

Characterisation of PAHs, PASHs, and O-PAHs in fugitive, stationary emissions and ambient air samples from a coke oven plant in the UK

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In the process of converting coal into coke (carbonisation of coal or coking) using a by-product recovery coke oven, the volatile matter in the coal (about 35% is a typical range for coking coals) is vaporized and driven off by heating in the absence of oxygen (air) in large ovens. The resulting gases and tars (volatile matter) are drawn off into a by-product plant to be separated into coke oven gas, tar, benzole and ammonia. The treated coke oven gas is returned to the coke oven battery where it is burnt to provide heat for the coking process and the waste combustion products from the underfiring process are emitted to atmosphere via a stack. The remaining metallurgical coke product has a volatile content of less than 2%. Potential sources of pollution in a coke oven plant are fugitive emissions caused by leakages from the coke oven sealing surfaces such as oven doors, lids and ascension pipes and stationary emissions from the main underfiring stack.

Coke ovens potentially constitute a significant source of organic micro-pollutants, particularly semi-volatile organic compounds (SVOCs) such as PAHs (polycyclic aromatic hydrocarbons), PASHs (polycyclic aromatic sulphur heterocycles) and O-PAHs (oxygen-polycyclic aromatic heterocycles). In 1999, the European commission created a working group to review the knowledge on PAHs in ambient air and to consider the need for regulations under the Air Quality Framework Directive (96/62/EC). The working group issued a position paper in July 2001 where it recommended that ambient concentrations of PAHs should be below 1.0 ng B[a]P / m³, annual mean and, therefore that the EU should adopt an air quality limit of between 0.5 -1.0 ng B[a]P / m³, annual mean, to be achieved by 2010¹. A limit of 1.0 ng B[a]P / m³ was subsequently endorsed by the European Parliament in 2004 to be reached by December 2012. Corus, a major European steel-making group, operates four integrated steelworks including seven coke oven plants. Under a Research Programme of the Research Fund for Coal and Steel that started in 2004 (ERAMAC), the Environment Department of Corus R, D and T is carrying out investigations to characterise SVOCs in coke oven emissions and in ambient air in the vicinity of coke plants.

Preliminary work focused on the development of suitable analytical methods for the analysis and sampling of SVOCs. An analytical method was developed for the quantitative analysis of targeted PAHs, PASHs and O-PAHs by GC/MS using deuterated internal labelled standards. Briefly, samples collected on XAD-2 resin traps and/or polyurethane foams (PUFs) were extracted with dichloromethane using accelerated solvent extraction and the resulting extracts were submitted to a basic alumina clean up to separate aliphatic hydrocarbons from aromatic species. The analytical procedure was fully validated using a certified reference urban dust (NIST 1649a). Ambient air samples in the vicinity of the coke plant were collected using Graseby Andersen Hi-volume samplers equipped with a PUF plug and a glass fibre filter. Stationary sampling of both coke oven doors and underfiring emissions was achieved following a standard UKAS ISO 17025 method derived from US EPA method 23. However, for the sampling of fugitive door emissions, the presence of atmospheric and thermal turbulence around the coke oven battery meant that the collection of a representative sample from oven doors was difficult. To overcome this problem, a unique method of channeling emissions from the whole door and seals was devised. A flame-retardant blanket was fixed across the outer buckstays of the oven to be sampled, thus creating a flue whereby air was drawn in at the bottom that carried the door emissions through buoyancy to the top of the battery where the gas flow could be measured and the emission sampled using conventional methods. Trials were undertaken at a Corus coke oven plant in 2004 and 2005 to characterise PAHs, PASHs and O-PAHs concentrations in fugitive door and underfiring stationary emissions, and to monitor the quality of ambient air in the vicinity of the plant. This paper will present details of the analytical and sampling methods used by Corus for the determination of SVOCs, and discuss the concentrations of PAHs, PASHs and O-PAHs determined in fugitive, stationary and ambient air samples from a Corus coke oven plant.

¹ Ambient air pollution by polycyclic aromatic hydrocarbons. Position paper prepared by the working group on polycyclic aromatic hydrocarbons. Office for Official Publications of the European Communities, 2001. ISBN 92-894-2057-X.

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