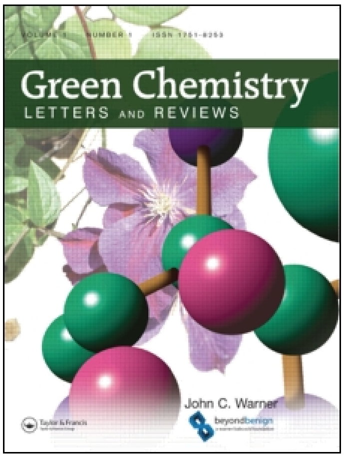

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"Green Star": a holistic Green Chemistry metric for evaluation of teaching laboratory experiments

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This paper presents a new semi-quantitative metric, Green Star (GS), for evaluation of the global greenness of chemical reactions used in teaching laboratories. Its purpose is to help choose the more acceptable reactions for implementing Green Chemistry (GC) and to identify suitable modifications of protocols to improve the greenness of the chemistry practiced by students. GS considers globally, in principle, all the Twelve Principles of GC. The metric consists in the evaluation of the greenness of the reaction for each principle by pre-defined criteria, followed by graphical representation of the results in an Excel radar chart – the fuller the chart, the higher degree of greenness. To illustrate the construction and the scope of the metric, a case study is presented – the iron(II) oxalate dihydrate synthesis performed under several sets of conditions to pursue the implementation of greenness.

Keywords: Green Star; green metrics; green synthesis; reaction greenness improvement; Green Chemistry education

Introduction

The contribution of chemistry for pursuing sustainability is proactively performed by Green Chemistry (GC, in broad sense, including Green Chemical Engineering) and therefore chemistry should nowadays be taught under this new posture. The basic objectives of GC were defined in the Twelve Principles of GC, with a qualitative nature, defined by Anastas and Warner (*1*) and presented in Table 1.

To instill in students the new mentality for doing chemistry constituted by GC, the experimental study of chemistry must use new or modified experiments, especially synthesis experiments, with an intentional objective of increasing their greenness. For this purpose, we have asked some pre-service teachers to perform synthesis experiments as described in the literature (traditional synthesis) and then challenged them to modify the protocols to obtain greener synthetic procedures ("revised synthesis" for GC). The analysis, construction, and implementation of protocols to reach this purpose press the students to feel what GC is – and that it has to be pursued with a purposeful determination.

In this context, it is necessary to use metrics for quick evaluation of greenness to allow the comparison of traditional and revised procedures. Greenness is a complex feature that involves several different aspects of the compounds involved in the reactions and the reactions themselves – their safety, health, and environmental effects, etc. For the purpose of comparisons, mass metrics (*2–6*) (addressed to evaluate the accomplishment of the first two GC principles) and environmental metrics (*7,8*) (addressed to measure the environmental benignness of the compounds and reactions, contemplated in the other principles) have to be used. However, the use of the simple metrics that have been introduced so far is not practical, as the variables to be considered in greenness are numerous, the number of metrics of both above types is large, their definition and calculation are complex, and the choice of the more suitable may be subjective and debatable. Therefore, metrics of larger scope addressing all the Twelve Principles of GC (*1*) in parallel are desirable.

The objective of this paper is to describe a new holistic metric developed for comparative evaluation of the greenness of reactions in undergraduate teaching laboratories, which we called Green Star (GS). GS was designed to address simultaneously all the principles of GC applicable in each situation.

To illustrate the construction of GS, the iron(II) oxalate dihydrate synthesis, performed in the laboratory under several sets of conditions to pursue increased greenness, is presented as a case study where GS is used for comparison of alternative procedures and identification of the most green. The new metric was evaluated against literature GC mass metrics.

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Table 1. The Twelve Principles of GC.

GC principle	Description
P1 – prevention	It is better to prevent waste than to treat or clean up waste after it has been created.
P2 – atom economy	Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
P3 – less hazardous chemical synthesis	Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
P4 – designing safer chemicals	Chemical products should be designed to effect their desired function while minimizing their toxicity.
P5 – safer solvents and auxiliary substances	The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
P6 – increase energy efficiency	Energy requirements of chemical processes should be recognized for their environmental and economic impacts should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
P7 – use renewable feedstocks	A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
P8 – reduce derivatives	Unnecessary derivatization (use of blocking groups, protection/deprotection, and temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
P9 – catalysts	Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
P10 – design for degradation	Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
P11 – real-time analysis for pollution prevention	Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
P12 – safer chemistry for accident prevention	Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents including releases, explosions, and fires.

The basic idea of Green Star (GS)

The Twelve Principles of GC are qualitative prescriptions and should be considered together in the evaluation of the greenness, because alterations of the conditions for executing the reactions may have different consequences with respect to different principles – the greenness may improve with reference to some of them but worsen with reference to others (*9*).

The basic idea of GS is to construct a star with a number of corners equal to the number of principles used for the evaluation of the synthesis reaction, all the 12 or only some if the remaining are not applicable, each corner with length proportional to the degree of accomplishment of the corresponding principle – a semi-quantitative view of the global greenness of the reaction can then be obtained by looking at the star and appreciating its area: the larger the area, the greener is the reaction.

Construction of Green Star (GS)

The construction of the metric consists in evaluating the greenness of the reaction for each principle (in a scale from 1 to 3, maximum value of greenness), by pre-defined criteria, followed by representing the

Table 2. Risks to human health and environment of substances involved.

Risks	Hazard symbols	Score (S)
Health	C – corrosive T – toxic T+ – very toxic	3
	Xi – irritant Xn – harmful	2
	No indication	1
Environment	N – dangerous for the environment	3
	No indication	1

Table 3. Risks of potential chemical accident due to substances involved.

Risks	Hazards symbols	Score (S)
Health	C – corrosive T – toxic T+ – very toxic	3
	Xi – irritant Xn – harmful	2
	No indication	1
Flammability	F – highly flammable F+ – extremely flammable	3
	No indication	1
Reactivity	E – explosive	3
	O – oxidizing agent	3
	No indication	1

Table 4. Degradability and renewability characteristics of substances involved.

Characteristics	Criteria	Score (S)
Degradability	Not degradable and may not be treated to render the substances degradable to innocuous products	3
	Not degradable but may be treated to render the substances degradable to innocuous products	2
	Degradable and breakable to innocuous products	1
Renewability	Not renewable	3
	Renewable	1

results in an Excel radar chart – the fuller the chart, the higher degree of greenness.

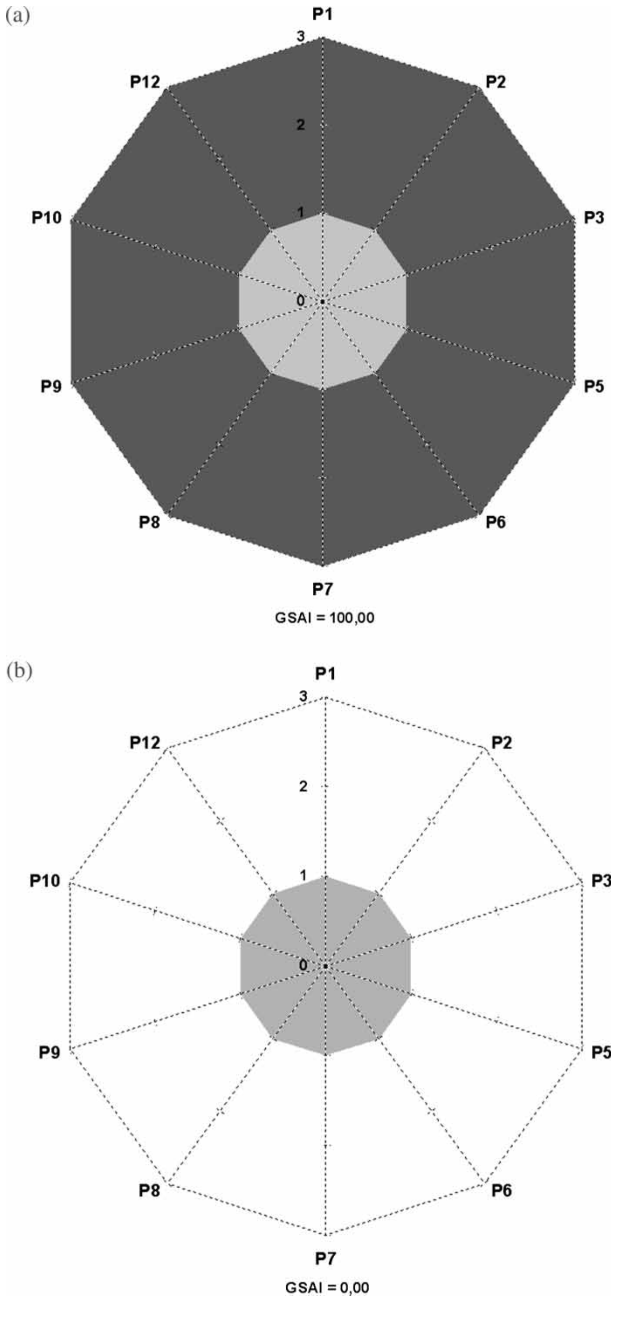
The construction of the GS for a synthesis experiment begins by examining its protocol and making an inventory of all the substances involved: feedstock, products, by-products, auxiliary substances (catalytic reagents, solvents, separation agents, etc.) and, if possible, wastes. Next, to evaluate risks to human health and the environment and of potential chemical accident, the hazard symbols for each substance are collected, as well as information to identify whether the substances are renewable and break down into innocuous degradation products. According to this information, every substance is then classified in a scale from 1 to 3 by criteria chosen to be easy to use

Table 5. Criteria and scores (S) to construct the GS.

GC principle	Criteria	S
P1 – prevention	Waste is innocuous (S = 1, Table 1)	3
	Waste involves a moderate risk to human health and environment (S = 2, Table 1, for at least one substance)	2
	Waste involves a high risk to human health and environment (S = 3, Table 1, for at least one substance)	1
P2 – atom economy	Reactions without excess of reagents (<10%) and without formation of by-products	3
	Reactions without excess of reagents (<10%) and with formation of by-products	2
	Reactions with excess of reagents (>10%) and without formation of by-products	2
	Reactions with excess of reagents (>10%) and with formation of by-products	1
P3 – less hazardous chemical synthesis	All substances involved are innocuous (S = 1, Table 1)	3
	Substances involved have a moderate risk to human health and environment (S = 2, Table 1, for at least one substance)	2
	At least one substance involved has a high risk to human health and environment (S = 3, Table 1)	1
P5 – safer solvents and auxiliary substances	Solvents and auxiliary substances are not used, but if used are innocuous (S = 1, Table 1)	3
	Solvents or/and auxiliary substances are used but have a moderate risk to human health and environment (S = 2, Table 1, for at least one substance)	2
	At least one solvent or auxiliary substance has a high risk to human health and environment (S = 3, Table 1)	1
P6 – increase energy efficiency	Room temperature and pressure	3
	Room pressure and temperature between 0 and 100°C when cooling or heating is needed	2
	Pressure different from room pressure and/or temperature >100°C or less than 0°C	1
P7 – use renewable feedstocks	All substances involved are renewable (S = 1, Table 3)	3
	At least one substance involved is renewable, water is not considered (S = 1, Table 3)	2
	None of substances involved are renewable, water is not considered S = 3, Table 3)	1
P8 – reduce derivatives	Derivatizations are not used	3
	Only one derivatization or similar operation is used	2
	More than one derivatization or similar operations are used	1
P9 – catalysts	Catalysts are not used and if used are innocuous (S = 1, Table 1)	3
	Catalysts are used but have a moderate risk to human health and environment (S = 2, Table 1)	2
	Catalysts are used and have a high risk to human health and environment (S = 3, Table 1)	1
P10 – design for degradation	All substances are degradable and break down to innocuous products (S = 1, Table 3)	3
	All substances not degradable may be treated to render them degradable to innocuous products (S = 2, Table 3)	2
	At least one substance is not degradable nor may be treated to render it degradable to innocuous products (S = 3, Table 3)	1
P12 – safer chemistry for accident prevention	Substances used have a low risk to cause chemical accidents (S = 1, Table 2)	3
	Substances used have a moderate risk to cause chemical accidents (S = 2, Table 2, for at least one substance)	2
	Substances used have a high risk to cause chemical accidents (S = 3,Table 2, for at least one substance)	1

(see Tables 2–4). For sake of safety, in case of lack of consistency of some of the information gathered about any of the items evaluated, the chosen value is that which most penalizes the item. The GS is then constructed giving the score 1, 2, or 3 to each of the Twelve Principles, following the criteria in Table 5.

For maximum greenness, the score will be 3 for every principle and the area of the GS will be the fullest as presented in Figure 1(a). On the other hand, when the greenness is minimum, all the scores will be 1 and the area of the GS will be minimum (zero, see below), as presented in Figure 1(b). These two GS have only 10 corners, as the fourth and 11th principles were not considered, because teaching experiments do not usually include the preparation of new products (moreover, when dealing with chemical experiments that do not refer to synthesis, the GS will be reduced to six corners as the second, third, eighth, and ninth principles are not applicable).



In certain cases, when comparing GS for evaluation of relative greenness of alternative protocols, it may be difficult to evaluate which has a larger green area by visual inspection. To overcome this difficulty, a Green Star Area Index (GSAI) was included in the GS (see Appendix 1). The index is calculated as the ratio of the area of the GS to the area of the GS of maximum greenness, expressed as a percentage ($100 \times$ area of the GS/area of GS of maximum greenness) and therefore varies between GSAI $= 100$ (maximum greenness) and GSAI $= 0$.

To illustrate the use of GS the iron(II) oxalate dihydrate synthesis is presented.

Synthesis of iron(II) oxalate dihydrate

A number of experiments were initially performed following a published protocol (*10*) in which the product was prepared from iron(II) sulfate heptahydrate and oxalic acid dihydrate. This protocol proposed a large excess of oxalic acid, the use of sulfuric acid to acidify the iron(II) sulfate solution, and heating the mixture at temperature near the boiling point. To increase the greenness, the experiment was optimized by looking for: (1) more benign reagents – sulfuric acid was substituted by ascorbic acid to reduce iron(III), eventually formed, to iron(II); (2) energy efficiency – the experiments were performed at room temperature; and (3) stoichiometry – instead of large excess of oxalic acid, proportions close to stoichiometry were used to reduce waste (these also favor the metrics of incorporation of atoms into the product).

For each experiment, the GS was constructed from the data and several quantitative mass metrics were calculated (*2–6*): yield, E-factor, mass intensity (MI), atom economy (AE), atom utilization (AU), relative mass efficiency (RME), and iron element efficiency (FeEE). The results were used to compare the response of GS and the other metrics when greenness increases.

Experimental procedure

First synthesis – traditional

A 5.0 g (18.0 mM) sample of iron(II) sulfate heptahydrate was dissolved in 25 mL of deionized water (*10*).

The solution was acidified with 0.5 mL of 2 mol L^{-1} sulfuric acid. A solution of 4.0 g (31.7 mM) of oxalic acid dihydrate in 25 mL of deionized water was added and the mixture stirred, heated to the boiling temperature, and left to settle at room temperature. The yellow precipitate of iron(II) oxalate dihydrate was washed with hot water, suction filtered, washed again with hot water, and allowed to dry in the filter for about 10 minutes before being placed in a desiccator for about a week. An excess of about 76% of oxalic acid was prescribed in this protocol (*10*). Three experiments were performed and a 92% yield was obtained (92.0 ± 1.9%, standard deviation).

The experiment was optimized in alternative procedures.

Second synthesis – first green improvement

To look for more benign reagents, 1 g (5.7 mM) sample of ascorbic acid was dissolved in 25 mL of deionized water and the iron(II) sulfate heptahydrate was dissolved in this solution (no sulfuric acid was used). After about 4 minutes, the oxalic acid was added. The mixture was heated to the boiling temperature and the initial protocol was then followed. Three experiments were performed with an excess 76% of oxalic acid and a 94% yield was obtained (93.6 ± 0.3%).

Third synthesis – second green improvement

To increase the energy efficiency, experiments were performed at room temperature using this last protocol (it was verified that the solubility of iron(II) oxalate dihydrate increases with temperature). A 96% yield was obtained (three experiments, 96.1 ± 0.2%).

Fourth synthesis – third green improvement

To look for proportions closer to stoichiometric, three experiments were performed at room temperature, with an excess of only 4% of oxalic acid. A 88% yield was obtained (three experiments, 87.5 ± 1.2%).

To characterize the product, IR spectra (Mattson ATI Genesis Series FTIR, KBr pellets) were obtained for samples prepared by each protocol and for known samples (Aldrich #307726). It was verified that the IR spectra were similar.

Green Star (GS)

From data on properties, as referred previously (see discussion about Tables 2–4), the risks for human health and for the environment of all the substances involved were collected in Table 6, from which the scores to construct the GS were obtained by the criteria in Table 5. The results are presented in Table 7.

The GS of the experiments performed under different conditions are presented in Figure 2. In this GS*n* denotes the GS for synthesis number ($n = 1$–4, see above). The visual comparison of the four GS shows that:

(1) When ascorbic acid was used instead of sulfuric acid (second synthesis), the scores for the third, the fifth, and the 12th principles increased, because ascorbic acid is less hazardous than sulfuric acid (Table 6 and 7); as a result the green area of GS increased, GS2 is greener than GS1 (Figure 2).
(2) When the experiments were performed at room temperature (third synthesis), the energy efficiency was increased and the score for the sixth principle increased (Table 6 and 7); as a result the green area of GS increased, GS3 is greener than GS2 (Figure 2).
(3) When conditions closer to stoichiometry were used (fourth synthesis), the excess of oxalic acid was reduced from 76 to 4%, therefore the incorporation of atoms from this reagent into the final product increased, although the incorporation of the atoms from the iron(II) sulfate into the final product decreased, as the yield decreased – indeed the increase of RME/AU (Figure 2) shows that the overall incorporation of atoms of reagents into the product increased; as a result, the score for the second principle increased and the green area of GS increased – GS4 is greener than GS3 (Figure 2).

The values for GSAI included in Figure 2 confirm the visual evaluation of the GS. However, the green area (GSAI = 46.25 for GS4) is far from the maximum.

Mass metrics (yield and GC mass metrics)

Using numerical data from the experiments, yields and the values of GC metrics were calculated as follows (see formula in Appendix 2). Water was not considered in the calculations (*11,12*) because its inclusion makes comparisons between different protocols difficult. More precisely, as the mass of water is 10 times larger than the total mass of stoichiometric and other auxiliary reagents, the inclusion of water leads to values of E-factor and MI so high that mask the effects of the increase of the mass of the other auxiliary reagents along the experiments.

Waste minimization

- *E-factor*, as the ratio of the total waste mass (total mass of reagents less mass of product) to the mass of product.

Table 6. Risks for human health and for the environment for the synthesis of iron(II) oxalate dehydrate.

Reagents used	Hazard symbols	Scores for substances used for construction of GS1 (sulfuric acid used)			Scores for substances used for construction of GS2–GS4 (ascorbic acid used)		
		Human health	Environment	Chemical accident	Human health	Environment	Chemical accident
Stoichiometric reagents							
Iron(II) sulfate heptahydrate	Xn	2	1	2	2	1	2
Oxalic acid dehydrate	Xn	2	1	2	2	1	2
Auxiliary substances							
Solvents							
Water	–	1	1	1	1	1	1
Other auxiliary substances							
Sulfuric acid	C	3	1	3	NU	NU	NU
Ascorbic acid	–	NU	NU	NU	1	1	1
Product							
Iron(II) oxalate dehydrate	Xn	2	1	2	2	1	2
Waste							
Sulfuric acid diluted	Xi	2	1	2	2	1	2
Oxalic acid in excess	Xn	2	1	2	2	1	2
Ascorbic acid	–	NU	NU	NU	1	1	1
Dehydroascorbic acid	–	NU	NU	NU	1	1	1

Note: NU, not used.

- *MI*, as the ratio of the total mass of reagents (stoichiometric reagents, solvents, other auxiliary reagents, etc.) to the mass of product.

Incorporation of atoms of reagents into the product

The following metrics evaluate the incorporation of atoms of reagents into the product. This is the purpose of the second principle of GC.

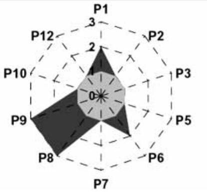
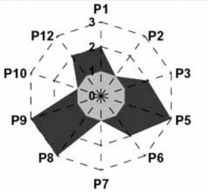
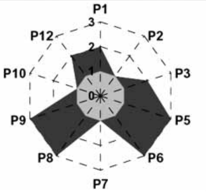
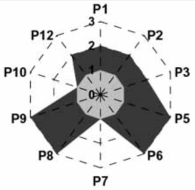
- *AU*, as the ratio of the mass of product to the mass of all the substances produced in the chemical reaction (product and by-products), expressed as a percentage.
- *AE*, as the ratio of the mass of atoms of stoichiometric reagents that are incorporated in the final product (molecular weight of the product) to the mass of total atoms of stoichiometric reagents (sum of the molecular weights of stoichiometric reagents), as a percentage (it was assumed that there were no losses in the process and that all stoichiometric reagents have been converted to product and by-products).
- *RME*, as the ratio of the mass of product to the mass of stoichiometric reagents, as a percentage.
- *FeEE*, as the ratio of the mass of iron in the product to the mass of total iron present in reagents, as a percentage.

The values of RME and AU were the same, as AU was calculated considering the mass of the waste and not the mass of by-products. The metrics RME and element EE (in the present case FeEE) are used in industrial processes and have been useful to evaluate the incorporation of atoms from the reagents into the product, because their calculation is easy (*12*).

The results are included in Figure 2. The values show that when ascorbic acid was used (second synthesis), a fuller GS (GS2) was obtained than for the traditional synthesis (GS1) and the GSAI increased (20.00 → 36.25). When the GC mass metrics are considered, the E-factor increased slightly (2.06 → 2.30) as well as MI (3.06 → 3.30), due to the increase of the mass of auxiliary substances, therefore the loss of atoms in wastes increased. At the same time, the values of AU, RME, and FeEE also increased slightly, therefore the incorporation of atoms from the reagents into the product also increased. These two conclusions are apparently contradictory: while the E-factor and MI suggest that the experiments are less green, the AU, RME, and FeEE indicate that the experiment is greener. This false contradiction may be explained as follows: (1) the use of the

Table 7. Scores used to construct the GS for the synthesis of iron(II) oxalate dehydrate.

	GS1		GS2		GS3		GS4	
	Sulfuric acid, boiling temperature, 76% excess of oxalic acid		Ascorbic acid, boiling temperature, 76% excess of oxalic acid		Ascorbic acid, room temperature, 76% excess of oxalic acid		Ascorbic acid, room temperature, 4% excess of oxalic acid	
GC principle	Score	Explanation	Score	Explanation	Score	Explanation	Score	Explanation
P1 – prevention	2	Oxalic acid, Xn diluted sulfuric acid, Xi	2	As in GS1	2	As in GS1	2	As in GS1
P2 – atom economy (incorporation of atoms into the product)	1	Excess of oxalic acid formation of by-products	1	As in GS1	1	As in GS1	2	Excess of oxalic acid $<10\%$
P3 – less hazardous chemical synthesis	1	Sulfuric acid, C	2	Xn – maximum hazard	2	As in GS2	2	As in GS2
P5 – safer solvents and auxiliary substances	1	Sulfuric acid, C	3	Water and ascorbic acid	3	As in GS2	3	As in GS2
P6 – increase energy efficiency	2	Temperature near 100°C	2	As in GS1	3	Room temperature	3	As in GS3
P7 – use renewable feedstocks	1	Substances not renewable	1	As in GS1	1	As in GS1	1	As in GS1
P8 – reduce derivatives	3	Without derivatives	3	As in GS1	3	As in GS1	3	As in GS1
P9 – catalysts	3	Without catalysts	3	As in GS1	3	As in GS1	3	As in GS1
P10 – design for degradation	1	Substances not degradable	1	As in GS1	1	As in GS1	1	As in GS1
P12 – safer chemistry for accident prevention	1	Sulfuric acid, C	2	Xn – maximum hazard	2	As in GS2	2	As in GS2

Metric	GS1 Sulfuric acid, boiling temperature, 76% excess of oxalic acid	GS2 Ascorbic acid, boiling temperature, 76% excess of oxalic acid	GS3 Ascorbic acid, room temperature, 76% excess of oxalic acid	GS4 Ascorbic acid, room temperature, 4% excess of oxalic acid
GS				
GSAI	20.00	36.25	41.25	46.25
Yield %	92.0±1.9	93.6±0.3	96.1±0.2	87.5±1.2
E-factor	2.06±0.06	2.30±0.01	2.217±0.006	1.96±0.04
MI	3.06±0.06	3.30±0.01	3.217±0.006	2.96±0.04
AE	44.52	44.52	44.52	44.52
RME = AU	33.1±0.7	33.7±0.1	34.54±0.06	38.4±0.5
FeEE	92.0±1.9	93.6±0.3	96.1±0.2	87.5±1.2

* Number of experiments for every GS, N = 3
MI - Mass intensity
AE - Atom economy
RME – Relative mass efficiency
AU - Atom utilization
FeEE - Iron element efficiency

Figure 2. Green Stars and mass metrics for iron(II) oxalate dihydrate synthesis*.

innocuous auxiliary substances had a negative influence on the E-factor and MI because the total mass of auxiliary substances was increased; and (2) the yield increased and this had a positive influence on AU, RME, and FeEE, which are calculated considering only stoichiometric reagents. In summary, the increase of greenness was detected by GS, but was not perceived by the values of GC mass metrics, as their results are contradictory.

The values in Figure 2 also show that for experiments at room temperature (third synthesis), the GS (GS3) is fuller than for the second synthesis (GS2), the GSAI increased (36.25→41.25); with reference to the mass metrics, the E-factor and MI decreased slightly and AU, RME, and FeEE increased slightly. These variations in the GC mass metrics are due to an increase in the yield, as these metrics do not respond to the energy efficiency.

Finally, when experiments were performed near stoichiometry (fourth synthesis), the GS (GS4) was found to be fuller than for the previous case (GS3), the GSAI increased (41.25→46.25) and both the E-factor (2.22→1.96) and MI (3.22→2.96) decreased. At the same time, the values of AU/RME (34.5→38.4) increased, although the yield decreased about 9%. In this case, the increase of greenness (productive use of atoms) was confirmed by the values of the mass metrics. When this final protocol is compared with the initial, it was found that the GSAI increased to more than twice its initial value (20.00→46.25) and the E-factor decreased (2.06→1.96), MI decreased (3.06→2.96), AU and RME increased (33.1→38.4).

The value of AE is the same for all experiments, as it is calculated for theoretical conditions, considering that there were no losses in the process and that all stoichiometric reagents were converted to product and by-products.

The increase in greenness along the green synthesis optimization procedure is better observed in the GS animation (online edition).

Discussion

Comparisons of the results of GS (evaluation of benignness) with GC mass metrics (evaluation of the efficient use of atoms in a chemical reaction) seem to indicate that the two types of metrics, when used together, allow a fuller initial evaluation of the green quality of a synthesis process. Indeed, GS and GC mass metrics provide different but complementary indications about the greenness.

With reference to the waste formed, GS considers only its deleterious nature, while the E-factor and MI evaluate the mass of waste, which is an important factor for loss of greenness. However, when GC mass metrics are considered alone, the results can be misleading, for example, if a small mass of very toxic waste is produced, a low value of the E-factor is obtained, although the high toxicity is very deleterious to greenness.

The same happens when solvents and other auxiliary substances are at play, as GS considers their nature but GC mass metrics do not distinguish between toxic or innocuous solvents, evaluating only the masses involved. This is particularly relevant when the solvent is water. The water quantity used, although often discarded in calculations, may be evaluated through GC mass metrics, but as it is an innocuous solvent, it has no effects in GS.

The substitution of reagents for more benign ones may have a negative impact on GC mass metrics if that implies a larger mass, a decrease of the yield and/or a waste increase. The yield of a chemical reaction has a high influence on the GC mass metrics, but none directly in GS.

The improvement of the greenness of a process may imply the increase of its costs, but this may not be the case if the amount of waste and the cost of waste treatment and disposal, together with potential risks of chemical accidents, are considered. The optimization of the GS may imply less favorable GC mass metrics, but the economic calculation of alternatives should consider environmental costs.

In summary, the advantage of GS is that it allows one to consider aspects which are not dealt with by mass metrics: (i) energy efficiency (sixth principle); (ii) the use of renewable feedstocks (seventh principle); (iii) reduction of derivatives (eighth principle); (iv) the use of catalysts and their toxicity (ninth principle); (v) the degradation of the substances involved (tenth principle); and (vi) risks to human health and to the environment caused by the nature of the substances (first, third, fifth, ninth, and 12th principles).

Conclusion

These results seem to indicate that GS is useful to evaluate the greenness of synthetic procedures, although more experiments involving other synthesis are required to test other factors which may affect it (further studies of other cases are now under progress). This conclusion is supported by several GS characteristics:

- GS may be used to evaluate of the greenness of a chemical reaction without performing the experiment, from a protocol, if enough detail is provided in it.
- GS allows the comparison of the greenness of different alternative experimental procedures by mere visual analysis, although a number between 1 and 100 can be used as result of the metric (GSAI).
- GS allows easy identification by visual analysis of the aspects that should be optimized to improve greenness.
- GS is easy to construct, although sometimes it may be difficult to obtain at the start all the information needed, specially about the degradability of the substances involved.
- GS responds holistically to a large number of features that must be considered when the greenness of a chemical reaction is under discussion, as it deals with all the relevant Twelve Principles of GC in a global and systematic way.

The incorporation of GC in the teaching environment is adequate to help develop a new look on chemistry by the students, hopefully more optimistic than the present, without compromising the integrity of chemistry knowledge. It is important that students change their posture to look for optimization of the greenness of chemical reactions, and when designing and performing several experiments under different conditions for this purpose, the GS seems to be a useful metric.

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Appendix 1. Calculation of the Green Star (GS) area and Green Star Area Index (GSAI)

The calculation of GSAI is exemplified for the case of GS4 in the text (see Figure 3). The calculation is based on the expression for the area of the triangle (see insert in Figure 3). For the branch of the star between the P1 and P2 axes (scores p_1 and p_2, respectively) the area of the triangle defined by the scores p_1 and p_2 (triangle 022, area A1′+ A1, base p2, height h,), as $h = p_1 \sin \alpha$, is:

$$A1' + A1 = p_2 h/2 = p_2 p_1 (\sin \alpha)/2.$$

Similarly, for the central triangle 011 (light colored), for which $p_1 = p_2 = 1$, the area is

$$A1' = (\sin \alpha)/2.$$

Therefore, the contribution to the area of the GS (dark colored trapezoid) is:

$$A1 = (p_2 p_1 - 1)(\sin \alpha)/2.$$

The total area of GS is calculated by addition of these areas for the 10 branches of the star:

$$\text{GS Area} = \Sigma_1^{10} A_i = [\Sigma_1^{10}(p_i p_{i+1} - 1)](\sin\alpha)/2,$$

where the sum index refers to the axes (not the principles). For maximum greenness all the scores would be $p_i = 3$ and the area of the full star would be:

$$\text{Full Area} = 10(3 \times 3 - 1)(\sin\alpha)/2 = 80(\sin\alpha)/2$$

therefore,

$$\text{GSAI (\%)} = 100(\text{GS Area}/\text{Full Area}) = [\Sigma_1^{10}(p_i p_{i+1})]/0.80.$$

Appendix 2. Calculation of Green Chemistry (GC) mass metrics for a chemical reaction

$$A + B \rightarrow P + D$$

In the above equation, A and B represent stoichiometric reagents, P the product, and D the by-products. In the formula below, m_w represents the mass of total waste, m_P the mass of the product, m_A and m_B the masses of the stoichiometric reagents, m_D the mass of by-products, m_{aux} the mass of auxiliary reagents, AW_{Fe} the atomic weight of iron, MW_A, MW_B, and MW_P the molecular weights of stoichiometric reagents and the product and n_{FeP}, n_{FeA}, n_{FeB} the number of iron atoms in the molecular formula of the product and of the stoichiometric reagents, respectively. The GC mass metrics were calculated using the formulae presented below.

E-factor

$$E = m_w/m_p$$
$$m_w = m_A + m_B + m_{aux} - m_P$$
$$E = (m_A + m_B + m_{aux} - m_P)/m_P$$
$$E = (m_A + m_B + m_{aux})/m_P - 1 = MI - 1.$$

MI

$$MI = (m_A + m_B + m_{aux})/m_P.$$

AU

$$AU = 100(m_P/(m_P + m_D))$$
$$m_D = m_A + m_B - m_P$$
$$AU = 100(m_P/(m_A + m_B)) = RME.$$

AE

$$AE = 100(MW_P/(MW_A + MW_B)).$$

RME

$$RME = 100(m_P/(m_A + m_B)).$$

FeEE

$$FeEE = 100(m_P n_{FeP} AW_{Fe}/MW_P)/ ((m_A n_{FeA} AW_{Fe}/MW_A) + (m_B n_{FeB} AW_{Fe}/MW_B)).$$

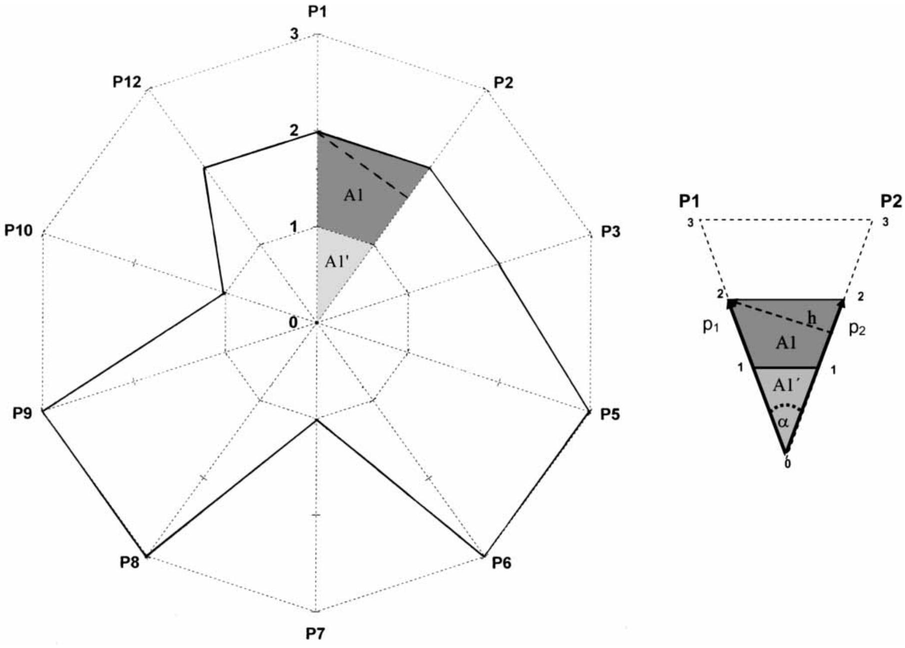

Figure 3. Calculation of the GS area and GSAI.