	15.4
CH_4	%	5.0	1.9	4.2
Particle	mg/m^3_n	200	1,000	20,000
$c_{particles}$	Kg/m^3_n	$2 \cdot 10^{-4}$	$1 \cdot 10^{-3}$	$2 \cdot 10^{-2}$
Tar	mg/m^3_n	100,000	1,000	20,000
c_{tar}	Kg/m^3_n	0.1	$1 \cdot 10^{-3}$	$2 \cdot 10^{-2}$
Gas yield Y_{gas} according to Eq. 3-8	m^3_n/kg (daf)	1.84	2.73	2.23
Fraction of C in particles, bottom ash and tar	% of total C in gas	11.3	1.0	15.5

Table 27.1 Calculated producer gas yields from various gasifiers using wood as fuel
Remarks: A survey of typical gas composition, tar and particle concentrations from various gasifier reactor types is given in Appendix F.2. Carbon content of the fuel is 47 wt% (see previous page) (typical for wood); carbon content in particles, bottom ash and tar are estimated from typical experimental data.

27.5 Calculation of nozzle diameter

The nozzle diameter is chosen in order to adjust the velocity in the nozzle to the surrounding duct velocity. Furthermore, the correct choice of nozzle contributes to obtain a suitable duration of sampling and a suitable sample flow rate. The suitable sample flow rate through impinger bottles is often a barrier for proper isokinetic sampling. Several CEN standards recommend a flow rate between 8 and 33 l/min for Midget and Greenburg-Smith impingers and a flow rate between 1 and 3l/min for impinger bottles with frits. A specially designed VTT impinger is suitable for the range of 2 to 10l/min.

With a maximum flow rate of 10 l/min and a minimum nozzle diameter of 5mm it is possible to make isokinetic samplings up to a maximum gas velocity of 8.5m/s on the condition that there are constant gas conditions through the sampling train. As producer gas normally contains some moisture and has a higher temperature than the gas in the sampling train, the velocity will be higher than 8.5m/s in practice.

A general expression for calculation of nozzle diameter based on known gas velocity (measurement with pitot tube including moisture content) can be derived from the following equations:

$$v'_N \cdot a \cdot 3600 \quad = \quad q'_{VN} \quad = \quad q_{Vg}\,(1+\frac{f_n}{0.804}) \cdot \frac{p_{am}+p_g}{p_{am}+p_a} \cdot \frac{273.15+\Theta_a}{273.15+\Theta_g} \qquad \text{(Eq. 3-9)}$$

where the nozzle face area *a*:

$$a \quad = \quad A \cdot \frac{q_{Vg}}{q'_{Va}}(1+\frac{f_n}{0.804}) \cdot \frac{p_{am}+p_g}{p_{am}+p_a} \cdot \frac{273.15+\Theta_a}{273.15+\Theta_g} \qquad \text{(Eq. 3-10)}$$

where $0.1 \leq q_{Vg} \leq 0.6$ m^3_n/h and the nozzle diameter d_N is calculated as follows:

$$d_N = \sqrt{\frac{4 \cdot a}{\pi}} \qquad \text{(Eq. 3-11)}$$

A general expression for calculation of nozzle diameter based on the assumption of a gas yield shown in Table 27.1 appears from the following equation. With a gas yield value from Table 27.1, which fits the present object, it is possible to calculate the wet producer gas flow q'_{Va} and the gas velocity v'_a as follows:

$$q'_{Va} = Y_{gas} \cdot \dot{m}_{fuel} \cdot \frac{101300 \cdot (273.15 + \Theta_a)}{273.15 \cdot (p_{am} + p_a)} \cdot (1 + \frac{f_n}{0.804}) \qquad \text{(Eq. 3-12)}$$

$$v'_a = \frac{q'_{Va}}{A \cdot 3600} \qquad \text{(Eq. 3-13)}$$

The appropriate nozzle area is expressed by:

$$a = A \cdot \frac{q'_{Vg}}{q'_{Va}} = A \cdot \frac{q_{Vg} \cdot (1 + \frac{f_n}{0.804})}{q'_{Va}} = A \cdot \frac{q_{Vg} \cdot 273.15 \cdot (p_{am} + p_a)}{Y_{gas} \cdot \dot{m}_{fuel} \cdot 101300 \cdot (273.15 + \Theta_a)} \qquad \text{(Eq. 3-14)}$$

According to ISO 9096 the minimum nozzle size should be 4 mm.

where a = Nozzle face area [m^2]
A = Producer gas duct cross section area [m^2]
v'_a = Wet producer gas velocity in duct [m/s]
v'_N = Wet gas velocity in nozzle [m/s]
q'_{Va} = Wet producer gas flow through duct [m^3/h]
q'_{VN} = Wet producer gas flow through nozzle [m^3/h]
q_{Vg} = Dried volumetric gas flow rate through the gas volume meter [m^3_n/h]
Δp_{Pt} = Pressure difference of pitot tube [Pa]
p_{am} = Ambient pressure [Pa]
p_a = Static pressure in producer gas duct [Pa]
p_g = Static pressure in the gas volume meter [Pa]
Θ_a = Temperature in producer gas [°C]
Θ_g = Remperature in gas volume meter [°C]
f_n = water vapour concentration in dried sample gas [kg/m^3_n]
ρ'_a = Density of wet producer gas [kg/m^3]
$\dot{m}_{fuel}$ = Fuel feeding rate [kg dry biomass / h]
Y_{gas} = Producer gas yield [m^3_n / kg dry biomass]

28. GC analysis to measure tar compounds

28.1 Scope

The method given in this chapter is an example of how to measure tar compounds with GC-FID. The method is an example, meaning that the actual method to be used can be chosen freely as long as the requirements that are given in the Technical Specification are met. These requirements are given in the chapters "Preparation of analysis" and "Analysis procedures" of the Technical specification.

This method is designed for determination of the total GC-tar content (calculated as naphthalene) in isopropanol (2-propanol) samples.

The method may be extended to include additional specific compounds, provided that the method is validated for each individual case.

28.2 Normative references

The following normative document contains provisions, which through reference in this text constitute the provisions of this method.

VDI 2457 part 1 and ISO 11338-2:2003.

28.3 Analysis procedure

In this paragraph, an example of a GC method is given including conditions. Other conditions are possible. The requirements that the GC method should fulfil, are given in the Technical Specification.

28.3.1 Principle

The tar content sampled in iso-propanol is analysed by gas chromatography using a flame ionization detector.

This method includes two different methods for the calibration procedure, by external calibration only and by using an internal standard.

28.3.2 Reagents

Isopropanol, min. 99.5% cas. no. [67-63-0]
Naphthalene [91-20-3]
n-Heptane [142-82-5]
n-Triacontane [638-68-6]
o-Terphenyl [84-15-1]
Hydrogen, min. 4.5
Helium, min. 4.6
Nitrogen, min. 4.8
Synthetic air min 4.0 or purified pressurised air (hydrogen free)
Standard stock solutions

Standard stock solutions are prepared by dissolving pure or - if available - certified reference standards in a suitable solvent.

Unless the manufacturer's information or stability trials indicate otherwise, the solutions should be stored at around +4°C in the dark.

Prior to use, the solutions should be brought to ambient temperature.

Intermediate standard solutions
Prepare intermediate standard solutions by a suitable dilution of the stock solution (3.2.11) with iso-propanol to a concentration of 0.1 mg/ml.

Working standard solution
Prepare at least five different concentrations by suitable dilutions of the intermediate standard solution (3.3.5) with iso-propanol.
The lifetime of these solutions is limited to one week.

28.3.3 Apparatus

Gas chromatograph
The (or A) Gas chromatograph is (or should be) fitted with a capillary column, a flame ionization detector and a data processing system. The stationary phase of the capillary column should be bonded poly(5% diphenyl/95% dimethylsiloxane). The recommended dimensions are an internal diameter of 0.25 to 0.32 mm and a length of 30 to 60 m. It should be noted that this length is suited to the defining of total GC-tar but for determining individual compounds the length may be too short.

The use of an autosampler is strongly recommended, especially when using external calibration, because it reduces the errors caused by injection.
If there is any risk that ferrules may be in contact with the sample gas, ferrules made up of no more than 49% graphite (e.g. 60% polyimide/40% graphite) shall be used at the GC column injection inlet to avoid possible absorption of tar compounds.

Microliter syringes
For injecting samples into the gas chromatograph, for making calibration and internal standard solution.

Miscellaneous glassware
Laboratory glassware can be cleaned according to good laboratory practice, for example by using e.g. a cleaning agent (laboratory detergent), followed by an annealing treatment at 500°C for 2 hours.
The efficiency of the treatment shall be randomly verified experimentally using blank determinations to ensure that no interfering contamination has occurred.

28.3.4 Sample preparation

Until required for laboratory preparation, samples should be stored in sealed containers protected from the light at temperature below 5°C. Samples shall be extracted within one month after sampling has been completed. In some cases (when oxygenated tars are expected, e.g. in raw gases of updraft gasifiers) it may be necessary to store the solution in a sealed, dark bottle under nitrogen atmosphere.

28.3.5 GC analysis

In general
The detection limit depends on the volume injected on column and the detector sensitivity. Other factors influencing on the detection limit are purity of the gases and solvents used.

Sample pretreatment
Prior to analysis, the sample is mixed thoroughly to insure homogeneity. The sample is then transferred into the GC vial and diluted with the internal standard. The concentration of the internal standard should preferably be exactly the same as in the calibration standards, otherwise a

correction factor is required when calculating quantitative results. The dilution can be performed for example by a factor of 1:1 corresponding to a concentration of the internal standard of 12.5µg/ml.

Instrument parameters
Typical gas chromatograph parameters are:

- Column temperature program: 50°C for 5 minutes. to 325°C at 8°C/min, stop for 5 minutes.
- Injector: Split, 1:75
- Injector temperature: 275°C
- Detector temperature: 300°C
- Injection volume: 1-2 µl
- Carrier gas: Hydrogen or helium, column pressure adjusted so that the linear velocity of hydrogen is 30 – 55 cm/s and of helium 20-40 cm/s. WARNING: Special caution is required when using hydrogen because of the risk of explosion.

It should be noted that the parameters above may not be suited to the determination of individual compounds.

28.4 Calibration

28.4.1 In general

The result of the analysis depends on the response factor of the compound(s) used for calibration. Naphthalene is selected for the external calibration procedure, and o-Terphenyl as the internal standard. If the sample contains significant amounts of oxygenated compounds e.g. phenols or guaiacols, the result generated by this procedure will be too low.

The integration interval is defined by the retention time from the apex of n-Heptane to the apex n-Triacontane. Prior to running the samples and calibration standards, a iso-propanol solution of 10µg/ml n-Heptane and n-Triacontane is analysed.

Two different calibration models are described below. The calibration procedure described under paragraph 28.4.3 is recommended for usage with an internal standard. The use of an internal standard will enhance the reproducibility of the analytical method significantly. Furthermore, the peak from the internal standard can be used as a functionality test for every GC run.

If the sample analysed contains considerably high number of different tar compounds, it can be difficult to recover the peak of the internal standard. In these cases the calibration procedure described under paragraph 28.4.2 can be applied.

28.4.2 Calibration using external standards without internal standards

External calibration standards of naphthalene shall be prepared at a minimum of five concentration levels. One of the calibration standards shall be at a concentration near the quantification limit, and the other concentrations shall correspond to the range of concentrations expected in the samples or shall define the working range in the GC-FID system.

A table of values is drawn up which consists of the masses mj in the standard solutions and of the associated measured values Aj (j = number of value pairs). The calibration line can be determined from these values by linear regression using equation (1):

$$A_{Naphthalene} = k * m_{Naphthalene} + b \qquad \text{(Eq 4-1)}$$

Where

$A_{Naphthalene}$: Measurement value for naphthalene as a function of m
$m_{Naphthalene}$: Mass of naphthalene in the calibration solution
k : Slope of the calibration line
b : Intercept of the calibration line

The linearity of the calibration function is to be checked and must be better than r2 = 0,995.

28.4.3 Calibration using internal standards (ISTD)

The procedure of the internal standard described in this paragraph is restricted to the addition of o-Terphenyl to all samples and working standard solutions.

Follow a procedure similar to the calibration using external standards (paragraph 28.4.2), except that each sample and working standard solutions are spiked with o-Terphenyl to attain the same end concentration for all working standard solutions, for example 12.5 µg/ml. If the concentration of internal standard is not the same in the sample and calibration standards a correction factor is required when calculating the results.

Use the same solvent composition and internal standard concentration for the working standard solutions and the samples.

To determine the calibration line, a series of measurement values is drawn up. It consists of the ratios of the masses m_j of naphthalene to the mass m_{Is} of the internal standard and also of the ratios of the measured values A_j / A_{Is} of the naphthalene peak to the o-Terphenyl peak. From these pairs of values, the calibration line is determined by linear regression using equation (2):

$$(A_{Naphthalene} / A_{Is}) = k * (m_{Naphthalene} / m_{Is}) + b \qquad \text{(Eq 4-2)}$$

where

$A_{Naphthalene}$: Measurement value for naphthalene as a function of mNaphthalene
A_{Is} : Measured value for o-Terphenyl as a function of mIs
$m_{Naphthalene}$: Mass of naphthalene in the calibration solution
m_{Is} : Mass of o-Terphenyl
k : Slope of calibration line
b : Intercept of the calibration line

The linearity of the calibration function is to be checked and must be better than r2 = 0,995.

28.5 Calculation

28.5.1 In general

To calculate on the tar content, the following assumption is made: There is a functional relationship defined by the calibration function between the signal obtained for all substances m_{Tot} and the mass injected $m_{Naphthalene}$. The evaluation solves the appropriate calibration function for $m_{Naphthalene}$.

28.5.2 Calculation using the external standards without internal standards according to 28.4.2

If an external standard is used, the evaluation is performed using equation 4-3:

$$m_{Tot} = (A_{Tot} - b) / k \qquad \text{(Eq 4-3)}$$

m_{Tot} : Total mass of chromatogram between the apex of n-Heptane to the apex n-Triacontane subtracted the internal standard.
A_{Tot} : Total measured value of chromatogram between apex of n-Heptane to the apex n-Triacontane subtracted the internal standard.
B : Intercept of the calibration line
K : Slope of calibration line

28.5.3 Calculation using internal standard ISTD according to 28.4.3

If an internal standard is used, the evaluation is performed using equation 4-4:

$$M_{Tot} = (m_{Is} / k) * ((A_{Tot} / A_{Is}) - b) \qquad \text{(Eq 4-4)}$$

See equations 4-2 and 4-3 for symbols.

28.6 Results

28.6.1 Summary

When the procedure described is applied, it provides one individual result (the total GC-tar content calculated as naphthalene) for each sample. If more than one analysis is done on each sample the standard deviation of the result is reported.

28.6.2 Expression of results

The tar concentrations shall be reported in micrograms per normal gas cubic meter (normal conditions: 273,15K, 101325Pa = 1,01325bar, dry)

29. Preparation of Sampling Equipment

29.1 Design of the sampling line

The sampling line should be kept as short as possible. To prevent plugging problems, the inside diameter of the sampling line should be at least 3mm. The sample nozzle diameter can be calculated according to paragraph 27.5. The minimal nozzle diameter is 4mm according to ISO 9096 and 5mm according to VDI 2066, part 2. The nozzle diameter should be at least 4mm. Design parameters for nozzle shapes used to isokinetic measurements can be found in ISO 9096 or VDI 2066.

The sample probe is either positioned in the same direction as the flow or at a 90° angle to it. The sample line is heat-traced at a constant temperature over the filter. The probe is maintained above the tar condensing temperature, to prevent any condensation in the probe. The determination of the temperature level depends on the gasification application. Since high temperature gas cools very quickly, tubes made of stainless steel are appropriate. For gas temperatures below 200°C, PTFE or glass tubing can be used. For gas temperatures above 600°C, material such as Inconel is preferred. The temperature of the stainless steel sampling probe (AISI 310, AISI 316) should be kept below 700°C to prevent changes to the concentrations of tar compounds.

Gas contact times with all parts of the sampling line should be minimised.

In atmospheric sampling the sampling probe is cleaned after each sample run either by flushing with nitrogen pulses or by dismantling and cleaning it manually. As it is not possible to dismantle the probe between sample runs in pressurised conditions, the probe and the filters are cleaned by nitrogen purge.

29.1.1 Measurement of actual gas velocity

Isokinetic measurement requires the knowledge of the actual gas velocity at the sample point or the use of an O-type probe (see chapter 27).

Gas velocities in producer gas streams at near ambient pressure should be measured with (calibrated) pitot tubes or can be calculated according to paragraph 27.4. The instructions for using pitot tubes are given in ISO 9096; an example of the layout is given in Figure 11. Pitot tubes must be heated to process temperature, back-flushing facilities being advantageous.

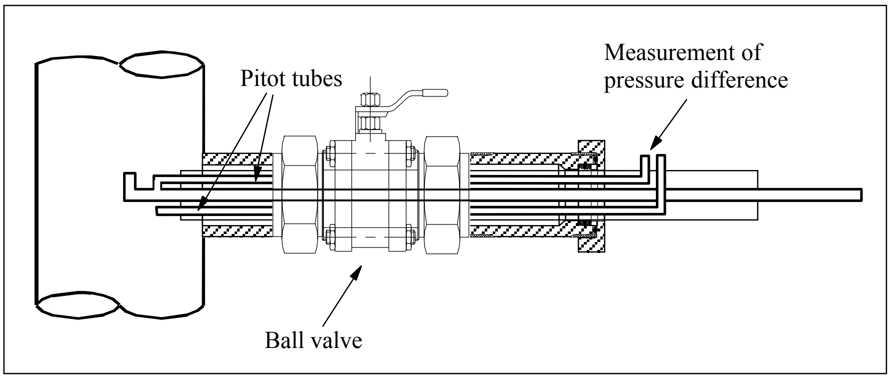

Figure 11: Pitot tubes for measurement of the producer gas flow.

In pressurised gasification applications removable pitot tubes cannot be used and hence gas velocities at the probe tip cannot be measured. Alternatively, an O-type probe has been found to work well for pressurised producer gases (Figure 3-3). The O-type probe is also suitable for atmospheric applications.

If there is no velocity meter available calculation is performed according to Paragraph 27.4.

29.2 Design of the sampling port

Sufficient space must be available to ensure easy access to sampling ports and placement of sampling equipment, typically an area of $4m^2$. There should be good ventilation in the sampling site and exhaust gases must be safely vented to atmosphere. Work in the vicinity of pressurised systems should be avoided or kept to a minimum.

In pressurised gasification processes, the O-type probe (Figure 3-3) or other sampling probe(s) must be mounted before the start-up of the plant. The nitrogen flush through the probe tip must be continuous except during the sampling.

In atmospheric processes, probe mounting during operation is possible. The mounting must be carried out safely both for producer gases with positive or negative pressure since combustible and poisonous sample gas exhibits a potential risk of explosion, fire and poisoning.

The joint of the atmospheric sampling probe is illustrated in Figure 12. The sampling port includes a main shut-off valve (a 2inch (5,08cm) ball valve) which must be assembled before plant start-up. The sampling probe with the gas tight joint (stuffing box) can be mounted during gasifier operation. The stuffing box structure enables mounting the probe, warming the probe after mounting and displacing the probe without the danger of a gas leak.

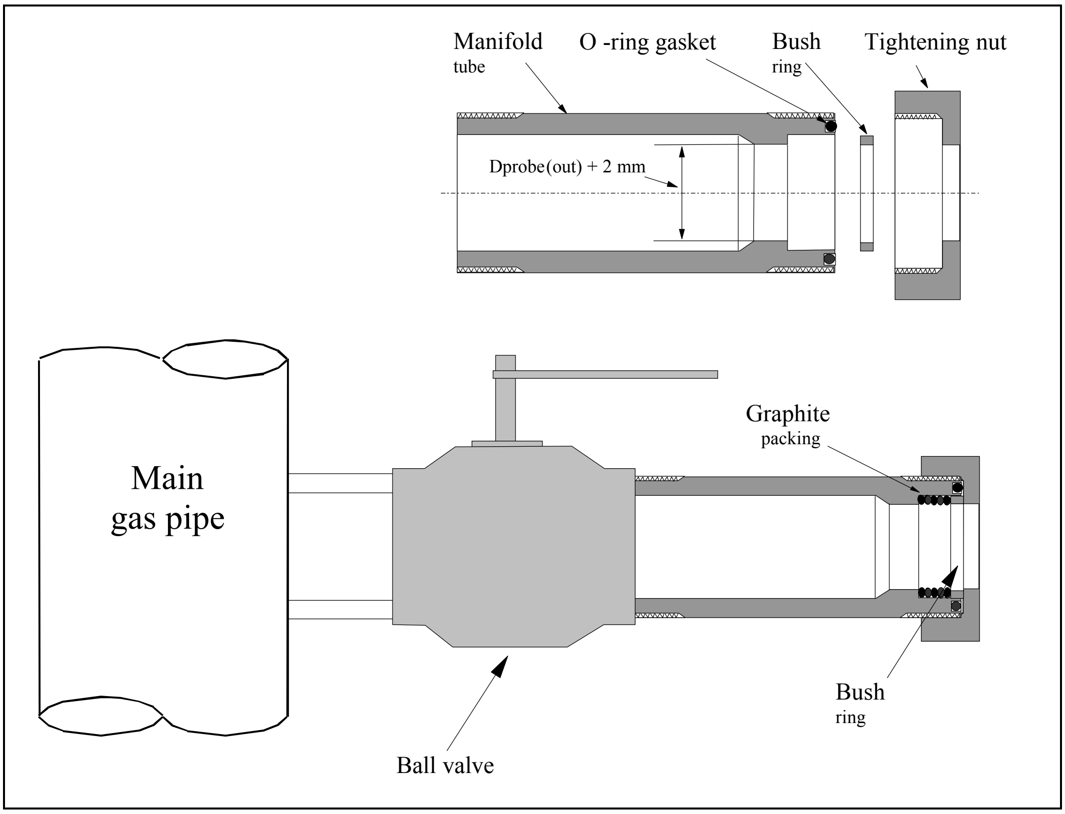

Figure 12: Sampling port with lock consisting of a ball valve and stuffing box (the sampling probe is not shown)

29.3 Preparation of the sample train

29.3.1 Gas velocity meter

The pitot tube is the only measurement principle described within this Technical Report which allows a measurement of the absolute gas velocity in the main gas stream. However, its use is limited to gases near atmospheric pressure. Accurate gas velocity measurement requires calibrated pitot tubes. The pitot tubes are preferentially heated to process temperature. Possible plugging can be tested e.g. by gently blowing nitrogen through the tube. The preparation and calibration instructions of pitot tubes are found in ISO 9096.

29.3.2 Particle filter

Filter thimbles must be preconditioned according to the instructions given in the Technical Specification. A fast, easy and gas-tight clamp system should be used at both ends of the filter holder.

The filter holder including the filter is heated to its set value.

29.3.3 Moisture collector

Prior to sampling the moisture collector cooling or heating system is checked. The preparation procedure depends on the chosen collector system. However, sufficient time should be allowed to ensure that the cooling system reaches the required temperature.

In cases where a liquid quench system is used, the re-circulating system is filled with the chosen liquid. After that, the liquid pump is switched off.

29.3.4 Tar impingers

The required amount of solvent is added to the impingers bottles or to the Petersen column. The impinger bottles or the Petersen column is then heated or cooled to the required temperature. The amount of solvent and the required temperatures are given in the Technical Specification. The impingers bottles or to the Petersen column require approximately 30 minutes to reach the respective heated and cooled bath temperatures.

The cooling liquid can either be a mixture of ice/salt/water or of isopropanol/dry ice or by cryostatic cooling of isopropanol. When using an ice/salt/water cooling mixture operators must ensure that the mixture is wet.

29.3.5 Cleaning of equipment before site measurements

Before using the equipment in connection with a site measurement, all glass equipment shall be cleaned according to an internal laboratory instruction. An example of suitable cleaning procedures is given below. 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:

- Prewash with softened water
- Mainwash at 85°C or at maximum achievable temperature 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. The cleaning procedure should be regularly checked by analysis of the rinsing liquid. After washing, the tubes are sealed with plastic wrap (parafilm).

29.3.6 Choice of correct nozzle size

The diameter of the sampling nozzle is normally determined by the requirement that the isokinetic sample flow at the beginning of a sample run should equal approximately 70% of the sampling trains pump capacity. In the Technical Specification the sample flow rate through the impinger bottles is limited to 0.1 - 0.6 m^3_n/h (see also footnote[14]). The calculation of the correct nozzle size can be found in Paragraph 27.5.

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[14]: For high gas flow rates, requiring a flow rate through the nozzle higher than 0,6 m_n^3/h to meet isokinetic conditions, this requirement plus the requirement on the minimum nozzle diameter can only be met under isokinetic conditions if the sample flow rate through the nozzle is higher than 0,6 m_n^3/h and if the sample flow is split before the impinger bottles.

29.3.7 Gas suction and volume metering

The calibrated gas volume meter and the pump are connected to the sampling line and to the vent gas line. The temperature and the atmospheric pressure are measured.

29.4 Sampling train leak test

Leaking of the sampling train can be tested either by over-pressurising or evacuating the entire sampling train starting from the particle filter inlet to the gas meter inlet. The test should be done at a pressure, which is 0.2bar above or below the maximum sampling over or under pressure. Step by step instructions for these procedures are given in the Technical Specification.

Pressurising of the train is carried out gently feeding gas from a cylinder into the particle filter inlet and the rest of the sampling train. The exit of the gas pump is locked by a ball valve. The pressure in the sampling line is monitored/observed by a pressure indicator (should stay constant). Possible leaks can also be detected as gas bubbles in the impingers or by using other leak indicators. Carefully opening the shutoff valves after the pump terminates the leakage test. The pressure release procedure must be undertaken with utmost care and should last for at least one minute.

The vacuum leakage test is done by using the gas metering pump. A shut-off valve is placed in a closed position at the inlet of the particle filter. The gas pump is turned on and the pressure is gently reduced to its desired value. Possible leaks are detected as gas bubbles in the impingers or in the Petersen column, or by monitoring the gas meter reading. Termination of the leakage test is performed by carefully opening of the ball valve at the particle filter inlet while the pump is still displacing. When gas bubbles are visible in the solvent, the gas flow rate is reduced by gently opening the bypass valve over the pump. The pressure release procedure must be performed with utmost care and should last for at least one minute.

30. Reporting and Documentation

30.1 General

Analysis data and results obtained in the laboratory during sampling and at the completion of experimental work are typically recorded and stored in a standardised computer format suitable for easy dissemination. Similarly analysis quality control data should be stored in a suitable master database. Such data typically contain information on gasifier parameters, analysis instrument type and analytical conditions, calibration data including precision and accuracy, etc. Reported analysis values should have been rounded off to its maximum allowed number of significant figures, i.e. the smallest number in any factor.

30.2 Analytical report

Final results of all analyses (particles and tar) are provided in a standard computer file format and forwarded to the requester with cover memorandum. The reports are prepared on the basis of raw data from sampling logs and analysis result files. Examples of sampling logs are given below in Appendix F.4. The raw log data can be customised to suit a particular report or usage.

Five different numbers are reported with the method for sampling and analysis of tars and particles from biomass producer gases. These five numbers are:

1. The concentration of gravimetric tar in g/m_n^3;
2. The concentrations of individual tar compounds as measured by GC (a suggestive list is given in Appendix F.3) with a GC retention time of the compounds ranging from benzene to coronene;
3. The sum of concentrations of GC-detected, identified compounds (sum of compounds reported in Annex B of the Technical Specification);
4. The sum of concentrations of GC-detected compounds in the range from and excluding benzene to coronene, calculated as naphthalene (so benzene is excluded from this sum and coronene is included in this sum), given that this concentration can be determined. For the analysis of tars from some gasifier types and/or conditions (e.g. updraft gasifiers, fluidised bed gasifiers operated at 750°C or lower) the number of compounds might be so high that the baseline cannot be properly determined. As this will result in an erroneous amount of GC detected, non-identified compounds, this number will then not be reported;
5. The concentration of particles in mg/m^3_n.

Remarks using suitable designations should be provided with reported data to alert the user to any specific conditions that may have affected the data.

Essential information that should be included in a report may contain the following:

- The name of the laboratory (or factory), from which the sample was received
- The date of sampling and analysis
- Analyst and/or examiner name
- The type of reactor, fuel type, fuel moisture, test number and operation parameters including actual power output (kW), actual fuel feeding rate (kg wet/h), dry raw gas flow rate (m_n^3/h), gasifier start
- Sampling location, i.e. in which part of the reactor the sample was taken
- Sampling technique and essential parameters including tar trapping solvent, ambient temperature and pressure, duct diameter, diameter of sampling nozzle and particle filter temperature
- Sample treatment, solvent, dilution factors etc.
- Sample storage technique
- Analytical technique and parameter settings
- Target analyte values, usually reported in kg/m_n^3 or g/m_n^3

- Level of analytical precision and accuracy

30.3 Sampling log

It is essential to keep records of the principal operating parameters of each gasification run. Examples of typical sampling logs are given in Appendix F.4.

31. Health and Safety

This section is intended to briefly list potential dangers associated with tar analysis and recommended precautions to avoid exposure to hazardous chemicals and accidents. Take care of the common standards on safety on

- site measurements and procedures
- pre and post sampling, transport, storage and laboratory routines
- special safety measurements for the use of chemicals and laboratory equipment

to be described in the further paragraphs.

For a more comprehensive description of chemical safety issues, the reader should consult the reference sources at the end of the section.

31.1 Introduction

No chemical work is completely risk free but the likelihood of accidents during tar analytical work will be greatly reduced if adequate safety precautions are followed. Health and safety legislation in most countries place duties on employers to ensure health and safety by providing employees with adequate information and training in the inherent hazards of chemical work. Safety issues are usually addressed jointly by supervisors, employees, the local safety representatives and the employer.

31.2 Hazards

Since tar analytical work typically involves handling of relatively small quantities of material the likelihood of acute overexposure to chemical vapour and serious injuries during normal work are less likely. However, acute toxicity hazards may arise during sampling from leaking reactor or sampling system or during sample preparation from spillage and splashes. One should also bear in mind that many sub-operations including operating vacuum devices and handling compressed gases are potentially hazardous and require attention to safety requirements.

General hazards during on site measurement

Before starting measurements on site, the operator has to introduce about the safety measures and actions which have to be considered during the stay at the plant for the preparation of the measurement(s). Discuss the configuration of the sampling equipment and the connection to the plant with the operator + check the compliance with the safety requirements of the sampling with the operator.

Chemical hazards

The use of chemicals is always potentially associated with health, fire and explosion hazards. The health risks associated with accidental exposure to the chemicals being handled depend mainly on their physio-chemical properties, the exposure concentration and exposure time. Toxic body responses can be either reversible or irreversible and response time may be immediate or delayed several days depending on the rates of absorption, bio-transformation, distribution and excretion as well as other factors. Nearly all chemicals found in tar matrices are more or less toxic and for that reason, great care should be exercised in handling samples, solvents and reagents and lengthy exposure above safety limits must be avoided.

The most probable routes to exposure may be through inhalation of non-polar organic solvent vapours since they are the most volatile chemicals. In contrast to water-soluble chemicals and large molecules non-polar solvents diffuse readily through the blood-brain barrier. About 90%

of all occupational poisoning are caused by inhalation of non-polar solvents and in particular aromatics and halogenated solvents, which are the most toxic. Solvents can effect the nervous system, the respiratory system, eyes, internal organs including reproductive systems and damage the skin by de-fatting, irritation, sensitisation or dermatitis. Dichloromethane, an often-used tar solvent is a probable human carcinogen and should be handled with great caution and if possible replaced by another safer solvent. For this Technical Specification, 2-Propanol (isopropanol) has been selected as a less toxic alternative to dichloromethane. Skin absorption is the second route of concern. The rate of skin penetration for solid chemicals is significantly increased if they are dissolved in an organic solvent.

Tar samples can contain many groups of organic compounds depending on the conditions of their formation. The long-term health implications of exposures to such substances are essentially unknown but available literature data that refer to coal-tars present evidence for carcinogenicity to humans. Biomass tars obtained at high temperatures (~900°C) typically contain several of the carcinogenic polycyclic aromatic hydrocarbons (PAH) found in coal tars. Benzene and some of the polyaromatics found in biomass tars have been reported to be carcinogenic for all routes of exposure although skin absorption is the most likely route for PAHs due to their low volatility. Such substances are indirect acting carcinogens and their acute toxicity is generally low. Benzofuran found in low temperature tar is possibly carcinogenic.

Examples of other substances considered most likely to pose a potential risk to human health may be toluene, phenol and its derivatives. The acute toxicity of individual substances may be roughly assessed by comparison with available data (see references). Accordingly, low level exposure to toluene has its primary effect on the CNS and is more acutely toxic than benzene. Phenols are relatively lipophilic and are readily absorbed via the lungs, the digestive organ and skin. Phenol is corrosive to skin, which increase the rate of penetration also for other compounds. It is also toxic to the kidneys and can cause skin allergy, especially following chronic exposure. Many experts consider phenol as a co-carcinogen.

In view of the low volatility and pungent odour of many compounds excessive exposure to vapours does not seem likely unless heating or leakage from the gasifier or sampling system generates fumes. Therefore, the most toxic effects of low volatility substances are expected from dermal exposure. Phenol derivatives, i.e. cresols, xylenols and guaiacyl type phenols are less toxic and corrosive than the mother compound.

Vacuum hazards

Solvents are typically removed under a moderate vacuum of about 1000Pa in a rotary evaporator. Similarly samples are often dried under vacuum in a desiccator.

When working with such devices the operator must be aware of implosion hazards that may result in flying glass and airborne chemicals. Always check for signs of damage (stars or cracks) before use. For greater protection, use a desiccator shield during and after evacuation and wear safety spectacles.

Compressed gas hazards

Compressed gases present potential mechanical and chemical hazards and cylinders and regulators must therefore be handled carefully. Cylinders must always be secured by chains or strong straps to prevent tipping and regulators must always be accessible. Flammable gases must be stored in a well-ventilated area and kept away from open flame and spark sources. Piping system must regularly be checked for leaks. Always use safety glasses when connecting and disconnecting gas regulators and lines.

Sampling hazards

Product gases typically contain high levels of carbon monoxide and benzene, both of which are toxic and inhalation of fumes that may result from leaking gasifiers and sampling system pose an obvious health hazard to the workers. With adequate general laboratory ventilation short-term and long-term exposure levels will not be exceeded.

Acute toxicity hazards can also arise from leaks and solvent splashes from impingers caused by a rapid change in gas pressure.
A Plexiglas shield around the sampling system provides a suitable safety. Furthermore the use of a personal carbon monoxide detector is recommended.

31.3 Safety precautions

One key to prevent accidents is to use the safest possible practices in laboratory and on the plant. Only individuals with proper training and experience to deal with the expected risks and hazards during laboratory operations should therefore perform all chemical work.
All work spaces must be equipped with first aid kits, safety showers, eyewash fountains, fire extinguishers and fire blankets and a laboratory safety manual and Material Safety Data Sheets (MSDS) should be available. Plans for medical and chemical accident response must have been established and emergency telephone numbers must be readily available. Organic solvents shall be stored in specialised flammable and well-ventilated storage areas and chemicals should have well-ventilated storage places. The laboratory should be equipped with clean-up equipment for chemical spills including appropriate absorbents (vermiculite[15], clay, dry sand, or towelling) for collecting and disposal containers.
Waste chemicals must be collected in suitable containers and stored in a properly ventilated place until disposed of according to safe disposal procedures that is commonly handled by a chemical hygiene officer.
The following basic personal safety rules should be followed when work on the plant orlaboratory is being conducted:

- Be instructed to the safety measurements and procedures of the plant by the operator. Discuss the configuration of the sampling equipment and the connection to the plant with the operator + check the compliance with the safety requirements of the sampling with the operator.
- Make sure that the ventilation system is switched on and is working before starting chemical work.
- Protective helmet should be worn at the sampling site.
- The sampling system should be checked for leaks before sampling.
- Wear eye protection (safety spectacles with side-shields, goggles, face-shield), protective gloves[16] and a chemical and fire-resistant laboratory coat as needed for the work at hand.
- Handle chemicals, solvent and samples in an efficient chemical fume cupboard.
- Carry out sampling in a well-ventilated area.
- Do not eat, drink or smoke in the laboratory or sampling area.
- Do not wear open shoes.

For more about this topic, the following Internet link may be useful: Chemical guide and permeation tables for laboratory gloves are available at http://www.pp.okstate.edu/ehs/hazmat/gloves.htm

31.4 Accidents

In the event of splashes on the skin, immediately rinse with water for 15 – 30 minutes and final cleaning with soap. In the event of large splashes on the body, remove contaminated clothing and promptly use the safety shower. Lipophilic substances can be rinsed of with polyethylene glycol. Splashes of chemicals in the eye are promptly flushed of with copious amounts of water for 15-30min using the eyewash and then seek medical advice.

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[15]: Hydrated magnesium-aluminium-iron silicate that can absorb large quantities of liquids.

[16]: There is no single glove material that is resistant to all chemicals and they should be chosen for each specific job. For compatibility and breakthrough characteristics of different glove material, an excellent information is ***Guidelines for the Selection of Chemical Protective Clothing*** published by the American Conference of Governmental Industrial Hygienists (ACGIH) or information provided by glove manufacturers.

Spills of chemicals should be cleaned up as they occur, using a suitable absorbent -dry sand or towelling- to collect and then dispose of residues according to safe disposal procedures.
Avoid breathing vapours of spilled chemicals and do not touch the spill without protective gloves.

31.5 Safety and health information resources

A broad coverage of chemical hazard topics is freely available on Internet resources. Here are some useful links:

- National Institute for Occupational Safety and Health (NIOSH) provides International Chemical Safety Cards (ICSCs) database including index with chemical names and synonyms. http://www.cdc.gov/niosh/ipcs/icstart.html
- The National Library of Medicine's Toxnet: http://toxnet.nlm.nih.gov/
- The United States Environmental Protection Agency (EPA) provides the Integrated Risk Information System (IRIS) database:
  http://www.epa.gov/iriswebp/iris/index.html
- Minimal Risk Levels (MRLs) for hazardous substances can be found at Agency for Toxic Substances and Disease Registry (ATSDR): http://www.atsdr.cdc.gov/mrls.html
- Chemical guide and permeation tables for laboratory gloves are available at http://www.pp.okstate.edu/ehs/hazmat/gloves.htm

Additional information about chemical characteristics and hazards can also be found in the following sources:

- Material Safety Data Sheets (MSDS) or International Chemical Safety Cards (ICSCs)
- Merck Index
- The Kirk-Othmer Encyclopaedia of Chemical Technology
- Sax's Dangerous Properties of Industrial Materials
- Bretheric´s Handbook of Reactive Chemical Hazards
- Patty's Industrial Hygiene and Toxicology
- Dictionary of Substances and their effects

References

CEN Technical Specification "Biomass Gasification – Tar and Particles in Producer Gases – Sampling and Analysis", prepared by CEN task force BT/TF 143 WI CSC 03002.4TC, 2005.

Ramackers, Heynis, v.d.Weide; Engines and Adaptation of Engines for Producergas, The second international producer gas course and conference, Bandung, Indonesia, March 1985.

T.Milne, N.Abatzoglou and R.J.Evans; Biomass gasifier "tars": their nature, formation and conversion, Golden, CO (USA), NREL, NREL/TP-570-25357, 68 p., 1998.

Appendix F Liquid Quench

The working principle of liquid quench with circulating fluid is shown in Figure 131. Liquid injection into the sample gas stream must occur immediately after the particle filter outlet. A liquid flow rate in the order 10 - 50ml/min (depending on the sample gas flow rate) is sufficient to cool the gas from 250 to 50°C.

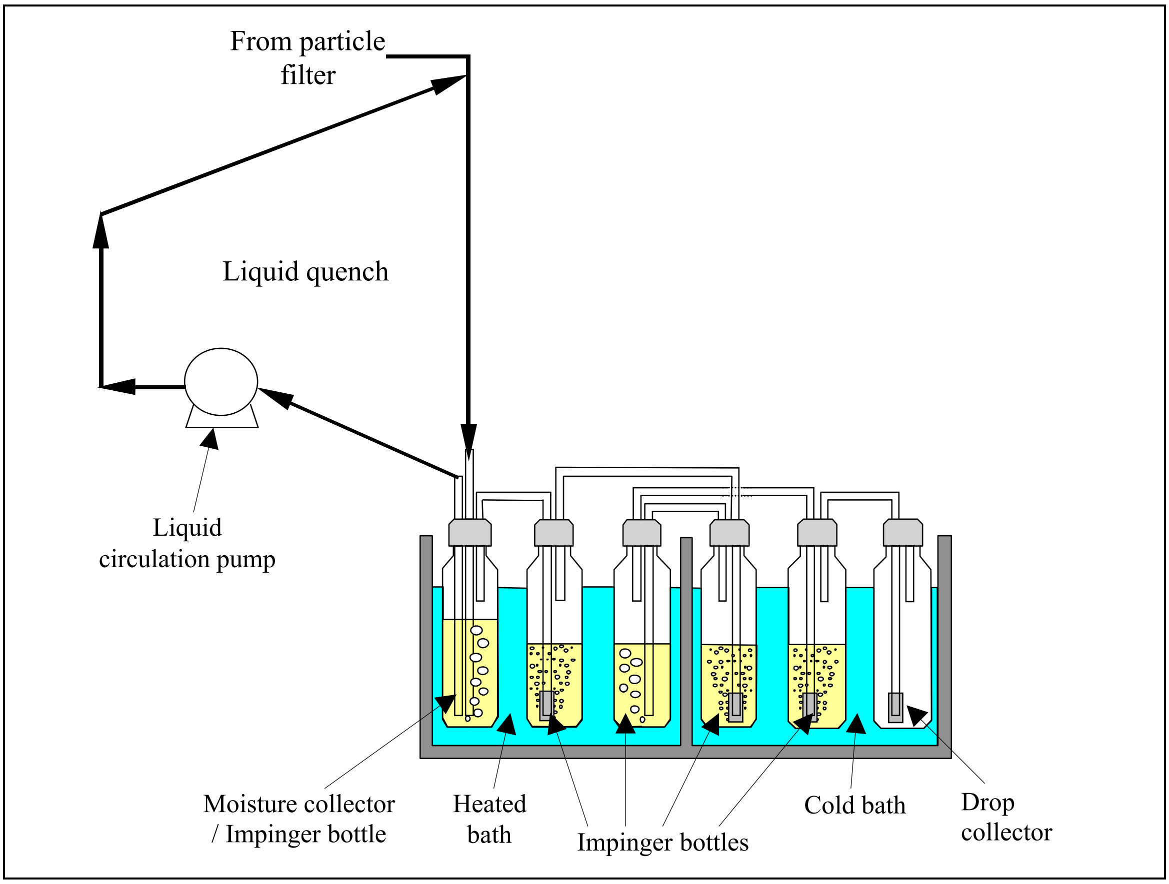

Figure 13: Example of a liquid quench system as part of the sampling train arrangement

F.1 Modified (VTT) design of Impinger Bottles

The mass and heat transfer in impinger bottles can be improved by modifying the design of impinger bottles. An modified design by VTT is shown in Figure 14. Glass bends using ball ground joints ensure correct connection of the impinger bottles. To ensure impinger bottle connections (conical and ball ground joints) are gas tight, only PTFE gaskets, PTFE tapes or solvent are accepted as the sealing media.

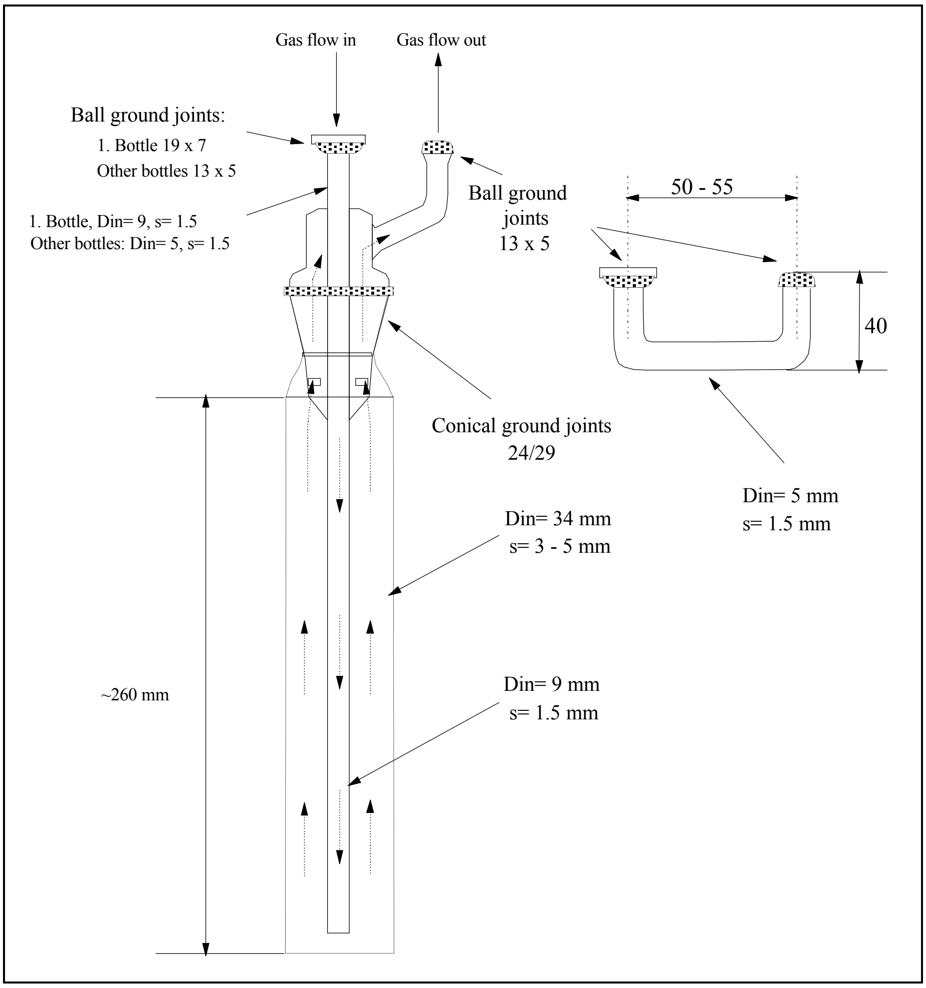

Figure 14: The impinger bottle and the glass bend used by VTT.

F.2 General design and operating conditions of gasifiers

Gasification is a thermochemical process, which converts solid carbonaceous fuels into gas by mixing the fuel with an appropriate gasification agent. Most of the gasifiers fall into four categories (see Figure 15) based on the capacity and flow direction of the feedstock and the design, feedstock and on the gasification agent. These four types are:

1) Fixed-bed updraft (or countercurrent)
2) Fixed-bed down-draft (or cocurrent)
3) Fluidised-bed and
4) Entrained-flow.

Within the gasification reactor, the processes of fuel drying, pyrolysis, reduction and oxidation occur. The oxidative gasification agent converts char and tar from the pyrolysis process into gas. As the gas generation is an endothermic process, some of the gasification agent is required to supply the chemical energy by combusting a fraction of the fuel. The combustion process generally is internal.

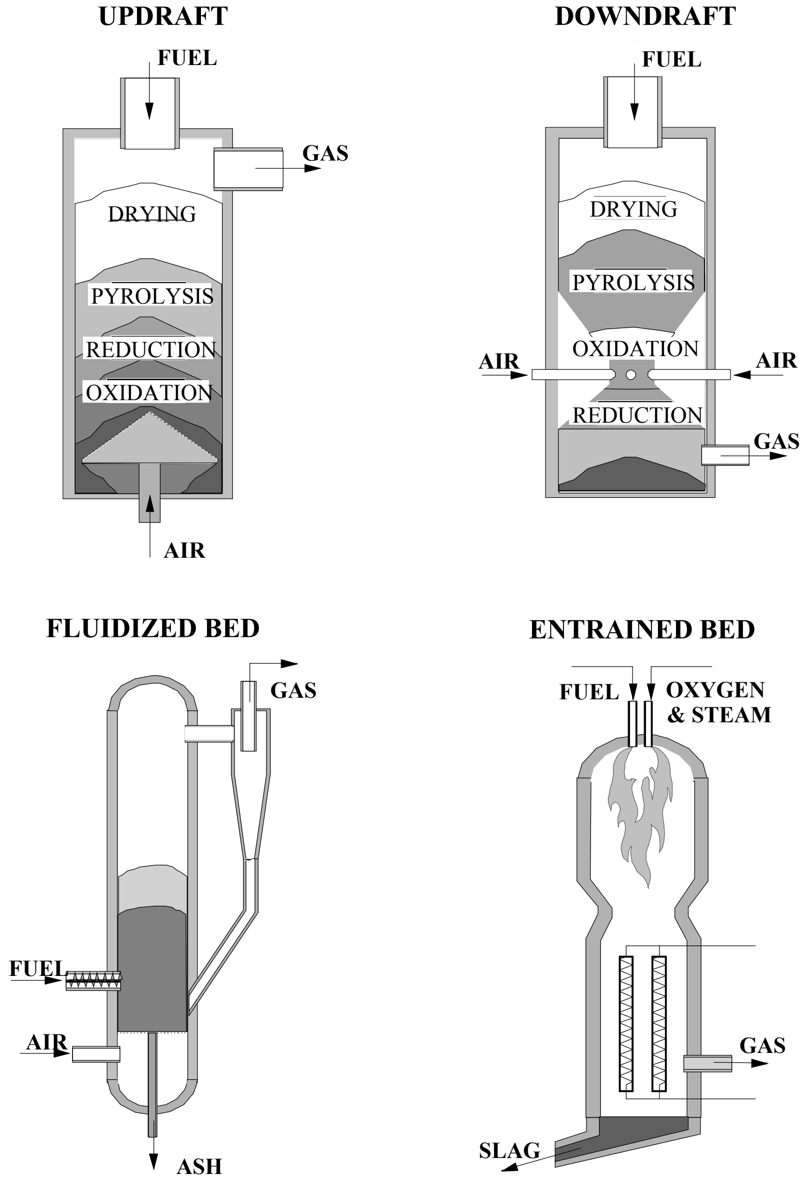

Figure 15: Schematic drawing of four basic gasifier types

In updraft gasifiers, the fuel generally moves from the top downwards and the gasification agent moves from the bottom upwards (updraft). As the gas leaves the reactor near the pyrolysis zone, the gas generated in updraft gasifiers exhibit a high level of organic components (tar). The solid carbon in the fuel is completely converted into gas and tar. Updraft gasifiers can be used for wet fuels and are relatively insensitive to the fuel size.

In cocurrent gasifiers, the fuel and gasification agent flow cocurrently, hence the gas leaves the reactor near the hottest zone and the tar levels are much lower than in updraft gasifiers. Also the amount of tar compoounds, present in updraft gasifier gas, is much higher than the amount of tar compounds present in downdraft or fluidised bed gasifier gas. A list of species that can be present is given in Appendix F.3.

The cold gas efficiency (conversion of fuel carbon into non-condensable gases) of cocurrent gasifiers is generally higher than in updraft gasifiers. Generally, cocurrent gasifiers can only be used with dried fuel (typically 15 wt%) and the size of the fuel are in narrow limits.

With increasing expansion of the fuel bed, the reactor behaviour transforms from a fixed bed to a (stationary) fluidised bed (FB) reactor and further to a circulating fluidised bed (CFB) reactor. The highest heat and mass transfer rates are observed in CFB reactors. A further increase leads then to entrained flow reactor types. FB and CFB gasifiers are characterised by high gas throughputs and require dried fuel with sizes typically <2cm. CFB type gasifiers can be designed both for near atmospheric pressure and for pressurised applications.

Entrained flow gasifiers operate at elevated pressure and are found in coal gasification. The flow of fuel and gasification agent is cocurrent. In contrast with the other principles, the temperatures in the reactors are above the melting point of the ashes, which therefore leave the gasifier as molten slag.

In the Table 31.1, typical operating conditions and gas composition are displayed for some of the gasifier principles. No data were found for entrained flow gasifiers fuelled with biomass.

		Countercurrent	**Cocurrent**	**CFB**
Typical heat output	kW_{th}	1’000 – 10’000	100 – 1’000	>10’000
Fuel moisture	wt% (daf)	50	16	15
Typical gas composition				
Carbon dioxide (CO_2)	%	10.0	12.9	15.0
Carbon monoxide (CO)	%	20.0	18.0	15.4
Hydrogen (H_2)	%	14.0	14.2	14.8
Methane (CH_4)	%	2.5	1.9	4.2
Nitrogen (N_2, by diff.)	%	53.5	53.0	39.6
Typical contaminant levels				
Particles	g/m_n^3	0.1 – 0.5	0.1 – 1	20 - 60
Tar (generic definition)	g/m_n^3	50 – 150	0.5 – 2	7 – 10

Table 31.1: Typical operating conditions and gas compositions of various wood fuelled gasifiers at atmospheric pressure. Data source (tar and particles): Milne et al 1998

F.3 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 explicitly not a list of compounds to be determined by this Technical Specification, hence this is an informative list. See also Chapter 1 "Scope" and Annex A and Annex B of the Technical Specification, in which the compounds are mentioned for which the Technical Specification applies.

Table 31.2- 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			

Group / common name	**Other / (more) trivial name**	**Chemical Abstract Service (CAS) Registry Number**	**Boiling point (°C) (Handbook of Chemistry and Physics, vol. 77)**
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,	78-98-8	72

Group / common name	**Other / (more) trivial name**	**Chemical Abstract Service (CAS) Registry Number**	**Boiling point (°C) (Handbook of Chemistry and Physics, vol. 77)**
	pyruvaldehyde)		
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
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	109-06-08, 108-99-6,	129,3; 144,1;

Group / common name	**Other / (more) trivial name**	**Chemical Abstract Service (CAS) Registry Number**	**Boiling point (°C) (Handbook of Chemistry and Physics, vol. 77)**
	(2- 3- 4-)Picoline	108-89-4	145,3
Quinoline	1-Azanaphthalene	91-22-5	237,1
Isoquinoline	Benzopyridine	119-65-3	243,2

[1]: sublimates

F.4 Example test and analysis logs for sampling and result documentation

F.4.1 Parameter log for sampling of P&T

Sampling of P&T from Biomass Producer Gases						
					Examiner:	X
Gasifier Type/Site:		X			Date:	X
Test No.:		X				
Gasifier parameter						
Actual power output:			kW	(max. .... kW)		
(based on fuel fuel input)						
Raw gas flow rate (dry):			[m_n^3/h] (if calc., spec. gas rate:			m_n^3/kg **wet**
Gasifier start *:				stationary since *:		
Fuel type *:						
Fuel moisture *:			[%, dry basis]			
Actual fuel feeding rate *:			[kg wet/h]			
Sampling parameters						
Sampling site (hot/cold end):						
Tar trapping solvent:						
Ambient temperature:			[°C]			
Ambient pressure:			[mbar]			
Duct diameter:			cm			
Diameter of sampling nozzle:			mm			
Particle filter temperature:			[°C]	Filter tube no.:		
		init. weight	**final weight**			
Solvent stock bottle:						
Solvent storing bottle:				[g]		
Summary protocol						
Solvent from P&T sampling:			[g]			
Approx. mass of condensate:			[g]			
Solvent from Soxhlet extraction:			[g]			
Total particle mass in filter tubes:			[mg]			
Normalised sampled gas flow rate:			[m_n^3/h]			

Remarks:			

F.4.2 Parameter log for gas meter reading

Sampling of P&T from Biomass Producer Gases						
Gasifier Type/Site:		X				
Sampling site (hot/cold end):					Date:	X
Test No.:		X				
Rated sampling gas flow rate (dry):			m_n^3/h (calculated set point;			
10% over isokinetic)						
P+T sampling start:			P+T sampling end:			
			Temperature in gas meter	Pressure In gas meter		
Gas meter protocol			[°C]	bar		
Time	Gas temperature	Reading			Δp pump	Sampling
	in duct	gas meter				Flow rate
[hh:mm]	[°C]	[m^3]			[mbar]	[m_n^3/h]

Remarks:						
Averaged sample flow rate:			m_n^3/h			
Total amount of gas sampled:			m_n^3			
Total sampling duration:			hours			
Mean gas meter temperature:			°C			

F.4.3 Log for particulate measurement

Sampling of P&T from Biomass Producer Gases						
Gasifier Type/Site:		X			Date:	X
Sampling site (hot/cold end):					Test No.:	X
Particle filter pre-treatment						
Type of particle filter used:					Filter tube no.:	
Preconditioning temperature:				°C		
Preconditioning duration:				hours		
Initial tube weight after preconditioning:				g		
Tar extraction from particle filter with Isopropanol						
Soxhlet extraction		Start:			hh:mm	
		End:			hh:mm	
		Duration:			hours	
	tara weight	**gross weight**		**net weight**		
Storing bottle					[g]	
Remarks:						
Particle filter post-treatment						
Post-conditioning temperature:				°C		
Post-conditioning duration:				hours		
Final tube weight after post-conditioning:				g		
Remarks:						

F.4.4 General logbook of test performer

This chapter contains the information mentioned in the logbook of the test performer. It describes all the relevant aspects regarding the sampling site, the sampling and analysis procedures should be given.

The following information should be given in a number of log-parts:

- Installation description (type of gasifier, gas cleaning, capacity, year of construction .....)
- Fuel characterisation (origin, moisture, size (distribution) .....)
- Description of sampling site and (gasifier) operation conditions
- Sampling train set-up (arrangement of type of modules used)
- Sampling (duration, temperatures, pressure, flow rate ....)
- Sample(s) post treatment
- Type of analysis used (incl. calibration methods)
- Tables with results