

AT-LINE ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS IN ALUMINIUM PRIMARY PRODUCTION

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Abstract

Emissions of Polycyclic Aromatic Hydrocarbons (PAH) from prebake anode production are closely monitored. The PAH concentrations downstream the gas treatment facility are normally in the ultra-trace range[1]. Rigorous sampling and analytical procedures are required in order to estimate the PAH release. The time from sampling to analytical result is therefore long. It is often of interest to study the dynamic gas composition. In this work, the applicability of Thermal Desorption (TD) combined with a transportable Gas Chromatography/Mass Spectrometry (GC/MS) instrument was investigated. The analytical setup was found to be capable of PAH quantification in the parts per trillion range. With short sampling times required, the total analytical time required was about 30 minutes. The limiting factor was the GC elution time. The analytical methodology was used to evaluate the efficiency of a prebake anode factory dry scrubber. At-line analysis made possible the direct evaluation of PAH emission as function of the operational set points.

Introduction and Theory

Polycyclic aromatic hydrocarbons (PAH) are released when heating coke and pitch in numerous industrial processes. For the aluminium industry the anodes are the main source of PAH. Most of it is released during mixing and later baking (for prebake anodes). There are several reported health hazards related to the different PAH components. Such as respiratory effects and decreased fertility. In addition, they are classified as Group B2 carcinogenic substances according to EPA[2]. PAH constitutes a range of different organic components from the very small and volatile components to very large organic structures. PAH can be present in off gas streams in several different states, these are gas, liquid droplets, particles or adsorbed on dust particle. Combined with the differences in boiling point comprehensive sampling and recovery of aromatics and PAH in off gas streams is challenging.

The emissions of these components are strictly regulated by national governments, as well as international rules [3]. Control on the emissions as well as process tuning to reduce the emissions is therefore essential. However, there are not any easy available methods to sample the entire range of PAH in a fast and reliable way. For comprehensive emission monitoring, samples are often sent to laboratories and results can take more than a week to get back to the plant. This might be good enough for emission monitoring and reporting, but real time process tuning and optimisation where results of parameter changes are needed rapidly, are impossible.

In order to analyse the entire range of PAH components multiple technologies will have to be applied. The lightest of the PAH components are in gas phase already at room temperature, and often along with other organic compounds, this fraction is well

suitable for analysis with Fourier Transformed Infra Red Spectroscopy (FTIR). The intermediate range between C4 and C8n rings are easiest identified by GC or GCMS technology, whereas the really heavy components with the highest boiling points needs to be sampled manually in a suitable solvent and analysed by GC/MS and or Fourier Transform Ion-Cyclotron Resonance spectrometry (FT-ICR). A potential procedure is to split a side stream from the off gas, in fractions suitable for the different analysis technologies, capture them and finally analyse them.

In this paper we propose and evaluate a procedure for sampling and splitting the entire range of PAH, as well as more detailed studies of the options for analysis of the different fractions.

FTIR is based on adsorption or emission of light waves in the infrared spectra, and is a well-known technology [4]. Different molecules will adsorb the IR radiation at different wave lengths and to different extent. Fourier transforms are used in order to collect data from the entire spectra in short time. This gives accurate and reproducible analysis, and is compact and robust enough to easily be transported into the field.

GC/MS is a powerful method to analyse gas samples. The gas is first passed through a traditional GC column which is a long thin column packed with a substrate that interacts differently with different gas components. In this way, the gas species that have a tendency to bond on to the substrate will be retarded on the way through the column and release later than the one who does not interact with the substrate surface.

In GC analysis the components are separated by the time they use to emerge from the column. Standards with known constituents as well as knowledge of the column properties are used to estimate the retention time for each component, and in that way identify the components as they emerge. Several detectors are available for GC analysis of which Thermal Conductivity (TC) perhaps being the most common. In a GC/MS a mass spectrometer (MS) is used as a detector. In an MS, the gas are passed through an electron beam, which ionizes the components in the gas. The molecules are then passed through a vibrating electric field and the weight of the molecules can be determined based on how much their path is bent when passing through the field. Larger organic molecules are fractionated by the electron beam and hence the atomic weights we detect are the fragments of these large molecules[5].

The combination of GC and MS gives us both the differenced retention times, but also the knowledge of which components that emerges from the column at the given times. This makes it easy to do reliable analysis and identification of the different components, and the GC/MS technology is well suited to analyse the mid range of PAH constituents, which covers a large and

representative share of the PAH emitted from i.e. anode baking furnaces.

Both analytical methods (FT-IR and GCMS) can be utilized directly on a process gas stream. However, to protect the instrument gas streams are in general filtered and controlled at some given temperature so that heavy compounds can condense. The filter will trap aerosols, droplets and particles to certain extend. PAH in solid or liquid states will therefore not be registered in a subsequent analysis.

Sampling methodology

In order to get a complete sampling of all PAH constituents along with other Volatile Organic Compounds, VOC, present in the off gas, we propose a 3 way sampling method where the light (gas phase below 180°C), intermediate (possible to adsorb on tubes), and heavy PAH constituents are separated and collected using different methods. As the more volatile components are in gas phase at room temperature, the heaviest starts to condense above 450°C. It is therefore necessary to split the gas stream and use 3 different capturing and analysis technologies.

The lightest fraction will be in gas phase at all times and should be analysed with an online **FTIR** analyser giving real online data.

The middle fraction, starting from benzene and upwards to chrysene (BP 448°C), can easiest be analysed by **GCMS** with tube adsorption / desorption technology, which is a rather rapid method with sampling intervals less than 30 minutes. NotePlease note that, the lightest components will not be captured by the adsorbent in the tubes and will therefor pass straight through the system, but from benzene and upwards, all components with a higher boiling point will generally be adsorbed. Also heavier PAH present in the gas stream will be trapped in the desorption unit along with particles. Depending on the maximum desorption temperature it is not certain to which extend the high boiling compounds are released during desorption of the tubes.

Thus, both analytical methods (FT-IR and GCMS) can be utilized directly on a process gas stream. However, to protect the instrument itself, gas streams are in general filtered through temperature controlled filters. Where heavy compounds will condense from the gas stream, further the filter will trap aerosols, droplets and particles to certain extend. Heavy PAH in these states will therefore not be registered in a subsequent analysis applying FTIR or GCMS.

The heaviest fraction of PAH, however, is more challenging. They can easily be captured through manual sampling by liquid absorption, e.g.: using a series of bubbling flasks / impingers containing a solvent that dissolves PAH. The challenge is to find a suitable solvent that can handle the properties of the operational conditions such as gas matrix, temperature of the off gas, water and dust concentration. The benefit with this sort of collection method is that the solvent will simultaneously capture aerosols and particles as well, thus dissolving PAH adsorbed on the surface of other particles. This means that all dissolved PAH will be accounted for and nothing will be prevented from reaching the analysis in a GCMS by being captured in a filter.

However, there is one limitation of the combination manual sampling and GCMS, namely the elution of solvent, aromatics

and PAH from the GC-column into the MS. PAH species with boiling point lower than the adsorbent chosen will be masked due to the high background signal from the adsorbent. For example, when using 2-methoxyethanol (EGME) as a solvent only PAH-compounds with more than 10-C atoms can be detected using this methodology. On the other hand, if a too volatile the adsorbent is chosen there will be a problem with vaporization during sampling.

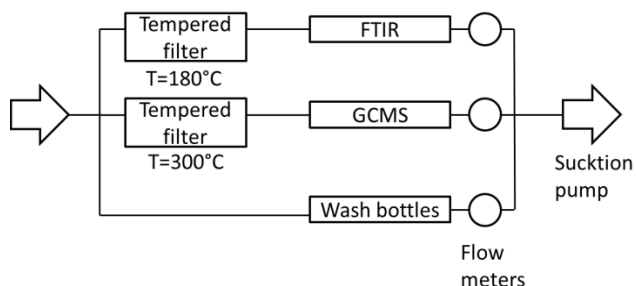


Figure 1: Sketch of proposed setup for total sampling of PAH.

Applying a procedure where the sample gas stream is splitted requires some considerations because it is essential to keep track of how much gas that passes through each section. Installation of individual volume flow sensors in each of the sampling lines after a sampling / analysis device is a feasible way of controlling the individual volume flows.

With the proposed setup, a FTIR can be taken into the field accompanied with a GCMS for analysis of light and medium weight (linear, isomeric and aromatic) hydrocarbons. However, analysis of the heaviest components can not be reliably preformed on equipment that are light and robust enough to be taken out of the laboratory. Samples of the heaviest fraction of PAH components will therefore have to be analyzed off site.

Examples of analysis

Although a complete collection setup like this have not yet been tested in the field, each of the technologies proposed have been tested and are proven to be valuable.

Analysis of intermediate fraction

An Agilent 9075 connected to a Marks Unity2 Airserver and tube desorption unit was used in these experiments. The Agilent 9075 is made by Agilent to be robust enough to be used in mobile applications while maintaining the high precision of an advanced laboratory instrument.

The measurements were taken before and after the gas treatment center of an anode baking furnace.

Adsorbent tubes were used to adsorb PAH by using only a small setup at the actual sampling site. The tubes were then subsequently desorbed into the cold trap of the Unity2 allowing for the GCMS and Unity2 to be assembled in a fixed location.

In our experiments there were 4 steps in the analysis:

- 1.) Gas from the baking furnace is passed through the sampling tubes where the PAH components are adsorbed.
- 2.) The sampling tubes are heated while they are flushed with helium to release the PAH, after which the PAH is transferred to the cold-trap kept at -20°C.

- 3.) The cold trap is rapidly heated and the PAH is transferred into the GC column.
- 4.) As the components emerge on the other end of the GC column they are fed into the MS where the molecular fractions are analysed on a weight basis.

The gas was sampled using a regular suction pump and gas volume measurement. The sampled gas was drawn through adsorbent tubes (Tenax GR), and gas volume along with sampling time was recorded. Typical sampling times are between 5 and 10 minutes giving a gas volume in the range of 2-3 L. The tubes will generally adsorb components heavier than C₄, but components with a high boiling point will condense in the sampling system of the GCMS, hence it will not be possible to do reliable quantifications on these components. This defines the limits upwards for this methodology.

The tubes were then desorbed into the cold trap using 50 mL/min helium and a temperature of 320°C, the cold trap was held at -20°C. Reversed gas flow was used during desorption, forcing the components out of the tube through the same end as they were sampled. This will most efficiently desorb the heavy components, which might take long to pass all the way through the adsorbent matrix of the tube if the flow was not reversed.

Subsequently, the cold trap was flash heated to 320°C within 2 seconds and purged with 20 mL/min helium. This helium stream was fed into the GC column on the GCMS where the flow was splitted to give the right flow of gas through the GC column. The excess gas was purged through a trap and discarded.

The column was operated in a constant flow mode of 1.2mL/min to achieve a constant split ratio of the gas flow before the column. The column was heated in a temperature program from 170°C to 280°C, and then held at 280°C

This is the temperature limit of the HP-5 column that it should be operated at. High temperatures at the end resulted in excessive column bleed and reduced signal to noise ratio, which limited the ability to quantify the heaviest PAH components with high accuracy.

One set of samples were sent to for standard analysis to a commercial analytical laboratory where several tubes were analysed on the GCMS setup.

The results are presented in Table I

Table I: Analytical results from commercial analysis, test 1 and test 2 are taken downstream the gas cleaning facility, whereas test 3 is taken upstream

uG/m ³	After ahex-1	After ahex-2	Before ahex
Acenaphthene	0.71	0.73	8.79
Acenaphthylene	<0.2	<0.2	11.2
Benz[a]anthracene	<0.2	<0.2	4.85
Benzo[b/j/k]fluoranthene	0.37	0.62	
Benzo[ghi]perylene	<0.2	<0.2	<0.2
Benzo[a]pyrene	3.12	6.05	10
Chrysene	<0.2	<0.2	15
Dibenz[a,h]anthracene	<0.2	<0.2	0.34

Fluoranthene	1.14	1.18	98.1
Fluorene	<0.2	<0.2	5.5
Indeno[1,2,3-cd]pyrene	<0.2	<0.2	0.22
Naphthalene	19.6	22.09	84.3
Anthracene / Phenanthrene	15.6	18.9	
Pyrene	6.71	7.84	59.4

Our sampled tubes from the campaign were analysed on the GCMS and we did observe the same PAH components as were described in the report. However, due to an uncontrolled dilution occurring after a valve malfunction we were not able to quantify these samples, we did however see the same trends and species as reported in the results.

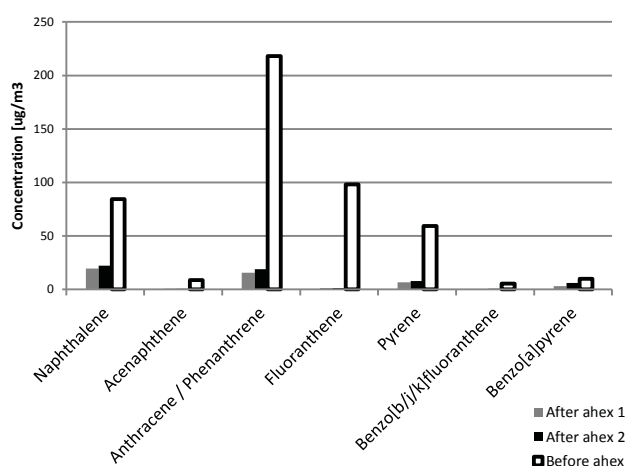


Figure 2: Concentration of the different PAH identified in the samples.

In Figure 2 the data analyzed at a commercial analytic laboratory from the same field work is presented. It can be seen that the PAH levels significantly decrease when comparing the levels before and after the heat exchanger. There is also a shift in the distribution of PAH, as expected, because after the heat exchanger the content of the lightest fractions are more dominant, when compared to before the heat exchanger where the heavier Phenanthrene was the dominant species.

To determine the detection limits of the setup we conducted further laboratory studies using a synthetic EPA 610 standard [6] from Sigma-Aldrich containing a mixture of the 16 most important PAH constituents. Out of these we could identify all except for the 4 heaviest as they are not suitable for the HP5 column that we had chosen to install in the GC.

By loading the tubes with small amounts of the EPA 610 mixture we determined that the detection limits of the analyser were between 0,5 ng and 3 ng loading of the given PHA species on the tube. This relates to 20 min of 250 mL/min sampling gas containing 0,1 – 0,6 ug/m³ PHA. This is well below what was detected in the gas samples taken from the anode baking furnace (Table I), and shows that the performance of our setup is capable of quantifying gases with a useful sensitivity.

Table II: PAH 610 standard analyzed, first column gives actual injected amount on the tube, and second column gives the corresponding concentration in a gas if the tube had been sampled for 20 minutes at 250 mL/min.

Acenaphthene	10 ng	2 ug/m ³
Acenaphthylene	20 ng	4 ug/m ³
Anthracene	1 ng	0.2 ug/m ³
Benz[a]anthracene	1 ng	0.2 ug/m ³
Benzo[b]fluoranthene	2 ng	0.4 ug/m ³
Benzo[k]fluoranthene	1 ng	0.2 ug/m ³
Benzo[ghi]perylene	2 ng	0.4 ug/m ³
Benzo[a]pyrene	1 ng	0.2 ug/m ³
Chrysene	1 ng	0.2 ug/m ³
Dibenz[a,h]anthracene	2 ng	0.4 ug/m ³
Fluoranthene	2 ng	0.4 ug/m ³
Fluorene	2 ng	0.4 ug/m ³
Indeno[1,2,3-cd]pyrene	1 ng	0.2 ug/m ³
Naphthalene	10 ng	2 ug/m ³
Phenanthrene	1 ng	0.2 ug/m ³
Pyrene	1 ng	0.2 ug/m ³

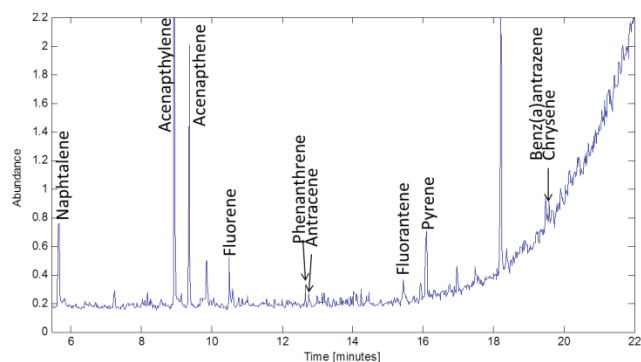


Figure 3: GCMS chromatogram showing signal for a sample load corresponding to Table II. The three highest peaks corresponds to Naphtalene, Acenaphthylene and Acenaphthene. The increase in column bleed can be seen at the end of the chromatogram.

In order to investigate if a higher sensitivity could be achieved we reduced the split of the gas before the GC column. The column flow could not be increased so the total purging flow through the cold trap would have to be reduced. This was expected to give less pronounced and sharp peaks in the GC chromatogram as the total time to empty the cold trap and inject it into the column would increase. We found that a reduction to 12 mL/min through the cold trap gave acceptable results, and almost doubled the sensitivity making it possible to quantify components as low as 0.25-1.5 ng on the tube, and by 20 min 250 ml/min sampling be able to quantify gases containing 0.05 to 0.3 ug/m³.

However, the low flow through the cold trap made it impossible to separate the peaks of anthracene and phenanthrene as they now became much more interlaced. A further reduction of the desorb flow was not investigated as that would have made these effects even worse.

Another way to increase the sensitivity is to increase the volume of gas through the tubes when sampling. This would require a prolonged sampling time, but in return it can virtually increase the sensitivity to any desired level.

For applications where increased sensitivity could be needed the sampling time in the duct can be increased, which would relate to a identical increase in detection limits.

The GCMS analysis gave good separation between the different PAH components and we were even able to differentiate between anthracene and phenanthrene, which usually is considered difficult to separate using GC methodology.

All these analysis described here can also be performed in the field with an analysis time of approximately 30 minutes.

Heavv fraction

A sampling setup to recover the heavier fraction of the PAH has been designed (see Figure 4) and tested in a gas stream from the furnace at a ferro alloy plant with up to 200 °C and a dust load in the order of 100 g/Nm³. For analysis a laboratory high temperature capable GCMS unit was used in combination with liquid injection of the solutions from the five absorbers.

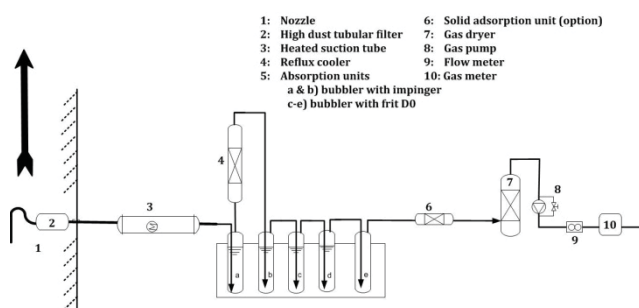


Figure 4: Sampling setup for liquid adsorbent.

For capturing PAH compounds from the raw gas stream of a furnace, a setup consisting of five wash bottles was used. The solvent for the given application was ethylene glycol methyl ether (EGME, 2-methoxyethanol) as it has a boiling point of 125°C and an auto ignition temperature of 285°C fulfilling HES requirements at site. The solvent combined good properties for dissolving both polar and non-polar PAH's of interest, however, all components with lower boiling points than the adsorbent liquid will be excluded from the analysis by a GCMS due to simultaneous evaporation of the adsorbent and analytes.

Table III: Results from samples taken with liquid adsorbent from the furnace.

Compound ($\mu\text{g}/\text{m}^3$)	Before gas cleaning	After gas cleaning
Naphtalene	20321	885
Acenaphthylene	9085	443
Acenaphthene	478	103
Fluorene	6455	142
Phenanthrene	18648	0
Antracene	19365	199
Fluoranthene	18967	91
Pyrene	19365	99
Benz(a)antrazene	11715	0
Chrysene	11715	62
Benzo(b)fluoranthen	10758	91
Benzo(k)fluoranthen		
Benzo(a)pyrene	3347	36
Idenol(1,2,3-cd)pyrene	1036	0
Benzo(ghi)perylene	2710	0

In this analysis all the heaviest components of the EPA 610 standard were successfully quantified. However, careful attention is needed to avoid deposition of PAH components on the inlet and sides of the wash bottles, which require proper handling of the absorbers after performed sampling to ensure that a representative sample is taken.

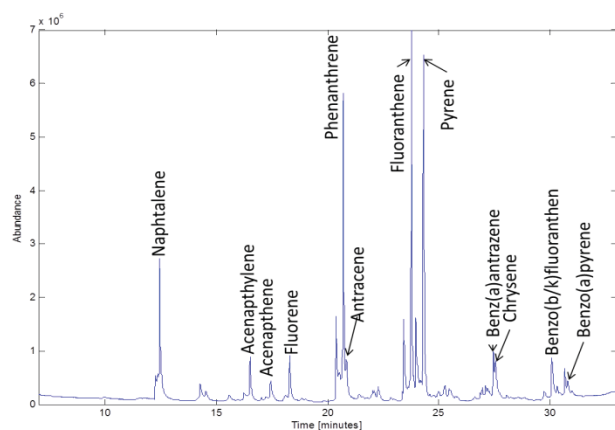


Figure 5: GCMS chromatogram corresponding to the data in Table III.

One other factor is that the lightest PAH components can not be detected with this methodology. PAH components with boiling point lower than the liquid adsorbent will elute together with the adsorbent from the GC, thus detection/quantification is not possible.

On the contrary for the solid adsorbent where the components with high boiling points could not be identified since the adsorbent in that case should not be heated above the desorption temperature of compounds. In some cases higher than the decomposition temperature of the solid adsorbent.

In Table III the same trend as from the data for the anode baking facility can be observed. The main part of the PAH distribution is moved towards the lighter PAHs after the gas cleaning facility. For the example in Table III it would be possible to use the at site methodology with tube adsorption / desorption GCMS to analyse the gas after the gas treatment centre without compromising anything except some accuracy on the quantification of the low amounts of Benzofluoranthen.

Conclusions

The proposed methodology gives a setup for analysing the entire range of PAH components along with most VOC components. The lightest components can be analysed on a FTIR, the mid-range components is suitable for field GCMS analysis whereas the heaviest have to be dissolved in liquid solutions and analysed off-line by laboratory GCMS equipment.

FTIR-analysers for organic compounds are readily available for installation on-site for online monitoring provided proper calibration. A GCMS combined with tube desorption is a suitable technology for at-site monitoring of PHA components. This technology is now light and robust enough to be moved out from the laboratory and to the industrial plant, giving the possibility of fast and accurate analysis of PAH components. GCMS works well for components up to Chrysene with a boiling point as high as 448°C, and with reduced sensitivity on benzopyrene and dibenzantracen. The heaviest PAH components, such as indeno[1,2,3-cd]pyrene, needs to be sampled manually by means of liquid absorption and followed by analysis in a laboratory.

Limitations of analysis from the liquid sampling can be overcome by utilization of ultrahigh resolution FT-ICR, Mass spectrometry is a relatively new technology that allows determination of elemental formula of compounds in very complex samples. FT-ICR MS is well suited for characterization of heavier PAHs, especially those that are so heavy that they not can be analyzed by GCMS. The applicability will be tested in the near future.

Although the full setup with liquid extraction is proven to be better, the performance of the tube desorption technology and portable GCMS setup seems to be suitable for most applications. For most of the applications the gas treatment facility removes the heavier fractions more efficiently, which means that the PAH components that are most interesting to monitor will be the lighter PAH that efficiently are adsorbed and desorbed from tubes. The detection limits for this type of setup are more than adequate to quantify any relevant source of PAH emissions and the speed of the process makes it ideal for process tuning feedback. Combined with its simplicity and flexibility, the tube adsorption technology combined with at site analysis can give fast and sufficient information of a systems performance.

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