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WHITE ANALYTICAL CHEMISTRY: A COMPREHENSIVE APPROACH FOR INTEGRATING SUSTAINABLEDEVELOPMENT PRINCIPLES IN ANALYTICAL CHEMISTRY

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ABSTRACT

White Analytical Chemistry (WAC) is introduced as an evolution of Green Analytical Chemistry (GAC). The 12 WAC principles were introduced to replace the current 12 GAC principles. The WAC improves the environmental aspects of GAC by incorporating extra critical factors that influence method quality, encompassing analytical (red) and practical (blue) dimensions. Like the RGB color model, the combination of red, green, and blue creates an appearance of white. A WAC method illustrates the integration and balance of analytical, ecological, and practical characteristics. The notion of whiteness can be evaluated by examining certain concepts, providing an appropriate standard for comparison, and identifying the best suitable methodology. The WAC aligns more closely with sustainable development principles due to its comprehensive approach, which seeks to attain a balance that does not sacrifice functionality for environmental considerations. This review overviews recent advances, including the potential use of a hybrid approach. By integrating WAC principles with experimental design, offering a cost-effective, environmentally sustainable, and user-friendly alternative for developing analytical methods.

KEYWORDS: Green Analytical Chemistry, White Analytical Chemistry, RGB color model.

INTRODUCTION

Rising levels of environmental pollution have significantly heightened public awareness of the need to combat global warming. Environmental preservation, economic feasibility, and social quality are the three tenets of sustainability that are currently the focus of a worldwide movement. Analytical chemistry aids sustainability in two ways. One positive aspect is that it can be useful for tracking contaminants in the ground, air, and water. However, using several harmful chemicals, solvents, and reagents is essential. Green analytical chemistry (GAC) was created in 1998 by Paul Anastas and John Warner and has led to innovative approaches and techniques that reduce and remove dangerous substances during chemical analysis and to lessen the harmful effects on persons and the environment [1]. Green Analytical Chemistry (GAC) has been documented in the literature for over two decades. Green Chemistry was developed in the 1990s to aid chemists in minimizing health and environmental risks in all chemical processes.

Improving upon the idea of GAC, White Analytical Chemistry (WAC) was developed to lessen the negative effects of analytical procedures on the environment without compromising their sensitivity, accuracy, or precision, hence, WAC is an advancement of GAC. Green Chemistry research focuses on analytical methods.[2] Adding green chemistry to analytical method evaluation should be a natural progression in chemistry and meet its broader purpose. Green chemistry principles, including waste prevention, better solvents and auxiliaries, energy efficiency, safer chemistry, and instrumental technique development, are directly related to analytical chemistry.[3] Armenta et al. discussed and detailed the integration of green chemistry into analytical techniques by delineating specific strategies to reduce solvent use and improve method efficiency.[4] In 2013, Gałuszka et al. formulated the critical principles of GAC, introducing a systematic framework of 12 essential concepts that will enhance environmental and human safety while advancing analytical procedures.[5]

12 principles of GAC

1. Aim for a small sample size and a small number of samples.
2. Measurements should be taken in situ.
3. Direct analytical procedures should be used to prevent sample treatment.
4. Formations of derivatives from chemical compounds must be avoided.
5. Integrating analytical processes and operations saves energy and reagents.
6. Large-scale analytical waste generation should be prevented, and appropriate analytical waste treatmentshould be provided.
7. Techniques utilizing many analytes or parameters are favoured over those utilizing a single analyte at atime.
8. There should be more emphasis on the operator's safety.
9. Energy usage ought to be kept to a minimum.
10. It is best to use agents that come from renewable sources.
11. It is best to replace or remove toxic reagents.
12. Automated and miniaturized techniques should be chosen.

Green analytical metrics are helpful tools that are increasingly being used to assess how analytical processes used in industry and research affect the environment. Green Analytical Chemistry has its own set of metrics, including the Analytical Eco-Scale (AES), the Analytical Greenness Metric (AGREE), and the Green Analytical Procedure Index (GAPI).[6] The GAC metrics use pictograms to assess an analytical method's environmental impact both qualitatively and visually. These measurements consider variables, including the number and toxicity of the reagents, waste production, energy usage, process complexity, miniaturization, and automation.[7] By using thesemeasurements, it is possible to determine how analytical processes affect the environment and take steps to reduce any negative consequences, which promotes more environmentally friendly production practices.[8] The analytical greenness metric and its sample preparation variant (AGREE prep) cover several factors that support the environmental sustainability of sample preparation.[9]

White Analytical Chemistry (WAC) is a complete strategy that uses a red-green-blue (RGB) color to solve environmental, analytical, and practical concerns in analytical chemistry, such as sustainability, efficiency, and cost-effectiveness. This strategy enhances analytical methods while promoting sustainability.[10] Analytical methods environmental impact must be evaluated against their efficiency. Accuracy, precision, and sensitivity are required to produce reliable and valid analytical results. Achieving a balance between sustainability and performance is challenging. Cost, speed, and simplicity are all essential considerations besides technical excellence. Sustainable concepts must be incorporated into the innovation process, even if they are more expensive or take longer. By doing so, we may create modern, eco-friendly technology that ensures civilization's progress coincides with environmental protection. Strong rules and regulations can help industries and researchers adopt sustainable practices while progressing.[11] By establishing standards and rewarding sustainability, these policies can balance prosperity and environmental protection.

In contrast to GAC, sustainable development must consider the environment, society, and economics. The RGB model, along with other global assessment tools, offers a structured framework for evaluating and optimizing analytical procedures while considering a variety of parameters. This technique combines GAC principles with practical decision-making to uncover effective, long-term, and cost-effective choices. WAC organizes and integrates several criteria of RGB model (**Fig 1**).

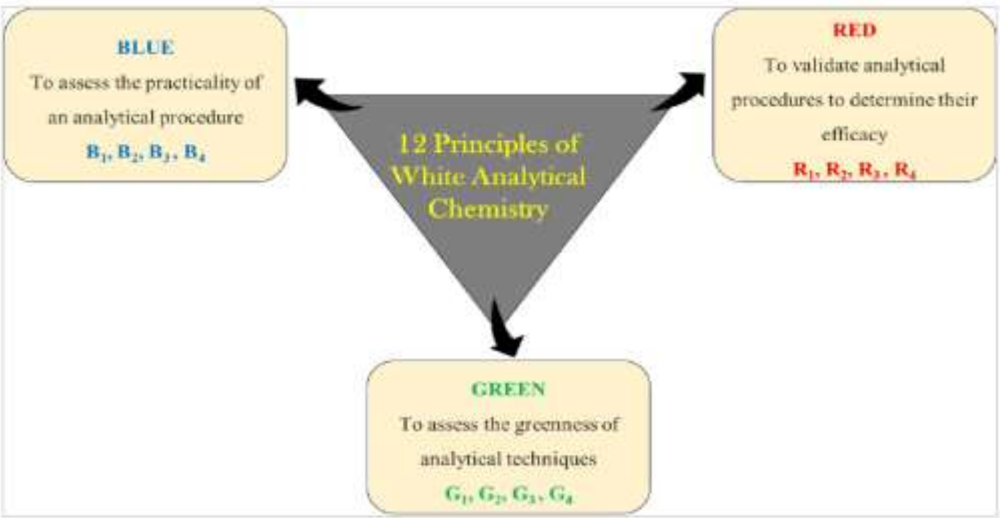

Figure 1: RGB Model of White Analytical Chemistry (WAC)

Twelve GAC principles are separated into four "green" rules, which include the most significant and mutually independent parts of GAC (G1-G4), which establish the 12 WAC principles.[12] The complete set of 12 WAC principles includes four "red" (R1-R4) and four "blue" (B1-B4) principles for analytical and practical efficiency, respectively (**Table 1**). To ensure sustainability, WAC emphasizes that all colors and principles are equal.

RED (R)
The validation of analytical procedures is done to ascertain their effectiveness.
R1: Multi-analyte detection, linearity, sample compatibility, and interference resistance should be comprehensive.
R2: Analytical procedures should be specific i.e. minimize detection and quantification limits.
R3: For maximum precision, analytical processes should be repeatable and reproducible.
R4: Analytical procedures should minimize relative error, maximize recovery, and be stable.

GREEN (G)
To evaluate the environmental sustainability of analytical methodologies.
G1: Analytical procedures should prioritize biodegradable and renewable reagents with low toxicity.
G2: Analytical procedures should reduce reagent usage and waste, regardless of toxicity.
G3: Analytical procedures should conserve energy by reducing electricity and other utility use. For this, use on-site, automated, high-throughput technologies.
G4: Analysis should not harm humans, animals, or the environment. Toxic drugs, genetic alterations, and other harms should be avoided.

Blue (B)
To evaluate the environmental sustainability of analytical methodologies.
B1: Analytical procedures must be cost-effective. Considering instrument, material, media, and labor costs, theyshould be developed to minimize costs.
B2: Another important analytical factor is time efficiency. All analytical workflow steps, including method development, should be designed to finish the analysis quickly.
B3: Minimum practical criteria for analytical methods include sample size, advanced equipment, people qualifications, and laboratory infrastructure.
B4: Analytical procedures require simple operations. They should be miniaturized, integrated, automated, andportable to facilitate their use.

A "white" analytical approach is attained when a method excels in all three primary domains, analogous to how white light is produced by a combination of red, green, and blue light. A well-balanced approach will be practical for analytical efficiency, environmental sustainability, and practicality.[13]

Table 1: RGB Model of White Analytical Chemistry (WAC).

RGB Model	Specifications	
Red (R) Validation of analytical procedures to determinetheir efficacy	R1	Linearity and sensitivity
	R2	Specificity
	R3	Accuracy and precision
	R4	Stability
Green (G) To assess the greenness of analytical techniques.	G1	Waste creation
	G2	Use of toxic and hazardous solvents
	G3	Power consumption
	G4	The protection of human and animal life
Blue (B) To assess the practicality of an analyticalprocedure.	B1	Cost-effectiveness
	B2	Time efficiency
	B3	Steps of sample analysis
	B4	Instrument handling abilities

Working Principle of the RGB 12 algorithm
RGB 12 algorithm's color assignment is another result display approach. According to the RGB color coding concept, background formatting saturation is linearly dependent on numerical values, making findings easier to comprehend and recall. This differs from the RGB method, which evaluated results using nine colors. This is simplified by the RGB 12 algorithm, which evaluates total "whiteness" using black and white. This method aids colorblind and black-and-white analysis. The contribution of red, green, and blue primary characteristics is clearly shown by R (%), G (%), and B (%) numbers and cell formatting.[11]

Complete the Excel template spreadsheet's red, green, and blue tables to evaluate the RGB 12 algorithm. In orderto conclude the assessment, appropriate scores must be entered in the grey columns. In the figure, three model methods were evaluated in tabular form by awarding exemplary scores as the worst (1), appropriate (2), and intermediate (3) (**Fig 2**). This template compares up to ten methods simultaneously. Only scores in the grey columns are needed, with 0 reflecting the worst outcome and 100 indicating the method's suitability for a planned application. Extra merit points (scores over 100) are acceptable. Enter 1 if animal and GMO use is used at any procedural stage, 0 otherwise Set these scores objectively and rationally. Evaluation of individual criteria concerning the method's intended use is vital. Consider whether the values are appropriate for the analysis type, analyte chemical nature, sample matrix, etc. Koel's intelligent debate emphasized that the main concern should be whether the method suits its aim.[14] Thus, we do not prescribe minimal parameter values for specific scores; the evaluator should adjust this decision to the assessment's situation and circumstances. A score of 50 means a result is unsatisfactory but tolerable in some situations, 75 means suitable but not adequate for all expected scenarios, and 100 means a method is suitable for its target application and fully compliant with a principle. Methods that offer significantly greater LOD than required can receive scores above 100 if the application may benefit from or need it in the future. The scores should reflect actual benefits, not linearly correspond with parameter values.[15]

When employed with capillary isoelectric focusing, Whole Column Imaging Detection (WCID) technology has become the biotechnology industry standard for product development and quality assurance. While WCID is lesssensitive and selective than MS detection, it is still the recommended approach for quality control despite its "redness" reduction. Because of its sensitivity, WCID can analyze low-complexity, high-concentration protein mixtures. The approach is appealing since it significantly improves "green" and "blue" qualities. The MS detector may receive a 120 score for LOD and LOQ values, whereas WCID may receive 100 because these values meet current criteria. The MS detector's 20 points reflect potential benefits when studying "unusual" samples.

RED PRINCIPLES (analytical performance)			R1: Scope of application	R2: LOD and LOQ			R3: Precision			R4: Accuracy		
	Method number	Method name	0-100	LOD	LOQ	0-100	RSD% (repeatability)	RSD% (reproducibility)	0-100	Relative error (%)	Recovery (%)	0-100
	1	The worst	0			0			0			0
	2	Appropriate	100			100			100			100
	3	Intermediate	50			50			50			50
	4		0			0			0			0
	5		0			0			0			0
	6		0			0			0			0
	7		0			0			0			0
	8		0			0			0			0
	9		0			0			0			0
	10		0			0			0			0

GREEN PRINCIPLES (green chemistry)			G1: Toxicity of reagents (impact and biodegradation)		G2: Amount of reagents and waste			G3: Concumption of energy and other media	G4: Direct impacts (safety, use of animals and GMOs)			
	Method number	Method name	Total number of pictograms	0-100	Reagent consumption	Waste production	0-100	1-100	Occupational hazards	Safety of users (0-100)	Use of animals (0 if no, 1 if yes)	Use of GMO (0 if no, 1 if yes)
	1	The worst		0			0	0		0	1	1
	2	Appropriate		100			100	100		100	0	0
	3	Intermediate		50			50	50		50	0	1
	4			0			0	0		0	1	1
	5			0			0	0		0	1	1
	6			0			0	0		0	1	1
	7			0			0	0		0	1	1
	8			0			0	0		0	1	1
	9			0			0	0		0	1	1
	10			0			0	0		0	1	1

BLUE PRINCIPLES (practical side)			B1: Cost-efficiency		B2: Time-efficiency		B3: Requirements			B4: Operational simplicity		
	Method number	Method name	Total cost	0-100	Speed of analysis	0-100	Sample consumption	Sample consumption (0-100)	Other needs: advanced instruments, skills, facilities (0-	Miniaturization (0-100)	Integration and automation (0-100)	Portability (0-100)
	1	The worst		0		0		0	0	0	0	0
	2	Appropriate		100		100		100	100	100	100	100
	3	Intermediate		50		50		50	50	50	50	50
	4			0		0		0	0	0	0	0
	5			0		0		0	0	0	0	0
	6			0		0		0	0	0	0	0
	7			0		0		0	0	0	0	0
	8			0		0		0	0	0	0	0
	9			0		0		0	0	0	0	0
	10			0		0		0	0	0	0	0

Figure 2: Working Principle of RGB 12 algorithm [11]

This objective method estimates whiteness without underestimating or overestimating. Consider the estimated number of superior alternative ways in challenging scoring conditions like green criteria. Methods in the top 20% for an element may score 100 or higher. Compliance is average for rules with several method features, such as B4 (operational simplicity). Evaluation results are automatically calculated and displayed in clear tables after scores are entered. WAC compliance is shown numerically and graphically using primary color saturation (0 for black, 100 for maximum saturation). Arithmetic means for important attributes R, G, and B are shown, along with an overall whiteness score (%) that averages all 12 principles (**Fig 3**).

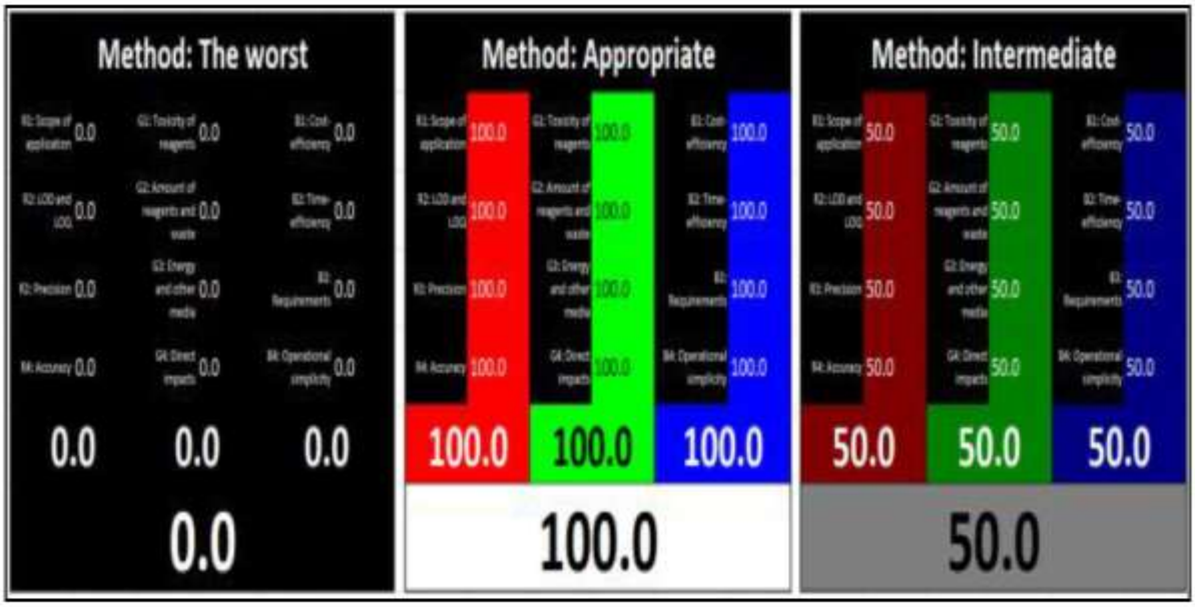

Figure 3: Visualization of the evaluation results of the three model methods according to the RGB 12 algorithm.[11]

Comparison of WAC and GAC

There is conformity between the outcomes produced by the RGB 12 and AGREE algorithms when comparing the WAC and GAC approaches to greenness assessments. Both algorithms reference the most environmentally friendly approaches. The disparities between the two measurements may be more pronounced in other comparisons, thus, it's important to be aware of the different evaluation criteria and techniques. In contrast to AGREE's use of rigid, predetermined models to assess conformity with specific principles, RGB 12 employs a more flexible and synthetic approach, considering only four independent green parameters such as toxicity, amount of reagents/waste, energy consumption, and direct impacts/risks. Keep in mind that many factors might affect these parameters. For example, GAC has its own set of regulations for derivatizing reagents, even if this should be considered when considering the toxicity of the chemicals employed in the WAC concept.[16] While RGB 12 does not evaluate automation, instrument mobility, integration of analysis processes, or throughput independently, these aspects can influence assessments of energy consumption, reagent use, and waste. Animal testing and genetically modified organisms (GMOs) are two further WAC components linked to environmental friendliness.

If analytical and practical factors are insignificant at evaluation, the GAC concept works best when greenness is essential. Alternative approaches are scored for greenness, and only those with a minimum score are subsequentlyanalyzed using a different algorithm against additional parameters to get the final rating. Finding a balance between red, green, and blue is crucial. Whiteness is a simple and comparable measure of technique quality; however, relying only on it to choose the best method may be unfeasible because of the bottleneck of one or morefactors, such as accuracy, LOD, cost-effectiveness, etc. Thus, one should evaluate all regulations and the possibility of such traps. AGREE allows for the direct description of weights to rules, while the RGB 12 algorithm does not. The specificity of a technique should be represented in the level of criticality when examining its important rules.[17]

Recent advancement of the wac approach

Many recent advancements have demonstrated a hybrid approach, merging WAC principles with experiment design, resulting in safe, environmentally friendly, and cost-effective solvents. Drug analysis employing analytical quality by design (AQbD) reduces the amount of organic solvent used and waste. AQbD combines Quality Risk Assessment (QRA) and Design of Experiments (DoE). WAC and AQbD allow for more sensitive, precise, robust, cost-effective, environmentally friendly, rapid, and accurate bioanalysis. A few examples of recentadvancements are listed below.

Ibrutinib (IBR) is a drug that targets the β-carotene ketolase enzyme and has low solubility and high permeability. Significant first-pass metabolism lowers oral bioavailability to 2.9 %. To increase drug releaseand bioavailability, researchers used DoE-based hot melting ultrasonication to make IBR-NLCs (NanostructuredLipid Carriers). Using WAC and AQbD, a sensitive and green spectrofluorimetric method was developed for IBR-NLC drug release kinetic studies *in vitro*. The results show that the NLC-IBR estimation method is sensitive,eco-friendly, cost-effective, rapid, and user-friendly. Finally, employing white WAC and AQbD, the BR-NLC drug release kinetic evaluation approach improved the drug release profile and was efficient and environmentally friendly.[18]

Benzodiazepines are widely used as antidepressants, tranquilizers, and sedative-hypnotic agents. Their global consumption is also due to their accessibility and addiction potential. Harmful uses include suicide, abduction, and drug-facilitated crimes. Thus, their study of food, biological, and environmental matrices is necessary for food safety, clinical research, and environmental analysis. This study examines diverse sample preparation methods utilized for the analysis of benzodiazepines in both biological and non-biological contexts using the recently proposed WAC approach. WAC evaluates analytical procedures based on RGB12 validation parameters.[19]

The WAC-based RP-HPLC-PDA method has been developed and validated for the simultaneous analysis of antihypertensive drugs, including azilsartan medoxomil (AZL), chlorthalidone (CLT), and cilnidipine (CIL) in human plasma, FDCs, and laboratory mixtures. Principle component analysis (PCA) and Partial Least Square Analysis (PLSA) were used to apply the AQbD approach for regulatory compliance with ICH specifications. The developed approach uses IPA, a Class 3 organic solvent according to ICH Q3C (R8).[20]

Epilepsy, neuropathic pain, fibromyalgia, restless leg syndrome, opioid withdrawal syndrome, and generalized anxiety disorder are treated with pregabalin (PGB). Several spectrofluorimetric methods have detected PGB in pharmaceutical dose forms. Most published PGB analysis methods use hazardous, costly solvents and reagents at high temperatures. They disrupt aquatic life and the environment, making them less eco-friendly and user-friendly. WAC introduced a cost-effective, eco-friendly, and user-friendly for building analytical processes. Using WAC principles, green and sensitive spectrofluorimetric analysis of PGB was accomplished utilizing distilled water as an environmentally friendly solvent.[21]

CONCLUSION

This review presents White Analytical Chemistry (WAC) concepts and the RGB model. The framework incorporates analytical (red) and practical (blue) criteria alongside greenness (green), employing standardized principles and a unified assessment tool. According to the WAC concept, a method is classified as "white" or appropriate when it meets various requirements, indicating comprehensiveness. The RGB 12 model is presented as an alternative assessment tool to Green Analytical Chemistry (GAC) concepts currently prioritized in the discipline. WAC is better aligned with the Sustainable Development (SD) paradigm, promoting a balanced approach between environmental issues and other essential variables that influence a strategy practicality and efficacy. The authors emphasize the significance of addressing sustainability, although they warn against excessively stressing it to the detriment of usefulness or completely neglecting it. This strategy seeks to assist the analytical chemist in assessing novel advancements, contrasting techniques, and defining future directions. Furthermore, it can aid industrial and researchers in evaluating technique adoption and investigating analytical technologies focusing on sustainability. The WAC concept and RGB 12 algorithm are intended to assist in selecting the best solutions for particular applications, evaluating newly developed techniques, and comparing existing and innovative approaches. This review covers current advances, some of which involve hybrid approaches that can be helpful; for example, by integrating WAC principles with experimental design, we can develop solvents that are safe, environmentally friendly, and cost-effective. This approach allows the analytical chemist to contextualize developments and make intelligent choices regarding future research directions. Moreover, it assists industries and researchers in assessing technique validation and exploring analytical technologies to achieve a sustainable future.

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