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An outline of R&D work supporting the Tar Guideline

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Overview

In implementing an applicable Tar Guideline, the accepted reality is that the data generated from practical test-work essentially provides the basis for development and improvement of analysis methods. The required R&D activities reported here were co-ordinated from within the EU 5th framework project ***Tar Protocol*** but aided by national funds and performed outside this project. The participants in the practical work were DTI (Danish Technological Institute, Denmark), Verenum Research (Switzerland), VTT (Technical Research Centre of Finland), BTG (Biomass Technology Group, The Netherlands) and ECN (Energy research Centre of the Netherlands). BTG and ECN performed the investigations in close co-operation.

Tar analysis is complicated by the fact that organics found in samples can range from low-molecular weight components to very complex structures of different polarity and boiling point which put special requirements on the design of the sampling system and the absorbent solvent. It is therefore a necessity to use both gravimetric and gas chromatographic (GC) methods to measure the total tar mass. One of the best universal solvents for complex organic samples is dichloromethane (DCM), which was used for the 1st version of the Guideline. This solvent was excluded from the **Guideline** at an early stage due to its potential hazardous properties and it was therefore decided to replace it by a safer solvent. The new solvent must meet additional specifications including good tar solubility properties and a boiling point that is compatible with the requirements of all analytical steps. In an early stage of the project a number of solvents were suggested for various physical examinations. Later on three solvent candidates (ethanol, 2-propanol and methoxypropanol) remained for further practical tests together with DCM that served as a reference. Reliable measurements of tar levels in producer gases imply the ability of the sampling system to collect a representative sample. It also relies on reproducible procedures for the subsequent analytical steps as well as good instrumentation. To arrive at accurate analysis methods require a great deal of practical work including tests of different sampler designs and various sampling variables as will be described below. Details of the R&D tests are given in the individual participant reports and published elsewhere.

Objectives

The overall objectives of this research were to inventory solvent candidates, improve sampler design and develop procedures for tar measurement. To accomplish this requires the set-up of numerous experiments and adjustment of their processing variables (i.e., train configuration, impinger temperature, etc) as stated in the document *Short –term R&D requirements* (*Tar Sampling Guideline*). The following did this:

- Testing absorption properties of the selected candidate solvents (ethanol, 2-propanol and 1-methoxy-2-propanol) under different sampling conditions
- Examination of evaporative loss of solvent during sampling and evaporation rate during gravimetric tar measurement
- GC analysis of the pure solvent candidates to confirm that their blank values are low (≤ 0.001 wt%) and that they do not co-elute with target analytes
- Evaluation of collection efficiency for different sampling approaches by means of real producer gases and synthetic gas mixtures containing selected authentic tar compounds of known concentration.

- Testing of the solvent ability to remove tar from particle filters and to dissolve different kinds of tar.
- Tests for sampling train breakthrough by means of a back-up train or an adsorbent tube.
- Evaluation of the accuracy and reproducibility of all analytical steps

In the next chapters, the results of the experimental work as performed by the different institutions will be summarised. These results do not always have a direct link to procedures for sampling and analysis as described in the Guideline. The link will be given in the chapter "Rationale for decisions taken" which describes which R&D results and which explanations for observations during the R&D led to decisions to change or update procedures in the Guideline.

Laboratory Tests

Selection of solvent

One of the important driving forces behind the development of the Guideline is the selection of the proper solvent. A good starting point may be to apply the rule of thumb "Like dissolves like" or using knowledge from passed experience on solvent-solute interactions but often trial-and-error must do this. The choice of solvent may also be facilitated by the use of vapour-liquid equilibrium data (VLE) for single tar model components. For this work VTT used VLE-data obtained by using the Aspen simulation program. A solvent should generally meet the following requirements:

- Low toxicity
- Good tar solubility
- Boiling point must be lower than target analytes
- Good tar trapping efficiency
- Suitable evaporation rate with respect to sampling and gravimetric measurement
- Compatibility with GC and gravimetric measurement
- Biologically degradable
- Resistant to chemicals
- Inexpensive

It may be assumed that sampling efficiency is mainly related to the solubility power of the solvent and the sampling temperature. To assess the tar solubility properties of the solvent candidates the following test procedure was used by DTI:

5 grams of heavy tar from an updraft gasifier was shaken with 50 grams of solvent in a clear glass bottle. Then, the bottle is left standing and the solubility of the tar is visually estimated. Subsequently, 10 ml of water is added and the bottle is shaken again. After 30 minutes of rest the solubility once again is visually estimated. The bottles are then emptied and rinsed twice with 10 ml of solvent.

The visual judgment was marked according to the scale: bad – medium – good. The results of these tests are summarised in Table 1.

Table 1 Visual check for the solvent candidates tar solubility properties (updraft tars)

Solvent	5 g of tar + 50 ml of solvent		5 g of tar + 50 ml of solvent + 10 ml of water		Remarks	Suitable Solvent
	Sediment	Obnoxious smells	Sediment	2 phases		
N-Pentane	Yes	No	Yes	Yes	Bad solubility, inflammable	No
DCM	Yes	Yes	Yes	Yes	Bad solubility, health risk	No
Acetone	No	Yes	No	No	Good solubility	Yes
Methanol	No	No	(Yes)	No	A little undissolved tar: medium solubility	No
Ethyl acetate	No	Yes	(Yes)	Yes	Viscous fraction at the bottom: medium solubility	No
Ethanol	No	No	No	No	Good solubility	Yes
Isopropanol	No	No	No	No	Good solubility	Yes
Isooctane	Yes	No	Yes	Yes	Bad solubility	No
Methylisobutylketone (MIBK	No	Yes	(No)	Yes	A little undissolved tar: medium solubility	No
1-Methoxy-2-Propanol	No	No	No	(No)	Good solubility but formation of foam	Yes

From Table 1 it is evident that Acetone, Ethanol, 2-propanol and 1-Methoxy-2-propanol was considered as good solvents for updraft tars, although the latter was not suitable for GC because it co-elutes with ethylbenzene and the xylene isomers. The solvents were free from contaminants as confirmed by GC.

Verenum has performed a comparison of several of the above-mentioned requirements mentioned above. From this comparison, a large number of solvents were excluded as future candidates for the Guideline. This comparison is further described at the end of this report ("Rationale for decisions").

BTG and ECN investigated the solvation efficiency of 1-methoxy-2-propanol and 2-propanol for tar extraction from particle filters that had been kept at 250 ºC and 325 ºC in different gasifiers (downdraft, CFB, BFB). The risk of thermal decomposition of some sample components was considered when selecting the upper filter temperature. As expected no GC-amenable tar compounds were trapped on the filter. At 325 °C, only 1 wt% of the total tar mass was captured on the filter compared to 5 wt% at 250 °C. It is therefore recommended that the filter temperature should be set to 325 °C to collect most of the tar compounds in the impingers. It was concluded that the extraction efficiency of 1-methoxy-2-propanol was slightly better (78-93%) than 2-propanol (61-85%).

Verenum performed tar extraction tests on filters that had been operated in an open-top downdraft gasifier at 150 and 300 ºC. Organic materials trapped on a filter is typically removed by Soxhlet extraction using one or more solvent. In this case one solvent was used. For comparison, liquid-solid extractions (LSE) were also carried out at ambient temperature. The tested solvents were ethanol, 2-propanol, and 1-methoxy-2-propanol. It was concluded that Soxhlet extraction is a requisite for optimal tar recovery and that all three solvents have comparable extraction efficiency. At a filter temperature of 300 °C, between 10 wt% and 20 wt% of the total gravimetric tar was found on the filter, and at 150 °C between 50 wt% and 60 wt% of the gravimetric tar was deposited on the filter. It was also found that the GC amenable

low boiling tar compounds contributed from 70 wt% to 90 wt% of the total tar mass. The quantitation of the impinger and adsorbent solutions were performed by GC-MS at VTT. For control purposes, the filter (Soxhlet) and some impinger solutions were also quantitated by GC-MS at ECN. Comparison of the results obtained at ECN and VTT showed large deviations between identical samples.

VTT evaluated the solvent candidates (dichloromethane, ethanol, 2-propanol, and 1-methoxy-2-propanol) using fluidised bed tars by means of two different approaches: Firstly, solubility properties for candidate solvents including estimation of their activity coefficients in binary systems were obtained by the Aspen simulation program using SLE (solid-liquid equilibrium) and VLE (vapour-liquid equilibrium) data for binary systems. Secondly, the solubility of tars was tested by adding the solvent to a tar sample in room temperature and then gravimetrically determines how much tar was dissolved.
Of the tested solvent, dichloromethane had the best dissolving power but some of the other solvents were also acceptable.

Sampling

The sampling step is most important in all analytical procedures since it strongly affects the accuracy of subsequent analyses for individual compounds and total sample mass. The recognised sampling principle of the Guideline procedure is to simultaneously collect particles and most of the heavy tar and particulate matter with a heated glass-fibre-filter under isokinetic conditions. Light tar passing through the filter is collected downstream by solvent trapping in a train that consists of six gas washing bottles with in-line glass frit. The bottles are connected in series with ground glass fittings. The bottles are connected so that the outlet of one bottle flows into the inlet of the next. Five bottles contain an absorbing organic solvent and one is empty. The sampling system is also equipped with an optional liquid quench. A schematic of the recommended Guideline sampling set-up is shown in Figure 1.

This set-up or modifications of the same constitutes the sampler configurations used by all participating research groups for performing tests on different sampling variables with a view to determine which are important to the analytical performance. In the course of the development efforts a number of modifications of the basic train have been tested together with different absorbing solvents over a wide temperature range. Table 2 lists the different train configurations and experimental variables investigated. All sampling runs were carried out under stable gasification conditions.

VTT investigated the efficiency of different sampling modifications using a sampling train arranged as in Figure 2. Two different sampling set-ups simultaneously conducted sampling: The VTT original train, used as a reference method, and different modifications of the Guideline train. The VTT original method uses dichloromethane (DCM) as absorbing liquid in six gas washing bottles which were cooled from 0 °C to –70 °C. Samples were taken from a bench scale fluidised bed and from different PDU scale test rigs: circulated fluidised bed (CFB), bubbling fluidised bed (BFB) and a downdraft type fixed bed gasifier.

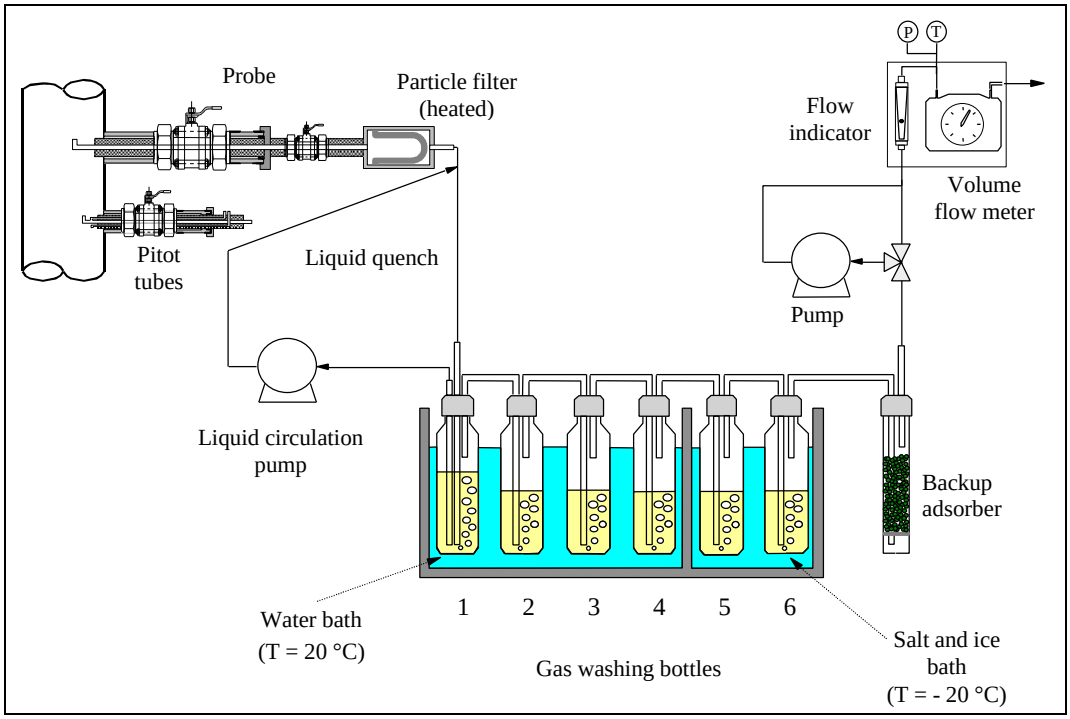

Figure 1 The current Guideline sampling set-up: atmospheric and isokinetic sampling train for tar and particles with removable probe and pitot tubes for flow measurement

To check for breakthrough and thereby make possible to determine the collection efficiency of the other systems, a second backup-train (VTT original) was connected to the outlet of the test-trains as seen in Figure 2.

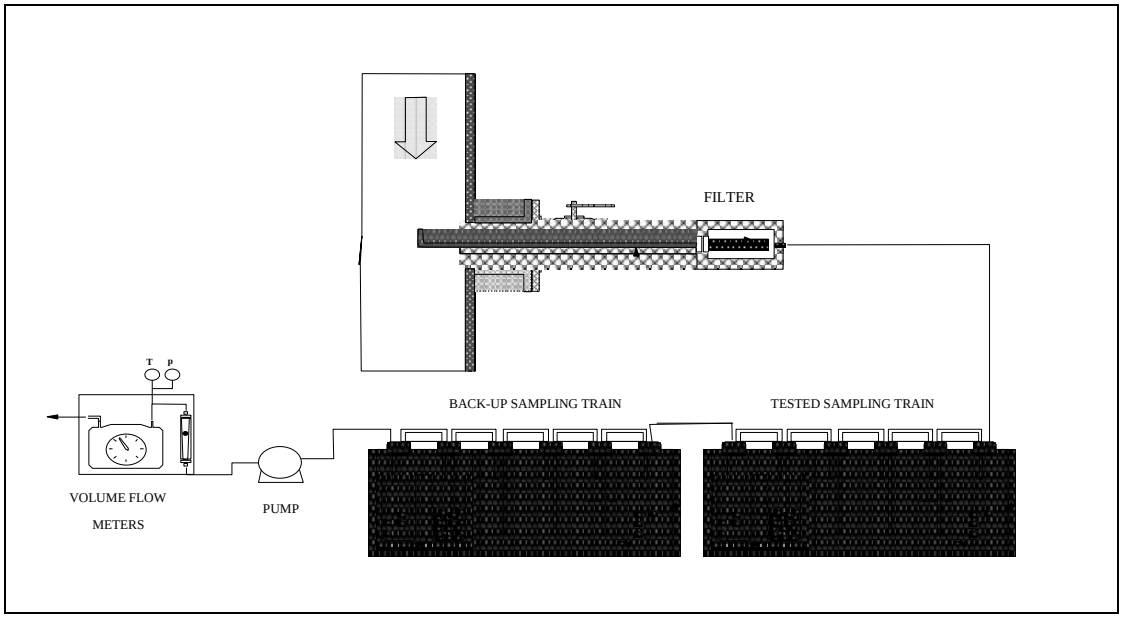

Figure 2. The VTT sampling procedure to evaluate the collection efficiency

The trapping efficiency of the tested solvents was remarkably high (almost 100 % for light tar from pyridine to 2-ethylnaphthalene) while the efficiency for heavier tars

(from acenaphtylene to pyrene) was significantly poorer possibly due to losses caused by aerosols. This is illustrated in two test series where the tar distribution among the six impingers was investigated. It was found that 35-43% of the sample was captured in the first impinger and between 9 and 18 % in each of the other impingers. The results are illustrated in Figure 3.

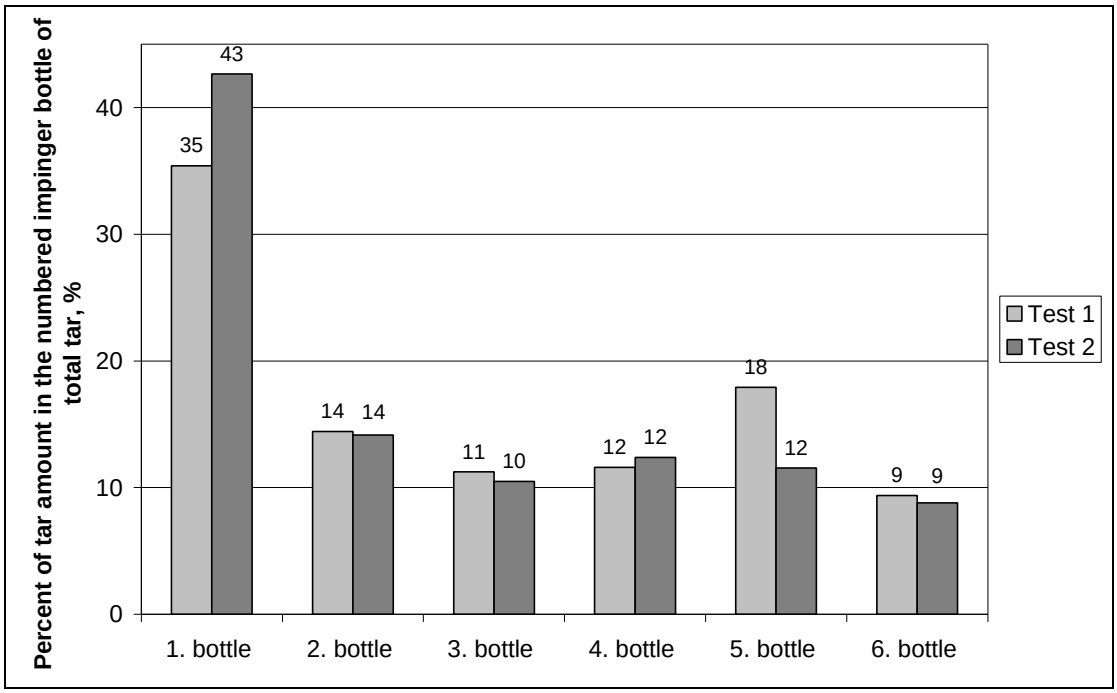

Figure 3. The percent of tar in each impinger bottle of the sampling train (solvent MP, 6 bottles, consecutive cooling baths of 0 ^{o}C and -70 ^{o}C, quarz in the last impinger).

The collection efficiency was best with DCM using the same kind of train. Different approaches to improve the sampling efficiency was tested including more effective cooling, insertion of quartz fibre into the last impinger, increasing the number of impingers, decreasing sampling rate. In spite of these actions the collection efficiency did not remarkably improve with the exception of one sampling modification where the first impinger was kept at 40 °C and the others at –70 °C in which case the efficiency was 97 %. The evaporation rate of the solvents at the same vapour pressure was investigated. It was observed visually that MP (methoxypropanol) did not vaporise as much at 40 °C as DCM at 0 °C. This may be explained by the fact that evaporation rates of solvents are not generally correlated to vapour pressures.
Similar trends were observed by DTI. Beyond tests with the Guideline train, an entirely new type of sampling device was used at DTI: The “Petersen column” (Figure 4) as it is called, for which a patent has been applied was invented at DTI. This sampler is reported to provide almost quantitative tar collection efficiency. Since the “Petersen column” consists of a single unit, it is easier to handle than the Guideline train (cf. also Figure 1) that consists of six impingers. Consequently, the new sampler might have the potential to replace the current Guideline train. However, the new sampler also has drawbacks like the fact that it is custom made and that currently less experience has been gained with this train compared to the six impinger bottle train.

Table 2 Summary of the tests performed with the sampling train for raw gas trapping

Sampling train set-up and operation conditions	**R&D Group**				
	BTG	**ECN**	**Verenum**	**VTT**	**DTI**
Parallelsampling	v	v		v	v
Gasifier type	CFB, BFB, downdraft, updraft	CFB, BFB, downdraft, updraft	Downdraft	CFB, BFB, downdraft fixed bed	Updraft
Synthetic sample collection				v	
Particle filter temp (ºC)	250	325	300	300	Not reported
Sampling flow rate (l/min)	Not reported	Not reported	4.6	Not reported	Not reported
Absorbent Solvents					
Ethanol	v	v	v	v	
2-Propanol	v	v	v	v	
1-Methoxy-2-propanol	v	v	v	v	
Dichloromethane				v	v
Impingers*					
Number of impingers	6	6	5	6 – 8 (VTT design)	6
ml of solvent/impinger	Not reported	Not reported	50-150	100	150 (75 in bottle 5)
Empty impinger no	6		5	Last bottle (6 or 8)	6
Liquid quench	v		v		
Glass frit					
In 3rd impinger	v		v		
In 4th impinger	v				
In all impingers		v			
Glass wool					
In 6th impinger				v	
Glass beads				v	
In 1st , 5th, and 6th impinger					v
Impinger temp (ºC**	-10	40 to -20	-20	40 to -70	0 to -70
Back-up devices					
Similar to main sampling train				v	
Activated charcoal			v		
filter (not specified)	v	v			

*Two different types of impinger were tested at DTI: the specially made VTT model and a commercially available standard gas-washing bottle. Since no significant differences was found the standard type gas-washing bottle used for the tests.
** Range of impinger temperatures used. Tests were performed at more than ten different combinations of impinger train temperatures in order to optimise the collection efficiency.

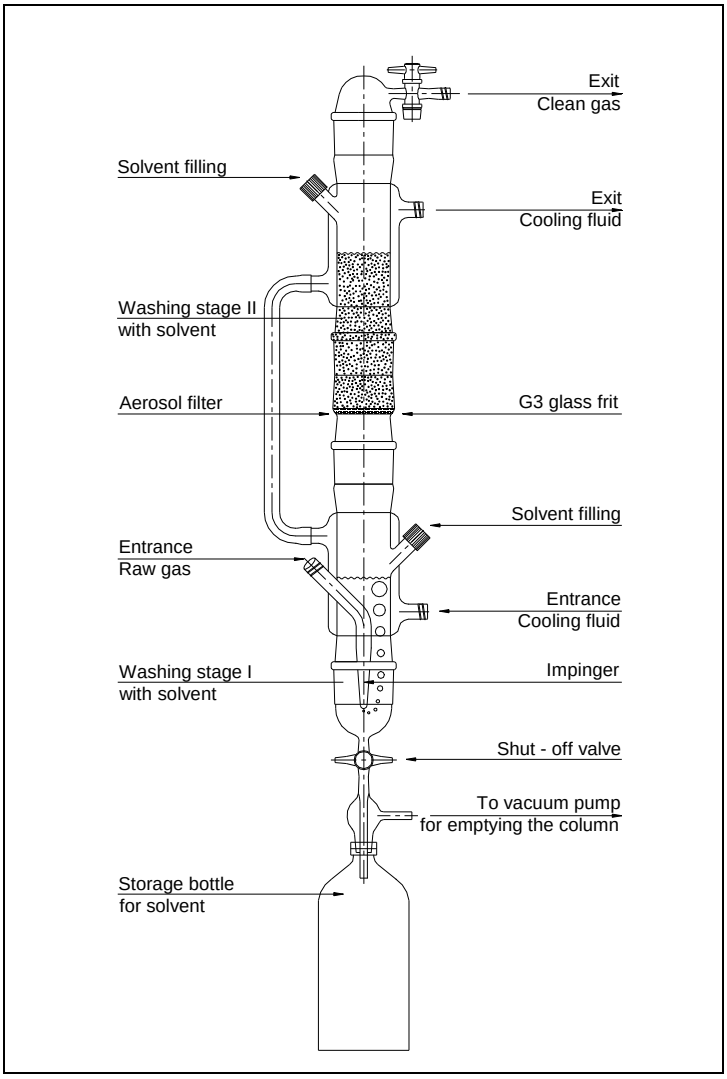

Figure 4 The "Petersen column"

Verenum used a modified version of the Guideline type train, which had also been used in previous test runs for measurements at a technical scale Xylowatt gasifier (300 kW) in Chatel-St-Denis. The train was composed of five impingers. The 1st impinger was cooled to about 0°C and the following five impingers to –20 °C. Due to the low vapour pressure of many tar compounds, they are prone to form aerosols. To solve that problem, the 3rd impinger was equipped with a glass frit (G3), which is a common technique to break aerosols. The 5th impinger is empty and the others contain approximately 50 ml of solvent. A backup trap containing an adsorbent was used to protect the pump unit from VOC. The solvent tested were 1-methoxy-2-propanol, 2-propanol and ethanol. DCM was used as a reference solvent. The train was tested for breakthrough by means of a backup trap containing silica based amino-phase adsorbent. It was concluded that all solvents show comparable efficiency and that a frit must be included in one of the impingers to achieve collection efficiencies >99% for tar compounds from benzene to pyrene.

BTG and ECN performed tar collection experiments in closed co-operations using 1-methoxy-2-propanol, 2-propanol and ethanol as absorbing solvents. They used a sampling train that in all essentials has the same architecture as the Guideline set-up

(Fig. 1). Sampling is often complicated by the fact that producer gases contain aerosols and sub micron particles that can carry tar through the entire sampling train and by that reduce trapping efficiency. By using a fritted disc (cf. also the Verenum train) in the second and third impinger of the train it was possible to break aerosols and thereby significantly improve the sampling efficiency. In the BTG approach the impinger bottles were chilled to – 10 °C and the particle filter temperature was 250 °C. All solvents captured between 96 and 100 wt% of the individual tar compounds. The results were confirmed by comparison with those obtained by parallel sampling using the adsorbent-based SPA method.

ECN performed experiments with and without a liquid quench and a temperature of the first and third impingers of 40 °C while the others were held at -20 °C. The particle filter temperature was 325 °C. All impingers were provided with a fritted disc in the inlet. Quantitative (100%) collection efficiency was observed for this sampling approach. The influence of the liquid quench on the collection efficiency was found to be negligible. Further it was concluded that the use of fritted discs in combination with a wide temperature gradient in the entire sampling train instead of isothermal conditions improves the collection efficiency by breaking aerosols.

The results suggest that the optimal conditions for sampling with the Guideline type train are as follows:

- Five solvent traps
- 2-Propanol as absorbent liquid
- One empty bottle
- Fritted disc in all impingers (G1 frit in impingers no. 1, 3, 5 and 6, G3 frit, in impingers no. 2 and 4).
- Temperature gradient: first impinger at 40 °C; second at -20°C, third at 40°C and fourth to sixth at -20°C

Influence of gas washing bottle design on tar collection efficiency

To come to a decision on the influence of impinger design on collection efficiency two different types of impinger were tested at DTI: a specially made VTT impinger and a standard impinger (NS 29/32).
The impingers are shown in Figure 5. Raw gases and clean gases were sampled simultaneously from the same sampling line with both impingers during six experimental runs using DCM as an absorbing liquid. The samples were subsequently quantitated by gravimetry. The results show no significant differences in trapping efficiency between the impingers. In addition, it was also found that using the VTT impinger that has an internal pipe diameter of 10 mm avoid the problems with ice formation experienced with the standard impinger that has an internal diameter of 6 mm.

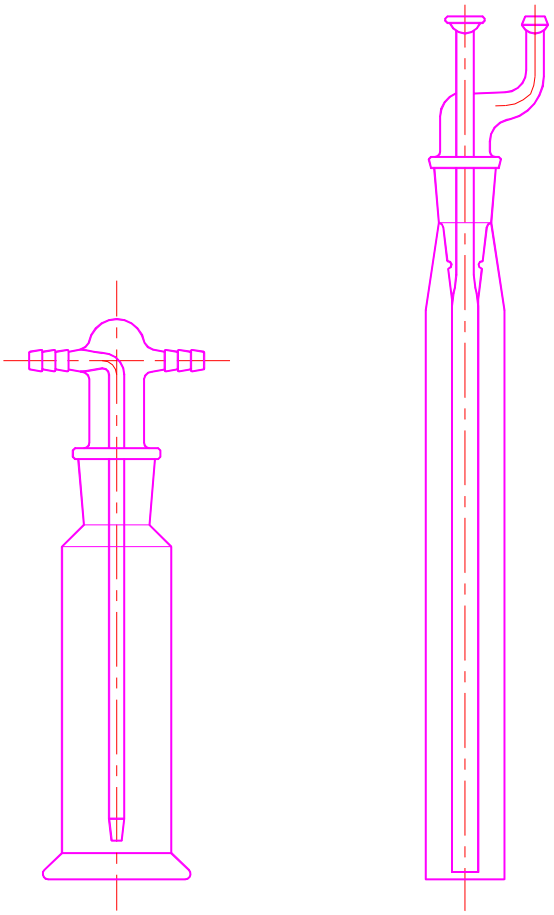

Figure 5 Standard gas-washing bottle NS29/32 and VTT gas washing bottle

Gravimetric tar measurements

Gravimetric tar is a quantitative measurement of the mass of the portion of a tar sample that is not amenable for GC analysis. A known volume of the combined solutions from the Soxhlet extraction (cf. also above: *Selection of solvent and tar Solubility*) and impingers are evaporated to constant weight. Two different approaches to measurement of heavy tar were investigated: 1) rotary evaporation under reduced pressure and 2) evaporation in an oven. Verenum used an own method based on evaporation at 105 °C and ambient pressure in an oven for 16 h.

DTI performed parallel sampling experiments in raw and clean gases from an updraft gasifier with two sampling trains using DCM, MP, IP and EtOH (ethanol). The DTI method applied rotary evaporation under reduced pressure to remove sample solvent. Samples collected in DCM were evaporated at 35 °C and 30 mbar final pressure. Samples collected in MP were evaporated at 50 °C and 30 mbar final pressure. It was found that a 32 % increase in sampling efficiency was obtained with EtOH relative to DCM. When using MP a 22 % increase in efficiency was obtained. IP (isopropanol, 2-propanol) gave a 14 % increase. Clearly, ethanol is the most efficient of the solvent investigated for gravimetric measurement of tar in updraft gases. As expected, the majority of the GC-amenable compounds were lost during evaporation.
BTG and ECN used rotary evaporation to remove solvent. Samples collected in IP (bp 82 °C) and MP (bp 120 °C) were tested. The influence of the tar concentration in the

impingers on the gravimetric estimation was investigated. It was concluded that the ideal rate of evaporation is 1-2 drops per second to finish the evaporation in 15 to 30 minutes. BTG performed evaporation tests at 125 mbar and ECN performed tests at 30 mbar. The highest losses of tar compounds were obtained with samples in MP due to the high bp of this solvent. For that reason it is recommended to use IP as the Guideline solvent instead of MP.
It was also found that the overall loss of tar compounds increased with increasing evaporation pressure. BTG and ECN have both reported standard deviations of 5 % in determination of gravimetric tar. Furthermore, it was found that the concentration of tar has influence on the gravimetric tar determination. At decreasing tar concentrations, the relative amount of tar, which is lost during rotary evaporation, increases. This means that the existing Guideline procedure has to be further tested and improved to ensure that the determined gravimetric tar concentration is independent of the dilution of tars with solvent during sampling and analytical procedures.
From the results as shown in the sub-reports of BTG and ECN and from results of DTI, an updated procedure for determination of gravimetric tar was developed. This procedure can be found in Paragraph 8.1.4. of the Guideline.

Measurement of individual Components

Identification and quantification of individual compounds were achieved by gas chromatography (GC) with flame ionisation detection (FID) or GC coupled to mass spectrometry (GC-MS) using a nonpolar capillary column and temperature programming. The identification of unknown compounds by GC analysis was based on comparison of retention times relative to authentic compounds. For GC-MS analysis identification of unknowns was based on comparison with retention time data and reference mass spectra of authentic compounds. VTT used GC-FID methods based on multi-level calibration to generate response factors and suit the different solvent candidates. The impinger samples obtained at Verenum were analysed by GC-FID at VTT while the filter extracts were analysed by GC-MS at ECN. Comparison of results from identical samples between ECN and VTT showed large deviations. DTI used a GC-MS method to quantify individual compounds. Details of the methods and analytical conditions are published elsewhere.

Verification of Efficiency of Sampling Procedures

It is not possible to verify accuracy on the basis of recovery data from producer gas samples since the real tar concentration is unknown. Instead such data may be obtained indirectly by comparison with an alternative well-established method or by running sampling tests with synthetic gases containing known amounts of authentic compounds. Once a method is established, precision may be determined by suitable replicated experiments. Since the error in measurement increases with decreasing sample mass it is important that a sufficient sample volume is collected to reduce such errors.

Rationale for decisions taken

This Chapter describes the Rationale of the decisions to change or update procedures in the Guideline, referring back to the R&D described in the previous chapters.

Temperature of the particle filter

Gravimetric tar and tars analysed by gas chromatography ("GC tars", e.g. PAH) show different separation behaviour in the filter. Almost all GC analysed tar components pass through the filters at a higher filter temperature, whereas this is not necessarily true for the gravimetric tar. (Hence the filter is Soxhlet extracted, see later in this chapter). It was found that at a particle filter temperature of 325°C only 1% of the "GC tars" is kept on the filter (ECN, Fluidised Bed (FB) tars). At lower temperature higher numbers were found: 10-20% at 300°C (Verenum, downdraft tars), 5% at 250°C (BTG, FB tars) and 50-60% at 150°C (Verenum, downdraft tars). Therefore, the particle filter temperature in the Guideline is set at 325°C. For updraft tars, DTI has found that high filter temperatures leads irreversible to polymerisation of tars and, hence, to a lower "GC tar" content and a higher gravimetric tar content. Therefore, the particle filter temperature of updraft gasifiers is limited to 125°C.

Solvent in the Guideline

Many solvents have been evaluated during the R&D work supporting the Guideline. At an early stage, it was anticipated that many of the solvents do not fulfil a limited number of important criteria. The two most important were that solvents could not be toxic or (suspected) carcinogenic, that they have a moderate volatility (to avoid a too high loss of solvent during sampling) and do not have a too high freezing point (enabling to sample at -20 or -30°C). A number of solvents did not meet these criteria, amongst which dichloromethane (DCM) that is a suspected carcinogen and therefore prone to restricted use in some countries. Three polar solvents met all criteria: ethanol, 2-propanol, and 1-methoxy-2-propanol. These were further tested in the R&D. At sampling temperature of -20°C in the impinger arrangement used, all three solvents (ethanol, 2-propanol, and 1-methoxy-2-propanol) showed comparable extraction efficiencies. In GC-analysis, it is difficult to avoid overlap of the peak of 1-methoxy-2-propanol with the peaks of benzene and toluene. Besides, the evaporation in the determination of gravimetric tar is more difficult compared to ethanol and 2-propanol, and finally the commercially available 1-methoxy-2-propanol contains impurities which interfere with benzene and toluene in theGC analysis. Therefore, this solvent was not further considered. A disadvantage of ethanol is its restricted use (leading to much paperwork) in some countries as it is a human drug. As a result, 2-propanol was chosen to be the solvent in the Guideline.

Use of a frit and temperatures of impinger bottles in sampling train

Many experiments were performed to optimise the collection efficiency of the sampling train. For instance, see Table 2 for a range of conditions. In many of these experiments, the slip of a small to larger amount (10-40 weight % of total amount) of tars was observed. After discussions and further testing it was concluded that formation of tar aerosols (small droplets of tar) causes this slip. Small tar aerosols are able to pass impinger trains, causing that only part of the tars are collected, that all five liquid containing impinger bottles collect significant amounts of tar and that a considerable fraction of tars is not captured by the sampling train. Figure 3 nicely illustrates this in the report. Therefore, experiments were performed to optimise the collection of these aerosols. Effective measures proved to be a temperature increase of the first impinger bottles, the use of small frits and the use of two temperature gradients. A too high temperature is, however, not possible due to solvent loss. With the use of 2-propanol, sampling up to a temperature of 40°C is feasible without loosing a too large amount of solvent during sampling from the first impinger bottle.

Based on these observations the temperatures of the impingers were chosen as four times 20°C and two times -20°C. This combination proved to be effective in VTT experiments. Besides, based on ECN experiments, the use of G3 frits is prescribed in the Guideline. Course frits (G1) were found to remove only part of the aerosols, whereas fine frits (G3) remove aerosols efficiently. This is nicely shown visually 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 frit in the second impinger bottle removed all or virtually all visible droplets. In order to not increase the pressure drop too much, only two fine frits are prescribed in the second and fifth impinger bottle. There is logic for this choice: the frits are placed as early in the impinger train as possible after temperature gradients (in which the aerosols form). No frit is placed in the first impinger bottle as it has a heavy tar load, which might block a fine frit. After removing the (largest part of) the aerosols, the remainder of the liquid tars might re-evaporate before entering the cooling step from 20 to -20°C in which 2-propanol will condense on existing droplets (if any) which are then removed in the frit in the fifth impinger.

Analytical procedures (Paragraphs 8.1 and 8.2 in the Guideline);
Analysis of identical sampling solutions at different laboratories using different analysis procedures result in large differences in identified concentrations of total tar or of individual tar compounds. Therefore it is essential that identical analysis procedures be applied.
In the experimental work performed by Verenum it was found that cold extraction of tar at ambient temperature resulted in incomplete tar extraction. Therefore, after sampling tars are removed from the particle filter by Soxhlet extraction.
In experiments by Verenum, BTG, DTI and ECN, it was found that the analysis of gravimetric tar by evaporation under a reduced pressure leads to reproducible results. However, time control needs to be very accurate. This accuracy is met by the procedure developed (see Paragraph 8.1.4 of the Guideline).

Conclusions and Recommendations

General conclusions from this R&D work performed at several European R&D laboratories are:

- A Guideline has been developed for sampling and analysis of tars that is found to perform very well, after a number important updates were made to the draft Guideline. The R&D described in this report has led to this updates: choice of the solvent, use of a frit to collect tar aerosols, choice of impinger bottle temperatures and update of analytical procedures.
- The results of this study prove that the Guideline functions well (is workable and leads to reproducible results) for tar concentrations in the range of 1000 – 12000 mg/m_n^3. Further testing with low concentrations of tar must prove that the accuracy is also good at low tar concentrations;

More specific conclusions are:

- The filter temperature strongly influences the amount of tar components, both gravimetric and individual compounds, deposited on the filter. It is recommended to

use particle sampling at identical temperature for the particle filter in the raw gas and in the clean gas (e.g. 300°C).

- A new sampling train has been developed: the "Petersen column". It turned out to be easier to use than the sampling train with 6 impinger bottles. Further testing under several conditions and tar concentrations must show whether this new sampling train performs as good as the train with six impinger bottles.

Recommendations resulting from this R&D work are the following:

- Evaluate the costs for the proposed methods in the Guideline;
- Measure the pressure drops over the particle filter and over the sampling train to check for blocking as a function of sampling flow rate;
- Determine the accuracy and reproducibility at low tar concentrations of 10-100 mg/m_n^3.
- Perform a good reproducibility test, for example a parallel test like the ones performed in Denmark in 1998.
- Exchange tar samples for comparison of GC analysis methods (Round Robin test)

From this work, long term R&D requirements were formulated which can be found at www.tarweb.net.

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Web Site www.tarweb.net, which contains the Guideline, conference proceedings, this report, and a list of long-term R&D requirements.

Appendices

VTT: *Summary of the Research and Development Work performed in VTT related to the project Tar Guideline (project no NNE5-00507*)

DTI: *Verification and validation of Manual Tar Measurement Method - Staus Report*

BTG & ECN: *R&D work supporting the development of a Guideline for sampling and analysis of tars in biomass producer gases*

Verenum: *Investigationsfor the Tar Protocol in Switzerland*