

Sampling of contaminants from product gases of biomass gasifiers

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VTT Energy



ISBN 951-38-5297-0 (nid.)

ISSN 1235-0605 (nid.)

ISBN 951-38-5298-9 (URL: <http://www.inf.vtt.fi/pdf/>)

ISSN 1455-0865 (URL: <http://www.inf.vtt.fi/pdf/>)

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JULKAISIJA – UTGIVARE – PUBLISHER

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Technical editing Maini Manninen

Oy EDITA Ab, ESPOO 1998

Ståhlberg, Pekka, Lappi, Maija, Kurkela, Esa, Simell, Pekka, Oesch, Pia & Nieminen, Matti. Sampling of contaminants from product gases of biomass gasifiers. Espoo 1998, Technical Research Centre of Finland, VTT Tiedotteita – Meddelanden – Research Notes 1903. 49 p. + app. 46 p.

Keywords gasification, biomass, combustion products, gas sampling, air contaminants, environmental protection, air pollution

Abstract

Reliable sampling and analysis of products from biomass gasification are essential for the successful process development and economical operation of commercial gasifiers. One of the most important and most difficult analytical tasks is to characterise the emissions from the gasifiers. This report presents a review of the sampling and analytical systems employed and developed when doing research on coal and biomass gasification. In addition to the sampling systems published in the literature, experiences obtained in various biomass gasification R&D projects of VTT in 1985 - 1995 are described. The present sampling methods used for different gas contaminants at VTT are also briefly presented.

This report focuses mainly on the measurement of tars, nitrogen compounds and sulphur gases. Isokinetic and non-isokinetic sampling train systems are described and, in addition, special sampling apparatus based on liquid-quenched probe and gas dilution is briefly outlined. Sampling of tars with impinger systems and sampling of heavy tars with filter techniques are described in detail.

Separate sampling of particulates is briefly discussed. From inorganic compounds the sampling systems used for H₂S and other sulphur gases, NH₃ and HCN and HCl are presented. Proper storage of the samples is also included in the report.

Preface

This review on sampling of contaminants from biomass gasifiers has been prepared within the Gasification and Analytical Groups of VTT Energy. The literature review of the study was conducted in 1991 - 1994 as the Finnish contribution to the Thermal Gasification of Biomass Activity of the IEA Bioenergy Agreement. This Activity was led by Dr. Suresh P. Babu of Insititute of Gas Technology, U.S.A.

In addition to the sampling systems published in literature, the experiences obtained in various biomass gasification R&D projects of VTT in 1985 - 1995 are described. The present sampling methods used for different gas contaminants at VTT are also briefly presented. As the literature review work was mainly conducted in 1991 - 1993, the most recent developments carried out elsewhere are not included in this study.

The work on this study was conducted within several gasification projects financed primarily by the Finnish Ministry of Trade and Industry (KTM) and the Technology Development Centre Finland (Tekes) as well as by VTT Energy and the Finnish industry.

Espoo, March 1998

Authors

Contents

Abstract	3
Preface	4
1. Introduction	7
1.1 Biomass gasification effluents	7
1.2 Particulates	9
1.3 Tars	10
1.4 Nitrogen compounds	13
1.5 Other effluents (S, HCl, Metals)	13
2. Sampling systems	15
2.1 Introduction	15
2.2 Isokinetic sampling trains	15
2.3 Non-isokinetic sampling trains	18
2.4 Separate sampling of particulates	20
2.5 Sampling with a liquid-quenched probe	21
2.6 Sampling using gas dilution	23
3. Sampling of tars	25
3.1 Impinger systems	25
3.2 Sampling of polyaromatic compounds	27
3.3 Other systems	29
4. Sampling of inorganic compounds	31
4.1 Sampling of H ₂ S and other sulphur gases	31
4.2 Sampling of NH ₃ and HCN	34
4.3 Sampling of HCl	36
5. Storage of samples	38
6. Conclusions and suggestions	39
References	42
Appendix A: Gas samples, sampling. Sampling lines	
Appendix B: Tar samples, sampling	
Appendix C: Heavy tar samples, sampling	
Appendix D: Tar samples, analysis	

1. Introduction

Reliable sampling and analysis of products from biomass gasification are essential for the successful process development and economical operation of commercial gasifiers. One of the most important and most difficult analytical tasks is to characterise the emissions from the gasifiers. This report presents a review of the sampling systems employed and developed when doing research on biomass and coal gasification. It focuses mainly on the measurement of tars, nitrogen compounds and sulphur gases. Sampling of particulates and other types of effluents is only briefly outlined.

1.1 Biomass gasification effluents

When biomass or other solid fuels are gasified to produce a gaseous fuel, gas impurities of different types are also formed. These effluents may cause problems in downstream process equipment or they may be environmentally harmful. The effluents can be divided into the following categories:

- Particulates entrained from the gasifier
- Low- and high-molecular-mass organic compounds (tars)
- H₂S, COS and other sulphur gases
- NH₃, HCN and other nitrogen-containing impurities
- Other gaseous impurities such as HCl and vapour-phase metals (alkali and heavy metals).

The wide variety of biomass fuels includes feedstocks of different types from very clean woody biomass to more problematic waste materials containing considerable amounts of nitrogen and/or sulphur, as can be seen from Table 1, which shows compositions typical of some selected biomass types. Some agricultural residues and wood wastes also contain high amounts of chlorine. Generally biomass feedstocks are low-sulphur fuels with a much higher volatile matter content than in the coal grades. Hence, the formation of gaseous effluents in biomass gasification is highly dependent on the decomposition of the volatilisation products in gasification processes.

Different types of gasifiers have been constructed for experimental and commercial use. Most of the gasifiers fall in four categories based on the contact type of the feedstock and on the gasification agent. The four main types are: 1) fixed-bed updraft, 2) fixed-bed down-draft, 3) fluidised-bed and 4) entrained-flow. The yields of tars, particulates and other effluents depend greatly on the gasifier type. The basic types of gasifiers are shown schematically in Figure 1.

Table 1. Examples of ultimate analyses for selected biomass materials and peat (wt% dry basis) (Baker 1986, Simell et al. 1994, Wiltsee 1992, Saviharju 1990).

Material	C	H	O	N	S	Ash
Pine saw dust	50.2	6.1	43.4	0.1	0.0	0.2
Pine bark	54.5	5.9	37.0	0.3	0.05	1.7
Black liquor ¹	39.0	4.0	33.4	0.1	4.5	19
Poplar	49.5	5.9	43.6	0.5	0.0	0.5
Wheat straw	48.5	6.4	40.2	0.7	0.1	4.1
S. cane bagasse	45.9	5.7	42.9	1.7	0.0	3.8
Rice husks	37.8	4.7	33.6	0.2	0.3	23.4
Low-mire peat	54.5	5.6	33.6	1.8	0.2	4.3

¹ Spent pulping liquor (ash = sodium content)

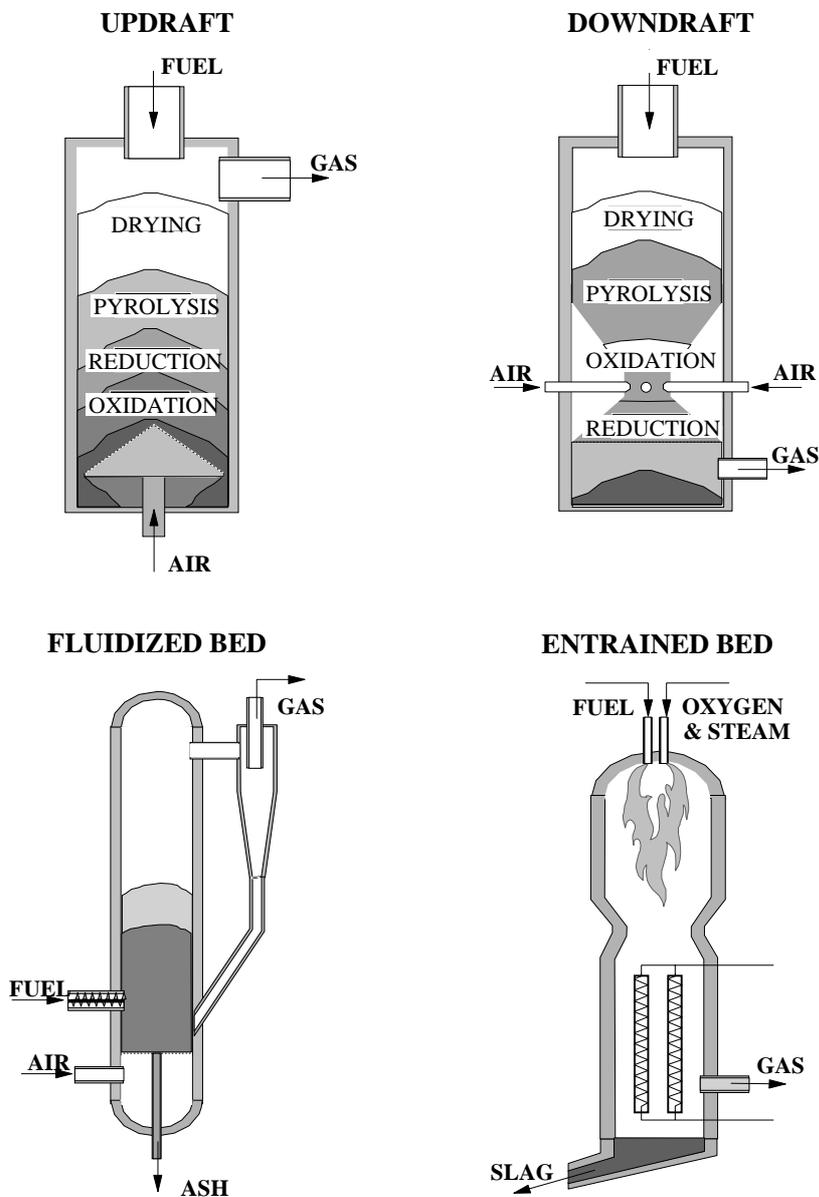


Figure 1. Schematics of the basic gasifier types.

In the fixed-bed updraft gasifier, the fuel is fed from the top and it flows down slowly through drying, pyrolysis, gasification and combustion zones. Gasification agents (air/O₂ and steam) are introduced from the bottom and the product gas is removed from the top of the gasifier. This counter-current flow of fuel and gas together with a long feedstock residence time and low gas velocities result in product yields and composition that are completely different from those of any other gasifier types. One advantage of the fixed-bed gasifier is the low entrainment of particulates, since the fuel has to be mainly piece-shaped and the gas velocities are low. On the other hand, the pyrolysis products and fuel moisture are drawn more or less directly into the product gas without thermal decomposition reactions. This results in much higher concentrations of condensable tars and oils in the product gas than in other types of gasifiers. Since the product gas temperature is generally very low (70 - 300 °C), the bulk of pyrolysis organics is present as tar aerosols, which sets limits to the usability of product gas of this type. For this reason, the reliable sampling and analysis of the effluents from the updraft gasifier is also a more challenging task than in other types of gasifiers.

In the other types of gasifiers, the tar formation temperature is generally much higher than in updraft gasification and consequently, the pyrolysis products are thermally decomposed to yield a different gas composition. After thermal decomposition, most of the tars leave the gasifier in a gas phase, which makes it easier to separate particulates from other effluents in sampling systems. However, these gasifiers also produce a wide variety of organic compounds from light oils to high-molecular-weight polyaromatic hydrocarbons, and careful and well designed sampling strategies are required for the reliable analysis of gasifier effluents. The particulate loading in fluidised-bed and entrained-flow gasifiers is generally higher than that in fixed-bed gasifiers, which normally means that efficient particulate filters are also needed in all sampling trains designed for collecting gaseous impurities.

1.2 Particulates

The particulate emissions of gasifiers vary a lot depending on numerous factors, including the type of the gasifier, feedstock properties and gasifier operation conditions. Hence, no general figures for particulate emissions can be given. However, typical ranges for fixed-bed and fluidised-bed gasifiers, which are the main gasifier types used for biomass gasification, are shown in Figure 2.

The size of particulates carried out with the product gas depends primarily on gas velocity, gasifier type and feedstock properties. Quite large particles (of the order of 100 microns) can be elutriated from the fluidised-bed reactors, while the particles escaping from correctly operating fixed-bed gasifiers are much smaller. However, the fluidised-bed gasifiers are normally equipped with cyclones, which separate most of the larger particles. From

cyclones the particles are returned back to the gasifier. Thus, the main particle size after the recycling cyclone(s) of the fluidised-bed gasifier is generally less than 10 microns.

Particulates from gasifiers of different types are comprised of inorganic constituents of the feedstock, partly converted or unconverted feedstock and soot. There may be great variations in the particle size and density as well as in other properties of particles of different origin, which creates some problems to be handled in particulate sampling and separation. In updraft gasifiers, the particulate sampling gives a mixed sample composed of 'real' particulates and tar aerosols, and it is rather difficult to separate these from each other.

1.3 Tars

Tar that is formed in gasification is a complex mixture of organic compounds ranging from light compounds like benzene to heavy polyaromatic hydrocarbons. Formation conditions affect the tar composition resulting in variation of the composition of tar in different processes. Thus quite a number of different meanings can be offered for the definition of 'tar'. It can refer to a sum of components with boiling points higher than 150 °C (Brown et al. 1986) or it can be based on vacuum evaporation residue obtained at 50 °C and 2 kPa (Brage et al. 1996). The sampling and analytical systems used for tar characterisation have also varied from simple "colour of the cotton wool" type of methods (Walawender et al. 1985) to sophisticated and complicated systems, by which different components from light oils to high-molecular-weight PAH components can be collected and analysed (Brage et al. 1996).

Different levels of information on tars are required for different purposes. Most detailed information, including all compounds, is needed in scientific research and often also in order to calculate accurate elemental material balances for gasifiers. On the other hand, only the concentrations of heaviest tar compounds have to be determined when evaluating potential problems in using product gas in applications which do not require cold gas cleaning steps. In the gasification research of VTT (Kurkela et al. 1993), benzene is usually presented separately as it stays in the gas phase in the majority of potential applications of biomass gasification. Compounds heavier than benzene are usually divided into light oils, naphthalene and tar compounds heavier than naphthalene. In this report, the generic term tar is used for the sum of organic compounds from benzene (C₆H₆) to high-molecular-weight components.

The temperature at which fuel pyrolysis takes place has a very pronounced effect on tar composition and accordingly tars can be divided to low- and high-temperature tars (Aristoff et al. 1981, McNeil 1981). Low-temperature tar is formed at temperatures lower than about 650 °C and it is composed mainly of components that are primary

decomposition products of the fuel structure (Aristoff et al. 1981). Hence, the feedstock used has a strong influence on the composition of low-temperature tar (Aristoff et al. 1981). High-temperature tar in turn refers to a high temperature of tar formation typical of fluidised-bed and downdraft gasifiers and is composed of mono- and polyaromatic compounds formed mainly in secondary reactions of the primary pyrolysis products of fuel (McNeil 1981).

Each type of gasifier has different reaction conditions and, consequently, different tar compositions and production yields. Figure 2 presents typical tar loadings in biomass gasifiers as reported by Brown et al. (1986). The updraft fixed-bed gasifier generates a high yield of tar, which is a mixture of the original low-temperature-pyrolysis products and more thermally processed products from the lower parts of the pyrolysis zone. Typical tar concentrations in updraft gasification range 100 - 200 g/m³, i.e., about 20 wt% of the input carbon of the wood is converted into liquids. The gas outlet temperature generally ranges 70 - 300 °C. At these temperatures, the tars mostly appear as condensed droplets in the gas phase. In updraft gasification the gas condensate sample is divided into two liquid phases: an aqueous phase containing very oxygenated, water-soluble organic compounds, and a separate heavy organic tar phase containing components typically found in the "settled tar" from charcoal manufacture. The lighter aqueous phase is highly acidic and contains a large amount (20 - 25 wt%) of dissolved organic material much like "pyroligneous acid".

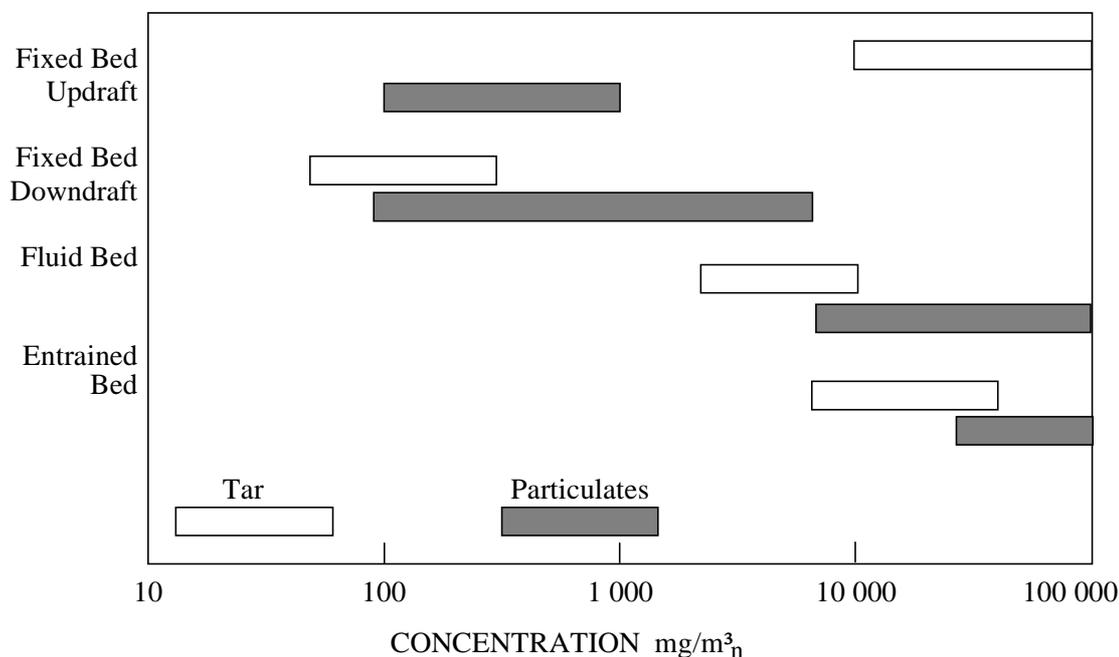


Figure 2. Typical particulate and tar loadings in biomass gasifiers (Brown et al. 1986). In this figure, tar refers to compounds boiling higher than at 150 °C.

Tar formation temperature is high in down-draft and fluidised-bed gasifiers, which usually generate relatively low amounts of tar (content < 20 g/m³). These tars are mainly in the gas phase at the gasifier outlet temperatures. In a correctly operating down-draft gasifier the pyrolysis products pass through a hot char containing combustion zone, in which the tars are cracked thermally and oxidised. In theory, the organic vapours from down-draft gasifiers should be decomposed totally, while in practice the amount of tars is mainly a function of the temperature, the efficiency of the combustion zone and the channelling of the bed. The fluidised-bed gasifiers operate almost isothermally. The high temperature (700 - 1 000 °C) and the good gas-solid contact result in partial cracking of the tarry pyrolysis products. The final tar concentration with a particular feedstock is a function of reaction temperature, pressure and residence time.

Table 2 shows an example of the biomass tar characterisation results obtained by Elliott (1983, 1985, 1986, 1987), who analysed tar condensates from different biomass gasification and pyrolysis plants. Elliott found out that the tar compositions are a continuous chain from an oxygenated "pyrolysis tar", obtained with a short contact time at 500 °C, to a highly aromatic oxygen free "high-temperature tar". The more severe the reaction conditions (high temperature and high pressure), the more aromatic the tars. The tar measurements of VTT made in the pressurised fluidised-bed PDU gasification tests with various fuels (at 5 - 7 bar) showed that at temperatures above 850 °C, the tars are almost entirely composed of aromatic compounds (Kurkela 1996).

Table 2. Results of the biomass tar characterisation. (Elliott 1985, 1986, 1987).

	Fluidised bed/ Entrained flow		Updraft		Downdraft	
	480 °C	880 °C	Tar	Aqueous	Tar	Aqueous
Carbon, %	52.7*	84.0*	70.9*	11.3	67.2* - 0**	7.0 - 0.5
Hydrogen, %	6.2	5.7	7.2	-	5.8 - 0	-
Oxygen, %	40.5	8.7	21.7	-	25.0 - 0	-
Ash, %	0.6	1.6	0.2	0.1	2.0 - 0	1.4 - 0.02
pH	-	-	-	2.1	-	3.0 - 5.3
Viscosity, cps	220 - 1 300	9 800 - 26 800	410	-	7 500 - 41 000	-
	@ 40 °C	@ 51 °C	@ 40 °C	-	@ 78 °C	-
Moisture, wt-%	16.00	20 - 28	8.00	-	12 - 13	-
Density, g/ml	1.26 - 1.28	1.14 - 1.16	1.13	-	1.16	-

* elemental and ash analyses for tars are reported on a dry basis

** downdraft gasifiers may or may not produce a separate tar phase depending on the specific operation

1.4 Nitrogen compounds

In gasification, one part of fuel nitrogen is released in pyrolysis and the other part in char gasification and combustion. It has been found that fuel nitrogen is gasified to a slightly greater extent than fuel carbon (Zand et al. 1985, Kilpatric 1986, Leppälahti & Koljonen 1995). Consequently, fuel nitrogen is almost completely released to the gas phase in gasifiers with high carbon conversion efficiencies. In the product gas of the updraft gasifier a considerable amount of fuel nitrogen is bound in organic tar components. In processes operating at higher gas outlet temperatures, the main nitrogen compounds are ammonia and cyanide. The thiocyanate found is most probably a reaction product of cyanide, sulphur and hydrogen compounds. All these nitrogen compounds have a tendency to form NO_x in gas combustion, and thus it is very important to get reliable data on the fate of fuel nitrogen in gasification. Table 3 shows typical ammonia and HCN concentrations measured for different feedstocks in the pressurised fluidised-bed PDU of VTT. Similar results for other high volatile feedstocks have been published by Zand et al. (1985), Purdy et al. (1985), and Kilpatric (1986). The measured ammonia concentrations are generally much higher than the equilibrium ones (Leppälahti et al. 1994, Kilpatric 1986, Case 1978).

Table 3. Typical ammonia and hydrogen cyanide content of gas in the VTT PFG gasifier with different fuels (Leppälahti & Koljonen 1995).

		Peat	Brown coal	Wood saw dust
NH ₃	ppm	6 000 - 9 000	2 500 - 2 800	330 - 450
HCN	ppm	10 - 200	50 - 90	10 - 30
Fuel-N	wt-%	1.7 - 2.0	0.8	0.1
Pressure	bar	4 - 10	4	5 - 7
Freeboard temperature	°C	810 - 910	860 - 940	910 - 1 000

1.5 Other effluents (S, HCl, Metals)

Biomass feedstocks normally contain very small amounts of sulphur. However, some biomass-based waste materials, such as spent pulping liquors, contain sulphur at least the same amount as most coals. Hence, the sampling and analytical methods for sulphur compounds have to be included in this report. The main sulphur-containing gas released in gasification is hydrogen sulphide (H₂S), which typically represents 80 - 95% of the total gas-phase sulphur in fluidised-bed gasifiers (Ma et al. 1989, Bryan et al. 1988, Kurkela et al. 1991). Feedstock decomposition and secondary gasification reactions also lead to the formation of other sulphur gas species including carbonyl sulphide (COS), carbon disulphide (CS₂) and various thiophens and mercaptans (Ma et al. 1989).

Some biomass feedstocks are also abundant in chlorine, which is released mainly as HCl in gasification. Especially some heavily fertilised agricultural residues (straw) may contain as much as 0.5 wt% of chlorine. Very little data is published on typical HCl concentrations in biomass gasification. Aqueous phases from different biomass gasifiers have been found to contain 8 - 44 ppm of chloride (Elliott 1986). Hardwood tar from the BCL fluidised-bed PRU gasifier has contained 110 ppm of chlorine (Elliott 1985). Concentrations peaking up to 90 ppm HCl in gasification gas have been reported by Simell et al. (1996).

The heavy metal contents of biomass feedstocks are generally very low compared to those of coal or peat. However, the biomass raw materials often contain relatively high amounts of alkali metals, which are potential sources for high-temperature corrosion in gas treatment lines and gas turbines. Part of the alkali metals are released to the gas phase in gasification and part of them stay in condensed phase and are removed with the particulate removal or with the bottom ash. Sampling of the sub-ppm concentrations of vapour-phase alkali metals from hot product gases is a problematic task and is not handled in this report. Information can be found from publications by Kurkela et al. (1993), Mojtahedi et al. (1987, 1990), Ciliberti (1984), Haas et al. (1984), Ma et al. (1989) and Häyrinen & Hernberg (1996).

2. Sampling systems

2.1 Introduction

The greatest difficulties in sampling in gasification processes are commonly related, according to VTT's experience, to the separation of particulates, water and tars in the system. In general, three different phases are formed: 1) solid particulate matter, 2) tar and 3) water phase, all more or less mixed with each other in the different parts of the sampling facility. To get a complete tar analysis every phase has to be treated with solvents.

The problems related to the separation of tars from the particulates and to the blocking of the sampling lines due to tar condensation can be minimised by considering the following aspects:

1. The sampling probe for tars should be constructed preferably after some particulate removal equipment (e. g., after process cyclones).
2. The final particulate removal from the sample gas should be carried out preferably 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 (Simell et al. 1994)]. This method is suitable for high-temperature sampling tasks, where the tars are completely in gas phase.
3. An isokinetic sampling is needed for low-temperature sampling points, where part of the tars are as aerosols in the gas. Then, the sampling system should be designed so that all parts can be washed by a proper solvent.
4. A continuous gas flow and heating is necessary in the sampling systems for biomass gasification tars.
5. Blocking problems can be minimised by using two parallel sampling lines equipped with facilities for purging and solvent washing.

2.2 Isokinetic sampling trains

Most of the sampling methods used in the gasification research and development projects in different parts of the world originate from the different versions of the EPA Method 5, illustrated in Figure 3 (EPA 1979, 1983, 1987). This method was originally designed for sampling particulate emissions from combustion flue gases. In addition to particulate sampling, this method is used for collecting gas and organic liquid samples from stack gases. Several modifications have to be done, when this method is used in different biomass gasification systems. For example, a cyclone pre-separator for particulates is often

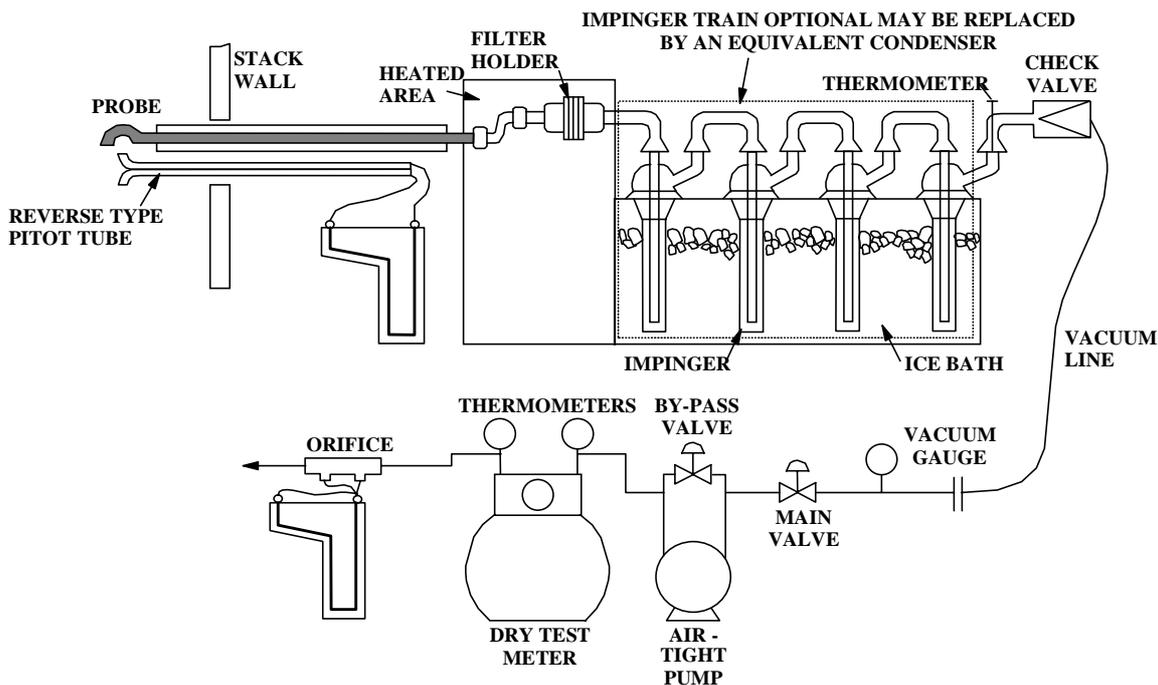


Figure 3. The standardised EPA method for collecting particulates from combustion stack gases (EPA 1983).

needed to reach long enough sampling times without blocking the filter or the sampling lines. The concentrations and vapour pressures of tars are often several orders of magnitude higher in biomass gasification than in combustion flue gases. That is why the temperature of the probe and the filter must often be higher in gasification applications than in the standard EPA method.

The EPA Method 5 has been the basis for the Canadian (McDonald et al. 1983, Esplin et al. 1985) and American systems (Freeburn & Houck 1989) for comprehensive sampling of biomass gasifiers. By these systems, particulate, condensate and gas samples can be taken. The major modifications to the standardised procedures are hot gas flow measurement with a heated orifice, a pre-separator cyclone for particles removal and an additional backup resin trap for trapping the most of the volatiles (Freeburn & Houck 1989). The advantage of the hot orifice meter is that the isokinetic rate at the probe nozzle is more easy to adjust, because gas moisture is not removed. For a successful flow measurement, however, the conventional orifice meters require relatively constant flow conditions and sufficient flow rates. These may be sometimes difficult to attain, if gasifier streams are fluctuating or variable or if there are liquid impingers on line. Neither does the 0-probe used in sampling of particulates work well with inferior sample flows.

The protocol initially developed in the Canadian ENFOR project (ENFOR 1983, McDonald et al. 1983, Esplin et al. 1985) has been successfully used for isokinetic

sampling of non-pressurised biomass gasifiers. This system with a slightly modified absorption liquid arrangement is shown in Figure 4. The system has been found suitable for sampling from fluidised-bed and down-draft gasifiers, and also at points, at which a low gas temperature causes condensation or aerosol formation in the process (McDonald et al. 1983). The probe and cyclone are uncooled and kept near the temperature of the sampling point, up to about 800 °C (Esplin et al. 1985). The length of the probe is kept as short as possible. Hot particles and aerosols are collected in the cyclone and stored in a cyclone catch at the ambient temperature. After the cyclone the gas is led through a conditioning coil which stabilises it to a constant temperature before the glass fibre filter, which removes the fines and tar aerosols. The coil condenses part of the tar and prevents the plugging of the filter.

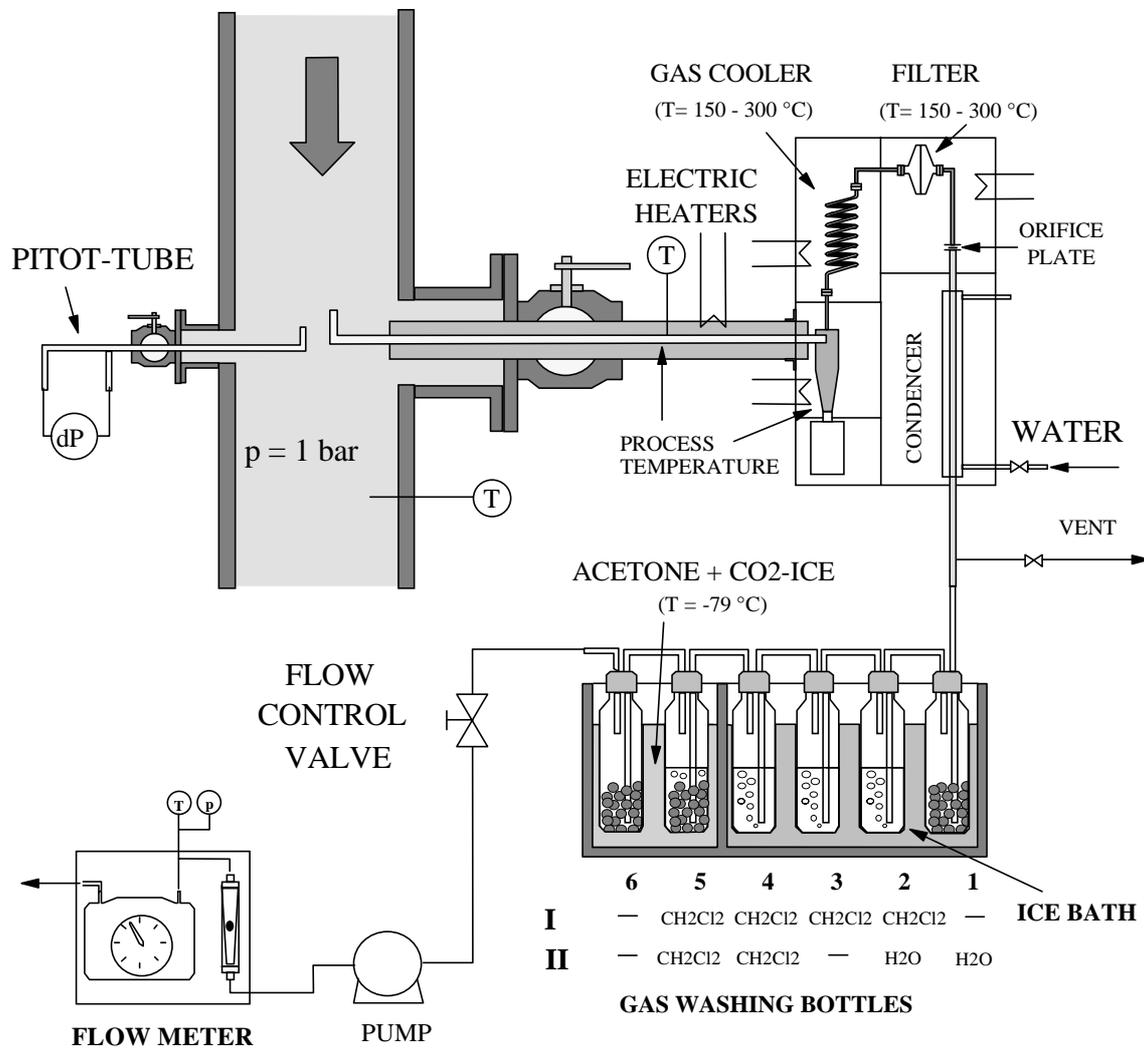


Figure 4. Isokinetic sampling train for gasification products in non-pressurised systems (modified from reference (ENFOR 1983)).

If the filter temperature can be kept high enough the pre-condensation of gas might not be necessary. In a closely similar atmospheric-pressure sampling system (Freeburn & Houck 1989) the probe is controlled via an external water cooling to allow long periods of sampling at high temperatures. Hence, the gas temperature is lowered already in the probe and is not maintained close to the process conditions. A mildly heated cyclone and a heated quartz fibre filter (about 175 °C) are positioned after the probe. This relatively low-temperature arrangement may lead to premature condensation of tar on surfaces of the probe and the cyclone.

In most processes tar condensation cannot be avoided after the temperature letdown. The lower the filter temperature the higher the tar accumulation rate. The temperature of the filter is critical and has to be chosen as high as possible to prevent filter plugging caused by the tar build-up, but low enough to prevent further reactions of tar on the filter surface. Consequently, temperatures from 150 to 300 °C have been used. In the applications mentioned earlier they have been in the range 160 - 200 °C (Esplin et al. 1985, Mann et al. 1985, Freeburn & Houck 1989, Ellman et al. 1979), whereas VTT has used temperatures in the range of 200 - 300 °C (Kurkela et al. 1993).

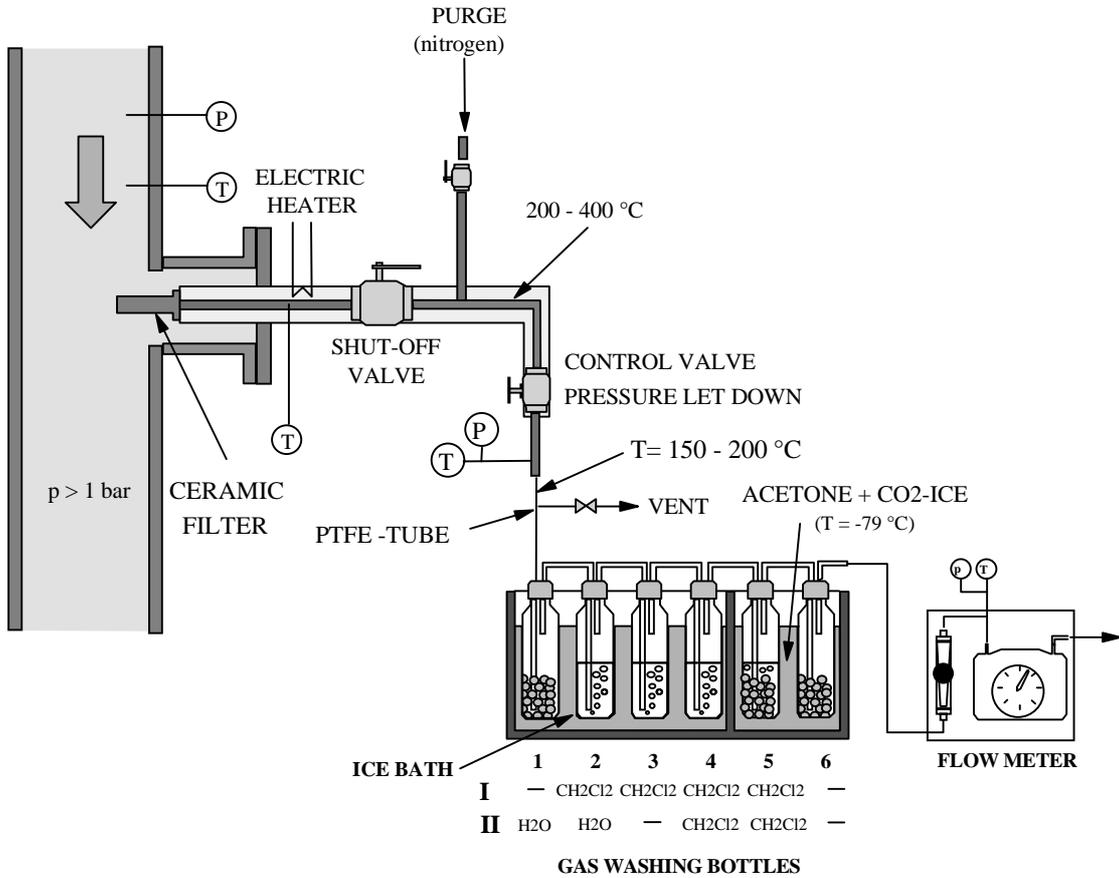
The use of the sampling system shown in Figure 4 for collecting tars from biomass gasification is somewhat tedious, since tars partly condense in the coil, partly are collected by the filter and finally collected into a solvent. All parts of the sampling system have to be carefully washed by the solvent after each sample.

2.3 Non-isokinetic sampling trains

The sampling strategy generally used for high temperature gasifiers is based on separate sampling of particulates and gaseous effluents (Pochan & Massey 1978, Piernock 1979). Isokinetic sampling with realistic probe dimensions requires, even at ambient pressures, very high flow rates, e.g., 25 - 30 dm³_n/min. Especially high flow rates are needed in pressurised systems to maintain isokinetic conditions and this is unpractical for impinger sampling using liquids. Therefore, a non-isokinetic sampling arrangement shown in Figure 5 has been used for condensables from pressurised systems at temperatures above the condensation point, e.g., > 450 °C. Systems of this kind have been widely used for sampling organic and inorganic constituents from pressurised coal gasification streams (see, e.g., Pochan & Massey 1978, Piernock 1979).

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, since the probe cannot be removed from the gas line during pressurised operation. The probe is headed either along with the flow or positioned at an 90° angle to it. Both straight-ended nozzles and those angled at 45° are used (Page 1978, Mayer et al. 1979). The sampling line is heat-traced at the process temperature over the

A) FILTER " IN THE SOURCE"



B) FILTER "OFF THE SOURCE"

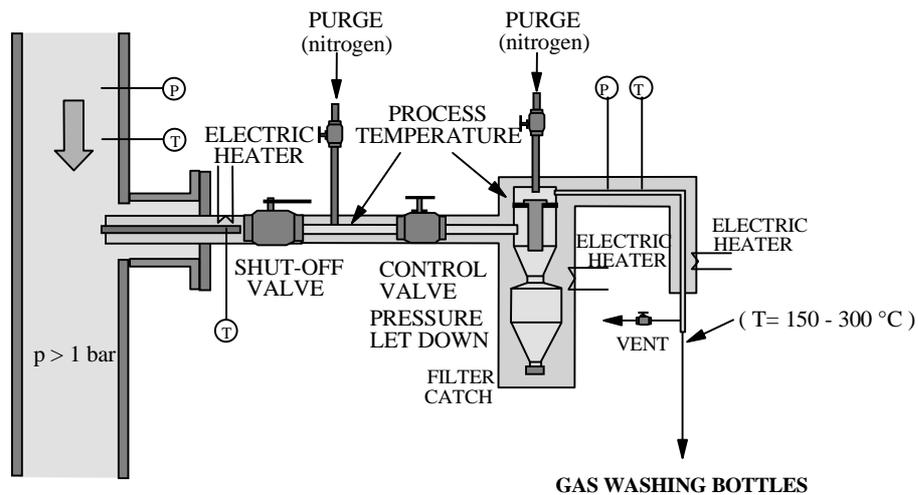


Figure 5. A non-isokinetic sampling train for high temperature gasification applications and pressurised systems: a) filter in the source, b) filter at a reduced temperature.

pressure relief valve, after which it is cooled for the fibre filter and impingers. The impingers are the same as in the isokinetic sampling train.

In the non-isokinetic systems improvements were made for reducing the accumulation of particles and tar on the sampling lines and on the filter. This was first accomplished by replacing the cyclone, the cyclone catch and the ceramic or glass fibre filter of the sampling line with a ceramic primary filter straight inside the unit and at the process temperature, as seen in Figure 5. The unpractically large and complex surface areas for the tar to stick were also minimised by removing the gas conditioning coil present in the isokinetic sampling train. The sampling line was thus made more compact and short. After the filter and before the absorption bottles the gas is quenched in a heat exchanger and led through a series of impingers containing proper absorption liquids. The condensing unit is washed with the same liquids.

The ceramic filter can be equipped with a pressurised reversed flow N₂ purging to clean off the cake of particles. In process conditions with a very high loading of solids, e.g., when lime/dolomite is used for sulphur removal, an impermeable cake may block this filter surface too quickly. In such cases the 'filter in the source' method has to be replaced with the conventional combination of cyclone and secondary filter for the removal of particles (Figure 5).

2.4 Separate sampling of particulates

Sampling arrangements for particulates from atmospheric pressure producer gas systems follow typically the principles of the EPA methods described in section 2.2. In order to get reliable results particles must be sampled at an isokinetic flow rate. From non-pressurised gasifiers particles and condensables can be usually sampled simultaneously with only one probe but in pressurised systems the most practical arrangement is based on two sampling lines: one isokinetic and one non-isokinetic line. In the PDU-scale pressurised fluid-bed gasification tests of VTT (Kurkela et al.1993) the particulates were sampled from two points of the product gas line: the first point was located directly after hot cyclones and the other after the ceramic filter unit. Sampling is carried out with an O-probe (balanced pressure) type system (Figure 6). When the sample is taken from a pressurised gas stream, in which the solids content is high, the straight O-type probe has been found to operate most reliably. The O-probe technique described above has been commonly used for sampling particulates (Nguyen et al. 1989, Narjes 1964, 1965). The particulate sample is collected on a quartz-fibre filter placed in a heated casing. The temperature of the sample filter is kept in the range of 200 - 300 °C during sampling that lasts typically 1 - 3 minutes at the first sampling point (after the second cyclone) and 5 - 60 minutes after the ceramic filter vessel.

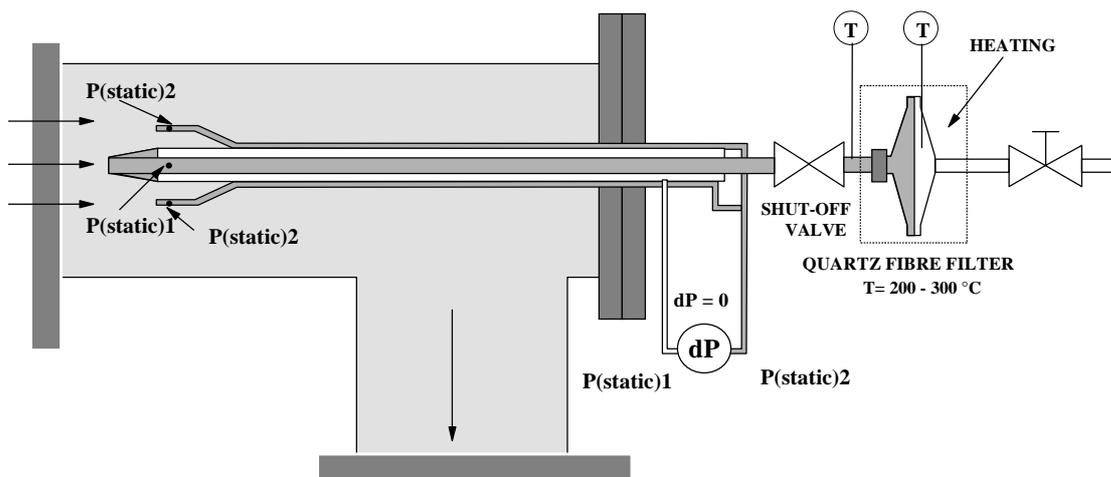


Figure 6. Isokinetic sampling probe (0-probe) for measuring particulate concentration.

Each sample filter is weighed both before and after the sampling and the difference is used to calculate the particulate concentration. Before weighing the sample filters are dried at 110 °C for two hours and cooled to ambient temperature in an exsiccator.

Selected particulate samples after the ceramic filter are also analysed for solubles. The sample filters are extracted in dichloromethane to determine the amount of tars in the sample. A general problem of this type of extractive particulate sampling is that part of the particles collected by the sample filter may have been in gaseous form in the product gas. This has turned out to be especially problematic in biomass gasification at the second sampling point located after the ceramic filter. At this point the concentration of "real" particulates is of the order of 10 mg/m³_n or less, while the amount of heavy tars may be even higher than 1 000 mg/m³_n. Part of these tars condense on the sample filter and they may also polymerise creating soot particles in the sampling probe or on the filter. In addition, part of the heaviest tar compounds are insoluble in dichloromethane. This type of problem is typical of biomass gasification only, while the tar concentrations in coal gasification are so low that similar problems do not exist (Kurkela et al. 1993). The 0-probe technique described above has been commonly used for sampling of particulates (Nguyen et al. 1989, Narjes 1964, 1965).

2.5 Sampling with a liquid-quenched probe

Instead of the conventional sampling train with liquid impingers and a considerable distance between the 'source' and the trapping solution, a sampling probe based on a continuously flowing liquid introduced right to the gas exit could in principle be used for inorganic as well organic effluents. This type of system called "Liqued Quenched Probe" was developed at the International Flame Research Foundation for collecting NH₃ and HCN from combustion gases without the fear of secondary reactions in the probe and in

the sampling lines (IFRF 1987). The principle can also be applied to other inorganic gas species, like H₂S, HCl, as well as to organics provided that they are trapped quantitatively in the chosen liquid. In the IFRF system the sampling rate of the gas was 3 - 3.5 dm³/min and the trapper solution flow rate about 0.08 dm³/min. A filter was located at the inlet side of the trapper solution line to prevent recycling of solids to the probe tip and obviating blockages. The solution (with particles) passed into a sample container. If necessary the solution was recycled to obtain a sufficient concentration for analysis. The total volume of gases extracted was measured using a positive displacement gas meter.

Corresponding sample probe systems operating at a liquid quenching principle have also been utilised in making a total gas, liquid, and solid sample collection from coal gasification and combustion processes (Smoot & Hedman 1979, Price et al. 1983, Burkinshaw et al. 1983).

One possible arrangement, which can also be used in pressurised gasifiers, is shown schematically in Figure 7. In this application the hot raw gas is filtered at the source by a SiC filter and the particle-free sample gas is quenched by the solvent solution. This type of probe might be very applicable in sampling high-molecular-weight tars, which are difficult to collect without any potential for probe reactions. The absorption liquid should be an organic solvent that has a relatively high boiling point and a low vapour pressure and should be thermally stable. The development of the 'tar' probe would, however, require considerable experimental work on different solvents and in variable conditions.

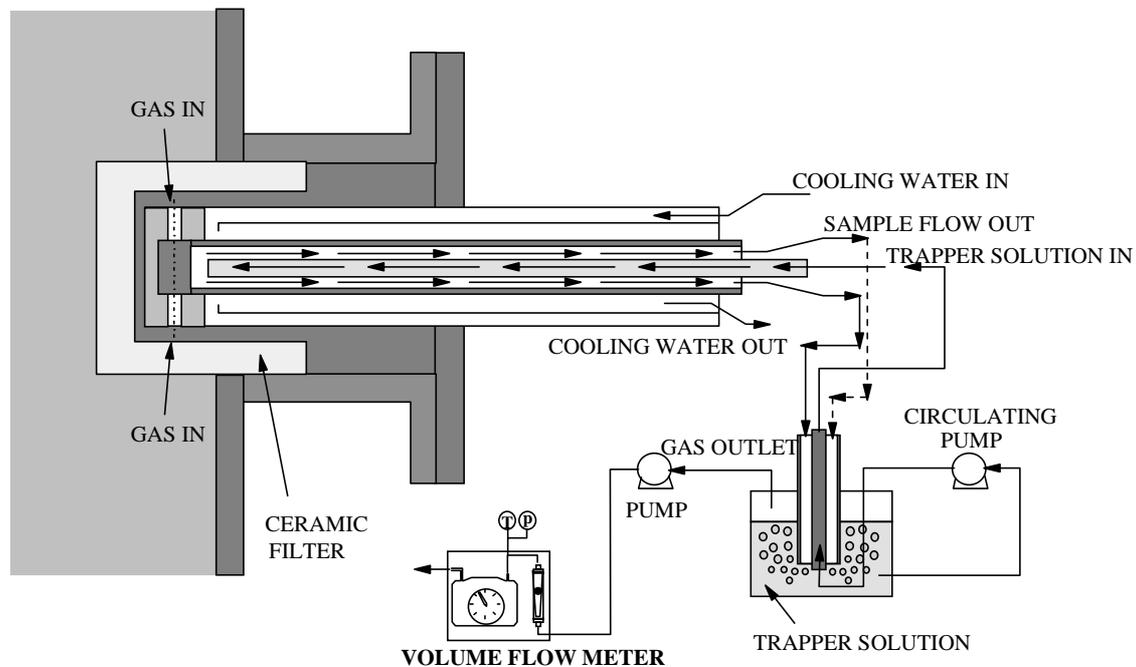


Figure 7. A principle of the Liquid Quenched Probe [modified from IFRF (1987)].

This method has also been tested at VTT by using a sampling apparatus constructed according to Figure 7. It was constructed in connection to the pressurised fluidised bed gasifier test rig. The total flow rate of the sample gas was 5 - 6 dm³_n/min and the flow rate of the solvent (CH₂Cl₂) was 13 - 20 ml/min. Liquid samples of 1 dm³ in size were obtained and they were analysed by GC as normal tar samples. Promising initial results were obtained indicating that tar main components were trapped as reliably as with the reference method shown in Figure 5. However, the development work was not continued mainly because the reliability of the ordinary and more simple methods (Figure 5) was found to be high enough in the studied high-temperature gasification application and there was no real need for this more sophisticated method.

2.6 Sampling using gas dilution

Conventional stack and exhaust sampling trains occasionally use gas dilution to prevent the condensation of high-molecular-weight compounds before the sampling point (EPA 1987). After dilution the condensables are collected on a glass fibre filter at a reduced temperature (Williams 1990).

Raw gas dilution has also been tried for sampling coal gasification gases (Hanson et al. 1982, Newton et al. 1979). The product gas was mixed with dry nitrogen by a radially injected diluter to yield an aerosol. For particle and vapour-phase collection the diluted gas was led through a glass fibre filter and a Tenax GC polymer adsorbent at a flow rate of 12 dm³/min. No evaluation of the operation has been presented. Supposedly, this method is suitable for relatively clean gases with low contents of tar and particulates.

VTT has also developed a diluting sampling system that has been employed in the measurement of hydrogen sulphide, carbonylsulphide (COS) and ammonia (Ståhlberg et al. 1995). This system is shown schematically in Figure 8. It was assembled in connection with the PDU-scale pressurised fluidised bed gasifier. In the sampling system gas is diluted with heated N₂ to such an extent that the dew point of the gas decreases to below 10 °C allowing the condensation of the heaviest tar fraction. After this step gas is cooled and filtered and slightly heated up to a temperature level that prevents fouling of the analysers. This system has been successfully tested in gasification tests for the measurement of H₂S and COS (Ståhlberg et al. 1995), but preliminary results with NH₃ indicate that slightly higher gas cooling temperatures should have been needed (to avoid cold surface temperatures).

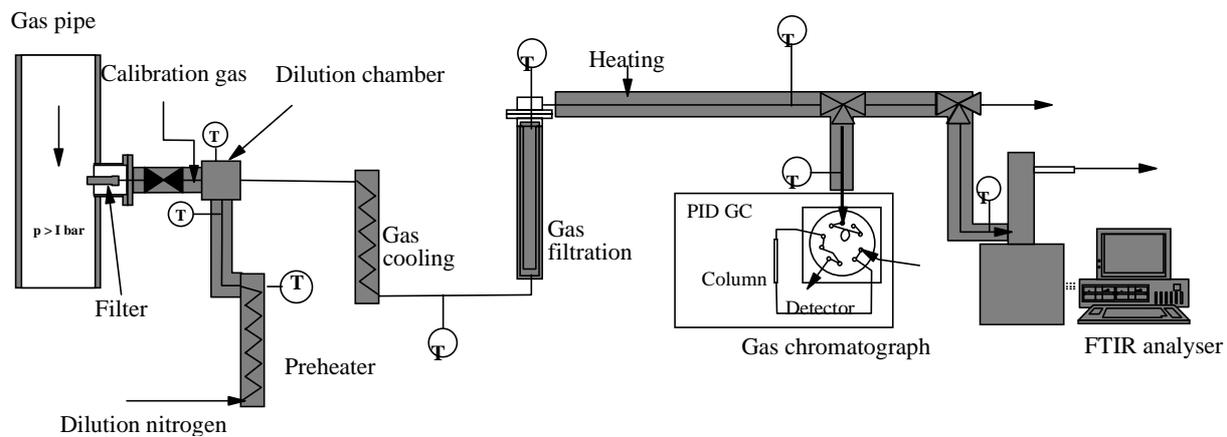


Figure 8. The principle of the diluting sampling system of VTT used for H_2S , COS and NH_3 measurements.

3. Sampling of tars

3.1 Impinger systems

The sampling method most often used for biomass gasification tars is based on the use of an impinger train arranged according to one of the alternatives shown in Figures 4 and 5. The detailed sampling arrangement depends most of all on the gasifier type and on the temperature of the sampling point. A complicated sampling system is needed with updraft gasifiers and mild gasification applications if complete tar analysis is required. In these processes the tar contains a lot of compounds of different chemical nature including an abundance of water-soluble compounds. In high-temperature gasifiers the tar composition is not so sophisticated and a simplified set-up of the sampling system can also be employed.

The tars are analysed for the combined samples mainly by GC methods described, e.g., by Hartung & Lies (1990), Simell & Bredenberg (1990), Brage et al. (1996) and Oesch et al. (1996). The use of simple gravimetric methods based on evaporating the solvent and weighing the tar residue often leads to incorrect results, since the "tar concentration" depends very much on the evaporation temperature and time, tar composition and tar concentration in the solvent (Simell 1988). Sample contamination, such as water condensation and particles, can also cause errors in gravimetric analyses.

A rather complicated sampling system is required for the most extensive and reliable tar analysis. A series of water impingers in an ice bath followed by CH₂Cl₂ impingers in acetone/CO₂ bath (temperature -79°C) (Figures 4 and 5) have been used for sampling low-temperature tars. The pre-cooled sample gas is cooled to below 5 °C in the water impingers, which hold most of the water-soluble tars and part of other compounds. The CH₂Cl₂ solvent after the water impingers traps quantitatively the rest of the tars including those with the highest vapour pressures, e.g., benzene. The last step is a backup container being either a) an empty bottle at a cryogenic temperature, or b) a bottle filled with CH₂Cl₂ and at a cryogenic temperature, or c) contains adsorption resin like XAD-2 at, e.g., 0 °C. The flow rate of the sample gas has to be low enough to allow sufficient cooling and a good gas-liquid contact in the impingers (typically less than 10 dm³_n/min).

According to VTT's experience the arrangement shown in Figure 5A (filter in the source) has proved to be practical, if the temperature of the sampling point is high enough to keep the tars in the gas phase. The sample line after the filter is also heated until the pressure letdown (in pressurised systems). Then, the sample is pre-cooled to a constant temperature in a simple tube, which is easily washed by the solvent after each sample. The final cooling takes place in the first impinger bottles. The potential problems of this sampling system, such as reactions of tars in stainless steel (AISI 310 and AISI 316) probes, in SiC

filters and in the dust cake formed on the sample gas filter, were systematically tested by VTT in a three-year project (Ståhlberg et al. 1994, 1995, 1996). These studies were carried out using product gases derived from wood, peat and coal in a pressurised fluidised-bed gasifier operating at gas outlet temperatures of 850 - 1 000 °C. With this type of highly aromatic tar, it was concluded that the sampling probes and the SIC filters can be safely heated up to 600 - 800 °C without any signs of change in the concentrations of tar compounds. However, if the gas contains a lot of catalytically active particulates (e.g., CaO), the temperature of the sampling line should be limited to below 700 °C or a different dust removal method should be applied (cyclone and filter of the source as illustrated in Figure 5B).

At low-temperature sampling points, where part of tars may be in the form of aerosols, an isokinetic system (Figure 4) is required for the complete collection of tars. Special attention should be paid to the effective solvent washing of the whole sampling device. This is quite easy to arrange in atmospheric processes, but extremely difficult in pressurised systems. When using the sampling system shown in Figure 4, different particulate and condensate samples are obtained that have to be separated from each others:

1. solvent-washed cyclone catch
2. prefilter wash, i.e., combined solvent wash of particulates and all parts before the filter
3. filter extract
4. post-filter wash, i.e., combined solvent wash from all parts after the filter in which most of the tar is trapped.
5. light part of the tar plus condensed water are scrubbed in an absorption liquid, including water as the first phase and solvent as the second phase.

Instead of CH₂Cl₂, other solvents such as acetone and methanol can be used for collecting tars. Methanol and acetone are polar solvents and thus efficient for the polar tar components (abundant in low temperature tar) and water. Methylene chloride is, however, practically insoluble in water resulting in two separate phases in sampling. If sampling condensables of lower molecular weight than benzene, CH₂Cl₂ has to be replaced by a higher boiling solvent. In GC methods methylene chloride overlaps the most volatile compounds. E.g., benzyl alcohol (b.p. 205 °C) has been used for this purpose. Benzyl alcohol dissolves 8.4 wt% of water; the solvent might be used for sampling the most water-soluble low-molecular-weight compounds, which are otherwise lost or analysed directly from the water phase.

In sampling of high-temperature tars, that have a poor solubility in water, all liquid impingers are filled with CH₂Cl₂ [impingers II in Figure 4 (Hanson et al. 1982, Farzam et al. 1985, Kurkela et al. 1993)]. The first absorption bottles are kept at 0 °C and the last

ones at a cryogenic temperature, e.g., $-79\text{ }^{\circ}\text{C}$ (Hanson et al. 1982, Newton et al. 1979). This means that the organics soluble in the water phase become extracted with CH_2Cl_2 and the water is neglected without analysis. The impingers filled with an organic solvent trap more effectively large tar amounts from producer gases than the corresponding aqueous absorbents or polymeric resins. Glass pearls or steel wool is used to disperse the gas flow. A backup Tenax resin is unnecessary when using several impingers in series.

A detailed description of the tar sampling and characterisation methods of VTT is given in appendices A, B and D.

3.2 Sampling of polyaromatic compounds

Polyaromatic compounds (PAC) may exist in gasification conditions either in the liquid or in the gas phase or as adsorbed onto particulates. They are often present in complex mixtures associated with other organic and inorganic gasification products. PAC occur over a wide boiling point range, e.g., naphthalene with two aromatic rings has a boiling point of $218\text{ }^{\circ}\text{C}$ and coronene with seven aromatic rings has a boiling point of $525\text{ }^{\circ}\text{C}$. These compounds can be sampled together with other tar compounds by using the systems described in chapters 2.2, 2.3 and 3.1. However, systems originally developed for the emission measurements of diesel engines and other combustion applications can also be employed for PAC collection.

The high vapour pressure of PAC means that even at ambient temperatures significant concentrations of PAC with boiling points up to $400\text{ }^{\circ}\text{C}$ can be present in the gas phase. Hence, the sampling strategies should include a collection of liquid-phase, solid adsorbed and gas-phase PAC. This is usually achieved by using glass fibre or quartz filters and downstream solvent traps, cold traps or organic polymeric resin traps. An example of these systems is shown in Figure 9. In PAC sampling a third sample may be formed from the separating condensable water, which contains water-soluble compounds.

The distribution of polyaromatic compounds between filter trapping and cold or resin trapping is dependent on the sample temperature at the filter. Figure 10 shows the distribution between filter and organic polymeric resin trap for coke oven emissions collected at $50\text{ }^{\circ}\text{C}$.

In the gasification gases aromatic compounds with 1 - 4 rings are still mainly in the gas phase at the sampling temperature of $200\text{ }^{\circ}\text{C}$. Hence, during sampling all parts of the sampling system should be kept heated at the sampling temperature. This filter temperature is high enough to prevent water condensation as well. After sampling all surfaces becoming in contact with the gas at a lower than the process temperature are washed with proper solvents, and the washes are combined with the actual sample.

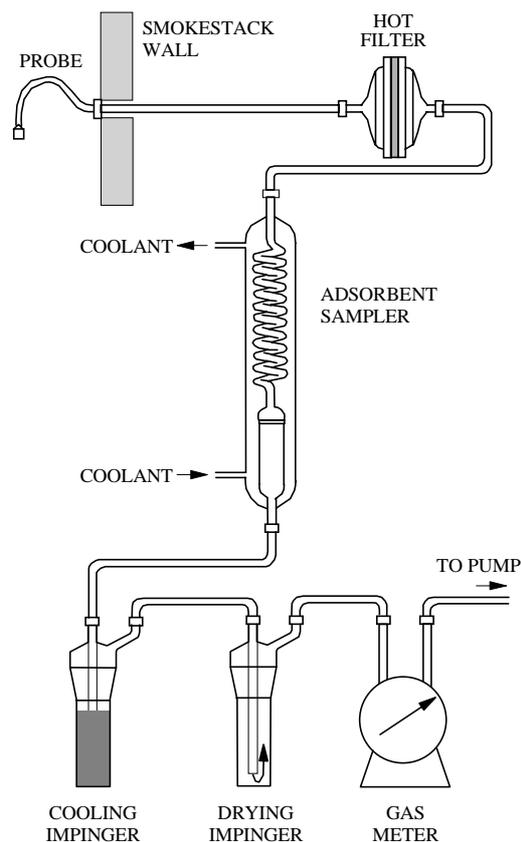


Figure 9. Sampling system for PAC compounds according to Williams (1990).

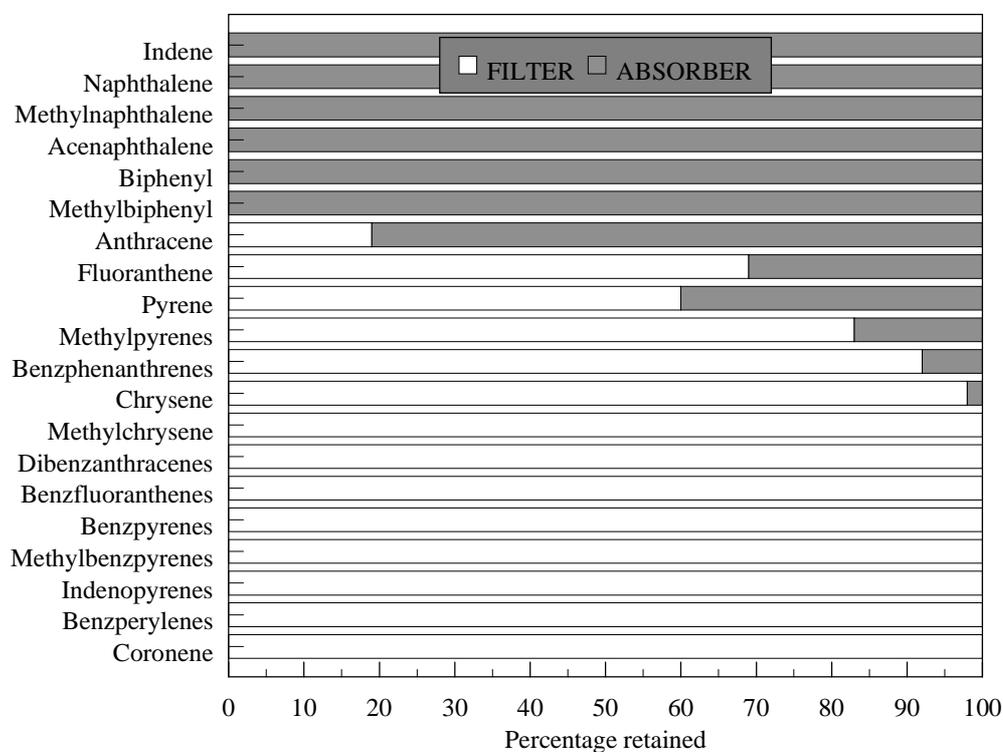


Figure 10. Distribution of PAC compounds between a filter at 50°C and a downstream cold polymeric resin (XAD-s) (Williams 1990).

Dilution with hot inert gas, nitrogen, is commonly used to minimise sample condensation before the traps. After filtration, the constituents in the gas phase are either washed by a solvent in an impinger system or trapped in Amberlite XAD-2 or Tenax GC polymeric resin. The temperature of the resin should be kept low (< 50 °C) to prevent decrease in sampling capacity. The resin is then extracted with an organic solvent (Nelson 1989). The most common solvents used for (Soxhlet) extraction of PAC compounds (2 - 4 rings) have been dichloromethane, cyclohexane and mixtures of benzene and methanol. Equally good extraction efficiencies have been found for PACs, while benzene/methanol extracts more alkanes than the other solvents do (Williams et al. 1986). Diethyl ether has been found more efficient than toluene for extracting heavy PAH compounds (Claessens et al. 1991). The result of the PAH analysis of samples containing particulates, like char or soot collected on fibrous filters, is highly dependent on the extraction method used for the PAHs (Claessens et al. 1991). It has been reported that the PAHs adsorbing on soot particles may degrade during the sampling procedure (Williams 1990). The filter-trapped PAH/PAC compounds also tend to change under storage. The tendency to filter-particulate interactions related to the filtering 'in the source' is not known.

The sampling system for PAC based on condensing of tars at 150 °C was taken into use in wood gasification tests at VTT in 1991 (Kurkela et al. 1993). This system is illustrated in Figure 11 and it has been described in detail by Oesch et al. (1996). The sample gas is first filtered at the process temperature and pressure. Then, after the pressure letdown, the sample gas is cooled in a cooling tube to 150 °C. Part of the condensables are thus collected on the walls of the tube and rest of the condensed tar aerosols on a quartz-fibre filter, which is placed in a heated casing (150 °C). Immediately after the sampling the devices are cooled to ambient temperature and then tars are washed by CH₂Cl₂. After sampling, the total amount of "heavy tars" is determined gravimetrically in the laboratory. The tar-containing solvent is first filtered to remove any particles and then the solvent is evaporated at room temperature. The tar residue weighed corresponds to the total amount of the tars condensing at 150 °C in atmospheric pressure. Hence, the amount of tar obtained is dependent on the vapour pressures of the components and does not give the correct concentration for compounds that have a considerable vapour pressure at 150 °C. Generally the samples contain mainly compounds heavier than fluoranthene and they can be partly analysed by gas-chromatography in addition to the gravimetric determination.

A detailed description of the heavy tar sampling and characterisation methods of VTT is given in appendices A, C and D.

3.3 Other systems

Other tar collecting arrangements than impingers have also been used. Evans et al. (1985) and Farzam et al. (1985) collected tars in empty pressurised stainless-steel containers operated at reduced temperature. Direct condensation of the liquid effluent in cold traps at

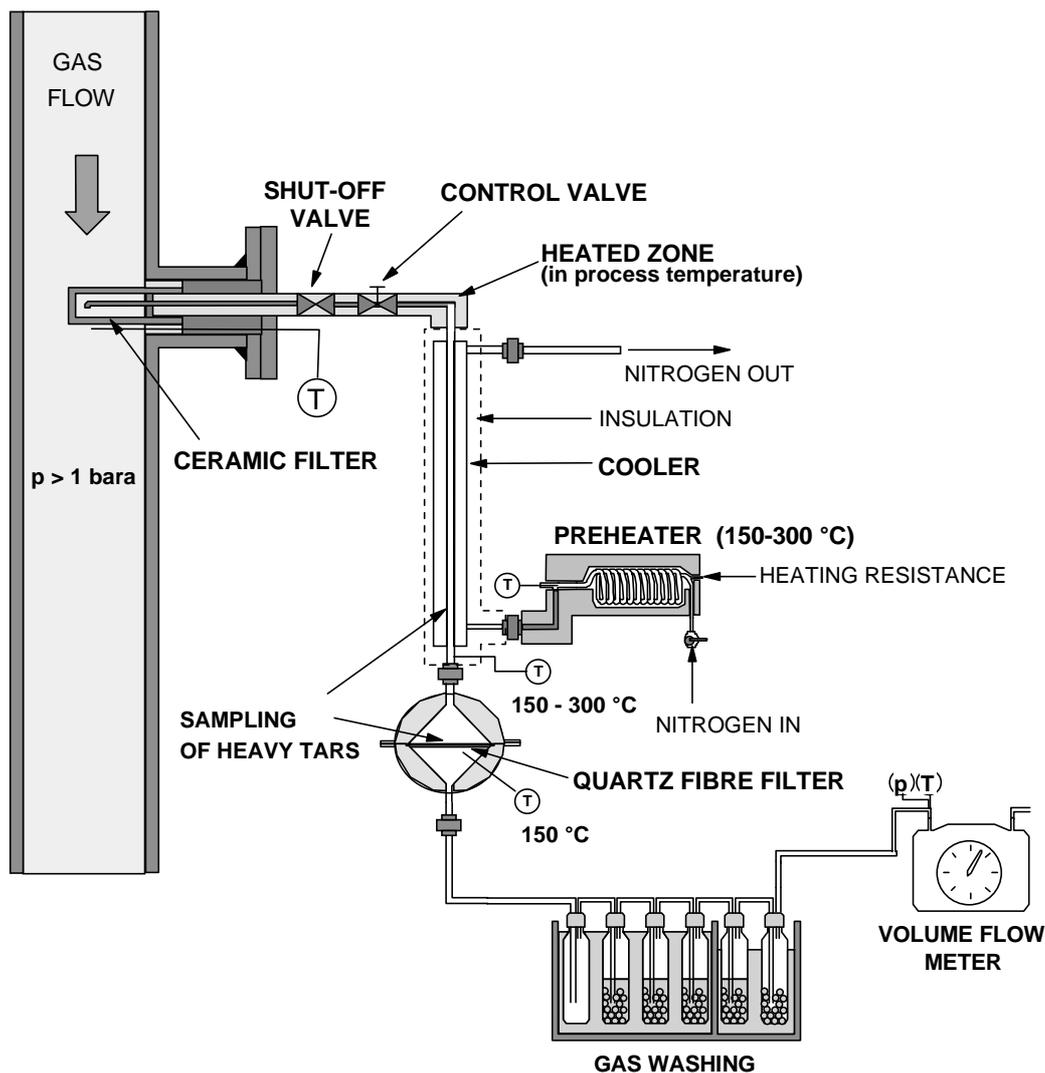


Figure 11. Method for sampling heavy tar compounds from pressurised gasifiers (Oesch et al. 1996).

extremely low temperatures has also been employed. The problem of these sampling systems is that there is no diluting medium like a solvent present making, at least in principle, further reactions of the sampled tars possible. Furthermore, the use of solvents cannot be avoided even in these cases as the whole sampling system has to be washed in order to collect the tar for further analysis.

A method based on solid-phase adsorption (s.p.a.) of tars has been reported by Brage et al. (1997). The authors have tested this method to product gases derived from biomass thermolysis and observed that components ranging from benzene to coronene can be trapped by it. Using eluotropic elution, adsorbates are selectively desorbed into aromatic and phenolic fractions and then determined by gas chromatography (with FID). The advantage of this type of method is simplicity in sampling and that it is possible to take samples in short intervals producing more information of the process observed.

4. Sampling of inorganic compounds

The reliable sampling and analysis of all polar inorganic compounds, like H₂S, NH₃ and HCl, is difficult, as these compounds are particularly sensitive to reactions with the surfaces of the sampling system as well as with the moisture and other impurities of the gas. The special features of sampling sulphur compounds, nitrogen gases and HCl are discussed separately in the following chapters.

4.1 Sampling of H₂S and other sulphur gases

Material aspects are of primary importance in sampling reactive sulphur compounds, like H₂S and thiols containing a reactive SH group. Selective adsorption of reactive sulphur compounds on glass or metal surfaces is a common problem in low concentrations and with moist gas streams (Lindgren 1990, Deprez et al. 1986, Graydon & Grob 1983). In principle this problem could be avoided by using only inert materials (ceramics and different PTFE, e.g. teflon, types of materials) in the sampling lines. However, since it is almost impossible to avoid the use of stainless steel in the high-temperature part of the sampling system, the following solutions have been used to minimise the adsorption problems.

- The stainless steel part have been designed as short as possible followed by inert PTFE parts immediately when the gas temperature is low enough (De Souza 1987, De Souza et al. 1978).
- The sample gas flow has been maintained continuous and the flow rate high enough to keep the sulphur adsorption in control. Flow rates of 2 - 3 dm³_n/min in a 6 mm (1/4") tubing have been sufficient to avoid severe adsorption problems. Moisture condensation in the sampling lines has been prevented by heating the lines (Clemons et al. 1981, Lindgren 1990).
- The sampling line has been reconditioned when a considerable concentration change has taken place in the product gas. This means that the analysis has not been started too soon after changing the operating conditions. Occasionally, for example, between two sampling periods, the sampling line has been back-flushed by nitrogen.
- An electrochemically polished, low-porosity and low-specific surface stainless steel tubing with chromium oxide surface has been used successfully at VTT in the hot parts of the sampling system shown in Figure 9.

Another problem is the removal of particulates, tars and water vapour from the sample gas. The information available in the literature on the effects of water and tar removal from the product gas prior to H₂S analysis is contradictory. For example, Beckers (1988) found out that moisture causes problems to the H₂S detection, and got best results when

water was cold-trapped from the sample gas immediately before the analysis. Lindgren (1990), De Souza (1987) and De Souza et al. (1978), used heated sampling lines and no water condensation in their successful systems for H₂S analysing systems.

Robbie and Paterson (1981) have observed that carbonaceous dust adsorbs effectively H₂S at the ambient temperature. Hence, for a successful H₂S analysis, the particulate matter should be removed at such a high temperature that H₂S is desorbed from the char. Temperatures between 400 - 800 °C have been used (Robbie & Paterson 1981). Any supplementary traps should be avoided, because H₂S is held easily by condensed moisture, glass wool and other materials, like tar and char dust on the filter, especially at lowered temperatures. Stainless steel filters have also been used for the hot particulate removal (Page 1978, Robbie & Paterson 1981) although there is a risk for sulphur reactions with the filter material especially at lower temperatures. On the other hand, some researchers (Krabbe & Hobucher 1982) have found out that the particulate removal at 200 °C by a glass fibre filter does not interfere with the analysis of inorganic species. This experience was from coal gasification, and it is quite evident that different particulates behave differently.

The conventional wet chemical methods for H₂S capture in aqueous alkaline and cadmium absorbents are no more widely used due to the instability of the sample, toxicity of the Cd absorbent and tediousness of the preparation and analysis. Moreover, carbonyl sulphide COS is not held quantitatively in aqueous solutions and it is most easily analysed from the gas phase.

H₂S and other sulphur compounds are most commonly analysed by gas chromatography. If on-line gas analysis by GC is not possible, the samples should be collected preferably in PTFE bags and analysed as soon as possible. In addition to PTFE bags, good results have been achieved with aluminium-coated sample bags, which Arendt (1988) has found to be safe and non-problematic for sampling sulphur, chlorine and fluorine compounds. Glass bulbs or any other glass parts should not be used, since H₂S is very reactive with glass surfaces. Different inertising methods for glass materials have been tried but with a very limited success. Glass surfaces have been coated with silylating agents, like dichlorodimethylsilane (Tangerman 1986) or hexamethyldisilazane (HMDS) (Mann et al. 1985). With moist gases this surface treatment has not been found satisfactory for sampling hydrogen sulphide. The OH groups of water react readily with the silylated layer of the glass transforming the surface again active for H₂S. COS and CS₂ sampling is not as problematic (Page 1978). Other experiences from the trials to inertise glass surface have been described by Deprez et al. (1986), Page (1978) and Farwell & Gluck (1989). No satisfactory deactivation was achieved by coating glass surfaces by permanent films of Carbowax materials or by any other material.

According to the experience gained at VTT, H₂S and other sulphur gases are most reliably analysed by on-line gas chromatography. In fluidised-bed gasification tests with biomass, peat and coal at VTT, good material balance closures for sulphur were achieved by the system shown in Figure 12. The particulates are removed at the process temperature and pressure by a SiC sampling filter. The filter can be back-flushed by nitrogen to remove the dust cake. After a short stainless steel part, where the gas is cooled to below 250 °C, the rest of the sampling line is of teflon-lined steel tubing. The second quartz filter shown in Figure 10 is just for protecting the gas chromatograph from the particulates in case of failure in the first-high temperature filter. Teflon solenoid valves are used for alternation and the chromatograph is equipped with heated PTFE lines for the sample gas inlet. The construction of the sampling and conditioning system is such that both the calibration and process gas can be taken automatically through the same gas pathway. This operated

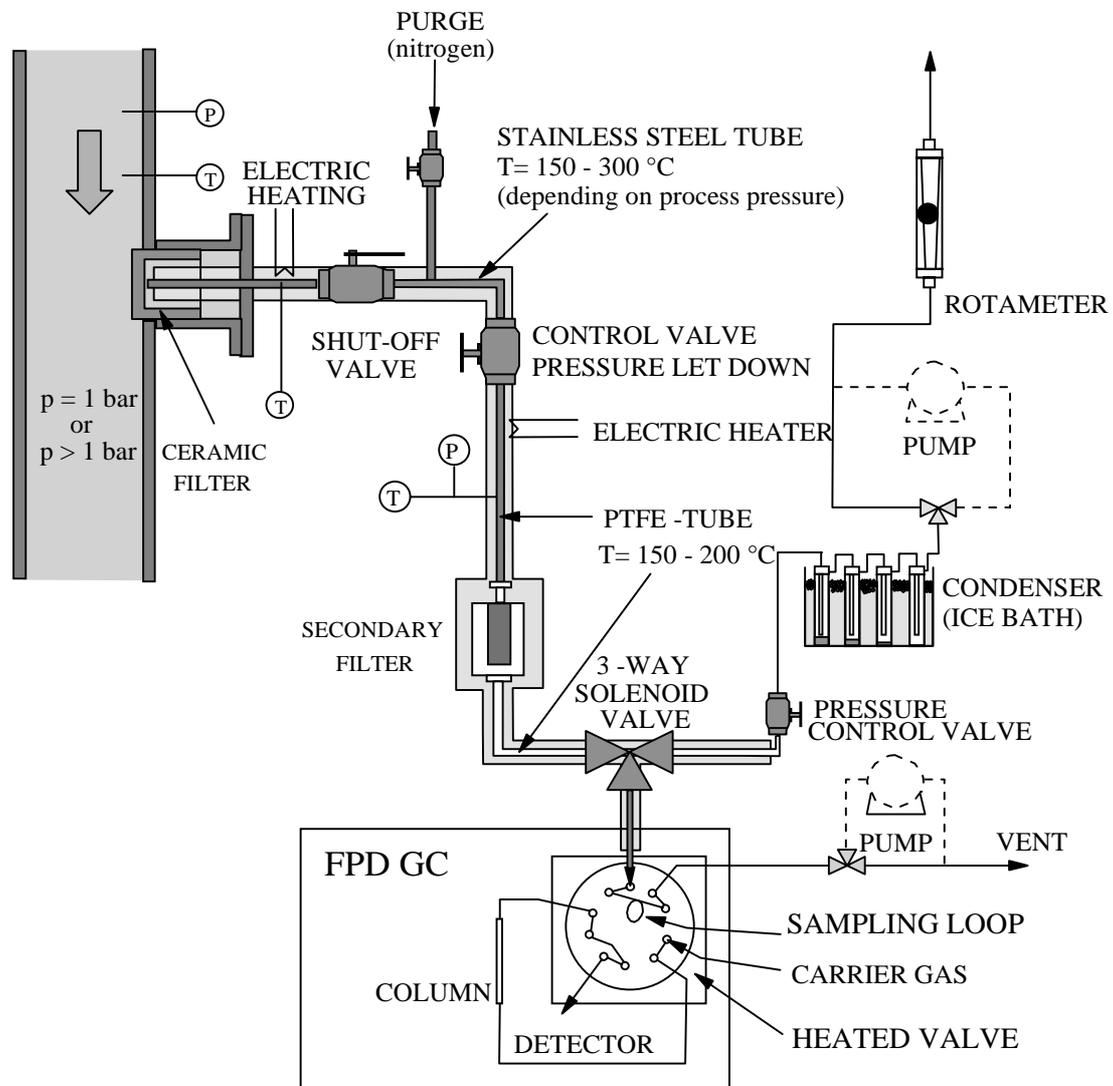


Figure 12. Sampling train for semi-continuous analysis of sulphur compounds in the gas phase.

very well in peat and coal gasification, while tar condensation caused problems and yielded a lot of tars in some wood gasification conditions. Reliable results were then achieved by taking the samples into PTFE bags through the heated line used for the semi-continuous sampling. When the gas bags were cooled to room temperature most of the moisture and part of the tars condensed on the walls of the bags and then the samples were successfully analysed without tar problems in the GC-system (the samples were analysed within 5 hours).

The best solution to avoid tar and moisture condensation problems is perhaps the use of dilution with heated nitrogen. This together with heated sampling lines should enable the analysis of biomass-derived gases without moisture or tar removal (see chapter 2.6). This is, however, difficult to attain when gas tar content is high and the process is operated at atmospheric pressure.

The apparatus shown in Figure 5B was tested by VTT and proved to be quite unreliable for sulphur sampling. In this system the particulates were removed at a reduced temperature (200 - 300 °C) and the whole sampling line was made of stainless steel (AISI 316).

4.2 Sampling of NH₃ and HCN

The outlines for the design of sampling lines and materials for H₂S sampling should in general be applied to nitrogen compounds as well. The probe reactions as well as the interaction between nitrogen compounds and other gas impurities and the materials of the sampling systems are, however, even less studied than those of the sulphur gases. It should be mentioned that in some conditions (high pressure, certain temperature range and the presence of catalysing surfaces) ammonia may be formed in the sampling systems through ammonia synthesis reaction (Case 1978).

In conventional sampling protocols for gaseous inorganic nitrogen containing species (Piernock 1979, Pochan & Massey 1978), these compounds are sampled in parallel aqueous impingers with an arrangement shown in Figure 13. Ammonia as a basic compound is generally sampled in acidic solutions, e.g., dilute sulphuric acid, and acidic compound HCN in basic solutions, e.g., dilute NaOH. Basic inorganic compounds may also be collected in HCl instead of H₂SO₄. The concentrations of the absorption solutions have varied in a wide range depending, e.g., on the gas composition and sampling time. Quite strong concentrations are generally needed to keep the pH of the sample in the right range. Ferrell et al. (1980) used the following concentrations in a coal gasification study: NH₃ was absorbed in 5% H₂SO₄ solution, and HCN plus SCN in 5% NaOH solution. For pH sustainability strong NaOH solutions are necessary when sampling gas streams containing high amounts of CO₂. The recommendation for ammonia collection is to keep pH below 1.0 and for HCN to keep pH >10 (Pochan & Massey 1978). For HCN and SCN

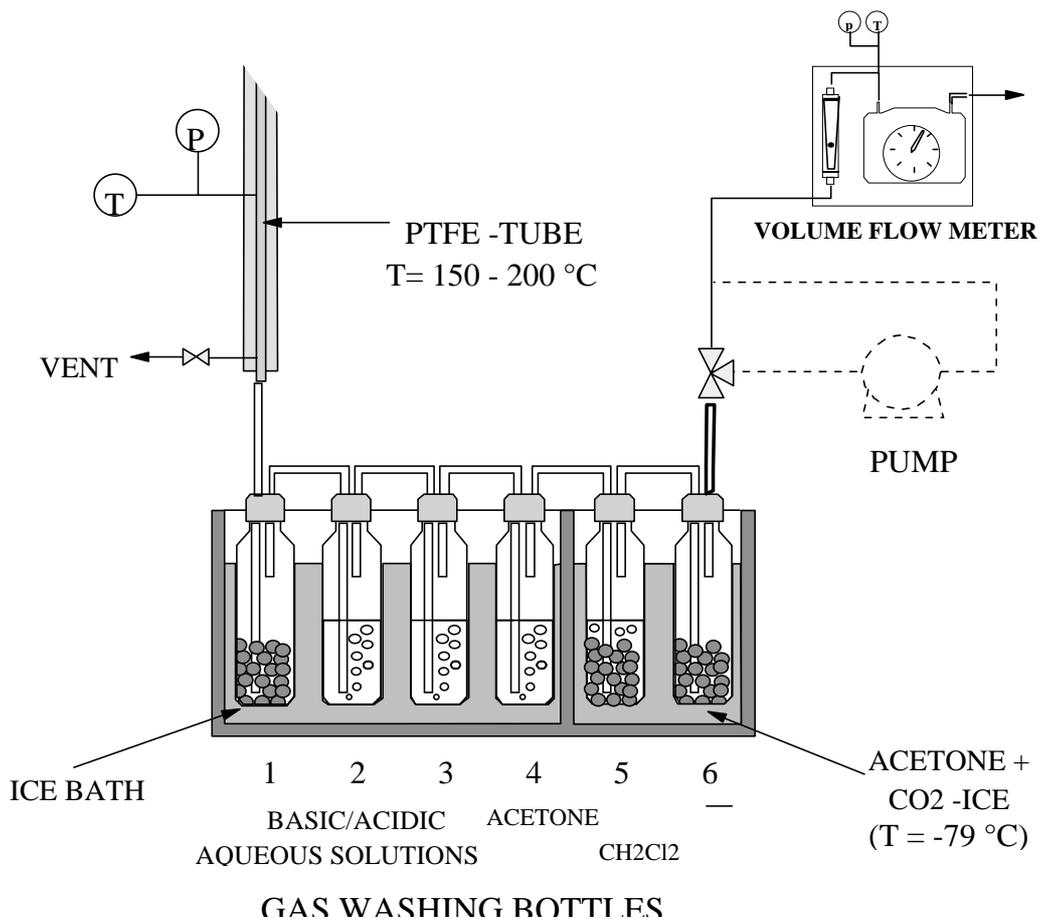


Figure 13. Impinger system for collecting inorganic effluents from biomass gasification.

even pH of 12 and higher have been suggested (Piernock 1979). The absorption efficiency of NH_3 in an H_2SO_4 solution is practically 100% and that of HCN in NaOH 97.7% (Smart & Maalman 1987).

VTT has successfully used the arrangement shown in Figure 13 for collecting different inorganic effluents from biomass, peat and coal gasification streams. The effluents are collected depending on the sampled compound into neutral, basic or acidic solutions in the first three impingers placed in an ice-water bath. The concentrations of 5% H_2SO_4 (for NH_3) and 5% NaOH (for HCN) have in most cases been satisfactory also in wood, peat and coal gasification experiments carried out at VTT. The fourth bottle contains acetone and the fifth CH_2Cl_2 . The final sixth bottle is empty. The last two impingers are placed in an acetone/ CO_2 ice bath. This final step is needed to remove all the remaining tars before the flow measurement (to protect the equipment). The acetone bottle is needed to prevent ice build-up in the fifth bottle.

The reliability of the NH_3 and HCN sampling systems of VTT has been studied by Ståhlberg (1995, 1996). According to the study stainless steel probes can be safely used at

least in the sampling of fluidised-bed gasifiers. No significant probe reactions were found in the temperature range of 300 - 800 °C.

A semi-continuous monitoring system in Figure 12 was designed primarily for the analysis of gaseous sulphur compounds. However, it can also be applied to all such inorganic species, like ammonia, that can be separated and detected by gas chromatography. This type of arrangement requires particulate-free sample gas and is described in detail, e.g., by Mayer et al. (1979) and Lindgren (1990).

4.3 Sampling of HCl

In gasification processes chlorine and fluorine are released mainly as hydrogen halogenides. Hydrogen chloride is extremely soluble in aqueous solutions. Its aqueous solution is a strong acid, and in water HCl is practically completely dissociated into chloride ions. Hence, chloride may be easily trapped quantitatively in any aqueous solution: neutral, acidic or basic. The trapping liquid is normally chosen according to the requirements of the subsequent analytical method. In ion chromatography (IC) the most suitable solvents are distilled water and dilute sulphuric acid (0.5% H₂SO₄). Alkaline NaOH solutions require the removal of Na⁺ ions before IC analysis (IEA 1992).

Gas-phase HCl is a very aggressive gas and reacts very easily with surfaces in gasifier and in down stream components. This leads easily to the loss of HCl until surfaces have reached more or less equilibrium conditions. In practice this results in a "memory effect", which means, that a stable operation of several hours or days is usually required before the stable HCl level is reached. The phenomenon is of special importance when changing from strong concentrations to dilute gases, as the adsorbed HCl is released (Huston & Wachter 1989). For example, a continuous stable operation of 3 - 4 days is required in VTT's pressurised gasifier until the stable HCl level is reached at the sampling point located after the hot gas filter. Due to the high corrosiveness and reactivity of HCl in the presence of moisture, inert materials, like quartz and PTFE, should be used in the sampling train. In general, principles similar to those described earlier for H₂S should be applied in the design of sampling systems for HCl too.

An interesting sampling method for an on-line measurement of HCl from high-temperature and high-pressure coal gasification processes has been presented by Huston & Wachter (1989). Sampling was performed in the presence of all matrix components formed in the fluidised-bed oxygen-blown gasification of coal. The sample gas coming from the process was maintained at about 500 °C to prevent the formation of NH₄Cl and then led into a long Ni-tubing kept at 1 000 °C, at which the tars and ammonia were effectively decomposed (aided by the catalytic effects of the nickel material). After this point the sampling line was maintained above the dew point, at 150 °C, and the tar-free

gas was led through analysers without condensation and soot problems. However, careful flow rate measurements are needed, since the cracking of tars and light hydrocarbons will increase the total gas flow rate quite substantially in biomass gasification applications, which has to be taken into account when calculating the concentration of HCl in the original raw gas.

A vapour-phase halogen (HCl, HF) sampling system developed by VTT is shown in Figure 14. It is based on the use of quartz liners everywhere inside the sampling tubes, also in the parts that are under process pressure. The only point where gas can be in contact with a metal surface is the valve chamber where gas is fed through the valve opening. After pressure letdown the valve gas is cooled and scrubbed by injecting purified halogen-free water (flow rate 10 ml/min) into the opening of the quartz liner immediately after the valve. The flow rate of the sample gas is 5 dm³_n/min and it is washed in four stages after cooling. The first washing stage also collects the water injected into the liner. The first stage washing is able to capture more than 98% of the total halides captured and only the content of the first stage washing bottle is analysed. A capillary electrophoresis system is applied for halide analyses. This sampling system has been successfully used in gasification tests, both in pressurised and atmospheric processes since 1995.

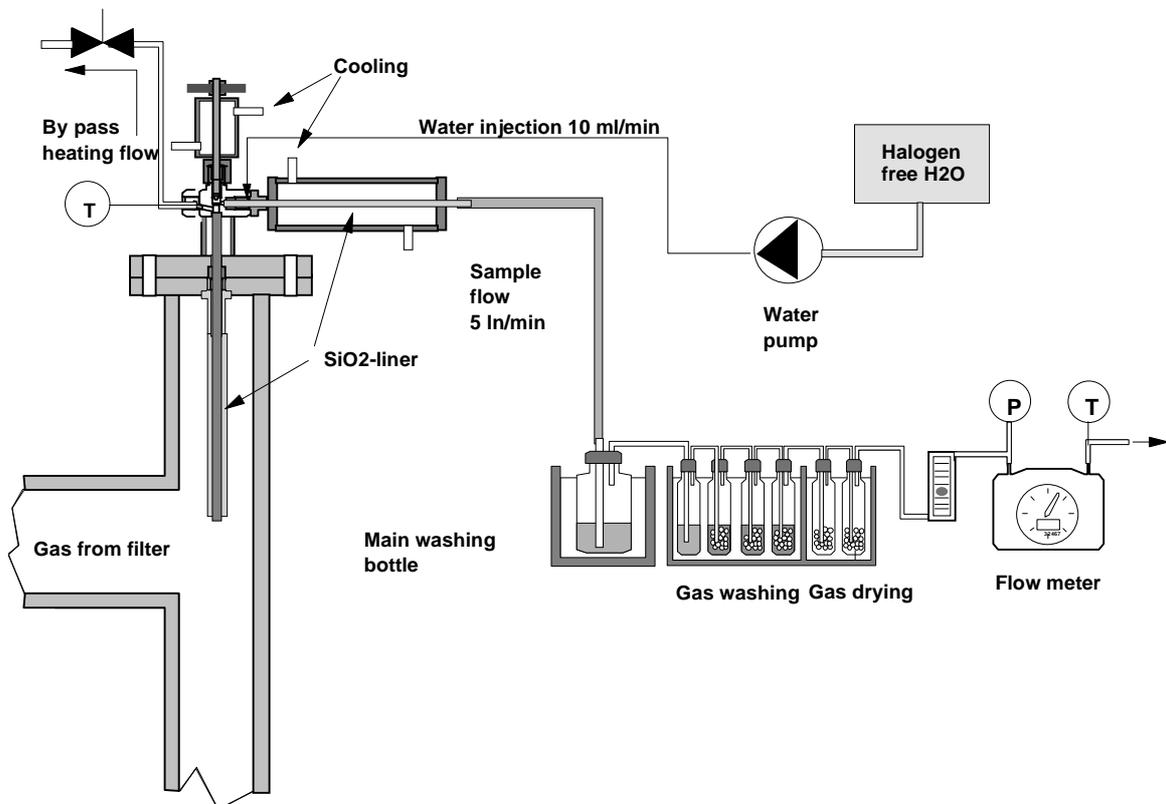


Figure 14. Vapour-phase halogen sampling system of VTT Energy.

5. Storage of samples

According to sample stability tests carried out at VTT (Ståhlberg et al. 1995, 1996) tar samples solved in dichloromethane can be stored in a cold ($< 5\text{ }^{\circ}\text{C}$) and dark place without changes for months. The right storing vessel for tar samples is made of glass.

Instructions for storing and treating aqueous samples are given in, e.g., ISO 5667/3 and NPR 6601 standards (ISO 1985, Smart & Maalman 1987). According to these HCN and SCN solutions can be stored for a maximum of 24 h (ISO 1985). Shorter storage time, in maximum 6 h, is used in ASTM D2036-82 (ASTM 1982). However, according to tests performed at VTT HCN should be analysed preferably immediately after sampling (Ståhlberg et al. 1994, 1995). HCN samples are stored at pH 11 - 12.5 (SFS 1975, Karst et al. 1980). Thiocyanate, SCN, is biodegradable, and samples that may contain bacteria are stored acidified at pH < 2 (Franson et al. 1985).

Despite the fact that ISO 5667/3 recommends a short storage time also for NH_3 , the experiences in practice show that ammonia samples can be stored for a longer time than HCN samples (Skinner 1985, Mann et al. 1985). According to the stability tests carried out at VTT ammonia samples can be stored in a cold and dark place without changes at least for a month (Ståhlberg et al. 1996). Ammonia samples should be stored at $2 - 5\text{ }^{\circ}\text{C}$ and acidified with H_2SO_4 to pH 2 (ISO 1985).

Certain inorganic compounds, like cyanides and sulphides, must be stabilised for storage. When sampling CO_2 -rich gases, like gasification effluents, the samples are stabilised with lime (Franson et al. 1985, ASTM 1982). Following the instructions of ISO standards the stabilisation for cyanide determination is necessary already at the sampling site (ISO 1985). In cyanide sampling sulphide makes an interference and it is removed by precipitation with lead or zinc acetate or lead carbonate (Smart & Maalman 1987, IFRF 1987). The oxidation products of sulphide convert HCN into SCN in a short time, especially at high pH values. HCN has been found to disintegrate even at a rate of 50% per hour, when the sulphide concentration in a solution was 500 mg/l. Precipitates are filtered off before pH stabilisation. Other oxidising agents are removed with sodium sulphite Na_2SO_3 (SFS 1975). Most interferences are removed by distilling HCN off from an acidified sample solution (IGT 1986, Ferrell et al. 1980, Mann et al. 1985, EPA 1979). Conventionally, all sulphur and nitrogen compounds are analysed separately using specific analytical methods for each (Karst et al. 1980).

Borosilicate or sodium-lime glass may release cations in an aqueous solution, and metals can be adsorbed on the containers walls. However, it is recommendable to use glass vessels instead of plastic ones (except for PTFE teflon), as plastic material is less inert. If plastic is used, polyethylene containers should be pretreated by letting them stand in 1 mol/l HNO_3 or HCl for 1 - 2 days. Freezing improves the storage stability of the samples. Plastic vessels are used in freezers (ISO 1985).

6. Conclusions and suggestions

Taking a representative sample from an elevated-temperature gas stream, which contains carbon particles, complex organics including high-molecular-weight polyaromatic compounds (PAC), water vapour as well as sulphur and nitrogen compounds, offers a difficult problem for the development of an effective sampling method. The withdrawal of a sample along the length of a probe and through a filter may cause chemical interactions, involving, e.g., transformations from gas to particulates.

At present there are no standardised overall sampling methods available, which would meet all the requirements of the different gasification applications. The heterogeneity of gasification processes and feedstocks results in a formation of a wide variety of products of different chemical nature. The required level of information about the gasification products also 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. That is why the sampling and analysing systems have to be more or less tailor-made for each application.

The system operating pressure is an important variable in sampling train considerations. With high pressure equipment lower volumetric gas flow rates are used, which results in a more effective gas contact in scrubbers and a better vapour/liquid disengagement. The tendency of premature condensation of the effluents in the sampling lines is, however, more problematic in high-pressure systems than in atmospheric gasifiers.

Several variables have an effect on the behaviour of the gasification effluent on its way from the original process conditions to the final sample container:

- chemical nature of the effluent
- moisture and particulate matter content of the gas
- temperature of the gas
- probe temperature and pressure
- probe material and dimensions
- gas velocity and residence time in the sampling lines.

There is scarce information available on these interactions. It is supposed that in incorrect sampling conditions probe materials can induce very severe reactions of the effluents in the sampling system. As the exact conditions and effects of these reactions are not well-known, a fast temperature letdown or dilution of the product should be attained. However, recent studies show that in sampling tars, NH_3 and HCl from fluidised-bed gasifiers operating at above 800 °C ordinary stainless steel probes and SiC filters can be safely used at least up to 600 - 700 °C. Sampling of HCl , H_2S and alkali metals is a more challenging task and very special methods are required for obtaining reliable results.

Although it is not possible to design one universal sampling method for all gasification applications, the following general design issues should be considered when planning a protocol for reliable sampling of gasifier effluents:

1. The filtering temperature should be kept so high that solids are cleanly separated from the volatile material, i.e., the volatiles do not condense on filters. In non-particulate sampling the primary ceramic filter is at best positioned at the sampling point, i.e., inside the gasifier or in the gas pipe. The initial filter is kept at or near the process temperature. Reverse flow, high-pressure nitrogen purge should be available to clean the filter from particulates.
2. The probe is kept near the process temperature, but above tar condensing temperature, to prevent any condensation in the probe. Rapid quenching or dilution of the effluent as soon as possible is preferable after the sampling point to maintain the original product composition.
3. If the sample gas has to be filtered at a lowered temperature, the temperature of the filter should be in the range 175 - 600 °C. Too low a temperature can plug the filter and terminate sampling, whereas too high temperatures can result in the thermal or catalytic cracking of tars.
4. Gas contact times with hot parts of the sampling line should be kept as short as possible; especially hot metal surfaces are a potential risk to the 'nativity' of the gas. Inert refractory materials (ceramics, quartz) should be used as probe materials whenever possible.
5. The condensate should be collected in a solvent (supplemented with a backup adsorbent resin), preferably not in a cold trap in which there is no 'diluting surroundings' to suppress further reactivity.

The available stack gas sampling protocols for gaseous, liquid and solid products are not very suitable for sampling hot and heavily tar-contaminated product gases. The up-to-date sampling systems for biomass gasifiers are modified from the EPA method for sampling emissions from combustion systems (EPA 1979). The protocol initially developed in the Canadian ENFOR project (Esplin et al. 1985) is recommended for isokinetic sampling of condensables and particles from non-pressurised biomass gasifiers, which produce gases with a high content of particulates and tar (Figure 4, chapter 2.2).

For the non-isokinetic sampling of condensables from pressurised gasifiers and high-temperature product gases, the sampling lines shown in Figure 5 are recommended. For sampling particles from pressurised systems an O-type probe configuration (as in Figure 6), combined with the pre-separation cyclone (and a conditioning coil) shown in Figure 4, depending on the temperature required, is the best choice. This type of probe has been found to operate relatively well under pressure. The O-probe is also suitable for sam-

pling particles from non-pressurised systems. The temperature of the downstream secondary fibre filters cannot be fixed, but is chosen according to the process conditions (temperature, pressure, raw material) and is variable at least between 150 and 400 °C .

Direct condensation of the liquid effluent without diluting media, e.g., with cold trapping can result in further reactions of the trapped compounds. The reactivity is suppressed by using a diluent like a diluting gas, an absorbing liquid or an adsorbent resin.

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APPENDIX A:

GAS SAMPLES, SAMPLING SAMPLING LINES

1. Object

This method is applied for conducting a sample gas flow from the product gas formed in thermal reactors either to on-line analysers or into a sampling vessel.

2. Scope of application

The method is suitable for moist product gas formed in continuously operating thermal reactors. The product gas may contain solids and condensing impurities (e.g., tar). The sampling point may be at overpressure or at low pressure.

The method cannot be applied to gases that adsorb on metal, plastic and glass surfaces of the sampling line or that react with these materials or with solids deposited on the filters.

3. References

Mann, R. et al. Environmental, health and safety data base for the KRW coal gasification process development unit. Final report. Chicago: Gas Research Institute, 1985.

Segeler, C. G. (ed.). Gas engineers handbook. Fuel gas engineering practices. Section 6, Chapter 1. New York: The Industrial Press, 1966.

Ferrell, J. et al. Coal gasification/gas cleanup test facility. Vol. V. North Carolina: North Carolina State University, Dept of Chemical Engineering, 1983. 89 s.

4. Definitions

Subscript n : standard state, $p = 1.013 \text{ bar}$, $T = 273 \text{ K}$

5. Sampling lines

5.1 Preparation

5.1.1 Cleaning of sampling line

The sampling lines are rinsed with a solvent, water or steam and/or flushing with air or nitrogen. If the sampling line is connected with a gas line containing combustible gases, inert rinsing agents have to be used.

5.1.2 Checking the tightness of the sampling line

The sampling line is pressurised either with gas from process pressure or from a gas cylinder, and possible leaks are detected by leak indicators or organoleptically (odour, auditory perception).

If the gas mixture to be studied does not contain oxygen, the leaks can be detected by an oxygen analyser connected to the sampling line.

5.2 Principle of sampling

Prior to sampling the sampling line is filled with the sample gas. If the sample is collected into a gas bag or a gas bulb with flow-through, the gas is let to flow a sufficiently long time (= the amount of gas flown through is at least 10-fold compared with the volume of the whole sampling line) through the gas bulb or the gas bag before shutting off the gas flow.

If flow-through cannot be employed when filling the sampling line (e.g., 1-valve gas bags, gas absorption), the sample gas is let to flow, a sufficiently long time, through the by-pass line located in the sampling line immediately prior to gas collection (ref. the previous chapter) to make sure that the sampling line is filled with the gas to be studied.

The gas sample is led through the sampling line either with the aid of process pressure or a pump included in the sampling line to analysers or to a sample vessel. The flow rate of the sample gas is monitored during sampling. If necessary, the total amount of sample gas and the temperature and pressure of the gas just prior to the flow meter are recorded.

5.3 Description of sampling lines

5.3.1 General

The sampling line shall always be as short, small in volume and simple as possible. Additional joints, valves, filters, etc., should be avoided due to leak risks. When designing the sampling line, cleaning of the line, sufficient cleaning of sample gas and prevention of condensation shall be considered. Examples of sampling line construction are shown in Figures 1 - 3.

The sampling line in Figure 1 can be applied for clean gases, if the cold trap can be placed close to (1 - 2 m) the sampling connector. An example of a long sampling line suitable for a sample gas containing solids and an abundance of condensing substances (water, tar) is shown in Figure 2. In Figure 3, an example of sampling line for pressurised gas containing an abundance of solids and condensing substances is shown.

5.3.2 Sampling line for clean gases

The sampling line in Figure 1 can be used when

- the sampling line is short (1 - 2 m) and can be made inclining (when condensing water does not form a “water lock” in the hose),
- the solids content of the sample gas is $<1 \text{ g/m}^3_n$ (absorption: solids content $\sim 0 \text{ g/m}^3_n$)
- the tar content of the sample gas is $<10 \text{ g/m}^3_n$.

If the sampling point is at normal atmospheric (= 1.013 bar) or low pressure, no control valve is required at the beginning of the sampling line. If the sampling point is at overpressure, neither a pump nor a control valve are required.

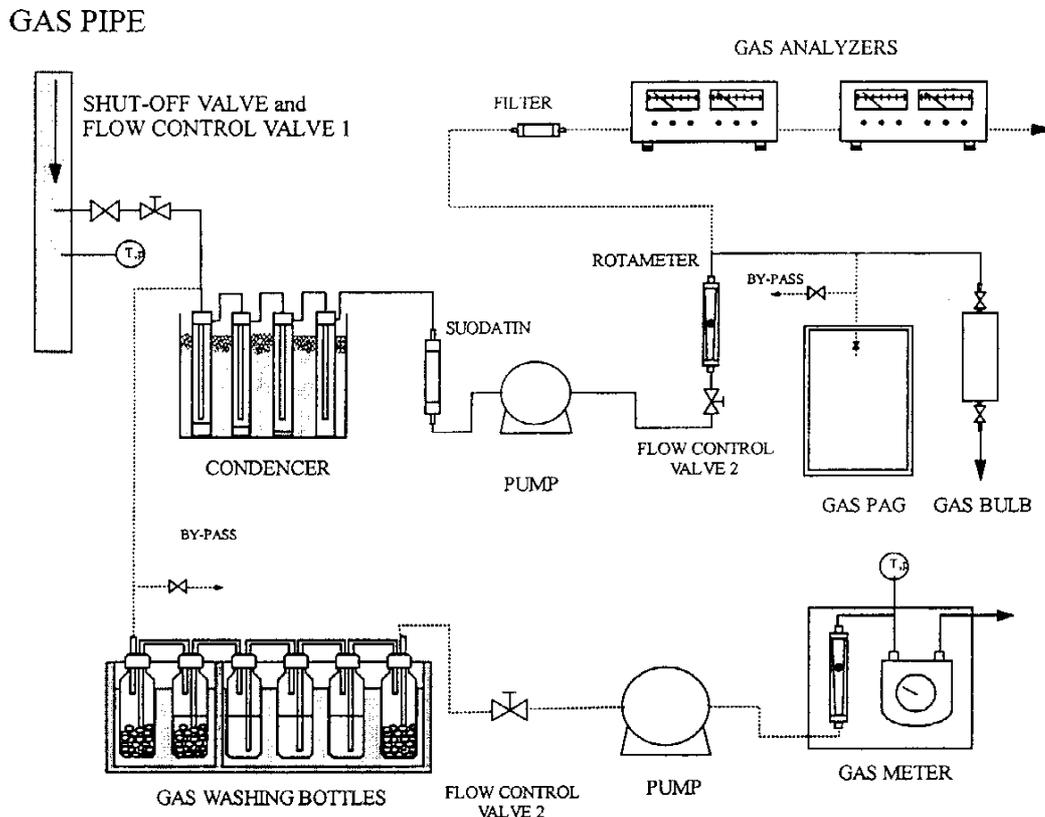


Figure 1. Sampling line for clean gas.

- The tip of the sampling line is installed in the gas line either co-current or right-angle to the gas flow (reduces the solids content of the sample gas).
- Pressure and temperature of gas at the sampling point are measured.
- Sample gas is led through a PTFE or silicone hose into the cold trap. If the sample is collected by absorbing in the liquid, the cold trap is replaced by a sample vessel. The sampling line shall be as short as possible and washable with the liquid used for absorbing.
- Water vapour and the heaviest tar components are condensed in the cold trap by cooling the gas to 2 - 5 °C. For example, an ice bath or a compression cooler can be used as cold trap.

- The flow of sample gas is controlled by flow control valve 2 (from a pressurised process, pressure relief and flow control with control valve 1).
- By-pass lines are used when filling the sampling line with the sample gas in case flow-through cannot be applied.
- Gas flow during filling of the sample line and during sampling is monitored with a rotameter.
- The sample is led into the sample vessel or to gas analysers.
- The sampling lines, cold trap and filter are cleaned when necessary.
- The exhaust gases from by-pass lines and sample gas are led safely outside the sampling room.

5.3.3 Sampling line for unclean gases

Figure 2 shows a heated sampling line in which the solids are removed with a hot quartz fibre filter. Electric heating prevents both water vapour and tar from condensing on the surfaces of long sampling lines.

This kind of sampling line can be used when

- the sampling line is long and/or twisting (the cold sampling line is clogged by condensing water vapour and tar)
- the solids content of sample gas is $< 5 \text{ g/m}^3_n$
- the tar content of sample gas is $< 150 \text{ g/m}^3_n$

The temperature of sample gas in the gas line and hot filter is regulated at 150 - 350 °C by electrical heating or by steam. The temperature level is dependent on the condensing impurities in the gas (ref. chapter 5.4). Otherwise the sampling is carried out as presented in chapter 5.3.2.

GAS PIPE

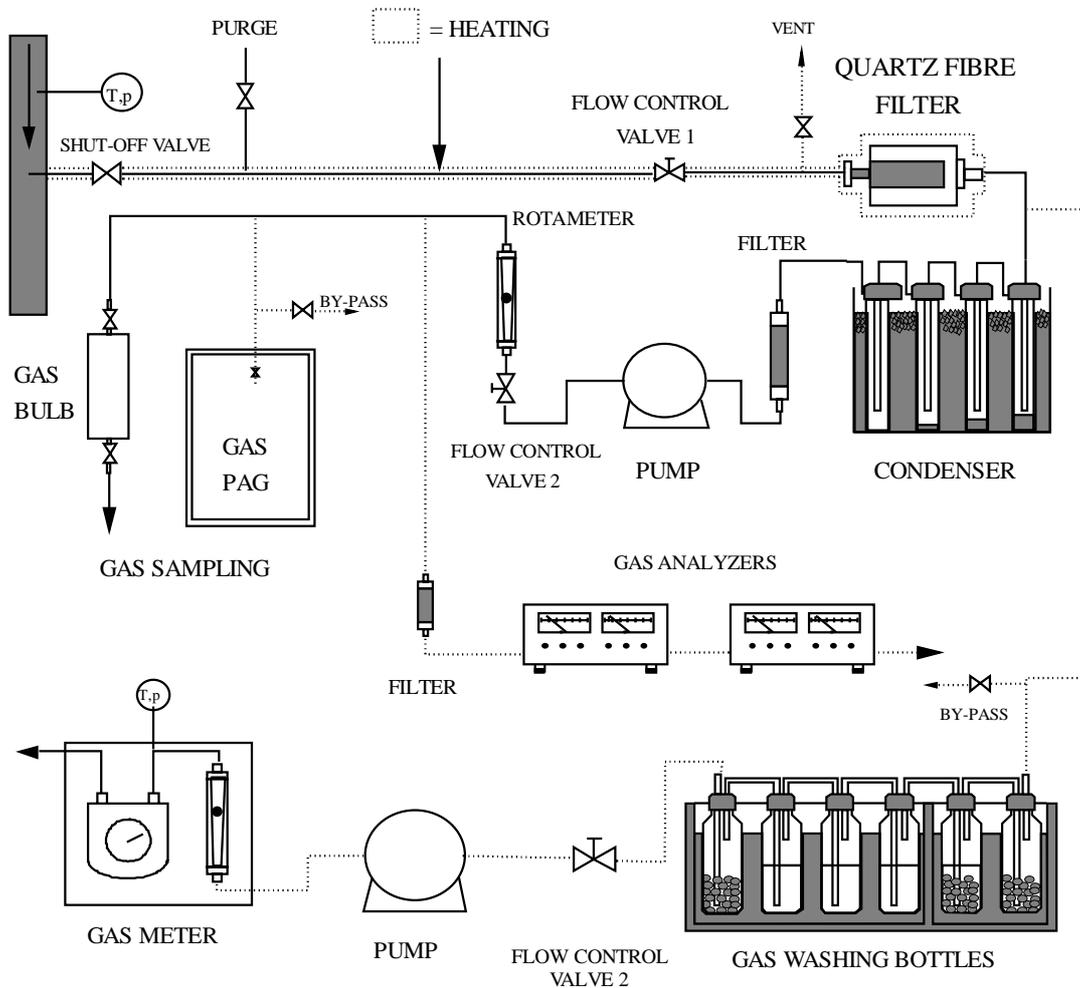


Figure 2. Sampling line for gases containing solid and gaseous impurities.

Figure 3 shows a sampling line with electric heating, which allows an on-line sampling of several days from pressurised process gas containing an abundance of solid and gaseous impurities. This kind of sampling line can be used when

- the sampling line is long and/or twisting (the sampling line is clogged by condensing water vapour and tar)
- the solids content of the sample gas is $< 50 \text{ g/m}^3_n$
- the tar content of the sample gas is $< 150 \text{ g/m}^3_n$

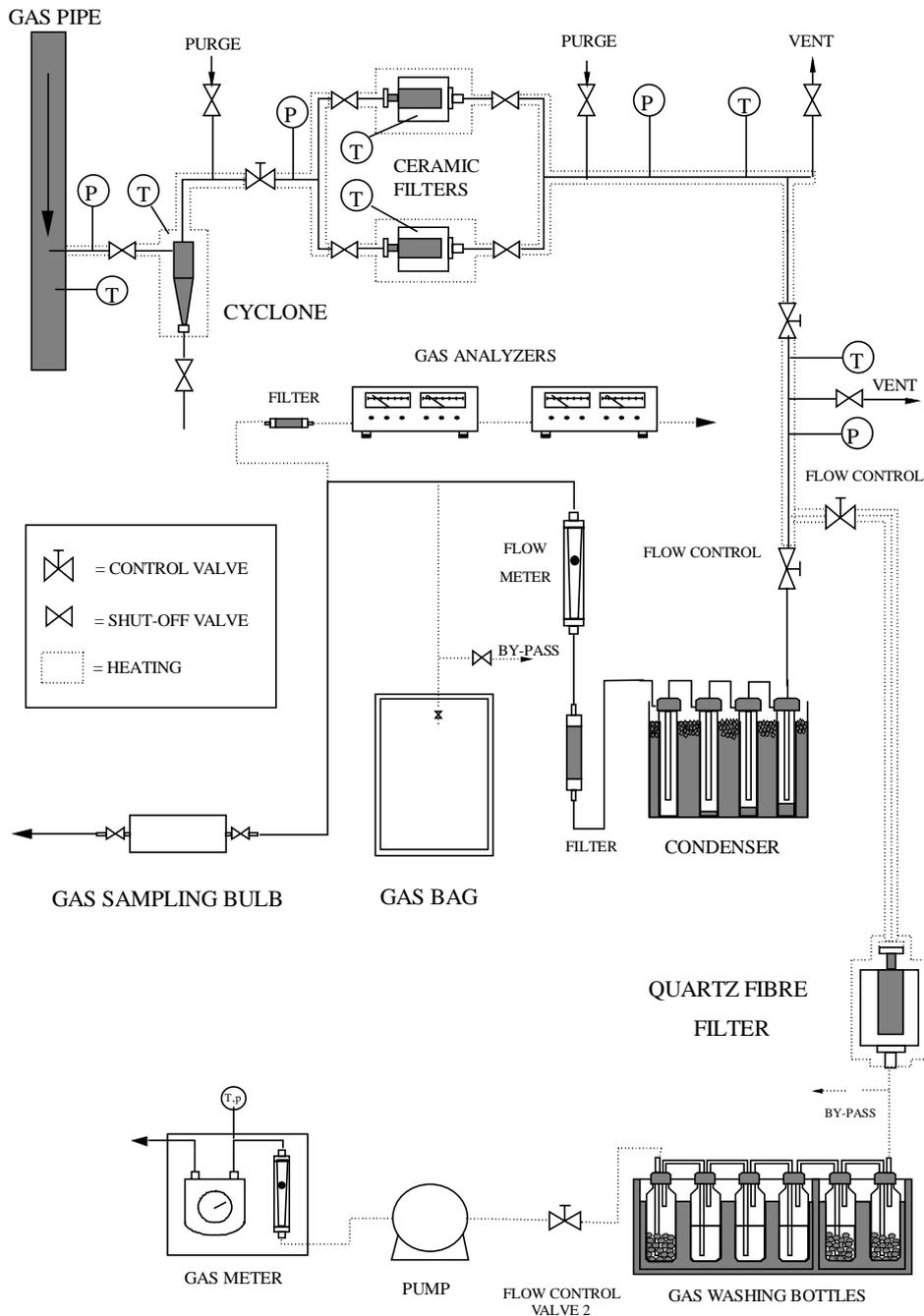


Figure 3. An example of sampling line for a pressurised process.

- The tip of the sampling line is installed in the gas line either co-current or right-angle to the gas flow (reduces the solids content of the sample gas).
- The pressure and temperature of gas at the sampling point is measured.
- There shall be a shut-off valve first in the sampling line for shutting off the line *at any time* (also in case of leaks). This valve should be resistant to *process temperature*.
- Removal of solids with cyclone, ceramic hot filter and cold trap. The parallel hot filter lines enable on-line sampling and change of filter in clogging situations. The type and number of particulate separators in the sampling line is chosen on the basis of solids contents in the sample gas (ref. chapter 5.3). Quartz and fibreglass filters can also be used as hot filters.
- If the sample gas is absorbed into liquid, the cold trap is replaced by the absorption liquid, and a hot quartz fibre filter is added to the sampling line (before absorption).
- Pressure relief is carried out in stages with three manual control valves. It can also be performed with one valve only (flow control), but a steadier pressure relief and higher reliability in service (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.
- Nitrogen flush lines are placed in such a mode that the most important valves and gas lines can be cleaned in both directions.
- By-pass lines are used for cleaning gas lines, regulating pressures and filling the gas line with the sample gas.
- Condensation of water vapour and condensable gases (clogging of the sampling line) before the cold trap is prevented by electric heating keeping the gas at 150 - 350 °C.
- The flow of sample gas is regulated by the last control valve of the line, from which the gas is led through as short a silicone or PTFE hose, or through a glass pipe into the cold trap or the absorption vessel.
- In the cold trap, water and tars are condensed from gas by cooling the gas to 2 - 5 °C.
- For example, an ice bath or a compression cooler can be used as the cold trap.
- The gas flow during the removal of flushing gases and essential sampling is monitored with a rotameter.

- The sample gas is led either to analysers or to a gas bulb or a gas bag.
- The sampling lines, the cold trap and the filters are cleaned when necessary.
- The exhaust gases from by-pass lines and sample gas are led safely outside the sampling room.

5.4 Operating conditions

The method can be used for sampling gases at 0.8 - 50 bar (abs.) and < 850 °C.

The filtration methods of sample gas and the temperature level of electric heating are primarily dependent on the solids content of the product gas and on the amount and quality of condensing substances. In addition, they are also affected by the placing of the cold trap with regard to the sampling connector, the density and duration of sampling, and the cleanability of sampling lines, filters and cold trap between samplings.

If the gas contains solids, a fibre filter (absolute filter) shall always be used prior to absorption in the sampling based on absorption.

In long-term continuous sampling, a fibre filter is required before the cold trap when the solids content $1 \text{ g/m}^3_{\text{n}}$. Smaller solids contents can be removed in the cold trap (ice bath) and then with cotton wool and/or fibre filters. In addition, the on-line analysers always require filters of their own.

If the solids content exceeds $5 \text{ g/m}^3_{\text{n}}$, a ceramic filter is required as a pre-filter, and if the solids content exceeds $20 \text{ g/m}^3_{\text{n}}$, additionally an cyclone filter is required.

The temperature in the sampling line of the product gas of the updraft gasifier is kept at 250 - 350 °C, in downdraft and fluidised-bed gasification at 200 - 250 °C and for flue gases at 150 - 200 °C.

5.5 Equipment and materials

Sampling lines with electric covering heating:	Acid-proof steel, AISI 316
Cold sampling lines:	Silicone or PFTE hoses
Cold trap:	Acid-proof steel, AISI 316, Gas volume 4 x 0.4 l, ice bath Compression cooler, e.g., H&B CGEK 4

Filters:	Munktell MK 360, quartz fibre, 30 x 77mm, Max. temperature 950 °C Retention capacity 99.998% (0.3 m), DOP-stand. Munktell MG 160, fibreglass, 30 x 77 mm Max. temperature 500 °C Retention capacity 99.998 % (0.3 m), DOP-stand.
Ceramic filter:	Silicon carbide, 50 x 30 x 135 mm H&B order no. 23005-4-0874725
Pumps (e.g.):	Sartorius GmbH, membrane pump Type SM 16612, 120 W Sartorius GmbH, membrane pump Type SM 16692, 80 W
Rotameters (e.g.):	Fischer & Porter D10A1017
Gas meter:	Ritter NB 3 (dry) KIMMON N3

5.6 Safety

The sample gases are often combustible and poisonous.

Sampler:	Eye protectors, personal CO alarm device, safety gloves, additionally pressurised processes: helmet, face shield
Sampling site:	Good air-conditioning, exhaust gases shall be led outside work rooms, staying in the vicinity of pressurised lines shall be avoided.

6. Assessment of the method

Weaknesses of the method:

- It is difficult to detect leaks in atmospheric sampling (low pressure in the sampling line).
- Part of gases may adsorb on the sampling line or on solids deposited on filters or they may condense.

APPENDIX B: TAR SAMPLES, SAMPLING

1. Object

This method is used for determining the content of condensable organic compounds (tars) in gas. It can be applied for collecting compounds having molecular weight range from benzene (C_6H_6 , MW 78 g/mol) up to pyrene ($C_{16}H_{10}$, MW 202 g/mol). Tars in this context comprise compounds heavier than benzene.

2. Scope of application

The method is suitable for separating organic compounds formed in gasification of solid fuels from the gas phase to a solvent. The gas to be sampled may contain solids and water vapour, in addition to gaseous components. The organics may exist as gas phase components and/or as aerosols.

The method has been applied for atmospheric updraft, downdraft and fluidised-bed gasification processes and for pressurised fluidised-bed gasification processes. The temperature of gas has ranged 50 - 900 °C in these processes. The sampling line to be used is selected by the process, while tar absorption is in principle always carried out in the same way.

If the temperature of the gas under study is so low at the sampling site that the organic compounds are condensed and form aerosols and/or drops, isokinetic sampling should be applied. In such a case instructions given in the standards ISO 9096 or VDI 2066 for sampling of flue gases should be followed.

The sampling lines should be heated in order to prevent tar compounds from condensing. However, to avoid thermal decomposition of compounds, the temperature should not be too high. In updraft gasification the temperature should be below 400 °C, while in downdraft and fluidised-bed gasification it can rise to nearly 800 °C at the tip of the sampling probe, if catalytic substances decomposing tar (i.e. dolomite, limestone) are not collected on the filters. According to experiences in practice, 200 - 300 °C is suitable gas temperature in the sampling line before tar absorption.

3. References

1. Kurkela, E., Ståhlberg, P. & Laatikainen, J. Pressurized fluidized-bed gasification experiments with wood, peat, and coal at VTT in 1991 - 1992. Part 1. Test facilities and gasification experiments with sawdust. Espoo: Technical Research Centre of Finland, 1993. (VTT Publications 161).
2. Simell, P. Tarry impurities developed in the gasification of indigenous fuels. Espoo: Technical Research Centre of Finland, 1988. (VTT Research Reports 531). In Finnish.
3. Environmental Protection Agency (EPA) Method 5. Determination of particulate emissions from stationary sources. Federal Register, 1971. Vol. 36, No. 247, p. 24888 -24895.
4. SFS 3866. Determination of dust emission. Helsinki: Finnish Standards Association, 1978.
5. Niskanen, V. & Puustinen, M. Emission measurements at VTT's Laboratory of Heating and Conditioning. Espoo: Technical Research Centre of Finland, 1982. (VTT Research Notes 129). In Finnish.

4. Definitions

Subscript n: standard state, pressure $p = 1.013$ bar and temperature $T = 273.15$ K

Light tar compounds: molar mass 79 - 202 g/mol

Heavy tar compounds: molar mass >200 g/mol.

5. Sampling

5.1 Preparation

Preparation of sampling lines is described in method description POVKN 01/90.

The sampling probe or the gas line is heated to its set value.

The solvent used for tar absorption (dichloromethane) and the glass beads used for improving material and heat transfer are dosed in gas wash bottles. The bottles are placed in the cold bath and let to cool to the temperature of the bath (min. 10 min).

5.2 Principle

Gas is led from the reactor or the gas pipe via the sampling line to the gas bottles in the cold bath. The organic compounds are absorbed to the solvent in the bottles. The amount, temperature, pressure and flow rate of the gas flowing through the equipment are measured after the bottles.

After sampling the contents of the impinger bottles, including the glass beads, are decanted into a storage bottle, which is stored tightly closed at cool, <5 °C, temperature for later analysis (see Method description ENEKA 102/94 Analysis of tar samples).

5.3 Sampling equipment

The sampling equipment is presented in detail in method description POVKN 01/90. The principle of the sampling system is shown in Figures 1 - 3.

In atmospheric sampling the probe is loosened and cleaned after each sampling. As it is not possible to loosen the probe between samplings in pressurised conditions, the probe and the filters are cleaned by nitrogen purge.

The impinger train comprises of six bottles connected in series:

- The first and the sixth bottle are half-filled with glass beads.
- The second, third and fourth bottle contain 70 ml solvent.
- The fifth bottle is half-filled with glass beads and contains 30 ml solvent.
- The first four bottles are placed in an ice bath, temperature 0 °C.
- The two last bottles are placed in an acetone-CO₂ ice bath, temperature <70 °C.

If the aim is to determine water-soluble compounds for the sample gas, ion-exchanged or distilled water is used in the first two bottles (see Figure 2) .

The dimensions of the gas wash bottles are given in chapter 5.5 and Figure 4, and the structure of the ice and dry ice bath is shown in Figure 3.

5.4 Operating conditions

The volume of the gas drawn to the tar sample is dependent on the tar content of the gas. A suitable sample volume in pressurised fluidised-bed gasification (tar $<20 \text{ g/m}^3_n$) is $50 - 100 \text{ dm}^3_n$ and in updraft gasification (tar $100 - 200 \text{ g/m}^3_n$) $30 - 50 \text{ dm}^3_n$. The total content of tar in the solvent should be about 10 g/dm^3 for gravimetric determination and about 2 g/dm^3 for gas chromatographic analysis. However, the detection limit is significantly lower for single components (0.25 ppm).

The gas flow rate in sampling cannot exceed $15 \text{ dm}^3_n/\text{min}$ with the impingers and solvent amounts applied. Normally the flow rate is significantly lower, being in the range of $5 - 10 \text{ dm}^3_n/\text{min}$. In isokinetic sampling the flow rate of gas can be affected by the choice of the tip diameter of the probe.

The maximum temperature of the gas can be slightly above $800 \text{ }^\circ\text{C}$ at the sampling site. In the sampling line, the gas temperature is kept at $350 - 400 \text{ }^\circ\text{C}$, from which it decreases to about $200 \text{ }^\circ\text{C}$ prior to the impingers. In the ice and dry ice baths the gas is then further cooled. Problems can arise, if the ambient temperature is below $0 \text{ }^\circ\text{C}$, as water and tar are condensed and frozen in bends and joints connecting the impinger bottles.

5.5 Materials

- Sample lines: (pump, measuring apparatus, etc.), see ENEKN 01/90
- Probe: Acid-proof steel, AISI 316 or
Fire-proof steel, AISI 310
- Filtration: Filter holder: Acid-proof steel, AISI 316
Filter 1: Munktell MK 360, quartz fibre $30 \cdot 77 \text{ mm}$
max. temperature $950 \text{ }^\circ\text{C}$, retention capacity 99.998%
Filter 2: Sampling filter
Silicon carbide, o.d. 12.7 mm , i.d. 20.5 mm , length $100 - 300 \text{ mm}$
Manufacturer: Refractron Technologies Corporation
- Gas wash bottles: a) bottle
volume 250 ml , o.d. 40 mm , i.d. 34 mm , length 300 mm
inside conical ground joint NS 24/29
ground stopper

b) inside
pipe, o.d. 12 mm, i.d. 10 mm
outside conical ground joint NS 24/29
inside ball ground joint S 19/7 and 13/5 (gas in)
outside ball ground joint S 13/5 (gas out)
c) glass bends
length about 60 mm
inside and outside ball ground joint S 13/5
Material is standard laboratory glass.

Glass beads: o.d. 6 mm

Solvent: dichloromethane (methylene chloride), p.a.

Cold bath: Acid-proof steel, AISI 316

CO₂ ice, preferably pellets

Acetone, technical

Sample bottles: 500 ml storage bottle with PPN screw plug (GL45) and pouring ring

5.6 Safety

The sample gases are combustible and poisonous.

Dichloromethane is readily vaporised, is a respiratory poison, causes headache, dizziness and nausea. Solvent vapours irritate mucous membranes (sore throat) and eyes, see Information about operational safety.

Acetone is readily vaporised and inflammable, irritates mucous membranes and eyes, see Information about operational safety.

Sampler: Eye protectors, personal CO alarm device, safety gloves, respirator mask when working with solvents, helmet and face shield in pressurised processes

Sampling site: good air-conditioning, exhaust gases must be led outside workrooms, staying in the vicinity of pressurised lines shall be avoided.

Solvent handling: good air-conditioning, the inflammability of acetone should be considered.

6. Assessment of the method

The heaviest tar components can be condensed on the walls of the sampling lines in the conditions presented above. Solids derived from unfiltered gas may deposit in particular in bends and chokes.

Safety hazards due to solvents should be considered. Wash bottles should be filled and samples recovered in an air-conditioned room, for example in a fume cupboard of the laboratory.

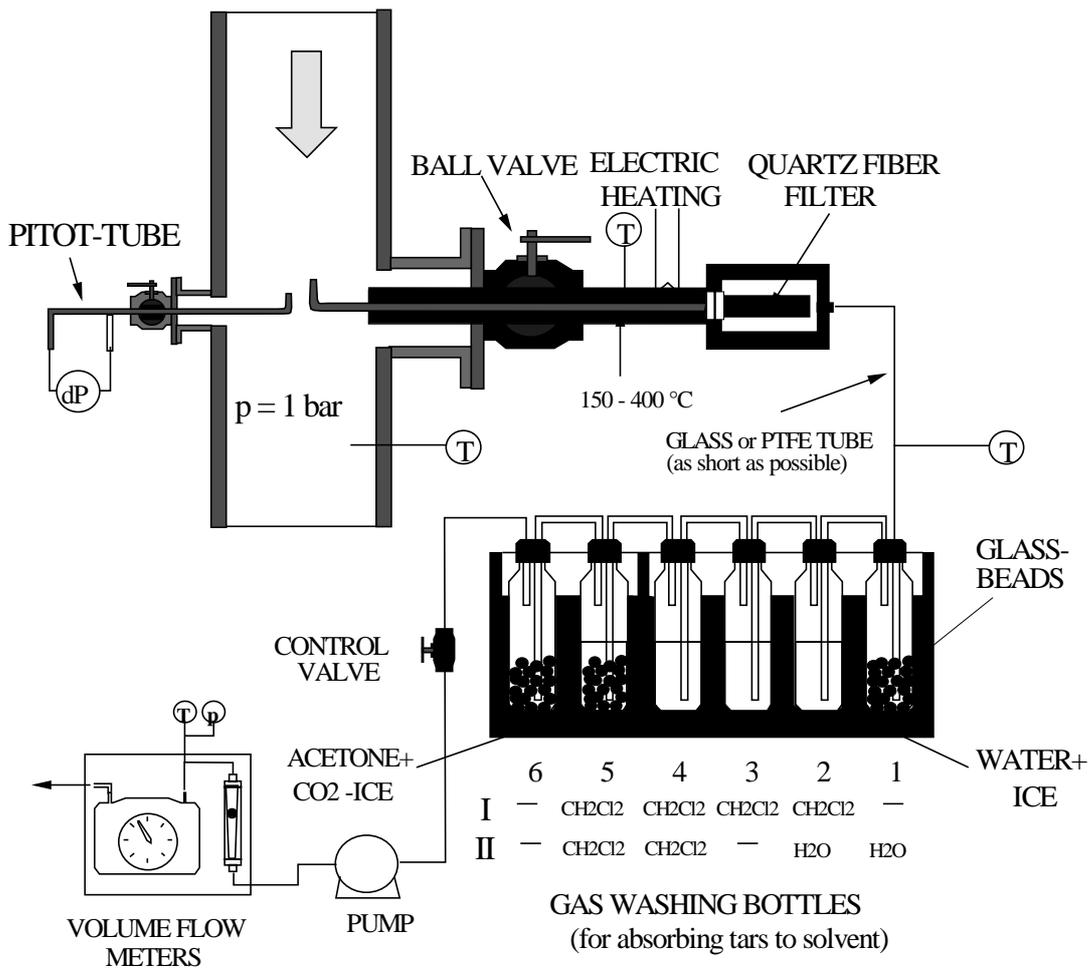


Figure 1. Atmospheric and isokinetic sampling of tars.

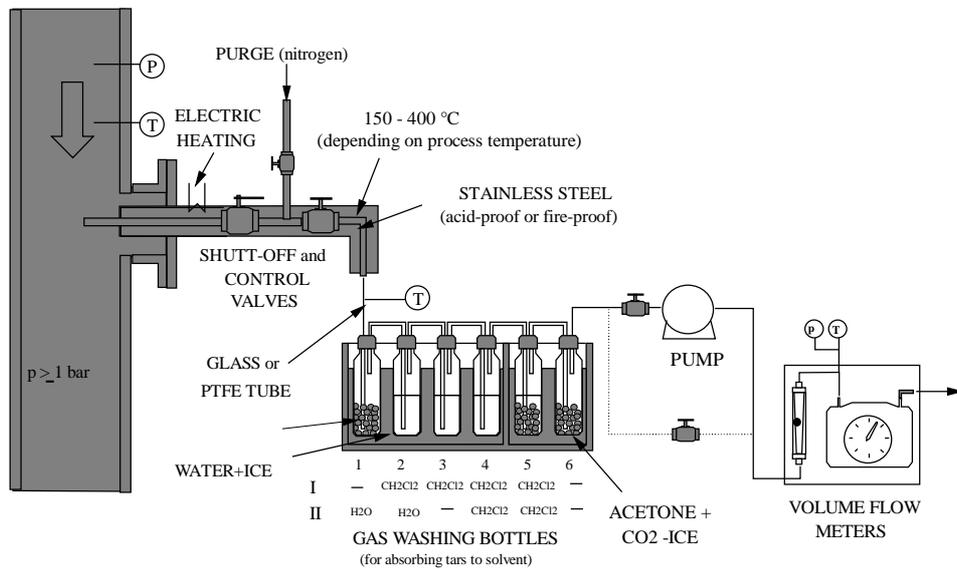


Figure 2. Tar sampling from solids free (filtered) gas.

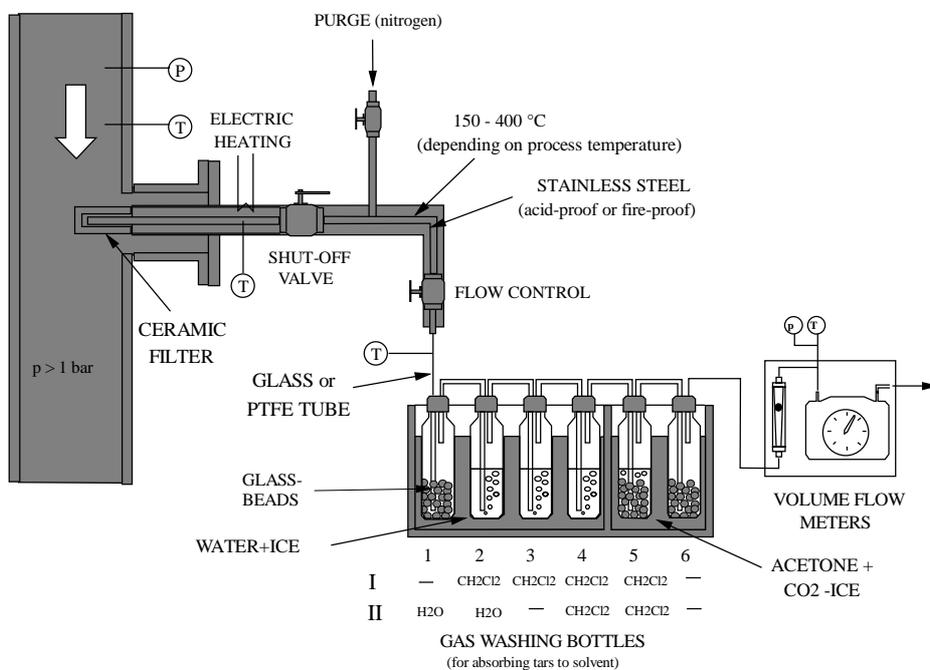


Figure 3. Tar sampling from pressurised gas containing solids.

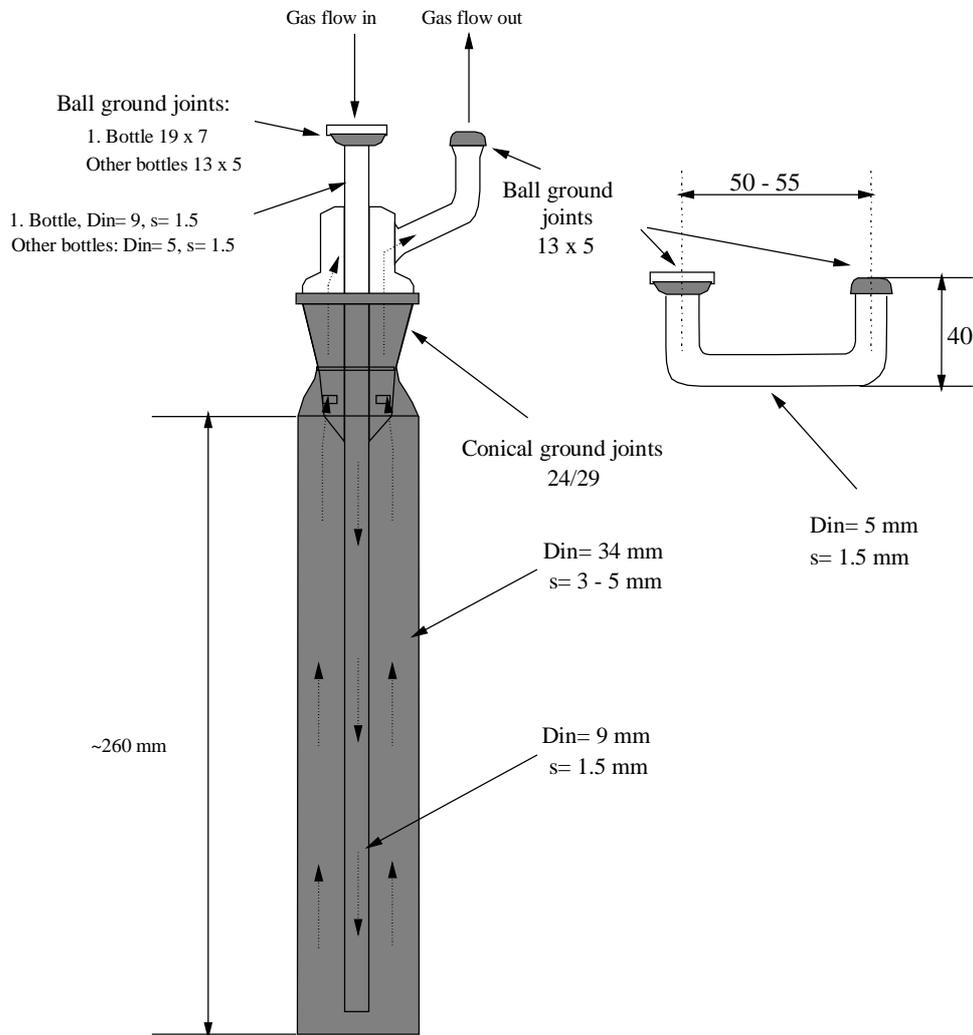


Figure 4. The gas washing bottle and the glass blend.

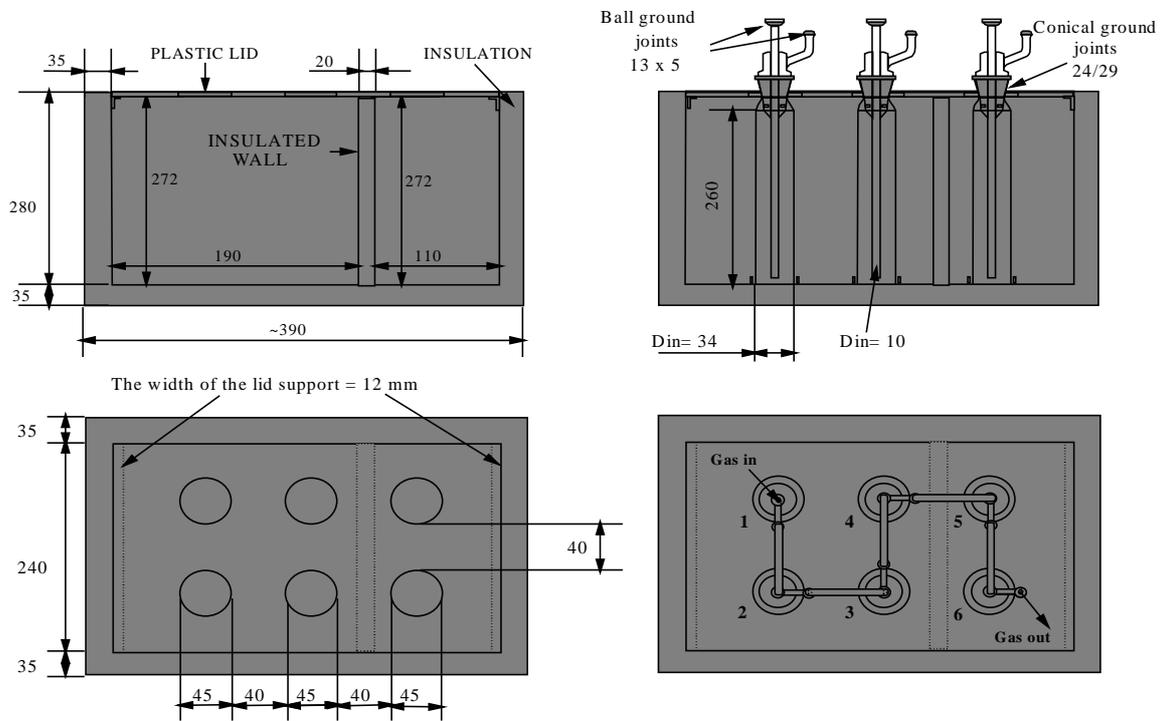


Figure 5. The gas washing bottles and the cold bath.

APPENDIX C:

HEAVY TAR SAMPLES, SAMPLING

1. Object

This method is used for the measurement of the content of condensable polyaromatic compounds (heavy tars) in gas. The heavy tars comprise in this context compounds with a molar mass higher than 200 g/mol and a boiling point higher than 350 °C. The method can be applied in the determination of the total content and composition of tar compounds condensable at 150 °C.

2. Scope of application

The method is suitable for sampling organic compounds formed in the gasification of solid fuels with a molar mass higher than 200 g/mol. Sampling is carried out by condensing compounds from the gas phase on the surface of a cooling pipe and on a filter. The gas may contain solids in addition to gaseous components. The method cannot be applied for compounds that are condensable or form aerosols in the process conditions prevailing at the sampling site.

As the condensation of different compounds at different temperatures is affected by their content/vapour pressure in the gas, compounds with a molar mass of 120 - 200 g/mol (naphthalene 128 g/mol) are also often condensed in the sampling. These compounds in the heavy tar sample are analysed by gas chromatography. In addition to the content of the tar compounds and the vapour pressure, condensation is affected by the pressure and the temperature of the process. The temperature should be above 400 °C at the sampling site of heavy tars. To prevent tar compounds from condensing too early, the sampling line prior to the collecting equipment should be heated to the process temperature.

The method has been applied for pressurised fluidised-bed gasification processes, but it is also applicable, with the restrictions given above, for atmospheric fluidised bed, downdraft and updraft gasification processes.

3. References

The method has been modified for gasification gases by the Gasification Research Group of VTT Energy. A similar method has been used for determining polycyclic aromatic compounds (PAC) in flue gases and car exhaust gases.

1. Williams, P. T. Sampling and analysis of polycyclic compounds from combustion systems: a review. J. of Institute of Energy, 1990. March, pp. 22 - 30.
2. Kurkela, E., Ståhlberg, P. & Laatikainen, J. Pressurized fluidized-bed gasification experiments with wood, peat, and coal at VTT in 1991 - 1992. Part 1. Test facilities and gasification experiments with sawdust. Espoo: Technical Research Centre of Finland, 1993. (VTT Publications 161).

4. Definitions

Subscript n: standard state, pressure $p = 1.013$ bar and temperature $T = 273.15$ K

Light tar compounds: MW 79 - 202 g/mol

Heavy tar compounds: MW >200 g/mol.

5. Sampling

5.1 Preparation

Preparation of sampling lines is described in method description POVKN 01/90.

The temperature of process gas at the sampling site is measured, and the sampling probe and the gas line are heated to the set values.

The temperature of the gas cooling pipe is set 10 - 30 °C above that (150 °C) of the filter used in sampling by leading hot nitrogen into the mantle pipe of the cooling pipe.

Weighed filters, weighing precision 0.0001 g, are used for condensing the heavy tars. Prior to weighing the filters are dried at 110 +/- 5 °C for 2 hour and then cooled to room temperature in an exsiccator for 1 hour. The filter is heated to the condensing temperature prior to sampling.

5.2 Principle

Sample gas is led via the sampling line kept at the process temperature into the cooling pipe and further to the quartz fibre filter kept at the standard temperature of 150 °C. The heavy tar compounds contained in the gas are condensed both in the cooling pipe and on the filter. After filtering the remaining light tar and *heavy tar* compounds and water vapour are removed either in a cold tarp or in impinger bottles, and the gas is led to metering. After sampling, the cooling pipe is washed and the filter is extracted with dichloromethane. The solvent used in the wash of the cooling pipe is recovered and combined with that used in the extraction of the filter. The combined solvent is placed in a storage bottle, which is stored tightly closed in cool place (<5 °C) for later analysis (see Method description ENEKA 102/94, Analysis of tar samples).

5.3 Sampling equipment

The so-called hot part (at process temperature) of the sampling equipment should always be as short, small in volume and simple as possible.

The main components of the sampling assemblies listed in Figures 1 - 3 are:

- Ceramic filter
- Electrically heated probe
- Shut-off valve
- Pressure relief/constant flow valve
- Gas cooling pipe and preheater of cooling nitrogen
- Sampling filter (quartz fibre filter)
- Condenser (ice bath), gas wash bottles (see method description ENE KN 04/94)
- Gas pressure, temperature and flow metering

The sampling assemblies showed in Figures 1 - 3 differ from each other only at the site of the ceramic hot filter. The filter cannot be placed at the tip of the sampling line, if the temperature of the sampling site exceeds 700 °C.

5.4 Operating conditions

The volume of the gas drawn to the tar sample is dependent on the tar content of the gas. A suitable sample volume in pressurised fluidised-bed gasification (tar <20 g/m³_n) is 100 - 600 dm³_n and flow rate 4 - 6 dm³_n/min. The total content of tar in the solvent should be about 10 g/dm³ for gravimetric determination and about 2 g/dm³ for gas chromatographic analysis. However, the limit of detection is significantly lower for single components (0.25 ppm).

The temperature of the gas can be 400 - 850 °C at the sampling site. When the temperature exceeds 700 °C, the temperature of the gas in the sampling probe can be lowered to 650 - 700 °C. The ceramic hot filter of the sampler is placed at the site, where the temperature of the gas is below 700 °C. This prevents the catalytic solids (e.g., dolomite) possibly deposited on the filter from affecting tar compounds.

5.5 Materials

Sample lines:	(pump, measuring apparatus, etc.) see POVKN 01/90
Probe:	Acid-proof steel, AISI 316 or Fire-proof steel, AISI 310
Hot filtration:	Filter holder: Acid-proof steel, AISI 316 Filter 1: Munktell MK 360, quartz fibre, o.d. 90 mm max. temperature 950 °C, retention capacity 99.998% Filter 2: Sampling filter Silicon carbide, o.d. 12.7 mm, i.d. 20.5 mm, length 100 - 300 mm Manufacturer: Refractron Technologies Corporation
Condenser: (ice bath)	Acid-proof steel, AISI 316
Solvent:	dichloromethane (methylene chloride), p.a.
Sample bottles: and pouring ring	500 ml or 1 000 ml storage bottles with PPN screw plug (GL45)

5.6 Safety

- The sample gases are combustible and poisonous.
- The operation and condition of the sampler should be controlled over the whole sampling time.
- Staying in the immediate vicinity of hot and pressurised sampling lines should be avoided.

Dichloromethane is readily vaporised. It is a respiratory poison and causes head-ache, dizziness and nausea. Solvent vapours irritate mucous membranes (sore throat) and eyes, see Information about operational safety.

- Sampler:** Eye protectors, personal CO alarm device, safety gloves, respirator mask when working with solvents, helmet and face shield in pressurised processes
- Sampling site:** good air-conditioning, exhaust gases must be led outside work-rooms, staying in the vicinity of pressurised lines shall be avoided.
- Solvent handling:** good air-conditioning, the inflammability of acetone should be considered.

6. Assessment of the method

The heaviest tar components can be easily condensed on the walls of the sampling lines in the conditions presented above. However, good results have been obtained with the method, considering how difficult the compounds are to collect.

Safety hazards due to the solvents should be considered. The probe should be washed with dichloromethane in a well air-conditioned room, and it should be cooled thoroughly prior to washing.

Sample analysis: Method description ENE KA102/94.

SAMPLING TRAIN for HEAVY TARs

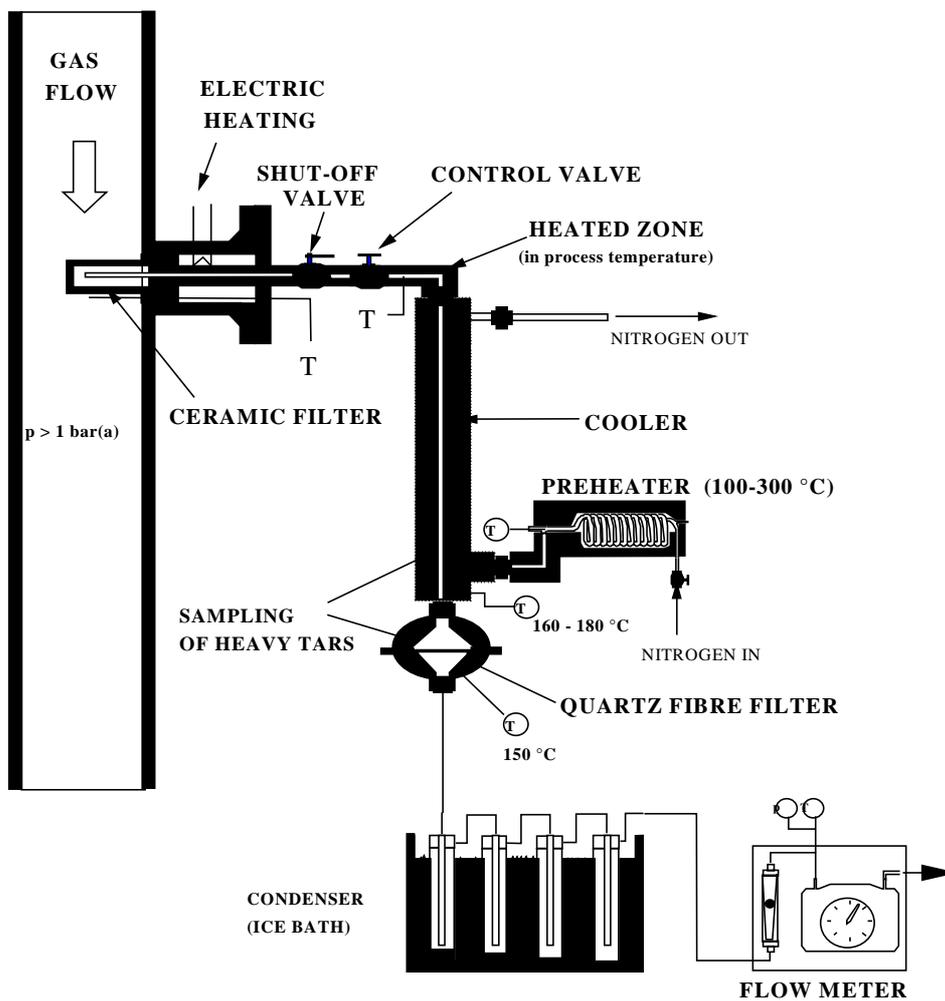


Figure 1. Sampling train for heavy tars.

SAMPLING TRAIN for HEAVY TARs

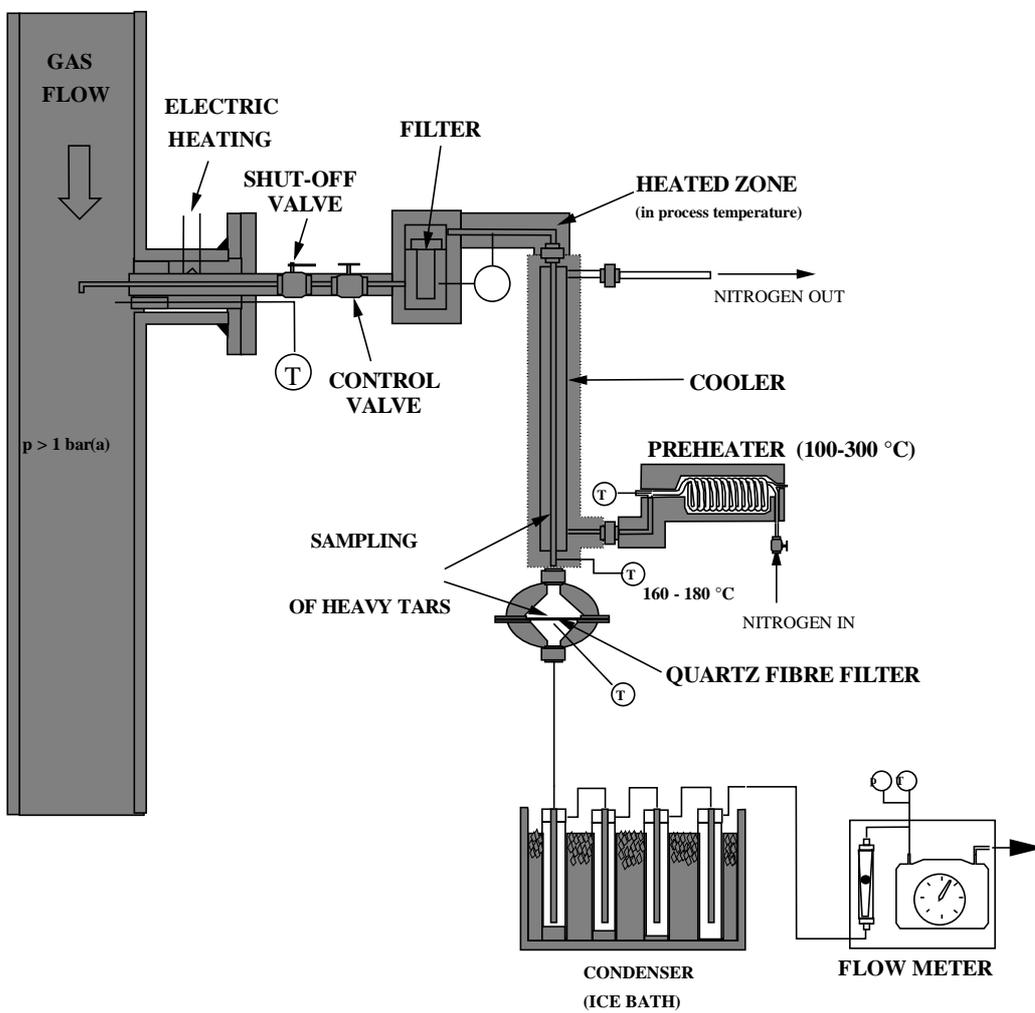


Figure 2. Sampling train for heavy tars.

SAMPLING TRAIN for HEAVY and LIGHT TARs

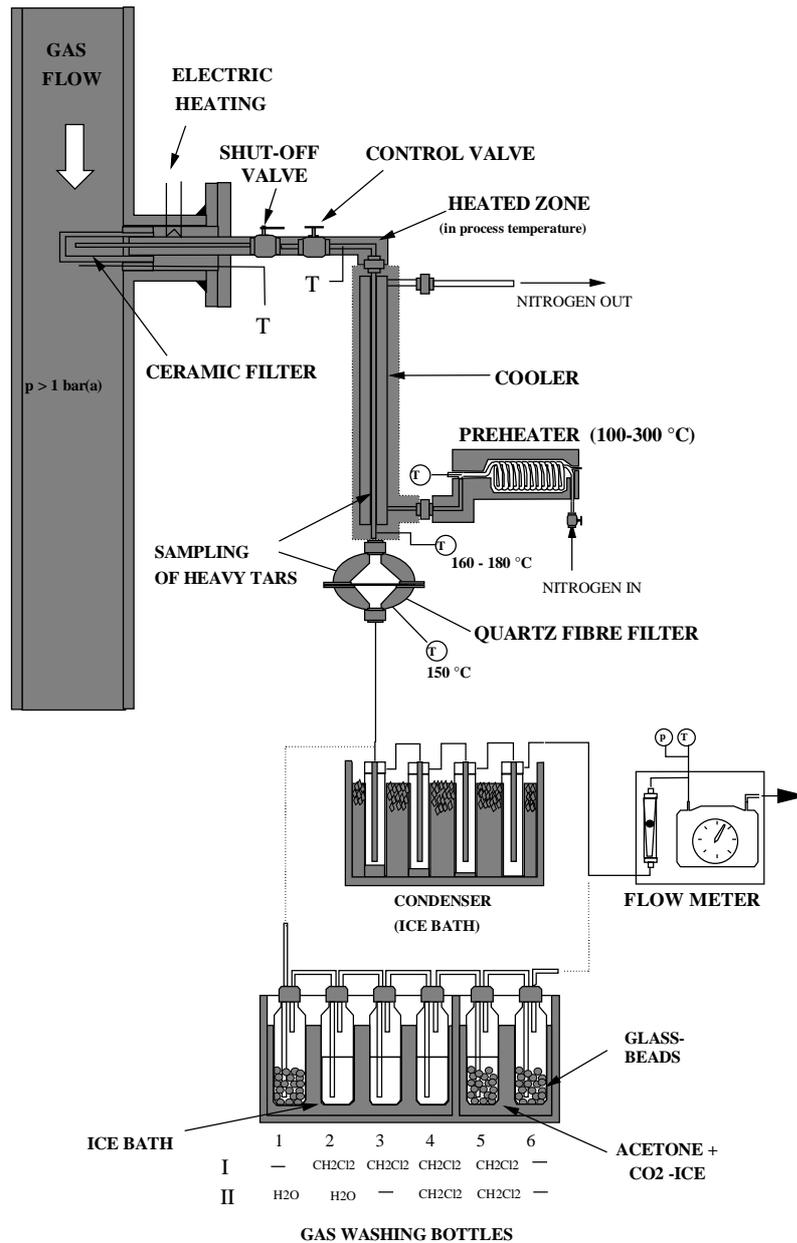


Figure 3. Sampling train for heavy and light tars.

APPENDIX D: TAR SAMPLES, ANALYSIS

1. Object

These methods are used for determining the content of condensable organic compounds (tars) in samples absorbed in a solvent.

2. Scope of application

The methods are suitable for tar samples drawn from the product gas of the gasification of solid fuel by absorbing tar compounds in a solvent. In addition to the solvent and organic tar components, the sample may contain solids and water. In this method description, tar means organic compounds heavier than benzene (C_6H_6 , molar mass 78 g/mol). The gas chromatographic method for light tars is also suited for the analysis of benzene.

The method of analysis to be applied is dependent on the way of formation and the content of the tarry substance to be determined. Gas chromatographic analyses are suitable for samples consisted of volatile organic compounds. Such samples are obtained from processes, in which the tarry substances are formed at high temperature ($>700\text{ }^\circ\text{C}$), for example in fluidised bed and downdraft gasification. The total content of analysable compounds is usually less than 20 g/m^3_n in these processes.

Gravimetric methods are suitable for monitoring the tar content of samples that are drawn from peat and biomass gasification and contain poorly volatile and heavy organic compounds, and for evaluating and comparing the total tar content. Vaporisation at room temperature is suitable only for samples that do not contain water or tar compounds lighter than phenanthrene ($C_{14}H_{10}$, molar mass 178 g/mol).

In updraft gasification the content of the heavy tar fraction analysed gravimetrically has typically been $>10\text{ g/m}^3_n$, and the total tar content $>50\text{ g/m}^3_n$. In downdraft and fluidised-bed gasification the amount of heavy tar compounds is usually less than 3 g/m^3_n , while the total tar content is about 20 g/m^3_n .

3. References

1. Kurkela, E., Ståhlberg, P. & Laatikainen, J. Pressurized fluidized-bed gasification experiments with wood, peat, and coal at VTT in 1991 - 1992. Part 1. Test facilities and gasification experiments with sawdust. Espoo: Technical Research Centre of Finland, 1993. (VTT Publications 161).
2. Simell, P. Tarry impurities developed in the gasification of indigenous fuels. Espoo: Technical Research Centre of Finland, 1988. (VTT Research Reports 531). In Finnish.

4. Definitions

Subscript n and NTP: standard state, pressure $p = 1.013$ bar and temperature $T = 273$ K

Light tar compounds: molar mass 79 - 202 g/mol

Heavy tar compounds: molar mass >200 g/mol.

5. Sampling

Sampling of light tar compounds is specified in method description ENEKN 04/94 and sampling of heavy tars in method description ENEKN 06/95.

6. Analysis

6.1 Principle

Water and possible solids are separated from the mixture of tar and solvent obtained in sampling. The volume of the sample solution is measured. The tar contained in the solvent is analysed by gas chromatography and/or gravimetrically, depending on the quality of the sample.

Tar consists of volatile organic compounds and is formed in gas phase reactions at high temperature, for example, in fluidised-bed and downdraft gasification. It is analysed both by capillary gas chromatography with flame-ionisation detector (FID detector) and gravimetrically. A mass selective detector (MSD) is used for the identification of the tar compounds. Two gas chromatographic methods are used for quantitative analysis: 1) light tar and 2) heavy tar method.

The content of tar (or tar fraction) that contains poorly volatile compounds can be described with gravimetric methods based on the evaporation of the solvent in standard conditions and on weighing of the evaporation residue. Tar of this kind is formed abundantly in updraft gasification, and minor amounts also in downdraft and fluidised-bed gasification.

The evaporation residue obtained in oven at 105 °C represents the content of the tar fraction formed by heavy and high-boiling (b.p. >300 °C) compounds. The distillation residue contains more lighter compounds and hence corresponds more closely to the total amount of tar. This factor has been discussed in further detail in reference [2]. If the heavy tar sample has been taken according to method description ENEKN 06/95 (on hot filter 150 °C) the evaporation can be carried out at room temperature.

6.2 Equipment and materials

6.2.1 Sample preparation

- graduated flask 500 ml or 1 000 ml
- Büchner funnel
- storage bottle 500 ml
- glass fibre filter paper (Whatman GF/A)
- filter flask 1 000 ml
- dichloromethane (p.a.)

6.2.2 Gas chromatographic analysis

- a) Sample preparation
 - pipette 5 and 20 ml
 - graduated flask 25 and 200 ml
 - disposable pipette
 - GC sample flask with stopper
 - dichloromethane (p.a.)
- b) ISTD solution
 - graduated flask 1 000 ml
 - decanter 10 ml
 - funnel
 - dodecane (C₁₂H₂₆), GC quality (99.5%)
 - dichloromethane (p.a.)

c) Model compound solution

- pipette 1 ml
- graduated flask 1 000 ml
- funnel
- decanter 10 ml
- spatula
- dichloromethane (p.a.)
- model compounds (p.a., see Enclosure)

d) Gas chromatographic analysis

- GC column HP Ultra 2 (50 m x 0.32 mm i.d., phase 0.52 μ m) for light tar compounds, or HP Ultra 2 (25 m x 0.32 mm i.d., phase 0.52 μ m) for heavy tar compounds
- HP 19251-60540 split-splitless liner
- gas chromatograph (HP 5890A) and integrator (HP 3396A)
- Sperry 3070-09 PC, or other MS-DOC PC with HP SERVER.EXE program.

6.2.3 Gravimetric analyses

a) Evaporation at 105 °C

- pipette 50 ml
- evaporating dish 60 ml
- exsiccator
- fume cupboard
- heating chamber, 105 °C
- analytical balance

b) Evaporation at room temperature

- pipette 50 ml
- round-bottomed flask 100 ml
- funnel
- cotton wool
- fume cupboard
- analytical balance
- dichloromethane (p.a.)

- c) Distillation 75 °C
- pipette 50 ml
 - conic flask 10 ml
 - exsiccator
 - drop funnel
 - Liebig cooler
 - distillation lamp
 - Erlenmeyer flask 100 ml
 - water bath, 75 °C
 - analytical balance

6.3 Sample preparation

1. The samples are allowed to warm up to room temperature.
2. Büchner funnel is placed on the graduated flask and the sample with glass beads is poured into the funnel.
3. The sample flask and the glass beads in the funnel are rinsed with a small amount of dichloromethane.
4. The volume of the sample and the amount of water in the sample are recorded.
5. The samples are stored in a cool place (<5 °C).

If the sample contains an abundance of solids, it is filtered prior to pouring into the graduated flask. The sample is filtered through a glass fibre filter paper placed in the Büchner funnel into the filter flask. Slight suction is applied when necessary. However, care should be taken not to let dichloromethane and light tar compounds to vaporise in filtration.

6.4 Gas chromatographic analysis

6.4.1 Preparation of internal standard solution (ISTD)

1. A small amount of dichloromethane is placed at the bottom of the 1 000 ml graduated flask.
2. The 10 ml decanter is tared on the analytical balance.
3. 1 g dodecane is weighed into the decanter, the exact amount is recorded.
4. Dodecane is poured into the graduated flask by rising with dichloromethane.
5. Dichloromethane is added to the graduated flask up to the mark.

6.4.2 Preparation of the model compound solution

(see Enclosure)

1. A small amount of dichloromethane is placed at the bottom of the 1 000 ml graduated flask.
2. Each component of the model compound is weighed in its own decanter in the following way:
 - 10 ml decanter is tared on the analytical balance.
 - Model compound is weighed in the flask and the exact amount is recorded (the amount of each component should be as close as possible to that of the actual sample).
 - Model compound is poured into the graduated flask by rinsing with dichloromethane.

Note! The lightest model substances, being readily volatile, should be treated quickly.

6.4.3 Analytical preparations

1. 5.0 ml of solution containing internal standard and 20.0 ml of sample at room temperature are pipeted into the graduated flask of 25 ml. The flask is shaken lightly and marked.
2. Sample is drawn from the 25 ml flask to the GC sample flask, the flask is shut and labelled clearly with the name of the sample.
3. A dilution is prepared from the model compound solution for calibration by pipeting 20.0 ml into the 200 ml graduated flask and by diluting with dichloromethane up to the mark.
4. A sample is prepared from the dilution of model compound solution for GC analysis as from tar samples (20 ml of solution is pipeted into the 25 ml graduated flask + 5 ml ISTD).

Separate measuring equipment shall be reserved for each sample!

6.4.4 Gas chromatographic analysis

Note! Exact instructions for the operation of the gas chromatograph are given in the operator's manual.

1. Capillary column HP Ultra 2 is put into use as follows:
 - It is installed when the oven is at room temperature.
 - One end of the column is fastened to the injector
 - Helium flow is switched on, the column pressure is adjusted to 146 kPa for the light tar analysis and to 88 kPa for the determination of heavy tars.
 - The column is rinsed with carrier gas for 15 min.
 - The oven is heated: from 30 °C to 300 °C (3 °C/min) and hold at 300 °C (60 min).
 - The oven can be kept at >200 °C over night to recover the column.
 - As soon as the oven has cooled the other end of the column is fastened to the FID detector.

Note! The maximum temperature of the oven is 325 °C for HP Ultra 2.

2. The septum of GC and the needle of the autosampler are checked. Make sure that there is solvent in the wash bottles and the so-called split-splitless liner in the gas chromatograph.
3. The valves of the gas lines (synthetic air, N₂ and H₂) are opened and the flame of FID ignited. The helium flow (flow A ~24 ml/min for light tars or ~21 ml/min for heavy tars) and the column pressure (see point 1) are checked.
4. The sample bottles are placed in the sampler tray and the sample identification data is typed in the integrator (EDIT SEQ).
5. The run programme (*.MET) and the calibration data (*.CAL) of the gas chromatograph are loaded in the integrator from the 3.5 in diskdrive connected to it. A separate manual is available on the use of the calibration programs.
6. A 3.5" DD diskette is formatted with the integrator and a 5.25" diskette with the PC for saving the results. The PC is connected through its serial port to the serial port of the integrator. HP fileserver program SERVER.EXE is booted from the PC, and then its hard disk operates as the drive unit H: of the integrator. The BASIC programs of the integrator, used for handling the integrator report, are on the hard disk of the PC. When analysing light tars, the program to be booted after the run in the integrator, STERVA6.BAS is determined by writing command ASSIGN 0,H:STERVA6.BAS in the integrator. The corresponding program for heavy tars is RTERVA6.BAS. The number given in the title of the programs is the number of version in use, and can later be changed when the programs are updated.
7. Before the samples, a pure ISTD solution is run to verify the consistency of retention times with calibration. If necessary, the flow of helium gas in the column is adjusted.

8. To check the condition of the column, pure solvent is initially run.
9. The run with the samples is started with the command keys: SEQ START.

6.5 Gravimetric analysis

6.5.1 Evaporation residue of tar in the heating chamber at 105 °C

1. The evaporating dishes are tared by keeping them in the heating chamber at 105 °C for about half an hour and then in the exsiccator for two hours. The dishes are weighed on the analytical balance.
2. 50 ml of tar sample at room temperature is pipeted to a tared evaporating dish. Five parallel determinations is made for each sample.
3. The blank test is carried out with pure dichloromethane.
4. The evaporating dishes are kept in the fume cupboard overnight.
5. The next day the dishes are moved to a fumed heating chamber at 105 °C for one hour (1.0 h).
6. The dishes are cooled in the exsiccator (~ 2 h) and are weighed exactly in the same way as when tared.

6.5.2 Evaporation residue of tar at room temperature

1. A clean glass flask is weighed accurately three times on the analytical balance.
2. 50.0 ml of heavy tar sample is measured and poured into the flask through cotton wool to filter the solids.
3. The wool is rinsed with dichloromethane and the flask is placed in the fume cupboard.
4. The solvent is evaporated over about 24 hours, and the flask is reweighed (weighing result is the mean of three weighings).
5. Parallel determinations are carried out for the samples.

6.5.3 Distillation residue of tar

1. The distillation equipment is installed in the fume cupboard (see Enclosure) in such a way that it is easy to remove from the water bath. The temperature of the water bath is adjusted to 75 °C.
2. The conical flask of 10 ml with the stopper is tared by drying it in the exsiccator at least over two hours, and then it is weighed on the analytical balance.
3. The tared flask is connected to the distillation equipment.
4. 50.0 ml of tar sample at room temperature is pipeted into the drop funnel. Sample solution is poured into the flask half full and the equipment is immersed in the water bath. A distillate collection flask, e.g., an Erlenmeyer flask of 100 ml, is placed.
5. As soon as distillation begins the valve of the drop funnel is opened in such a way that the flask is continuously half-filled with sample solution. The suitable rate of distillation is on average 1 drop/s. Distillation takes about 30 min.
6. When distillation has stopped the flask is let to be coupled to the distillation apparatus and to stay in the water bath over three minutes, after which it is loosened and shut with the stopper.
7. The stopped flask is placed in the exsiccator for at least two hours, and then it is weighed as when tared.
8. The blank test is carried out with dichloromethane.

6.6 Calculation of results

6.6.1 Gas chromatographic analysis

The tar compounds are identified by the mass selective detector (MSD) in the gas chromatograph (GC) and by running model compounds. The GC-MS run data and other data used for identification are kept in the gas chromatography room.

The calculation of analysis results is carried out as follows: The report of the calibrated gas chromatographic analysis is saved as EXTENDED REPORT in the hard disc of the PC, from which it is read line by line back to the integrator and handled with the BASIC program of the integrator. The program modifies the .RTP-ending file and saves the modified file as .UA2-ending file, which can be read directly to spreadsheet programs.

The program requires data on the gas collecting conditions of the sample in certain form for the sequence sample sheet. In column REPORT MEMO, the collecting data on each sample is given according to the following example: K=99,T=25.2,L=520,. The decimals are set off by full stop and data by comma. The last value is also followed by comma. In the example K=99 means that the collecting volume of gas has been 99 l, T=25.2 gives the temperature of the gas meter (°C), i.e. the temperature of gas when measured, and L=520 is the total liquid volume of washing bottles (ml).

The gas chromatograph is calibrated to give the concentrations of the sample solutions in mg/l. The program calculates the contents for the gas sample in NTP conditions according to ideal gas laws. In addition, the program has data statements that contain the elemental analysis of the calibrated substances in calibration order. At the end of the UA2-ending report the calculated elemental analysis of the whole sample is given. If the order of calibration is modified or new substances are added to calibration, the DATA statements of the programs shall also be updated.

In the timetable data of the integrator, the integration is started after the solvent peak. At this point the BASIC program is able to give data on the proportion of identified substances on the basis of the area relations of the chromatogram. The correctness of this data is significantly dependent on the starting time of integration.

The printout of the BASIC programs are kept in the gas chromatograph room. The programs are saved on the hard discs of the PCs coupled to the integrators as well as on backup copy diskettes.

The integrator reports (.RPT) and calculated results (.UA2) are saved on the hard disc of the PC. The .UA2-ending files are copied on the diskette of the PC, after which the files can be deleted from the hard disc. The .UA2-ending files are read by SYMPHONY command File - Import - Structured. The sheet obtained does not contain any calculation formulas, i.e. when modifying some concentration value the sum and the results of the elemental analysis are not updated.

6.6.2 Gravimetric analysis

Tar content of gas is calculated from the evaporation residue:

$$C = m_{ka} \times v_{TL} \times (T_{KN} + 273) / (v_1 \times V_{KN} \times 273)$$

where C is tar content of gas ($\text{g}/\text{m}^3_{\text{n}}$)

m_{ka} evaporation residue as the mean of parallel samples (g)

v_1 volume of the tar solution sample analysed (ml)

v_{TL} total volume of the tar solution sampled (ml)

V_{KN} volume of sample gas (m^3)

T_{KN} temperature of gas in sampling ($^{\circ}\text{C}$).

The evaporation residue is calculated from the mean of at least four determinations, and the result of the blank test, being also the mean of at least four determinations, is reduced from it. The distillation residue is calculated from the mean of at least two determinations and the result of the blank test is reduced from it.

6.7 Accuracy and repeatability

Error sources of tar analysis:

- tar loss in sample preparation stages
- sample residuals in glass beads (despite rinsing)
- measuring, weighing and pipeting errors
- identification errors of compounds in gas chromatographic analysis.

A typical error in parallel tar sample determinations in gas chromatographic analysis has been less than 3% for single components.

6.8 REPORTING

The contents of compounds analysed by gas chromatography are given in $\text{mg}/\text{m}^3_{\text{n}}$, to the nearest 1 mg.

The result of gravimetric tar determination is given in $\text{g}/\text{m}^3_{\text{n}}$, to the nearest tenth. The evaporation temperature and time applied are also given.

6.9 Safety at work

Dichloromethane, used as solvent, is readily vaporised and a respiratory poison. The solvent vapours irritate mucous membranes (sore throat) and eyes and cause headache, dizziness and nausea (see safety information).

Tar contains benzene and polyaromatic hydrocarbons (PAH compounds), which may cause occupational cancer. Most of the tar model substances are especially dangerous to health (see safety information).

All sample handling shall be carried out in the fume cupboard. Safety gloves and respirator masks shall be used.

7. Assessment of methods

The gas chromatographic analysis is laborious, and requires high expertise and experience from the operator. The automatically starting BASIC program requires that the run conditions of the chromatograph stay very stable. Identification of peaks shall be checked with a model solution prior to each series of analysis, and the calibration data of the integrator is edited accordingly when necessary.

Starting values of gas collection cannot be corrected in the report of analysis if fed incorrectly in the sample sheet. The data shall be corrected in the sample sheet, and a new chromatographic analysis shall be carried out. On the other hand, if calibration data should be corrected, a new .UA2 report can be formed by the ANALYZE command of the integrator without any new gas chromatographic analysis.

The gravimetric determinations are suitable for characterising the total content of the heaviest tar compounds, for example, when monitoring variations in the tar content in a certain process. The results are affected by the concentration and composition of the sample solution, and consequently, the measuring results obtained for different types of processes or for samples taken by different methods are not necessary comparable with each other.

Enclosure to Appendix D

1 Light tar determinations

Equipment: HP 5890 gas chromatograph
HP 3396A integrator

Column: HP Ultra 2 (Crosslinked 5% Ph Me silicone)
length 50 m, diameter 0.32 mm, film thickness 0.52 µm

Detector: FID (temperature 310 °C)

Injector: Split/splitless injector, temperature 280 °C

Carrier gas: Helium, injector pressure about 120 kPa, total flow about 20 ml/min

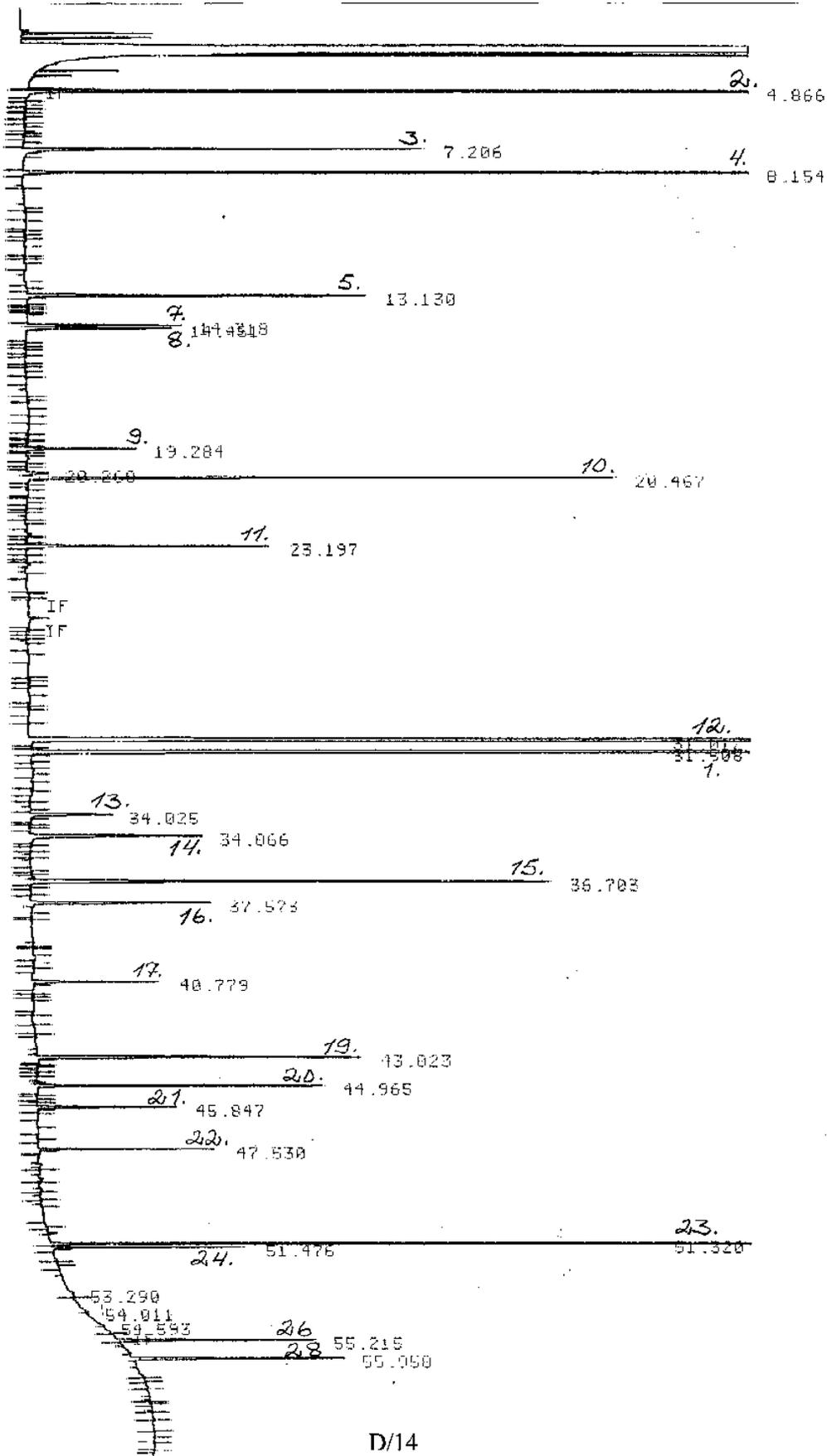
Oven: Start 50 °C, initial holding time 5 min, heating rate 3.0 °C/min to
160 °C, then heating rate 10.0 °C/min to 290 °C, holding time 15 min.

Injection: Autosampler 1 µl, split injection, sample in dichloromethane.

Calibration:

- 1 Dodecane ISTD
- 2 Benzene
- 3 Pyridine
- 4 Toluene
- 5 M-Xylene
- 6 Ethynylbenzene
- 7 Styrene
- 8 O-Xylene
- 9 Phenol
- 10 4-Methylstyrene
- 11 Indene
- 12 Naphthalene
- 13 Quinatsoline
- 14 Isoquinatsoline
- 15 2-Methylnaphthalene
- 16 1-Methylnaphthalene
- 17 Biphenyl
- 18 2-Ethyl-naphthalene*
- 19 Acenaphthylene
- 20 Acenaphthene
- 21 Dibenzofurane
- 22 Fluorene
- 23 Phenanthrene
- 24 Anthracene
- 25 4II-Cyclopenta(def)phenanthrene*
- 26 Fluoranthene
- 27 Benz(e)acenaphthylene*
- 28 Pyrene

* not in the chromatogram enclosed

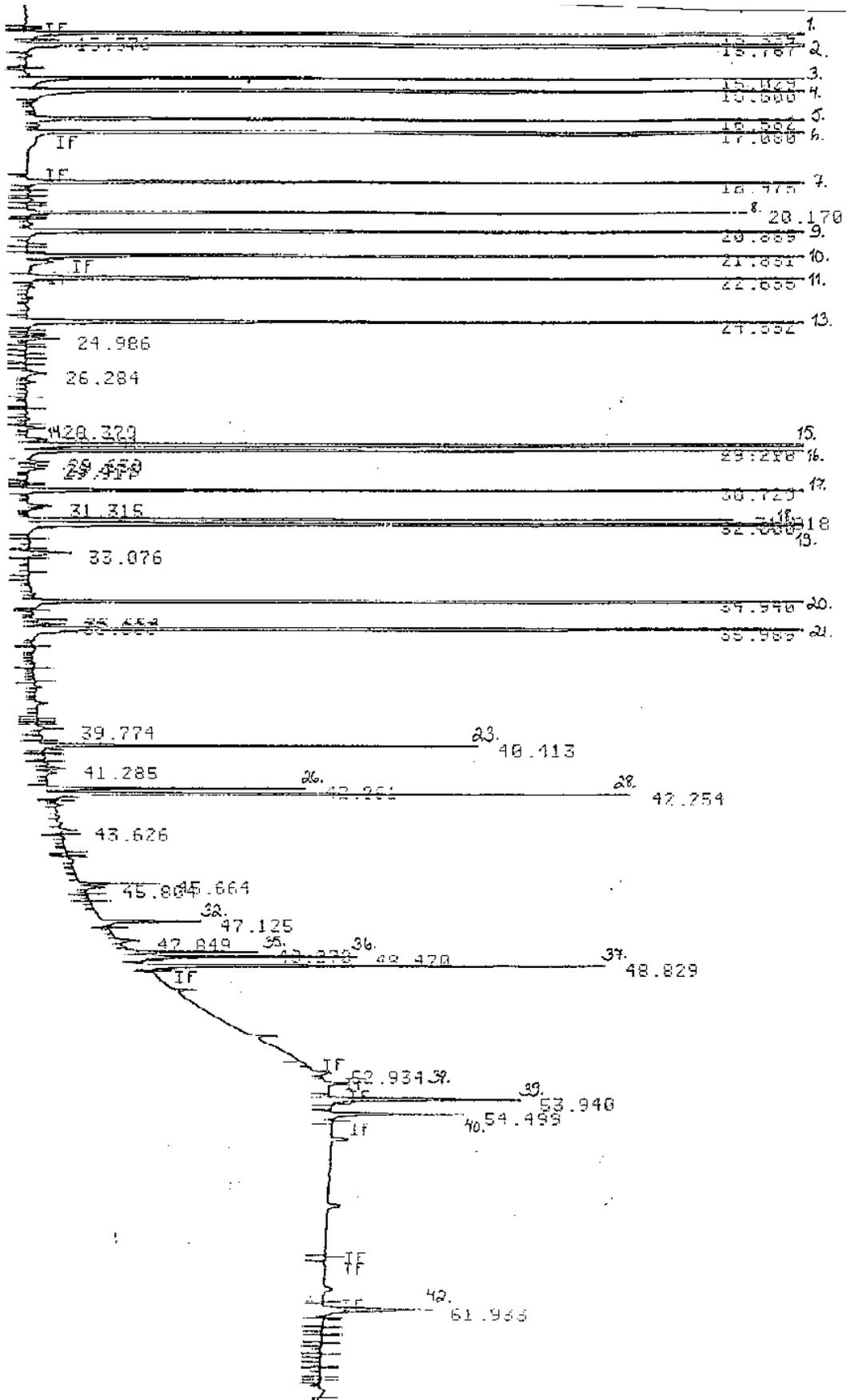


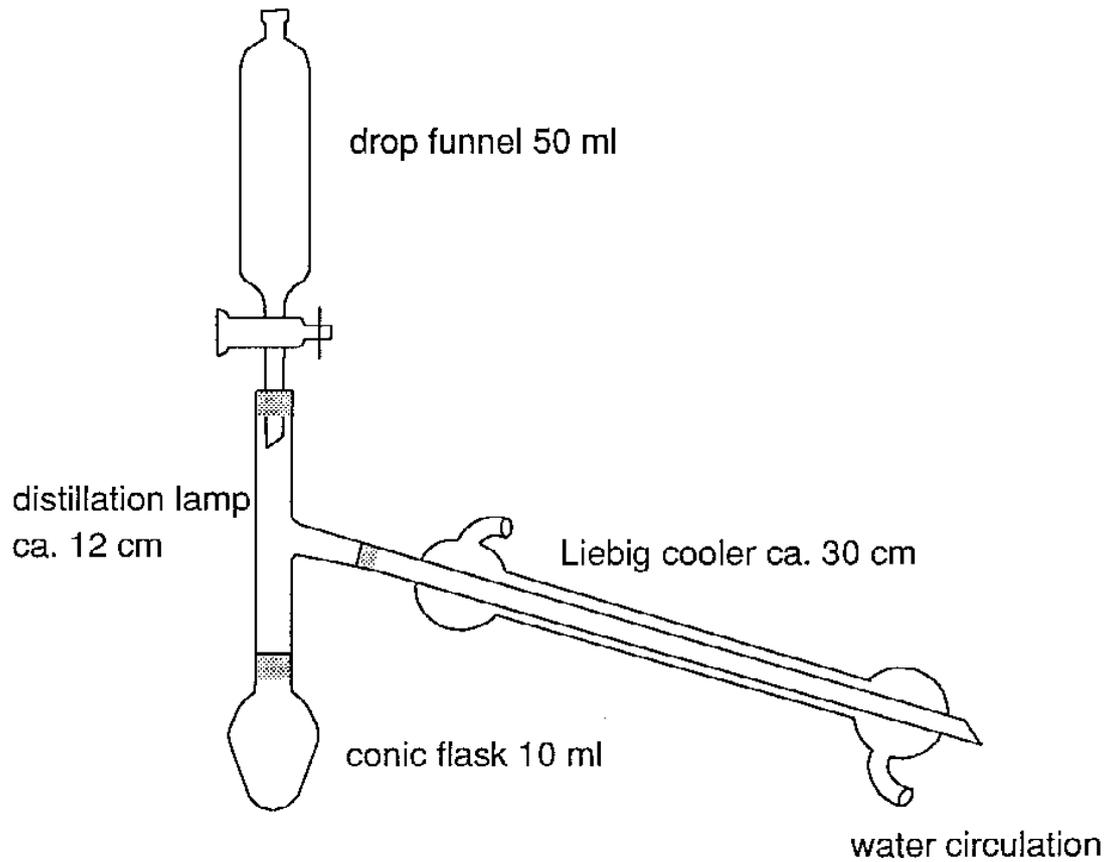
2 Heavy tar determinations

Equipment:	HP 5890 gas chromatograph HP 3396A integrator
Column:	HP Ultra 2 (Crosslinked 5% Ph Me Silicone) length 25 m, diameter 0.32 mm, film thickness 0.52 µm
Injector:	Split/splitless injector, temperature 300 °C
Carrier gas:	Helium, injector pressure about 70 kPa, total flow about 21 ml/min
Detector:	FID (temperature 310 °C)
Oven:	Start 60 °C, initial holding time 2.00 min, heating rate 5.0 °C/min to 300 °C, holding time 30 min
Injection:	Autosampler 1 µl, split injection, sample in dichloromethane
Calibration:	<ol style="list-style-type: none">1 Naphthalene2 Dodecane ISTD3 Quinatsoline4 Isoquinoline5 2-Methylnaphthalene6 1-Methylnaphthalene7 Biphenyl8 1,6 Dimethylnaphthalene9 Acenaphthylene10 Acenaphthene11 Dibenzofurane12 2-Methyl-1-naphthol*13 Fluorene14 Dibenzothiophene*15 Phenanthrene16 Anthracene17 1-Phenylnaphthalene18 2-Methylanthracene19 4H-Cyclopenta(def)phenanthrene20 Fluoranthene21 Pyrene22 2,3-Benzofluorene*23 1,1' Binaphthyl24 Benzo(g,h,i)fluoranthene*25 Cyclopenta(cd)pyrene*26 1,2 Benzanthracene27 Triphenylene*28 Chrysene29 2,3 Benzanthracene*30 1-Methylchrysene*31 2,2' Binaphthyl*32 Benzo(b)fluoranthene

- 33 Benzo(j)fluoranthene*
 - 34 Benzo(k)fluoranthene*
 - 35 Benzo(c)pyrene
 - 36 Benzo(a)pyrene
 - 37 Perylene
 - 38 Indeno(1,2,3,-cd)pyrene
 - 39 Benzo(ghi)perylene
 - 40 Anthanthrene
 - 41 Dibenz(a,l)pyrene*
 - 42 Coronene
 - 43 Dibenz(a,e)pyrene*
 - 44 Dibenz(b,def)chrycene*
- *not in the chromatogram enclosed*

** not in the chromatogram enclosed*





Distillation equipment.