

SIMULTANEOUS DETERMINATION OF SELECTED INSECTICIDES
AND ATRAZINE IN SOIL BY MAE–GC–ECDHANNA BARCHAŃSKA^{1*}, MARIANNA CZAPLIKA^{1,2}, ANNA GIEMZA¹¹Department of Analytical Chemistry, Silesian University of Technology, Gliwice,
M. Strzody 7, Poland²Institute of Non – Ferrous Metals, Gliwice, Sowińskiego 5, Poland

*Corresponding author's e-mail: hanna.barchanska@polsl.pl

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Abstract: The procedure for simultaneous extraction from soil and determination by means of GC–ECD insecticides: aldrin, dieldrin, endrin and herbicide: atrazine was worked out. The proposed GC–ECD technique provides limits of detection in range 12 µg/mL – 18 µg/mL and 2 µg/mL, for insecticides and atrazine, respectively. Two different types of extraction: microwave assisted extraction (MAE) and ultrasound assisted extraction (UAE) with different solvents were tested to choose the procedure that provides the highest recoveries of analytes and low detection limits, typical for trace analysis (100 ppm or 100 mg/g, IUPAC). On the basis of recoveries and precision both extraction methods were compared. The insecticides recovery from soil samples obtained by UAE were in range 40–85%, coefficient of variation (CV): 1.3–5.0%, whereas for atrazine recovery was below 15% (CV: 8–18%). The most efficient and precise extraction procedure turned out to be MAE with *n*-hexane: acetone. The recoveries were in range 70–85% for insecticides and 84% for atrazine, CV: 0.4–2.2% and 5.3% for insecticides and atrazine, respectively. The presented MAE–GC–ECD procedure enables extraction and determination of aldrin, dieldrin, endrin and atrazine in soil samples with high recoveries, precision and limits of detections in range 6 ng/g – 8 ng/g in the case of insecticides and 1.5 ng/g for atrazine.

The MAE–GC–ECD procedure was applied for the above mentioned pesticides determination in environmental samples. Soils were collected in agricultural as well as rural areas in Poland. In all cases atrazine was determined in concentration range: 0.0187 mg/g – 0.1107 mg/g. Aldrin and dieldrin was detected in soil samples from two locations.

INTRODUCTION

Agriculture plays a key role in the world. Fast industrial progress and the reduction of the rural area, force the increase and effectiveness of cultivation. To cope with these requirements, the application of pesticides is necessary.

Chloroorganic insecticides are used for insects annihilation in agriculture, forests and households. Since they are toxic for human and persistent in the environment, they were withdrawn in many countries, among others in Poland. Nevertheless, they are present in the environment because of their stability (30 years) and threat to the environment [7, 12, 21, 24, 41].

Herbicides are used to fight weeds. One of the most common group of herbicides are triazines, used in crops, especially corn and potatoes cultivations. These compounds as well as their degradation products are stable in the soil.

Atrazine (herbicide), aldrin, dieldrin and endrin (insecticide) are the objects of this study. Their physical-chemical properties are listed in Table 1 [11, 27].

Aldrin, dieldrin and endrin are soluble in fats. They are persistent in the environment (half-life of 2 years) [13]. They are carcinogenic, cause dermatological diseases, coronary heart disease, arteriosclerosis, hypertension and diabetes [21, 30, 41].

Atrazine has been applied on agricultural soil since 1950, being one of the most widely used herbicides in the world. The persistence of atrazine and its ability of translocation in the environment are key factors influencing its potential to contaminate the terrestrial and aquatic environments. Due to its possible carcinogenic, endocrine disrupter and teratogen properties, atrazine has been classified as one of the major target anthropogenic pollutants [12, 29, 31, 43]. Even though, atrazine is withdrawn from application in the European Union, it is still detected in European environment.

Monitoring of the contamination level of environment underlies the assessment of the threat of human health. Therefore, sensitive and selective analytical methods for the determination of atrazine, aldrin, dieldrin and endrin residues in soil matrices are desirable. Pressurised liquid extraction (PLE) and microwave-assisted extraction (MAE) are techniques that can be used instead of shake – flask or Soxhlet extraction. They are rapid and require fewer solvents in comparison to traditional liquid – solid extraction.

Ultrasound assisted extraction (UAE) provides an efficient contact between the solid and the extractant, usually resulting in a good recovery of the analyte. Tadeo [50] established, that the efficiency of UAE was dependent on the type of solvent, temperature, character of analytes and sample matrix. Therefore, it is necessary to optimise the extraction process taking into account the above mentioned parameters.

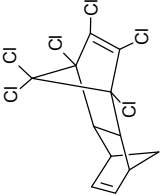
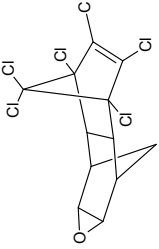
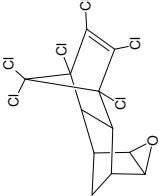
Microwave assisted extraction provides high recoveries of analytes in a short time, is easy to automation, however, there is a risk of decomposition of compounds sensitive to temperature [14].

Determination of pesticides in soil is a complex task, it usually includes four stages: soil pre-treatment (drying, grinding, sieving), analytes extraction from the matrix, clean up the extract and the analyse – identification and quantitative analyse of compounds. The recovery of analytes is influenced by the following soil factors: granulometric composition, mineral and organic matter content (mainly fulvic and humic acids) as well as pH of soil [38, 39].

Ultrasound assisted extraction is a useful tool for aldrin, dieldrin and endrin extraction from soil samples. According to [40, 51], the above mentioned insecticides were extracted from the soil samples with the mixture of petroleum ether and acetone or dichloromethane, for the first extraction solvent the additional clean – up was conducted on Al_2O_3 sorbent. The analytes recoveries were between 93–101%.

Microwave assisted extraction is another extraction technique that enables fast separation of pesticides from soil matrix. Concha-Graña and co-workers [10] applied the mixture of hexane – acetone for aldrin, dieldrin and endrin extraction from soil. Subsequently, the extract was cleaned on Florisil. The recoveries were 102–129%. Similar procedure was described in [18, 34], however, the head space – solid phase microextraction (HS–SPME) was applied for analytes concentration. The microwave energy was about 800–950 W, temperature 115°C. The recoveries were 84–100%.

Table 1. Physical – chemical properties of selected pesticides

No	Pesticide	Chemical structure	Melting point, (°C)	Boiling point, (°C)	Density (20 °C), (g/cm ³)	Solubility in water (20°C), (mg/L)	logK _{ow}	logK _{oc}	Vapor pressure (25 °C) (mPa)
1	Aldrine		104	145	1.70	0.027	6.50	4.59	3
2	Dieldrin		177	385	1.75	0.14	3.70	4.08	0.024
3	Endrin		226-230	245	1.65	0.24	3.20	4.50	0.09

The detailed literature overview reveals that the most popular procedure for atrazine extraction from soil samples is liquid–solid extraction (LSE), carried out with shaking, sonication or in the presence of microwaves. Usually methanol, mixture of methanol–water (different proportions) [2, 8, 16, 17, 28, 33, 37, 46, 47, 49, 53] acetonitrile, acetonitrile – water, or acetonitrile-hexane (different proportion) [1, 14, 22] or chloroform [4] are used. In some cases solid phase extraction (SPE) on octadecyl (C18), phenylsulfonil acid (PhSO_3H) or multi-walled carbon nanotubes (MWNTs) sorbents was carried out [2, 4, 33, 37, 44, 47]. The atrazine recovery was about 85–93%.

Soil sonication with mixture of acetonitrile – dichloromethane, acetonitrile – water, ethyl acetate, water with addition of chloroform was applied by [4, 24, 25, 31–33, 35, 42]. The recovery was in the range of 50–95%.

Microwave assisted extraction is also used for atrazine extraction from soil samples. In [48], the mixture of dichloromethane – methanol as a solvent was applied, microwave power was 950 W. After filtering, solid phase microextraction (SPME) was conducted. The recovery was 76.6–85.7%. For pesticides determination in environmental samples chromatographic methods are usually applied, capillary electrophoresis as well as immunenzymatic procedures [6].

For pesticides detection, the most often applied are liquid chromatography with fluorescence detection (FL), ultraviolet or diode array detection and mass detector (MS). Another technique for pesticides determination is gas chromatography with mass or nitrogen phosphorus (NPD) detector [26]. Liquid chromatography with UV detection provides LOD in the range of 0.019 $\mu\text{g/L}$ –0.2 $\mu\text{g/L}$, 0.04 ng/g –0.05 ng/g [19, 22, 35, 47], whereas with DAD detection: 2.0 $\mu\text{g/L}$, 0.5 ng/g [5, 21, 42, 45, 52]. According to Gong [16], fluorescence detection enables to detect pesticides at 1.2 ng/g level. The lowest value of LOD (0.188 ng/g) was obtained by means of LC – MS/MS by Jablonowski [20]. Gas chromatography with nitrogen – phosphorus detector provides limit of detection around 0.005 mg/L [35], 1.5 ng/g – 2 ng/g [3,5,9,15,32] while with mass detector 0.3 $\mu\text{g/L}$, 4 ng/g – 8.3 ng/g [9, 23, 24, 25, 33, 36].

The aim of this study was to work out the analytical procedure for the simultaneous determination of insecticides and herbicides in environmental samples by means of gas chromatography coupled with electron capture detector (GC–ECD). The influence of the type of extraction (UAE or MAE) as well as extraction solvents on the analytes recoveries was also presented. The obtained parameters of analysis, i.e., mass of sample, volume of solvent, extraction recovery, limit of detection and quantification were critically discussed with the literature data. On the basis of the detailed literature review, it follows that there were no trials of simultaneous determination of chloroorganic compounds and compounds with nitrogen atom(s) in soil. Taking into account the specificity of ECD detector, it was usually applied for chloroorganic insecticides determination. In the present paper, the innovative application of ECD detector for simultaneous determination of insecticides and triazine, provided limit of detection in the range of 6 ng/g – 8 ng/g for insecticides and 1.5 ng/g for atrazine.

METHODOLOGY

Chemicals and reagents

The standards for aldrin, dieldrin and endrin were provided by Supelco (Bellefonte, USA), atrazine was obtained from Reidel-de-Haen, (Seelze, Germany). All applied compounds

were used without purification. Stock standards solutions were prepared by dissolving standard in *n*-hexane (for insecticides), atrazine was dissolved in methanol. Working standard solutions were prepared by dilution of suitable aliquots from stock solution in appropriate solvent. The concentrations of these solutions are presented in Table 2.

All solutions were stored at 4°C in the dark. Helium (99.9999%) and nitrogen (for ECD) were purchased from Linde (Germany). Acetone was bought in Z.B.P. HEMED, (Gliwice, Poland), methylene chloride was from CHEMPUR, (Piekary Sl., Poland), methanol, *n*-hexane and sodium sulphate (VI), anhydrous, were provided by POCH. S.A., (Gliwice, Poland).

Apparatus and equipment

For the pesticides extraction from soil samples a microwave oven Multiwave 3000 SOLV Anton Paar, (Graz, Austria), equipped with microwaves generator (2.45 GHz), temperature and pressure sensors IR and p/T, respectively, power 1400 W, rotator for 8 and 16 samples. Ultrasound bath POLSONIC 2, (Warsaw, Poland), frequency 40 kHz, ultrasound power 2x100 W, was used for UAE.

Qualitative and quantitative analyses were preformed using Perkin-Elmer Clarus 500 gas chromatograph (GC) equipped with an electron capture detector (ECD), and a 30 m × 0.25 mm i.d. DB-5MS column with a film thickness of 0.25 µm.

Analysis conditions

The column temperature was programmed to increase from 150°C to 275°C, at 10°C/min, held for 3 min, and then from 275°C to 300°C, at 16°C/min; the temperature of injector was 250°C, temperature of detector 310°C.

Investigated compounds were identified by their retention times. The quantitative analysis was performed with the use of the external standard method. An exemplary chromatogram of pesticides standard mixture is showed in Fig. 1.

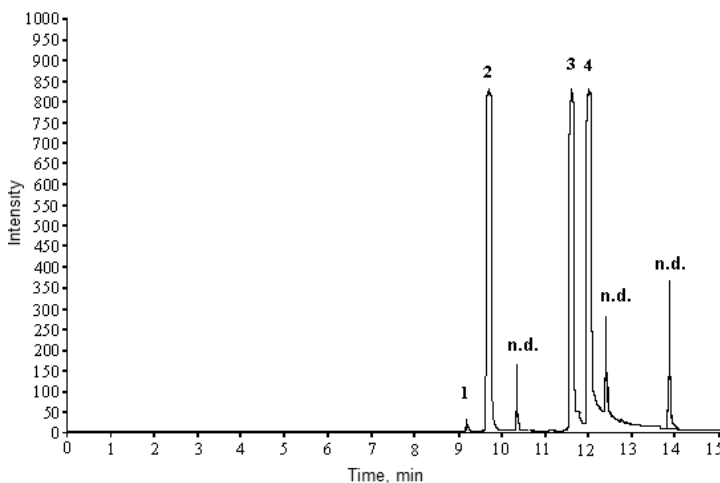


Fig. 1. Chromatogram of standards mixture solution, 1 – atrazine, 2 – aldrin, 3 – dieldrin, 4 – endrin; n.d – not determined

Table 2. Working standards solutions concentrations [mg/mL] on six concentration levels

Analyte	Level I	Level II	Level III	Level IV	Level V	Level VI
Aldrin	0.403	0.602	0.802	1.003	1.302	1.496
Dieldrin	0.406	0.606	0.808	1.010	1.312	1.508
Endrin	0.407	0.608	0.810	1.013	1.315	1.512
Atrazine	0.139	0.207	0.277	0.346	0.449	0.516

Table 3. Precision of the procedure for pesticides determination

Analyte	LOD [mg/mL]	LOQ [mg/mL]	Linearity range [mg/mL]	Equation of calibration plot	R ²
Atrazine	0.002	0.005	0.139 – 0.516	$y = 480252 x - 19021$	0.994
Aldrin	0.014	0.042	0.403 – 1.496	$y = 2620071 x + 4696462$	0.995
Dieldrin	0.016	0.049	0.406 – 1.508	$y = 3064620 x + 4100559$	0.997
Endrin	0.012	0.036	0.407 – 1.512	$y = 3335272 x + 5130203$	0.998

Validation of pesticides determination procedure

Six nonzero calibration standards for aldrin, dieldrin, endrin and atrazine, covering the concentration range given in Table 2, were prepared. The analysis was repeated six times for each concentration level. The detailed parameters of calibration curves are presented in Table 3, whereas, the plots are presented in Fig 2.

Extraction procedures

Ultrasound assisted extraction (UAE)

Spiked soil sample (5.0 g) was placed in shake-flask, 55 mL of *n*-hexane was added and the mixture was sonicated for 20 min. The sonication was repeated three times. Subsequently, the sample was filtered, solvent evaporated and the residue, prior to analysis, was dissolved in 0.5 mL of methanol (Procedure I). For the Procedure II, the conditions of extraction were the same as for Procedure I, however, methylene chloride was applied.

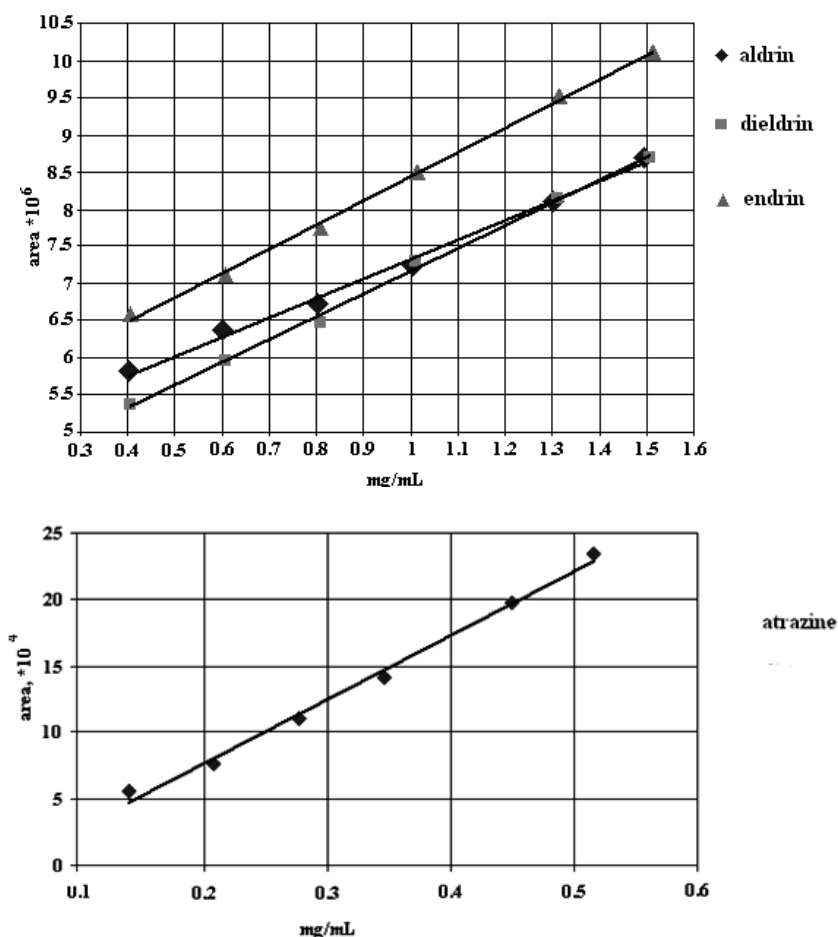


Fig. 2. Plots of calibration curves

Microwave assisted extraction (MAE)

Spiked soil sample (0.5 g) was extracted with 17.5 mL of *n*-hexane and 7.5 mL of acetone, the temperature programmed to 120°C at 24°C/min and held for 20 min. Microwaves energy was 1200 W. After cooling, the extract was filtrated in the presence of sodium sulphate (VI), then evaporated to dryness. The residue was dissolved in 0.5 mL of methanol and the chromatographic analysis was conducted (Procedure III).

Recovery determination

To estimate the recoveries of MAE and UAE, the reference soil sample was prepared according to the following procedure. Soil was dried on filter paper for 24 h. One hundred grams of pulverized, sieved through a 0.8 mm sieve soil was poured with 125 mL of methylene chloride. Subsequently, the ultrasound assisted extraction (20 min.) was conducted. The extraction procedure was repeated three times. Then, after filtering, soil was dried till the solvent was completely removed. The extract of the methylene chloride was discarded. To evaluate the extractions efficiencies, 0.5 and 5.0 g of dried and deprived of organic matter soil were weighted out for MAE and UAE, respectively. Soil was spiked with 1.0 mL and 0.5 mL of pesticides standards solution for UAE and MAE procedure, respectively. The concentration of this solution is presented in Table 2, Level VI. After two hours the references samples were analyzed. The recovery was determined for six references samples. The comparison of recoveries of pesticides from reference soil samples are presented in Fig. 3.

The highest recoveries of all investigated compounds were obtained by means of Procedure III, therefore, the detailed validation parameters of this procedure are presented in Table 4.

The blank sample (without standards addition) was prepared, according to the above described Procedure III, to estimate the precision of the procedure of pesticides determination in soil samples.

Limits of detection of the procedure (LOD) were calculated based on signal to noise ratio S/N for blank sample, limits of quantification (LOQ) as threefold LOD. Values of LOD and LOQ are given in Table 5.

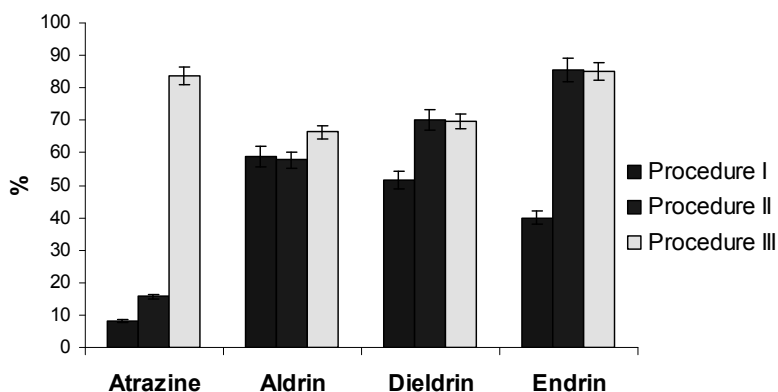


Fig. 3. Recoveries of pesticides from references soil samples

Environmental samples

Top soil samples were collected from five different locations in Poland, both agricultural and urban areas. Detailed characteristics of soil samples are given below:

Agricultural area: S1 – soil from wheat cultivation, S2 – rye cultivation, S3 – maize cultivation; urban area: S4, S5 soil from heavy polluted areas and former waste storage yard. Soil samples were collected according to standard PN-R-04031:1997. Stones and residues of plants were removed and the pesticides were extracted according to the Procedure III. The masses of the samples taken for analysis were in the range of 0.5–5.0 g depending of pesticides concentration.

DISCUSSION

On the basis of the detailed literature review, it follows that there were no trials of simultaneous determination of chloroorganic compounds and compounds with nitrogen atom(s) in soil. Taking into account the specificity of ECD detector, it was usually applied for chloroorganic insecticides determination. In the present paper, the innovative application of ECD detector for simultaneous determination of insecticides and triazine, provided limit of detection, found in the range of 12 $\mu\text{g/mL}$ – 18 $\mu\text{g/mL}$, for insecticides and 2 $\mu\text{g/mL}$ for atrazine. In this range the linearity responses were obtained. The acceptance criteria for the correlation coefficient, R^2 , of the calculated regression curves were 0.994 or higher. The detailed parameters of calibration curves are presented in Table 3, whereas, the plots are presented in Fig. 2.

Recovery study

In the course of experiment, according to the methodology described in Extraction procedures, the recovery of investigated compounds from soil was determined and relative standard deviation (RSD%) was computed and graphically presented in Fig. 3.

Table 4. Recovery study of investigated pesticides by means of Procedure III

Analyte	Added [mg]	Measured [mg]	Recovery [%]	R.S.D. (n=6)
Atrazine	0.516	0.432	83.8	0.052
Aldrin	1.496	0.992	66.3	0.004
Dieldrin	1.508	1.049	69.6	0.022
Endrin	1.512	1.288	85.2	0.018

Table 5. Limits of detection and quantification of Procedure III

Analyte	LOD [mg/mL]	LOQ [mg/mL]	R.S.D. (n=6)	CV (%)
Atrazine	0.002	0.005	0.146	14.59
Aldrine	0.014	0.042	0.084	8.43
Dieldrine	0.016	0.049	0.096	9.56
Endrine	0.012	0.036	0.061	6.08

The CV computed for six samples was 18% for atrazine and in the range of 3.3–5.0% for insecticides, for the Procedure I; 8.0% for atrazine and 1.3–2.3% for insecticides, for Procedure II. The lowest values of CV for all compounds were observed for the Procedure III, namely 5.3% for atrazine and 0.04–2.2% for insecticides. Such CV values indicated good precision of the method.

Ultrasound assisted extraction with *n*-hexane as solvent gave the lowest recoveries of all compounds, for insecticides 40–59% and 8% for atrazine. Moreover, this procedure was characterized by the highest values of CV. The exchange of *n*-hexane for methylene chloride improved the recoveries of endrin (85.5%), dieldrin (70.1 %) and atrazine (15.8%), whereas, the recovery of aldrin remained unchanged (57.8%), nevertheless still too low for quantitative analysis. According to our previous study [5], low recoveries of atrazine obtained by means of ultrasound assisted extraction is not connected with the solvent neither with ultrasound bath (the recoveries of other compounds were satisfactory). The extractions with chloroform, acetone, mixture acetone – water (1:1, v/v), methanol, mixture methanol–water (1:1, v/v), buffers (pH 1.5–5.0) were also conducted. In all cases the recoveries did not exceed 50%, that was noticed for methanol as a solvent. The same solvents were used for shake – flask extraction. In this technique recoveries were above 70%, the highest value was recorded for chloroform (97%) [3, 5]. Low recoveries of atrazine obtained by UAE were also observed by Lesueur [24]. According to our best knowledge, there is no profound explanation of this phenomenon in the literature.

The highest recoveries were observed for microwave assisted extraction and were in the range of 66–85% for insecticides and 84% for atrazine. The recoveries of investigated herbicide and insecticides are presented in Table 4.

The obtained results indicate that satisfactory recoveries of all investigated analytes (above 60%) were achieved by means of microwave assisted extraction with the mixture of *n*-hexane and acetone and the detection by GC–ECD. Therefore, this procedure was chosen for pesticides determination in environmental samples.

For the Procedure III, the precision of pesticides determination was calculated, taking into consideration the recoveries of analytes and quantitative determination (Table 5). The obtained limits of detection are in the range of 6 ng/g – 8 ng/g for insecticides and 1.5 ng/g for atrazine.

Analysis of real soil samples

The highest recoveries of all investigated compounds were obtained by MAE extraction – Procedure III, therefore this procedure was chosen for the pesticides extraction from real soil samples

In soil samples (S1–S3) collected in agricultural areas, atrazine was determined in all cases, at levels in the range from 30.4 to 110.7 µg/g, aldrin was detected in soil from wheat and rye cultivation, in latter also dieldrin was detected. Chromatogram of the soil extract (S2) is presented in Fig. 4.

In soil samples from rural areas atrazine was determined in samples S4 and S5 at the concentration levels 18.7 µg/g and 56.7 µg/g, respectively. High concentration of atrazine determined in real soil samples is connected with intensive usage of this herbicide in the past.

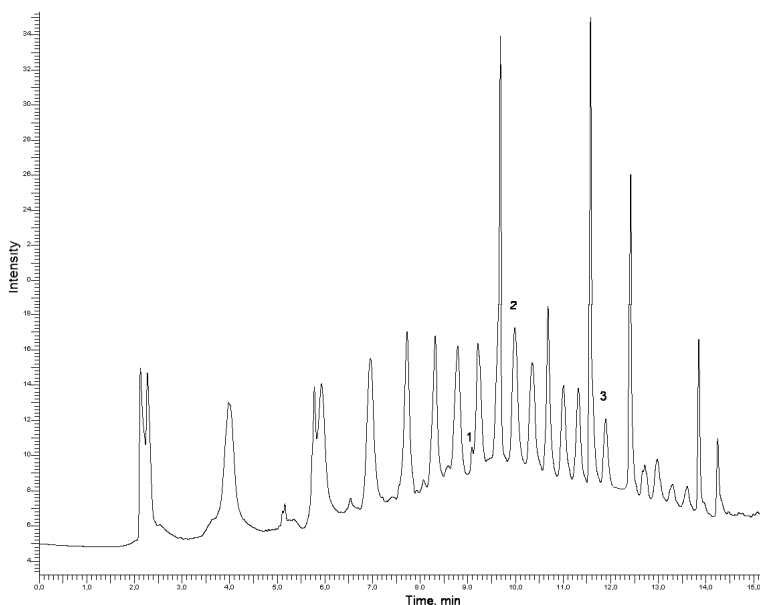


Fig. 4. Chromatogram of soil sample extract obtained by Procedure III, 1 – atrazine, 2 – aldrin, 3 – dieldrin

CONCLUSION

The presented MAE–GC–ECD method enables to extract and determine aldrin, dieldrin, endrin and atrazine in soil samples with high recoveries, precision and limits of detections in the range of 6 ng/g – 8 ng/g in the case of insecticides and 1.5 ng/g for atrazine. The application of electron capture detector enables to determine simultaneously both chloroorganic insecticides as well as herbicides with nitrogen atoms in the structure. The comparison of results obtained by different techniques sometimes is questionable, therefore, the proposed procedure may describe this issue.

Microwave assisted extraction provides higher recoveries of analytes in comparison to ultrasound assisted extraction, regardless of solvent.

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RÓWNOCZESNE OZNACZANIE WYBRANYCH INSEKTYCYDÓW I ATRAZYN W GLEBIE TECHNIKĄ MAE–GC–ECD

Opracowano procedurę MAE–GC–ECD umożliwiającą równoczesną ekstrakcję i oznaczenie insektycydów: aldryny, dieldryny i endryny oraz herbicydu: atrazyny z gleb. Zastosowana metoda GC–ECD charakteryzuje się granicą wykrywalności w zakresie 12–18 µg/ml dla insektycydów oraz 2 µg/m for dla atrazyny. W celu opracowania procedury analitycznej o wysokim odzysku analitów i granicy oznaczalności typowej dla analizy śladowej (100 ppm lub 100 mg/g wg. IUPAC) przeprowadzono badania z zastosowaniem ekstrakcji rozpuszczalnikowej wspomaganą ultradźwiękami (UAE) oraz mikrofalami (MAE) dla różnych rozpuszczalników. Dokonano porównania precyzji oraz odzysków analitów dla obu technik ekstrakcyjnych.

Wydzielanie insektycydów z próbek gleb na drodze ekstrakcji rozpuszczalnikowej wspomaganą ultradźwiękami przeprowadzono z odzyskiem 40–85% (CV: 1,3–5,0%), natomiast atrazyny 15% (CV: 8–18%). Najwyższą precyzją i odzyskiem charakteryzowała się metoda MAE z zastosowaniem mieszaniny *n*-heksan–aceton. Odzyski mieściły się w tym przypadku w zakresie 70–85% (CV: 0,4–2,2%) dla insektycydów oraz 84% (CV: 5,3%) dla atrazyny. Opisana procedura MAE–GC–ECD umożliwia ekstrakcję i oznaczenie aldryny, dieldryny, endryny oraz atrazyny w próbkach gleb. Charakteryzuje się wysokimi odzyskami, precyzją i granicami wykrywalności mieszczącymi się w granicach 6–8 ng/g, w przypadku insektycydów oraz 1,5 ng/g dla atrazyny. Metodyka MAE–GC–ECD została zastosowana do oznaczanie wymienionych pestycydów w próbkach gleb pobranych z terenów rolniczych oraz przemysłowych. We wszystkich próbkach gleb oznaczono atrazynę, której stężenie mieściło się w granicach od 0,0187 mg/g do 0,1107 mg/g w zależności od pochodzenie próbki. Aldryna i dieldryna została wykryta w dwóch próbkach na poziomie poniżej granicy oznaczalności.