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Trends in the new generation of green solvents in extraction processes

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Abstract

Analytical chemistry, like other scientific fields, has undergone a number of changes to make it more consistent with the concept of sustainable development. Among the various steps of chemical analysis, without a doubt, sample preparation is the bottleneck in regard to following a green protocol, especially in terms of solvent consumption. Therefore, many attempts have been made to improve the environmental friendliness of this stage, mainly through the developing approaches for miniaturized sample preparation as well as application of new green solvents. This review offers a brief discussion of current trends in analytical applications that have been less studied and discussed: a new generation of green solvents, such as bio-based solvents, supercritical fluids, and liquefied. We believe that this mini review is a good starting place for readers interested in the future of green analytical chemistry.

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Green solvents, Extraction, Analysis, Bio-based solvents, Supercritical fluid extraction, Liquefied gases.

Green analytical chemistry: challenges in sample preparation

The development of analytical chemistry is clearly moving towards the increasing application of the principles of green analytical chemistry (GAC). It is imperative to reduce the use of reagents and excipients in general and to eliminate the use of hazardous solvents, in particular, or to at least replace them with safer ones. On the other hand, the priorities for the development of analytical procedures especially include the validation characteristics of the methods, such as their sensitivity, selectivity, accuracy, precision, and robustness. Therefore, analytical chemists around the world are looking to find a balance between the conflicting demands of the present era. We would like to add that these requirements are sometimes only seemingly contradictory, and the introduction of new, more sustainable, and energy-efficient alternatives also leads to improvement in the metrological characteristics of the new procedures. Automation, acceleration, miniaturization, and simplification, as well as the use of environmentally friendly chemicals and innovative materials, have fueled the development of numerous green analytical procedures. The degree of "greenness" attained by several of them is notable. The elimination of sample preparation by conducting direct analysis is the first principle of GAC. However, in most chemical analyses, a sample preparation step is compulsory for the cleanup and preconcentration of analytes [1]. Perhaps the most commonly used sample pretreatment technique is liquid extraction. The primary disadvantage of this approach is the extensive use of organic solvents and the resulting laboratory waste.

At present, omitting solvents completely from analytical procedures seems to be almost impossible; therefore, many research groups have focused their efforts on developing and examining new generations of green solvents to be applied in the extraction process.

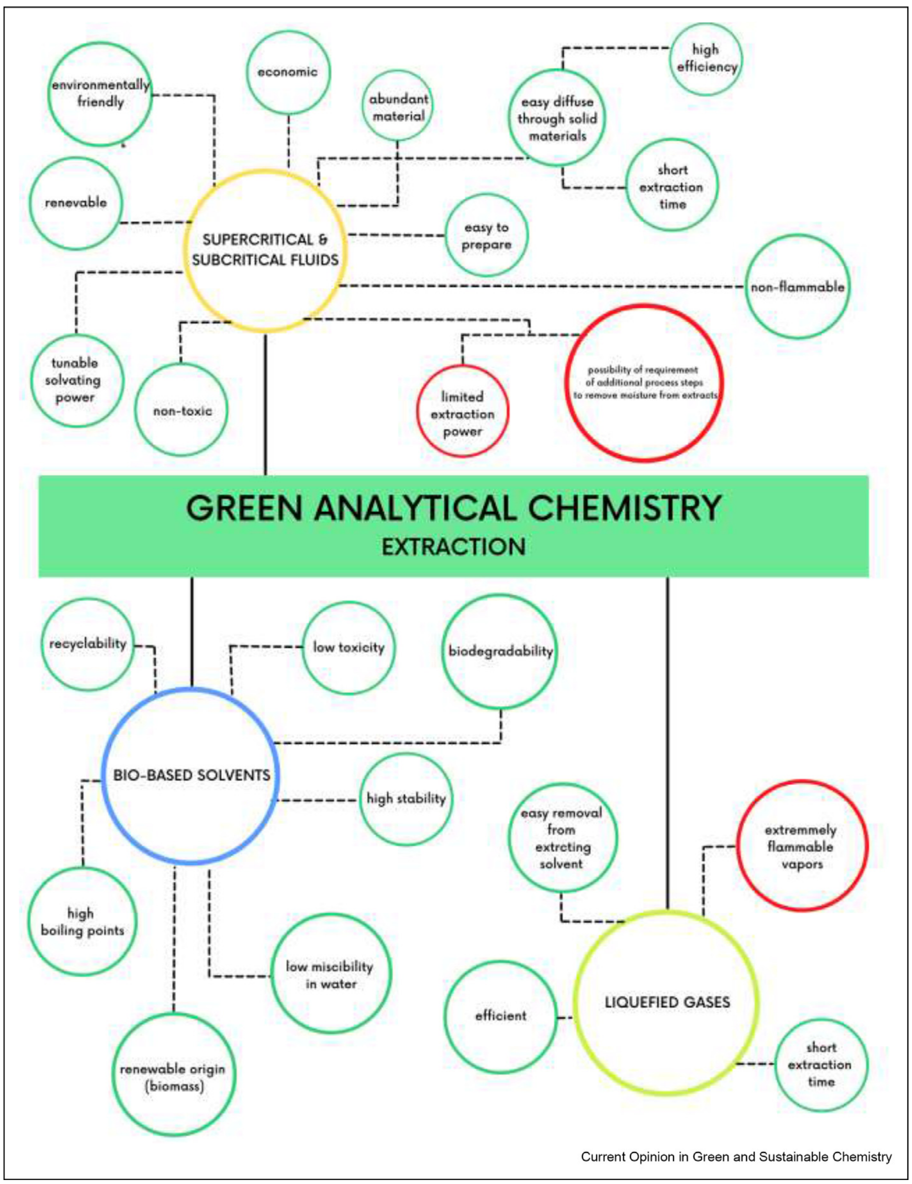
A new generation of green solvents applied in the extraction process

Organic solvents commonly used in analytical chemistry are obtained from crude oil, a nonrenewable source [2]. According to the GAC principles introduced by Namieśnik [3] and Anastas and Warner [4], an ideal "green" solvent for analytical applications should have low toxicity, low environmental impact, and low cost; they should be biodegradable, reusable, and easily obtained from renewable sources and should have high extraction ability and selectivity [2]. The requirements for green solvents are relatively demanding, but research on environmentally friendly solvents is advancing rapidly [5,6]. Over the last two decades, new environmentally friendly solvents — called "green" solvents — have been designed and introduced. Although green solvents that have recently appeared include, for example, switchable-hydrophilicity solvents [7] and deep eutectic solvents [8–11], we do not address them in this review because a great amount literature on them is already available. We focused instead on less discussed topics, namely bio-based solvents, supercritical fluids, and liquefied gases (Figure 1).

Supercritical and subcritical fluids

Supercritical fluids are substances that have their pressure and temperature above their critical points. In the supercritical region, the surface of demarcation between

Figure 1



Characteristic of green solvents used in extraction processes.

Table 1

Selected applications of supercritical/subcritical solvent extraction.

Solvent	Extraction technique	Target	Matrix	Extraction conditions			Extraction yield [%]	Ref.
				Sample to solvent ratio	Extraction time [min]	Temp. [°C]		
Subcritical water	SWE	Non-polar flavonoids (hesperidin, narirutin)	Defatted orange peel	1:24 (g/mL)	Not mentioned	150	21.0 ± 0.2	[21]
Subcritical water	SWE	TPC, TFC	Kiwifruit peels	1:50 (kg/L)	20	160	19.0 ± 0.1	[22]
Subcritical water	SWE	TPC	chestnut shells	1:10 (μg/mL)	30	220	9.01 ± 0.22	[23]
Subcritical water	SWE	Polysaccharides	Mushroom	–	15	150	11.35 ± 0.44	[24]
Subcritical water	SWE	Polysaccharides	Leaves	1:30 (g/mL)	16	1701	25.60 ± 0.22	[25]
Subcritical water	SWE	Polysaccharides	Leaves	1:25 (g/mL)	16.71	129.83	20.67 ± 0.10	[26]
Subcritical water	SWE	EO compounds	Leaves	0.025 g/mL	29	174	2.14 ± 0.03	[27]
Subcritical water	SWE	EO compounds	Leaves	1:5 (w/w)	25	156	2.66 ± 0.08	[28]
Supercritical CO_2; ethanol	SFE, PLE	SLs	Microalga	1:10 (g/mL)	495	50, 125	22.1 ± 0.1	[29]
Supercritical CO_2; 10% ethanol	SFE	TPC	Olive pomace	1:23 (g/mL)	–	60	8.80 ± 0.08	[30]
Supercritical CO_2; 2% ethanol	SFE	Cannabinoids	Cannabis seeds	–	120	40	9.7 ± 0.7	[31]

EO, essential oil; PLE, pressurized lipid extraction; SFE, supercritical fluid extraction; SLs, Microalgal saponifiable lipids; SWE, subcritical water extraction; TFC, total flavonoid content; TPC, total phenolic content.

gas and liquid disappears, causing the unique physicochemical properties of a supercritical fluid to appear between these two phases. Supercritical fluids have higher density in comparison to the gas phase and lower viscosity in comparison to the liquid phase. Their solvating power is tunable by small changes in the pressure and temperature [12]. These properties make them an excellent alternative to traditional organic solvents in liquid extraction.

Supercritical fluid extraction (SFE), in general, is characterized by shorter extraction time, better efficiency and selectivity and easy removal of the extracting solvent [13]. Moreover, it meets the requirements of GAC, since the extraction fluid in many instances is CO_2 which is non-flammable, nontoxic, abundant, renewable, easy to prepare and does not produce waste. SFE is widely used to extract natural compounds from food products as well as essential oils and drugs from natural sources. However, one of its drawbacks is its nonpolar nature; therefore, its use is limited mainly to the extraction of nonpolar and moderately polar compounds. To overcome this limitation, addition of a small volume of a polar cosolvent, such as methanol or ethanol, is necessary [8]. Unfortunately, this approach reduces the green nature of the method. Greener modifiers that enable both an increase in the polar character and the maintaining of a low environmental footprint are water [14] as well as vegetable and nut oils [15–18]; however, reaching the critical point for extraction can be more challenging.

Subcritical water extraction (SWE) is an effective alternative, above all, to classic extraction methods due to its environmentally friendly nature and faster process. It also requires much simpler equipment, which significantly reduces costs [19]. However, the extraction power of water is limited, and removing moisture from the extracts may require additional steps, such as evaporation, chemical dehydration, or precipitation [20]. Superheated water has gained popularity for the extraction of flavonoids and phenolic acids [21–23], polysaccharides [24–26], and essential oils [27,28] from fruits and vegetables (Table 1).

Liquefied gases

Another group of alternative extraction solvents that has recently caught the attention of researchers is that of liquefied gases, i.e., gases used in a liquid state at low pressures. Commonly used liquefied gases include n-butane, n-propane, dimethyl ether, trans-1,3,3,3-tetrafluoroprop-1-ene, and 1,1,2-tetrafluoroethane [32], which require only gentle pressure (<1 MPa) to remain in a liquid state and can be evaporated easily at low temperatures. Therefore, liquefied gas extraction can be carried out at room temperature with minimal energy consumption, and only a negligible residual

Table 2

Selected applications of liquefied gas extraction.

Solvent	Extraction technique	Target	Matrix	Extraction conditions			Extraction yield [%]	Ref.
				Sample to solvent ratio	Extraction time [min]	Temp [°C]		
Compressed n-propane	CPE	Tocopherol, phytosterol	Oil	–	80	80	5.56 ± 0.19	[36]
Compressed n-propane	CPE	Fatty acids	Sesame seed	1:8 (g/g)	50	60	27.4 ± 0.1	[37]
1,1,1,2-tetrafluorethane	LGE	Cinnamal, coumarin	Barks of cinnamon	–	75	18	17.34 ± 0.1	[41]
LPG	LGE	Terpenoids	Agroindustrial and forest waste	1:3 (g/g) per cycle	20	35	5.36 ± 0.01	[42]
lDME	LGE	Lipids	Microalgae	–	–	25	30.0 ± 0.1	[43]
lDME	LGE	Lipids	Wet biomass	–	10	20	46.1 ± 0.1	[44]
lDME	LGE	Lipids	Macroalgae	–	33	25	33 ± 0.1	[45]

CPE, compressed n-propane extraction; lDME, liquefied dimethyl; ether; LGE, liquefied gases extraction; LPG, liquefied petroleum gas.

Table 3

Bio-based solvents and their application in extraction.

Solvent	Extraction technique	Target	Matrix	Extraction conditions			Extraction yield [%]	Ref.
				Sample to solvent ratio	Extraction time [h]	Temp. [°C]		
D-limonene	Solid–liquid extraction	Rice bran oil	Rice bran	2:1 (wt/wt)	0.5	163	15.8 ± 0.2	[50]
hexane				3:1 (wt/wt)	2	69	18.9 ± 0.5	
				5:1 (wt/wt)	0.5		19.2 ± 0.2	
				2:1 (wt/wt)	2		21.1 ± 0.1	
				3:1 (wt/wt)	0.5		20.7 ± 0.1	
				5:1 (wt/wt)	2		24.5 ± 2.5	
					0.5		14.4 ± 1.1	
					2		17.0 ± 0.4	
					0.5		15.7 ± 0.1	
					2		18.4 ± 0.9	
					0.5		17.3 ± 0.5	
					2		18.4 ± 1.5	
D-limonene	Soxhlet extraction	Olive oil	Aglandau olive	Not mentioned	8	163	48.6 ± 2.2	[51]
n- hexane						69	40.3 ± 0.7	[51]
Solvent	Extraction technique	Target	Matrix	Extraction conditions			Extraction yield [%]	Ref.
				Sample (mass); solvent (volume)	Extraction time [min]	Temp. [°C]		
D-limonene	Soxhlet extraction	Microalgae oil	Microalgae	10 g;	8	176	38,4	[53]
α-pinene			chlorella vulgaris	300 mL		155	27.1	[53]
ρ-cymene						176	45.2	
n-hexane						69	26.2	
2-methyltetrahydrofuran	Solid–liquid extraction	Aromas	Hop cones	17 g;	2	80	16.6 ± 0.5	[66]
Hexane				175 mL	2	69	12.7 ± 0.7	
2-methyltetrahydrofuran	Soxhlet extraction	Aromas	Hop cones	30 g;	6	80	20.2 ± 0.3	[66]
Hexane				200 mL	6	69	17.9 ± 0.2	
Solvent	Extraction technique	Target	Matrix	Extraction conditions			Extraction yield [%]	Ref.
				Compound concentration; sample to solvent ratio	Extraction time [min]	Temp. [°C]		
2-methyltetrahydrofuran	Liquid–liquid extraction	p-hydroxybenzoic acid (HA),	Water samples	100 mg/l;	30	25	100	[48]
Cyclopentyl methyl ether		p-hydroxybenzoic acid (HA),		1:1 (v:v)			97.48 ± 0.14	
Ethyl acetate		p-hydroxybenzoic acid (HA)		100 mg/l;			96.94 ± 0.14	
2-methyltetrahydrofuran		Vanillic acid	Water samples	1:1 (v:v)	30	25	100	[48]

Table 3. (continued)

Cyclopentyl methyl ether		Vanillic acid					96.73 ± 0.67	
Ethyl acetate		Vanillic acid					97.71 ± 0.66	
2- methyltetrahydrofuran	Liquid–liquid extraction	Vanillin	Water samples	100 mg/l; 1:1 (v:v)	60	25	97.9 ± 0.14	[46]
cyclopentyl methyl ether							90.5 ± 0.25	
D-limonene							59.5 ± 1.83	
ethyl acetate							96.8 ± 0.05	
2-methyltetrahydrofuran	Liquid–liquid extraction	Vanillic acid	Water samples	100 mg/l; 1:1 (v:v)	60	25	94.0 ± 0.12	[46]
Cyclopentyl methyl ether							71.3 ± 0.10	
D-limonene							8.9 ± 0.09	
ethyl acetate							91.5 ± 0.12	

amount of solvent will remain in the extracts [33]. Compressed or liquefied gases have the ability to dissolve natural substances at relatively lower temperature in comparison to conventional organic solvents [34]. Despite these advantages, its use is still limited, however, liquefied gas poses a serious hazard due to the extremely flammable vapors. Among all the gases used, only tetrafluoroethane is nonflammable, but it is classified as a potent greenhouse gas. Moreover, it requires a special design for extraction [35], which has already been commercialized. This extracting device has no pump; it has a compressor that reduces energy consumption and the cost of maintenance.

Thus far, this technique has been used successfully to extract a wide range of compounds, from hydrocarbons to lipids (Table 2). For example, compressed n-propane was applied as an extraction solvent for lipids from the Perilla plant [36] and for fatty acids and antioxidants from sesame seeds [37]; n-butane was used to extract fatty acids from dried carrots and sunflower seeds [33], and dimethyl ether for the isolation of lipids from a single-celled alga [38,39] and hydrocarbons from a green microalga [40]; 1,1,1,2-tetrafluoroethane was used to extract essential oil from Ceylon cinnamon tree [41]; and liquefied petroleum gas (a mixture of isomers of propane and butane) was employed to extract terpenes from agro-industrial and forest waste [42]. All of the subsequent studies demonstrated similar characteristics, indicating that extraction by liquefied gases provides satisfactory extraction yields in relation to classical organic solvents. Moreover, due to easy separation after extraction, the stripping step was easily omitted. A good example showing a comparison of the classical lipid extraction methodology with extraction by compressed n-propane can be found in the work of Silva et al. [36].

Bio-based solvents

Bio-based solvents are defined as solvents that are of renewable origin obtained by chemical or biochemical transformations of a wide range of biomass sources, such as (i) agricultural crops rich in carbohydrates (corn, wheat and sugar beets), (ii) forest products (e.g. wood), (iii) aquatic biomass (e.g. algae), and (iv) waste materials [8,46]. They can be obtained through carbohydrate fermentation, extraction of vegetable oils and steam distillation of wood. The products of these processes include a wide range of compounds, such as alcohols, esters, glycerols, terpenes, furfurals, and furans, some of which have the potential to be applied in green extraction processes due to their low miscibility with water, relatively high boiling point, and enhanced stability in comparison with the other solvents, as well as their low toxicity, biodegradability under normal environmental conditions, and solvent recyclability [47,48]. However, the number of

Table 4

Comparison of selected green solvents used in extraction processes.

	Supercritical fluids Subcritical fluids	Liquefied gases	Bio-based solvents
Examples	Carbon dioxide, water	n-butane, n-propane, dimethyl ether Trans-1,3,3,3-tetrafluoroprop-1-ene, 1,1,2-tetrafluoroethane	Limonene, α-pinene, β-pinene p-cymene, glycerol
Toxicity	Low	Significantly higher than the others	Low
Flammability	Low	High	Relatively low
Advantages	- Environmentally friendly nature - Does not produce waste - Diffuse easily through solid materials - Short extraction time - Efficient - Economic - Abundant - Renewable - Easy to prepare - Tunable solvating power - Easy removal from extracting solvent	- Easy removal from extracting solvent - Efficient - Short extraction time - Minimal energy consumption required to use as an extractant	- Renewable origin (biomass) - Low miscibility in water - High stability - Biodegradability - Recyclability
Disadvantages	- Possibility of requiring additional steps to remove moisture from extracts - Limited extraction power - Nonpolar nature of CO_2.	- Serious hazard due to extremely flammable vapors	- Complicated sourcing processes
Polarity	Carbon dioxide – low polarity Water – polar	Low polarity	Low polarity
Applications	- Extraction of natural compounds from food products - Extraction of essential oils and drugs from natural sources	- Extraction of fatty acids and antioxidants from food products - Extraction of essential oil from plants - Extraction of terpenes from agro-industrial and forest waste	- Extraction of natural compounds from food products - Extraction of lipids inter alia from microalgae, fly larvae, seeds - Extraction of aromas from hop pellets

analytical procedures that utilize bio-solvents is still relatively low.

One of the most frequently used greener alternative solvents is D-limonene, extracted from the peels of citrus fruits mainly via steam-distillation or centrifugal separation [49]. The first report on the use of this terpene for extraction was published by Mamidipally and Liu in 2004. In this case, the extraction of oil from rice bran samples was carried out in a comparison with the same extraction using hexane. The performance of the extraction and quality of the crude oil extracted were found to be comparable [50]. Similar or even better results were also obtained in the extraction of fats and oils from olive seeds [51], lipids from salmon tissue [52], oil from microalgae [53], and fatty acids from grape seeds [54]. Moreover, D-limonene has been successfully employed in place of other hazardous petroleum solvents, such as toluene [46] and chlorinated organic solvents [55].

A review of the literature showed that not only D-limonene but also other terpenes, such as α-pinene, β-pinene, and p-cymene, have also been used as a valuable renewable alternative in natural products extraction from a variety of feedstocks [56–59]. Another bio-based solvent used for analytical purposes is 2-methyltetrahydrofuran (2-MeTHF), obtained by hydrogenation or hydration of furfural derived from corn cobs or sugar cane. The compound 2-MeTHF was found to be a suitable alternative for hazardous solvents such as tetrahydrofuran, toluene, dichloromethane, hexane, diethyl ether, and ethyl acetate [48,60]. Due to its low solubility in water, the main area of its application was the extraction of lipids inter alia from microalgae [61,62], fly larvae [63], and some seeds [64,65]. More recently, it was used in a solid–liquid extraction to obtain aromas from hop pellets, and its use resulted in higher extraction yields and showed faster kinetics than hexane [66]. Further, an investigation aimed at discerning the best bio-solvent among cyclopentyl methyl ether (CPME), 2-MeTHF, and D-limonene in the liquid–liquid extraction of nine phenolic acids compounds from an aqueous matrix showed 2-MeTHF to have the best potential for extraction, providing very high recoveries in some cases (equal to or slightly lower than 100%) [48]. Similar results were found in a paper focused on a comparison of the extraction performances of hydrophobic solvents (2-MeTHF, CPME, D-limonene and three hydrophobic deep eutectic solvents) and ethyl acetate to isolate vanillin and vanillic acid from aqueous samples [47]. In that case, the highest recoveries were obtained using 2-MeTHF (91.96–95.37%). Apart from the above-mentioned solvents, soybean oil methyl esters [67,68], CPME [61,69], polyethylene glycol, and diethyl carbonate [70,71] have also proved to be efficient and sustainable for obtaining compounds of interest from different matrices. Table 3 summarizes bio-based solvents and applications that have thus far been applied for the extraction of different analytes.

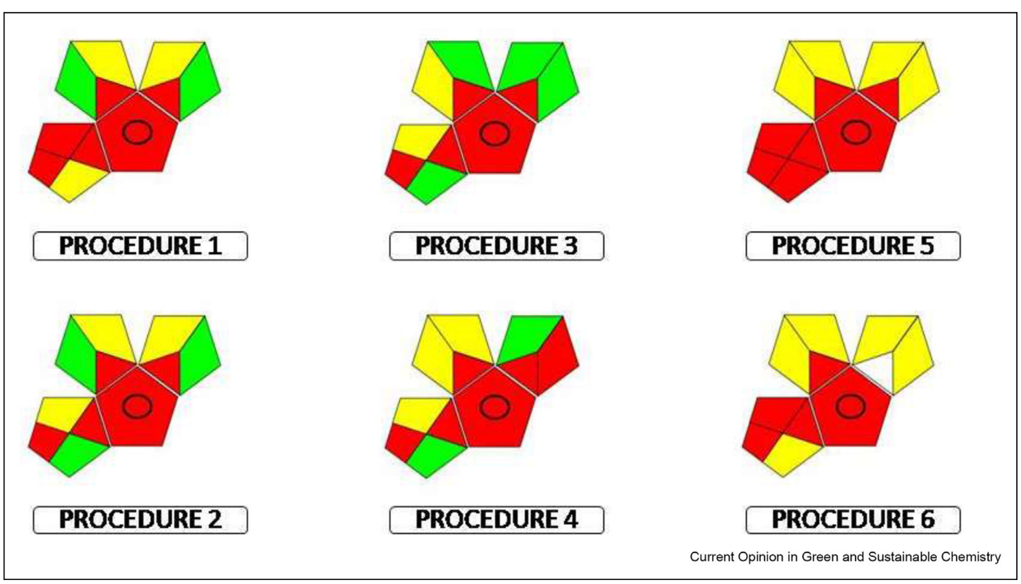
Conclusions

GAC has compelled analysts to find and introduce new extraction techniques based on miniaturized methods to reduce or even eliminate the use of harmful organic solvents in order to significantly decrease the adverse environmental effect of chemical analyses. At the same time, the finding and applying of a new generation of green solvents which can be used in extraction process has attracted extensive attention. Besides being environmentally friendly, such solvents should possess other properties, such as custom tunability, ease of preparation, low volatility, high selectivity, low cost, and biocompatibility (Table 4). The application of bio-based solvents is promising since they are of renewable origin and can be obtained from many different waste parts of plants.

Although it seems that due to the wide range of analyte polarity no universal solvent exists that can be used in a universal extraction process, if we manage to replace conventional solvents (hexane, toluene, and chloroform) with a suitable green solvent, we can achieve a significant reduction of analysis costs as well as a reduction of the negative impact on people and the environment.

Water, as the most important and readily available solvent, should be more considered in this regard. Water is highly polar and does not seem to be a proper extracting

Figure 2



GAPI assessment of the green profile of the evaluated procedures for the determination of fatty acids in food samples using supercritical fluids [72,73] (Procedure 1, Procedure 2), liquefied gases [32,33] (Procedure 3, Procedure 4) and bio-based solvents [50,51] (Procedure 5, Procedure 6).

solvent for organic analytes; however, this is true only under ambient conditions. Changing its temperature at putting it under higher pressures can heavily affect its dielectric constant and therefore its solvation power, such that it will be able to solubilize nonpolar molecules as well. This is perfectly shown by comparison of the green character of analytical procedures based on bio-based solvents, supercritical fluids, and liquefied gases using the GAPI tool (Figure 2).

Declaration of competing interest

There are no conflicts to declare.

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