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Corresponding Author	Family Name	**Kjos**
	Particle	
	Given Name	**Ole**
	Prefix	
	Suffix	
	Role	
	Division	
	Organization	SINTEF Industry
	Address	0314, Oslo, Norway
	Email	ole.kjos@sintef.no
Author	Family Name	**Aarhaug**
	Particle	
	Given Name	**Thor Anders**
	Prefix	
	Suffix	
	Role	
	Division	
	Organization	SINTEF Industry
	Address	7034, Trondheim, Norway
	Email	taarhaug@sintef.no
Author	Family Name	**Gaertner**
	Particle	
	Given Name	**Heiko**
	Prefix	
	Suffix	
	Role	
	Division	
	Organization	SINTEF Industry
	Address	7034, Trondheim, Norway
	Email	heiko.gaertner@sintef.no
Author	Family Name	**Håland**
	Particle	
	Given Name	**Bente**
	Prefix	
	Suffix	

	Role		
	Division		
	Organization	Elkem Carbon	
	Address	Oslo, Norway	
	Email	bente.sundby-haland@elkem.com	
Author	Family Name	**Fjelldal**	
	Particle		
	Given Name	**Jens Christian**	
	Prefix		
	Suffix		
	Role		
	Division		
	Organization	Elkem Carbon	
	Address	Oslo, Norway	
	Email	jens.christian.fjelldal@elkem.com	
Author	Family Name	**Jakovljevic**	
	Particle		
	Given Name	**Katarina**	
	Prefix		
	Suffix		
	Role		
	Division		
	Organization	Norwegian University of Science and Technology	
	Address	Trondheim, Norway	
	Email	Katarina.jakovljevic@ntnu.no	
Author	Family Name	**Espeland**	
	Particle		
	Given Name	**Oscar**	
	Prefix		
	Suffix		
	Role		
	Division		
	Organization	Nemko Norlab	
	Address	Porsgrunn, Norway	
	Email	oscar.espeland@nemkonorlab.no	
Author	Family Name	**Kero**	
	Particle		
	Given Name	**Ida**	
	Prefix		
	Suffix		
	Role		
	Division		
	Organization	SINTEF Industry	
	Address	0314, Oslo, Norway	
	Email	ida.kero@sintef.no	

Abstract

New measurement techniques aiming to achieve a better understanding of the PAH emissions dynamics during production of electrode paste briquettes were tested. Traditional sampling method requires several hours of sampling to get enough PAH components on the adsorbent material to perform reliable analysis. As the process is changing from one batch to the next, emissions cannot be expected to be constant over time. Better time resolution is essential to increase the understanding of emission variations. Thermal desorption (TD) tubes allow for sampling times as short as 10 min. The SINTSENSE, a standalone photo ionization detector (PID) implementation allows for continuous emission monitoring providing online data second by second. However, the SINTSENSE will only report a total hydrocarbon estimate, with no differentiation between individual components. Comparing results from these 3 methodologies gives interesting findings on the emission dynamics and variations in composition, in addition to benchmarking the individual measurement techniques.

New Methods to Determine PAH Emission Dynamics During Electrode Mass Processing

Ole Kjos, Thor Anders Aarhaug, Heiko Gaertner, Bente Håland, Jens Christian Fjelldal, Katarina Jakovljevic, Oscar Espeland, and Ida Kero

Abstract

New measurement techniques aiming to achieve a better understanding of the PAH emissions dynamics during production of electrode paste briquettes were tested. Traditional sampling method requires several hours of sampling to get enough PAH components on the adsorbent material to perform reliable analysis. As the process is changing from one batch to the next, emissions cannot be expected to be constant over time. Better time resolution is essential to increase the understanding of emission variations. Thermal desorption (TD) tubes allow for sampling times as short as 10 min. The SINTSENSE, a standalone photo ionization detector (PID) implementation allows for continuous emission monitoring providing online data second by second. However, the SINTSENSE will only report a total hydrocarbon estimate, with no differentiation between individual components.

Comparing results from these 3 methodologies gives interesting findings on the emission dynamics and variations in composition, in addition to benchmarking the individual measurement techniques.

Keyword

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Introduction

Polycyclic Aromatic Hydrocarbons (PAH) are hydrocarbons consisting of two or more aromatic rings. The lightest PAH component is naphthalene, with only two connected rings. Due to their different sizes and molecular weights the PAH components have varying physical properties such as boiling point and vapor pressure. Emissions to air can be either as gas or condensed (liquid or solid) onto dust particles.

Almost all industrial processes involving the use of carbon materials at elevated temperatures have the potential to release PAH components, but PAH emissions are of particular concern when the carbon materials also contain pitch and tar. Classical metallurgical industries such as silicon, ferrosilicon and ferromanganese production [1, 2] as well as production and use of anodes in aluminum industry [3] are well-known sources of PAH emissions.

Conventional reporting of PAH emissions is usually based on a few hours of sampling once or twice every year, as full sampling in accordance with relevant standards such as EPA0010 or similar is complex and expensive. The yearly emissions are typically estimates of PAH content per Nm^3 air/off-gas, based on analysis of these samples, assuming that the emission profile during sampling is representative for the entire year. This assumption is known to be erroneous, and strange deviations from trends in reported emissions can be seen when studying yearly trends in open databases such as the Norwegian PRTR database [4]. It is very difficult to

O. Kjos (✉) · I. Kero
SINTEF Industry, 0314, Oslo, Norway
e-mail: ole.kjos@sintef.no

I. Kero
e-mail: ida.kero@sintef.no

T. A. Aarhaug · H. Gaertner
SINTEF Industry, 7034 Trondheim, Norway
e-mail: taarhaug@sintef.no

H. Gaertner
e-mail: heiko.gaertner@sintef.no

B. Håland · J. C. Fjelldal
Elkem Carbon, Oslo, Norway
e-mail: bente.sundby-haland@elkem.com

J. C. Fjelldal
e-mail: jens.christian.fjelldal@elkem.com

K. Jakovljevic
Norwegian University of Science and Technology, Trondheim, Norway
e-mail: Katarina.jakovljevic@ntnu.no

O. Espeland
Nemko Norlab, Porsgrunn, Norway
e-mail: oscar.espeland@nemkonorlab.no

assess the degree to which a sample is actually representative with regards to variations in raw materials, production and process, or the impact of ambient conditions such as moisture, atmospheric pressure or wind.

Use of alternative sampling and measurement technologies, which can be conducted more frequently, or ideally continuously, can improve emission estimates and process understanding. Although these methodologies may be less accurate in themselves, the possibility to sample more frequently and hence better cover the process variations might improve the overall accuracy of the emission estimates [5]. In addition, the move towards industry 4.0, with more process control systems being digitized and requesting online data to be used as feedback, is providing insight in how and which sensors can be used in the industry. It is also desirable to combine the more frequent sampling by simple methodologies with the certified standard high precision sampling methods to establish correction factors for the simplified methodologies.

A production plant producing electrode paste briquettes and cylinders for Søderberg electrodes in metallurgical industries was used as a test site to evaluate different measurement strategies. The production of paste is a batch process and involves heating, mixing and casting operations of different pitch and raw materials like calcined anthracite and for some products also calcined coke materials. All of these processes may result in the release of PAH components. The amount and composition of the emissions will depend on the content of the coal-tar pitch, the softening point as well as the actual temperatures and time.

Two different emission points were selected to evaluate the performance of short-term sampling on thermal desorption (TD) tubes as well as online measurement with a photo ionization detector (PID) implementation. Conventional extractive sampling on filter and adsorbent (XAD2) was selected as reference measurements.

Measurement Principles

Three different measurement strategies were used, conventional extractive sampling on filter and XAD2, sampling on TD-tubes as well as online monitoring with a PID implementation. Each of these approaches has different sampling times, accuracies, and measurement challenges associated with them. Previous experience and historical, unpublished measurement data from various relevant industries have indicated that the gaseous PAH fraction tends to be significantly larger than the particle-bound fraction of the total PAH emissions. Hence, the measurement methods applied in this study were selected on the assumption that the gaseous fraction dominates the PAH picture.

Extractive Sampling

The extractive sampling was conducted using constant volumetric flow sampling. Two different setups with equipment from different manufacturers were used, but both had the same functionality and capability to sample gas and particulate matter in a representative manner in accordance with VDI 2066, EN 13,284–1, EPA5, and ISO 9096. The two setups were "ITES Automatic isokinetic sampler" (ITES) by Paul Gothe GmbH, Germany and "TPS4-ISOK4" by Environment AS, Germany (ISOK4). These setups were used to collect 2 and 24 h extractive samples, where the particulate matter was captured on glass microfiber thimble filters (MK160) with analytical purity, and gaseous PAH components by XAD2 adsorbent. The filter and sampling probe were kept at 120 °C to avoid condensation of PAH or water prior to the XAD2 adsorbent. Both the XAD2 and filter were then shipped to a commercial certified laboratory for analysis. A typical setup can be seen in Fig. 1, and it consists of several heavy components such as a high-capacity suction pump, control unit, filter, and sampling probe. Typical overall weight for a setup is 20–30 kg.
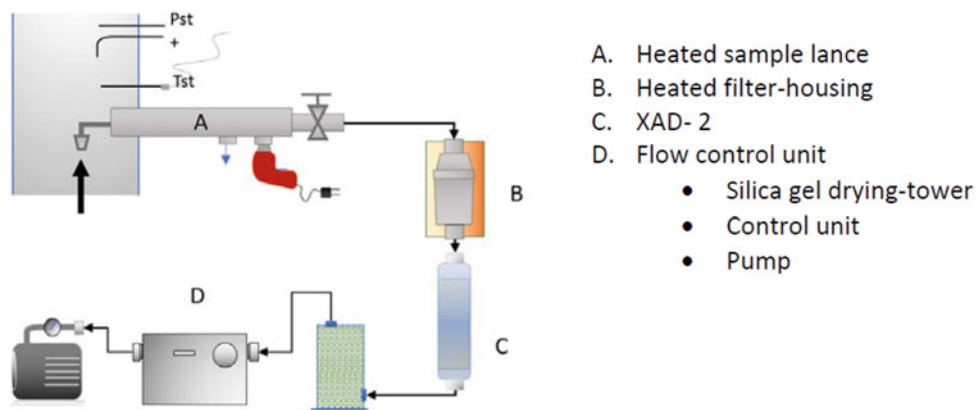
TD Tubes

Sampling by TD-tubes represents a significantly simplified sampling procedure compared to the standardized extractive sampling methods. A small flow, typically between 20 and 500 mL/min is sampled directly onto an adsorbent that is packed in a ¼" tube. Duration of a sample will vary depending on flow and expected concentrations but could be anything between a few minutes up to some hours.

TD-tubes have a widespread use for working environment monitoring but are not frequently used for emission monitoring. There is no separation between particles and gaseous components and the TD-tubes are not suitable for very dusty environments, although small amounts of particulate matter are usually not a problem. Analysis of TD-tubes is performed by heating the tube with the adsorbent and purging it by a clean gas to directly transfer the sample into a gas chromatograph (GC) for analysis. This is a simple 1-step procedure, and much simpler than the liquid extraction of PAH from XAD2 and filter as in the case of extractive sampling.

A typical kit with a battery-operated sampling pump, tubing, and a set of TD-tubes can easily fit in a backpack and will be lighter than 1 kg. For these experiments Carbograph TD1 from Markes International was used as an adsorbent due to availability. For better recovery of the heavier fraction of PAH components other adsorbents such as Tenax TA and XRO-440 [6], Carbopack C or glass beads. There are also

Fig. 1 Schematic view of the sampling system

A. Heated sample lance
B. Heated filter-housing
C. XAD- 2
D. Flow control unit
- Silica gel drying-tower
- Control unit
- Pump

purpose paced TD-tubes such as Markes PAH-tubes that are claimed to give good and linear response for the entire EPA-16 range of PAH components [7]. Sampling time was 10 min, and flow was 125 mL/min, controlled by a SKC PocketPump Touch.

Photo Ionization Detection, PID

SINTSENSE, an inhouse developed PID implementation is based on a Raspberry PI as a controller and logger and was created as a low-cost online monitoring system to follow trends in VOC and light PAH emissions. It does not have a selective response for each individual component but will show a trend for the total gaseous hydrocarbon emissions. It has been demonstrated to work satisfactory for up to 8 weeks in the off-gas of a Fe–Mn smelter [8].

A PID works by ionizing the targeted components in the gas mix by light and then measures the current generated when the ions hit a detection electrode. PID will not be selective as it will ionize all gaseous molecules that can be ionized by the output energy from the lamp. The PID used for these trials had a 10.6 eV lamp and will ionize all cyclic organic compounds. A PID has a fast response time, and by recording the value every 5 s we got a continuous trend. The PID outputs a voltage change as a response to changing hydrocarbon content, this voltage can be calibrated to a concentration, but only for a single hydrocarbon or a pre-defined mix of hydrocarbons. It is not possible to separate the contributions from each individual PAH component that is part of the signal. All results in this paper will be reported as naphthalene equivalents, which is the concentration of naphthalene that would give the recorded voltage of the sensing electrode. Since a PID electrode sensitivity generally increases with molecule size, a mixture of naphthalene with heavier PAH components would most likely result in a high estimate [9]

The results are mixed contributions from all PAH and other VOCs in gas phase calculated by the factory naphthalene calibration slope. For permanent use at a given PAH source this factor could be calibrated to increase accuracy.

The main aim for using the SINTSENSE in these trials is to get information about dynamics and how much hydrocarbon emission changes during the 2 and 24 h samples. By comparing PID results to the extractive sampling it is possible to get a lot of information about trends and time variations in the process emissions that cannot be captured by other means.

Results

In these studies, 2 different PAH sources on a carbon electrode paste plant were studied. The first source is the exhaust gas from a mixer, and the second is the draft from the casting line of this mixer. The emission points from the mixer have an adsorption system and dust filter where PAH is returned to the mixer by using the carbon (raw) material as a dry-scrubbing agent. The emission point from the casting does not have such a filter, but a wide stack with a condensation trap.

The ventilation from the casting had sufficient cross section to allow for all measurements to be conducted simultaneously. In Fig. 2 the complete setup at the stack over the castling line can be seen. The ISOK4 sampling line is on the left-hand side, while the ITES sampling line is seen just to the right of the center of the stack. TD-tubes and SINTSENSE sampling was conducted on a small hole at the back of the stack. There was no filtering of the gas at this stack, just a condensation trap at the bottom. The stack from the mixer had too small a diameter for simultaneous sampling, and sampling of 2 and 24 h samples had to be done in sequence.

Fig. 2 Picture of the casting emission point with all equipment installed

Reference Measurements

The fraction of PAH captured on the sampling filter (i.e. the particle-bound fraction) constitutes less than 1% of the overall emissions from the mixer, while from the casting around 10% of the overall PAH emissions were recovered from the filter. This confirms the assumption that the main part of PAH emissions is gaseous, and hence that our approaches to focus only on gaseous components are valid for this application.

Figure 3 shows the concentration estimates from the sampling on the casting stack. Measurements by all 3 methodologies are overlayed in the same figure. The width of the red, blue, and green bars represents the timeframe from which the samples are collected, and hence their value can be viewed as an average emission for that timeframe.

We can clearly see that there is a significant variation between each 2 h sample. The total PAH in the 3rd 2 h sample is only 26% compared to the 2nd sample. A typical routine sampling for reporting would consist of 2 such samples, and it is clear to see that two of these samples do not cover the full picture. Even for a 24 h timeframe, the representativity of two 2 h samples is poor.

Emissions from the mixer, shown in Fig. 4, had to be collected in sequence due to the stack diameter. The total PAH variation between the samples here is lower but significant. The lowest 2 h sample is only 85% of the highest sample even though they were collected within a 40 h timeframe.

PID measurements with SINTSENSE

In Figs. 3 and 4, the SINTSENSE signal is indicated by the black trendline, providing high time resolution data from which the dynamics in the emission profile can be studied. Events such as filling, mixing, and tapping can clearly be identified in the emissions from the mixer. It is also clear that the average PID signal represented by the magenta lines follows the same trend as the analysis of the total PAH from conventional sampling. Emissions from the casting line seem to have less variations from minute to minute and do not appear to be so affected by production events. However, the correlation between the averaged SINTSENSE signal and the conventional sampling is still strong.

Another finding is that the signal from the SINTSENSE indicates significant variation of PAH emissions between production batches. This is unexpected, as process estimations would have suggested that each batch of the same recipe should be identical when it comes to emissions. Possible explanations here are differences in mixing time before casting, and possibly also changes in the draft profile

Fig. 3 Comparison of naphthalene trends (upper) and total PAH trends (lower) for all 3 methodologies during the 24 h timeframe. Width of columns represents the sampling time covered
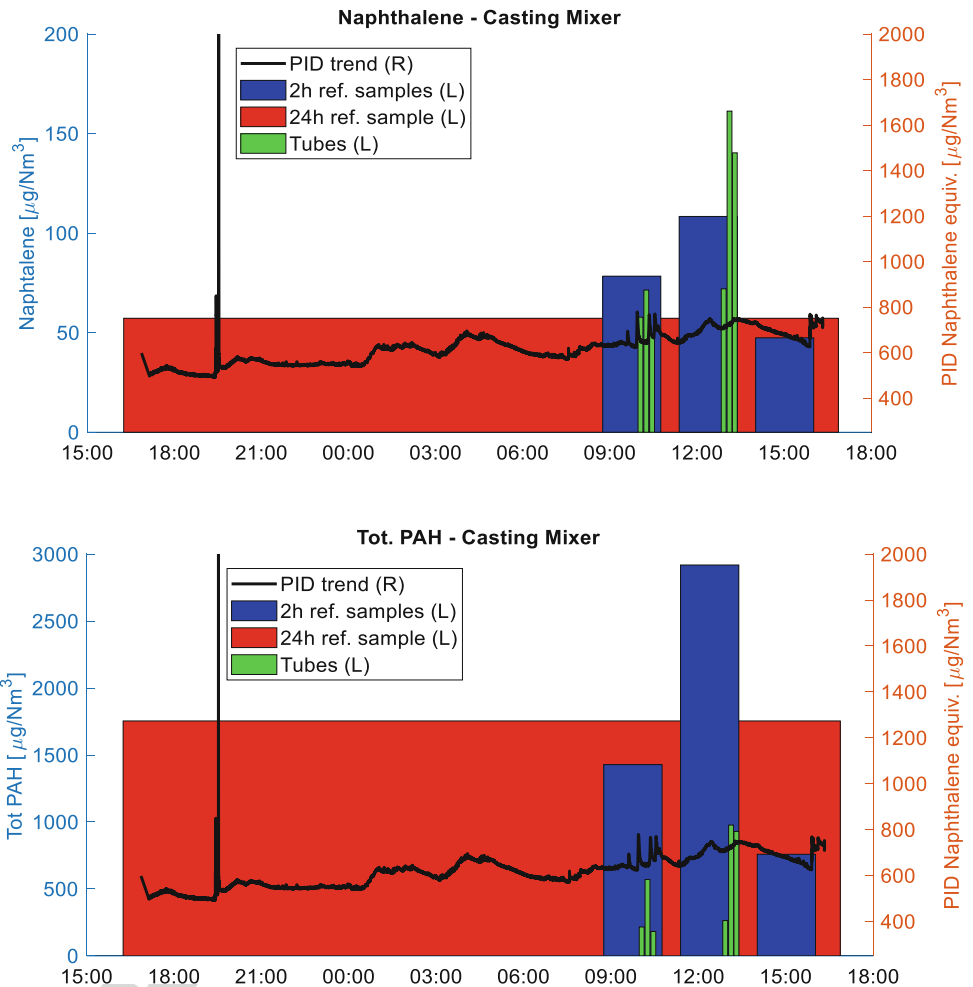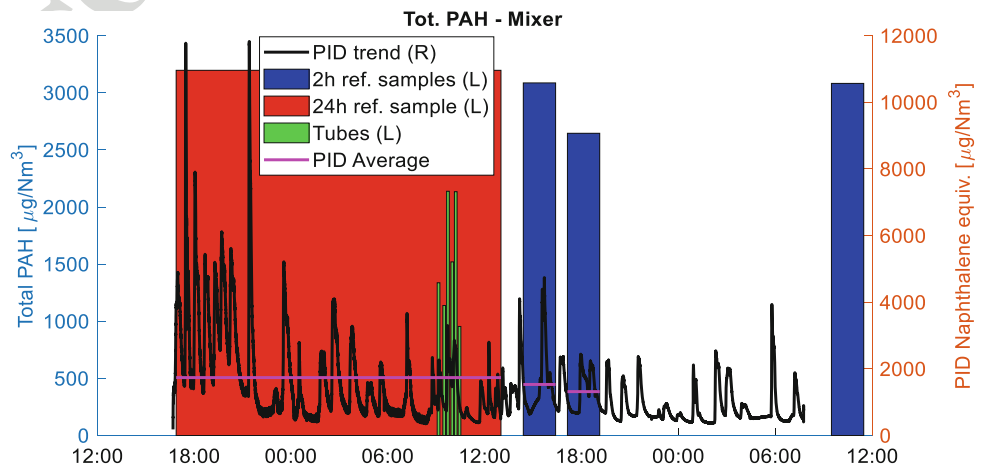

Fig. 4 Comparison of total PAH trends for all 3 methodologies during the collection of samples. The planned 24 h sample had to be slightly shortened for logistic purposes and ended up around 20 h. The width of columns represents the sampling time covered

in the building due to operation of drive gates, natural convection around high-temperature equipment (hall wind) or outside wind conditions and atmospheric pressure.

TD Tubes

Naphthalene estimates from TD-tubes and reference measurements using XAD2 and filter seen in upper part of Fig. 3 have a good agreement quantitatively. The TD-tube samples (green bars) vary within the expected range for the XAD2 sample (blue bars), at least when taking into consideration that the three 10 min samples only cover 25% of the sampling time of the 2 h sample.

For total PAH seen in the lower part of Fig. 3, the TD-tubes clearly underestimate the emissions compared to the reference samples. There are two explanations for this. Firstly, the TD-tubes have a limit for how much they can be heated. Hence it is challenging to completely desorb the heavy PAH components, especially in this case as the adsorbent is stronger than it ideally should be. This will impact recovery of heavy PAHs as to high heating will lead to decomposition of PAH. Secondly, the sampling is not isokinetic and the actual sampling itself will therefore under-sample particulate matter and the particle-born PAH is known to carry most of the heavy PAH components.

A comparison of the recovery of 6 PAH components from TD-tubes and reference measurements can be seen in Fig. 5. At least up to anthracene, the TD-tubes seems to produce results that are meaningful when comparing with the 2 and 24 h samples, especially when considering that there is not a complete overlap in sampling time between these samples. This is best seen in the samples from the

casting (right) as these samples had a higher total content of heavier PAH due to the absence of any filtering, and hence naphthalene is not so dominant in the overall results.

An improved adsorbent such as Tenax in the TD-tubes would probably allow for better recovery of more heavy PAH components [6]. The gas chromatography mass spectroscopy (GCMS) methodology might also be limiting, depending on the setup of the laboratory.

To be able to estimate the total PAH emissions based on results from TD-tubes it would be necessary to establish a correlation factor between certain of the light PAHs and the heavier ones, especially in cases with more particulate matter (higher dust concentrations) since the particle-bound fraction is quite poorly recovered by this methodology. Such correlations could potentially be established by yearly reference measurements.

In Fig. 6 we can see an enlargement of the section in Fig. 4 where the TD-tubes are sampled. Note that SINT-SENSE response is plotted at the right axis, while the other values are on the left axis. The SINTSENSE response is given in naphthalene equivalents so a direct comparison of numbers is not possible, but the overall agreement is very good, nevertheless. The average PID signal from the time periods where the TD-tubes were sampled has a high degree of correlation. It is worth to keep in mind that both these methodologies have the same bias when it comes to only being sensitive towards gaseous PAH components. This bias is less of a concern for emission points equipped with a filter (such as the mixer case in this study) since the main part of PAH components would be expected to be in the gaseous state anyway. For emission points with unfiltered gas, and thus more dust particles present, the effect of this bias would be more significant.
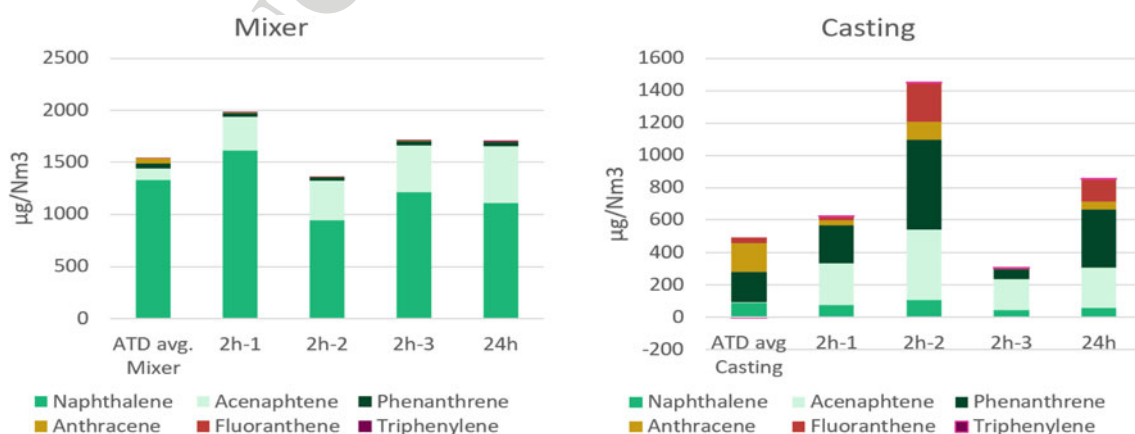

Fig. 5 Variations in the 6 most volatile PAH components in off-gas from the mixer (left) and casting from the mixer (right). For TD-tubes all 6 samples from each sampling point are averaged, giving a total sampling time of 60 min
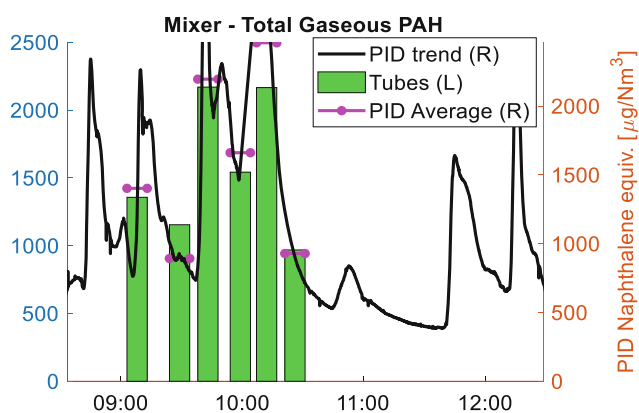
Fig. 6 Average PAH recovered from TD-tubes with SINTSENSE trend and averages overlayed
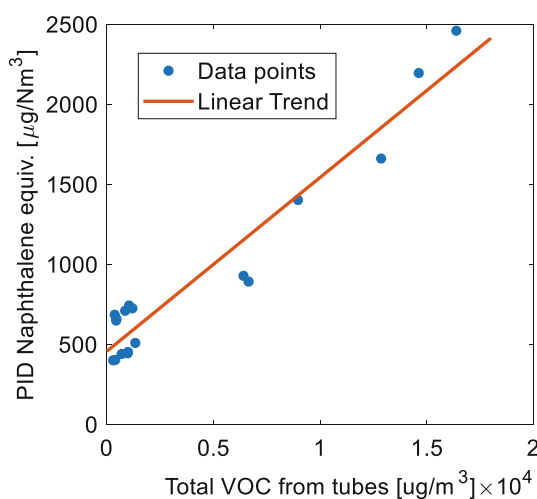

Fig. 7 Correlation between PID naphthalene equivalents estimated by the SINTSENSE and total VOC estimate from the TD-tubes gives $R^2 = 0.93$

In Fig. 7 we can see the overall agreement of the SINT-SENSE signal and the TD-tubes for all simultaneous samplings conducted in this trial. The correlation is strong and linear over the entire concentration span and the actual slope seems to be very consistent. However, there appears to be some baseline shift in the data from the SINTSENSE resulting in a shift along the y-axis for one of the groups of data.

The rapid response from the SINTSENSE could be useful to improve or tune a process with regards to minimizing emissions, or to build an understanding of the process variations over time. Having a PID detector constantly monitoring the emissions in the weeks before and after a yearly certified extractive sampling could, for example, place that sample in an informative context, indicating if the analysis were performed in a timeframe with average conditions or if the emission profile of the sampling day were deviating from normality.

Conclusions

There is no single way of measuring PAH emissions that are precise, easy, and cheap to conduct. A combination of certified reference measurements that can be supported by more frequent sampling by simplified low-cost measurements could improve the understanding of process variations and emission dynamics. It could also improve the representativity of the yearly emission estimates used in environmental reports.

The fraction of PAH captured on the sampling filter (i.e. the particle-bound fraction) constitutes less than 1% of the overall emissions from the mixer, and around 10% from the casting. Hence, the PAH emissions from the processes studied here are dominated by the gaseous PAH fraction. The simplified measuring methods focus primarily on gaseous components and are deemed valid for these applications. It is clear, however, that the dust concentration in the sampled off-gas is decisive for the suitability of these methods.

Both TD-tubes and the PID-based SINTSENSE show results that are in good agreement with expectations. Both correlate well with each other and with reference sampling using filter and XAD2. The results show that there are significant variations in the emissions both from second to second as well as between two 2 h samples taken back-to-back.

PID implementations such as SINTSENSE can capture trends and have short response time and low noise. Despite not being quantitative, it can give useful process information. This information has a significant potential to gain insight in process variations and planning of sampling strategies as well as for tuning and improvements of process control.

TD-tube sampling with Carbograph TD1 seems to give a representative and good analysis of anthracene and lighter PAH components, a weaker adsorbent would improve the method for heavier PAH-components. Sampling on TD-tubes can easily be conducted by plant personnel, and ease of sampling and comparably low cost of analysis could enable frequent sampling intervals with useful quantitative results as a way of capturing emission fluctuations between certified reference measurements.

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