

## EVALUATION OF GREEN SAMPLE PREPARATION TECHNIQUES FOR ORGANIC COMPOUNDS

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### **Abstract**

Nowadays, Green Analytical Chemistry (GAC) idea is of high importance, with impact on the rapid growth in the sample preparation area with special emphasis on sample preparation simplification, miniaturization and automation. Due to the fact that GAC is of high importance today, this study is focused on the evaluation of green sample preparation techniques for organic compounds. It is well known that sample preparation is considered a crucial part of analytical procedures in particular in samples characterized by complex matrices composition. Previously the parameter of „greenness” is as important as selectivity in order to avoid using harmful organic solvents in sustainable extraction techniques. These solvents can generate hazardous, toxic waste while consuming large resources volume, thus, developing new, eco-friendly and benign solvents which would meet technological and economic demands is perhaps the most popular aspects of Green Chemistry. Some examples of these “green” solvents are given in this work. In addition, several new miniaturized extraction techniques are described. Here you can highlight solid phase microextraction (SPME) and liquid phase microextraction (LPME). However, the best option would be to use direct methods of analysis, where sample preparation is not required. Given study shows also the possibilities and limitations of using Eco-Scale and GAPI tools for the assessment of green character of selected analytical procedures. Both tools were applied to assess 9 different analytical procedures and both showed similar results presented in a different manner.

Key words: Green Analytical Chemistry, SPME, LPME, GAPI, Eco-Scale

### 1. Introduction

Analytical chemistry is crucial when it comes to deal with the environmental protection aspects. It enables monitoring of pollutants in many mediums like air, water, soil etc. However, it involves lots of reagents and solvents for its procedures, which by itself may be toxic and generate dangerous wastes. Thus, there is more and more attention put for the Green Analytical Chemistry. It is a new branch of the analytical chemistry, that copes with the problems of organic solvents toxicity, waste generation and consumption of large volume of resources. To cope with the idea of green chemistry, 12 principles have been stated, which

focus on the renewable resource usage, minimization of the scale of analytical procedure and is targeted on the most important aspect of sample preparation and miniaturization of the extraction techniques [1,2].

The aim of this paper is to present the range of green solvents involved in the green sample preparation processes, that may be used in the analytical operations and a wide range of the miniaturized extraction techniques, all of them designed to cope with the sustainable and environmentally friendly chemical techniques of sample analysis. We believe that this manuscript is of high importance and can help readers to choose the best “green” solutions in the future practice.

## 2. Green solvents

Sample preparation is very important stage of the analytical procedures, especially when it comes to deal with complex matrices. Its performance may strongly influence the whole analysis. Green way of sample preparation concentrates mainly on the reduction of solvents used, its recovery and reuse and what is more application of green media, that are less toxic and less harmful for the environment from organic, that are commonly used [2]. The process of designing of green solvents includes several aspects presented in Figure 1 [3].

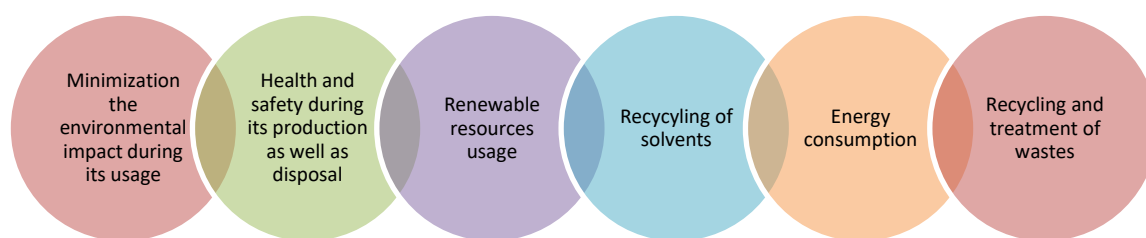


Figure 1. Criteria for designing green solvents.

There are several types of green solvents commonly applied in the analytical processes:

- **Superheated water** – water is the most widely and the most popular solvent used in analytical chemistry. Thanks to the process of heating in the temperatures between its boiling point (100°C) and critical point (374°C) in pressure higher than atmospheric, it gains specific properties important from the green chemistry perspective. It becomes less polar and has lower permittivity, surface tension, viscosity and higher diffusion rate. What is more its dielectric constant decreases from 80 to 27 at 250°C. Thanks to its wide range of polar and non-polar substances are soluble in water. There are lots of advantages of using subcritical water as a solvent since it is non-toxic, easily available and cheap. However, it should be noticed, that it has limited power of extraction and may cause lots of problems with further separation of targeted analytes from the aqueous phase [3].
- **Supercritical fluids** – are substances subjected to the pressure and temperature above their critical points, possessing the physicochemical properties between

liquid and gas. Due to their low viscosity and high diffusivity, lots of parameters of extraction with the use of these solvents are improved: better mass transport from solid samples, higher efficiency and reduction of dangerous waste since no toxic residues are left. To choose solvents appropriate, to put under the supercritical conditions, it is important to consider several factors like toxicity, physicochemical properties, that may affect the conditions of the supercritical state, technical viability and cost. The most commonly used supercritical fluid is carbon dioxide, because it is non-flammable, easily accessible and easy to achieve. However, there are also propane and ethane both characterized by better extraction efficiency than CO<sub>2</sub>. What is more, supercritical ethane is obtained in a lower pressure than CO<sub>2</sub>, thus it consumes less energy, what also acts in favor [3,4].

- **Surfactants** – amphiphilic, surface-active compounds with polar “head” group bonded to the non-polar “tail” group. Depending on the type of groups in the “head” there can be distinguished four different kinds of surfactants presented in Figure 2.

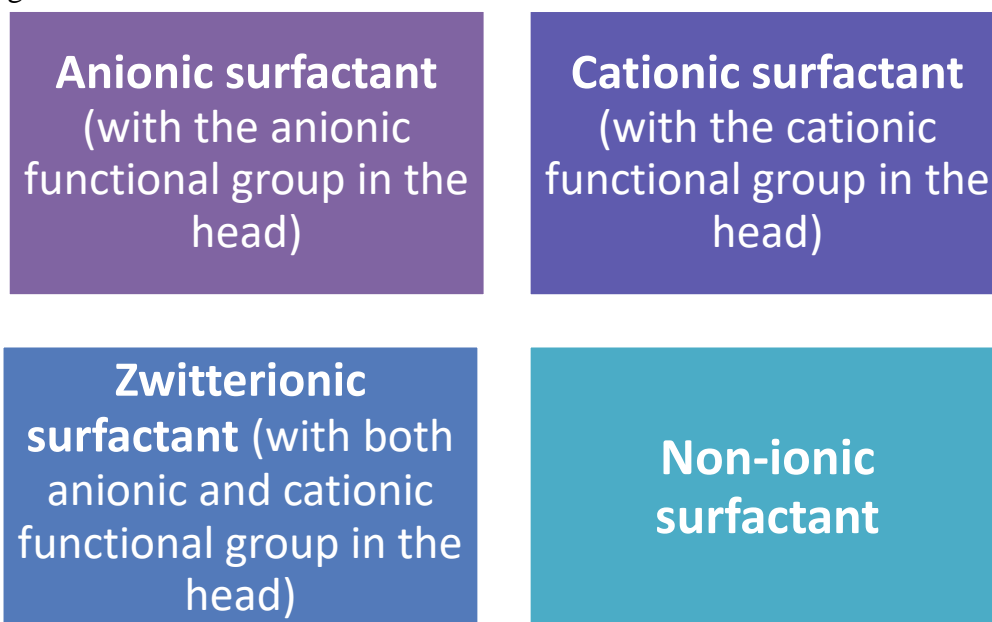


Figure 2. Four types of surfactants.

Under the characteristic concentration – critical micelle concentration, they start to form clusters, what results in formation of cloudy solutions. However, the size of this colloidal system is smaller, than visible light wavelength so the transparency of the solution is preserved. According to the characteristic of the media, they are acting with, they behave in a different way. When the polar media is present, micelle aggregate with the hydrophobic tail oriented toward the centre. While acting with the non-polar medium, they behave in the opposite way with the head oriented toward the centre. The main advantage of discussed surface active agents is the significant increase of the solubility of compounds poorly soluble in water or hydrophilic substance poorly soluble in organic phase [3].

- **Ionic liquids** – usually molten salts, consisting of a big asymmetric organic cation and smaller inorganic anion, with the boiling point below 100°C. They are

characterized by low vapor pressure, high thermal stability, which increases with increasing anion size and what is more universal, a wide range of organic and inorganic substances are soluble in this medium. Moreover, their heat capacity increase with temperature and an increasing number of atoms in their structure. Selection of the appropriate cation and anion enables the design of ionic liquid with physicochemical characteristic needed for the specific analysis [3,5].

### 3. Green microextraction techniques

The use of green solvents in favour of the more common organic solvents is one of the most active areas of green chemistry [6]. However, it is not always possible to find a replacement for toxic, hazardous reagents. Because of that, it is necessary to reduce the amounts of solvent and reagents by miniaturizing the instruments and the scale of analytical operations. Both solid and liquid phase microextraction techniques could be used in order to collect and prepare the samples in accordance with green analytical chemistry.

#### 3.1. Solid-phase microextraction techniques

Solid-phase microextraction (SPME) was at first introduced into analytical practice in 1990 by Pawliszyn and Arthur. Due to a decrease in the scale of solid-phase extraction, it was possible to eliminate its two disadvantages – the need to use organic solvents and the length of extraction time [7]. In SPME, silica fibres are coated with a suitable sorption material in order to absorb the target analytes. Depending on their position in relation to the sample, microextraction may take place in two manners: by direct immersion (DI, Figure 3a), in which the analytes are transferred directly from the sample to the stationary phase on the fiber immersed in the solution or absorption from the headspace (HS, Figure 3b), where the fiber is placed in the gas phase in direct contact with the sample, the analytes are transferred into the headspace before being absorbed on the stationary phase. In both DI-SPME and HS-SPME, absorbed analytes may be easily freed with the thermal desorption technique and analysed with gas chromatography. However, the effectiveness of the analyte pre-concentration by SPME depends on various parameters such as the type and length of the fibre, the thickness of stationary phase, temperature and mode of extraction. It is not always possible to find a type of stationary phase with sufficiently high affinity to specified analytes and/or stability in extraction conditions.



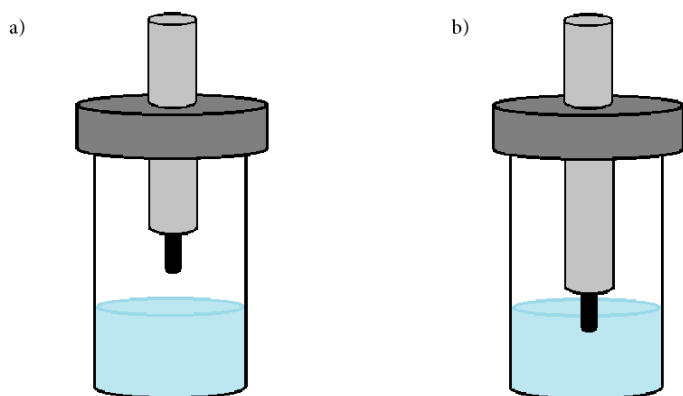


Figure 3. Modes of solid-phase microextraction: a) direct immersion (DI-SPME), b) headspace (HS-SPME).

An alternative to the SPME is the use of solid-phase dynamic extraction (SPDE). In this technique, the internally-coated needle is used instead of coated fibre. Different localization of the sorbent material increased the inter-phase contact which led to the decrease of both analysis time and sample capacity. Because of that, SPDE has found application in the analysis of volatile compounds in food and drug determination in hair samples, as well as pesticides in water samples [8]. However, localization of the sorbent material on the inner wall of the needle may cause the carry-over problems, since some analytes tend to remain in the needle even after thermal desorption.

Micro-SPE is another solution related to SPME. In porous membrane-protected  $\mu$ SPE ( $\mu$ SPE) the sorbent bag is made of the porous membrane and filled with small amount of the sorbent [9]. This technique enables the extraction of analytes from suspensions or semi-solid samples without the risk of sorbent contamination and thus reduces the matrix effect. Moreover, the use of  $\mu$ SPE provides high enrichment factor and is both easier and less time-consuming than conventional solid-phase microextraction. For that reason, this technique has found application in the extraction of pesticides from water or detection of trace materials in environmental samples [1].

A different technique of microextraction is the adsorptive microextraction ( $A\mu E$ ) in which the analytes are transferred from the aqueous medium to the sorbent nanostructure.  $A\mu E$  can be performed using two geometrical variants: bar ( $BA\mu E$ ) or multi-sphere ( $MSA\mu E$ ). Because of the vast number of available sorption materials and high recovery factor, both  $BA\mu E$  and  $MSA\mu E$  have found use in monitoring the contaminants in environmental samples or food samples and anti-doping control.

Alternative solutions related to SPME are various modifications of stir-bar sorptive extraction (SBSE) (Figure 4): stir-cake sorptive extraction (SCSE) in which the stationary phase is placed in a specially prepared cake holder, rotating-disc sorbent extraction (RDSE), where extraction device is a Teflon disk filled with the stationary phase and stir-rod sorptive



extraction (SRSE) in which there is a metal rod coated with the monolithic polymer. All three methods exhibit high recovery level and lower friction loss of the coating material than SBSE.

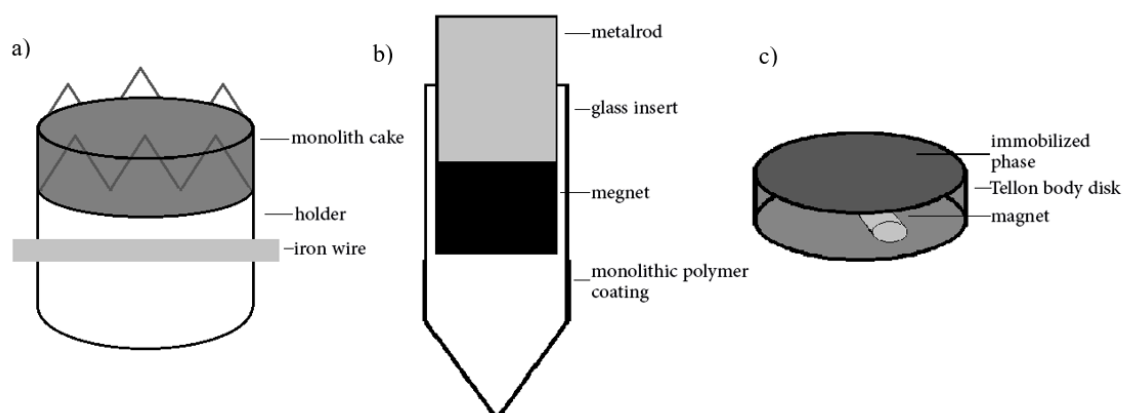


Figure 4. Devices used for a) stir-cake sorptive extraction (SCSE), b) rotating-disc sorbent extraction (RDSE), c) stir-rod sorptive extraction (SRSE)

### 3.2. Liquid-phase microextraction techniques

Liquid-phase microextraction (LPME) is a technique developed in order to overcome the disadvantages of the liquid-phase extraction (LLE) such as large amount of organic solvents used, long time of extraction and emulsion formation that prevents its automation. In LPME only several microliters of a water-insoluble solvent and analyte in an aqueous phase. In addition, this technique can be coupled with various identification techniques such as gas chromatography or high-performance liquid chromatography [10]. The use of LPME enables extraction both organic (e.g. pesticides, pharmaceutical products) and inorganic (e.g. arsenic (III), arsenic(V), fluorine) substances from water, food or biological samples [11].

One of the modes of LPME is single drop microextraction (SDME) (Figure 5). In this technique, the extraction medium forms a drop at the tip of the needle that is stabilized by the mechanical equilibrium and can be retracted after extraction and further analyzed [12]. There are several types of SDME that can be classified depending on the number of phases coexisting at equilibrium as either two-phase or three-phase technique. The most commonly used modes are direct immersion (DI-SDME), which is the type of two-phase technique, where the extractant phase is directly immersed into stirred liquid-sample solution and headspace (HS-SDME), a three-phase technique where the solvent microdrop is placed either in the sample's headspace or in an air sample stream. DI-SDME and HS-SDME are probably popular due to their simplicity and inexpensive equipment needed for them [13].



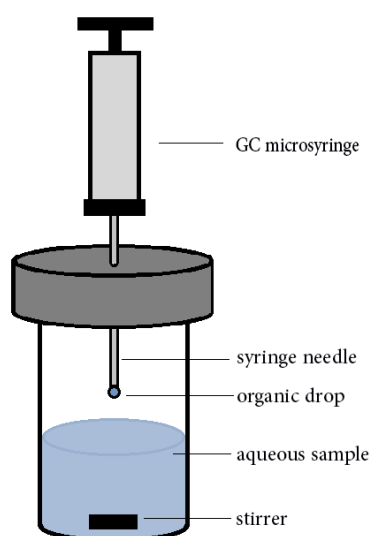


Figure 5. Single drop microextraction

An alternative to SDME is a hollow-fibre liquid-phase microextraction (HF-LPME) in which the porous hollow fibre is dipped in an organic solvent that is water immiscible. The supported liquid membrane that is formed in the process is then placed in the sample vial containing continuously stirred sample donor phase and the analytes are extracted through the liquid membrane into the acceptor phase that can be then removed and analysed. Depending on solution agitation and the type of the acceptor, HF-LPME can be classified as two-phase, three-phase, dynamic or static mode. All modes of this technique are applied mostly for environmental and bioanalytical analysis.

Another option is electromembrane extraction (EME) that derived from HF-LPME. In this technique, analytes are extracted through organic solvent sustained as this supported liquid membrane in the pores of a fibre and then into an acceptor solution. Like HF-LPME, EME has found its application in the bioanalytical analysis. However, the process is based on electrokinetic migration in an electrical field and due to the application of the electrical potential, the extraction time is significantly shorter than in hollow-fibre liquid-phase microextraction [14]. Because of that, it is used in the analysis of wastewater, biological samples and drugs.

Dispersive liquid-liquid microextraction (DLLME) is a relatively new mode of liquid-phase microextraction. In this technique, the mixture of non-miscible with water extraction solvent and dispersive solvent are rapidly injected into an aqueous sample. A cloudy solution is formed. The contact between fine droplets and the analyte speeds up the mass-transfer, the hydrophobic solutes are enriched in the extraction solvent with great efficiency. The phase containing analytes can be collected after centrifugation and analysed [15]. DLLME is mainly used to extract and concentrate metal ions and organic compounds from water samples.

Liquid-liquid-liquid microextraction (LLLME) is a technique, where at first, the analyte is extracted from the donor phase into the several microliters of an organic phase. After that,

from the organic phase, it is extracted into an acceptor phase. There are several criteria, which the organic solvent should fulfil to be suitable for this process, like:

- to be easily immobilized in the pores of polypropylene hollow fibre;
- to be of low volatility and immiscible with water;
- to be more soluble for analytes than the donor phase.

Hollow fibre protects against carryover and cross-contamination. Additionally, changing the organic phase, give the possibility to use this technique to extract variable analytes [16].

Other techniques of microextraction have been invented in order to improve already existing techniques. The efficiency of the extraction can be further enhanced e.g. with the use of vortex agitation (Vortex-assisted liquid-liquid microextraction, VALLME). Ultrasound-assisted emulsification microextraction (USA-EME) use sonification instead of the dispersive solvent to overcome the disadvantages of DLLME, such as the need to use the third component or a difficulty to automate. A bell-shaped extraction device liquid-phase microextraction (BSED-LPME) was developed to improve SDME and reduce its instability [11].

#### 4. Evaluation of green character of selected procedures based on microextraction techniques

Currently, Green Analytical Chemistry idea is of high interest of researchers, with impact on the rapid growth in the sample preparation area with special emphasis on sample preparation simplification, miniaturization and automation. Although the microextraction techniques were developed in order to minimize the environmental risk and to make the analysis more “green”, sometimes it is impossible to eliminate the use of harmful solvents.

Above presented literature depicts some examples of microextraction techniques which present several opportunities to move toward GAC practices. In order to present the differences in the green nature of selected procedures, several analytical methodologies applied in biogenic amines determination in wine [1-3], sulfonamides [4-6] and organophosphate pesticides determination in water [7-9] with the use of different types of methodologies based on microextraction techniques, that are mentioned in this paper are assessed in respect to the green character. To evaluate these selected protocols, Analytical Eco-Scale and Green Analytical Procedure Index (GAPI) were used.

Analytical Eco-Scale is a tool of greenness assessment in which parameters of the analytical procedure such as amount and toxicity of the reagents, utility of the method and volume of waste, are evaluated. The penalty points (PPs) are assigned for every aspect of the procedure, that falls short of the green analytical chemistry guidelines and then are subtracted from the base of 100. Based on the resulting score it is possible to assess the greenness of the procedure: the higher the score, the greener and more economical procedure is.

Analytical Eco-Scale is a good evaluation tool for laboratory practice and educational purposes. It is simple to use and not time-consuming. Moreover, it appraises many aspects of environmental impact under well-defined criteria of evaluation and enables easy comparison between techniques. However, it also has some limitations, since Analytical Eco-Scale is only semi-quantitative and does not provide the information about the reasons for the





environmental impacts of the assessed techniques [17]. Because of that, more information can be obtained by application GAPI tool.

GAPI is a tool in which the result of greenness evaluation of each stage of the analytical procedure is presented using a three-stage colour scale. Assessment of the analytical methodology is presented in the form of the pictogram consisting of five pentagrams out of which each represents a separate stage of analytical procedure: sample collection, sample preparation, reagents and compounds used, instrumentation, type of general method and quantification. Three colours are used for assessment: green representing low environmental impact, yellow representing medium environmental impact and red meaning high impact on the environment [18].

In Table 1, the PPs are presented for evaluated procedures, while Figure 6 presents the pictogram obtained by application of GAPI.

Considering the penalty points (PPs), calculated for each procedure used for wine analysis (Table 1), it can be concluded, that all of the evaluated procedures can be assigned green (more than 75 PPs), however, the best result is achieved for Procedure 1 based on DI-SPME-GC-MS [19] (Score: 84 PPs). The worst evaluated here procedure in term of “green” profile is Procedure 3 [21]. The same results are presented in Figure 6. It is visible at first glance, that all of the evaluated procedures require advanced sample preparation meaning extraction and derivatization procedure, however, Procedure 1 and Procedure 2 are based on micro-scale extraction. However, the GAPI pictogram obtained for the procedure based on SPME presents better results in case of consideration reagent and solvents used as well as occupational hazards; thus, from this point of view, it can be considered greener than the other two methodologies.

All of the procedures used for the sulfonamides determination have similar environmental characteristics, what can be noticed both in the Ecoscale (where the score oscillate in the narrow range between 71-79 points) as well as in GAPI tool (where Procedure 4 and 5 look identical and procedure 6 only slightly differs). The rule of Ecoscale assessment is as follows the higher the score, the greener and more economical the procedure is. The scores obtained for sulfonamides determination in water are not fully satisfied. The procedure is considered as green while the scores are equal 75 or more. Only one procedure, using HF-LPME-HPLC-VW [23] obtained such results, rest is below. The biggest problem appearing in all procedures is waste generation. Since all methodologies are based on HPLC, lots of solvents are used creating big amount of waste. Some reagent like formic acid or methanol even if were used in small amount (amount was expressed in  $\mu\text{L}$ ) obtained big number of penalty points (PPs) due to their properties and harmfulness. It is reflected in the colors in the GAPI tool where the sample harmfulness and safety is marked by the red color.

Three procedures applied in the determination of organophosphate pesticides in water were also assessed with the use of Analytical Eco-Scale and GAPI tool. Based on the results obtained using Eco-Scale, it can be concluded that the differences between Procedures 7-9 are not prominent. All three methods can be considered green, even though their application require the use of toluene. The highest score was obtained for the Procedure 8 [25] (85 points), as there are no additional toxic reagents. Procedures 7 and 9 (with scores of 80 and 82



respectively), can be considered slightly less green than the Procedure 8. The results of greenness evaluation with the use of GAPI further suggests, that green character of these procedures is very similar. Nevertheless, it can be seen that the Procedure 8 obtained the best results overall, especially in the subject of sample preparation

Table 1. The penalty points (PPs) for BAs determination in wine samples by evaluated procedures [1-3], for the sulfonamides determination in water samples [4-6] and determination of organophosphate pesticides in water samples [7-9].

| PROCEDURES FOR BAs DETERMINATION IN WINE |      |  |      |   |      |
|--|------|--|------|---|------|
| PROCEDURE 1: DI-SPME-GC-MS [19]          |      | PROCEDURE 2: DLLME-GC-MS [20]                                    |      | PROCEDURE 3: SPE-HPLC-fluorescence detection [21] |      |
| Reagents                                 | PPs  | Reagents   | PPs  | Reagents  | PPs  |
| NaCl                                     | 0    | Pyridine   | 1    | MeOH (12.1 mL)                                    | 8    |
| Internal standards                       | 4    | Internal standard  | 4    | Internal standard                                 | 4    |
| Isobutyl chloroformate (50 µL)           | 8    | HCl (55 µL)  | 3    | H <sub>3</sub> PO <sub>4</sub> (1.8 mL)           | 1    |
| Water (5 mL)                             | 0    | Chloroform (400 µL)  | 2    | NaOH (2.7 mL)                                     | 1    |
|  |      | Isobutyl chloroformate (110 µL)                                  | 8    | CaCl <sub>2</sub> (1.4 mL)                        | 0    |
|  |      | MeOH (215 µL)  | 6    | HCl (100 µL)                                      | 3    |
|  |      |  |      | Sodium acetate trihydrate (3.3 mL)                | 1    |
|  |      |  |      | Trihydrate triethylamine (3.3. mL)                | 2    |
|  |      |  |      | AQC (20 µL)                                       | 3    |
|  | Σ 12 |  | Σ 24 |   | Σ 23 |
| Instruments                              | PPs  | Instruments  | PPs  | Instruments                                       | PPs  |
| Transport                                | 1    | Transport  | 1    | Transport   | 1    |
| GC-MS                                    | 2    | GC-MS  | 2    | HPLC-fluorimetric detection                       | 2    |
| Occupational hazard                      | 0    | Occupational hazard  | 0    | Occupational hazard                               | 0    |
| Waste                                    | 1    | Waste  | 1    | SPE   | 2    |
|  |      |  |      | Waste   | 5    |
|  | Σ 4  |  | Σ 4  |   | Σ 10 |
| <b>Total PPs: 16</b>                     |      | <b>Total PPs: 28</b>   |      | <b>Total PPs: 33</b>                              |      |
| <b>Score: 84</b>                         |      | <b>Score: 82</b>   |      | <b>Score: 77</b>                                  |      |
| PROCEDURES FOR SULFONAMIDES IN WATER     |      |  |      |   |      |
| PROCEDURE 4: SD-LPME-HPLC-VW [22]        |      | PROCEDURE 5: HF-LPME-HPLC-VW [23]                                |      | PROCEDURE 6: LLLME-HPLC-UV [16]                   |      |
| Reagents                                 | PPs  | Reagents   | PPs  | Reagents  | PPs  |
| Formic acid                              | 8    | [C <sub>8</sub> MIM][PF <sub>6</sub> ]                           | 3    | Acetonitrile                                      | 3    |
| Acetonitrile                             | 3    | KH <sub>2</sub> PO <sub>4</sub> -K <sub>2</sub> HPO <sub>4</sub> | 1    | KH <sub>2</sub> PO <sub>4</sub> (13 mL)           | 2    |
| [C <sub>8</sub> MIM][PF <sub>6</sub> ]   | 3    | Acetonitrile   | 3    | NaOH  | 1    |
| HCl                                      | 3    | Acetone  | 4    | Deionized water                                   | 0    |
| NaCl                                     | 1    | NaOH   | 1    | MeOH  | 6    |
|  |      |  |      | HCl   | 3    |



|   |             |                                       |             |  |             |
|---|-------------|---------------------------------------|-------------|--|-------------|
|   |             |                                       |             | Acetone  | 4           |
|   | $\Sigma$ 18 |                                       | $\Sigma$ 12 |  | $\Sigma$ 19 |
| <b>Instruments</b>  | <b>PPs</b>  | <b>Instruments</b>                    | <b>PPs</b>  | <b>Instruments</b>                                     | <b>PPs</b>  |
| Transport   | 1           | Transport                             | 1           | Transport  | 1           |
| HPLC-VW   | 2           | HPLC-VW                               | 2           | HPLC-UV  | 2           |
| Occupational hazard                                       | 1           | Occupational hazard                   | 1           | Occupational hazard                                    | 1           |
| Waste   | 5           | Waste                                 | 5           | LLLME  | 1           |
|   | $\Sigma$ 9  |                                       | $\Sigma$ 9  | Waste  | 5           |
|   |             |                                       |             |  | $\Sigma$ 10 |
| <b>Total PPs: 27</b>                                      |             | <b>Total PPs: 21</b>                  |             | <b>Total PPs: 29</b>                                   |             |
| <b>Score: 73</b>  |             | <b>Score: 79</b>                      |             | <b>Score: 71</b>                                       |             |
| <b>PROCEDURES FOR ORGANOPHOSPHATE PESTICIDES IN WATER</b> |             |                                       |             |  |             |
| <b>PROCEDURE 7: SDME-GC-FID [24]</b>                      |             | <b>PROCEDURE 8: VALLME-GC-MS [25]</b> |             | <b>PROCEDURE 9: USAEME-GC-<math>\mu</math>ECD [26]</b> |             |
| <b>Reagents</b>   | <b>PPs</b>  | <b>Reagents</b>                       | <b>PPs</b>  | <b>Reagents</b>  | <b>PPs</b>  |
| Internal standards  | 4           | Internal Standards                    | 4           | Internal standards                                     | 4           |
| Methanol  | 6           | Water                                 | 0           | Water  | 0           |
| Toluene (1 $\mu$ L)                                       | 6           | Toluene (40 $\mu$ L)                  | 6           | Acetone  | 4           |
|   |             |                                       |             | Toluene (20 $\mu$ L)                                   | 6           |
|   | $\Sigma$ 16 |                                       | $\Sigma$ 10 |  | $\Sigma$ 14 |
| <b>Instruments</b>  | <b>PPs</b>  | <b>Instruments</b>                    | <b>PPs</b>  | <b>Instruments</b>                                     | <b>PPs</b>  |
| Transport   | 1           | Transport                             | 1           | Transport  | 1           |
| GC-FID  | 1           | GC-MS                                 | 2           | GC-FPD   | 1           |
| Occupational hazard                                       | 1           | Occupational hazard                   | 1           | Occupational hazard                                    | 1           |
| Waste   | 1           | Waste                                 | 1           | Waste  | 1           |
|   | $\Sigma$ 4  |                                       | $\Sigma$ 5  |  | $\Sigma$ 4  |
| <b>Total PPs: 20</b>                                      |             | <b>Total PPs: 15</b>                  |             | <b>Total PPs: 18</b>                                   |             |
| <b>Score: 80</b>  |             | <b>Score: 85</b>                      |             | <b>Score: 82</b>                                       |             |



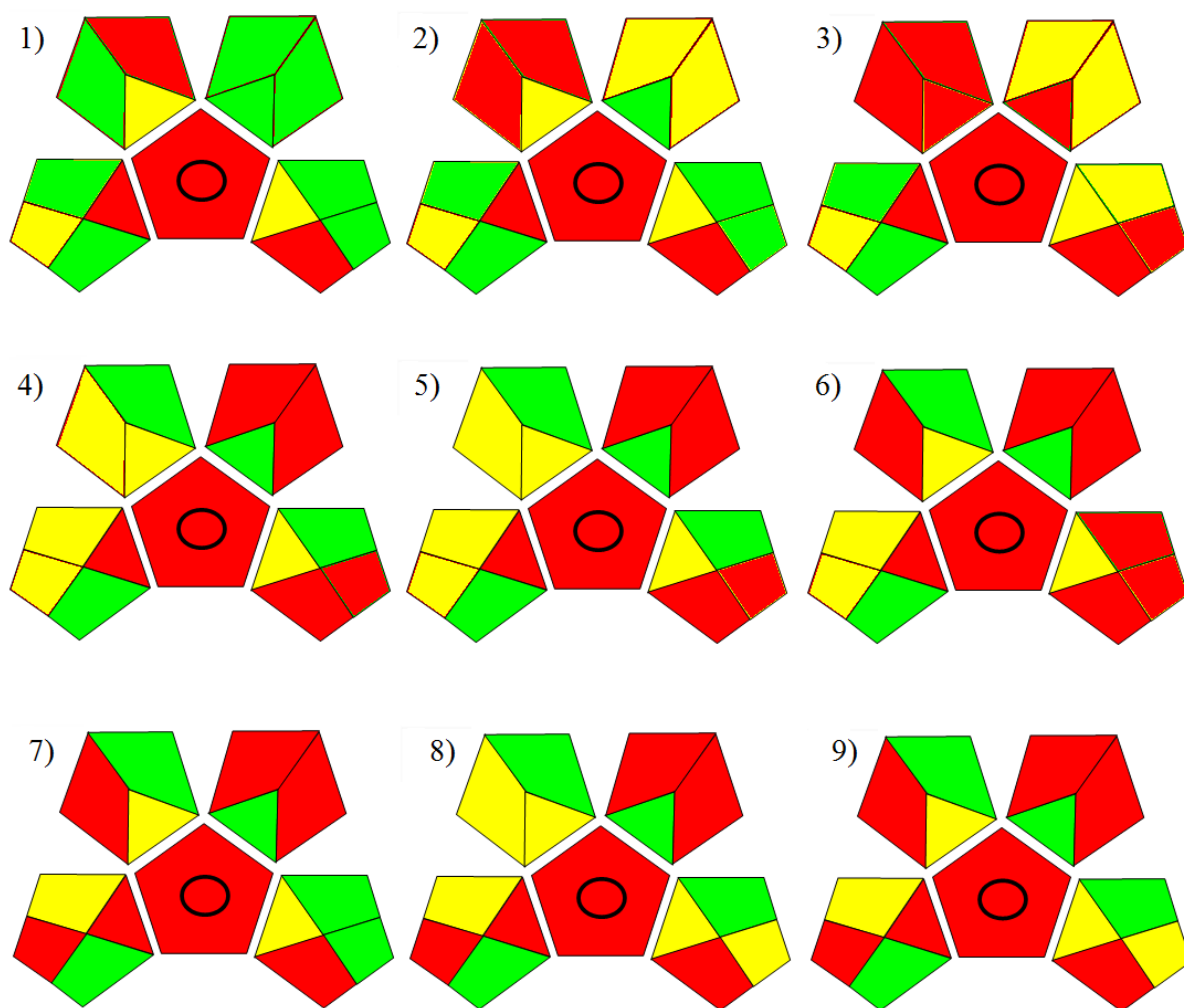


Figure 6 Assessment of green profile of evaluated procedures for BAs determination in wine samples by (Procedures 1-3), for the sulfonamides determination in water samples (Procedures 4-6) and determination of organophosphate pesticides in water samples (Procedures 7-9), using GAPI tool.

## 5. Summary

Due to sample preparation being a critical element of the analytical process, it is one of the most active areas of green analytical chemistry. Various modes of both liquid-phase and solid-phase microextraction can be used in order to decrease the amount of used reagent. These techniques have numerous advantages including simplicity of the operation, short time of extraction and relatively low cost of instrumentation. Moreover, high temperature, ultrasound energy and other factors are applied not only to enhance the effectiveness of the procedure, but also in order to reduce their influence on the environment. Furthermore, green media, such as ionic liquids, supercritical fluids or bio-derived solvents, can be used instead of more commonly used organic solvents. Because of their physicochemical properties, they are not only benign to the environment, but also bring the advantages in the extraction processes.

However, the avoidance of using harmful and toxic solvents as well as the miniaturization of the scale of extraction cannot completely eliminate the influence of the sampling preparation on the environment. Because of that, moving towards the use of direct methods of analysis, in which this stage is not required, should be the next goal to achieve.

As the aim of this work was to summarize the most popular solutions in the area of green sample preparation, we believe that this manuscript is of high importance and can help readers in the future practice to choose the best “green” solutions. In addition, we hope that presented ways of the evaluation of analytical procedures allow the readers to follow such practice.

#### Conflict of interest

Magdalena Fabjanowicz declares that she has no conflict of interest. Kaja Kalinowska declares that she has no conflict of interest. Jacek Namieśnik declares that he has no conflict of interest. Justyna Płotka-Wasyłka declares that she has no conflict of interest.

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