Electronic Supplementary Material (ESI) for Analyst.

Supplementary Material

Greener Chemistry in Analytical Sciences - from Green Solvents to Applications in Complex Matrices. Current Challenges and Future Perspectives: A Critical Review

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Figure and Tables

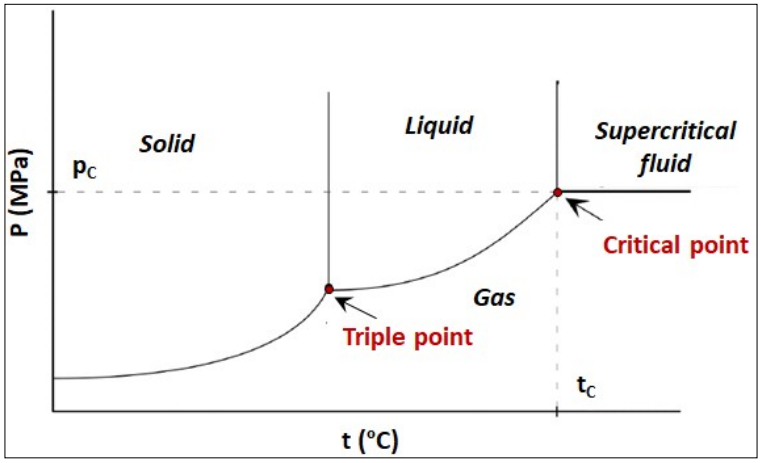

Fig. S1 Phase diagram of a pure single-component system.

Table S1 Parameters for the NEMI diagram.

Principle	Description	Color
Persistent, bioaccumulative, toxic chemicals are used	Yes	White
	No	Green
Hazardous chemicals are used	Yes	White
	No	Green
The pH value of the sample is in the range of 2–12	Yes	Green
	No	White
The amount of generated waste does exceed 50 g	Yes	White
	No	Green

Table S2 The penalty points (PPs) to calculate analytical Eco-Scale.

Reagents			Total PP
	Amount	<10 mL (g)	1
		10–100 mL (g)	2
		>100 mL (g)	3
	Hazard	None	0
		Less severe hazard	1
		More severe hazard	2
			Amount PP x Hazard PP
Instruments	Energy	<0.1 kWh per sample	0
		<1.5 kWh per sample	1
		>1.5 kWh per sample	2
	Occupational hazard		0
			3
	Waste	None	0
		<1 mL (g)	1
		1–10 mL (g)	3
		>10 mL (g)	5
		Recycling	0
		Degradation	1
		Passivation	2
		No treatment	3

Table S3 Green Analytical Procedure Index parameters description.

Category	Description	Color
Sample Collection (1)	In-line	Green
	On-line or at-line	Yellow
	Off-line	red
Sample Preservation (2)	None	Green
	Chemical or physical	Yellow
	Physico-chemical	Red
Sample Transport (3)	None	Green
	Required	Yellow
	-	Red
Sample Storage (4)	None	Green

	Under normal conditions	Yellow
	Under special conditions	Red
Type of method: direct or indirect (5)	No sample preparation	Green
	Simple procedures, eg. filtration, decantation	Yellow
	Extraction required	Red
The scale of extraction (6)	Nano-extraction	Green
	Micro-extraction	Yellow
	Macro-extraction	Red
Solvents/reagents used (7)	Solvent-free methods	Green
	Green solvents/reagents used	Yellow
	Non-green solvents/reagents used	Red
Additional treatments (8)	None	Green
	Simple treatments (clean up, solvent removal)	Yellow
	Advanced treatments	Red
Reagent and solvents: Amount (9)	<10 mL (< 10 g)	Green
	10–100 mL (10–100 g)	Yellow
	>100 mL (> 100 g)	Red
Reagent and solvents: Health hazard (10)	Slightly toxic, slight irritant; NFPA health hazard score = 0 or 1.	Green
	Moderately toxic; could cause temporary incapacitation; NFPA = 2 or 3.	Yellow
	Serious injury on short-term exposure; known or suspected small animal carcinogen; NFPA = 4.	Red
Reagents and solvents: Safety hazard (11)	The highest NFPA flammability or instability score of 0 or 1. No special hazards.	Green
	Highest NFPA flammability or instability score of 2 or 3, or a special hazard is used.	Yellow
	Highest NFPA flammability or instability score of 4.	Red
Instrumentation: Energy (12)	≤0.1 kWh per sample	Green
	≤1.5 kWh per sample	Yellow
	>1.5 kWh per sample	Red
Instrumentation: Occupational hazard (13)	Hermetic sealing of analytical process	Green
	-	Yellow
	Emission of vapours to the atmosphere	Red
Waste (14)	<1 mL (< 1 g)	Green
	1–10 mL (1–10 g)	Yellow
	>10 mL (< 10 g)	Red
Waste treatment (15)	Recycling	Green
	Degradation, passivation	Yellow
	No treatment	Red
Circle in the middle of GAPI: Procedure for qualification and quantification No circle in the middle of GAPI: Procedure only for qualification		

Table S4 AGREE tool parameters description.

Category	Description	Score
1. Sample pretreatment activities	Remote sensing without sample damage	1.00
	Remote sensing with little physical damage	0.95
	Noninvasive analysis	0.90
	In-field sampling and direct analysis	0.85
	In-field sampling and on-line analysis	0.78
	On-line analysis	0.70
	At-line analysis	0.60
	Off-line analysis	0.48
	External sample pre-and treatment and batch analysis (reduced number of steps)	0.30
	External sample pre-and treatment and batch analysis (a large number of steps)	0.00
2. Type of analysis (sample size mg or µL)	Ultramicroanalysis (<1)	1.00
	Microanalysis (1–10)	= -0.142 × ln (amount of sample in g or mL) + 0.65
	Semimicroanalysis (10–100)	
	Macroanalysis (>100)	
3. Instrumental Position	In-line	1.00
	On-line	0.66
	At-line	0.33
	Off-line	0.00
4. Number of steps in analytical process	Three or fewer 1.00	1.00
	Four	0.80
	Five	0.60
	Six	0.40
	Seven	0.20
	Eight or more	0.00
5. Level of automation and miniaturization	automatic, miniaturized	1.00
	semi-automatic, miniaturized	0.75
	manual, miniaturized	0.50
	automatic, not miniaturized	0.50
	semi-automatic, not miniaturized	0.25
	manual, not miniaturized	0.00
6. Derivatization status	No derivatization applied	1.00
	Derivatization applied	= $DA_1 \times DA_2 \times DA_3 \times \ldots \times DA_n$ where DA_i is the score corresponding to the particular derivatization agent.
7. Amount of waste	0.1 g (mL)	1.00
	10 g (mL)	0.40
	25 g (mL)	0.25
	100 g (mL)	0.10
	Any other amount	= -0.134 × ln (amount of waste in g or mL) + 0.6946
8. Number of analytes per hour	1	0.00
	10	0.50
	50	0.90

	70	1.00
	Any other number of analytes	= 0.2429 × ln (number of analytes determined in 1 h) - 0.0517
9. Amount of energy per sample	<0.1 kWh 1.0	1.00
	0.1–1.5 kWh	0.50
	>1.5 kWh	0.00
10. Condition (toxic reagents)	No toxic reagents or solvents are used	1.00
	Toxic reagents or solvents are used	= -0.156 × ln (amount of reagent or solvent in g or mL) + 0.5898
11. Condition (reagents obtained from renewable source)	No reagents are applied, or all are from bio-based sources	1.00
	If some of them are derived from bio-based sources, while others are not	0.50
	None of the reagents originates from bio-based sources	0.00
12. Threats (The threats shouldn't be toxic to aquatic life, bioaccumulative, persistent, highly flammable, highly oxidizable, explosive or corrosive)	All threats avoided 1.0	1.00
	One threat present	0.80
	Two threats present	0.60
	Three threats present	0.40
	Four threats present	0.20
	Five or more threats present	0.00

Table S5 Comprehensive green analytical procedure index parameters description.

Category	Description	Color
Yield (I)	>89%	Green
	70–89%	Yellow
	<70%	red
Temperature/time (II)	Room temperature, <1 h	Green
	Room temperature, > 1 h Heating, < 1 h Cooling to 0°C	Yellow
	Heating, > 1 h Cooling < 0 °C	Red
Relation to the green economy Number of rules met (III)	5-6	Green
	3-4	Yellow
	1-2	Red
Reagents and solvents Health hazard (IVa)	Slightly toxic, slightly irritant; NFPA health hazard score is 0 or 1	Green
	Moderately toxic; could cause temporary incapacitation; NFPA = 2 or 3	Yellow
	Serious injury on short-term exposure; known or suspected small animal carcinogen; NFPA = 4	Red
Reagents and solvents Safety hazard (IVb)	Highest NFPA flammability, instability score of 0 or 1. No special hazards	Green

	Highest NFPA flammability or instability score is 2 or 3, or a special hazard is involved	Yellow
	Highest NFPA flammability or instability score is 4	Red
Instrumentation Technical setup (Va)	Common setup	Green
	Additional setups/semi-advanced instruments used	Yellow
	Pressure equipment >1 atm; glove box	Red
Instrumentation Energy (Vb)	≤0.1 kW h per sample	Green
	≤1.5 kW h per sample	Yellow
	>1.5 kW h per sample	Red
Instrumentation Occupational hazard (Vc)	Hermetization of the analytical process	Green
	-	Yellow
	Emission of vapors to the atmosphere	Red
Workup and purification of the end product (VIa)	None or simple processes	Green
	Application of standard purification techniques	Yellow
	Application of advanced purification techniques	Red
Purity (VIb)	>98%	Green
	97–98%	Yellow
	<97%	Red

Table S6 AGREEprep tool parameters description.

Category	Description	Score
Criterion 1. Favor in situ sample preparation	*In-line/In situ*	1.00
	On-line/In situ	0.66
	On-site	0.33
	Ex situ	0.00
Criterion 2. Use safer solvents and reagents	Solvent-free and reagent-less sample preparation procedures	1.00
	>10mL or 10 g of hazardous solvents and reagents	0.00
	Any other amount	= -0.145 × ln (amount of hazardous substances in g or mL) + 0.3333
Criterion 3. Target sustainable, reusable, and renewable materials	Only sustainable and renewable materials are used several times	1.00
	> 75% of reagents and materials are sustainable or renewable	0.75
	50-75% of reagents and materials are sustainable or renewable and can only be used once	0.50
	Materials are not sustainable or renewable and are used several times	0.50
	25-50% of reagents and materials are sustainable or renewable	0.25
	< 25% of reagents and materials are sustainable or renewable and can only be used once	0.00
Criterion 4. Minimize waste	<0.1 g (mL)	1.00
	> 50.0 g (mL)	0.00
	Any other amount	= -0.161 × ln (sample mass or

		volume in g or mL) + 0.6295
Criterion 5. Minimize sample, chemical and material amounts	Any amount	= -0.145 × ln (sample mass or volume in g or mL) + 0.6667
Criterion 6. Maximize sample throughput	Any amount	= 0.2354 × ln (number of prepared samples per hour)
Criterion 7. Integrate steps and promote automation	≤2 steps	1.00
	3 steps	0.75
	4 steps	0.50
	5 steps	0.25
	≥6 steps	0.00
	fully automated systems	1.00
	semi-automated systems	0.50
	manual systems	0.25
	The final score for principle 7 is the product of both sub-scores.	
Criterion 8. Minimize energy consumption	<10 Wh per sample	1.00
	between 10 and 500 Wh per sample	= -0.256 × ln (Wh/sample) + 1.5886
	>500 Wh per sample	0.00
Criterion 9. Choose the greenest possible post-sample preparation configuration for analysis	Simple, readily available detection (information technology and communications equipment such as smartphones, desktop scanners, etc.)	1.00
	Molecular optical spectroscopic techniques (e.g. UV-vis spectrophotometry, fluorimetry, chemiluminescence, etc.), surface analysis techniques, voltammetry, potentiometry	0.75
	Gas chromatography with non-mass spectrometry (MS) detection, atomic absorption spectroscopy, capillary electrophoresis	0.50
	Liquid chromatography (due to mobile phase consumption, usually being or containing organic solvents), gas chromatography with quadrupole mass spectrometric detection	0.25
	Advanced mass spectrometry techniques (due to high energetic requirements), inductively coupled plasma-optical emission spectroscopy (ICP-OES), ICP-MS (due to noble gas consumption)	0.00
Criterion 10. Ensure safe procedures for the operator	no hazards	1.00
	1 hazard	0.75
	2 hazards	0.50
	3 hazards	0.25
	4 or more hazards	0.00