

# Comparative sampling of gas phase volatile and semi-volatile organic fuel emissions from a combustion aerosol standard system

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## Highlights

- A CAST system generated a consistent source of fuel combustion emissions.
- A novel graphene wool sampler was tested for gaseous VOCs and SVOCs.
- More analytes were detected on the graphene wool sampler than other samplers.
- The graphene wool sampler provided better % RSDs compared to other samplers.
- The standard activated charcoal sampler was unsuitable due to high background.

## Abstract:

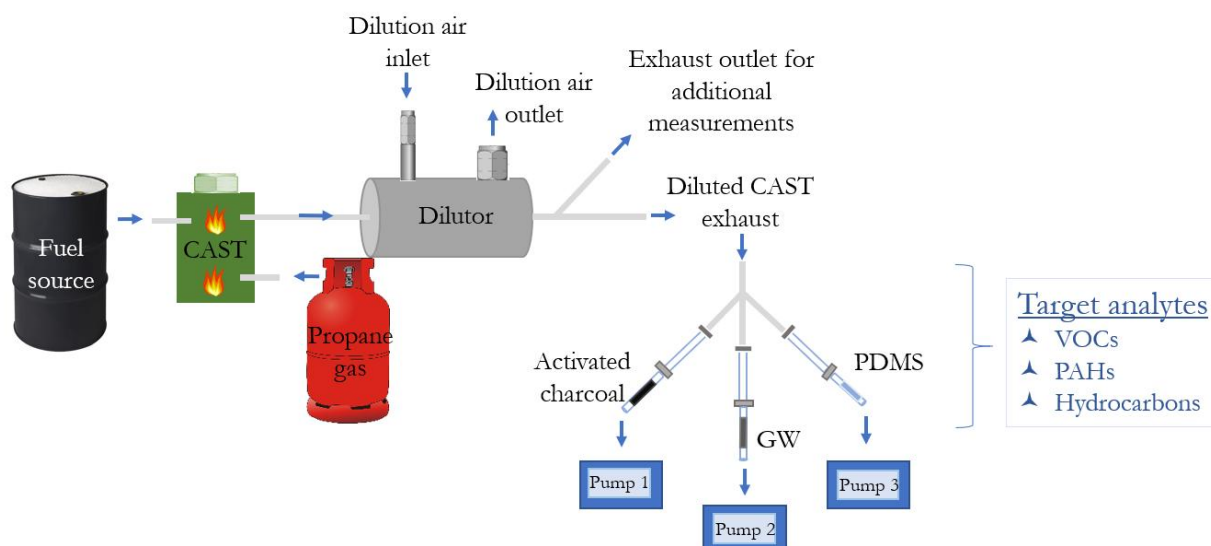
The incomplete combustion of fossil fuels generates hazardous gaseous compounds which have been linked to various adverse environmental and human health effects worldwide. Cleaner alternatives such as gas-to-liquid (GTL) and biofuels such rapeseed oil methyl ester (RME) have therefore been investigated. In this study, a Combustion Aerosol Standard (CAST) was used to generate a diluted, consistent and relatively stable source of fuel emissions from the combustion of diesel, GTL and RME, respectively. Gas phase sampling was carried out by removing particulates using a filter upstream of three different samplers: i) a commercialised activated charcoal sampler; ii) a validated polydimethylsiloxane (PDMS) sampler; and iii) a novel graphene wool (GW) sampler. The latter two were thermally desorbed, whilst the charcoal sampler was solvent extracted. All three samplers were analysed for trace levels of selected volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) by means of gas chromatography - mass spectrometry (GC-MS).

The GW sampler outperformed the PDMS and activated charcoal samplers as the GW sampled the most compounds and had a lower variability in VOC and SVOC (selected polycyclic aromatic hydrocarbon and n-alkane) concentrations sampled, especially in the case of the n-alkanes (average %RSDs of the GW, PDMS and activated charcoal samplers were found to be 23.8%, 43.1% and 52.9%, respectively). The activated charcoal sampler was found to be unsuitable in this study due to the low number of detected compounds, as well as high benzene and toluene backgrounds of the sorbent. Combustion of diesel was found to emit a total VOC and SVOC concentration 4-5 times that of GTL and RME, respectively, based on GW sampler analyses. This study therefore further supports GTL and RME as cleaner fuel alternatives to petroleum derived diesel.

## Capsule:

A novel graphene wool sampler allowed for the detection of more gaseous VOCs and SVOCs with better reproducibility than other samplers, including standard activated charcoal.

## Graphical abstract:



## Keywords:

CAST; graphene wool sampler; PDMS sampler; diesel combustion; biodiesel

## 1. Introduction

The detection of hazardous gaseous compounds has become ever more critical as an increasing number of studies link various adverse environmental and human health effects to increasing ambient air pollution (Landrigan et al. 2019; Goldemberg et al. 2018; Yan et al. 2018). Commonly known constituents of air pollution include compounds such as  $\text{NO}_x$ ,  $\text{SO}_x$ , CO and particulate matter (PM) in addition to volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs). Recent literature shows that vehicular emissions are generally reported in terms of the CO,  $\text{CO}_2$ ,  $\text{NO}_x$  and PM produced (Dagaut et al. 2019; Borillo et al. 2018; He 2016). There are multiple studies which have focused on the adverse side effects of PM (Bae and Hong 2018; Gautam et al. 2018; Hime et al. 2018; Chen et al. 2017; Künzli et al. 2005; Peters et al. 1997), which thereby warrants combustion emissions being reported in terms of PM production, however, it is also crucial to be cognisant of gaseous emissions, such as VOCs and SVOCs, as these have also shown to be detrimental to human health (Points 2019; Mirzaei

et al. 2016; Yu and Kim 2010; Jia et al. 2008; Kawamura et al. 2006). VOCs and SVOCs have been noted to be potentially carcinogenic and may cause the enhancement of respiratory, cardiovascular, infectious and allergic diseases through contact with the skin or through inhalation (Helen et al. 2019; Lerner et al. 2018; Raza et al. 2018; Bernstein et al. 2004; Finlayson-Pitts and Pitts Jr 1999 and 1997; Hemminki and Pershagen 1994). It has been noted that a trend towards using biodiesel over petroleum-derived diesel has arisen due to lower reported PM emissions from biodiesel combustion, therefore it is generally considered a cleaner alternative fuel (Damanik et al. 2018; Knothe and Razon 2017). However, little has been reported on the gaseous organic by-products released by the combustion of these biofuels.

As research into the effects of VOCs and SVOCs has progressed over the years, governing environmental bodies have made it ever more imperative to create a means by which to monitor even lower trace concentrations of these analytes. Currently, VOCs are typically sampled onto retaining media such as commercially available Carbotrap, Carbosieve<sup>TM</sup>S-III and Tenax<sup>®</sup> which are either carbon- or polymer-based samplers. SVOCs are commonly sampled onto the same retaining media as the VOCs in addition to retaining media such as multi-channel polydimethylsiloxane (PDMS) traps (Munyeza et al. 2018; Forbes and Rohwer 2009; Ortner and Rohwer 1996).

The use of carbon-based air samplers is not a novel concept in the field of environmental analysis, however a novel class of carbon nanostructures, known as graphene, is gaining attention in analytical chemistry due to many of its innately attractive properties. Graphene has been calculated to have an impressive theoretical specific surface area of 2630 m<sup>2</sup>g<sup>-1</sup> (Züttel et al. 2004) which is far above the 1000 m<sup>2</sup>g<sup>-1</sup> required of a “strong” sorbent (United States Environmental Protection Agency, 1999). Due to the ultrahigh surface area graphene possesses in combination with its non-polar nature, Schoonraad and Forbes developed a means to synthesize graphene in a way which allows facile use thereof as an adsorbent in an active air sampler, called a graphene wool (GW) sampler, as shown in Figure S1 in the Supplementary Information. (Schoonraad and Forbes, 2019a, 2019b) (Schoonraad et al. 2020).

A CAST generator, which is based on a laminar propane co-flow diffusion flame, is a useful way to produce stable trace level emissions that mimic the physical and chemical properties which are characteristic of real-world emissions from the combustion of selected fuel sources (Moore et al. 2014). To solve the difficulty of analysing combustion aerosols, which have a tendency to

coagulate, particles need to be produced instantaneously in a continuous process with reliable reproducibility (Kasper 2009) from a regulated aerosol generator. It is from this need that the CAST generator was developed, in which soot particles are formed when the combustion process is quenched with inert “quenching” gas, and its operation has been investigated by various authors (Mueller et al. 2015; Moore et al. 2014). In this study, trace level gas phase emissions which are simultaneously produced from a CAST generator were utilised to evaluate the performance of three different air samplers. Due to the various methods implemented to stabilise the exhaust emissions from the CAST generator, it has been viewed as a stable and repeatable source of PM of a certain size range (Mueller et al. 2015) and therefore the diluted exhaust stream may also be a source of trace levels of organic gas phase combustion emission products.

Here we describe the sampling of gas phase VOCs and SVOCs from a CAST generator utilising a filter upstream of each sampler to capture the PM and thereby only sample the gas phase analytes. The VOCs of interest included benzene, toluene, ethylbenzene and xylenes (BTEX), whilst SVOCs included n-alkane hydrocarbons and polycyclic aromatic hydrocarbons (PAHs). Emissions from each of three different fuel types were sampled from the CAST exhaust in parallel by three different samplers of interest, namely a multichannel PDMS sampler prepared in-house, a commercial activated charcoal sampler, and a novel GW sampler prepared in-house. The activated charcoal sampler was selected due to its use in VOC methods published by the International Organisation for Standardisation (ISO) and Methods for the Determination of Hazardous Substances (MDHS) (ISO 9487:1991 (E); ISO 16200-1:2001 (E) and MDHS 96 (2000)). Activated charcoal is also a cheaper alternative to graphitised materials such as Carbotrap<sup>®</sup>. The CAST system was utilised in this comparison of the performance of the chosen samplers due to the improved stability of emissions the system produces in comparison to real-world emissions, which typically would vary over time which in turn introduces sampling uncertainties. Other gas standard emission generators tend to produce only one compound at a time, and standard gas cylinder mixtures of VOCs cover a very limited range of analytes. The CAST system therefore provides a suitable means to evaluate the performance of the selected samplers, thereby allowing for the determination and evaluation of the strengths and weaknesses of each type of sampler in determining the concentrations of the target organic gas phase analytes at trace levels.

## **2. Materials and methods**

### **2.1. Reagents and materials**

The three fuels that were tested, namely petroleum derived diesel with no added biodiesel (B0), gas-to-liquid (GTL) and rapeseed oil methyl ester (RME) fuels were all purchased from ASG Analytik-Service GmbH, Neusäss, Germany. An ultrasonic bath was utilised to degas each fuel for 30 min prior to use.

Individual stock standards of 36 volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) along with 13 internal standards were purchased from the suppliers listed in Table S1 of the supplementary information. Working solutions were prepared by appropriate dilutions of the stock solutions prior to use. For the extraction of analytes from the activated charcoal sampler, anhydrous carbon disulphide (CS<sub>2</sub>) (>99% purity) was purchased from Merck, Germany.

### **2.2. Sampler details**

Each of the polydimethylsiloxane (PDMS) traps consisted of twenty-two 55 mm long parallel PDMS tubes (Technical Products, Inc., Georgia, USA) of 0.3 mm i.d. which were housed in a 89 mm long Supelco glass TD tube with an i.d. of 4 mm. Graphene wool (GW) was synthesised in-house as per the optimised conditions described by Schoonraad et al. (2020) using a quartz wool substrate (Acros, Industrial Analytical, South Africa). For the assembly of the GW samplers, approximately 120 mg of GW was weighed out using a calibrated Sartorius Entris analytical balance and then packed into the same glass tubing as the PDMS traps, whilst maintaining a bed length of 60 mm for the GW sampler. The sorbent was held in place by stainless steel screens (Sigma Aldrich, South Africa) which are designed for Gerstel TD tubes of the same i.d.. The traps were then conditioned using a multi-tube conditioner (TC-20 MARKES International, Germany) at 250 °C for 8 hrs under hydrogen gas flow and were then sealed using Shimadzu stainless steel tube caps. The activated charcoal type BIA tubes were purchased from Dräger, Germany.

### **2.3. CAST setup**

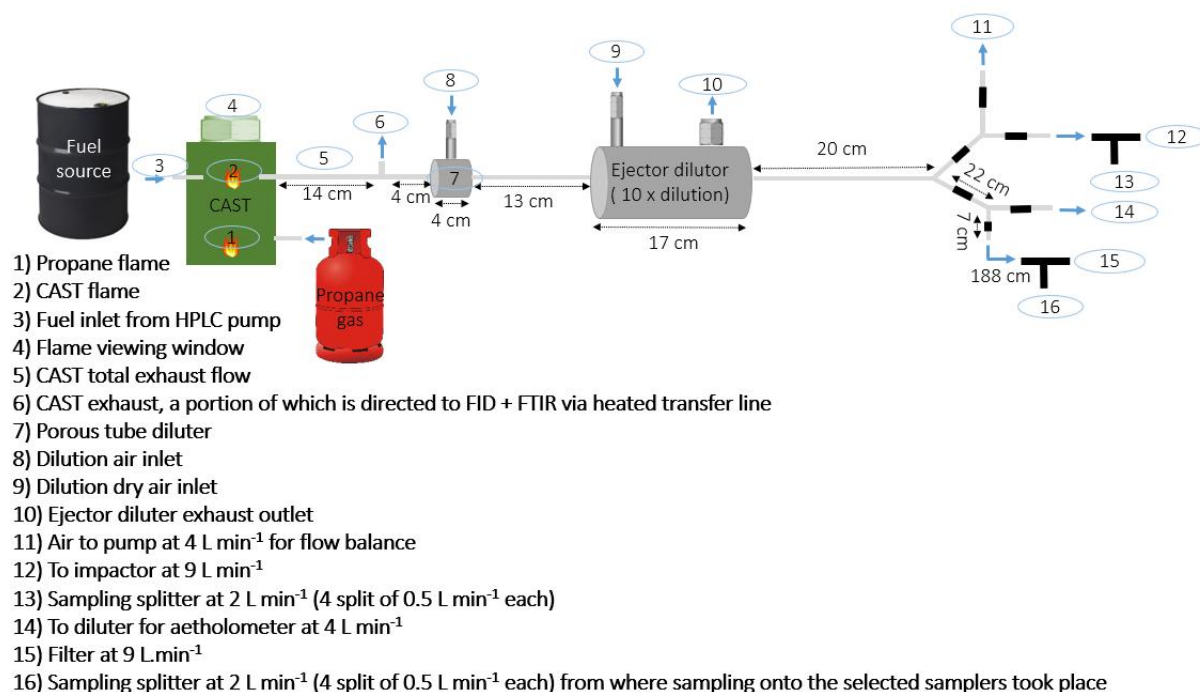
A Combustion Aerosol Standard generator (diesel CAST, Jing mini-CAST 5201D, Switzerland) was operated with propane (99.95%, Linde AG, Germany). The settings were as follows:

dilution air ( $10 \text{ L}\cdot\text{min}^{-1}$ ), oxidation air ( $2.2 \text{ L}\cdot\text{min}^{-1}$ ), quenching gas ( $10 \text{ L}\cdot\text{min}^{-1}$ , fixed), propane fuel ( $30 \text{ mL}\cdot\text{min}^{-1}$ , fixed) (refer to Mueller et al. (2016) for further details regarding the operation of the CAST). The fuel of choice was supplied to the CAST generator using an inlet from a high-performance liquid chromatography (HPLC) pump at  $50 \text{ mL}\cdot\text{min}^{-1}$ . In the viewing window, illustrated by number 4 of Figure 1, it could be seen that the flame changed from blue to orange once the fuel of interest was added to the propane already combusting in the CAST generator. A photograph of the CAST setup is shown in Figure S2 in the Supplementary Information.

The fuel was introduced to the CAST generator using polytetrafluoroethylene (PTFE) tubing (50 cm) and polyurethane (PU) tubing (5 cm) using a HPLC pump (Kontron, type 420, Germany) and then subsequently, copper tubing was used to connect the HPLC pump to the CAST generator. Antistatic polyurethane hose of 12.0 mm o.d. x 8.0 mm i.d. (Riegler, Germany) was used for all the connections between the CAST and various dilutors, splitters and sampling instrumentation involved in this study. The CAST generated  $22 \text{ L}\cdot\text{min}^{-1}$  of undiluted combustion exhaust. From the CAST generator, an exhaust outlet, shown by number 6 in Figure 1, allowed for the undiluted excess exhaust emissions to be released whilst continuously sampling  $0.3 \text{ L}\cdot\text{min}^{-1}$  of this exhaust over the course of the 10 min sampling period for analysis by a flame ionization detector (FID) (SK-Electronik, GMBH), calibrated with propane (30 ppm) in nitrogen (Linde, Germany), and a Fourier-transform infrared spectroscopy (FT-IR) Gas Analyser (Gaset, Model: DX4000, Finland). The FID sampled the undiluted CAST exhaust using a  $380 \text{ }^\circ\text{C}$  heated transfer line. Thereafter,  $0.3 \text{ L}\cdot\text{min}^{-1}$  ( $1.5 \text{ L}\cdot\text{min}^{-1}$  for GTL and RME) of the undiluted CAST exhaust was introduced to a porous tube dilutor (Mikro-Glasfaser Filterelement, Type GF-12-57-80E) to which  $2.7 \text{ L}\cdot\text{min}^{-1}$  ( $1.5 \text{ L}\cdot\text{min}^{-1}$  for GTL and RME) of dry air was added to make up a total diluted flow of  $3 \text{ L}\cdot\text{min}^{-1}$ . The ejector dilutor then drew the  $3 \text{ L}\cdot\text{min}^{-1}$  from the porous dilutor and further diluted the CAST exhaust with laboratory air that was first cleaned by passing through Intersorb Plus (Intersurgical, Sankt Augustin, Germany) to remove  $\text{CO}_2$ , and then activated charcoal (Carl Roth, Karlsruhe, Germany) and finally through Silicagel (Azelis, Sankt Augustin, Germany) at  $27 \text{ mL}\cdot\text{min}^{-1}$ . Any overpressure which may have occurred in the ejector dilutor was released through the outlet shown as number 10 in Figure 1.

From the ejector dilutor, a custom-built three-way Y-piece stainless steel splitter allowed for the diluted flow of the CAST exhaust to be directed to various sampling instrumentation as well

as to the selected samplers. Two of the Y-piece exits lead directly to two sampling stations to which selected samplers were attached and diluted CAST exhaust was drawn through these at  $500 \text{ mL}\cdot\text{min}^{-1}$  for 10 min by Gillian® GilAir® Plus Air Sampling Pumps (Sensidyne®, USA).



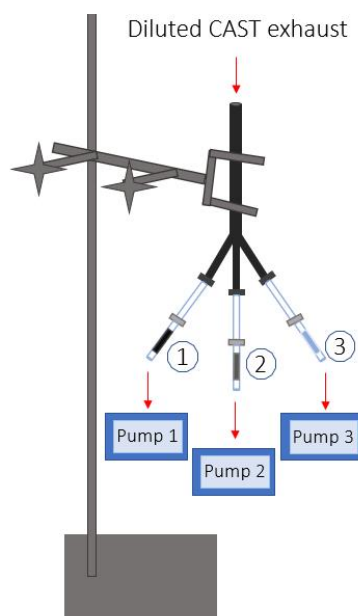
**Figure 1:** Schematic diagram of the CAST generator sampling set-up.

The second Y-piece was utilised for the measurement of the light absorption properties of the CAST aerosols measured online by means of an Aethalometer® (Magee Scientific, Model AE33-7, Slovenia), which had an optimised diluted flow using a PALAS® VKL 10E dilutor as the Aethalometer® typically required a dilution of 1:10 000 in order to not over saturate the instrument. From the same PALAS® VKL 10E dilutor, the diluted CAST exhaust was additionally measured by a Condensation Particle Counter (CPC, TSI, Model 3022A, USA) and an Electrostatic Classifier (TSI, Model 3082, USA) connected to a CPC (TSI, Model 3750) in order to determine the stability of the particle number concentration produced from the CAST after changing fuel sources. The particulate matter (PM) measurements were conducted in order to check the stability of the emissions and suitability of the dilution ratios of the different fuels. The combustion of diesel (B0) resulted in higher PM emissions than the other fuels, therefore the emissions required different dilutions for gas phase sampling. The fuel of interest was thus combusted in the CAST generator and the exhaust thereof passed through a porous tube

dilutor and an ejector dilutor, in which the dilution flows were adjusted to dilute diesel (B0) emissions by a factor of 100 and to dilute the GTL and RME emissions by a factor of 20.

#### 2.4. Sample collection and extraction

Prior to introducing a new fuel into the CAST generator, the system was cleaned with cotton swabs, Kimtech wipes and a vacuum cleaner. Once cleaned, the selected degassed fuel was introduced into the CAST generator using the HPLC pump and the combustion emissions were monitored by the particle counter and the aethalometer to ensure that the CAST generator was stable and producing a consistent concentration of aerosols. A stainless-steel filter holder assembly was positioned between an empty glass tube upstream and the selected sorbent sampler downstream. The filter holder contained a 13 mm quartz-microfibre disc (Ahlstrom Munksjö, T 293) with a precipitation area diameter of 10 mm. Each sampler was connected to a Gilian® GilAir® Plus Air Sampling Pump (Sensidyne®, USA) using Teflon tubing (Figure 2), which was operated at 500 mL.min<sup>-1</sup> for 10 min. A photograph of the set-up is shown in Figure S3 in the Supplementary Information.



**Figure 2:** Schematic of the sampler setup where numbers ①, ② and ③ illustrate the positions of the activated charcoal, GW and PDMS samplers, respectively, during CAST sampling events.

These sampling pumps were all calibrated for each specific sampler used prior to sampling by means of a Gilibrator 2® (Sensidyne®, USA). This accounted for the individual differing back



pressures of the different sampler types. A Kestrel 4500 weather station (Envirocon, South Africa) was used to measure the ambient conditions at the time of the sampling event which are shown in Table S2 of the Supplementary Information. After sampling, PDMS and GW samplers were end-capped and were subsequently wrapped in aluminium foil, sealed in zip lock polyethylene bags and were stored in a freezer at -18°C until analysis took place within 72 hrs.

The charcoal tubes were opened with an adjustable ORBO™ Tube Cutter after the sampling event, and the charcoal was emptied into 20 mL amber vials. 3 mL of CS<sub>2</sub> was added, the vials were then sealed and allowed to extract for 12 hr in a fume hood at room temperature. Although accredited methods such as the ISO 9487: 1991 (E) state that 500 µL of solvent be used in the extraction of analytes from activated charcoal sorbents, it was found that 3 mL of solvent was required to completely submerge the activated charcoal. After overnight extraction, the extract, with the activated charcoal still in contact with the solvent, was sonicated (Allpax Palsonic, Germany) for 15 min. The supernatant extract was subsequently transferred into a 5 mL amber GC vial and stored in a freezer at -18 °C until batch-wise analysis was conducted within 72 hrs.

## 2.5. GC-MS analysis

The PDMS and GW samplers were thermally desorbed using a Thermal Desorption System (TD-20, Shimadzu, Japan) using 60 mL.min<sup>-1</sup> helium from 80 °C to 250 °C for the PDMS and to 280 °C for the GW sampler, both with a hold time of 30 min. The cooled injection system (CIS) method started at 5 °C and ended at 330 °C with a hold time of 30 min. A GC-2010 Plus was coupled to a MS-QP2010 Ultra (both Shimadzu, Japan) and helium was used as carrier gas at a flow rate of 1.6 mL.min<sup>-1</sup>. A split ratio of 10:1 was applied whilst the column used was a VF-XMS 30 m x 0.25 mm i.d. x 0.25 µm d.f. column (Agilent, Netherlands). The GC oven method started with a hold time of 6 min at 60 °C and was ramped to 250 °C at 5 °C.min<sup>-1</sup>. The transfer line temperature was set to 250 °C. The mass spectrometry method was set to scan from m/z 35 to m/z 500 with an electron ionisation energy of 70 eV and an ion source temperature of 230 °C.

The charcoal extracts were injected by a 1 µL hot injection at 280 °C. Helium was used as the carrier gas with a flow rate of 1.5 mL.min<sup>-1</sup>. A split ratio of 1:1 was applied and a SGE BX5 25 m

x 0.22 mm i.d. x 0.25  $\mu\text{m}$  d.f. column was used. The oven started with a hold time of 1 min at 40 °C and was ramped to 250 °C at 5 °C.min<sup>-1</sup> and then held for 2 min. The transfer line temperature was set to 270 °C. The mass spectrometry method was the same as for the PDMS and GW sampler analysis.

### 3. Results and discussion

#### 3.1. FID/FTIR analyses

Since this study occurred over a period of three days, it was of interest to investigate the inter-day CAST generator combustion and emission stability using the flame ionization detector (FID) and Fourier-transform infrared spectroscopy (FTIR) over the sampling period to determine the reliability of the CAST system for organic gas phase emission sampling. In order to do this, the sampling of the emissions from the CAST generator started with the diesel (B0) fuel type, which was used as a basis for comparison of the other two fuels tested, as petroleum-derived diesel is widely used throughout the world. The experiments then continued onto the gas-to-liquid (GTL) and rapeseed oil methyl ester (RME) fuel types, respectively, and ended with sampling the B0 fuel type as a bracket test to gauge the reproducibility of the CAST emissions between the duplicate measurements sampled over the course of the days over which the sampling took place. In Table 1, each fuel type is allocated numbers 1-4, where 1 and 2 designate the duplicate measurements of the first round of sampling the emissions from each fuel, which were carried out directly after each other, whereas numbers 3 and 4 relate to the duplicate measurements of the second sampling event of the same fuel which were carried out sequentially on a different day.

**Table 1:** Mean FID results for the sampling events of the undiluted fuel emissions over each 10 min sampling period.

Sampling event	<i>FID (ppm)</i>		
	B0	GTL	RME
1	8.87	7.33	5.60
2	8.75	7.27	5.57
3	7.63	7.09	5.30
4	7.60	7.05	5.49
Mean	8.21	7.19	5.49
SD	0.69	0.14	0.13
%RSD	8.42	1.89	2.46

As can be seen from Table 1, the response of the FID showed higher gas phase organic emissions from each fuel type during the first sampling event as compared to the second sampling event. Although the duplicate sampling events for each fuel type were carried out on different days, no rinsing occurred for intra-fuel sampling events of the GTL and RME fuel types. This could have in turn contributed to the smaller FID measurement difference (i.e. lower %RSD) in the combustion fuel emissions of these fuel types, measured between the duplicate fuel measurements, as compared to B0 which was sampled as a bracket test. Nevertheless, the fuel combustion emissions recorded by the FID, for all of the fuel types, showed that the combustion emissions were significantly different between days, using a statistical t-test at a 95% confidence level. This implies that it is preferable to conduct all tests of a particular fuel type sequentially on one day when using the CAST system, in order to reduce these uncertainties. During the sampling events of each fuel type, additional measurements were taken of the H<sub>2</sub>O, CO<sub>2</sub>, O<sub>2</sub> percentage and amount of CO (ppm) contained within the combustion emissions from the CAST exhaust. These values were found to not differ significantly during the sampling period (Table S3 in the Supplementary Information).

In order to compare the performance of the samplers, the results from the second sampling events of the B0 and GTL combustion were used, i.e. B0 and GTL 3 and 4 in Table 1, as these results proved to be more reliable from the FID measurements; in that lower %RSDs were recorded. Additionally, it was found that the first round of sampling of the B0 and GTL yielded concentrations that were significantly larger with greater variation than in the second round of sampling as shown in Figure S4 of the Supplementary Information. Since the RME fuel did not contain additives i.e. stabilizers, polymerisation of the combustion products occurred around the flame tip during the second sampling event causing a partial blockage with related potential inconsistencies in results, therefore the duplicates from the first sampling event for that fuel type, i.e. RME 1 and 2 in Table 1, were used for the comparison of the samplers and fuel types.

### **3.2. Comparison of the compounds detected on each sampler type**

The highest number of target analytes were detected from the emissions of diesel (B0), where thermal desorption of the PDMS sampler resulted in the detection of 33 target analytes, whilst 34 were detected upon analysis of the GW sampler. Analysis of the charcoal sampler extracts resulted in the detection of only two of the 36 target analytes in all fuel types sampled; namely

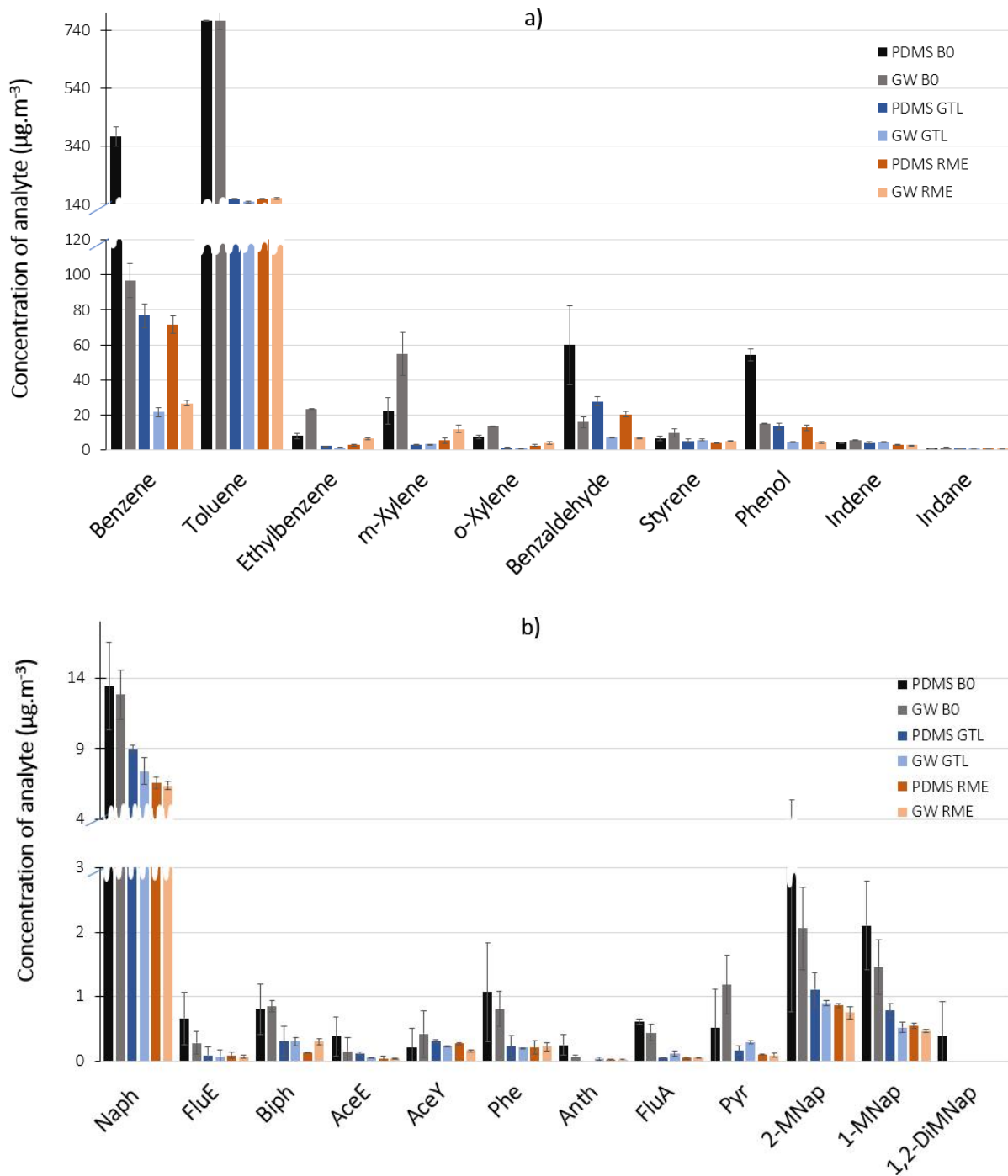
benzene and toluene, of which only benzene was above the limit of quantification (LOQ). The low number of analytes detected was likely due to the dilution volume. After analysis of a blank extraction of the activated charcoal sorbent, it was evident that the detected analytes were from the sorbent itself, which contained particularly high levels of benzene. The blank analysis data of the three samplers is shown in Table S4 in the Supplementary Information. Therefore, the comparison of the concentrations of benzene and toluene emitted upon combustion of different fuels is based only on the analysis of the PDMS and GW samplers (as shown in Figure 3 and detailed in Section 3.4).

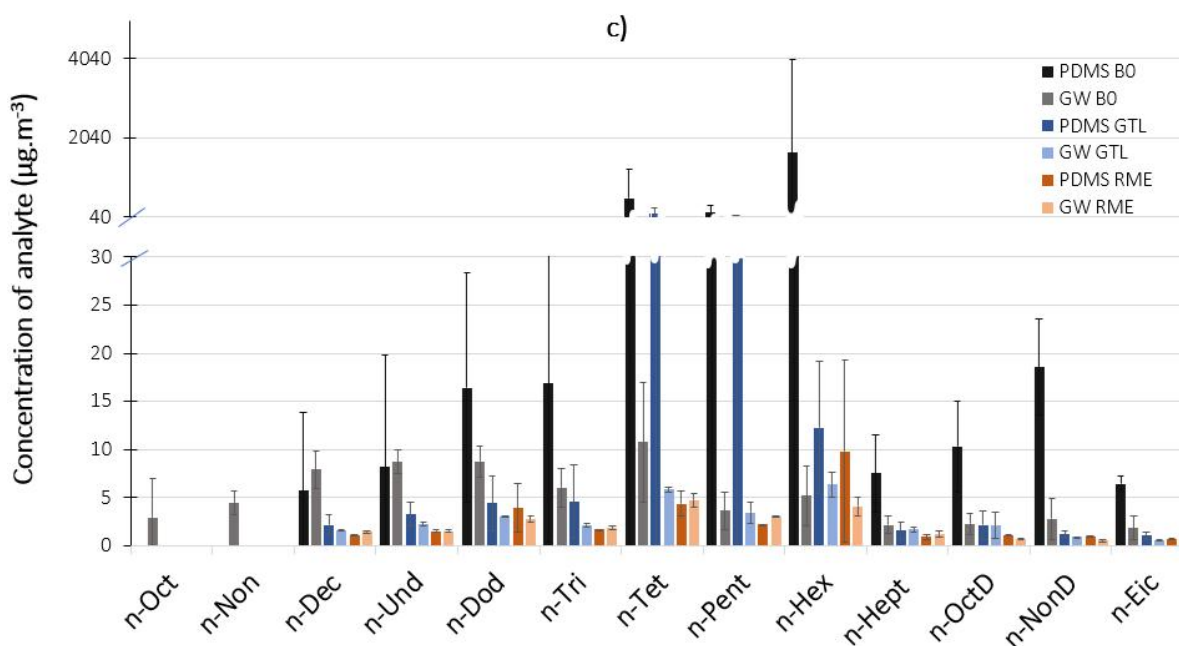
There are a number of factors contributing to the lack of analytes detected upon analysis of the activated charcoal sampler extracts as compared to the number of compounds detected upon analysis of the PDMS and GW samplers, as shown in Figure 4 (also refer to Tables S5 and S6). Firstly, the volume of solvent experimentally determined to be required (3 mL) for the extraction of the activated charcoal may have diluted the sampled analytes to below the limit of detection (LOD) of the analytical method. The charcoal sampler was preliminarily calibrated for only 8 of the 36 target analytes. Further calibration of the remaining 28 target analytes did not occur as no other target compounds other than benzene and toluene were detected upon analysis of the activated charcoal extracts. The LODs for the activated charcoal sampler were calculated to range from 0.48  $\mu\text{g}\cdot\text{m}^{-3}$  for naphthalene to 2.26  $\mu\text{g}\cdot\text{m}^{-3}$  for m-xylene (Tables S7a and S7b). Comparatively, the LODs for PDMS ranged from 0.0001  $\mu\text{g}\cdot\text{m}^{-3}$  for 1,2-dimethylnaphthalene to 0.80  $\mu\text{g}\cdot\text{m}^{-3}$  for n-octane, whilst the LODs for GW ranged from 0.002  $\mu\text{g}\cdot\text{m}^{-3}$  for toluene to 0.79  $\mu\text{g}\cdot\text{m}^{-3}$  for n-octane and n-nonane.

Another reason why the analysis of the activated charcoal extracts could have resulted in the detection of so few compounds is that the activated charcoal may have bound the analytes in an irreversible manner and this, in combination with the low gas phase analyte concentrations which the CAST system produces, could have resulted in the analytes not being detected. The lack of analytes detected occurred even though the activated charcoal was left in  $\text{CS}_2$  for 10 hrs as compared to the recommended extraction time of 30 min (ISO 9487:1991 (E)).

As can be seen from Figure 3c), the GW sampler was found to be more effective than PDMS in retaining the lighter n-alkanes such as n-octane and n-nonane. However, analysis of the GW sampler generally gave lower concentrations of each target analyte than the PDMS sampler (Figures 3a)-c)). This may be indicative of the GW sampler having a lower breakthrough volume

compared to the PDMS sampler however, the true cause is probably due to the thermal desorption parameters being optimised for the PDMS sampler and not for GW desorption. Therefore, the lower concentrations of analytes determined upon analysis of the GW samplers are most likely due to the incomplete thermal desorption of analytes from the GW sampler, which retains analytes more strongly by adsorption rather than by sorption as in the case of PDMS.





**Figure 3:** Detected concentrations of a) VOCs, b) PAHs and c) n-alkanes from the combustion of fuel types B0, GTL and RME sampled from the CAST generator exhaust using PDMS and GW samplers. *The error bars are based on the standard deviation (SD) of duplicate measurements and abbreviations can be found listed in Tables S7a and S7b.*

### 3.3. Comparison of the variability between the samplers

As previously stated, the analysis of the PDMS samplers reflected higher concentrations of the target compounds as compared to the GW samplers (Figures 3). However, the reported concentrations from the analysis of the PDMS samplers showed larger standard deviations as compared to the GW samplers. This could be due to PDMS functioning as a sampler through the action of absorption as opposed to the GW sampler, which functions by adsorbing analytes. Additionally, the structure of the GW sorbent itself, which involves a 2D monolayered structure of one atom thickness, leads to a large number of active sites being open and available for adsorption.

The range of target analytes were dominated by non-polar compounds which would theoretically tend to interact better with the non-polar GW sorbent as compared to the less non-polar PDMS sorbent. The lower standard deviation in the concentrations reported through the analysis of the GW samplers as compared to the analysis of the PDMS samplers is particularly noticeable for the concentrations of the polycyclic aromatic hydrocarbons (PAHs) detected (Figure 3b) but even more so for the concentrations of n-alkanes detected (Figure

**Table 2:** The relative advantages and disadvantages of GW, PDMS and charcoal samplers for the sampling of the selected VOCs, PAHs and n-alkanes at trace levels.

	<i>GW Sampler</i>	<i>PDMS Sampler</i>	<i>Activated Charcoal Sampler</i>
<i>Advantages</i>	Low background noise		
	Can be reused	Can be reused	Reasonable cost (€3.26 per sampler)
	On average, the lowest standard deviation in recorded duplicate measurements		
	Largest number of compounds detected	A large number of compounds detected	
	Similar analysis time to PDMS	Similar analysis time to GW	
	Can be thermally desorbed therefore requires no solvents in preparation for analysis	Can be thermally desorbed therefore requires no solvents in preparation for analysis	Does not require a lab equipped with a TD system
<i>Disadvantages</i>		Sorbent background (due to siloxanes)	Sorbent background (for toluene and benzene)
	Reasonably costly (€6.88 per sampler)	Most costly (€7.55 per sampler)	Single use
	Lower concentrations of several target analytes reported as compared to PDMS	Larger standard deviation in recorded duplicate measurements as compared to the GW sampler, especially for the n-alkanes	Largest standard deviation in recorded duplicate measurements of benzene
	Requires a lab equipped with thermal desorption system	Requires a lab equipped with a thermal desorption system	Lowest number of compounds detected
			Long extraction time
			Incomplete analyte recovery
			Toxicity of solvent used for extraction i.e. CS <sub>2</sub>

3c). Therefore, due to the lower degree of uncertainty in concentrations reported upon analysis of the GW sampler and the greater number of compounds detected by the GW sampler as compared to the other two samplers, the GW sampler proved to be the superior sampler as compared to the activated charcoal sampler and the PDMS sampler for the sampling of the selected trace level VOCs, PAHs and n-alkanes in this study. The strengths and weaknesses of the various samplers are summarised in Table 2.

#### **3.4. Effect of the different fuels on the combustion emission profiles**

Throughout the sampling period, the ambient temperature differed slightly from 26.8 – 27.7 °C with a standard deviation of 0.4 whilst the barometric pressure ranged from 955.5 – 956.2 hPa with a standard deviation of 0.2, as shown in Table S2. This showed that the ambient conditions during sampling were fairly consistent and thereby allowed for the comparison of the fuel measurements and the CAST system over the sampling period.

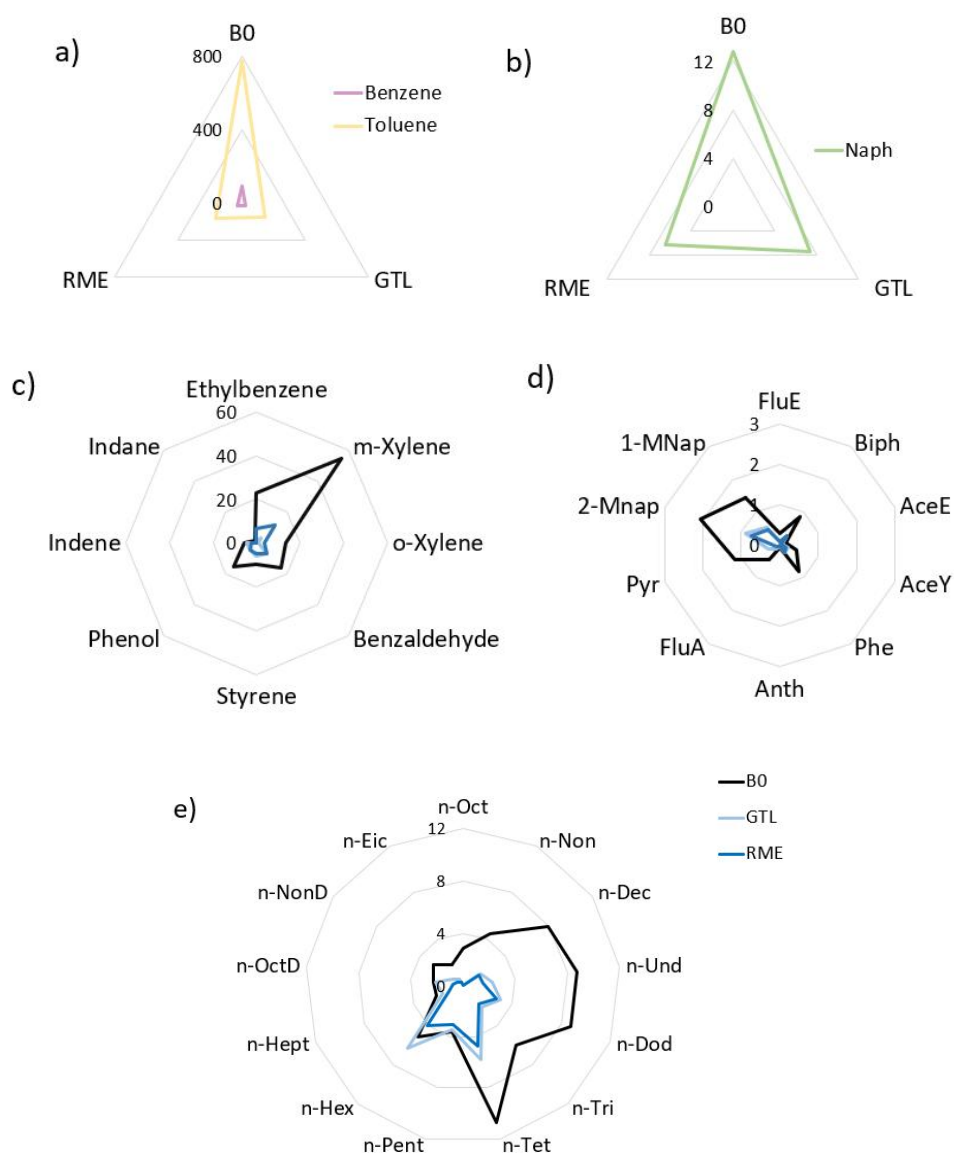
Most of the CAST combustion emission compound profiles for the different fuels tested reflected a similar trend as seen in Figure 3, when sampled by the PDMS and the GW sampler. Since it has been identified that the PDMS sampler had more variability in the resultant concentrations reported as compared to the GW sampler, the relative concentrations of target analytes within each fuel type emission profile will be discussed in terms of the results reported upon analysis of the GW samplers. Comparing the three fuel types sampled in this study, the combustion of diesel (B0) resulted in higher concentrations of target compounds in most cases, with the exception of the hexadecane in the combustion emissions of gas-to-liquid (GTL) (Figure 4). As expected, the combustion emissions of rapeseed oil methyl ester (RME) reflected lower concentrations of targeted VOCs and SVOCs as compared to diesel and GTL, with the exception of ethylbenzene and the xylene isomers in the case of GTL (Figure 4c).

These reported results align with the visual analysis of the filter papers which were placed upstream of the samplers. It can be seen in Figure 5 that the PM filter from B0 combustion is considerably darker than the filters relating to GTL and RME combustion. The same trend was also observed in the duplicate sampling events conducted with B0 and GTL and RME.

The percent carbon content and total unburned hydrocarbons (THCs) are typically reported in the literature to be the largest in diesel whilst GTL tends to have less, and biodiesels, such as RME, have been reported to have the lowest concentrations (Dagaut et al. 2019; Soriano et al.



2018; Damanik et al. 2018). The measurements are done on %w/w of the fuel before combustion or the measurements of the target molecules are accomplished through the analysis of the PM phase formed after the combustion of the fuel. The compounds present in the different fuels and the relative abundancies in terms of engine emissions are also reported. It is important to note that the CAST generator pyrolyzes the fuel by means of a diffusion flame therefore the combustion conditions and consequently the emissions, would differ to real-world engine emission scenarios making direct comparisons to other studies difficult.



**Figure 4:** Relative abundance ( $\mu\text{g}\cdot\text{m}^{-3}$ ) of various compounds detected upon analysis of the GW sampler after sampling the gas phase emissions from B0, GTL and RME combustion: a) benzene and toluene, b) naphthalene, c) VOCs, d) PAHs and e) n-alkanes.



**Figure 5:** PM filtered from a) B0, b) GTL and c) RME CAST emissions prior to gas phase sampling.

Furthermore, compounds present in various fuel sources are often reported in terms of total carbon (TC); which is the summation of elemental carbon (EC) and organic carbon (OC) fractions with little detail regarding which specific compounds are present in the OC fraction (Zhou, Zhou, and Zhu 2019; Atiku et al. 2016; Nyström et al. 2016; Shen et al. 2013). In terms of bettering the fuel source for many forms of machinery in order to reduce emissions which are potentially hazardous to human health, it will be important to determine emission profiles of fuels not only in terms of the particulate matter generated, but also specifically which volatile and semi-volatile organic compounds are being released into the atmosphere, as these can also be detrimental to the environment and to human health, even though they may not be visible.

#### 4. Conclusions

In this study it was found that the commercial activated charcoal sampler was not effective in sampling the trace levels of target analytes produced upon combustion of the fuels tested by the CAST. This could be due to the sample being too dilute and below the LOD due to the volume of the extraction solvent required, as well as the low levels of gas phase VOCs and SVOCs produced by the CAST system, and the small sample volume. In addition to the target analytes being below the LOD for the activated charcoal extracts, the activated charcoal sampler may have irreversibly adsorbed the target analytes. It is also noted that the extraction method for the activated charcoal sampler is time consuming and requires a toxic solvent, and high background concentrations were found for some target analytes. The activated charcoal sampler proved to be the cheapest however, with a once-off use, whilst the PDMS and GW have the advantage of being able to be reconditioned and reused.

The results of the PDMS sampler analysis reflected relatively higher concentrations of the VOC and SVOCs target analytes detected to that of the GW sampler. However, the results from the PDMS sampler analysis also showed a higher variability in the duplicate concentrations reported, particularly for the n-alkanes. The analysis of the GW sampler showed that target analytes were determined with lower uncertainties than with the PDMS sampler and lighter n-alkanes, such as octane and nonane, were detected with the GW sampler but not with the other two samplers. However, the analysis of the GW samplers did reflect lower concentrations of all target analytes sampled as compared to the concentrations reflected by the PDMS sampler. This could indicate that the GW has a lower breakthrough volume than the PDMS sampler or, most likely, that the TD parameters were optimal for the PDMS but resulted in incomplete desorption from the GW sorbent which therefore requires further optimisation such as a higher desorption temperature. Overall, the GW sampler has proven to be superior, as compared to the activated carbon as well as the PDMS sampler in the sampling of the selected trace levels of VOCs, PAHs and n-alkanes in this study. In terms of fuel comparisons, diesel (B0) produced the highest concentration of VOCs and SVOCs upon combustion in the CAST, as compared to rapeseed oil methyl ester (RME) and gas-to-liquid (GTL) fuels.

Regarding the CAST generator itself, it is suggested that one fuel type is used and sampled over a continuous period to definitively establish the reproducibility of the CAST, as significant variation was observed when sampling the fuel emissions on different days, although this variability was compounded by the low levels of target analytes produced by the CAST system. In future comparisons, the final extract volume for the charcoal sampler should be reduced to improve detection limits, especially in light of the low emission levels from the CAST system. It may also be of use to analyse the various fuel types before combustion to determine the aromatic content thereof and compare these to the combustion profiles reported in this study, as well as to compare the samplers using another combustion source which generates higher levels of target VOCs and SVOCs.

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