

PREPARATION OF WASTEWATER SAMPLES FOR GC-MS ANALYSIS
OF PAHS

MARIA WŁODARCZYK-MAKUŁA

Department of Chemistry, Water and Wastewater Technology, Częstochowa University of Technology
69 Dąbrowskiego Str, 42-200 Częstochowa
e-mail: mwm@is.pcz.czest.pl, tel.034 32-50-919, fax:034 32 50 496

Abstract: Standard EPA Method 8310 recommends the use of liquid chromatography with fluorescence detection for the determination of PAH compounds. Taking into consideration the advantages of gas chromatography – mass spectrometry (GC - MS) it is important to carry out investigations to optimise wastewater preparation for qualification and quantification of PAHs using this method. The aim of the investigation was to verify the procedure of wastewater preparation for PAHs analysis using GC-MS. The method was evaluated based on experimental recovery values of individual compounds. The experiments were carried out using both raw and biologically treated wastewaters collected from a municipal treatment plant.

Keywords: Wastewater, EPA – PAH, recovery, GC-MS, SPE

INTRODUCTION

When working on methods for PAHs determination, reference data, a lab's own expertise, available equipment and the expected concentration and overall composition of analytes, need to be considered. Two major types of chromatography are commonly used in PAHs analysis, namely, high-performance liquid chromatography (HPLC) and gas chromatography (GC). The UV, photoionization or flame-ionization detectors (FID) are the most used detectors in HPLC. In GC usually MS and FID detectors are used (Barcelo *et al.*, 1998; Helaleh *et al.*, 2005; Miege *et al.*, 2003; Wolska, 2002; Clesceri *et al.*, 1998). The most important steps in analyte preparation are extraction of the compounds from the matrix and fractionation of PAHs. PAHs concentrations obtained using various analytical methods are often diversified and difficult to compare because of at least two reasons. One of them is that the physicochemical properties of PAHs are heterogeneous and the second is that various chromatographic methods are applied. During sample preparation for chromatographic analysis all steps can be sources of analytical errors, including: sample collecting, storage, extraction and extract purification (Wolska *et al.*, 2005). PAHs are frequently analysed in surface waters (Manoli *et al.*, 2000), bottom sediments (Wolska *et al.*, 2005; Mc Groddy *et al.*, 1996) but also in soil (Maliszewska-Kordybach, 1993; Noordkamp *et al.*, 1997) and other media. Thus, they were also quantitatively analysed in aerosols from a sewage treatment plant and in sewage sludge (Perez *et al.*, 2001; Manoli and Samara, 1999; Rogers, 1996). In wastewaters PAHs are not now frequently analysed (Miege *et al.*, 1999; Włodarczyk-Makuła, 2005). In Poland, the concentration of PAHs in treated effluent is not regulated, however because of the carcinogenic and mutagenic properties of these compounds they are classified as substances harmful to the environment. This means that there is a need for the development and application of treatment techniques. The level of PAHs in treated effluent is limited in the European Union. In Poland, PAHs concentrations in effluents are hardly ever investigated. Moreover, there is no approved standard method of wastewater sample preparation for PAHs analysis. The results obtained by other

authors indicate that, despite the adsorption of PAHs into the solid particles during wastewater treatment, these micropollutants are present in treated effluents in measurable concentrations (Włodarczyk-Makuła, 2005). This was the reason for carrying out the investigations on elucidating an adequate solvent system for extraction of PAHs from wastewater (Włodarczyk-Makuła, 2004).

In this paper the results of investigations on the best method of PAHs fractionation from sewage are presented. PAHs recoveries are also reported.

MATERIALS AND METHODS

Influent and biologically treated effluent samples were collected from the municipal treatment plant ($Q > 20\,000\text{ m}^3/\text{d}$) at Czeszochowa in the south-east of Poland. This mechanical-biological-chemical treatment plant carries out both biological removal of nitrogen compounds and phosphorus precipitation.

Wastewater samples were analysed for pH, total suspended solids (TSS) and volatile suspended solids (VSS) as well as for total organic carbon. For PAHs extraction from wastewater samples, liquid-liquid extraction was used. Based on our earlier investigations a mixture of methanol: cyclohexane: dichloromethane (v/v 30:5:1) was used as extracting agent (Włodarczyk-Makuła, 2005). The properties of the compounds were various. The polarities of the extractants were 0, 3.4 and 6.6 for C_6H_{12} , CH_2Cl_2 and CH_3OH , respectively. Methanol was used as the agent for desorption of PAHs from solid particles (as recommended by the Polish standard on PAHs analysis in water with thin-layer chromatography). Organic matrix extraction was performed using a shaker with horizontal motion for 60 min. The extracts were then separated from the water phase in a laboratory separator, dried with anhydrous sodium sulphate and concentrated to 3 mL. Subsequently the extracts were purified under vacuum on silica gel or on silica-cyano (PAH soil) columns. The silica gel columns were conditioned with a cyclohexane: dichloromethane mixture. Next, the extracts were introduced into the columns. When PAH soil was used the hydrocarbons were eluted with acetonitrile: toluene mixture (v/v 3:1). Acetonitrile: toluene mixture was also used for conditioning the PAH soil columns. Cleaned extracts (with PAHs) were concentrated under nitrogen to 1 mL. Afterwards 16 PAHs – EPA were determined quantitatively and qualitatively using GC-MS. The experimental procedure is presented in Fig. 1.

To verify the method of wastewater sample preparation for PAHs analysis control samples spiked with known concentrations of PAH compounds were prepared.

A standard mixture of PAHs (deuterated hydrocarbons not included) (Accu Standard Inc. USA - PAH Mix) in benzene and dichloromethane (v/v 1:1) was spiked into the influent and effluent samples. Standard mixture concentration spiked into the samples was $30\mu\text{g/L}$. For chromatographic determination of individual PAHs a Fisons GC 8000 gas chromatograph equipped with an MD 800 mass spectrometric detector was used. The chromatographic analysis parameters were as follows: carrier gas - helium 70kPa, temperature program $40^\circ\text{C} - 120^\circ\text{C}$ ($40^\circ\text{C}/\text{min}$) to 280°C ($5^\circ\text{C}/\text{min}$) and 280°C for 20 min., interface temperature - 280°C , column – DB-5 (30m; 0.25 mm; 0.25 μm), integration system – MassLab. volume injection - 1 μL , injection system – on column injector. The extracts (in cyclohexane/dichloromethane or acetonitrile/toluene – depending on the extract preparation technique) were directly introduced into the precolumn (1.5 m length). The limits of detection values for individual compounds were as follows: naphthalene-0.14, acenaphthylene-0.31, acenaphthene-0.43, fluorene-0.46, phenanthrene-0.59, anthracene-0.54, fluoranthene-0.30, pyrene-0.22, benzo(a)anthracene-0.28, chrysene-0.28, benzo(b)fluoranthene-0.28, benzo(k)fluoranthene-0.27, benzo(a)pyrene-0.21, indeno(1,2,3,c,d)pyrene-0.24, dibenzo(a,h)anthracene-0.22, benzo(g,h,i)perylene-0.20 ($\mu\text{g/L}$). A Student-t test was used in order to assess the statistical significance of results. The critical value was read from tables for the specified degree of freedom (n-2) and a 95% confidence level.

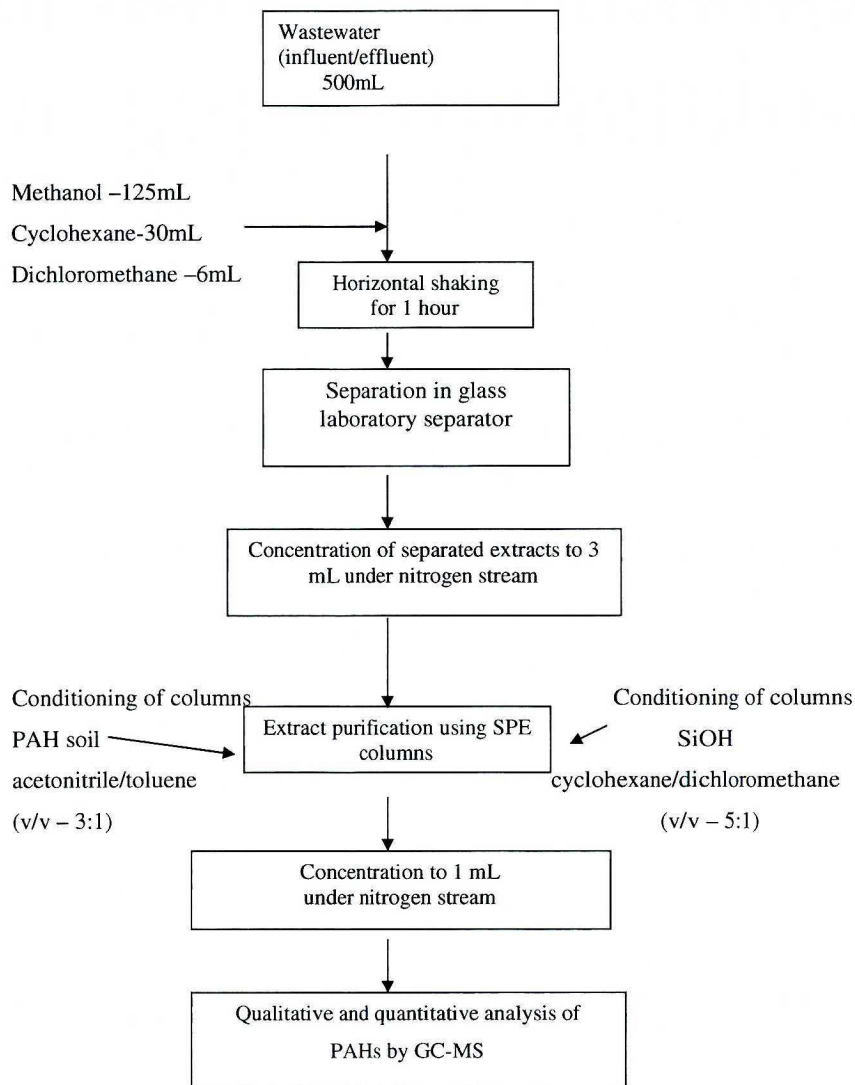


Fig. 1 Preparation of wastewater samples for the determination of PAHs by GC-MS

RESULTS AND DISCUSSION

In influent, a high concentration of total suspended solids was observed- 304 mg/L. Neutral pH and a COD value of 429 mg/L was also noted. Biological treatment of the wastewater decreased the

TSS concentration to 12 mg/L; the COD value in treated effluent was 27 mg/L. Individual PAHs recoveries from influents are presented in Fig 2. Recovery was calculated taking into consideration not only the spiked PAHs concentration but also initial concentration of individual compounds in the influent. PAHs recoveries varied between 48 and 95% when silica gel was used for extract purification. When the samples were purified using PAH soil columns, recoveries of 47 - 88% could be achieved. Average PAHs recoveries were in the range 71 - 72%. Despite purification the highest recovery (>80%) was obtained in the case of high molecular weight compounds ($\log K_{ow} > 7$). These compounds are considered to be adsorbable onto solid particles. The vapour pressure of these compounds is the lowest. The highest recovery values were obtained for hydrocarbons with water solubility of 62 to 260 $\mu\text{g/L}$ (at 20°C). The difference between recovery values obtained for influents with various purification methods was not statistically significant (statistical analysis was performed using Student-t test).

PAHs recoveries from effluents are presented in Fig. 3. As in the case of the raw wastewater no effect of purification method on the recovery of most PAH compounds from their matrix was observed. Only in the case of 4-ring PAHs, the recovery value was higher, at 16%, when silica gel columns were used for extract purification. Recoveries for individual compounds were in the range of 53 -119% and 56-111% for silica gel columns and PAH - soil columns, respectively. Both in treated and raw wastewaters the highest recovery values were obtained for hydrocarbons of water solubility 62 - 260 $\mu\text{g/L}$ (99%). Simultaneously high (>97%) recoveries were obtained in the case of hydrocarbons with $\log K_{ow}$ in the range of 5 to 6. The lowest recovery values were always obtained for naphthalene. This was probably connected with loss of this compound by evaporation. The average recovery from the standard mixture (volatile hydrocarbons omitted) was high and reached 93% and 73% for raw and treated wastewaters, respectively. Taking into account the high recovery values obtained for influents (containing high concentrations of TSS) it is obvious that proposed procedure may be used for qualification and quantification of PAHs. The recovery values obtained were within the range reported by other authors.

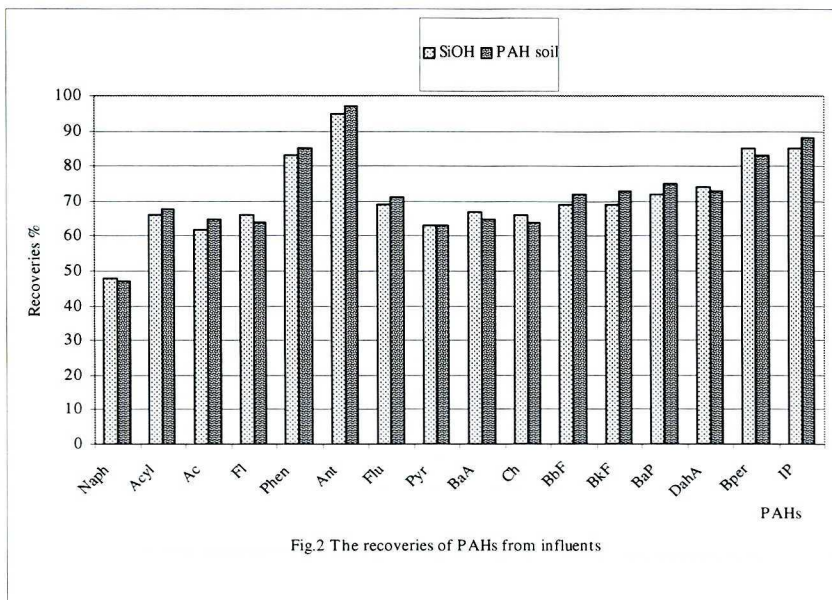


Fig.2 The recoveries of PAHs from influents

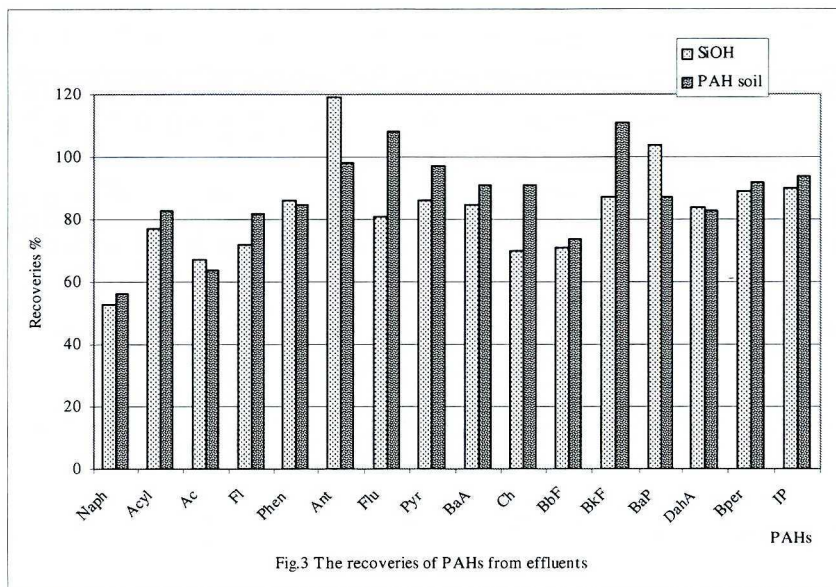


Fig.3 The recoveries of PAHs from effluents

In the case of petrochemical wastewaters containing high concentrations of volatile solids when the standard mixture was directly spiked into the sewage sample and then extracted with organic solvents recovery values for 6 PAH compounds were in the range 38-95% (average recovery 48 - 75%). In the case of rain, wastewaters recoveries of 14 PAHs (not including volatiles) varied between 80 and 120% (Miege *et al.*, 2003; Wolska, 2002; Helaleh *et al.*, 2005; Manoli and Samara, 1999).

CONCLUSIONS

The conclusions are as follows:

1. For the extraction of PAHs from wastewater samples a mixture of methanol, cyclohexane and dichloromethane and SPE purification is recommended,
2. Both silica gel and cyano-propyl phase (in PAH soil columns) were suitable to obtain high PAHs recoveries from the sewage.

Acknowledgement

This research was supported by the Committee of Scientific Research grants 4T09D 040 24

REFERENCES

- [1] Barcelo D., Oubina A., Salau J.S., Perez S., 1998. Determination of PAHs in river water samples by ELISA., *Analytica Chimica Acta*, 376, 49-53
- [2] Clesceri L S., Greenberg A.E., Eaton A.D., 1998, *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington
- [3] Heleleh M.I. H., Al.-Omar A., Nisar A., Gevao B., 2005. Validation of various extraction techniques for the quantitative analysis of polycyclic aromatic hydrocarbons in sewage sludge using gas chromatography-ion trap mass spectrometry, *Journal of Chromatography A*, 1083, 163-160

- [4] Lepri L., Bubba M.D., Masi F., Udisti R., Cini R., 2000. Particle size distribution of organic compounds in aqueous aerosols collected from above sewage aeration tanks, *Aerosol Science and Technology*, 32, 404-420
- [5] Maliszewska-Kordybach B., 1993. The effect of temperature on the rate of disappearance of polycyclic aromatic hydrocarbons from soils, *Environmental Pollution*, 79, 15-20
- [6] Manoli E., Samara C., 1999. Occurrence and mass balance of polycyclic aromatic hydrocarbons in the sewage treatment plant, *Journal of Environmental Quality*, 28
- [7] Manoli E., Samara C., Konstantinou I., Albanis T., 2000. Polycyclic aromatic hydrocarbons in the bulk precipitation and surface waters of Northern Greece, *Chemosphere*, 41, 1845-1855
- [8] Mc Groddy S.E., Farrington J.W., Gschwend P.M., 1996. Comparison of the *in situ* and desorption sediment-water partitioning of Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls, *Environmental Science and Technology*, 30, 172-177
- [9] Miega C., Bouzige M., Nicol S., Dugay J., Pichon V., Hennion M.C., 1999. Selective immunoclean-up followed by liquid or gas chromatography for the monitoring of polycyclic aromatic hydrocarbons in urban waste water and sewage sludges used for soil amendment., *Journal of Chromatography A*, 859, 29-39
- [10] Miega C., Dugay J., Hennion M.C., 2003. Optimization, validation and comparison of various extraction techniques for the trace determination of polycyclic aromatic hydrocarbons in sewage sludge by liquid chromatography coupled to diode-array and fluorescence detection, *Journal of Chromatography A*, 995, 87-97
- [11] Noordkamp E.R., Grotenhuis T.C., Rulkens W.H., 1997. Selection of an efficient extraction method for the determination of polycyclic aromatic hydrocarbons in contaminated soil and sediment, *Chemosphere*, 35, 9, 1907-1917
- [12] Perez S., Guillamon M., Barcelo D., 2001. Quantitative analysis of polycyclic aromatic hydrocarbons in sewage sludge from wastewater treatment plants., *Journal of Chromatography A*, 938, 57-65
- [13] Rogers H.R., 1996. Sources, behaviour and fate of organic contaminants during sewage treatment and in sewage sludges, *The Science of the Total Environment*, 185, 3-26
- [14] Włodarczyk-Makuła M., 2004. Analytical experiences with PAHs analysis in wastewater samples, *Laboratorium, Aparatura, Badania LAB*, 4, 9-12 (in Polish)
- [15] Włodarczyk-Makuła M., 2005. The Loads of PAHs in wastewater and sewage sludge of municipal Treatment Plant, *Polycyclic Aromatic Compounds*, 25, 183-194
- [16] Wolska L., 2002. Miniaturised analytical procedure of determining polycyclic aromatic hydrocarbons and polychlorinated biphenyls in bottom sediments, *Journal of Chromatography A*, 959, 173-180
- [17] Wolska L., Rawa-Adkonis M., Namieśnik J., 2005. Determining PAHs and PCBs in aqueous samples: finding and evaluating sources of error. *Analytical and Bioanalytical Chemistry*, 6, 1389-1397

Received: September, 2007; accepted: June, 2008.