



# RECOVERY OF THE ORGANIC SOLVENTS FROM THE MULTICOMPONENT MIXTURE IN THE PROCESS OF THE FRACTIONAL DISTILLATION AND THE VACUUM DISTILLATION

## ODZYSKIWANIE ROZPUSZCZALNIKÓW ORGANICZNYCH Z MIESZANINY WIELOSKŁADNIKOWEJ W PROCESIE DESTYLACJI FRAKCYJNEJ I DESTYLACJI PRÓŻNIOWEJ

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### Abstract

*In these times of sustainability, the purification and regeneration of used solvents is attracting a lot of interest for environmental reasons and to reduce production costs. The article presents research on the separation of organic solvents such as acetonitrile, methanol, acetone, and toluene from a multicomponent mixture of liquid organic waste. This is an element of the circular economy and prevents the emission of volatile organic compounds into the environment. In order to separate the mixture and recover the solvents, fractional distillation and vacuum distillation were used together with pre-treatment of the waste using sorption on silica gel and calcium oxide. The analysis of the waste composition and the mixture after the separation was performed by gas chromatography coupled with a mass spectrometer (GC-MS). As a result of the research, the acetonitrile concentration increased to 90.7% after fractional distillation.*

**Keywords:** fractional distillation, vacuum distillation, organic solvents, acetonitrile

### Streszczenie

*Aktualnie w czasach zrównoważonego rozwoju oczyszczanie i regeneracja zużytych rozpuszczalników cieszy się dużym zainteresowaniem ze względów środowiskowych i w celu obniżenia kosztów produkcji. W artykule przedstawiono badania nad wydzielaniem rozpuszczalników organicznych takich jak acetonitryl, metanol, aceton i toluen z wieloskładnikowej mieszaniny ciekłych odpadów organicznych. Jest to element gospodarki o obiegu zamkniętym i zapobiega emisji lotnych związków organicznych do środowiska. W celu rozdzielania mieszaniny i odzyskania rozpuszczalników zastosowano destylację frakcyjną i destylację próżniową wraz z wstępną obróbką odpadów metodą sorpcji na żelu krzemionkowym i tlenku wapnia. Analizę składu odpadów oraz frakcji po rozdziale mieszaniny przeprowadzono metodą chromatografii gazowej sprzężonej ze spektrometrem mas (GC-MS). W wyniku przeprowadzonych prób stężenie acetonitrylu po destylacji frakcyjnej wzrosło do 90,7%.*

**Słowa kluczowe:** destylacja frakcyjna, destylacja próżniowa, rozpuszczalniki organiczne, acetonitryl

### 1. INTRODUCTION

Organic solvents are widely used in many branches of industry (the greatest demand for solvents is recorded in the production of paints and coatings,

inks, and adhesives. chemical, pharmaceutical, paints, and varnishes) and laboratories due to their valuable properties, as it was described [1]. These include, first of all, the ability to dissolve other substances

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without changing their chemical structure. Desirable characteristics of solvents are also transparency and lack of colour, volatility, appropriate viscosity depending on the type of use, resistance to chemicals, non-corrosive to apparatus, anhydrousness, chemical, and physical stability, and cost. Since sustainable development also applies to solvent management, more and more attention is paid to the fact that solvents are non-toxic, biodegradable, odour-free, and regenerable, to minimize the exposure of workers during production and use of solvents to their harmful effects and to reduce the emission of volatile organic compounds (VOC) to the atmosphere, what was studied [2].

In recent years, the development of two directions in the economy of solvents can be noticed. The first is to replace traditional solvents, the so-called "green solvents". This direction was widely described [3-5], and the second is the regeneration of used solvents after various industrial processes. The so-called "green solvents" can be successfully used, inter alia, in the paints and varnishes sector, because it is in this production sector that the transition from solvent-based to water-based products can be observed. The development of the biological solvents production was widely described, such as bioethanol [6], butane 1-ol [7], acetic acid [8], 1-octanol [9], 1,3-diol butane, glycerol [1] were widely described. However, many branches of the chemical industry do not allow this type of solvents to achieve the desired product characteristics and classic solvents will still be used due to their chemical properties. The way to manage used organic solvents, which, mainly due to their volatility, pose a threat to the environment is their recovery. This allows not only the multiple use of solvents but also an ecological and environmentally safe method of disposal. Solvents used in chemical reactions, chemical analysis, or the pharmaceutical industry must meet high standards in terms of purity. This often requires the use of advanced and complex cleaning methods. The method that will be used to purify the solvents depends on the solvent itself and the type of impurities present in the mixture. The most commonly used and described are simple and fractional distillation techniques, membrane processes, and ion exchange [11-14]. Depending on the amount of waste, the nature of the mixture, and the process economy, the regeneration process is optimized, taking into account the technical possibilities, the scale of the process, and the required purity of the solvent. The solvent recovery process typically takes place in several steps, starting with the removal of solids that may be present in the waste stream, followed by a recovery, purification, and refinement step

where higher purity solvents are required, these steps were presented [15]. Methods of purifying a mixture of organic solvents are discussed in the literature [10-12, 15]. The most commonly used distillation methods involve a multi-stage purification process or the use of recycl of the distillation stream for repeated distillation. The basic difficulties encountered during the purification of solvents include the need to separate substances from a multicomponent mixture of organic solvents and other impurities, flammability and explosiveness. Another problem is the presence of water in the mixture, which promotes the formation of azeotropic mixtures [16-20].

Undoubtedly, a very important aspect is the energy consumption of the solvent recovery process, because the process of separating the mixture and purifying solvents requires energy in the form of heat. Of course, due to the scale of the process and the required final purity of the solvents, this parameter will vary. Technical and economic indexes of distillation processes were compared in [21] such as conventional single column distillation process, conventional single column mechanical vapour recompression (MVR), heat pump distillation process, split heat pump distillation (SHPD) with single-stage compression and SHPD with two-stage compression in process of the separation of acetone and water mixture. It was shown, that the conventional single-column distillation process compared with the conventional single-column MVR heat pump distillation process can save energy by 43.56%. The energy of SHPD with single-stage compression and the SHPD with two-stage compression was saved by 56.31% and 69.78%, respectively. Additionally, the SHPD process provides an effective energy-saving method for the separation of mixtures with large temperature differences and constant concentration.

One of the most widely used solvents is acetonitrile. Due to its low viscosity, high stability and high elution power, it has been widely used, among others, as a polar aprotic solvent in organic synthesis, fabric dyeing, lighting, and as an eluent in chromatographic techniques [18]. The leader in consumption is the Asia-Pacific region, where the annual growth rate of consumption will be 5% per year, while Europe and North America will show a more moderate growth of 4% per year [10].

Currently, many enterprises strive to optimize their production processes, minimize the impact of industrial activities on the environment and sustainably manage production. This results in the need to use solvent recovery systems that enable effective removal of a wide range of contaminants from the waste stream.

The solutions most often chosen by companies include solvent purification systems in evaporation processes using distillers and evaporators to regenerate contaminated solvents at atmospheric pressure and vacuum. These systems can be easily adapted to the individual needs of enterprises taking into account the nature of production, including daily efficiency, automation and ease of use. Additionally, these systems can be easily combined with a heat recovery system (heat exchangers) or coupling the solvent recovery system with the distillate purification system when high solvent purity is required, e.g. in the ion exchange process. The use of a system for recycling used solvents and their mixtures in the company not only reduces production costs, but also complies with the principles of “green chemistry” by saving raw materials and the principles of a closed-loop economy.

The aim of the work was to optimize the separation process of components of a waste mixture of volatile organic solvents, the dominant component of which was acetonitrile. The research was carried out on a laboratory scale and included five experiments where fractional distillation at atmospheric pressure and vacuum distillation were used to separate a multi-component mixture of organic solvents. The raw material for the tests was liquid waste, which was a mixture of volatile organic compounds with an admixture of water. The volatile components of a mixture of liquid organic waste were identified by using gas chromatography coupled with a mass spectrometer (GC-MS).

## 2. MATERIALS AND METHODS

The research material was liquid waste, which is a mixture of organic solvents, from research

and development laboratories in the polyurethane adhesives and foams industry.

Qualitative and quantitative analysis of the mixture components were performed by GC-MS and gas chromatography coupled with a flame ionization detection (GC-FID). The qualitative GC-MS analysis was performed on an Agilent 7890B apparatus with an MS 5977B detector. The DB-23 capillary column 60 meters long, 0.250 mm internal diameter from Agilent was used. Helium was used as the carrier gas at a pressure of 20 psi. The temperature program started at 50°C for 7 minutes and the temperature was programmed to increase at a rate of 20°C/min to 250°C. Identification of volatile organic compounds present in the samples was carried out based on the NIST mass spectral database updated in 2019.

Chromatographic quantitative analysis of raw material and collected fractions was carried out on an HP 5890 Series II apparatus equipped with a flame ionization detector under analogous conditions. The concentrations of individual components were determined using the standard curve method. The volatile organic compounds of p.a. quality were used as standards.

Figure 2 shows the chromatogram of raw material with fourteen identified components.

Infrared analysis was performed on the FT-IR Bruker Alpha spectrometer by ATR (Attenuated Total Reflectance, Germany) on a diamond P-type attachment.

In order to separate the components of the raw material, the following experiments were carried out. Figure 1 shows the fractional and vacuum distillation sets used for the experiments:

**Experiment 1.** The fractional distillation of raw waste. Fractional distillation was performed on



Fig. 1. Distillation sets used in experiments: a) BUCHI vacuum evaporator; b) fractional distillation set

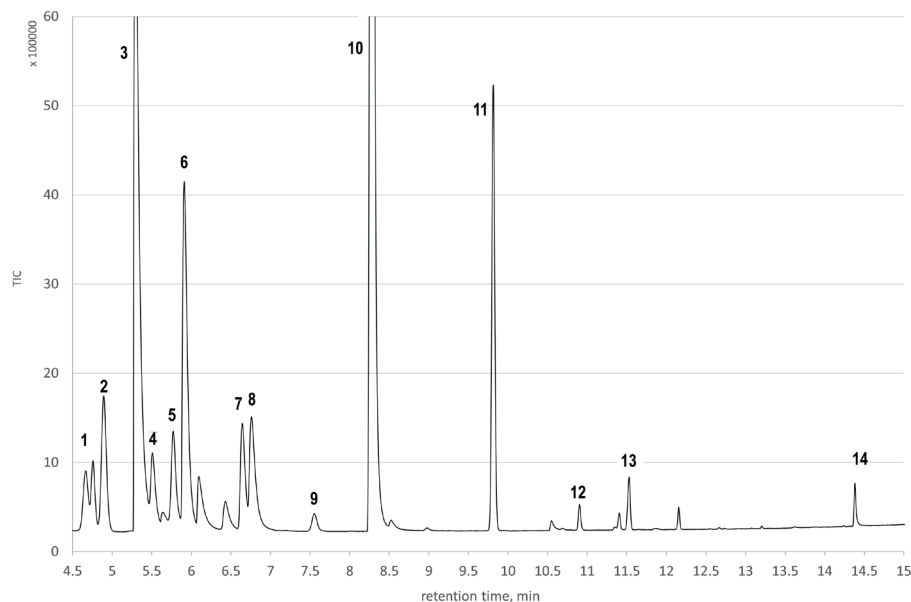


Fig. 2. Chromatogram of the raw material obtained by the GC-MS method. Peak numbering according to the compound numbers described in Table 1

a borosilicate glass column (800 mm, Simax). The individual fractions were collected in the temperature range of 50-80°C.

**Experiment 2.** Fractional distillation preceded by drying over silica gel (desiccant 2-5 mm, Merck, Germany). The crude waste was passed through a silica gel column to separate the water. Then, fractional distillation was performed as in experiment 1.

**Experiment 3.** Vacuum distillation. A rotary evaporator (ROTAVAPORR-300, Buchi Labortechnik AG, Switzerland) was used. The process was carried out at a temperature of 50°C. The pressure was reduced gradually over the range of 410-290 mbar while collecting the individual fractions.

**Experiment 4.** Vacuum distillation followed by drying over silica gel. The crude material stream was passed through a silica gel column as in experiment 2. Then the procedure was as in experiment 3.

**Experiment 5.** Vacuum distillation followed by drying with calcium oxide CaO (Chempur, Poland). Anhydrous calcium oxide in an amount of 65 g/l was added to the raw material and mixed for 1 hour. After CaO was filtered off, distillation was carried out as in experiment 3.

### 3. RESULTS

#### 3.1. Analysis of raw waste

After the quantitative analysis by the GC-FID method, it was found that raw waste contained acetonitrile methanol toluene and acetone in amounts of 55.4%, 22.4%, 4.13% and 2.04% by volume (Fig. 2). The water content in the mixture was 4% v/v. The remaining ten components of the mixture are in the range from 0.3 to 2% v/v. A detailed list of concentrations is presented in Table 1.

Table 1. The content of organic solvents in raw material

No.	Compound	Conc., % v/v	Boiling pt (°C)	No.	Compound	Conc., % v/v	Boiling pt (°C)
1.	1-methoxy-2-propanol	0.31	119.6	8.	ethyl acetate	1.38	77.1
2.	cyclohexane	0.80	80.7	9.	tetrahydrofuran	1.90	66.0
3.	methanol	22.45	65.0	10.	acetonitrile	55.41	81.6
4.	methyl acetate	0.50	57.0	11.	toluene	4.13	110.6
5.	hexane	0.40	68.7	12.	butyl acetate	0.38	125.0
6.	acetone	2.04	56.3	13.	xylene	0.64	139.0
7.	2-propanol	1.33	82.3	14.	N,N-DMF	1.12	153.0



### 3.2. Fractional distillation

Fractional distillation was carried out for raw material and material after prior drying. Drying was accomplished by passing the crude solvent mixture through a column containing silica gel. The distillate samples were collected at defined temperatures and subjected to chromatographic analysis.

The infrared spectroscopy analysis of the collected fractions was performed. It has been shown that during the temperature increase, the acetonitrile

content increases, which was confirmed by an increase in the intensity of absorption band in the range of 2200-2400  $\text{cm}^{-1}$ . At the same time, an increase in the intensity of the band coming from the C = O groups in the range of 1650-1780  $\text{cm}^{-1}$  can be noticed. As the temperature increases, the methanol content in the obtained fractions decreases, which is confirmed by the reduction of the band intensity in the range of approx. 1100  $\text{cm}^{-1}$ . A comparison of the infrared spectra of selected fractions is shown in Figure 3.

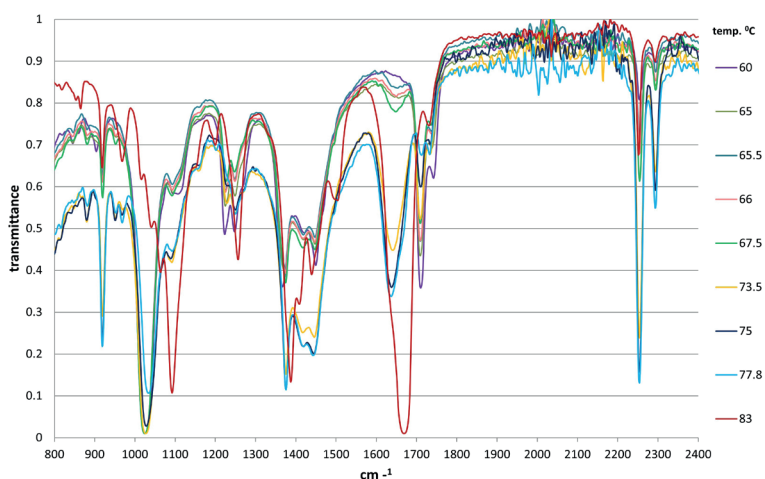


Fig. 3. Comparison of IR spectra of fractions obtained during fractional distillation

Table 2. The content of organic solvents (% v/v) depending on fractional distillation temperature

Temperature, °C	60.0	64.4	65.0	65.4	66.5	67.5	68.9	71.7	73.5	75.0	77.8	83.0
	Concentration, % v/v											
1-methoxy-2-propanol	–	–	–	–	–	–	–	–	–	0.49	0.99	8.76
2-propanol	1.33	0.51	0.58	0.63	0.79	0.97	1.10	1.38	1.42	1.28	0.93	–
acetone	10.4	9.68	9.52	9.27	7.98	6.34	5.45	3.35	2.13	1.15	0.45	–
acetonitrile	20.5	39.0	42.6	44.7	48.8	54.1	57.7	69.6	78.9	85.6	90.7	56.7
butyl acetate	–	–	–	–	–	–	–	–	0.61	0.86	1.25	3.52
cyclohexane	22.3	5.22	2.42	1.02	–	–	–	–	–	–	–	–
ethyl acetate	1.33	1.70	1.75	1.77	1.73	1.57	1.47	1.12	0.84	0.56	–	–
hexane	9.19	2.11	1.18	0.55	–	–	–	–	–	–	–	–
methanol	25.4	30.3	30.8	31.1	29.8	26.5	24.8	16.5	10.7	5.62	2.13	–
methyl acetate	2.03	1.34	1.21	1.03	0.79	0.56	0.43	–	–	–	–	–
N,N-DMF	–	–	–	–	–	–	–	–	–	–	–	29.9
tetrahydrofuran	3.58	3.41	3.34	3.23	2.69	2.01	1.63	0.84	–	–	–	–
toluene	3.13	5.16	5.39	5.53	5.52	5.06	4.69	3.43	2.44	1.62	0.96	–
xylene	–	–	–	–	0.46	0.57	0.65	0.87	0.98	1.03	1.04	1.35

The chromatographic analysis has shown, that changes in the composition of the individual fractions were temperature-dependent. This is particularly evident in the case of methanol and acetonitrile. With the increase in the boiling point of individual fractions, the content of acetonitrile increased until it reached almost 90% of the content. At the same time, the content of methanol was the highest around the boiling point (approx. 65°C), and then it systematically decreased to the level of approx. 2%. However, it is noteworthy, that due to the formation of azeotropes, it was not possible to separate all methanol at its boiling point and it appeared in higher-boiling fractions. Only above 70°C did its content drop significantly. Detailed results are presented in Table 2.

Experiment 2. Was performed by subjecting the raw waste to prior drying on a silica gel column. It is noteworthy that after drying the raw waste with silica gel, some components present in crude

material in small amounts, such as butyl acetate (No. 5 Table 1), 1-methoxy-2-propanol (No. 1 Table 1) or 2-propanol (No. 2 Table 1), didn't appear in the fractions obtained later during distillation. The content of low-boiling waste components such as cyclohexane and hexane, which constitute nearly 30% of the fraction obtained at 60°C for raw waste, has also significantly decreased (Table 2). After drying, the content of these compounds in the lowest boiling fraction dropped to 11%, and in the remaining fractions, they were practically absent. It should be assumed that these components were adsorbed on a bed of silica gel. As in the case of the raw waste, a significant content of N,N-dimethylformamide can be observed in the residue, with a simultaneous decrease in the content of acetonitrile (Table 3).

The comparison of the content of the main components of the mixture for both experiments using the fractional distillation process depending on the boiling point is shown in Figure 4.

Table 3. Composition of the fractions obtained after fractional distillation of dried material

Temperature, °C	63	65	67	68.2	70.5	72.8	75	83
	<b>Concentration, % v/v</b>							
2-propanol	–	2.43	2.20	–	2.64	2.48	2.31	–
acetone	10.54	8.98	7.93	7.35	5.20	3.47	2.03	–
acetonitrile	38.20	46.26	52.65	58.44	65.42	71.83	83.72	71.75
cyclohexane	8.30	1.57	–	–	–	–	–	–
ethyl acetate	–	–	–	–	–	1.24	–	–
hexane	3.48	–	–	–	–	–	–	–
methanol	30.74	30.99	28.76	28.34	22.03	15.93	9.73	–
methyl acetate	–	1.65	–	–	–	–	–	–
N,N-DMF	–	–	–	–	–	–	–	22.36
tetrahydrofuran	3.54	1.93	2.63	–	–	0.88	–	–
toluene	5.19	6.19	5.83	5.86	4.72	3.27	2.20	5.89
xylene	–	–	–	–	–	0.91	–	–

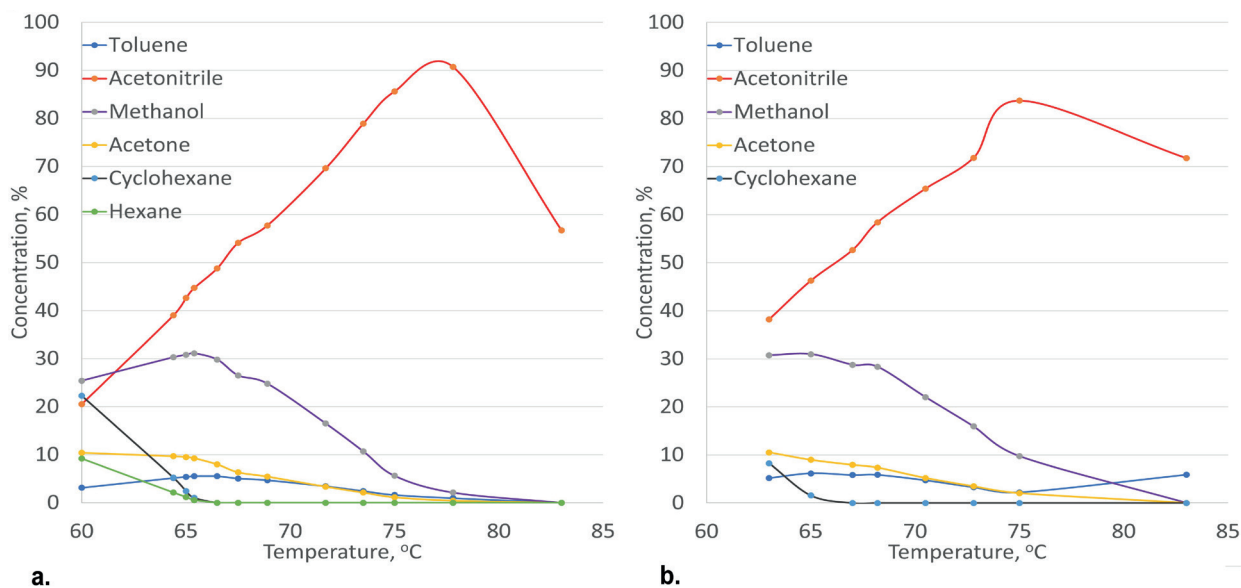


Fig. 4. The content of the main components of the fractions obtained: a) raw material, b) material after drying

### 3.3. Vacuum distillation

The process was carried out at a constant temperature of 50°C, gradually reducing the pressure. The collected fractions were subjected to chromatographic analysis and infrared spectroscopy. The differences in the pressures at which the fractions were collected for individual experiments result from the efficiency of the condensate streams, which for different samples allowed for collecting of appropriate volumes of distillate at different pressures.

The analysis of the IR spectra showed that as the pressure decreased, the acetonitrile content in the

obtained fractions increased. The comparison of the spectra of selected fractions is shown in Figure 5.

The results of quantitative determinations of the components of individual fractions are presented in Table 4. It can be seen that the separation of the substance when the pressure decreases is similarly to the increase in temperature during fractional distillation. Important for the separation of the main components is the much lower acetonitrile content – c.a 73% v/v (Table 4) in the richest fraction, while in the case of fractional distillation near 91% v/v (Table 2, Fig. 3) of acetonitrile content was achieved.

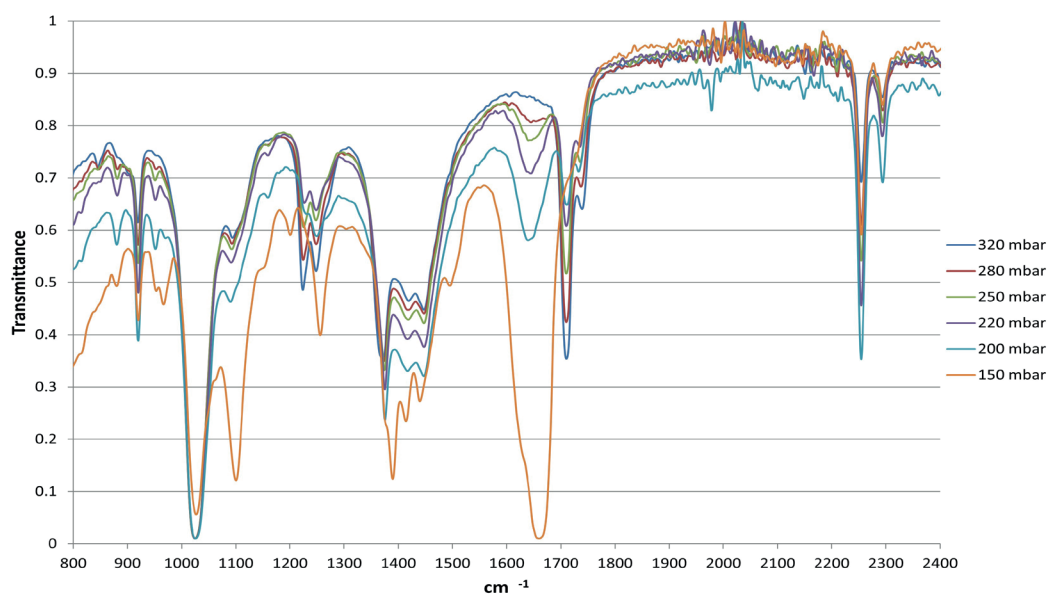


Fig. 5. Comparison of the IR spectra of the fractions obtained by vacuum distillation

Table 4. Composition of the obtained fractions of raw waste after vacuum distillation

Pressure, mbar	320	280	250	220	200	100
Concentration, % v/v						
1-methoxy-2-propanol	–	–	–	–	–	5.48
2-propanol	0.94	1.48	1.99	2.52	3.14	4.08
acetone	11.33	8.81	5.55	3.03	1.35	–
acetonitrile	39.04	50.84	59.34	67.34	73.31	54.51
butyl acetate	–	–	–	0.49	1.05	2.22
cyclohexane	6.44	0.71	–	–	–	–
ethyl acetate	1.75	1.72	1.46	1.11	0.71	–
hexane	3.15	–	–	–	–	–
methanol	26.86	26.63	23.36	19.21	8.28	3.71
methyl acetate	1.52	0.96	0.44	–	7.48	7.77
N,N-DMF	–	–	–	–	–	17.58
tetrahydrofuran	3.93	2.96	1.74	0.85	–	–
toluene	5.05	5.31	4.69	3.31	1.79	–
xylene	–	–	0.63	0.93	1.26	2.14

The next experiments were carried out after preliminary drying of the raw material with the use of silica gel (experiment 4) and calcium oxide (experiment 5).

As in the case of fractional distillation, drying with both silica gel and calcium oxide resulted in a significant reduction in the amount of some

components in the obtained fractions. This is especially true of hexane and cyclohexane. However, no butyl acetate and 1-methoxy-2-propanol were found in any of the fractions obtained. The results of the chromatographic analysis of the obtained fractions are summarized in Table 5.

Table 5. Composition of the obtained fractions of raw waste after drying and vacuum distillation

Sample	after silica-gel drying						after CaO drying					
	425	390	360	330	290	150	430	410	390	370	330	180
Concentration, % v/v												
2-propanol	–	2.12	2.54	2.81	3.03	3.42	1.72	2.03	2.37	2.71	2.99	–
acetone	10.6	6.23	4.19	2.37	1.09	–	8.95	7.16	5.42	3.91	2.99	3.43
acetonitrile	41.8	55.9	62.9	71.7	78.5	80.9	49.3	54.4	59.3	65.1	70.1	78.0
cyclohexane	2.68	–	–	–	–	–	–	1.46	–	–	–	–
ethyl acetate	1.79	1.59	1.34	0.97	–	–	1.66	1.51	1.33	1.11	0.89	–
hexane	1.45	–	–	–	–	–	–	–	–	–	–	–
methanol	29.6	26.6	22.6	17.6	12.7	7.86	28.9	25.6	24.3	21.2	17.7	10.9
tetrahydrofuran	3.57	1.99	1.22	–	–	–	3.03	2.30	1.67	1.11	–	–
toluene	5.58	5.06	4.05	2.62	1.24	0.34	5.21	4.79	4.34	3.60	2.66	1.20
xylene	–	–	–	0.99	1.12	0.90	–	–	–	–	1.10	1.09



A graphical comparison of the composition changes of the main components of raw waste in the vacuum distillation process is shown in Figures 6 and 7.

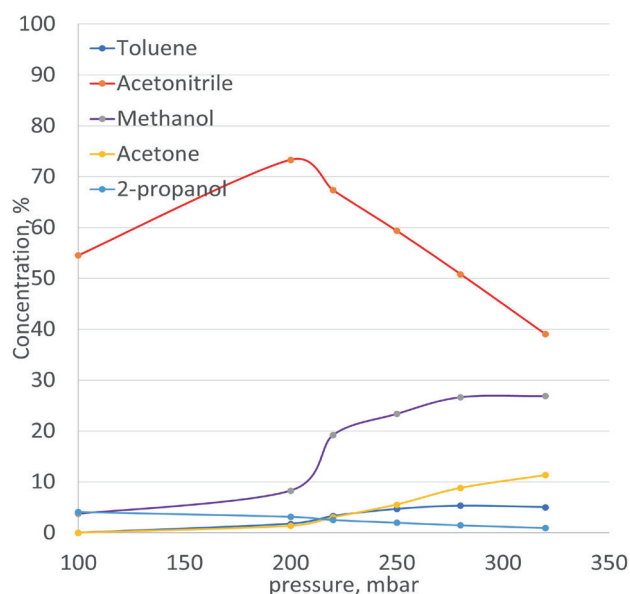
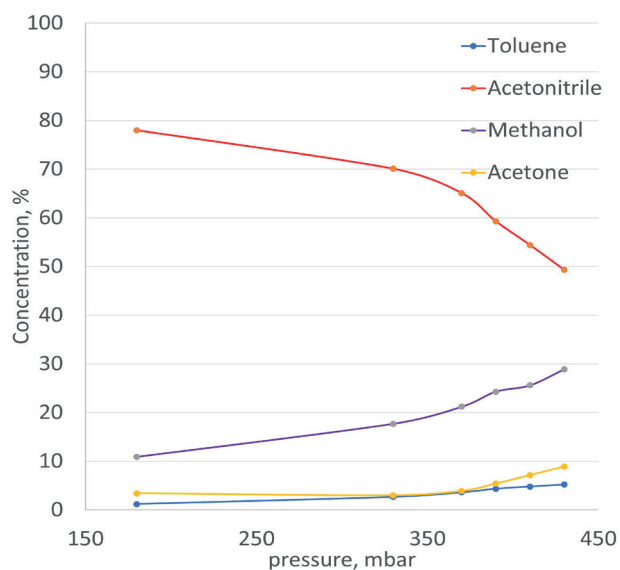
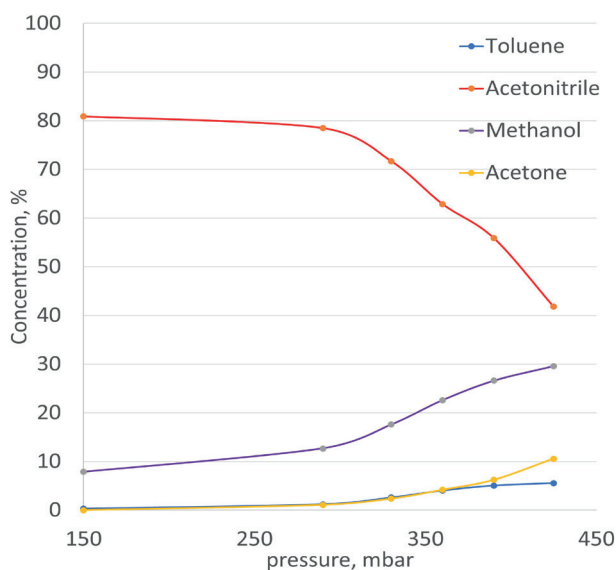


Fig. 6. The content of the main components of the fractions obtained in vacuum distillation



a.



b.

Fig. 7. The content of the main components of the fractions obtained in vacuum distillation: a) material dried on CaO, b) material dried on silica-gel

Comparing the methods used, fractional distillation turned out to be more effective in the recovery of acetonitrile. However, taking into account the energy efficiency of the process and the small difference between the achieved results, vacuum distillation can also be considered worth using for the waste tested.

None of the analyzed methods resulted in obtaining a solvent fraction of analytical purity, but for many industrial applications such purity is not required. A fraction containing approximately 90% acetonitrile may meet the necessary requirements depending on the technological process for which it is to be used. The choice of method should depend on the specific composition of the mixture of volatile organic solvents, which, as we know, depends on the source of waste origin.

#### 4. CONCLUSIONS

Global trends indicate an increase in the consumption of acetonitrile in the coming years. So we can expect the prices of organic solvents to increase. It will be beneficial for production plants to use solvent recovery, which is in line with the principles of sustainable development and green chemistry.

This article presents effective and cheap methods of recovering organic solvents from waste. Volatile organic components were separated by fractional distillation and distillation under reduced pressure.

In analyzed waste the main components of the volatile organic compounds were acetonitrile, methanol and toluene in amounts of 55%, 22.5% and approx. 4%, respectively. The mixture was also dried using cheap and easily available agents, such as silica gel and CaO. Initial drying of raw material

with silica gel and calcium oxide caused the sorption of some components present in low concentrations in the raw waste. As a result, the input stream to the next fractional distillation process was free from some impurities. The amounts of acetonitrile was 90.7% v/v after fractional distillation process (at a temperature of 77.8°C) (Table 2). This means that the concentration of acetonitrile after fractional distillation relative to the raw material increased by about 36%. In the process of vacuum distillation acetonitrile concentration in the obtained fractions was observed at a maximum of 80.9%, which is a value nearly 10% lower than in the case of fractional distillation.

The analyzed methods, such as fractional and vacuum distillation, are relatively simple and cheap

processes. It is worth emphasizing that the analyzed methods work well on a laboratory and semi-technical scale, which is a sufficient scale for many laboratories and small production companies. Due to differences in the design of the equipment, scaling the process to an industrial scale requires extensive optimization research. It should also be noted that the tested liquid waste had a specific composition, characteristic of the production industry. The recovery of organic solvents requires an individual approach depending on the quantitative and qualitative composition of waste generated in a given production process.

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