Sampling of tar from sewage sludge gasification using solid phase adsorption

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Abstract Sewage sludge is a residue from wastewater treatment plants which is considered to be harmful to the environment and all living organisms. Gasification technology is a potential source of renewable energy that converts the sewage sludge into gases that can be used to generate energy or as raw material in chemical synthesis processes. But tar produced during gasification is one of the problems for the implementation of the gasification technology. Tar can condense on pipes and filters and may cause blockage and corrosion in the engines and turbines. Consequently, to minimize tar content in syngas, the ability to quantify tar levels in process streams is essential. The aim of this work was to develop an accurate tar sampling and analysis methodology using solid phase adsorption (SPA) in order to apply it to tar sampling from sewage sludge gasification gases. Four types of commercial SPA cartridges have been tested to determine the most suitable one for the sampling of individual tar compounds in such streams. Afterwards, the capacity, breakthrough volume and sample stability of the Supelclean™ ENVI-Carb/NH_2, which is identified as the most suitable, have been determined. Basically, no significant influences from water, H_2S or NH_3 were detected. The cartridge was used in sampling real samples, and comparable results were obtained with the present and traditional methods.

Keywords Tar sampling · Gasification · Solid phase adsorption · Gas chromatography-mass spectrometry

Introduction

Sewage sludge refers to the waste product left from industrial and domestic wastewater treatment plants and contains amounts of heavy metals, organic toxins and pathogenic microorganisms. Sewage sludge is considered to be harmful to the environment and all living organisms, so its disposal represents one of the most important issues for environmental management in Europe [1, 2].

Although sewage sludge has been widely used as a fertiliser in many regions all over the world [1, 3, 4], there are some important limitations, such as the high metal content present in the sewage. Thus, the necessity of investigating alternative management options is evident [5]. Gasification is an alternative and sustainable process to sewage sludge disposal method.

Gasification is a technology that thermally converts the sewage sludge into gases that can be used to generate energy or used as raw material in chemical synthesis processes whilst reducing the volume of waste and leaving heavy metals in the residual solid ash for final disposal [1-3, 6]. However, one of the remaining problems still to be solved is the reduction of the high level of tar present in the product gas [7, 8].

Tar easily condenses on the surface of pipes and filters and may cause blockage and corrosion in the engines and turbines used in the application of the producer gas [8-12]. Hence, tar control and conversion is one of the most important technical barriers for a successful application of the technology in the power markets [10, 13]. To minimize tar content in syngas, the ability to quantify tar levels in process

streams is essential in gasification research and commercial gas production [14].

The technical specification CEN/TS 15439, Biomass gasification−Tar and particles in product gases−Sampling and analysis [15], defines tar as a "generic (unspecific) term for all organic compounds present in the gasification prod- uct gas excluding gaseous hydrocarbons (C1 through C6)". This definition excludes benzene as a tar despite being one of the major and more stable aromatic compounds in real gasification gas. Benzene may cause problems in catalytic gas conversion and has been classified by the EPA as a known human carcinogen of medium carcinogenic hazard [16, 17]. Therefore, monitoring benzene is important from the standpoint of environmental and occupational health.

Tar is a very complex heterogeneous mixture of organic molecules (aromatics, phenols, bases, asphaltenes, preasphaltenes and particulate matter) whose amount in the gas will depend on the operating conditions (temperature, residence time, pressure, bed height, feedstock, reactor design) [14, 18].

In fluidized bed gasification of biomass, the typical total tar content is in the range of 2-10 g/m^3 [9], and the main components are benzene and naphthalene [19].

Little information is available about sewage sludge gasification, but some studies have shown the aromatic characteristics of tar [18, 20, 21]. Polycyclic aromatic compounds with heteroatom substitution (mainly O and N) was observed, but naphthalene was one of the main compounds found [18, 20].

Methods for the sampling and analysis of tar can be on-line or off-line. The sampling part of the off-line methods is based on trapping the tar by condensation on cold surfaces or filters, by absorption in a cold organic solvent or, more recently, by adsorption on suitable sorbents. The analysis of tars is most often performed by gas chromatography (GC) or gravimetrically [10].

Traditional methods for tar sampling, based on cold trapping coupled with solvent absorption in impingers, are the most used by researchers; especially, the European tar protocol is the most popular and accepted by researchers [10]. The European tar protocol is developed in the technical specification CEN/TS 15439 which recommends a series of impinger bottles containing isopropanol for tar absorption. This sampling method has drawbacks due to the long period for sampling and troublesome preparations. Due to these disadvantages, some researchers used solid phase adsorption (SPA) for tar sampling [12, 22, 23].

The favourable features that distinguish SPA from traditional sampling methods include simplicity, speed of sampling, less solvent consumption, faster workup, accuracy and repeatability. However, this method is so far only applicable to light tar compounds up to a molecular weight of 300 (coronene) [12, 22].

The aim of this work was to develop an accurate tar sampling and analysis methodology alternative to impinger bottles filled with isopropanol using SPA in order to apply it to tar sampling from sewage sludge gasification gas. The principle of this method is that tar compounds in vapour phase can be trapped on a porous adsorbent at ambient temperatures [12]. Four types of commercial SPA cartridges have been tested to determine the most suitable one for the sampling of individual tar compounds in that stream. Then, the performance of the selected cartridge was evaluated. Relevant parameters have been studied: breakthrough volume, capacity, stability and influence of some gas components.

Experimental

Materials

Taking into account the main compounds found in tar generated in the gasification of sewage sludge, the following compounds were selected: benzene, toluene, naphthalene, phenanthrene and phenol. These compounds were obtained from Scharlau, Merck and Sigma-Aldrich as individual pure compounds with at least 99.5 % purity. Stock solutions (10,000 μg/mL benzene, 10,000 μg/mL toluene, 5,000 μg/mL naphthalene, 5,000 μg/mL phenanthrene and 5,000 μg/mL phenol) were prepared from pure compounds in dichloromethane. All standards prepared from stock solutions were placed in sealed flasks and refrigerated at −4 °C until their analysis.

As an internal standard, 4-bromofluorobenzene 2,000 μg/mL in methanol was obtained from Supelco. Dichloromethane (DCM), acetone, acetonitrile and 2-propanol of GC grade were acquired from SDS or Riedel-de Haën. Four commercial cartridges were selected for tar sampling: Discovery® DSC-NH_2, Supelclean™ ENVI-Chrom P, Supelclean™ ENVI-Carb/NH_2 and Supelclean™ ENVI-Carb II/PSA.

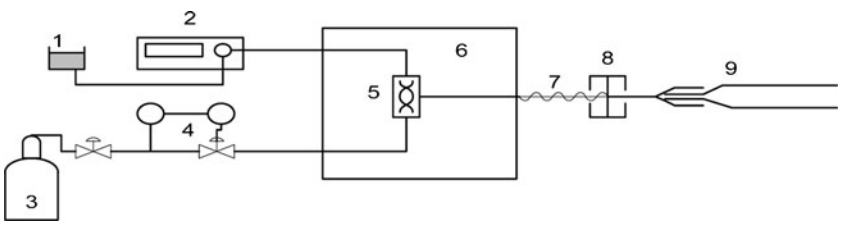


Fig. 1 Simplified diagram of Microactivity Pro unit. *1* Solution, *2* liquid pump, *3* gas cylinder, *4* mass flow controller, *5* homogenisation unit, *6* hot box, *7* hot pipe, *8* septum, *9* SPA column with needle

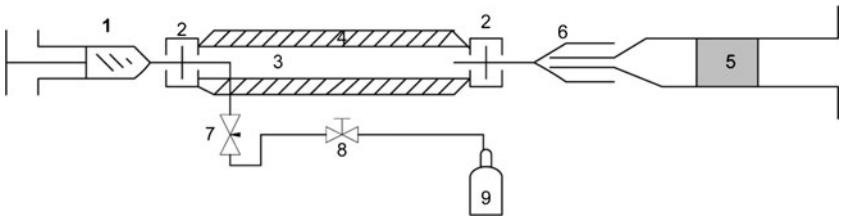


Fig. 2 TES device. *1* Standard GC syringe, *2* septum, *3* steel tube, *4* heating tape, *5* SPA cartridge, *6* needle, *7* needle valve, *8* stop valve, *9* gas cylinder

NH_2 cartridges were used by Brage et al. [14] for biomass gasification tar sampling. Chrom P cartridges are a highly cross-linked styrene divinylbenzene resin used to retain hydrophobic compounds with some hydrophilic functionality under reversed phase conditions (http://www.sigmaaldrich.com/spain.html). The PSA phase is a polymerically bonded ethylenediamine-*N*-propyl phase. It has greater capacity than DSC-NH_2 because it contains both primary and secondary amines (http://www.sigmaaldrich.com/spain.html). Carb and Carb II phases are graphitized non-porous carbons which improve the retention of volatile organic compounds.

Test facility

Two different systems were employed to produce test tar samples: a Microactivity Pro Unit which was used to select the cartridge most suitable for collecting tar and an in-house device, referred to in this article as tar evaporator system (TES), which was used for further characterization of the cartridge selected as the most promising.

Microactivity Pro Unit is a commercial lab-scale test rig which consists of a pump to provide the liquid tar solution, mass flow controllers to supply gas streams and a hot box (200 °C) where the liquid solution is evaporated and mixed with the gas stream.

The tar evaporator system consists of a custom-made device comprising an injector port with a controlled carrier gas supply and a tube heated up to 200 °C by means of an insulated heating tape coiled around the tube. The tar solution is introduced through the injector septum using a standard GC syringe. The tar solution vaporises in the flow of gas, allowing analytes to reach the SPA cartridges in the gaseous phase.

Both systems allow vaporising a solution of tar and mixing it with nitrogen to simulate the gas stream generated by a gasifier. The difference was that the Microactivity Pro Unit generates a continuous gas stream, whilst the TES device generates a discrete gas stream. Simplified diagrams of both systems are shown in Figs. 1 and 2.

The sampling setup consists of a syringe needle, SPA column without preconditioning and a syringe connected in series. Samples are taken by a septum port of a T-connection located at the outlet of the sampler system. A sample of 100 mL of gas is taken by pulling back the syringe plunger.

Analysis

After sampling, the cartridges were eluted immediately. Discovery® DSC-NH_2 cartridges were eluted with 2 mL of DCM and 2 mL of acetonitrile/2-propanol/DCM (8:1:1). Supelclean™ ENVI-Chrom P cartridges were eluted with 2 mL of DCM, and Supelclean™ ENVI-Carb/NH_2 and Supelclean™ ENVI-Carb II/PSA cartridges were eluted with 3 mL DCM and 2 mL of acetone. All extracts were analysed after adding the internal standard (4-bromofluorobenzene) using GC-MS. A Hewlett Packard 5890 series II chromatograph coupled to a Hewlett Packard 5971A mass spectrometer was employed. Volumes of 1 μL were injected. The operating conditions were as follows: initial oven temperature of 60 °C; held for 1 min then increased at a rate of 3 °C/min to 105 °C, increased at a rate of 8 °C/min to 250 °C, increased at a rate of 5 °C/min to 260 °C and held for 5 min; injector temperature of 250 °C; operation mode: splitless; carrier gas: He at 21 kPa; capillary column: ZB-624 (30 m×0.25 mm×1.40 μm); detector operated in electronic impact mode (70 eV); detector mode: SIM (78, 91, 94, 128, 178).

Quality of analytical methodology

To determine the quality of the analytical results, the following parameters were determined: precision, linearity, sensitivity, selectivity and quantification and detection limits.

To obtain calibration curves, five standard solutions with internal standard were analysed in triplicate and the least squares linear fit performed. Correlation coefficients obtained for all analytes were 0.999, except for naphthalene ($r^2$00.994). The sensitivity, defined as the slope of the calibration curve, the detection limits and the quantification limits are shown in Table 1. Blank cartridges were treated in

Table 1 Quality parameters of the analytical methodology

Compound	Sensitivity (mL/μg)	Detection limit (μg/mL)	Quantification limit (μg/mL)
Benzene	1.72	0.03	0.10
Toluene	1.61	0.15	0.48
Phenol	1.42	0.10	0.30
Naphthalene	2.29	0.01	0.03
Phenanthrene	1.14	0.06	0.21

Table 2 Recovery study 1-Discovery® DSC-NH_2, 2-Supelclean™ ENVI-Chrom P, 3-Supelclean™ ENVI-Carb/NH_2, 4-Supelclean™ ENVI-Carb II/PSA

Compound	R_1 (%)		R_2 (%)		R_3 (%)		R_4 (%)	
	With nitrogen stream[a]	Without nitrogen stream[b]	With nitrogen stream	Without nitrogen stream	With nitrogen stream	Without nitrogen stream	With nitrogen stream	Without nitrogen stream
Benzene	11±2	91±3	71±5	109±15	90±1	84±14	85±7	105±15
Toluene	74±3	104±9	79±3	94±14	93±1	100±15	88±5	90±6
Phenol	91±5	106±15	83±2	108±9	92±5	97±2	92±4	100±13
Naphthalene	90±3	103±7	81±2	96±7	103±1	103±11	89±2	97±15
Phenanthrene	95±2	104±15	76±2	105±8	75±8	76±11	76±10	72±11

[a] Elution after the application of a nitrogen stream

[b] Elution immediately after the addition of the standard solution

the same way that samples and no interferences were detected.

Results and discussion

Recovery study

Before doing actual tar sampling experiments on the devices described in "Test facility", a recovery study was performed. To evaluate the recovery of the selected compounds, 10 μL of a standard solution in DCM with 26.5 μg/μL of benzene, 30 μg/μL of toluene, 7 μg/μL of phenol, 8 μg/μL of naphthalene and 11.4 μg/μL of phenanthrene was added to each cartridge. Then, two methods were carried out: (a) elution with organic solvents was performed immediately after the addition of the standard solution, and (b) a stream of nitrogen was applied before proceeding to the elution with organic solvents of the retained compounds to simulate the flow of the gas stream through the cartridge. The recovery study was performed in triplicate for both methodologies; the samples were analysed by GC-MS (Table 2).

Some differences for Discovery® DSC-NH_2 and Supelclean™ ENVI-Chrom P cartridges in the recovery of the selected compounds between both methods were observed. In Discovery® DSC-NH_2 cartridges, when the stream of nitrogen flowed through them, a decrease of around 80 % in the recovery of benzene and 25 % in toluene was observed, which may be due to a low breakthrough volume or a low retention capacity for these compounds. In Supelclean™ ENVI-Chrom P cartridges, this effect is not so pronounced and recovery decreased just by 30 and 20 %, respectively. On the other hand, for the heavy compounds like phenanthrene, high recoveries are not obtained for any of the studied cartridges, except for the DSC-NH_2 cartridge, which may be due to irreversible adsorption.

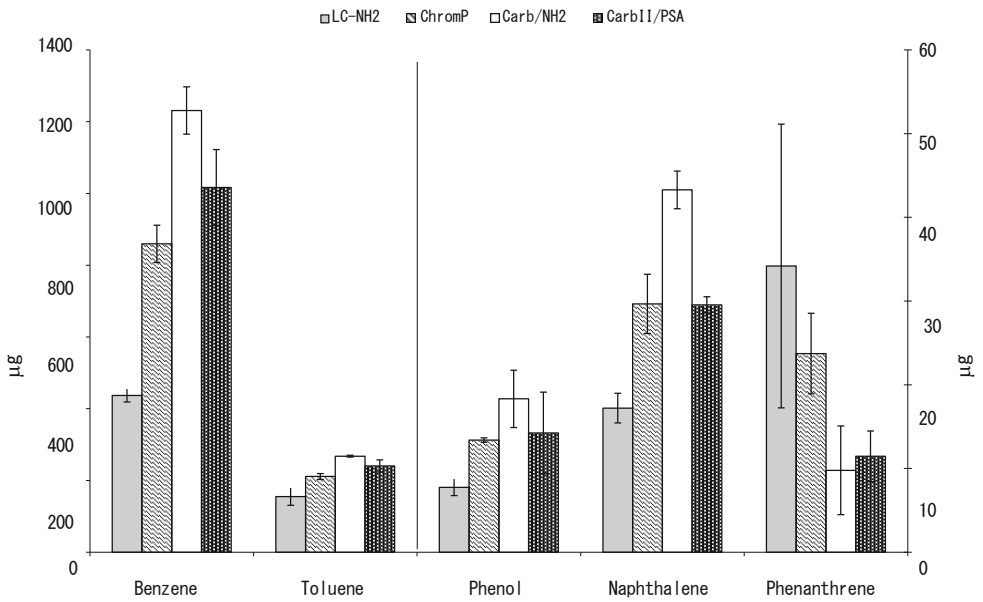


Fig. 3 Study of the retention of the different types of SPA cartridges

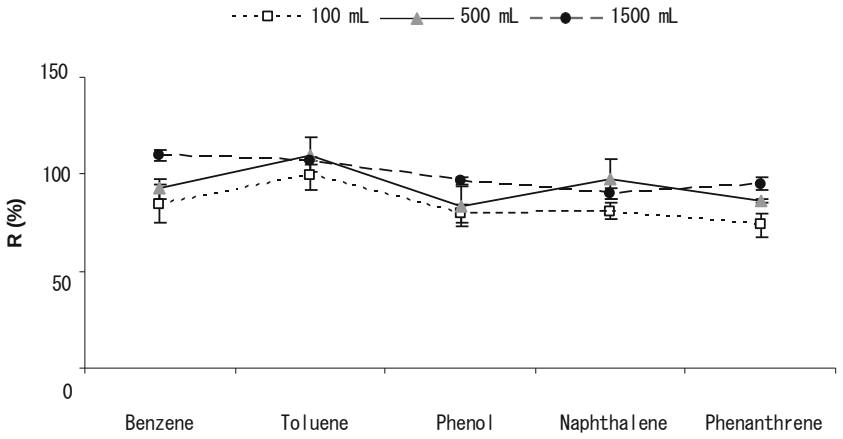


Fig. 4 Evaluation of the breakthrough volume of Supelclean™ ENVI-Carb/NH_2 cartridges

Selection of the most suitable cartridge for tar sampling

To study the most suitable cartridge for tar collection and analysis, a controlled stream of selected tar compounds was generated introducing into the Microactivity Unit a solution with 2,800 mg/L of benzene, 800 mg/L of toluene and phenol, and 200 mg/L of naphthalene and phenanthrene. Of the generated stream, 100 mL was sampled with each type of cartridge in triplicate. The results are shown in Fig. 3.

Of the four selected cartridges, Supelclean™ ENVI-Carb/NH_2 has shown greater capacity to sample compounds like naphthalene and benzene, which are usually the most abundant tar compounds in gasification gases. However, it has a low capacity to retain phenanthrene. This may be due to the low recovery obtained for this compound. Supelclean™ ENVI-Chrom P and Supelclean™ ENVI-Carb II/PSA cartridges have similar holding capacities, but lower than the Supelclean™ ENVI-Carb/NH_2 cartridge, whilst Discovery® DSC-NH_2 has shown the least holding capacity to the compounds studied, except for phenanthrene.

Study of the Supelclean™ ENVI-Carb/NH_2 cartridge breakthrough volume

The breakthrough volume was studied increasing gradually the volume of gas sampled whilst the tar concentration was maintained constant.

When collecting tar from gaseous sources using SPA methods, the gas volume usually sampled is 100 mL [14, 16]. This volume is generally enough to reach the analytical detection limits for most tar compounds. But it can be necessary to increase the volume of the sampled gas if one wants to determine other tar components which are in low concentrations in the gas stream. Therefore, it is important to ensure that there is no loss of analytes when the volume of the gas sampled is increased. To this aim, for this study, 100, 500 and 1,500 mL of gas were sampled.

In Fig. 4, the recoveries (R) against the sampling gas volumes are depicted. The results show that recovery does not decrease when the sampling gas volume increases, so the breakthrough volume was not reached under the studied conditions. The breakthrough volume for all compounds evaluated is >1.5 L.

Capacity of the Supelclean™ ENVI-Carb/NH_2 cartridges

To assess the capacity of the Supelclean™ ENVI-Carb/NH_2 cartridges, the amount of analytes injected into them was increased gradually, while the volume of the gas sampled was maintained as constant. The mass of individual compounds injected range from 0.1 to 4 mg for benzene, 0.1 to 3 mg for toluene, 0.02 to 0.6 mg for phenol, 0.03 to 0.5 mg for naphthalene and from 0.02 to 0.8 mg for phenanthrene.

As Figs. 5 and 6 show, no significant decrease in the recovery of the studied compounds was observed when the

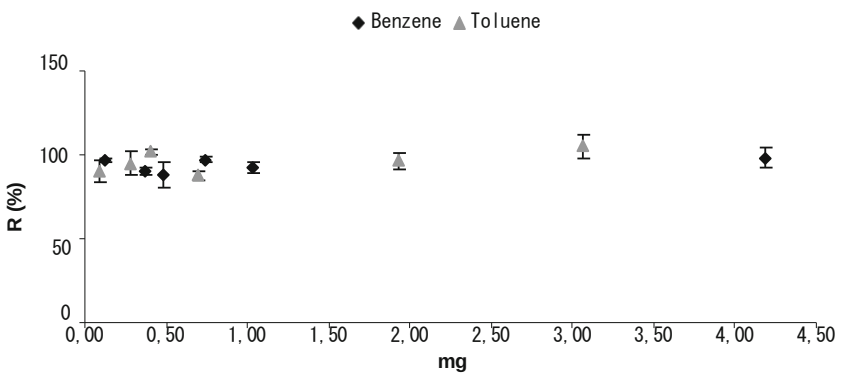


Fig. 5 Evaluation of the Supelclean™ ENVI-Carb/NH_2 cartridge capacity for benzene and toluene

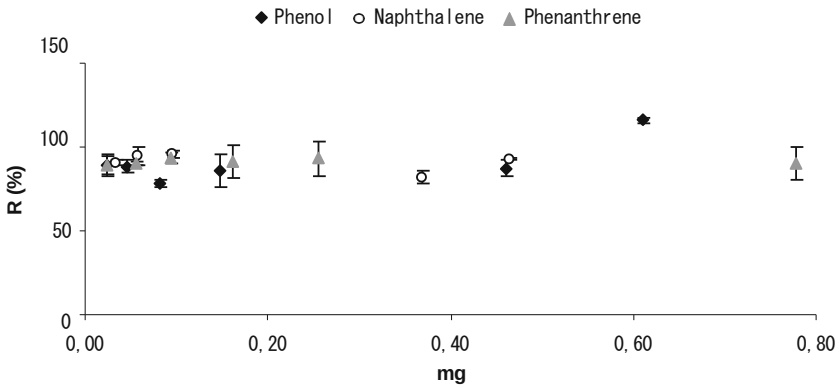


Fig. 6 Evaluation of the Supelclean™ ENVI-Carb/NH_2 cartridge capacity for phenol, naphthalene and phenanthrene

amount of analyte was increased. Therefore, the capacity was not exceeded for any of the compounds studied. It can be concluded that the Supelclean™ ENVI-Carb/NH_2 cartridge capacity is over 4.18 mg for benzene, 3.06 mg for toluene, 0.61 mg for phenol, 0.47 mg for naphthalene and 0.78 mg for phenanthrene.

The results indicate that with Supelclean™ ENVI-Carb/NH_2 is possible to sample gases with at least 42 g/Nm^3 of benzene, 31 g/Nm^3 of toluene, 6 g/Nm^3 of phenol, 5 g/Nm^3 of naphthalene and 8 g/Nm^3 of phenanthrene. Our experience in the sewage sludge gasification in a fluidized bed gasifier shows that the product gas has around 10 g/Nm^3 of tar in total, of which around 80 % are volatile compounds (benzene and toluene), so the values found are higher than the concentration level expected in gas from the gasification of sewage sludge; therefore, Supelclean™ ENVI-Carb/NH_2 cartridges would be suitable for tar collection.

Stability of the samples taken with Supelclean™ ENVI-Carb/NH_2 cartridges

The stability of the samples has been determined at different storage conditions. The samples were stored at 4 and −18 °C for 1–7 days. The results are shown in Fig. 7.

Regardless of the temperature used, the storage of samples for 1 day produces no loss of analytes, except for phenol for which there was a slight decrease that can reach 6 % loss. Storage for 7 days produces greater loss of compounds, which was more important in the case of storage at 4 °C in which losses of 33 % for phenol and 10 % for naphthalene were observed.

Influence of some gas components in the retention capacity of Supelclean™ ENVI-Carb/NH_2 cartridges

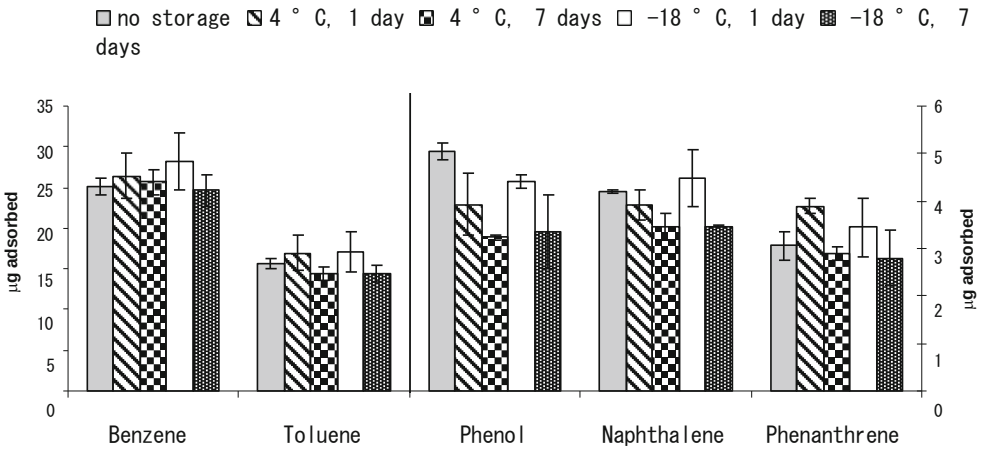
The influence of water, hydrogen sulphide and ammonia in the retention capacity of Supelclean™ ENVI-Carb/NH_2 cartridges was evaluated.

Actual gasification gases contain a significant amount of steam which is known to adsorb strongly on solid adsorbents. Hydrogen sulphide and ammonia are contaminants of the gas generated in the gasification of sewage sludge that can be trapped in the carbon phase of the selected cartridge. Therefore, the presence of any of these compounds in the gas could modify the holding capacity of the cartridges.

The influence of each compound was evaluated individually. To study the influence of water in the adsorption efficiency of the cartridges, a nitrogen stream was saturated with water. The stream was forced to bubble into an impinger bottle filled with water at an ambient temperature. To evaluate the influence of hydrogen sulphide and ammonia, experiments were conducted using mixtures with two concentration levels of hydrogen sulphide (100 and 1,000 ppm, *v*/*v*) or ammonia (1,000 and 5,000 ppm, *v*/*v*) in a nitrogen stream used as the carrier gas.

For the studied compounds, no significant differences were observed in the retention capacity when water or ammonia in the gas stream was present (see Electronic

Fig. 7 Results of the stability study of Supelclean™ ENVI-Carb/NH_2 cartridges



supplementary material (ESM) Figs. S1 and S2). Even a slight increase in the retention capacity for phenanthrene can be seen when the nitrogen stream was saturated with water. On the other hand, an increase in the variability of the results was observed due to the water vapour in the gas stream.

The presence of hydrogen sulphide does not interfere with the sampling of the compounds studied, except in the case of phenanthrene for which a poorer performance of the cartridge was achieved upon increasing the concentration of H_2S in the gas (see ESM Fig. S3).

Application to tar sampling from actual sewage sludge gasification gas

The developed SPA method was used to check one of the stages of gas cleaning. Real samples from an atmospheric bubbling fluidised bed gasifier with a capacity of 100 kg/h of dried sewage sludge were taken with Supelclean™ ENVI-Carb/NH_2 cartridges coupled with a needle and a syringe. Samples were taken by a septum port of a T-connection located at the outlet of the gasifier. A sample of 100 mL of gas is taken by pulling back the syringe plunger. Immediately after the sampling, cartridges were eluted with 3 mL of DCM and 2 mL of acetone, and extracts were refrigerated at −4 °C until their chromatographic analysis.

Sampling was accomplished fast, easily and successfully, proving that it can be implemented as an alternative method to the solvent absorption method recommended by the technical specification CEN/TS 15439. Table 3 shows the results obtained for samples before and after the cleaner filter. Expanded uncertainty calculated using a coverage factor of 2, which gives a level of confidence of approximately 95 %, is shown in parentheses. The results show that the SPA method is valid for determining the ability of tar removal in the filter.

The developed SPA method was compared with the traditional method which consists of a series of impinger bottles with isopropanol. Simultaneous sampling was carried out in the gasifier mentioned above. The first results are shown in Table 4. To evaluate the results, a *t* test was used. This test indicates that tar sampling with Supelclean™ ENVI-Carb/NH_2 cartridges yields tar concentration measurements which are comparable to those obtained when using impinger bottles, except for phenol.

Table 3 Performance of the cleaning system

Compounds	BF (g/Nm^3)	AF (g/Nm^3)
Benzene	2.80 (0.4)	1.51 (0.21)
Toluene	0.99 (0.17)	0.59 (0.10)
Phenol	0.02 (0.004)	-
Naphthalene	0.75 (0.08)	0.03 (0.003)
Phenanthrene	0.03 (0.003)	0.003 (0.0003)

Concentration and expanded uncertainty

BF before filter, *AF* after filter

Table 4 Comparison between the traditional sampling method and sampling with solid phase adsorption

Compounds	SPA (mg/Nm^3)	Traditional method (mg/Nm^3)
Benzene	344 (48)	319 (54)
Toluene	556 (95)	453 (68)
Phenol	105 (23)	287 (63)
Naphthalene	208 (31)	240 (60)
Phenanthrene	233 (26)	222 (42)

Conclusions

For this work, SPA cartridges were chosen instead of impinger bottles for tar sampling due to their potential advantages. Four types of commercial SPA cartridges have been tested to determine the most suitable one for the sampling of the individual tar compounds from sewage sludge gasification gas. Supelclean™ ENVI-Carb/NH_2 cartridges were shown as the most promising and were chosen for further studies because they presented more retention capacity for naphthalene and benzene, which are usually the most abundant aromatic species in gasification gases. The breakthrough volume for these cartridges was over 1.5 L. The results show that the capacity is higher than the expected levels for all the main tar compounds in gasification gases. The stability results indicate that the samples can be stored for 7 days at −18 °C, but with some losses of phenol and naphthalene. The presence of water, hydrogen sulphide or ammonia in gas stream does not produce significant alterations in the retention capacity of the selected cartridges. The Supelclean™ ENVI-Carb/NH_2 cartridges were successfully applied to tar sampling in a real gasification plant and was used to determine the efficiency of the cleaner filter. The first results show that comparable results are obtained with the traditional sampling method and with Supelclean™ ENVI-Carb/NH_2 cartridges.

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