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## CHROMATOGRAPHIC ANALYSIS IN THE CHARACTERIZATION OF COKING WASTEWATER

### ANALIZA CHROMATOGRAFICZNA W CHARAKTERYSTYCE ŚCIEKÓW KOKSOWNICZYCH

**Abstract:** Chromatography, the general term for the group of instrumental analytical methods, accepted nowadays as an extremely sensitive and effective analytical techniques, allows for qualitative and quantitative analysis of components of wastewater samples. In case of coking wastewaters, due to its complicated nature, a number of chromatographic techniques can be implemented in order to identify and determine the concentration of main hazardous pollutants, such as ammonia, cyanides, sulphides, thiocyanates, phenols and polycyclic aromatic hydrocarbons. Ion chromatography (IC), a type of liquid chromatography, is widely applied in measurement of concentrations of ionic species. Application of IC with suppressed conductivity detection allows to measure concentrations of major anions, i.e. chloride, nitrate, nitrite, sulphate and thiocyanate, as well as major cations such as sodium, ammonium, potassium, calcium, and magnesium. IC with pulsed amperometric detection (PAD) at silver electrode is applied in determination of sulphide and free cyanide concentration. Gas chromatography (GC), which can be used in conjunction with other methods to concentrate analytes, is predominant method of measurement of organic components present in the wastewater. Coupling the separation capabilities of GC with the detection properties of mass spectrometry (GC-MS) enhance the identification of organic pollutants, i.e. phenols and polycyclic aromatic hydrocarbons in coking wastewater samples. The paper presents the application of ion and gas chromatography with and without mass spectrometry detection in coking wastewater analyses.

**Keywords:** coking wastewaters, ion chromatography, gas chromatography

### Introduction

The composition of coke wastewater, coming from the condensation and cleaning of coke oven gas, is complex and variable depending on the technological processes of coke production, the type of coal used, the temperature of the coking process, methods used to recover by-products and methods of its physico-chemical and biological treatment. Raw coking wastewaters are highly contaminated with organic compounds, such as: polycyclic aromatic hydrocarbons, heterocyclic compounds, oils, tars and inorganic substances including cyanides, sulphides, sulphates, thiosulphates and ammonia [1]. 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, thiocyanates and tars are regarded as process inhibitors and have to be removed to a proper level during preliminary physico-chemical treatment. On the other hand,

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phenols and ammonia are main substances undergone to biodegradation, during which phenols act as carbon source for microorganisms responsible for decomposition of nitrates, which are the product of ammonia biological removal.

The concentration of mentioned substances has to be measured in priority in coke oven wastewater treatment (WWT) plant effluent, but also in the influent as well as at individual stages of its treatment. 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 [2]. 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.

Chromatography, the general term for the group of instrumental analytical methods, accepted nowadays as an extremely sensitive and effective analytical techniques, allows for qualitative and quantitative analysis of components of coking wastewater samples. Ion chromatography (IC), a type of liquid chromatography, is widely applied in measurement of concentrations of ionic species. Application of IC with suppressed conductivity detection allows to measure concentrations of major anions, i.e. chloride, nitrate, nitrite, sulphate and thiocyanate, as well as major cations such as sodium, ammonium, potassium, calcium, and magnesium. IC with pulsed amperometric detection (PAD) at silver electrode is applied in determination of sulphide and free cyanide concentration [3].

Gas chromatography (GC), which can be used in conjunction with other methods to concentrate analytes, is predominant method of measurement of organic components present in the wastewater. Coupling the separation capabilities of GC with the detection properties of mass spectrometry (GC-MS) enhance the identification of organic pollutants, i.e. phenols and polycyclic aromatic hydrocarbons in coking wastewater samples. In the article, authors present some basic experiences in the use of chromatography in the analysis of coking wastewater.

### **Ion chromatography**

A dual-channel reagent-free capillary Dionex ICS-5000 ion chromatograph, one of the most flexible IC systems, equipped with dual IC channels, each consisting of individual gradient pump, eluent generator cartridge, injection valve, column set and detector, as well as AS Autosampler, which can be differently configured was used for all chromatography experiments. A Chromeleon<sup>®</sup> 6.7 (Dionex) Data Management system was used for instrument control and data handling.

### **Ion chromatography with pulsed amperometric detection - free cyanide and sulphide anions**

Argentometric [4] and iodometric [5] titrations, potentiometry titration [6, 7], spectrophotometry [8, 9], gas chromatography, flow analysis with spectrophotometry and amperometry detection methods [10, 11] were proposed for determining cyanide and sulphide concentration in different matrices. However, some of them suffers from the interference from other ions, while others provides no information about analytes speciation or are time consuming and require sample preparation by distillation [12]. Since

hydrocyanic and hydrosulphuric acids are weak, its direct detection with suppressed conductometric detector is not possible. Nevertheless, ion chromatography with amperometric detection applied in determination of sulphide and free cyanide concentration is easy handle and shows excellent sensitivity. Standard procedure include isocratic separation of both anions in 15 min using Thermo-Scientific IonPac AS7 (250 mm×2 mm) analytical column and guard (50 mm×2 mm) column set with 600 mM degassed sodium hydroxide at a flow rate of 0.250 cm<sup>3</sup>/min and column temperature of 30 °C. Analytes are detected by PAD using a silver working electrode, in combination with pH-Ag/AgCl reference electrode in AgCl mode. The PAD waveform used for these experiments was a three-potential waveform optimized by detractor supplier for silver electrodes and cyanide, sulphide, iodide, and thiosulphate anions in a hydroxide eluent.

Electrochemical detector can work in two modes, i.e. DC amperometry and pulsed amperometry. Both modes are suitable for the detection of sulphide and cyanide. Nevertheless, when sulphide and cyanide are determined in real samples using a silver working electrode, the electrode surface is covered by products of the reaction, which alternate the sensitivity of the analysis over the time [13, 14]. Although the electrode can be reconditioned, the process requires interrupting the analysis and detector disassemble. The application of the pulsed amperometry with repeated multiple potentials (waveform) for detection, cleaning and conditioning can prevent electrode surface and extend their working time.

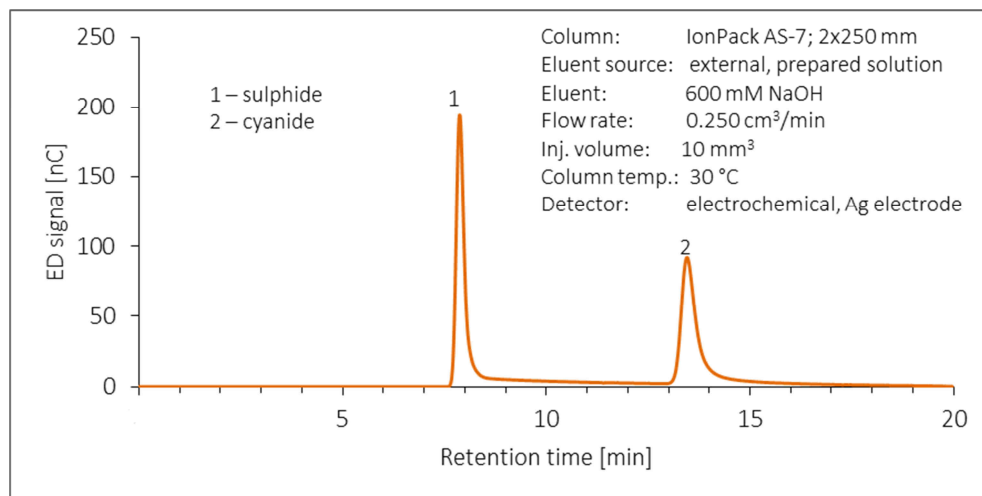


Fig. 1. Chromatogram of cyanide and sulphide standard solution recorded using IonPac AS-7 column

The type of column has a decisive influence on analytes separation and the result of the chromatographic analysis. In the literature, there are some examples of application of different columns in free cyanide and sulphide determination. Cheng et al. [15] used Thermo-Scientific IonPac<sup>®</sup> AS15 and IonPac AS16 columns. Literature reports indicate also on applicability of AS-7 columns [5, 6]. During the optimization of presented procedure, two analytical columns were tested - in addition to the mentioned

Thermo-Scientific IonPac AS7, AS-18 was also used. Tests carried out with AS-18, however, gave negative results. The separation of cyanide and sulphide anions obtained using this column proved to be insufficient. The cyanide signal overlapped with the sulphide signal, making it impossible to accurately measure the peak area (Figs. 1 and 2).

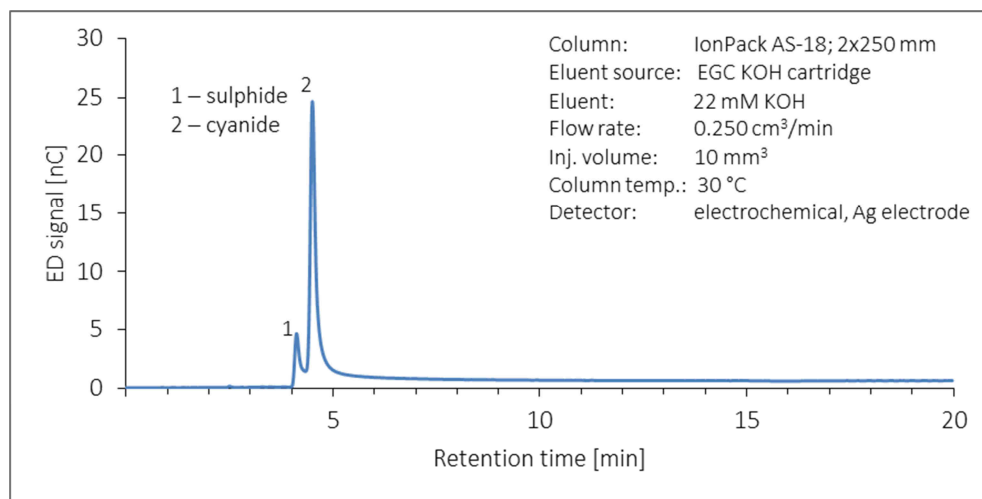


Fig. 2. Chromatograph of cyanide and sulphide standard solution recorded using IonPac AS-18 column

Different compositions of the eluent were also tested during studies. The recommended by the supplier eluent is a mixture of NaOH + CH<sub>3</sub>COONa + EDA (diaminoethane). The addition of acetic acid salt is intended to reduce peak tailing. EDA has the task of neutralizing divalent cations that could complex cyanides or cause sulphide precipitation. The last additive is very important due to the moderate purity of the other two components, which will always contain trace amounts of iron, magnesium and calcium compounds. However, the study showed, that the EDA is not completely inert and gives a signal on the electrochemical detector. Its presence in the eluent drastically increases the observed noise and makes it impossible to analyse traces. Subsequently, sodium acetate was removed from the eluent. Its lack did not significantly affect the tailing, but there were significant suspicions, that it may contain traces of impurities affecting detection. The remaining studies were carried out using an eluent containing only sodium hydroxide (600 mM).

Another issue is the strong tailing of signals from sulphides along with lowering their concentration in the sample. It is most likely that oxidation is responsible for this effect already on the ion exchange column. Along with the eluent, despite the degassing with helium, air enters the system. During the entire retention time of the sulphides on the column (about 8 min) they are in contact with oxygen. Hence, their slow oxidation to polysulphides, whose retention time is much longer, take place. To prevent this phenomenon, various antioxidants were added to the sample and their effect on the shape of the peak was checked. Sodium ascorbate, hydrazine and acetaldehyde were tested. No improvement in the shape of the peak was observed in any of experiments.

### Ion chromatography with conductometric detection

Application of IC with suppressed conductivity detection allows to measure concentrations of major anions, i.e. chloride, nitrate, nitrite, sulphate and thiocyanate, as well as major cations such as sodium, ammonium, potassium, calcium, and magnesium. IC is currently a standard method for the measurement of anions and cations in water and wastewater samples [16-18].

### Ammonia determination

There is a wide 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.

Ion chromatography method is based on the separation of ammonium ions from sample matrix by means of ion-exchange separation column. Column eluate is constantly analysed by conductivity detector. External standard method is utilized for quantitative analysis. The method is suitable for ammonia concentration from 0.05 to 5 mg  $\text{NH}_4^+$ /dm<sup>3</sup>. Apart from ammonia, the method enables simultaneous analysis of other cations presented in coking wastewaters, like sodium, potassium, calcium and magnesium.

The main problem connected with ammonia analysis in COW is high concentration of sodium cations, with may results in problem with those two analytes sufficient separation. However, properly selected separation column may solve this problem (Fig. 3).

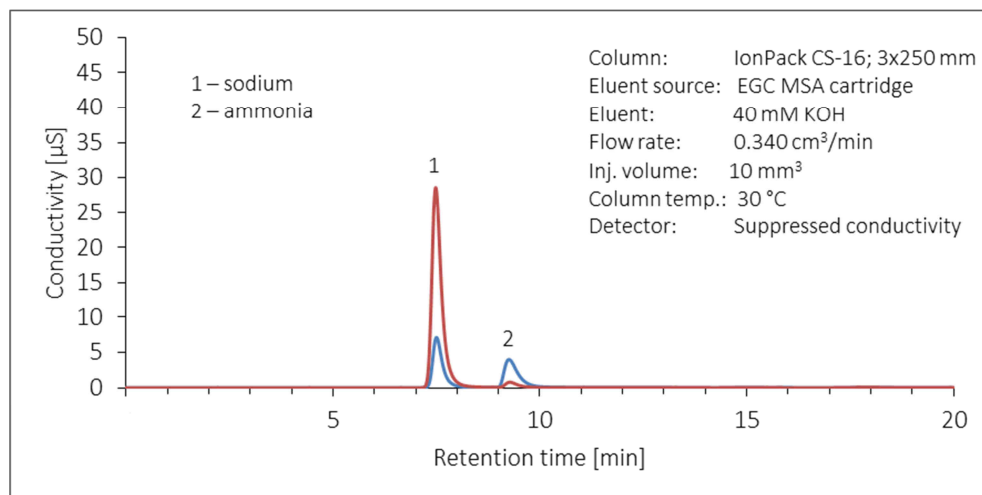


Fig. 3. Chromatograph of sodium and ammonia cations in coking wastewater sample recorded using IonPack CS-16 column

During studies, the application notes provided by columns supplier was followed. Since concentration of sodium in coking wastewaters is much higher in comparison with ammonia, for its efficient separation the IonPack CS-16 analytical column (250 mm×3 mm)

and IonPack CG-16 guard column were applied. External standard method using commercial 6-cation solution was utilized for quantitative analysis. 40-mM methanesulphonic acid eluent of high purity was electrochemically produced by eluent generator cartridge (EGC-MSA). The eluent flow was maintained at the rate of 0.340 cm<sup>3</sup>/min. Column and detector compartments were thermostated at 30 and 20 °C respectively to obtain a constant conditions. Chromatogram were recorded isocratically for 30 minutes.

### Anions determination

Taking into account the permissible discharge limits for coking wastewater treatment plant 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 [2], determination of concentration of anions such as nitrite, nitrate and thiocyanate in COW effluents is of great importance. Furthermore, monitoring of nitrogen compound concentration at different stages of wastewater treatment provide information on the activity of ammonia and nitrite oxidizing bacteria. On the other hand, thiocyanate ions are well known as nitrification inhibitors when presented in elevated concentration.

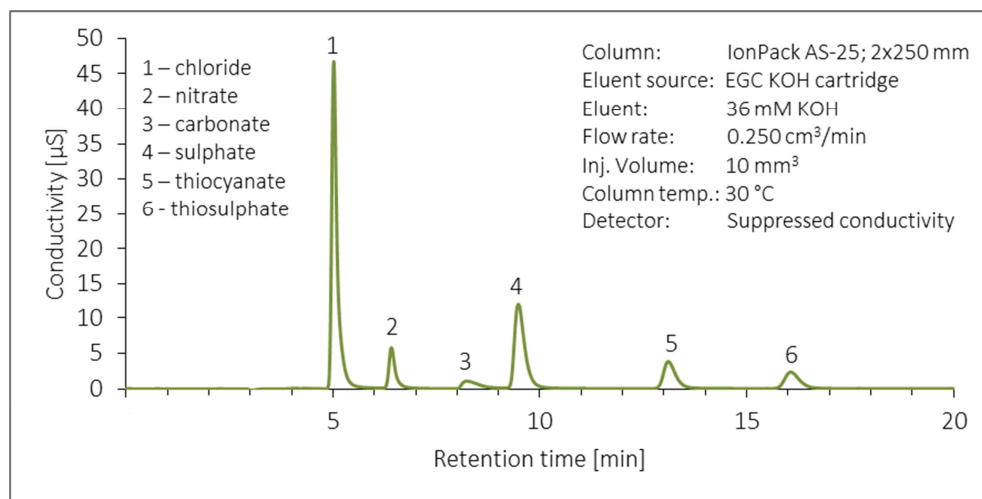


Fig. 4. Chromatograph of determined anions in standard solution recorded using IonPack AS-25 column

Standard anions like chloride, sulphates, phosphates and N-containing ones can be separated by means of a wide range of commercially available columns [19]. Authors studied applicability of two anion-exchange columns - IonPack AS-18 and IonPack AS-25. Both columns allows for separation of typically presented in coke wastewaters anions. Nevertheless, detection on thiocyanate anions with AS-18 is not possible. In order to get complete information about the content of interesting anions in a single analysis, employment of IonPack-25 column is recommended. External standard method using

self-prepared standard solution was utilized for quantitative analysis. 36-mM potassium hydroxide eluent of high purity was electrochemically produced by eluent generator cartridge (EGC-KOH). The eluent flow was maintained at the rate of 0.250 cm<sup>3</sup>/min. Column and detector compartments were thermostated at 30 and 20 °C respectively to obtain a constant conditions. Chromatogram were recorded isocratically for 20 minutes (Fig. 4).

### Gas chromatography

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.

### Phenols and polycyclic aromatic hydrocarbons (PAHs) determination by GC/GC-MS

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 [2], permissible concentration of sum of the 6 arbitrary chosen PAHs 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 (octanol-water partition coefficient  $\log K_{ow} > 3.3$ ) 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.

Wastewater samples are not homogenous. They contain solid particles as well droplets of tar. Due to extremely low solubility of PAHs in water they are either adsorbed on solid particles or dissolved in tar droplets. In order to extract them from the sample Solid Phase Extraction (SPE) technique was utilized. Coke oven wastewater sample (50 cm<sup>3</sup>) was passed through a cartridge containing non-polar adsorbent (LC-18). PAHs were then eluted with acetone (2 cm<sup>3</sup>) and toluene (2 cm<sup>3</sup>). Extract was marked with internal standards: toluene solution of triphenylmethane (TFM) and 9,10-dimphenylanthracene (9,10-DFA). Due to extremely low concentration of analytes pulsed splitless injection along with Selected Ion Monitoring (SIM) technique were utilized. An example chromatogram is shown in Figure 5. Detailed description of chromatographic analysis conditions of PAHs in wastewater samples are given in Table 1.

Content of phenols in wastewater was determined by gas chromatography with flame ionization detector. Quantitative analysis was conducted by internal standard calibration. Prior to analysis the sample was marked with aqueous solution of 2-methoxyphenol (guaicol) and 4-methoxyphenol. Depending on the phenols content in the sample, the quantity of the internal standard and the injection technique were selected. In case of

extremely low concentrations pulsed splitless injection technique was utilized (Table 1). Otherwise, split between 5 and 25 was chosen. An example chromatogram is shown in Figure 6. In order to determine concentration up to 10 mg/kg of methyl phenols and nitrogen compounds pulsed splitless injection had to be utilized.

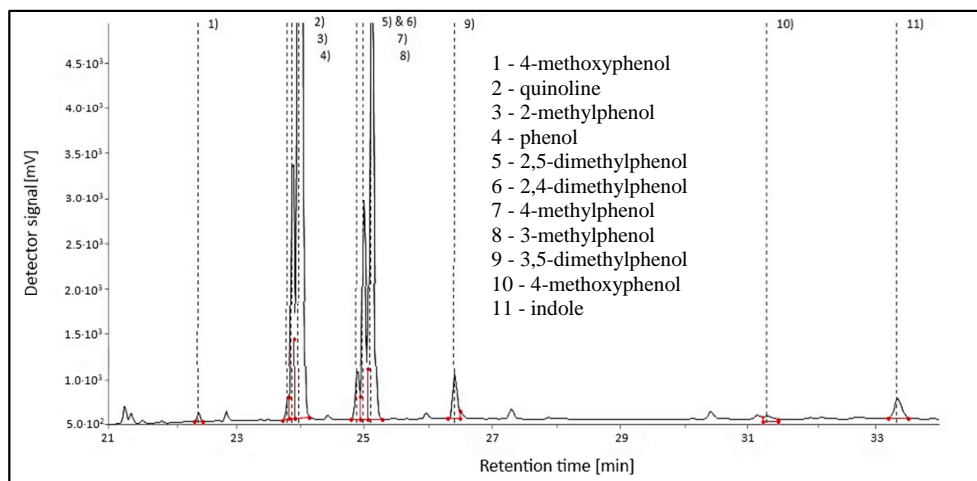


Fig. 5. Chromatographic analysis of phenols, quinoline and indole. Capillary column Stabilwax 60 m x 0.32 mm x 0.25  $\mu$ m; Pulsed splitless injection

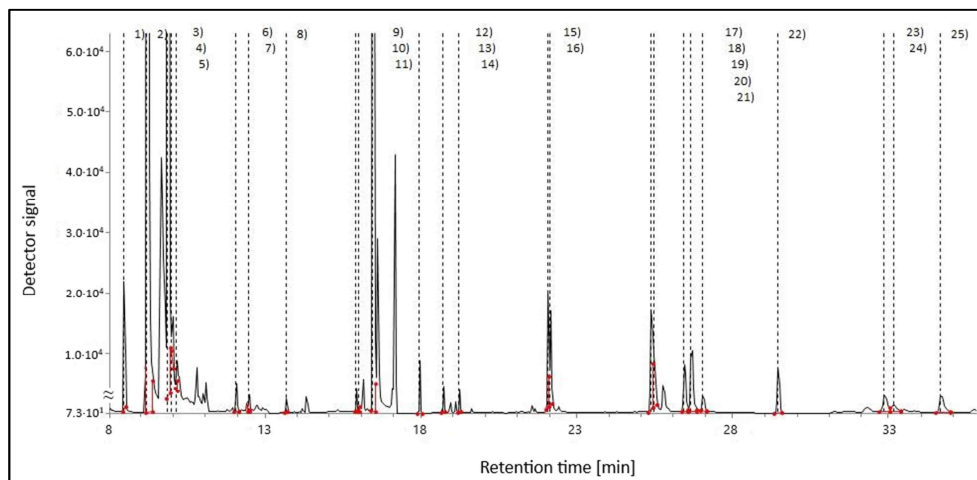


Fig. 6. Chromatographic analysis of PAHs. Capillary column HP-5ms 30m x 0.25 mm x 0.25  $\mu$ m. Pulsed splitless injection and Selected Ion Monitoring (SIM); 1 - naphthalene; 2 - quinolone; 3 - indole; 4 - 2-methyl naphthalene; 5 - 1-methyl naphthalene; 6 - acenaphthylene; 7 - acenaphthene; 8 - fluorine; 9 - phenantrene; 10 - anthracene; 11 - carbazole; 12 - TFM; 13 - fluoranthene; 14 - pyrene; 15 - benzo[a]anthracene; 16 - chrysene; 17 - benzo[b]fluoranthene; 18 - benzo[k]fluoranthene; 19 - benzo[e]pyrene; 20 - benzo[a]pyrene; 21 - perylene; 22 - 9,10-dimphenylanthracene; 23 - indeno(1,2,3-c,d)pyrene; 24 - dibenzanthracene; 25 - benzo[g,h,i]perylene



Table 1

Conditions of chromatographic analysis of phenols and PAHs in wastewater samples

	Analysis of phenols	Analysis of PAHs
<b>Detector</b>	Flame ionization detector	Quadrupole mass spectrometer Selected ion monitoring (SIM)
<b>Column</b>	Stabilwax 60 m x 0.32 mm x 0.25 $\mu$ m	HP-5ms 30 m x 0.25 mm x 0.25 $\mu$ m
<b>Injector</b>	Temp.: 240 °C, 2 min pulsed splitless, 250 kPa then split 5	Temp.: 280 °C, 2 min pulsed splitless, 250 kPa then split 5
<b>Carrier gas</b>	Helium 1cm <sup>3</sup> /min	Helium 1 cm <sup>3</sup> /min
<b>Oven</b>	50 °C (5 min) - 10 °C/min - 220 °C (13 min)	70 °C (1 min) - 10 °C/min - 280 °C (18 min)

## Summary and conclusions

The reliable and fast methods for the determination of the concentration of contaminants typical for the wastewater generated during coke production is crucial in the case of the wastewater treatment plant effluent discharge standards, but also in the case of WWT plant influent, as well as at individual stages of its treatment. Coking wastewaters samples can be analysed with different methods. Nevertheless, some of analytical procedures dedicated for qualitative and quantitative analysis of typical for coke oven wastewaters contaminants often allows the determination of only one analyte while being time-consuming. Furthermore, they often suffer from interferences from other analytes, especially thiocyanates and thiosulfates in case of spectrophotometric methods for cyanides and sulphides determination. Nevertheless, because of its advantages, i.e. good accuracy and precision, detection modes, high selectivity, speed, and separation efficiency, methods like ion and gas chromatography are becoming more and more popular in wastewater analysis. Simplicity in sample preparation and possibility to determine different analytes during single run makes those methods unrivalled even despite the fact, that they require higher investment cost. Furthermore, in comparison with

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## References

- [1] Znahg L, Hwang J, Leng T, Xue G, Wu G. Discussion on Coking Wastewater Treatment and Control Measures in Iron and Steel Enterprises. In: Ikhmayies SJ, Li B, Carpenter JS, Hwang JH, Monteiro SN, Li J, et al., editors. TMS2016 Annual Meeting - Proceedings Characterization of Minerals, Metals, and Materials 2016. New York: John Wiley & Sons, Inc.; 2016. ISBN 9783319482101. DOI: 10.1007/978-3-319-48210-1.
- [2] 2012/135/EU: 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 (notified under document C(2012) 903). 2012. <https://publications.europa.eu/en/publication-detail/-/publication/4ed6c72d-6dba-4274-870e-9a94ae826cbb/language-en>.
- [3] Weiss J. Handbook of Ion Chromatography. Weinheim: Wiley-VCH Verlag GmbH; 2004. ISBN 9783527619610. DOI: 10.1002/9783527619610.

- [4] Alonso-González O, Jiménez-Velasco C, Nava-Alonso F, Alvarado-Hernández F, González-Anaya JA. *Miner Eng.* 2017;105:1-21. DOI: 10.1016/j.mineng.2017.01.001.
- [5] Pawlak Z, Pawlak AS. *Talanta.* 1999;48:347-353, DOI: 10.1016/S0039-9140(98)00253-7.
- [6] Breuer PL, Sutcliffe CA, Meakin RL. *Hydrometallurgy.* 2011;106:135-140, DOI: 10.1016/j.hydromet.2010.12.008.
- [7] Tamele MW, Ryland B, McCoy N. *Anal Chem.* 1960;32:1007-1011. DOI: 10.1021/ac60164a034.
- [8] ISO 10530:1992. Water quality. Determination of dissolved sulfide - Photometric method using methylene blue. 1992. <https://www.iso.org/standard/18599.html>.
- [9] ISO 6703-2:1984. Water quality. Determination of cyanide - Part 2: Determination of easily liberatable cyanide. 1984. <https://www.iso.org/standard/13142.html>.
- [10] Ertek B, Vu DL, Cervenka L, Dilgin Y. *Anal Sci.* 2012;28:1075-1080. DOI: 10.2116/analsci.28.1075.
- [11] ISO 14403-2:2012. Water quality. Determination of total cyanide and free cyanide using flow analysis (FIA and CFA) - Part 2: Method using continuous flow analysis (CFA). 2012. <https://www.iso.org/standard/52208.html>.
- [12] Ma J, Dasgupta P. *Anal Chim Acta.* 2010;673:117-125. DOI: 10.1016/j.aca.2010.05.042.
- [13] Giuriati C, Cavalli S, Gorni A, Badocco D, Pastore P. *J Chromatogr A.* 2004;1023:105-122. DOI: 10.1016/j.chroma.2003.10.001.
- [14] Meher A, Labhsetwar N, Bansiwala A. *Food Chem.* 2018;240:131-138. DOI: 10.1016/j.foodchem.2017.07.041.
- [15] Cheng J, Jandik P, Avdalovic N. *Anal Chim Acta.* 2005;536:267-274. DOI: 10.1016/j.aca.2004.12.039.
- [16] PN-EN ISO 10304-1:2009. Water quality - Determination of dissolved anions by liquid chromatography of ions - Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate. 2009. <http://sklep.pkn.pl/pn-en-iso-10304-1-2009e.html>.
- [17] PN-EN ISO 10304-3:2001. Water quality - Determination of dissolved anions by liquid chromatography of ions - Part 3: Determination of chromate, iodide, sulfite, thiocyanate and thiosulfate. 2001. <http://sklep.pkn.pl/pn-en-iso-10304-3-2001p.html>.
- [18] PN-EN ISO 14911:2002. Water quality - Determination of dissolved Li<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mn<sup>2+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> using ion chromatography - Method for water and waste water 2002. <http://sklep.pkn.pl/pn-en-iso-14911-2002p.html>.
- [19] Michalski R. *Separations.* 2018;5:16-28. DOI: 10.3390/separations5010016.

## ANALIZA CHROMATOGRAFICZNA W CHARAKTERYSTYCE ŚCIEKÓW KOKSOWNICZYCH

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**Abstrakt:** Chromatografia, ogólne określenie grupy instrumentalnych metod analitycznych, obecnie akceptowanych jako niezwykle czułe i skuteczne techniki analityczne, pozwala na jakościową i ilościową analizę związków chemicznych występujących w ściekach. W przypadku ścieków koksowniczych, z uwagi na ich skomplikowany skład, identyfikacja oraz oznaczenie stężenia głównych zanieczyszczeń, takich jak amoniak, cyjanki, siarczki, rodanki, fenole i wielopierścieniowe węglowodory aromatyczne, wymaga zastosowania różnych technik analitycznych. Zastosowanie chromatografii jonowej (IC) z detekcją konduktometryczną z supresją pozwala mierzyć stężenia głównych anionów, tj. chlorków, azotanów, azotynów, siarczanów i rodanków, a także kationów, takich jak jon amonowy, sód, potas, wapń i magnez. IC sprzężona z pulsacyjną detekcją amperometryczną na srebrnej elektrodzie jest stosowana do oznaczania stężeń siarczków i wolnych cyjanków. Chromatografia gazowa (GC), która może być stosowana w połączeniu z różnymi metodami zateżenia analizatów, jest dominującą metodą oznaczania stężenia związków organicznych występujących w ściekach. Sprzężenie chromatografii gazowej ze spektrometrią mas (GC-MS) umożliwia wykonanie kompletnej analizy zarówno jakościowej, jak i ilościowej zanieczyszczeń organicznych, tj. fenoli i wielopierścieniowych węglowodorów aromatycznych w próbkach ścieków koksowniczych. W pracy przedstawiono i omówiono zastosowanie chromatografii jonowej i gazowej oraz GC sprzężonej ze spektrometrią mas w analizie ścieków koksowniczych.

**Słowa kluczowe:** ścieki koksownicze, chromatografia jonowa, chromatografia gazowa