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Method development and validation for total mercury determination in coke oven gas combining a trap sampling method with CVAAS detection

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ABSTRACT

Coke oven gas is one of the by-products of the coal coking process. It is used as a fuel in the coking plant, but also as a raw material in the chemical industry to produce methanol, syngas or environment-friendly, low-CO_2 hydrogen fuel. Due to the reasons mentioned above, the knowledge of coke oven gas pollutants such as mercury is a key issue. To determine the mercury in the cleaned coke oven gas a trap sampling method combined with CVAAS mercury detection was developed, optimized and validated. In order to perform the sampling process the traps filled with activated carbon were used. The determination of mercury in the traps material was performed by means of an MA-2 mercury analyzer. During the optimization of the method one selected the trap material, sample volume and flow rate. The optimal volume of the coke oven gas sample was 3 dm^3 and the flow rate was 18 dm^3/h (per one trap). The developed method was validated according to the Eurachem recommendation and was applied to determine mercury in the clean coke oven gas. The coke oven gas sampling was performed in a coking plant in Poland. The average concentration of mercury in the clean coke oven gas was 3.2 ± 0.3 μg/m$_N^3$ (k = 2) for n = 18.

1. Introduction

Coke oven gas is one of the products of the coal coking process. Coke oven gas is used mainly as fuel in the coking plant. Additionally, the high density of hydrogen predisposes the coke oven gas to be used as an environment-friendly, low-CO_2 fuel [1–3] or as a raw material in the chemical industry to produce methanol [4–8] or syngas [1–3,9,10]. Due to the reasons mentioned above, the knowledge of coke oven gas pollutants such as mercury is important. The source of mercury in the technological installation of the coking plant is the coking of coal that may contain various compounds of mercury [11,12]. The average concentration of mercury in charge coal measured in coals from four coking plants was 75 ± 9 μg/kg [13]. During the heating of coal the concentration of mercury in coal is reduced. The average concentration of Hg in coke measured by Konieczynski was 14 ± 7 μg/kg (about 20% of Hg which exists in charge coals) [13]. This means that about 80% of mercury from coal enters various products such as sulfur, coal-tar and coke oven gas or is emitted in disorganized emissions during coke oven battery loading [14]. Together with coke oven gas, mercury enters the technological circuit of the coking plant and then, with a flue gas, the environment.

Since 2007 all coking plants are subject to the European Pollutant Release and Transfer Register (E-PRTR) [15]. According to the legal regulations, coking plants are obliged to monitor the pollutants that are released and to issue reports. The threshold of mercury and its compounds released to the air, in accordance with the E-PRTR regulations, is 10 kg/year. The exceeding of this level obliges coking plants to inform the relevant authorities responsible for environmental pollution monitoring about this fact.

In the literature there is a lack of information on mercury determination in coke oven gas. Determination of mercury in the coal and solid or liquid products of the coking process such as: coke, desulfurization products or coal-tar is relatively simple and could be performed by means of a mercury analyze [16–21]. However, for the full balance, mercury should be also determined in the coke oven gas. The determination of mercury in process gases like flue gas is amply described in the literature [22–26], but from an analytical point of view, due to the rich organic matrix and hydrogen, coke oven gas is a much more complicated sample. The main components of coke oven gas are N_2, CO_2, CO, CH_4 and H_2, but even purified coke oven gas also contains a high amount of benzol (about 3 g/m$_N^3$) and naphthalene (about 0.5 g/m$_N^3$) [27]. For this reason, in the case of coke oven gas, the use of continuous analyzers or scrubber systems for the determination of mercury is impossible. In order to develop mercury balance in the

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coking plant, it was necessary to develop an effective and safe method for the determination of mercury in coke oven gas.

The main aims of this paper are as follows: to present the developed method of mercury determination and the concentration of mercury in the purified coke oven gas. To enable the determination of mercury in the coke oven gas a sampling method utilizing activated carbon traps combined with CVAAS detection was developed. The method was validated according to the Eurachem recommendation and used for mercury determination in real sample.

2. Experimental

2.1. Apparatus

For the collection of mercury, a trap system, designed for industrial use, was developed. Mercury from coke oven gas, collected in the activated carbon traps, was subsequently determined in the laboratory by means of an advanced MA-2 mercury analyzer (Nippon Instrument Corporation, Japan).

2.1.1. Coke oven gas sampling system

In order to take a sample, a clean coke oven gas system, shown in the Fig. 1, was designed and constructed. The coke oven gas enters the sampling system through the PTFE transfer line (1), then the gas flows through a pressure compensator with the function of water removal (2). All connections in the system are made from silicon tubing (3). The pressure compensator is connected with a glass tee connector (4). Mercury and organic compounds are captured at three sections of activated carbon traps (5). Then the gas passes through the scrubber (6), which is filled with a mixture of activated carbon and sorbent (sampling unit protection), and next reaches the sampling unit (7). The sampling unit (ASP-2 II, ZELMOT, Poland) with a flow rate of 10–70 dm^3/h (air) was used. The sampling place was situated in the second explosion zone (coke oven gas contains over 50% of hydrogen). Therefore the sampling line was not heated and the sampling of coke oven gas was performed when the air temperature was close (± 10 °C) to the temperature of the coke oven gas.

2.1.2. The MA-2 mercury analyzer

In order to determine the mercury in the trap materials one used an advanced MA-2 Nippon Instrument Corporation (Japan) mercury analyzer. In the MA-2 analyzer the analyzed sample is introduced into the first furnace, where the thermal decomposition or evaporation of mercury compounds occurs. Then mercury is atomized in the second furnace and Hg vapor forms an amalgam in the amalgamation unit (sand covered with gold). After the amalgamation process the amalgam is heated up to 600 °C to release atomic mercury, which is determined by means of a CVAAS detector at a wavelength of 253.7 nm in the absorption chamber. The detection limit of MA-2 analyzer is 0.01 ng. The analyzer has the capability to set a two-stage heating of the sample at different temperatures.

2.2. Materials

All reagents and standards were of an analytical grade or higher. Traps for the collection of Hg were constructed from a 10 cm-long, borosilicate glass tube with an internal diameter of 6 mm. Each trap consists of three sections. Sections were separated with quartz wool. A 6 mm PTFE tube was used as a transfer line. Activated carbon (AC) or a sorbent were applied as a filling material of the traps. The Coconut Activated Carbon (Storms, Sweden) properties were as follows: surface area: 1150 m^2/g; density: 480 $\mathrm{g/dm}^3$; hardness: 90%; grain size: 0.1–0.5 mm. During the method optimization, in addition to activated carbon, a Damasorb (IM-POL, Poland) sorbent was also used. The properties of the sorbent were as follows: name: chemical composition: SiO_2 – 75%, Al_2O_3 – 10%, Fe_2O_3 – 6%, CaO – 2%, MgO – 1%, $K_2O + Na_2O$ – 2%, other – 4%; density: 433 $\mathrm{g/dm}^3$; hydrocarbon absorbency: 98%; grain size 0.1–0.5 mm. To obtain a proper granulation of trap materials (0.1–0.5 mm) the AC and the sorbent were ground in a mortar and sieved. A 20% solution of HNO_3 (J.T. Baker, Holland) was used for cleaning of the trap. A 10% (w/v) aqueous potassium hydroxide solution from J.T. Baker (Holland) was used as a solution in the scrubber of the MA-2 analyzer. The B (Nippon Instrument Corporation, Japan) and M (POCH, Poland) additions, recommended by the manufacturer of the MA-2 mercury analyzer, were used during the determination of Hg in the activated carbon and sorbent samples. A MB-1 mercury vapor generator from Nippon Instrument Corporation (Japan) was used as a source of elemental mercury. Five and ten dm3 Teddlar bags were used to prepare the Hg° calibration gases.

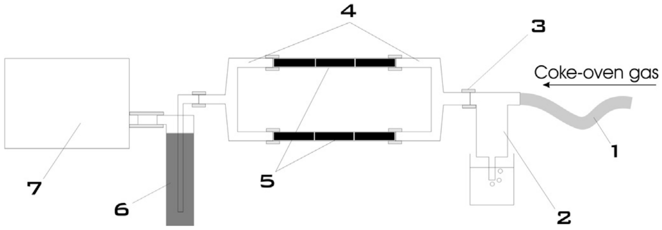

Fig. 1. Coke oven gas sampling system.

2.3. Procedures

2.3.1. The preparation of the trap

Each trap consisted of a borosilicate glass tube filled with activated carbon or sorbent. The material inside the trap was divided into three sections. Each section was about 33 mm long. The average weight of the material from one section was about 0.2 g. At the beginning and at the end of each section one placed quartz wool whose thickness was approximately 5 mm. The quartz wool separates the individual sections and prevents the trap material from being trapped during transport. The ends of the traps were closed with a glass stopper. During the transport traps were stored in a sealed polyethylene bag. The inlet and outlet of the trap and the direction of the gas flow were marked on the tube. After being filled with activated carbon or sorbent, the traps were combined in pairs on the basis of the measurement of flow resistance. This ensured the similar gas flow, during Hg pre-concentration, through two traps which constituted one set.

2.3.2. Coke oven gas sampling procedure

The samples of clean coke oven gas were collected in the coking plant after the benzol scrubber section. The air temperature during sampling was always above 20 °C. In the initial phase of sampling method testing, there was a problem with benzol (mixture of benzene, toluene and xylene) condensation, in the lower air temperatures, on the internal surfaces of the glass tube of the trap. This problem was detected during the thermal cleaning of the glass tubes in a MA-2 mercury analyzer. Therefore in the final sampling procedure the samples were taken at an air temperature (± 10 °C) similar to the temperature of the coke oven gas (typically 25 °C). Using the above procedure, mercury (bonded with organic compounds) was not found on the internal walls of the trap. The flow rate of coke oven gas was set to 36 $\mathrm{dm}_N^3/\mathrm{h}$ per set (18 $\mathrm{dm}_N^3/\mathrm{h}$ per single trap). The sampling volume was 3 dm_N^3 per single trap. At the beginning of sampling the sampling system was conditioning. Six dm_N^3 of coke oven gas were passed through the system in which the traps were replaced by glass tubes. After conditioning the glass tubes were replaced by traps filled with activated carbon or sorbent. The sampling volume and flow rate during sampling was the same as during the conditioning of the system. During the sampling day the field blanks traps were used. Two traps were opened (glass plugs were removed) for about one minute. Then traps were closed and inserted into a sealed polyethylene bag. Those traps were used to set the