ECOLOGICAL CHEMISTRY AND ENGINEERING A

Vol. 17, No. 12 2010

Ksenia RAMUS[1] and Tomasz CIESIELCZUK[2]

EVALUATING THE EFFICIENCY OF SELECTED EXTRACTION METHODS FOR PAHs ON THE EXAMPLE OF COMPOST FROM URBAN WASTES

EFEKTYWNOŚĆ WYBRANYCH METOD EKSTRAKCJI PAHs (WWA) NA PRZYKŁADZIE KOMPOSTU Z ODPADÓW KOMUNALNYCH

Abstract: Extraction methods are especially important during the stage of preparing the samples to the identification and separation of the elements from environmental samples. Analytes, which are mainly solid organic substances, can be separated from solid materials either by a gas or a solvent. Nevertheless, solvents are still the most popular and the most widely used extractants. Still, the efficiency of extraction depends not only on the particular type of solvent but also on the extraction method. In literature, there are all sorts of assaying processes. Qualitative or quantitative persistent chemical pollutants are among others, polycyclic aromatic hydrocarbons (PAHs). This research was to test two different organic solvents, ie hexane, dichloromethane and hexane with acetone, as well as different extraction methods in the process of isolating polycyclic aromatic hydrocarbons from compost originating from municipal wastes.

Keywords: extraction, PAHs, compost

Polycyclic aromatic hydrocarbons, which represent persistent organic waste, have been rousing interest for over 100 years since their cancerous properties were discovered [1, 2]. The prevalence of these compounds requires a monitoring of their content in the environment [3]. They can be of natural or anthropogenic origin [4]. Due to their low concentration levels, it was necessary to apply effective methods of isolating, purification and inspissation.

One of the essential elements of analytical procedures, which are especially important in the analysis of environmental samples, is preparing research material for analysis. According to many authors, more than 60 % of the time of the overall analysis cost is preparing samples, while the actual analysis is less than 10 % of the overall cost. It is mainly due to the necessity of preliminary purification and isolation of the analysed

[1] Helmholtz Centre for Environmental Research – UFZ, Department of Environmental Technology, Permoserstrasse 15, 04318 Leipzig, Germany.

[2] Department of Land Protection, Opole University, ul. Oleska 22, 45–052 Opole, Poland, phone: +48 77 401 60 27, email: tciesielczuk@uni.opole.pl

substance from a complicated mixture containing different kinds of multiple molecules. This stage of preparing the samples is called purification. The selected method used to prepare environmental samples for analysis depends mostly on the element and sample properties as well as on the required detection limit, possibilities of the process, etc.

The most common techniques of purification, separation and inspissation in analytical chemistry are extraction techniques [2, 5].

Extraction is a method of separating and purificating compounds from a liquid or solid mixture by using appropriately selected selective solvents. The process is based on moving compounds contacting each other by phases: solid body-liquid or liquid-liquid.

Therefore, extraction allows:

– Separation,
– Separating interfering components,
– Inspissating (enriching) elements in trace analysis of high purity materials.

We can distinguish the following extraction techniques:

– liquid-liquid extraction (LLE),
– solid-phase extraction (SPE),
– superfcritical fluid extraction (SFE),
– solid-phase microextraction (SPME),
– single-drop microextraction (SDME),
– accelerated solvent extraction (ASE),
– ultrasound accelerated extraction (UAE) and
– microwave assisted extraction (MAE).

The most common methods used for separation and inspissation in analytical chemistry are solid body-liquid and solid phase extraction.

The most important issue connected with the extraction process is the choice of a particular solvent, which has to be characterised by the following features:

– Easiness of precipitation from the extract,
– The lowest possible mutual phase solubility,
– Favourable division ratio between the extractant and phase extractant,
– The highest possible difference between the solvent density and extractant phase,
– High surface tension.

Solid-liquid extraction is a versatile technique that allows a more effective separation of different substances from complex mixtures due to the possibility of using specific reagents allowing, as far as possible, a selective separation of the desirable compound.

Materials and methods

Compost used in the research was taken from the MPGU compost facility in Zabrze, Poland, where composting material is organic waste. The samples were taken on 3rd October 2007. Air-dried compost was used in the research. A fine fraction under 2 mm was examined. Samples with a mass of 10 g were used. The quality assessment of compost, based on trade norms were carried out as well. The study included:

– Determining the content of organic substances in compost from municipal waste (trade norm BN-88 9103-07),
– Determining the content of organic carbon (trade norm PN-91 Z-15005).

In order to isolate PAHs, samples of compost are put through the fexIKA vario control cycle for a period of 5 hours or in an ultrasonic bath (underwent sonication) for 30 minutes [5–7] (Fig. 1). Solvents quoted in the literature: hexane, dichloromethane and acetone/hexane, in a ratio of 1:1 by volume, were used in the process of extraction. In the chromatographic analysis, reagents with HPLC purity were used [1, 2, 8, 9].

The extract was obtained after a preliminary inspissation process in a stream of

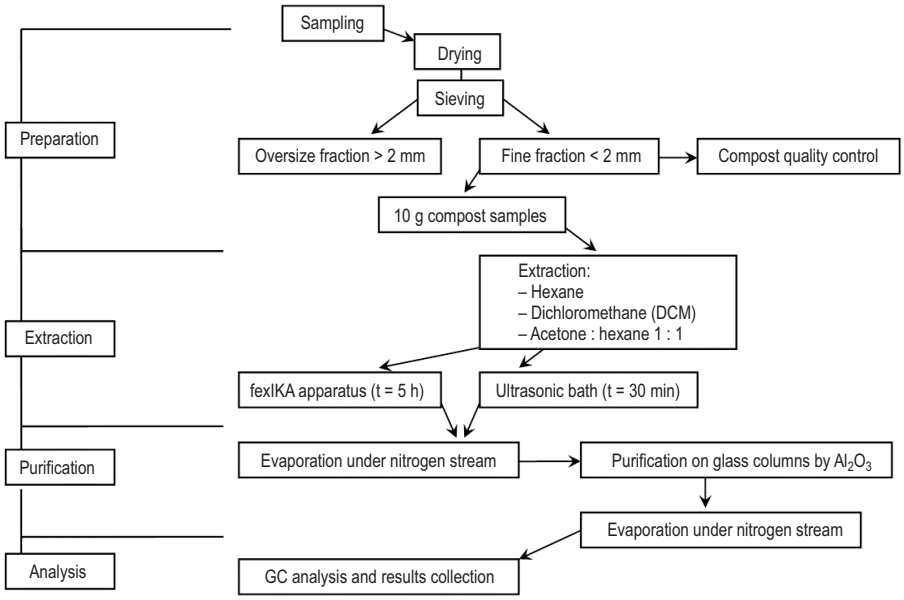

Fig. 1. Experiment scheme

neutral gas, purified by aluminium oxide on a glass column (height = 12 cm, diameter = 0.5 cm) [5]. The column was stopped by a glass wool cork and was filled with dichloromethane and then was filled in turns with:

– 0.5 cm of waterless sodium sulphate,
– 0.5 g of neutral aluminium oxide dried in 130 ^{o}C,
– 0.5 cm of waterless sodium sulphate.

When the process of filling was finished, dichloromethane was drained and the column was washed three times with 1 cm^3 of hexane, each time. The subsequent stage was to fill the column with hexane and slow drain it to the level of approximately 3 mm over the surface of sodium sulphate and put the sample on the prepared column. The column was washed again four times with 1 cm^3 of hexane and eluate was rejected each time. In order to leach the fraction containing PAHs, 40 % of DCM solution in hexane was used, after this the obtained eluate was inspissated to approximately 300 mm^3 (μl). Prepared in such a way the sample underwent analysis through a gas chromatograph Varian GC 3800 with the usage of ZB-5 column (length – 30 cm).

The procedure of extraction and quantity-quality measurements of PAHs in compost samples was carried out simultaneously in two attempts. Concentration of the analysed compounds were given in mg/kg d.m. With accuracy to the 0.001 mg/kg d.m. and as a percentage contents of particular PAHs with accuracy to the 0.01 %.

Results and discussion

The basic characteristic of compost, which underwent analysis, is presented in Table 1.

Table 1

Main characteristic of compost

Parameter	Unit	Value
Fraction	[mm]	< 2
pH_{H_2O}	—	7.78
Organic matter	[%]	33.8
Organic carbon	[%]	18.5
Humidity	[%]	4.4
Nitrogen	[% N_{Kjeld}]	0.86
Phosphorus	[% P_2O_5]	1.23
Potassium	[% K_2O]	0.65
Glass	[%]	< 0.1

When it comes to the basic characteristic of compost from the municipal waste it was proven that of all organic substances 54.73 % is organic carbon. The paper also examined extraction methods of the polycyclic aromatic hydrocarbons contained in compost from the municipal waste. The following extractants were used: hexane,

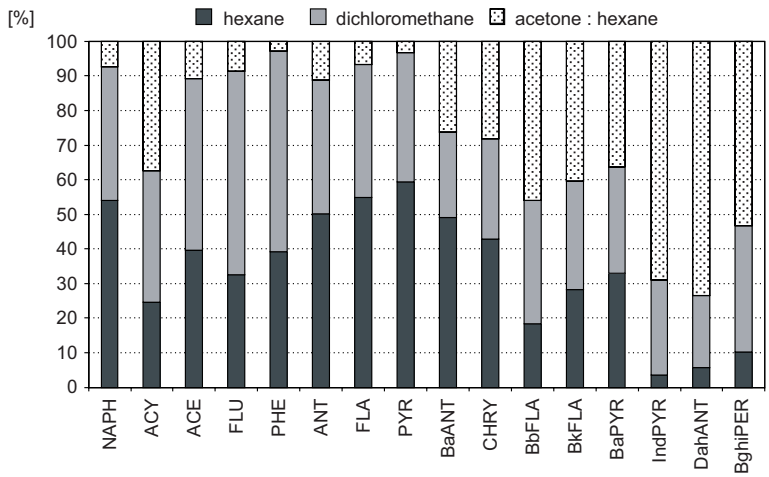

Fig. 2. The percentage participation of Polycyclic Aromatic Hydrocarbons (PAHs) in compost, which underwent extraction process in the ultrasonic bath

dichloromethane as well as acetone and hexane in a ratio of 1:1 by volume. When it comes to the process of separation the particular PAHs were carried out by using ultrasound and the fexIKA device.

The percentage participation of Polycyclic Aromatic Hydrocarbons (PAHs) in compost, which underwent an extraction process in the ultrasonic bath (Fig. 2).

In the compost samples extracted by hexane the definite majority constituted of compounds with three and four benzene rings arranged in a cluster spatial layout in the molecule. Among these the majority were: fluoranthine (20.13 %), pyrene (17.82 %) and chrysene (15.01 %).

A similar situation occurs when dichloromethane is used as an extractant. When extracting PAHs by acetone and hexane in a ratio of 1:1, six-cyclic hydrocarbons are the most easily separated, especially: indeno(1,2,3-c,d)pyrene (22.57 %) and benzo(g,h,i)perylene (16.11 %). Changes in the content of Polycyclic Aromatic Hydrocarbons (PAH) in compost extracted in the fexIKA device (Fig. 3).

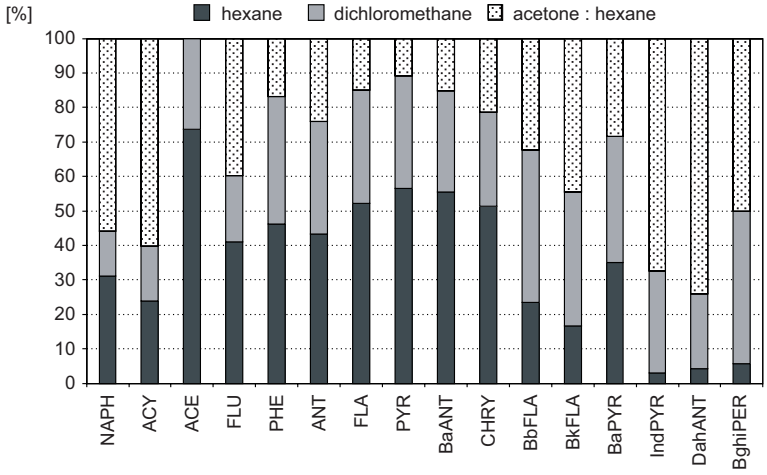

Fig. 3. Changes in the content of Polycyclic Aromatic Hydrocarbons (PAHs) in compost extracted in fexIKA

The biggest group was PAHs with three- and four-cyclic molecules, including cluster spatial layout, extracted by hexane. In this group of compounds the most common were: fluoranthene (19.83 %), pyrene (17.58 %) and chrysene (18.15 %). A similar content of Polycyclic Aromatic Hydrocarbons was noted in compost, which underwent the process of extraction by dichloromethane in comparison with the content of PAHs in compost extracted by hexane. The only exception were the six-cycle compounds, which are ideno(1,2,3)pyrene (11.81 %) and benzo(g,h,i)perylene (11.50 %). Using acetone and hexane in a ratio of 1:1 as an extractant, the best separated were six-cycle compounds, that is indeno(1,2,3)pyrene (26.79 %) and benzo(g,h,i)perylene (13.02 %). The comparison of extraction methods by selected solvents was carried out as well (Fig. 4).

The best solvent used in the extraction process of compost, containing polycyclic aromatic hydrocarbons in water bath was dichloromethane. By this extractant an overall

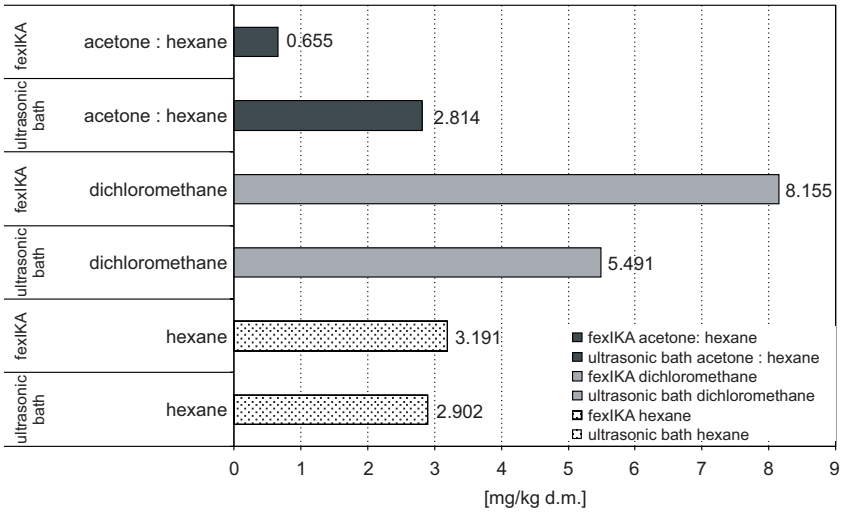

Fig. 4. Comparison of extraction methods using different solvents

PAH content of 5.491 mg/kg d.m. was obtained during the research. When comparing the overall concentration of 16 PAHs in compost which underwent sonication by hexane, the overall concentration of PAHs was 2.814 mg/kg d.m. The total concentration of PAHs in compost that underwent sonication by acetone and hexane in a ratio of 1:1 was 2.902 mg/kg d.m. It was found that these values are very similar [5]. The research shows that when using the fexIKA vario control cycle for the extraction process it is better to use dichloromethane as the extractant. By contrast, the least effective method of extraction was by acetone and hexane in a ratio of 1:1 by volume.

Conclusions

The research has led to the following conclusions:

Applying hexane as an extractant allows a separation of mainly three- and four-cyclic compounds. Six-cycle hydrocarbons are extracted most efficiently by acetone and hexane in a ratio of 1:1. Nonetheless, the best extractant in the process of PAHs extraction, either by ultrasounds or by the fexIKA device, is dichloromethane.

References

[1] Kluska M: *Dynamika sorpcji wielopierścieniowych węglowodorów aromatycznych przez glebę w pobliżu dróg o dużym natężeniu ruchu komunikacyjnego*. Arch. Environ. Protect. 2004, **30**(2), 83–93.

[2] Sun P., Weavers L.K., Taerakul P. and Walker H.W.: *Characterization of polycyclic aromatic hydrocarbons (PAHs) on lime spray dryer (LSD) ash using different extraction methods*. Chemosphere 2006, **62,** 265–274.

[3] Thiele S. and Brummer G.W.: *Bioformation of polycyclic aromatic hydrocarbons in soil under oxygen deficient conditions.* Soil Biol. Biochem. 2002, **34**, 733–735.

[4] Atanassova I. and G. Brummer.: *Polycyclic aromatic hydrocarbons of anthropogenic and biopedogenic origin in a colluviated hydromorphic soil of Western Europe*. Geoderma 2004, **120,** 27–34.
[5] Ratola N., Lacorte S., Alves A. and Barcel D.: *Analysis of polycyclic aromatic hydrocarbons in pine needles by gas chromatography-mass spectrometry. Comparison of different extraction and clean-up procedures*. J. Chromatogr. A 2006, **1114,** 198–204.
[6] Oleszczuk P.: *Persistence of polycyclic aromatic hydrocarbons (PAHs) in sewage sludge amended soil.* Chemosphere 2006, **65**, 1616–1626.
[7] Włodarczyk-Makuła M., Janosz-Rajczyk M., Zakrzewska E. and Karwowska B.: *Changes of PAHs contents in the sewage sludge and supernatants during anaerobic digestion process.* Chem. Inż. Ekol. 2003, **10**(7), 687–694.
[8] Boxall A.B. and Maltby L.: *The characterization and toxicity of sediment contaminated with road runoff*. Water Res. 1995, **29**(9), 2043–2050.
[9] Wilcke W., Krauss M., Lilienfein J. and Amelung W.: *Polycyclic aromatic hydrocarbons Storage in a typical cerrado of the Brazilian Savanna*. J. Environ. Qual. 2004, **33**(3), 946–955.

EFEKTYWNOŚĆ WYBRANYCH METOD EKSTRAKCJI PAHs (WWA) NA PRZYKŁADZIE KOMPOSTU Z ODPADÓW KOMUNALNYCH

[1] Helmholtz Centre for Environmental Research – UFZ, Department of Environmental Technology
[2] Katedra Ochrony Powierzchni Ziemi, Uniwersytet Opolski

Abstrakt: Techniki ekstrakcyjne odgrywają szczególną rolę na etapie przygotowywania próbek do identyfikacji i wydzielania analitów z próbek środowiskowych. Anality, będące głównie stałymi substancjami organicznymi, z materiałów stałych można wyodrębnić albo za pomocą gazu, albo przy użyciu rozpuszczalnika. W dalszym ciągu, jako ekstrahenty analitów, najbardziej popularnymi i najczęściej stosowanymi są różne rodzaje rozpuszczalników. Sprawność ekstrakcji nie zależy jednakże tylko od rodzaju rozpuszczalnika, ale też od metody ekstrakcji. W literaturze podawane są najróżniejsze metody oznaczania zarówno ilościowego jak i jakościowego trwałych zanieczyszczeń chemicznych, jakimi są m.in. wielopierścieniowe węglowodory aromatyczne. Praca ta miała na celu przetestowanie zarówno różnych rozpuszczalników organicznych, tj. heksanu, dichlorometanu oraz heksanu i acetonu, jak i różnych metod ekstrakcji w procesie izolacji wielopierścieniowych węglowodorów aromatycznych z kompostu pochodzącego z odpadów miejskich.

Słowa kluczowe: ekstrakcja, PAHs, kompost