### The innovative system for coke oven wastewater treatment and water recovery with the use of clean technologies



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#### **1. Introduction**

Coke oven wastewater (COW) is a highly loaded stream contaminated with a range of various organic and inorganic substances. Their presence in the stream has to be carefully controlled in order to assure the proper run of processes involved in the treatment cycle and fulfillment of coke oven wastewater treatment plant (COWTP) effluents standards. Considering both, technological requirements and regulations, one may distinguish a group of target contaminants, which has to be especially monitored, i.e. cyanides, sulphides, tars, phenols and ammonia. These contaminants can be classified due to their impact on biological processes involved in the treatment technology. Hence, cyanides, sulphides and tars are regarded as process inhibitors and have to be removed to a proper level during preliminary COW treatment with the use of physical and chemical operations. On the other hand, phenols and ammonia are main substances undergone to biodegradation, during which phenols act as carbon source for microorganisms responsible for decomposition of ammonia.

The concentration of all listed substances has to be measured in priority in coke oven wastewater treatment plant (COWTP) effluent, but also in influent and in selected technological processes' streams. The range of particular contaminants concentration in coke oven wastewater plant influent and the permissible concentration in COWTP effluent are shown in table 1. The latter values are based on Commission Implementing Decision of 28 February 2012 establishing the best available techniques (BAT) conclusions under Directive 2010/75/EU of the European Parliament and of the Council on industrial emissions for iron and steel production. Methods dedicated to their analysis should characterize with high accuracy, precision and selectivity accompanied with both, relatively short time and low costs, due to the high frequency of the analysis performance.

#### Table 1. Concentration of typical coke oven wastewater contaminants

Contaminant	Unit	Concentration usually observed in coke oven wastewater treatment plant influents <sup>(1)</sup>	Concentration usually observed in coke oven wastewater treatment plant effluents <sup>(1)</sup>	Permissible concentration in treated coke oven wastewater <sup>(2)</sup>
Chemical oxygen demand, COD	mg/dm <sup>3</sup>	2000 - 6500	75-280	<220
Biological oxygen demand for 5 days, BOD <sub>5</sub>	mg/dm <sup>3</sup>	800 - 3000	5-15	<20
Sulphides, easily liberatable	mg/dm <sup>3</sup>	n/a	0.01-0.05	<0.1
Thiocyanate SCN <sup>-</sup>	mg/dm <sup>3</sup>	150 - 380	0.5-3	<4
Cyanides, easily liberatable	mg/dm <sup>3</sup>	1-10	0.01-0.03	<0.1
Polycyclic aromatic hydrocarbons (PAHs) <sup>(3)</sup>	mg/dm <sup>3</sup>	200	< 0.05	<0.05
Phenols	mg/dm <sup>3</sup>	500-1500	< 0.1	< 0.5
Sum of ammonia- nitrogen $(NH_4^+-N)$ , nitrate-nitrogen $(NO_3^N)$ and nitrite- nitrogen $(NO_2^N)^{(4)}$	mg/dm <sup>3</sup>	35-300	10-35	<15-50

<sup>(1)</sup> In reference to Best Available Techniques (BAT) Reference Document for Iron and Steel Production

<sup>(2)</sup> In reference to BAT Conclusions for Iron And Steel Production

<sup>(3)</sup> Sum of Fluoranthene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene and Benzo[ghi]perylene

<sup>(4)</sup> Regarding the sum of ammonia-nitrogen ( $NH_4^+$ -N), nitrate-nitrogen ( $NO_3^-$ -N) and nitrite-nitrogen ( $NO_2^-$ -N), values of < 35 mg/dm<sup>3</sup> are usually associated with the application of advanced biological waste water treatment plants with predenitrification/nitrification and post-denitrification.

Within the task 1.1. of INNOWATREAT project, main goal of which was to select recommended analytical procedures for target contaminants determination, a number of methods based on chromatography, spectrophotometry, potentiometry and titrimetry was reviewed, investigated and evaluated.

### 2. Methods for cyanides determination

#### **2.1. General information**

Cyanides appear in coke oven wastewater as a result of presence of hydrogen cyanide (HCN) gas coke oven gas. Hydrogen cyanide is formed during coal coking process due to the high temperature, reducing atmosphere and the presence of nitrogen and carbon. The amount of hydrogen cyanide produced during the process is assumed at the level of 1.5-2% of the nitrogen content in the coal. During coke oven gas treatment, a portion of cyanide gas remains in the gas stream, while the rest leaves the coking system in the waste ammonia liquor – the basic constituent of coke oven wastewater.

In raw coke oven wastewater cyanides appear in the ionic form CN<sup>-</sup> and (in a lower extent) as a non-dissociated hydrogen cyanide. Those cyanides are known as free cyanide species. Due to the presence of various substances in coked coal, cyanides may also appear in the form of complexes with various metals e.g. Fe, Na, K, Ca, etc. However, the appearance of particular complex species is very difficult to be precisely identified. The list of weak and strong metal-cyanide complexes, which can be met in aqueous environments, is given in table 2. The sum of free and complex cyanide species gives the total amount of cyanides in the stream.

Classification	Cyanide species
Free cyanide	HCN, CN <sup>-</sup>
Weak metal- cyanide complexes	Ag(CN)OH <sup>-</sup> , Ag(CN) <sup>-</sup> <sub>2</sub> , Ag(CN) <sup>2-</sup> <sub>3</sub> , CdCN <sup>-</sup> , Cd(CN) <sub>2</sub> , Cd(CN) <sup>2-</sup> <sub>4</sub> Cu(CN) <sup>-</sup> <sub>2</sub> , Cu(CN) <sup>3-</sup> <sub>3</sub> , Cu(CN) <sup>3-</sup> <sub>4</sub> , NiH <sub>2</sub> (CN) <sup>0</sup> <sub>4</sub> , NiH <sub>3</sub> (CN) <sup>+</sup> <sub>4</sub> , Ni(CN) <sub>2</sub> , Ni(CN) <sup>-</sup> <sub>3</sub> , Ni(CN) <sup>2-</sup> <sub>4</sub> , NiH(CN) <sup>-</sup> <sub>4</sub> , NiH <sub>2</sub> (CN) <sup>0</sup> <sub>4</sub> , NiH <sub>3</sub> (CN) <sup>+</sup> <sub>4</sub> , Zn(CN) <sub>2</sub> , Zn(CN) <sup>-</sup> <sub>3</sub> , Zn(CN) <sup>2-</sup> <sub>4</sub> , HgCN <sup>+</sup> , Hg(CN) <sub>2</sub> , Hg(CN) <sup>-</sup> <sub>3</sub> , Hg(CN) <sup>2-</sup> <sub>4</sub> , Hg(CN) <sub>2</sub> Cl, Hg(CN) <sub>3</sub> Cl <sup>2-</sup> , Hg(CN) <sub>3</sub> Br <sup>2-</sup> ,

Table 2. Species of cyanides, which may appear in aqueous environment

Classification	Cyanide species
Strong metal- cyanide complexes	$BaFe(CN)_{6}^{2^{-}} BaFe(CN)_{6}^{-} Ca_{2}Fe(CN)_{6}^{0} CaHFe(CN)_{6}^{2^{-}} CaFe(CN)_{6}^{2^{-}} CaFe(CN)_{6}^{0} Ca_{2}Fe(CN)_{6}^{0} CaHFe(CN)_{6}^{2^{-}} Fe(CN)_{6}^{2^{-}} HFe(CN)_{6}^{3^{-}} H_{2}Fe(CN)_{6}^{2^{-}} Fe_{2}(CN)_{6}^{0} K_{2}H_{2}Fe(CN)_{6}^{0} K_{3}HFe(CN)_{6}^{2^{-}} Fe_{2}(CN)_{6}^{2^{-}} KFe(CN)_{6}^{3^{-}} K_{2}Fe(CN)_{6}^{3^{-}} KFe(CN)_{6}^{3^{-}} LiFe(CN)_{6}^{3^{-}} Li_{2}Fe(CN)_{6}^{3^{-}} Li_{2}Fe(CN)_{6}^{2^{-}} ShFe(CN)_{6}^{2^{-}} Fe(CN)_{6}^{3^{-}} MgFe(CN)_{6}^{2^{-}} NH_{5}Fe(CN)_{6}^{2^{-}} NH_{4}Fe(CN)_{6}^{3^{-}} Na_{2}Fe(CN)_{6}^{2^{-}} NaHFe(CN)_{6}^{2^{-}} SrFe(CN)_{6}^{3^{-}} Na_{2}Fe(CN)_{6}^{2^{-}} NaHFe(CN)_{6}^{2^{-}} SrFe(CN)_{6}^{3^{-}} , Au(CN)_{2}^{2^{-}} Co(CN)_{6}^{3^{-}} , Pt(CN)_{2}^{2^{-}} NaHFe(CN)_{6}^{2^{-}} NaHFe(CN)_{6}^{3^{-}} Na_{2}Fe(CN)_{6}^{3^{-}} NaHFe(CN)_{6}^{3^{-}} NaHFe(CN)_{6}^{3^{-}} Na_{2}Fe(CN)_{6}^{2^{-}} NaHFe(CN)_{6}^{2^{-}} NaHFe(CN)_{6}^{3^{-}} Na_{2}Fe(CN)_{6}^{3^{-}} NaHFe(CN)_{6}^{3^{-}} Na_{2}Fe(CN)_{6}^{3^{-}} NaHFe(CN)_{6}^{3^{-}} Na_{2}Fe(CN)_{6}^{3^{-}} NaHFe(CN)_{6}^{3^{-}} NaHFe(CN)_{6}^{3^{-}} Na_{2}Fe(CN)_{6}^{3^{-}} NaHFe(CN)_{6}^{3^{-}} NaHFe(CN)_{6}^{3^{-}} NaHFe(CN)_{6}^{3^{-}} Na_{2}Fe(CN)_{6}^{3^{-}} NaHFe(CN)_{6}^{3^{-}} NaHFe(CN)_{6}^{3^{-}} Na_{2}Fe(CN)_{6}^{3^{-}} NaHFe(CN)_{6}^{3^{-}} NaHFE($

#### 2.2. Analytical methods for cyanides determination

Due to character of cyanides' compounds, one can distinguish easily liberatable cyanides, i.e. ones which appear as free species or weak metal-cyanide complexes, also called weak acid dissociable (WAD) cyanides, and total cyanides. The subtraction of the former result from the latter one gives the amount of strong metal-cyanides complexes.

The difference between easily liberatable and total cyanides determination relies on the pretreatment of the sample by distillation. We have discussed both distillation methods in 2.2.2. Nevertheless, in our selection of the method used further within the project to cyanides determination, we have focused on the avoidance of distillation procedure for easily liberatable cyanides. As there is no data on weak metal-cyanides complexes appearance in coke oven wastewater we have assumed, that easily liberatable cyanides comprise only of free cyanides species.

There is a range of analytical procedures, which can be utilized for determination of easily liberatable cyanides. We have made a detail review on available methods, next we evaluated them due to accuracy, duration and external reagents requirement. In next subchapters, we have discussed particular methods and presented our evaluation.

#### 2.2.1. Cyanides containing sample preservation

Due to low stability of cyanides, especially those appearing as free or WAD species, samples must be analyzed either immediately after sampling or properly preserved. The simplest method of preservation is obtained by addition of sodium hydroxide in order to increase the overall pH of the sample to above 10. Such preservation allows to elongate the analytical period up to 24 hours. Longer preservation can be obtained by addition of both, sodium hydroxide and zinc sulphate. Such the method enables the preservation of sample for 7 days. Nevertheless, due to the formation of zinccyanide complex, such preserved sample has to be always pretreated with distillation due to cyanides recovery. Hence, in our project we have preserved wastewater samples with sodium hydroxide and performed all analyses within 24 hours from their sampling.

#### 2.2.2. Cyanides recovery

There are different available distillation procedures enabling the recovery of cyanides, in order to perform further analysis. Among them, one can distinguish methods dedicated to easily liberatable cyanides (WADCs) and complex/total cyanides.

#### Easily liberatable cyanides distillation

In conventional method, WADCs are released by means of combined distillation and air stripping at the presence of phosphoric acid and dedicated buffer solution. Released hydrogen cyanide is caught in washers containing sodium hydroxide solution. The distillation together with air stripping is carried out for 1 hour. Afterwards heating is stopped, while air stripping is continued for the next 15 minutes.

In the latest procedure WADCs species should be undergone to air stripping at pH = 4 and room temperature carried out for 4 hours. Released hydrogen cyanide gas is trapped in a washer containing sodium hydroxide solution.

#### Total/complex cyanides distillation

In conventional method for complex/total cyanides distillation, sample after distillation of WADCs (complex cyanides) or fresh sample (total cyanides) is acidified with sulphuric acid at presence of mercury and magnesium catalysts. Next, the distillation combined with air stripping are run for 1 hour and afterwards heating, the air stripping is continued for another 15 minutes. Released hydrogen cyanide is caught in two washers containing sodium hydroxide solution.

In the latest method total/complex cyanides should be undergone to thermal distillation combined with air stripping at presence of hydrochloric acid and copper catalyst,

carried out for 1 hour. Released hydrogen cyanide gas is trapped in a washer containing sodium hydroxide solution.

#### Disrupting/interfering substances

Thermal distillation of samples containing thiocyanate (SCN<sup>-</sup>) can result in low cyanides recovery. Thiocyanate decomposes to oxidized sulfur compounds during distillation, which react with cyanide in the absorber solution and cause a negative bias.

Distillation of samples containing sulphides may result in their appearance in distillate sample. Sulfides react with colorimetric reagents used for cyanides determination and are detected as cyanides. Hence, erroneously high recoveries may be established.

Sensitivity of every distillation method towards disrupting agents needs to be checked due to their effect on the analysis results using standard solutions.

#### Our evaluation of sample pretreatment by distillation

We have found that the latest methods for cyanides recovery seems to be more suitable for samples preparation than conventional ones, as they mostly eliminate the impact of interfering substances. On the other hand, the conventional method for WADCs is much shorter, and may be used for samples with lower concentration of disrupters, e.g. treated coke oven wastewater. Nevertheless, considering the fact that in our project large number of samples is to be analyzed and samples containing cyanides should be analyzed within 24 hours after sampling, we have decided to focus on determination methods, in which preliminary cyanides recovery (WADCs) is not required. Nevertheless, one have to be aware that in case of complex cyanides, the preliminary sample treatment is crucial and we have decided to use the latest procedure, which is also recommended in DIN 38405 D 13-2 called in Commission Implementing Decision of 28 February 2012 establishing the best available techniques (BAT) conclusions under Directive 2010/75/EU of the European Parliament and of the Council on industrial emissions for iron and steel production.

#### 2.2.3.Colorimetric benzidine-pyridine method

#### Idea

The procedure is based on the conversion of cyanides to Bromocyanate with the use of bromine at acidic conditions. Bromocyanate reacts with pyridine, and forms glutaconic aldehyde, which condenses with benzidine to yield polymethine dye. The intensity of the final color is directly proportional to cyanides concentration. Next, the spectrophotometric analysis at  $\lambda = 492$  nm is run and the concentration of cyanides is determined. The method is suitable for solutions containing 0.01-1.0 mg/dm<sup>3</sup> of CN<sup>-</sup>.

#### Procedure

In the method, 50 cm<sup>3</sup> of sample containing 0.001-0.02 mg of cyanides is placed in the separatory funnel. The pH of the sample should be equal to ca.7. Next, 3 cm<sup>3</sup> of bromine solution (0.5.% solution of bromine in diluted hydrochloric acid) should be added and the mixture must be carefully mixed. The extent amount of bromine can be removed with the use of sodium metaarsenite solution (2% solution). Next, 50 cm<sup>3</sup> of n-butanol is added to the mixture and it is again mixed. Next, 5 cm<sup>3</sup> of freshly prepared pyridine-benzidine agent is added and it is all mixed again and left for 30 min. Afterward, aqueous phase is removed from the funnel, and alcohol phase is filtered to dry 1 or 5 cm cuvette. First portion of the filtrate is removed. The spectrophotometric analysis at  $\lambda = 492$  nm should be run within 40-90 minutes after addition of benzidine-pyridine solution to the sample.

#### Disrupting agents

Cyanates, thiocyanates, urea and other substances, which can hydrolyze to cyanides, sulphides and sulphides containing compounds, color, turbidity.

#### Our evaluation

We have not found the method to be effective for cyanides analysis in coke oven wastewater. Mainly, because of the large amount of thiocyanates, which appear in the raw stream. Their impact on the analysis may be minimized by preliminary distillation, but it significantly elongates the overall procedure. The method itself is very time consuming, its accuracy may be affected due to the complexity of the procedure and it requires a number of external reagents.

#### 2.2.4. Titrimetric argentometric method

#### Idea

The method is based on the reaction of cyanides with silver to yield silver cyanide complex  $Ag(CN)_2^-$ . The excess of silver reacts with p-dimethylaminobenzylidene rhodanine and the sample color changes from yellow into red-orange. The method is suitable for solutions containing above 1 mg/dm<sup>3</sup> of CN<sup>-</sup>.

#### Procedure

In the method,  $100 \text{ cm}^3$  of sample is placed in  $200 \text{ cm}^3$  cone flask (if color of the sample is significant a smaller portion can be used and it should be diluted with distilled water to  $100 \text{ cm}^3$ ). pH of the sample should be adjusted to 11 or above with sodium hydroxide

solution. Next, 0.5 cm<sup>3</sup> of rhodanine solution (0.02% solution in acetone) is added. The sample is titrated with AgNO<sub>3</sub> solution (0.0192 mol/dm<sup>3</sup> solution in water) until the color changes from yellow into red-orange.

#### Disrupting substances

Cyanates, thiocyanates, urea and other substances, which can hydrolyze to cyanides, sulphides and sulphides containing compounds, fatty acids.

#### Our evaluation

We have found the method to be simple in procedure and it has not required a number of external reagents. However, due to the appearance of disrupting substances in coke oven wastewater as well as quite intensive color (significant dilution required) we have found it unsuitable for our project for the examination of raw stream, while it cannot be used for treated stream due to the high detection level (much higher than permissible one). In order to eliminate the impact of disruptors on the analysis as well as to preserve the proper amount of cyanides in the sample (> 1 mg/dm<sup>3</sup>), the preliminary treatment of the sample by means of distillation should be performed, but it significantly affects the overall duration of the procedure.

#### 2.2.5. Colorimetric barbituric-pyridine method

#### Idea

Cyanides react with free chlorine (from chloramine T) to yield chlorocyanate, which next reacts with pyridine to form glutaconic aldehyde, which finally condenses with barbituric acid to form red-purple polymethine dye. The intensity of the final color is directly proportional to cyanides concentration. Next, the spectrophotometric analysis at  $\lambda = 578$  nm is conducted and the concentration of cyanides is determined. The method is suitable for solutions containing 0.05-1.0 mg/dm<sup>3</sup> of CN<sup>-</sup>.

#### Procedure

In the method 25 cm<sup>3</sup> of the sample is added to 50 cm<sup>3</sup> cylinder (the amount of cyanides in the sample should be kept within 0.00025-0.01 mg CN<sup>-</sup>). Next, 7.5 cm<sup>3</sup> of sodium dihydrophosphate solution, 1 cm<sup>3</sup> of chloramine T solution, and, immediately, 2.5 cm<sup>3</sup> of barbituric acid solution is added. The solution is fulfilled to 50 cm<sup>3</sup> volume with distilled water and mixed. After 8, but before 30 minutes since sample preparation, absorbance of the solution at wavelength  $\lambda = 578$  nm using 1 or 5 cm cuvettes is measured.

#### Disrupting agents

Oxidizing compounds, hydrosulphide and sulphides, color, turbidity and thiocyanates. *Our evaluation* 

We have found the method to be unsuitable for analysis of cyanides in coke oven wastewater without preliminary treatment with distillation due to the presence of thiocyanates. Hence, the duration of the procedure is elongated. Moreover, the method can be applied for solutions of low cyanides content, and it cannot be used for raw coke oven wastewater without sample dilution. However, if the proper pretreatment of sample is performed, including dilution, the method is recommended to be utilized within the project.

#### 2.2.6. Photometric methods with the use of dedicated tests by HACH Lange

There are two methods dedicated for free and easily liberatable cyanides offered by HACH. Both are based on the spectrophotometric analysis.

#### 2.2.6.1. Method for free cyanides determination – LCK 315

#### Idea

Cyanides react with chlorine to yield chlorocyanate, which at the presence of barbituric acid condenses with pyridine and the color of the solution changes to purple. Method range is from 0.01-0.6 mg  $CN^{-}/dm^{3}$ . The method is a simplified modification of barbituric-pyridine method discussed in 2.2.5.

#### Procedure

1 cm<sup>3</sup> of sample is added to the analytical cuvette containing chloramine solution. Next, the sample is mixed with barbituric acid and 1 cm<sup>3</sup> of working solution is added. After 3 minutes the sample absorbance is analyzed at wavelength  $\lambda = 578$  nm.

#### Disrupting agents

Thiocyanates, formaldehyde, sulfites, and other compounds with affinity to chlorine.

#### Our evaluation

The method is very fast and simple in procedure. However, due to the presence of thiocyanates in coke oven wastewater it cannot be directly used for analytical purposes and the preliminary treatment of the sample by means of distillation is required. However, the method is recommended to be used for distillate samples due to its accuracy, simplicity and short duration. The method requires the dilution of the sample of distillate, however it does not affect the accuracy of measurements.

#### 2.2.6.2. Method for easily liberatable cyanides determination – LCK 319

#### Idea

During the reaction, liberated cyanides yield to hydrogen cyanide, which reacts with indicator and changes its color. The change of color is measured photometrically at wavelength  $\lambda = 575-590$  nm. The method range is from 0.03 to 0.35 mgCN<sup>-</sup>/dm<sup>3</sup>.

#### Procedure

 $2 \text{ cm}^3$  of sample is added to digestion cuvette and carefully mixed. Next, the digestion cuvette is connected with indicator cuvette by means of two side cap equipped with gas permeable membrane. The set of cuvettes is heated in thermostat at 100°C for 1 h. After cooling, the sample is analyzed at wavelength  $\lambda = 575 - 590 \text{ nm}$ .

#### Disrupting agents

The producer defines disrupting agents and their concentrations as given in table 3. *Table 3. Permissible concentrations of LCK 319 method disruptors and their effect on result* 

Higher erı	roneous cyanides recovery	Lower erroneous cyanides recovery		
$2000 \text{ mg/dm}^3$	Thiocyanate (SCN <sup>-</sup> )	$500 \text{ mg/dm}^3$	Cyanate (OCN <sup>-</sup> )	
$50 \text{ mg/dm}^3$	Nitrite (NO <sub>2</sub> ), dithionite ( $S_2O_4^{2-}$ )	$20 \text{ mg/dm}^3$	Disulphite $(S_2O_5^{2-})$	
$1 \text{ mg/dm}^3$	Sulphides ( $S^{2-}$ ), thiosulfates	$10 \text{ mg/dm}^3$	Cupper (Cu <sup>2+</sup> ), sulfite (SO <sub>3</sub> <sup>2-</sup> )	
r mg am	$(S_2O_3^{2-})$	$1 \text{ mg/dm}^3$	Formaldehyde (HCOH)	

#### Our evaluation

The method is suitable for analysis of coke oven wastewater. Together with included cyanides liberation the overall analysis lasts ca.1 h 15 minutes, while the procedure is very simple. The method avoids disrupting action of other substances present in the sample. We recommend this method for analysis of cyanides in all coke oven wastewater streams after suitable dilution.

#### 2.2.7. Potentiometric method with the use of argentometric titration

#### Idea

Cyanides are titrated by solution of silver ions which react to stable complex. The reaction is constantly monitored by potentiometric method. The highest change in the potential (indicating on the disappearance of free cyanides/appearance of free silver ions) observed per exactly established portion of titrating solution corresponds to the amount of cyanides present in the sample. The method can be used for wide concentration of cyanides from 0.05 up to  $100 \text{ mg/dm}^3$ .

#### Procedure

The sample of wastewater is mixed with sodium hydroxide solution and isopropanol. Next, electrochemical cell comprised of silver-sulphide electrode and reference glass electrode is placed in the mixture and the potential of the solution is measured. Depending on the expected concentration of cyanides, silver-based titrating solution is stepwise added to the sample solution in exactly defined amount and the change of the potential is observed. The highest ratio of the potential change to titrant portion corresponds to the appearance of free silver ions in the mixture, i.e. no further silver-cyanides complexation takes place, what allows to calculate the amount of cyanides present in the sample.

#### Disrupting agents

The impact of other substances present in coke oven wastewater on the analysis results has not been observed.

#### Our evaluation

We have found the potentiometric method for cyanides analysis to be suitable for application within our project. Due to the lack of indicated interferences among other substances present in coke oven wastewater, the method does not require preliminary sample treatment. The accuracy of the method is defined by the concentration of titrating solution. The concentration of the complexing agent may be easily modified and adjusted to the particular type of the sample. The final point of titration may be additionally observed by addition of indicator used in argentometric cyanides determination discussed in chapter 2.2.4.

### **2.2.8. Ion Chromatography analysis with Pulsed Amperometric Detection (PAD)** *Idea*

Method is based on separation of free cyanides from sample matrix by means of ionexchange chromatography. Column eluate is constantly analyzed by electrochemical detector equipped with silver electrode. The method is suitable for cyanides concentration from 0.05 to 5 mg CN<sup>-</sup>/dm<sup>3</sup>. External standard method is utilized for quantitative analysis.

#### Procedure

Sample is injected onto the chromatographic system via sample loop (10  $\mu$ l). Separation is conducted on IonPack AS-7 capillary column. Eluent consists of 0.6 M sodium hydroxide. Electrochemical detector in Pulsed Amperometric mode is utilized for concentration measurement.

#### Disrupting agents

In this application, electroactive anions (iodide, thiosulfate, bromide, thiocyanate, and sulfide) are potential inferences.

#### Our evaluation

We have found the method to be simple in application, and after proper equipment set up, it can be successfully applied for free cyanides species analysis. However, it requires chromatograph with proper detector and analytical column. We checked the impact of possible disrupting agent on the analysis results and we did not observe any effect on the analysis. Hence, we recommend the method for the analysis of free cyanides in all process streams, however we advise samples dilution (at least 50 times for raw stream and at least 20 times for treated streams) in order to assure the best analytical results.

# **2.2.9. Continuous flow analysis with photometric or amperometric detection** *Idea*

The method is dedicated for analysis of both, WADCs and complex cyanides (total cyanides). The pretreatment of the sample takes place in the device and UV mineralization at acidic pH is used for this purpose. The revealed hydrogen cyanide reacts with reagents used in colorimetric pyridine-barbituric method (chapter 2.2.5) and the concentration of finally formed dye is measured in photometric detector. In case of amperometric method, silver containing electrode operated at defined potential is used. The method is dedicated for cyanides concentration ranging from 0.002 to 0.5 mg/dm<sup>3</sup>. In case of higher concentrations a proper dilution of sample is required.

#### Procedure

The procedure for cyanides determination with the use of CFA is automated method discussed in 2.2.5 and 2.2.8. Released hydrogen cyanide reacts with proper reagent during its flow through reactor. The preparation of the sample is also performed automatically in the device.

#### Disrupting agents

Oxidants, at concentration sulphides >  $60 \text{ mg/dm}^3$ , salinity above  $10 \text{ g/dm}^3$ , aldehydes, thiocyanates.

#### Our evaluation

Due to the requirement of dedicated apparatus we have not investigated the method in detail. However, in our opinion the need for the dedicated (expensive) device is the main

disadvantage of the method. Considering the application of the method to coke oven wastewater, the observed impact of thiocyanates on the analysis results has to be carefully checked. For range of cyanides concentration met in COW (especially raw one) the sample requires significant dilution. The method can be applied for cyanides analysis within our project, but after careful determination of the impact of interferences on the analytical result.

#### 2.2.10. Summary

We have reviewed a number of methods for cyanides determination in wastewater and we have evaluated them due to the accuracy, procedure complexity, duration, disrupting agents and sample pretreatment requirement. Within all investigate methods we have decided, that within our project one of the methods presented in table 4 can be applied. We have confirmed, that coke oven wastewater does not contain weak metal-cyanide complexes. In order to determine the content of strong metal-cyanide complexes the pretreatment of sample with distillation has to be always carried out. We have decided, that the method with hydrochloric acid and copper sulphate catalyst is the most suitable for our purpose.

	Table 4.	Recommended	methods	of	<i>cyanides</i>	analysis	in cok	ke oven	wastewater
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Sample preservation	Alkalization with sodium hydroxide to pH >10.				
Cyanides recovery for easily liberatable species	Not performed (if needed air stripping at acidic environment is recommended).				
Cyanides recovery for strong metal-cyanides complexes	Distillation and air stripping with hydrochloric acid and copper sulphate catalyst.				
Determination of cyanides	Colorimetric barbituric-pyridine method (2.2.5); HACH Lange method for easily liberatable cyanides determination – LCK 319 (2.2.6.2); Potentiometric method with the use of argentometric titration (2.2.7); Ion Chromatography analysis with Pulsed Amperometric Detection (2.2.8); Continuous flow analysis with photometric or amperometric detection (2.2.9).				

#### 3. Methods for sulphides determination

#### **3.1. General information**

Sulphides appear in coke oven wastewater as a result of incomplete recovery of hydrogen sulphide in dedicated installations. There are several different processes, which can be used for removal of hydrogen sulfide from coke oven gas. The main desulfurization processes used nowadays are:

- Vacuum Carbonate Process (hydrogen sulfide is absorbed from the coke oven gas using a solution of potassium carbonate, then stripped out in a still);
- Ammonia Wash Process (hydrogen sulfide is absorbed from the coke oven gas using a solution of ammonia, then stripped out in a still this process is often combined with the ammonia removal system);
- Sulfiban Process (hydrogen sulfide is absorbed from the coke oven gas using a solution of monoethanolamine (MEA) then stripped out in a still).

In raw coke oven wastewater, sulphides may appear in the ionic form  $S^{2-}$  or  $HS^{-}$  or in a form of non-dissociated hydrogen sulphide. The species, in which sulphides appear in wastewater, mainly depend on pH. Thus, at pH  $\leq 6$  the dominant form is non-dissociated H<sub>2</sub>S, while at pH  $\geq 8$  it is hydrosulphide ion HS<sup>-</sup>. Sulphides ions S<sup>2-</sup> appear in the solution at pH >10. Sulphides of alkali metals (Na, K, Mg, Ba and others) are soluble in water, while sulphides of I<sup>st</sup> (Ag, Pb, Hg), II<sup>nd</sup> (Cu, Bi, Sn, Cd, As, Sb) and III<sup>rd</sup> (Al, Fe, Cr, Ni, Co, Mn, Zn) analytical group are water-insoluble. However, sulphides of III<sup>rd</sup> analytical group are soluble in diluted mineral acid, whereas sulphides of II<sup>nd</sup> analytical group are not.

#### 3.2. Analytical methods for sulphides determination

Sulphides can be divided into soluble and insoluble ones. The presence of former ones results in the appearance of free  $S^{2-}$  ions in the solution. In case of latter species, one can distinguish easily liberatable sulphides (i.e. ones which are soluble in diluted mineral acids) and insoluble sulphides. Within the report, we have distinguished three sulphides groups: water soluble, acid soluble and insoluble ones.

Similarly as in case of cyanides, a number of procedures for determination of sulphides in wastewater streams can be found. We have discussed and evaluated them in next subchapters.

#### 3.2.1.Sulphides containing sample preservation

The preservation of sample can be performed with the use of two methods. First one, which may be applied for samples analyzed up to 4 hours after sampling, is based on sample pH adjustment above 10. Hence, the sampling has to be done in a way, that avoids the mixing of sample with air, in order to prevent the oxidation of sulphides with oxygen.

The second method of sulphides preservation is the addition of zinc acetate and slight alkalization of the solution. Such the method can be applied in case, when further sulphides determination is carried out at acidic environment.

#### 3.2.2. Sulphides recovery

There are two methods utilized for sulphides recovery from samples preserved with zinc or from samples, in which the appearance of acid-soluble sulphides is expected. The first method is based on thermal distillation at presence of sulphuric acid solution accompanied with inert gas stripping. The second method avoids the application of heating and relies on inert gas stripping with the use of acidic buffer solution. In both methods, released hydrogen sulphide is trapped in washers containing zinc acetate. The obtained solution is suitable for analysis carried out at acidic conditions.

## 3.2.3. Colorimetric method for water soluble and acid soluble sulphides with p-aminodimethylaniline

#### Idea

The method is based on the formation of methylene blue during reaction of hydrogen sulphide with p-aminodimethylaniline at acidic conditions and at the presence of iron (III) chloride. The method is dedicated for samples containing up to 20 mg  $S^{2-}/dm^{3}$ .

#### Procedure

Fresh portion of wastewater is preserved with zinc acetate and alkalized with NaOH. The supernatant is decanted and the precipitate is diluted with distilled water (deoxidized). Into two volumetric cylinders, of volume 25 cm<sup>3</sup>, 7.5 cm<sup>3</sup> of well mixed sample is added. Next, to the first cylinder p-aminodimethylaniline is added, while to the second sulphuric acid solution is introduced. To both cylinders 2 drops of FeCl<sub>3</sub> solution are added and both solutions are well mixed. At the presence of sulphides, the color of solution in first cylinder will turn into blue. After 1-5 minutes diamono hydrophosphate solution should be added to both cylinders and both solutions are mixed. Next, to the second cylinder methylene blue solution is added with the use of microburette until the color is comparable with one in the

first cylinder. The amount of methylene blue added to the second cylinder corresponds to the amount of sulphides present is the first cylinder.

#### Disrupting agents

Reductive substances, sulfites, thiosulfates, nitrites.

#### Our evaluation

We have not found the method to be accurate in refer to eye relied comparison of both solutions' colors. Additionally, the method accuracy may be disrupted by improper mixing of ZnS with water. The method may be more suitable for matrices, which do not require preservation of sulphides with zinc acetate, however, we do not recommend the method for coke oven wastewater analysis.

## **3.2.4. Iodometric method for water and acid soluble sulphides** *Idea*

By acidification, sulphides are transformed into hydrogen sulphide, which is distilled at inert gas atmosphere to zinc acetate solution. Zinc sulphide precipitate is further oxidized in standard iodine solution to free sulphur, while the excess of iodine is titrated with sodium thiosulphate. The method can be utilized for solutions containing above 1 mg S<sup>2-</sup>/dm<sup>3</sup>. *Procedure* 

Distillation washers are filled with zinc acetate solution. Distilled water and concentrated sulphuric acid are added to the distillation flask and stripped with inert gas in order to remove oxygen. Next, well mixed sample previously preserved with zinc acetate is added to the distillation flask, which is brought to boiling and kept as such for ca. 1h. When the distillation is finished (lead paper test) the content of washers is placed in a volumetric flask and excess of standard iodine solution is added (as solution color turns to yellow). The flask is closed and well mixed and after 5 minutes the excess of iodine is titrated with sodium thiosulphate solution. Near the titration end point (slightly yellow color) starch solution is added and titration proceeds until the solution decolorizes.

#### Disrupting agents

All oxidative and reductive substances (eliminated by distillation), volatile substances (sulfites, cyanides) (impact eliminated by enhanced precipitation of zinc sulphide in washers). *Our evaluation* 

We have found the procedure to be very time consuming and complex, hence its accuracy could be affected. Due to the presence of both groups of disruptors in coke oven wastewater the sample would require sophisticated pretreatment by distillation and precipitation. Hence, we do not recommend the method for analysis of sulphides in coke oven wastewater.

# **3.2.5. Colorimetric method for water soluble sulphides with HMB and thiofluoroscein** *Idea*

The method relies on the introduction of excess o-hydroxymercuribenzoic acid salt (HMB) to the sample, which form complexes with sulphides. These complexes do not react with thiofluoroscein. The excess of HMB is titrated with thiofluorescein. The difference between titrant amount used to sample titration and control sample titration corresponds to the amount of sulphides present in the sample. The method is suitable for samples with sulphides concentration range 0.005 to 0.04 mgS<sup>2-</sup>/dm<sup>3</sup>.

#### Procedure

Analytical sample and control sample must be collected at the same time. Control sample is placed in a washer, acidified with sulphuric acid, stripped with air for 15 minutes and neutralized with ethanolamine. To analytical sample 1 cm<sup>3</sup> of HMB per every 100 cm<sup>3</sup> of sample is added. Both samples are placed in colorimetric cylinders (to control sample 1 cm<sup>3</sup> of HMB is added). To both samples, 1 cm<sup>3</sup> of formaldehyde is added. Solutions from both cylinders are titrated with thiofluorescein solution until the same blue color is reached.

#### Disrupting agents

Sulfites and thiosulfates do not interfere, while cyanides are removed by formaldehyde addition.

#### Our evaluation

We have found the method to be inappropriate for sulphides determination in coke oven wastewater due to the large dilution required by the method range. Even though the procedure is quite simple, the need for control sample analysis may affect the method accuracy. We do not recommend the method to be utilized for sulphides determination.

## 3.2.5.Photometric method for water and acid soluble sulphides with methylene blue formation

#### Idea

The idea of the method relies on the formation of methylene blue (as discussed in 3.2.3), but eye detection is replaced with measurements of absorption at  $\lambda = 655$  nm. The method is valid for sulphides range 0.04 to 1.5 mgS<sup>2-</sup>/dm<sup>3</sup>.

#### Procedure

The analysis is recommended to be preceded with sample inert gas tripping to zinc acetate containing washers. However, the method can be applied to samples preserved with zinc acetate at alkali environment. To the sample containing zinc acetate, precipitate obtained from a known volume of sample  $10 \text{ cm}^3$  of acidic N,N-dimethyl-1,4-phenylendiammoniuchloride and  $1 \text{ cm}^3$  of ammonium iron(III) sulphate are added. The sample is left for 10 minutes and afterwards the absorption is measured.

#### Disrupting agents

Cyanides (2 mg/dm<sup>3</sup>), iodides (20 mg/dm<sup>3</sup>), thiosulfates (900 mg/dm<sup>3</sup>), thiocyanates (900 mg/dm<sup>3</sup>), sulfites (700 mg/dm<sup>3</sup>) (the impact of interferences is eliminated by preliminary stripping or by decantation of supernatant from precipitate. Higher concentrations affect the stripping procedure due to the volatility of particular components).

#### Our evaluation

The procedure is simple, and even with preliminary sample treatment (which is not applied in our project) it is not time consuming. Hence, we do recommend the method for coke oven wastewater examination after proper dilution of samples with deoxidized water.

## **3.2.6. Photometric method with dedicated HACH Lange tests – LCK 653** *Idea*

The idea of the method is based on the colorimetric reaction described 3.2.5, i.e. the formation of methylene blue, intensity of which is measure photometrically and corresponds to the amount of sulphides present in the sample. The method itself is dedicated for water soluble sulphides, however in combination with MicroDist set, which is used for easily liberatable sulphides release, it can be applied for determination of both ones, i.e. water and acid soluble. The method is valid for sulphides range from 0.1 to 2.0 mgS<sup>2-</sup>/dm<sup>3</sup>.

#### Procedure

4 cm<sup>3</sup> of sample is added to the reaction cuvette and 0.2 cm<sup>3</sup> of iron containing solution is added. The sample is left for 10 minutes and photometric measurement of absorption is carried out at wavelength  $\lambda = 665$  nm.

#### Disrupting agents

Cyanides (2 mg/dm<sup>3</sup>), iodides (20 mg/dm<sup>3</sup>), thiosulfates (900 mg/dm<sup>3</sup>), thiocyanates (900 mg/dm<sup>3</sup>), sulfites (700 mg/dm<sup>3</sup>) (the impact of interferences is eliminated by preliminary treatment of sample with MicroDist procedure or conventional inert gas stripping. Higher concentrations affect the stripping procedure due to the volatility of particular components).

#### Our evaluation

We have found the method to be simplified version of procedure discussed in 3.2.5, hence the method is recommended for sulphides determination within our project, but only after preliminary preparation of sample by means of MicroDist or by inert gas stripping. We do recommend the method for sulphides determination in coke oven wastewater, but only with the use of pretreatment.

## **3.2.7.** Potentiometric method for water soluble sulphides analysis with argentometric titration

#### Idea

Potentiometric method for sulphides analysis relies on the reaction of silver ions with water soluble sulphides species present in the sample, which yield to formation of silver sulphide precipitate, at constant monitoring of the sample potential. The highest change of ratio of the potential per exactly established portion of silver ions (indicating on disappearance of sulphides in the solution) corresponds to the amount of sulphides present in the sample. The method can be used for wide concentration of cyanides from 0.05 up to  $100 \text{ mg/dm}^3$ .

#### Procedure

The sample is mixed with sodium hydroxide solution and isopropanol. Next, electrochemical cell comprised of silver-sulphide electrode and reference glass electrode is placed in the mixture and the potential of the solution is measured. Depending on the

expected concentration of sulphides, silver containing solution is stepwise added to the sample solution in exactly defined amount and the change of the potential is observed. The highest change of the potential corresponds to the appearance of free silver ions in the mixture, i.e. no further silver sulphide precipitation takes place), what allows to calculate the amount of sulphides present in the sample.

#### Note

The method can be simultaneously used for free cyanides analysis. The distinguish of particular contaminants can be made by means of potential value, at which their appearance is observed. Sulphides are present in the solution at the potential value > (+100) mV, while cyanides determination is performed at the potential range (-100) - (-200) mV.

#### Disrupting agents

The impact of other substances present in coke oven wastewater on the analysis results has not been observed.

#### Our evaluation

We have found the potentiometric method for sulphides analysis to be suitable for application within our project. Due to the lack of interactions with other substances present in coke oven wastewater, the method does not require preliminary sample treatment. The accuracy of the method is defined by the concentration of silver solution used for titration. The concentration of the complexing agent may be easily modified and adjusted to the particular type of the sample.

### **3.2.8.** Ion Chromatography analysis for water soluble sulphides with Pulsed Amperometric Detection (PAD)

#### Idea

Method is based on separation of water soluble sulphides from sample matrix by means of ion-exchange chromatography. Column eluate is constantly analyzed by electrochemical detector equipped with silver electrode. External standard method is utilized for quantitative analysis. The method is suitable for sulphides concentration from 0.05 to 5 mg S<sup>2-</sup>/dm<sup>3</sup>.

#### Procedure

Sample is injected onto the chromatographic system via sample loop (10  $\mu$ l). Separation is conducted on IonPack AS-7 capillary column. Eluent consists of 0.6 M sodium hydroxide. Electrochemical detector in Pulsed Amperometric mode is utilized for concentration measurement.

#### Note

The method can be simultaneously used for free cyanides analysis. The separation of particular contaminants can be obtained with the use of proper analytical column (AS7 type recommended). In case of sulphides analysis, eluent solution (0.6 mM NaOH) has to be prepared with the use of deoxidized water in order to prevent their oxidation on the column.

#### Disrupting agents

In this application, electroactive anions (iodide, thiosulfate, bromide, thiocyanate) are potential inferences.

#### Our evaluation

We have found the method to be simple in application, and after proper equipment set up, it can be successfully applied for water soluble sulphides species analysis. However, it requires chromatograph with proper detector and analytical column. We have checked the impact of possible disrupting agent on the analysis results and we have not observed any effect on the analysis, when dedicated AS7 column was used. Hence, we recommend the method for the analysis of water soluble sulphides in all process streams, however we advise samples dilution (at least 50 times for raw stream and at least 20 times for treated streams) in order to assure the best analytical results.

#### **3.2.9. Summary**

We have reviewed a number of methods for sulphides determination in wastewater and we have evaluated them due to the accuracy, procedure complexity, duration, disrupting agents and need of sample pretreatment. Within all investigated methods we have decided, that within our project one of the methods presented in table 5 can be applied. We have confirmed, that raw coke oven wastewater does not contain acid soluble sulphides, however ones may appear in the post-coagulation stream and in the effluent. In such cases sample pretreatment has to be applied. Table 5. Recommended methods of sulphides analysis in coke oven wastewater

Sample preservation	Alkalization with sodium hydroxide to pH >10, for samples undergone to pretreatment addition of zinc acetate is recommended.					
Sulphide recovery for easily liberatable species	Not needed for raw coke oven wastewater and for analytical procedure carried out at acidic environment. If needed for process sample (stream after coagulation, COWTP effluent) inert gas stripping at acidic environment is recommended.					
	Photometric method for water soluble and acid soluble sulphides with methylene blue formation (3.2.5);					
Determination of	Photometric method with dedicated HACH Lange tests – LCK 653 (sample pretreatment required) (3.2.6);					
sulphides	Potentiometric method for water soluble sulphides analysis with argentometric titration (3.2.7);					
	Ion Chromatography analysis for water soluble sulphides with Pulsed Amperometric Detection (3.2.8).					

#### 4. Methods for ammonia/ammonium determination

#### **4.1. General information**

Ammonia (NH<sub>3</sub>) is a by-product of the coking of coal. It is a constituent of the coke oven gas leaving the ovens, with a typical concentration in raw coke oven gas of  $6g/Nm^3$ . The solubility of ammonia in water leads to its presence in the coke battery flushing liquor with a typical concentration of  $5.0 - 6.0 \text{ g/dm}^3$  total ammonia. Consequently, due to the net production of flushing liquor in the coke plant, referred to as excess flushing liquor, but also known as coal water, virgin liquor or weak ammonia liquor, there arises a liquid stream as well as a gas stream from which ammonia must be removed. The quantity of excess liquor is approx. 12% by weight of the dry coal throughput, depending on the coal moisture content.

The continuous separation of the flushing liquor stream from ammonia liquor is a particularly vital feature, as this flow is required to cool the hot oven exit gases down to a temperature, which can be handled in the gas collecting system. The liquor contains dissolved ammonia as a wide variety of compounds. These are generally grouped as "fixed" or "free" compounds (table 6). The former ones are relatively stable whilst the "free" compounds can be decomposed solely by heating to approx. 100°C. The "free" compounds include the hydroxide, carbonate, bicarbonate, sulphide and cyanide; the 'fixed' compounds include the chloride, thiocyanate, thiosulphate and sulphate.

The appearance of ammonia in aqueous stream is a pH dependent factor, thus in solutions of pH<7, ammonia appears almost exclusively in the form of ammonium ion, while at higher pH non-dissociated NH<sub>3</sub> is found.

Free compounds <sup>*</sup>	NH <sub>4</sub> OH, (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> , NH <sub>4</sub> HCO <sub>3</sub> , (NH <sub>4</sub> ) <sub>2</sub> S,
	NH <sub>4</sub> CN
Fixed compounds	NH <sub>4</sub> Cl, NH <sub>4</sub> SCN, (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>

Table 6. Species of ammonia, which may appear in coke oven wastewater

\*usually these compounds are decomposed during ammonia removal from COG

#### 4.2. Analytical methods for ammonia/ammonium analysis

There is a range of analytical procedures, which can be used for ammonia/ammonium determination in coke oven wastewater. Due to the character of methods, ammonia/ammonium are determined as a sum, or they can be determined separately. In Commission Implementing Decision of 28 February 2012 establishing the best available techniques (BAT) conclusions under Directive 2010/75/EU of the European Parliament and of

the Council on industrial emissions for iron and steel production ammonia nitrogen, which needs to be controlled in coke oven wastewater treatment plant effluent is defined as ammonium nitrogen  $(N-NH_4^+)$ , hence, within the contaminant determination methods we recommend ones, which allow to determine ammonia/ammonium as a sum of both components.

#### 4.2.1. Ammonia containing sample preservation

There is no method used for the sample preservation in case of ammonia analysis. In literature, we have found the advice that the analysis should be performed as soon as possible after sampling. Nevertheless, during our studies we have found that if samples are kept in cool temperature, it does not affect the result even after 7 days since sampling.

#### 4.2.2. Ammonia recovery

In some methods for ammonia determination, the need for ammonia recovery by means of distillation can be met. However, within our studies we investigated mostly methods, in which the preliminary treatment of sample is not required.

#### 4.2.3.Direct Nesslerization

#### Idea

Ammonia reacts with Nessler's reagent to form yellow complex. Color intensity is directly proportional to ammonia content in the sample. The result is obtained by photometric measurements of absorption at a wavelength  $\lambda = 425$  nm. The range of method depends on the concentration of standard solutions used for calibration curve determination. *Procedure* 

A portion of the sample, containing up to 0.1 mg of ammonia nitrogen is added to 50 cm<sup>3</sup> in a Nessler tube. Next, 2 drops of sodium potassium tartrate solution (or disodium dihydrogen ethylenediamine tetraacetate) are added to prevent cloudy tubes, and the solution is mixed. Finally, 1 cm<sup>3</sup> of Nessler solution is introduced to the mixture and photometric measurement at a wavelength of  $\lambda = 425$  nm is run.

#### Note

For the first use of the method, a number of standards containing from 0.0-0.05 mg NH<sub>4</sub> in the sample has to be prepared and analyzed by the same procedure as sample.

#### Disrupting agents

Salts of calcium, magnesium, iron, turbidity, color, hydrogen sulphide, phenol, free chlorine, amines, chloroamines and other organic compounds react with Nessler reagents to give color. Hence, in case of coke oven wastewater the preliminary distillation at pH = 7 has to be carried out. There is no trapping solution required, but ca. 60% of sample needs to distilled in order to assure the complete recovery of ammonia.

#### Our evaluation

We have found the method to be simple however the number of interferences that are present in the coke oven wastewater seriously affects its applicability. Additional sample pretreatment (distillation) does not ensure the lack of disrupting agents like phenols and hydrogen sulphide. Hence, we do not recommend the method for the ammonia analysis within our project..

## **4.2.4. Ion-selective method**

#### Sodium hydroxide is added to the sample to convert ammonium ion to ammonia. The ammonia diffuses through a gas-permeable membrane of an ion selective electrode (ISE) and pН solution which. alters the of its internal in turn. is sensed by a pH electrode. The potential is measured by means of a pH meter or an ISE meter. If the pH meter is used, the ammonia content is determined from a calibration curve; if the ISE meter is used, the ammonia content is read directly from the meter. Method is applicable to the determination of ammonia nitrogen in the range from 0.5 to 1000 mg NH<sub>3</sub>N/dm<sup>3</sup>.

#### Procedure

Calibration: pH meter - calibration curves are prepared using a minimum of three standard solutions bracketing the expected concentrations of the samples. The standards are treated as analytical sample and the potential of each standard is measured and recorded in millivolts (mV). The standards and the sample must be at the same temperature, preferably about 25°C. The concentration of ammonia nitrogen in milligrams per dm<sup>3</sup> on the log axis against the corresponding electrode potential, in millivolts, on the linear axis, is plotted. The calibration curve has to be checked every 3 h when analyzing a series of samples.

ISE meter - calibration curves are prepared with three standard solutions, bracketing the expected concentrations of the samples. The calibration curve is checked every 3 h when analyzing a series of samples; otherwise, it is calibrated daily.

Analysis: 100 cm<sup>3</sup> of the sample (or an aliquot diluted to 100 cm<sup>3</sup>) is transferred to a 150 cm<sup>3</sup> beaker. The sample temperature must be the same as that of the standards used in calibration. The stirring bar is put in the beaker and sample is mixed on the magnetic stirrer. The sample cannot be mixed too rapidly to avoid air bubbles draw into the solution. The electrode is immersed into the sample, positioning it at an angle 20° to the vertical, making sure that no air bubbles are trapped on the membrane of the electrode. 1.0 cm<sup>3</sup> of NaOH solution is added to the sample. NaOH solution should be added just prior to measurement because ammonia may be lost to the atmosphere from a stirred alkaline solution. The pH of the sample is checked with pH paper and it must be greater than 11.0. If it is less, additional NaOH solution in 0.1 cm<sup>3</sup> increments is added until the pH of the solution exceeds 11.0. When the electrode comes to equilibrium, the electrode potential of the ammonia nitrogen concentration is measured. The ammonia nitrogen concentration is determined by means of a pH meter or a specific-ion meter:

- pH meter the observed potential in millivolts is recorded and converted to milligrams per dm<sup>3</sup> of ammonia nitrogen by means of the calibration;
- ISE meter the concentration reading directly from the logarithmic scale as milligrams of ammonia nitrogen per dm<sup>3</sup> is recorded.

#### Disrupting agents

Volatile amines, mercury, organic compounds that form ammonia readily (within 5 min) under alkaline conditions.

#### Our evaluation

Even though the method can be applied to a wide concentration of ammonia, we have not found it suitable for analysis performance within our project, as it requires timeconsuming calibration, which needs to be checked with high frequency. Hence, we do not recommend the method for ammonia determination in coke oven wastewater.

#### 4.2.5. Distillation method with titration

#### Idea

Sample of ammonia containing sample is distilled and released ammonia is collected in acidic solution, which, after distillation, is titrated with acid at the presence of indicator. *Procedure* 

The proper amount of sample (depending on expected ammonia content) is placed in the distillation flask and filled with ammonia-free distilled water to 350 cm<sup>3</sup>. Next, few drops

of indicator are added and, if required, pH adjustment is performed (the pH of sample should be within 6.0 - 7.4). Next, magnesium oxide is added in order to assure slightly alkali environment of distillation. Acidic solution is added to the collecting flask. The sample is heated up and the distillation is carried out until 200 cm<sup>3</sup> of distillate is collected. Next, the sample is titrated with standard acid solution and the amount of ammonia is calculated.

#### Disrupting agents

Urea, volatile amines, chloramines.

#### Our evaluation

Even though the method involves distillation process, it is time-effective, accurate, and simple. The collection of the required amount of distillate lasts usually 30 -35 minutes, while the titration is very accurate. Hence, we do recommend the method for ammonia analysis in coke oven wastewater.

#### 4.5.6.Manual spectrometric method

#### Idea

The method relies on spectrophotometric measurement of indophenol blue color intensity, which is formed after reaction of ammonia with salicylic and hypochlorite ions at presence of sodium pentacyanonitrosylferrate(II) (sodium nitroprusside) at pH 12.6. The use of 40 cm<sup>3</sup> analytical sample allows for determination of up to 1 mg of ammonia, while for higher concentrations proper dilution has to be applied.

#### Procedure

A proper amount of sample is placed in a volumetric flask, to which salicylic ions solution and alkali hypochlorite ions solution are added. The sample is mixed and put into the water bath at 25°C for 1 hour. Afterward, spectrophotometric measurement at wavelength  $\lambda = 655$  nm with the use of 10 or 50 mm cuvettes is run. Prior to ammonia concentration determination, the series of calibration solutions must be prepared with the use of ammonium standards.

#### Disrupting agents

Primary amines at high concentrations.

#### Our evaluation

We have found the method to be simple and accurate, however due to the timeconsuming water bath and required calibration we do not recommend it for the analysis of ammonia in coke oven wastewater.

### **4.5.7. Photometric method with dedicated HACH Lange tests – LCK 302, 303, 304, 305** *Idea*

At alkali environment (pH 12.6) ammonia reacts with hypochlorite and salicylic ions at presence of sodium nitroprusside (catalyst) to yield indophenol blue. Depending on the test number, the method is suitable for ammonia/ammonium concentration from 0.015 to 130 mgN-NH<sub>4</sub>/dm<sup>3</sup>. The method is a simplified modification of manual spectrophotometric method discussed in 4.5.6.

#### Procedure

A proper amount of sample is introduced to the analytical cuvette containing hipochlorites and salicylic ions mixture. Next, nitroprusside is added and the sample is left for 15 minutes, after which the intensity of solution color is measured photometrically at wavelength  $\lambda = 550$  nm.

#### Disrupting agents

The producer defines disrupting agents and their concentrations as given in table 7. *Table 7. Disrupting agents for LCK 302-305 method and their concentrations* 

Concentration	Interference	Concentration	Interference
$1000 \text{ mg/dm}^3$	Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	$25 \text{ mg/dm}^3$	Fe <sup>2+</sup>
$500 \text{ mg/dm}^3$	$K^{+}, Na^{+}, Ca^{2+}$	$10 \text{ mg/dm}^3$	Sn <sup>2+</sup>
$50 \text{ mg/dm}^3$	CO <sub>3</sub> <sup>2–</sup> , NO <sub>3</sub> <sup>–</sup> , Fe <sup>3+</sup> , Cr <sup>3+</sup> , Cr <sup>6+</sup> ,	$5 \text{ mg/dm}^3$	Pb <sup>2+</sup>
50 mg/dm <sup>2</sup>	Zn <sup>2+</sup> , Cu <sup>2+</sup> , Co <sup>2+</sup> , Ni <sup>2+</sup> , Hg <sup>2+</sup>	$2 \text{ mg/dm}^3$	$Ag^+$

#### Our evaluation

We have found the methods proposed by HACH to be simple in procedure and accurate. Hence, we do recommend them for analysis of ammonia content in coke oven wastewater.

#### 4.5.8. Ion chromatography with conductometric detector

#### Idea

Method is based on separation of ammonium ions from sample matrix by means of ion-exchange chromatography. Column eluate is constantly analyzed by conductivity detector. External standard method is utilized for quantitative analysis. The method is suitable for ammonia concentration from 0.05 to 5 mg  $NH_4^+/dm^3$ . Apart from ammonia, the method enables simultaneous analysis of lithium, sodium, potassium, manganese, calcium, magnesium, strontium and barium cations.

#### Procedure

Sample is injected onto the chromatographic system via sample loop (10  $\mu$ L). Separation is conducted on IonPack AS-18 capillary column. Eluent consists of 5 mM methanesulfonic acid. Column eluate is passed through suppressor which selectively removes methanesulfonic acid. That decreases conductivity and enables detection of trace levels of ammonia.

#### Disrupting agents

Aminoacids, aliphatic amines, cations:  $Zn^{2+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$ , etc. (in case of use of eluent solution without complexing agent or lack of suppression), imposition of sodium and ammonium ions at significant concentrations difference.

#### Our evaluation

We have found the method to be simple in procedure and accurate for analysis of ammonia in coke oven wastewater. However, it requires chromatograph with dedicated column and detector. Moreover, the presence of high concentration of sodium might influence obtained results. That is especially relevant, when sodium compounds are applied for pH adjustment in wastewater treatment plant. Nevertheless, we do recommend the method for ammonia analysis in coke oven wastewater.

## **4.5.9.** Flow analysis method (FIA and CFA) with spectrometric detection *Idea*

The idea of the method is based on formation of indophenol blue, which was discussed in 4.5.6 and 4.5.7. In this method, the reaction of nitroprusside with reaction mixture is carried out at elevated temperature (37-50°C) and the intensity of sample color is measured at wavelength  $\lambda$  range from 640 to 660 nm. The method is valid for ammonia concentration from 0.1 to 10 mg/dm<sup>3</sup>. Higher concentrations may be obtained by sample dilution before measurement.

#### Procedure

The method is fully automated version of methods discussed 4.5.6 and 4.5.7. *Disrupting agents* 

Volatile amines, improper pH adjustment (reaction pH <12), salinity >10g/dm<sup>3</sup>. *Our evaluation* 

Due to the requirement of dedicated apparatus we have not investigated the method in detail. However, in our opinion the need for the dedicated (expensive) device is the main disadvantage of the method. Considering the application of the method to coke oven wastewater, for range of ammonia concentration the sample requires dilution. Nevertheless, the method can be utilized for ammonia determination in coke oven wastewater.

#### 4.5.10 Summary

We have reviewed a number of methods for ammonia/ammonium determination in wastewater and we have evaluated them in terms of accuracy, procedure complexity, duration, disrupting agents and requirement for sample pretreatment. Within all investigated methods we have decided, that within our project one of methods presented in table 8 can be applied.

 Table 8. Recommended methods of ammonia/ammonium analysis in coke oven wastewater

Sample preservation	Not required.			
Ammonia recovery	Not required.			
Determination of ammonia	Distillation method with titration (4.2.5); Manual spectrometric method (4.5.6); Photometric method with dedicated HACH Lange tests (4.5.7);			
	Flow analysis method (FIA and CFA) with spectrometric detection (4.5.9).			

#### 5. Methods for phenols determination

#### **5.1. General introduction**

Phenols, also known as tar acids, appear in coke oven wastewater as a result of tars condensation during coke oven gas cooling. Part of phenols in coke oven wastewater comes from effluent from tars separation, composed mainly of phenols, which is partially directed to wastewater treatment. The second source is residue wastewater after ammonia distillation. Nowadays, the removal of phenols from coke oven wastewater is made with the use of biological methods. The proper content of phenol in coke oven wastewater is crucial for denitrification microorganisms, which are involved in removal of ammonia. On the other hand, the permissible content of phenols in coke oven wastewater plant effluent is established at very low level and equal to  $<0.5 \text{ mg/dm}^3$ .

#### 5.2. Analytical methods for phenols analysis

Phenols can be defined as aromatic compounds with at least one hydroxide group. Due to the appearance of multiple compounds, which can be defined as phenols, so called "phenol index determination" has been established. The index states for all compounds present in the sample, which undergo to mechanism of determination in the same way as phenol does.

#### 5.2.1. Phenols containing sample preservation

Determination of phenols can be made from unpreserved samples within 4 h from sampling. The sample may be preserved with acidification to pH = 4 with phosphoric acid solution and addition of copper sulphate (1 g of copper sulphate pentahydrate per 1 dm<sup>3</sup> of sample).

#### 5.2.2. Phenols recovery from sample

Within a range of methods for phenols analysis, a need for their recovery from the sample is required. The recovery is done by means of distillation, which is carried out at acidic condition and at the presence of copper sulphate (if the sample is preserved, the adjustment of pH and copper sulphate addition does not have to be done). 500 cm<sup>3</sup> of the sample is undergone to distillation, which is carried out until 80% of the initial sample volume is recovered in the form of distillate. Next, 50 cm<sup>3</sup> of distilled water is added to the distillation flask and the distillation is continued until 500 cm<sup>3</sup> of distillate is recovered.

#### 5.2.3. 4-aminoantipyrine method

The method can be run in two modifications discussed in subchapters 5.2.3.1 and 5.2.3.2.

#### General idea

Phenols react with 4-aminontipyrine and potassium ferricyanide at pH 10 to yield indophenol derivatives of yellow up to red color, in dependence of phenol concentration. The intensity of obtained color is measured spectrophotometrically.

#### Disrupting agents

Regardless of 4-aminoantypyrine method modification, the same group of interferences is defined. Those are oxidative and reductive substances, high pH, sulphur compounds, tars and oils. The impact of those compounds can be eliminated with sample predistillation.

#### Calibration

If the method is performed for the first time, a range of calibrating solutions containing the amount of phenols enabling its actual concentration bracketing has to be prepared and undergone to analysis with the use of dedicated procedure.

### 5.2.3.1 4-aminoantipyrine method with chloroform extraction

#### Idea

Indophenol dye is extracted from sample with the use of chloroform. The method is valid for phenols concentration from 0.001 to  $1.0 \text{ mg/dm}^3$ . It is the most sensitive method among 4-aminoantipyrine method modifications.

#### Procedure

The sample needs to be preliminary distillated due to 5.2.2. Next, the portion of distillate is placed in separatory funnel of volume 1000 cm<sup>3</sup>, and 5 cm<sup>3</sup> of ammonia buffer solution is added. The content of phenols in sample taken to analysis should not be greater than 0.05 mg. Next, 3 cm<sup>3</sup> of 4-aminoantipyrine solution and 3 cm<sup>3</sup> of potassium ferrocyanide sample 10 added. The mixed left for minutes. are is and Afterwards, 25 cm<sup>3</sup> of chloroform is added and sample is vigorously shaked for 3-5 minutes. After separation of chloroform from aqueous layer, the chloroform phase should be filtered through

filter with anhydrous sodium sulphate to a volumetric cylinder. The cylinder should be filled with chloroform to 20 cm<sup>3</sup> volume. The sample is analyzed at wavelength  $\lambda = 510$  nm.

#### Our evaluation

Due to complex procedure and range of the method we have not found it suitable for determination of phenols in coke oven wastewater. Moreover, the procedure of phenols determination in this case has to be always preceded with distillation. However, method can be applied for determination of phenols in coke oven wastewater treatment plant effluent, in which the concentration of contaminant should not be greater than 0.5 mg/dm<sup>3</sup>. Hence, we do recommend the method for determination of phenols in coke oven wastewater within our project, but only for effluent samples.

### **5.2.3.2 4-aminoantipyrine method without chloroform extraction** Idea

The analysis is based on the general idea and it is valid for phenols' concentration range from 0.1 to  $50 \text{ mg/dm}^3$ .

#### Procedure

The method requires preliminary distillation of the sample due to procedure discussed in 5.2.2. Next, a portion of distillate is placed in 250 cm<sup>3</sup> beaker and filled with distilled water to 200 cm<sup>3</sup>. The maximum amount of phenol in the sample must be not greater than 0.5 mg. Next, the sample pH is adjusted with ammonia buffer to pH = 10 and 2 cm<sup>3</sup> of 4-aminoantipyrine is added. The sample is mixed, 2 cm<sup>3</sup> of potassium ferrocyanide is added and the sample is mixed again. After 15 minutes the sample can analyzed at wavelength  $\lambda = 510$  nm.

#### Our evaluation

The procedure is simpler than in modification with chloroform extraction, however it still requires preliminary distillation of sample. Additionally, it can be used for higher phenols concentration. Hence, we do recommend the method for phenols determination in coke oven wastewater, however after proper dilution in case of streams sampled before biological treatment.

#### 5.3.4. Bromometric method

#### Idea

Determination of phenols relies on their bromination with bromate-bromide solution. As the result of this reaction, hydrobromic acid is formed, while the excess of bromine is measured iodometrically with thiosulphate titration. The method is dedicated for phenols concentration above  $10 \text{ mg/dm}^3$ .

#### Procedure

 $5 \text{ cm}^3$  of copper sulphate solution and  $1 \text{ cm}^3$  of phosphoric acid solution are added to the distillate obtained due to 5.2.2. The sample is placed in a separatory funnel. 150 g of NaCl is added and triple extraction with chloroform is performed with the use of  $50 \text{ cm}^3$  of chloroform/1 extraction. Chloroform extracts are mixed and undergone to further procedure, i.e. extraction with 75 cm<sup>3</sup> of NaOH, which is carried out two times. Alkali phases from both NaOH extractions are mixed in volumetric flask and  $10 \text{ cm}^3$  of bromate-bromide solution is added together with  $5 \text{ cm}^3$  of HCl solution. The solution is mixed. If the color caused by bromine is found to be unstable, next  $10 \text{ cm}^3$  portions of bromate-bromide solution are added until the color holds. The flask is closed and left for 10 minutes in dark place. Afterwards, 1 g of KI is added and after 5 minutes the solution is titrated with thiosulphate solution at the presence of starch as an indicator. The analysis has to be performed simultaneously with control sample analysis. Control sample is prepared with the use of phenol-free, distilled water.

#### Disrupting agents

The same group of interferences is defined as in case of 4-aminoantipyrine method. Those are oxidative and reductive substances, high pH, sulphur compounds, tars and oils. The impact of those compounds can be eliminated with sample predistillation.

#### Our evaluation

We have found the method to be complicated in procedure, and, despite complex sample preparation, it still required preliminary distillation. Hence, we do not recommend the method for determination of ammonia in coke oven wastewater. **5.3.5. Photometric method with dedicated HACH Lange tests – LCK 345** *Idea* 

Phenols react with 4-nitroaniline to form a yellow complex, color of which is measured in a photometer. The method is valid for phenols concentration range from 0.05 to 5 mg/dm<sup>3</sup>.

#### Procedure

 $2 \text{ cm}^3$  of sample is added to analytical cuvette. Next, 0.2 cm<sup>3</sup> of working solution A is added, the sample is mixed and left for 2 minutes, after which 0.2 cm<sup>3</sup> of working solution B is added. The sample is left again for 2 minutes, after which photometric measurement takes place.

#### Disrupting agents

The list of interferences of the method and their concentration supplied by the producer is presented in table 9.

Concentration	Interference	Concentration	Interference
$2000 \text{ mg/dm}^3$	$Na^{+}, K^{+}, SO_{4}^{2-}$	$25 \text{ mg/dm}^3$	$Al^{3+}, Mn^{2+}, Cr^{6+}, Cr^{3+}, Pb^{2+}$
$1000 \text{ mg/dm}^3$	Cl	$10 \text{ mg/dm}^3$	Sn <sup>2+</sup> , NH <sub>4</sub> <sup>+</sup>
$500 \text{ mg/dm}^3$	$Mg^{2+}$	$5 \text{ mg/dm}^3$	$Fe^{3+}$ , $Ag^+$ , $CN^-$
$250 \text{ mg/dm}^3$	NO <sub>3</sub>	$2.5 \text{ mg/dm}^3$	Fe <sup>2+</sup>
$125 \text{ mg/dm}^3$	Ca <sup>2+</sup>	$2 \text{ mg/dm}^3$	C1
$50 \text{ mg/dm}^3$	$Cu^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+}, NO_2^{-}$		

Table 9. Disrupting agents for LCK 345 method and their concentrations

#### Our evaluation

We have found the method to be extremely simple in procedure and accurate. As for our application, samples of coke oven wastewater streams before biological treatment need to be preliminary diluted at least 200 times, hence the impact of interferences present in the stream (especially ammonia and cyanides) is eliminated. We do recommend the method for analysis of ammonia content in coke oven wastewater.

# 5.3.6. Gas chromatography with flame ionization detector and mass spectrometer *Idea*

Sample without any pretreatment is a subject of gas chromatography analysis. All phenols present in the sample are identified by their retention time and/or mass fragmentation pattern. Both, flame ionization detector (FID) and mass spectrometer (MS) provide enough sensitivity for determination of 0.1 mg/dm<sup>3</sup> up to 100 mg/dm<sup>3</sup> of phenol. Afterwards the sum of all phenols is calculated.

#### Procedure

Wastewater sample is spiked with internal standard (1-butanol) and injected  $(1\mu)$  into chromatographic system equipped with a polar column, e.g. Stabilwax or SLB-60IL. Injector temperature should be 220°C or higher to ensure evaporation of all target compounds.

#### Disrupting agents

Co-elution of other organic compounds present in the sample might occur. That would generate serious errors, when FID is utilized. Analysis with MS provides additional dimension, which is usually sufficient to separate compounds with the same retention time. So far, we have not observed any influence of pH or concentration of suspended solid matter on analysis results. Neither acidification nor utilization of SPE technique (6.2.2.) changed the result obtained for untreated sample.

#### Our evaluation

Gas chromatography has an enormous potential in environmental analysis. It is capable of analysis trace level of organic compounds and do not suffer from matrix effects. Moreover it provides many additional information on sample composition like concentration of basic compounds (pyridine, quinolone, indole). Even though the method requires the use of chromatograph with dedicated detector coupled with mass spectrometer, we recommend it for phenols analysis within our project.

#### 5.3.7. Flow analysis

There are two modifications of that method: without distillation, but with chloroform extraction or with distillation, but without extraction. Both methods are discussed in subchapters 5.3.7.1 and 5.3.7.2. Both methods can be applied for samples containing from 0.01 to 1.0 mg of phenols/dm<sup>3</sup>.

#### 5.3.7.1. Flow analysis with extraction/without distillation

#### Idea

The method is based on the modification on 4-aminoantipyrine. The sample reacts sodium persulfate, which oxidizes phenols and products of this reaction react with 4-aminoantipyrine to yield colored condensation product. Those are extracted with chloroform, and the organic phase color intensity is measured spectrometrically at wavelength  $\lambda$  from 470 to 475 nm.

#### Procedure

The analysis is run in the dedicated device, in which all manuals are run automatically.

#### Disrupting agents

Aromatic amines, low sample pH.

#### Our evaluation

Due to the requirement of dedicated apparatus, we have not investigated the method in detail. However, in our opinion, the need for the dedicated (expensive) device is the main disadvantage of the method. Considering the application of the method to coke oven wastewater, for range of phenol concentration the sample requires dilution (except for effluents). Nevertheless, the method can be applied for phenol analysis in coke oven wastewater.

#### 5.3.7.2. Flow analysis without extraction/with distillation

#### Idea

The method is the automated version of 4-aminoantipyrine method without chloroform extraction discussed in chapter 5.2.3.2.

#### Procedure

The analysis is run in the dedicated device, in which all manuals are run automatically. *Disrupting agents* 

Aromatic amines, if sample is distilled at pH = 4. For distillation run at pH=0.5 or pH = 1.4 no interferences are listed.

#### Our evaluation

Due to the requirement of dedicated apparatus, we have not investigated the method in detail. However, in our opinion, the need for the dedicated (expensive) device is the main disadvantage of the method. Considering the application of the method to coke oven wastewater, for range of phenol concentration the sample requires dilution (except fir effluents). The method can be applied for phenol analysis within our project.

#### 5.4. Summary

We have reviewed a number of methods for determination of phenols in wastewater samples and we have evaluated them in terms of accuracy, procedure complexity, duration, disrupting agents and requirement for sample pretreatment. Within all investigated methods we have decided, that within our project one of the methods presented in table 10 can be applied.

Sample preservation	Acidification with phosphoric acid and copper sulphate addition - required for 4-aminoantipyrine method, for other methods not required (5.2.1)		
Phenols recovery	Distillation - required for 4-aminoantipyrine method, for othe methods not required (5.2.2.)		
	4-aminoantipyrine method (with chloroform extraction for COWTP effluent $-5.3.3.1$ , without chloroform extraction for other samples $-5.3.3.2$ .);		
Determination of phenols	Photometric method with dedicated HACH Lange tests – LCK 345 (5.3.5);		
	Gas chromatography coupled with flame ionization detector or mass spectrometer (5.3.6).		
	Flow analysis at both modifications (5.3.7.1 and 5.3.7.2)		

Table 10. Recommended methods of phenols analysis in coke oven wastewater

# 6. Methods for determination of polycyclic aromatic hydrocarbons (tars)

#### **6.1. General information**

Tars, which are generated during coal coking, are very complex in nature and comprise of a range of various compounds. They appear in wastewater is a result of condensation during coke oven gas processing and incomplete separation at plant site. Hence, in order to monitor their content in wastewater, the analysis of selected polycyclic aromatic hydrocarbons is performed.

Polycyclic aromatic hydrocarbons are a subject of interest due to their proven cancerogenic activity. According to Commission Implementing Decision of 28 February 2012 establishing the best available techniques (BAT) conclusions under Directive 2010/75/EU of the European Parliament and of the Council on industrial emissions for iron and steel production, permissible concentration of sum of the 6 arbitrary chosen PAHs (underlined in table 11) in treated coke oven wastewater should not exceed 0.05 mg/dm<sup>3</sup>. Surprisingly, two of the most cancerogenic compounds are excluded from that mandatory list.

Detection limit of 0.05 mg/dm<sup>3</sup> can be easily achieved by gas chromatography coupled with mass spectrometry. However, direct analysis of wastewater encounters one major problem, i.e. PAHs are water-insoluble (log  $K_{ow} > 3.3$ ) and are almost completely adsorbed on suspended solid matter. Therefore, their analysis requires sample pretreatment in order to obtain homogenous solution. So far, different techniques have been proposed for sample pretreatment. They are all based on high affinity of PAHs to nonpolar substances.

Subsequent, quantitative analysis might be conducted by gas chromatography (GC) coupled with mass spectrometry (MS) or flame ionization detector (FID) as well as by high-performance liquid chromatography coupled with ultraviolet (UVD) or fluorometric detector (FD).

Compound	Abbrevaition	TEF <sup>**</sup>	Log Kow
Dibenzo[a,h]anthracen	DBahA	5	6.50
Benzo[a]pyrene <sup>*</sup>	BaP	1	6.06
Benzo[a]anthracene	BaA	0.1	5.61
<u>Benzo[b]fluoranthene*</u>	BbFA	0.1	6.04
<u>Benzo[k]fluoranthene*</u>	BkFA	0.1	6.06
Indeno[123-c,d]pyrene*	IP	0.1	6.58
Anthracene	ANT	0.01	4.45
Benzo[g,h,i]peryIene*	BghiP	0.01	6.84
Chrysene	CHR	0.01	5.16
Acenaphthene	ACP	0.001	4.07
Acenaphthylene	ACY	0.001	3.98
Fluoranthene <sup>*</sup>	FA	0.001	4.90
Fluorene	FLR	0.001	4.18
Naphthalene	NPH	0.001	3.37
Phenanthrene	PHE	0.001	4.45
Pyrene	PYR	0.001	4.88

Table 11. Characteristics of 16 polycyclic aromatic hydrocarbons present in coke oven tars

\* compound listed in BAT requirements

\*\* toxic equivalency factor

#### 6.2. PAHs recovery methods

There are several methods suitable for recovery of PAHs from aqueous matrices. We have discussed them in detail in subchapters 6.2.1-6.2.3.

#### **6.2.1.Extraction with organic solvents**

#### Idea

High values of log  $K_{ow}$  ensure that all PAHs are transported to organic solvent. The method enables retrieval of PAHs from both, liquid and solid phase.

#### Procedure

The wastewater sample of  $10 - 50 \text{ cm}^3$  is extracted with 3 x 20 cm<sup>3</sup> of organic solvent immiscible with water (n-hexane, benzene or dichloromethane). Extraction is performed manually or by sonification. After phase separation, organic extracts are combined and

solvent is evaporated at reduced pressure (0.1 bar, 80°C). The sample is dissolved in 1 cm<sup>3</sup> of benzene with internal standards and analyzed by GC-MS.

#### Disrupting agents

We have examined that method with the utility of benzene and dichloromethane. Extraction has been conducted with both, manual shaking and sonification. In all cases, besides organic and water phase, a formation of transient phase has been observed. It has consisted of water, organic solvent and solid particles. Its presence has severely hampered proper separation of phases. Moreover, sonification has resulted in formation of an emulsion, which has separated after a few hours.

#### Our evaluation

Despite the fact that it is the simplest method of sample pre-treatment, it is also the most time consuming. Additionally, PAHs recovery suffer from formation of transient phase. Hence, we do not recommend the method for coke oven wastewater samples preparation.

#### 6.2.2.Solid phase extraction

#### Idea

The idea is essentially the same as described in 6.2.1, but in this case organic solvent is replaced by solid nonpolar phase, which adsorbs PAHs present in the liquid phase and filters suspended solid matter out. Afterwards, all adsorbed substances are liberated by small amount of organic solvent.

#### Procedure

Cartridge containing 500 mg of C18 sorbent (Supelclean LC-18) is conditioned by methanol ( $2 \times 2 \text{ cm}^3$ ) and washed with deionized water ( $3 \times 1 \text{ cm}^3$ ). Next, wastewater sample is passed ( $50 \text{ cm}^3$ ,  $2 \text{ cm}^3/\text{min}$ ), inorganic impurities are removed with deionized water ( $2 \times 2 \text{ cm}^3$ ). PAHs are desorbed by acetone ( $2 \times 2 \text{ cm}^3$ ) and benzene ( $2 \times 2 \text{ cm}^3$ ). Effluent consists of two phases, since acetone removes also trace amount of water that remained in the cartridge. All solvents are evaporated at reduced pressure (0.1 bar,  $80^{\circ}$ C), sample is redissolved in 1 cm<sup>3</sup> benzene containing internal standards and analyzed by GC-MS.

#### Disrupting agents

We have utilized the method for analysis of several wastewater samples with different amount of suspended solid matter. In some cases, cartridges clogged with solid particles, what disabled the extraction of the whole sample.

#### Our evaluation

It is one of the fastest method of sample pretreatment. Moreover, only small amount of organic solvents is required. It ensures high recovery of PAHs from both, water phase and suspended solid matter. Since concentration of PAHs increases with concentration of solid matter, clogging of cartridges should be prevented by reduction of sample size without loss of analysis precision.

### 6.2.3.Solid phase microextraction

#### Idea

The idea of SPME is to adsorb the target compounds on a fiber covered with nonpolar sorbent. Desorption method requires insertion of the fiber into chromatograph injector, where thermal desorption takes place.

#### Procedure

SPME fiber is first conditioned in the injector port of the gas chromatograph for 2 h at 300°C. The fiber is immersed in the wastewater sample with agitation at 60°C for 60 min. After extraction, the fiber is thermally desorbed at 300°C for 10 min in the injector port set to splitless mode.

#### Disrupting agents

SPME fiber might be easy saturated, if sample contains high concentration of organic impurities. Moreover the method does no ensure transfer of PAHs from suspended solid matter to SPME fiber.

#### Our evaluation

The method was originally designed for analysis of trace level PAHs in drinking water. Hence, we do not find it appropriate for our samples, due to the high content of organic compounds in the coke oven wastewater matrix.

#### 6.3. Chromatographic methods for PAH determination

## **6.3.1.Gas chromatography coupled with mass spectrometry** *Idea*

The idea of the method is based on separation of target compounds by gas chromatography and their subsequent analysis by quadruple mass spectrometer in SIM mode. Internal standard technique is utilized for quantitative analysis. Method can be coupled with all discussed pretreatment methods.

#### Procedure

 $1 \text{ cm}^3$  of homogenous sample containing mixture of PAHs and other organic compounds is spiked with internal standards (triphenylmethane and 9,10-diphenyl anthracene). Mixture is injected (1µL) onto chromatograph system and analyzed by quadrupole mass spectrometer in SIM mode. Separation is conducted on nonpolar stationary phases, e.g. HP-5 ms.

#### Disrupting agents

PAHs might co-elute with other organic compounds present in the sample. It may generate serious errors, when single FID analysis is utilized. Hence, its combination with MS provides additional dimension, which is usually sufficient to distinguish compounds with the same retention time.

Another problem is discrimination of high-boiling compounds. It is responsible for incomplete transfer of analytes from injector to column and results in lowering peak areas of compounds, e.g. IP and BghiP. The phenomenon is compensated by the utility of a proper internal standard with low volatility (usually 9,10-diphenyl anthracene).

#### Our evaluation

The method enables relatively fast analysis of all 16 PAHs (35 min). Utility of quadruple mass spectrometer extends method resolution and reduces effect of co-elution. Moreover, some additional information on sample composition might also be acquired. Hence, we recommend the use of this method for PAHs analysis in coke oven wastewater.

#### 6.3.2. High pressure liquid chromatography

#### Idea

The idea of the method is based on separation of target compounds with high performance liquid chromatography and their subsequent analysis by ultraviolet (UVD) or fluorometric detector (FD). Both, internal and external standard techniques can be utilized for quantitative analysis.

#### Procedure

 $1 \text{ cm}^3$  of homogenous sample containing mixture of PAHs and other organic compounds is injected (10µL) onto chromatograph and analyzed by UVD. Separation is conducted on octadecyl (C-18) stationary phase. Eluent consists of water: acetonitrile mixture.

#### Disrupting agents

Peak overlapping might disrupt analysis result. Compared to GC-MS, this method provides much worse separation.

#### Our evaluation

Compared to GC-MS, the method is much more sensitive to sample matrix. On the other hand, its greatest advantage is the lack of compounds discrimination. Nevertheless, due to the complexity of coke oven wastewater matrix we do not recommend it for PAHs analysis.

#### 6.4. Summary

We have reviewed a number of methods for determination of PAHs in wastewater samples. Within all investigated methods ,the sample pretreatment with SPE followed by GC-MS analysis is most suitable for research in our project (table 12). It reduces matrix effects and enables desired levels of detection.

Sample preservation	Not required.
PAHs recovery	Solid phase extraction (SPE) followed by desorption with acetone and benzene (6.2.2.).
Determination of PAHs	Gas chromatography coupled with FID (high concentration) or MS (trace level concentration). Quantitative analysis conducted by internal standard method (6.3.1.).

Table 12. Recommended methods of polycyclic aromatic hydrocarbons analysis in coke oven wastewater

#### 7. Conclusions

Within task 1.1. of INNOWATREAT project, a number of analytical methods has been investigated for analysis of target contaminants present in coke oven wastewater, i.e.:

- cyanides,
- sulphides,
- ammonia,
- phenols,
- tars.

The methods taken to the investigation have been selected on the basis of international and national standards and literature review. We have evaluated them according to accuracy, duration, procedure complexity, possible interferences and need for sample pretreatment. Except for last group contaminants, i.e. tars (analyzed as a defined group of polycyclic aromatic hydrocarbons), we have reviewed methods based on different analytical procedure, starting from titration methods, through photometric ones up to chromatographic procedures and flow analysis. Within every type of analysis, we have tried to indicate the most suitable for determination of a given contaminant in coke oven wastewater.

We have found, that the most demanding analyses had to be performed in case of cyanides and sulphides, which are the most instable in the wastewater matrix and their determination has to be run up to 24 hours since wastewater sampling. Moreover, procedures for their analysis usually require sophisticated sample pretreatment, which needs to be carefully done in order to assure the complete recovery of contaminant from the sample. Additionally, further determination procedures, especially in case of sulphides, have to be performed with the highest attention focused especially on oxidation prevention.

The methods investigated within the task have been performed simultaneously, in order to assure the highest comparability of analytical conditions. We have run the selected procedure until the agreement between the particular methods ranged between 10-15%. In case, when the accuracy of the given procedure have not reached the assumed correlation, we have recommended it for the analytical purposes within our project.

In tables 13-17, we summarize all investigated methods and present their basic characteristics: analyte concentration range without sample dilution, necessity of pretreatment, required equipment and recommendation for method to be applied in analysis of coke oven wastewater samples.

#### Table 13. Summary of methods for cyanides analysis

Method	Range of CN <sup>-</sup> concentration without sample dilution	Preliminary treatment*	Equipment	Recommendation
Colorimetric benzidine-pyridine method	$0.01-1.0 \text{ mg/dm}^3$	Yes	Distillation set Laboratory glass Set of reagents Spectrophotometer	No
Titrimetric argentometric method	above 1 mg/dm <sup>3</sup>	No	Laboratory glass Set of reagents	No
Colorimetric barbituric-pyridine method	0.01-1.0 mg/dm <sup>3</sup>	Yes	Distillation set Laboratory glass Set of reagents Spectrophotometer	Yes
HACH Lange LCK 315	$0.01-0.6 \text{ mg/dm}^3$	Yes	Distillation set Dedicated tests Spectrophotometer	Yes
HACH Lange LCK 319	0.03-0.35 mg/dm <sup>3</sup>	No	Dedicated tests Spectrophotometer	Yes
Potentiometric method with the use of argentometric titration	0.05-100 mg/dm <sup>3</sup>	No	Laboratory glass Set of reagents Dedicated electrodes Laboratory multimeter	Yes
Ion Chromatography analysis with Pulsed Amperometric Detection	0.05-5 mg/dm <sup>3</sup>	No	Ion chromatograph AS-7 analytical column Silver working electrode	Yes
Continuous flow analysis with photometric or amperometric detection	$0.002-0.5 \text{ mg/dm}^3$	No	Dedicated device Set of reagents	Yes

\*The need for preliminary treatment is given only in case of weak acid dissociated cyanides. In case of strong cyanides complexes the distillation has to be always performed before the analysis

#### Table 14. Summary of methods for sulphides analysis

Method	Range of S <sup>2-</sup> concentration without sample dilution	Preliminary treatment	Equipment	Recommendation
Colorimetric method for water soluble and acid soluble sulphides with p-aminodimethylaniline	up to 20 mg /dm <sup>3</sup>	No	Laboratory glass Set of reagents	No
Iodometric method for water soluble and acid soluble sulphides	$> 1 mg/dm^3$	Yes	Laboratory glass Set of reagents	No
Colorimetric method for water soluble sulphides with HMB and thiofluoroscein	0.005-0.04 mg/dm <sup>3</sup>	No	Laboratory glass Set of reagents	No
Photometric method for water soluble and acid soluble sulphides with methylene blue formation	$0.04-1.5 \text{ mg/dm}^3$	Yes	Laboratory glass Set of reagents Spectrophotometer	Yes
HACH Lange LCK 653	$0.1-2.0 \text{ mg/dm}^3$	Yes	Distillation set Dedicated tests Spectrophotometer	Yes
Potentiometric method for water soluble sulphides analysis with argentometric titration	0.05-100 mg/dm <sup>3</sup>	No	Laboratory glass Set of reagents Dedicated electrodes Laboratory multimeter	Yes
Ion Chromatography analysis for water soluble sulphides with Pulsed Amperometric Detection	0.05-5 mg/dm <sup>3</sup>	No	Ion chromatograph AS-7 analytical column Silver working electrode	Yes

#### Table 15. Summary of methods for ammonia analysis

Method	Range of N-NH <sub>4</sub> concentration without sample dilution	Preliminary treatment	Equipment	Recommendation
Direct Nesslerization	Depends on the concentration of standard solution used for calibration	Yes	Distillation set Laboratory glass Set of reagents Spectrophotometer	No
Ion-selective method for ammonia determination	0.5-1000 mg/dm <sup>3</sup>	No	Laboratory glass Set of reagents Dedicated electrodes Laboratory multimeter	No
Distillation method with titration	up to 100 mg/dm <sup>3</sup>	No	Distillation set Laboratory glass Set of reagents	Yes
Manual spectrometric method	up to 1 mg/dm <sup>3</sup>	No	Laboratory glass Set of reagents Spectrophotometer	No
HACH Lange LCK 302, 303, 304, 305	0.015-130 mg/dm <sup>3</sup>	No	Dedicated tests Spectrophotometer	Yes
Ion chromatography with conductometric detector	0.1-10 mg/dm <sup>3</sup>	No	Ion chromatograph Analytical column Conductometric detector	Yes
Flow analysis method (FIA and CFA) with spectrometric detection	0.1-10 mg/dm <sup>3</sup>	No	Dedicated device Set of reagents	Yes

#### Table 16. Summary of methods for phenols analysis

Method	Range of phenols concentration without sample dilution	Preliminary treatment	Equipment	Recommendation
4-aminoantipyrine method with chloroform extraction	0.001-1.0 mg/dm <sup>3</sup>	Yes	Distillation set Laboratory glass Set of reagents Spectrophotometer	Yes
4-aminoantipyrine method without chloroform extraction	0.1-50 mg/dm <sup>3</sup>	Yes	Distillation set Laboratory glass Set of reagents Spectrophotometer	Yes
Bromometric method for phenols determination	>10 mg/dm <sup>3</sup>	Yes	Distillation set Laboratory glass Set of reagents	No
HACH Lange LCK 345	$0.05-5 \text{ mg/dm}^3$	No	Dedicated tests Spectrophotometer	Yes
Gas chromatography with flame ionization detector and mass spectrometer	0.1-100 mg/dm <sup>3</sup>	No	Gas chromatograph PEG capillary column (Stabilwax) Flame ionization detector	Yes
Phenols determination by flow analysis	0.01-1 mg/dm <sup>3</sup>	No	Dedicated device Set of reagents	Yes

#### Table 17. Summary of methods for PAHs (tars) analysis

Method	Range of PAHs concentration without sample dilution	Preliminary treatment	Equi	pment	Recommendation
		Extraction with organic solvents	Laboratory glass	Gas chromatograph Apolar capillary column (Rxi-5)	No
Gas chromatography coupled with flame ionization detector	$0.02 - 100 \text{ mg/dm}^3$	Solid phase extraction	SPE cartridges		Yes
detector		Solid phase microextraction	Micro-syringe with attached SPME wire	Flame ionization detector	No
Gas chromatography coupled with mass spectrometry	0.001 – 10 mg/dm <sup>3</sup>	Extraction with organic solvents	Laboratory glass	Gas chromatograph Apolar capillary column (HP-5ms) Quadruple mass spectrometer High pressure liquid chromatograph Apolar analytical column (C-18) Ultraviolet detector	No
		Solid phase extraction	SPE cartridges		Yes
		Solid phase microextraction	Micro-syringe with attached SPME wire		No
High pressure liquid chromatography coupled with ultraviolet detector	$0.02 - 100 \text{ mg/dm}^3$	Extraction with organic solvents	Laboratory glass		No
		Solid phase extraction	SPE cartridges		Yes

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