Integration of Green Metrics in Analytical Chemistry: A Pathway towards Sustainable Chemical Analysis"

***Dr. Anita Prashant**

ABSTRACT

Although the idea of "green analytical chemistry" is not new, no mechanism for measuring its greenness currently exists. Metrics used in green chemistry that focus on product mass are inappropriate for evaluating analytical procedures. Analytical chemistry metrics have been the subject of some research and development. Some are easy to use, but they don't address the full range of ways analytical procedures might harm the environment. Some are easier to implement, while others are more thorough. There was no evaluation of the analytical reagents, however there are hints about their eco-friendliness in evaluations from other areas of chemistry. Analytical chemists must carefully evaluate the environmental friendliness of any new solvents and reagents they use. The selection of reagents and solvents, the disposal of analytical waste, the creation or selection of analytical techniques, and the energy needs of analytical processes all have an impact on the environment, which is why metrics systems are necessary.

Keywords: green analytical chemistry, eco-friendliness, environment.

Introduction

A philosophical movement known as "green analytical chemistry" has emerged to bring principles of sustainable development into traditional chemistry labs. While there are several approaches to introduce the GAC idea, some of the most crucial ones are using less hazardous solvents, using solventless extraction procedures, miniaturising sample preparation processes, and nal determination devices. These procedures are standard operating procedure in scientific and academic labs and have a long history of success.

It is standard practice to take performance attributes including LOD, recovery, accuracy, and linear range into account while developing analytical procedures. When developing new procedures, it is important to keep in mind that green analytical chemistry considerations are just as important. Results about preferred analytical techniques might vary when selecting analytical procedures based on three criteria: analytical performance, green analytical chemistry values, and economic expenses. It is obvious that these considerations must be taken into account when selecting an analytical technique.

Analytical process in the light of green chemistry

Why should we care about the environmental effect of analytical laboratories? That's an easy thing to ask. Some people in the general public believe that analytical chemistry has an effect that is little in

comparison to the chemical and pharmaceutical sectors. Here are the key points that highlight the importance and urgency of this problem:

With an estimated 130,000 units in operation, which amounts to a substantial 34 million litres per year, a typical liquid chromatograph produces over 1 litre of organic waste every day. Only liquid chromatographs produce this much solvent waste. To this figure, you must include the waste that results from the process of preparing the samples.

The geographical dispersion of analytical chemistry emissions is directly proportional to the number of analytical labs. This sort of pollution is notoriously difficult to regulate.

A branch of analytical chemistry known as "green chemistry" focusses on the field's contributions to global sustainability efforts. It is imperative that all fields of competence include sustainability principles into their work.

Oil refining uses an E-factor of 0.1, pharmaceutical manufacture uses an E-factor of 100, and nanomaterial synthesis uses an E-factor of 100,000.9 It is common practice to describe the amount of waste produced in kilogrammes per kilogramme of product in order to get the E-factor. In analytical chemistry, the computed E-factor is close to unity. Since the end outcome of an analytical procedure is a weightless substance, its mass is also zero. However, resources that end up in the trash are needed to get the analytical findings. The argument that analytical chemistry is harmful to the environment and that there is need for improvement in this area is well-made.

Analysts are familiar with the Ishikawa or shbone diagram, and it is useful for demonstrating the complexity of the environmental effect of analytical operations. Take, for instance, a standard liquid chromatographic technique that uses sample we will look at extraction-based preparation. The elements impacting the method's success are shown in the Ishikawa. The Ishikawa diagram depicting the procedure's effect on the environment. Keep in mind that the overall quality of the analytical result is dependent on each and every phase of the process. In the same way, the sum of all actions has an effect on the environment. Energy and material inputs are given. The materials used to conduct the analysis end up in the trash, as mentioned before.

Green analytical chemistry without metrics?

"Do we need green analytical chemistry?" asks a new paper, posing a crucial issue.11 Now that we know the answer is yes, we must ask the second, more natural question: "How to measure the greenness of analyt-ical methods?" There are no tried and true ways of determining GAC's "greenness," which is a major issue. As a field of study, green analytical chemistry is severely underdeveloped. There are a lot of analytical processes that authors claim to be environmentally friendly in the literature. Sadly, it is usual practice to make such claims without substantiating them with facts, such as applied greenness measurements or comparisons to established analytical or standard processes. Claims about how environmentally friendly a method is often to rest on the writers' subjective opinions or unproven assumptions. This kind of thinking is completely flawed in some passages of literature.

Despite the lack of a direct correlation to analytical chemistry in the given case, a comparison of

preparative HPLC and SFC techniques used in the pharmaceutical business does provide some intriguing insights. Preparative SFC is far more environmentally friendly than preparative HPLC, according to the intuitive comparison result (recall that intuition is the most widely used greenness evaluation technique at the moment). Indeed, SFC is 26.3% more efficient than conventional materials.

If energy is taken into account, nevertheless, HLPC outperforms SFC by 34.3%. The very high energy requirements of heating and cooling in SFC are the reason for this. A number of metrics systems have been established in the field of green chemistry. The most popular methods for determining if chemical processes used in organic synthesis are atomic economy, reaction mass efficiency, and environmental impact factor. In some fields, such as the fragrance or pharmaceutical sectors, specialised instruments are required. These measurements cannot be directly used to green analytical chemistry since they relate to the mass of the reaction product (17). At this point, the metrics may be computed "per analytical result" and can relate to material and energetic inputs.

Overview of the developed metrics

Weak and inconsistent approaches to evaluating the environmental friendliness of analytical processes abound in the literature. The first is NEMI labelling, which produces an easy-to-understand pictogram that indicates if the method uses toxic or corrosive chemicals or produces a significant quantity of trash. If the corresponding portion of the NEMI pictogram is green, it means: There is no bioaccumulation, toxicity, or persistence of the reagents. The analytical process does not use any solvents or reagents that are not included on the TRI list maintained by the EPA.

There is no risk associated with the chemicals used in the operation. Neither of the Resource Conservation and Recovery Acts include them on their separate lists.

The sample treatment and analysis process takes place in an environment free of corrosion. There is a range of 2–12 for the pH.

All all, less than 50 g of trash is produced throughout the analytical method. a sample of a NEMI pictogram. Because it requires extensive searches for each reagent to be included in lists containing dangerous, hazardous, or persistent substances, NEMI makes it difficult to evaluate analytical procedures.

On top of that, the study just provides qualitative results; it doesn't reveal how many risks there are. One of the first methods for measuring environmentally friendly analytical chemistry was the NEMI pictogram technique, however.

In contrast to NEMI, the Analytical Eco-scale incorporates a larger number of environmental effect criteria in its second evaluation phase. Subtracting penalty points from a base of 100 forms the basis of the eco-scale evaluation system. Analytical waste treatment methods (or lack thereof), the quantity and kind of reagents that might harm the environment, the analyst's possible exposure on the job, and the power consumption of electrical equipment all contribute to the total number of penalty points.

A highly straightforward method is used to score reagents. Each chemical-related danger pictogram is denoted by a penalty point. On top of that, the term "danger" doubles the amount of hazard pictograms when describing the chemical, however the word "warning" has no effect on the score. Multiply the quantity of the chemical by the number of penalty points associated with the chemical danger. For reagents and solvents with concentrations below 10 mL or 10 g, the danger score is multiplied by 1. For concentrations between 10 and 100 mL (g), the multiplication factors are 2 and 3, respectively. Additionally, three penalty points will be deducted for the release of vapours into the air while the analysis is being conducted. One penalty point is assigned for waste quantities less than 1 mL or 1 g, three points for amounts between 1-10 mL or 1-10 g, and five points for amounts more than that. Three bonus points are awarded in the event that the garbage is not processed in any manner.

Due to the presence of danger pictograms on chemical containers, the points associated with the chemicals utilised are readily apparent. Additional information is made more accessible by using danger pictograms on safety sheets. It is simple to compare the various analytical approaches since the scoring results are legible. However, the score does not include any information on the structure of the dangers, which is a major shortcoming of this technique. Because of this, the Eco-scale score is useless for finding the procedure's flaws and fixing them. The evaluation technique also takes dangers into consideration in a semi-quantitative manner, which is a drawback.

Although the first two methods may be used to any analytical process, the HPLC-EAT (environmental assessment tool) is specifically designed to evaluate liquid chromatographic operations with respect to the amount of mobile phase used and how it is disposed of.6 To complete the analysis, we must add up the potential risks to human health and the environment posed by each solvent used in the process. Results from solvent scoring using GSK's solvent selection guide validated the HPLC-EAT technique. This method of evaluation has the limitation of focussing on solvents alone when calculating possible environmental impacts.

There are analytical processes created for every possible analyte and matrix. There are numerous of techniques available for certain analytes that have good characterisation.

There are over 40 methods for determining chloroorganic pesticides in water samples or polycyclic aromatic hydrocarbons in bottom sediments, according to database searches. Benefiting from this knowledge, one may implement a strategy based on comparing operations inside this collection.

An established method in the field of chemistry, multivariate statistics forms the basis of the first strategy. The goal of the study is to classify the analytical processes into comparable categories. Green analytical chemistry metrics may make use of chemometrics if the variables utilised to characterise the analytical methods are those that relate to their environmental effect or greenness. It is possible to effectively use the relatively simple chemometric methods to group analytical processes, such as principal component analysis and cluster analysis. Because they can identify the most and least green outlying items, more sophisticated chemometric methods like self-organising maps (SOMs) provide more useful findings. The presence or absence of a positive or negative correlation between variables may be readily identified using SOMs. The findings from the evaluations conducted using self-

organising maps align with those from the NEMI and Eco-scale evaluations. Other intriguing dependencies in the collection may be uncovered by the findings, in addition to clustering according to greenness. Exhibiting complete independence from procedural material and energetic inputs, the findings reveal, for instance, that the number of analytes identified in a single chro-matographic run is uncorrelated with any other variable.

Multicriteria decision analysis (MCDA) is a lesser-known method in the field of chemistry. Instead of grouping, as is done in the chemometrics technique, it enables the rating of analytical processes based on their greenness. A multi-stage presentation is possible for the overall architecture of MCDA approaches. Once the purpose of the analysis has been defined, quantitative measures (such as analytical performance or greenness requirements) may be used to characterise it. The next stage is to find other ways to get there; in analytical chemistry, this may include trying out some new analytical techniques. We assign a weight to each criterion since their relative value varies. The next step is to use the appropriate MCDA algorithm to rank the analytical approaches that are alternatives. A few of MCDA's key benefits include the ability to evaluate several analytical techniques all at once and the simplification of numerous criteria into a single, easily understandable score.

The Method for Ranking Preferences According to How Close They Are to the Ideal Solution is an MCDA tool. Several analytical techniques for pharmaceutical determination in wastewater samples were evaluated using TOPSIS. Eight criteria were used to define the nineteen analytical techniques, with a focus on their analytical performance and greenness. The majority of the processes relied on the solid phase extraction technique, and the most suitable one was chosen. Curiously, the procedure's highest performance was with the multianalyte analysis; it did adequately, but not optimally, with the other criteria. Using a little quantity of in comparison to dichloromethane and hexane, methanol is thought to be less hazardous.

The second green analytical chemistry metric that is used using MCDA is PROMETHEEE, which stands for the Preference Ranking Organisation Method for Enrichment Evaluation. A thorough ranking of alternatives is the outcome of this outranking approach, which is similar to TOPSIS. It has been used to evaluate 25 methods for the measurement of chloroorganic pesticides in water samples using 9 criteria as inputs. The process characterised by the best overall performance was the one based on SPME followed by GC-ECD, according to the ranking data. Importantly, this study's ranking outcomes were consistent with Eco-scale findings and had no association with NEMI findings. Analytical procedures that performed well on the Eco-scale evaluation also performed well on the PROMETHEE scale.

It turns out that conventional procedures aren't eco-friendly when measured using any form of metric. The idea that conventional method development does not take green analytical chemistry concepts into account is completely incorrect. They are used in all regular studies and are often found in commercial analytical labs. Standard procedures account for the vast majority of reagents, solvents, emissions, and waste. When it comes to selecting or evaluating conventional analytical methods, MCDA is a great tool since it may be based on several criteria and you can find out how professionals regard each one. The existence or absence of high-tech equipment and the price of

reagents were also considered as input factors, in addition to conventional analytical parameters and environmental friendliness. Data from numerous analysts may be obtained thanks to the ease of evaluating the relative relevance of the criteria; this data can then form the foundation of an environmentally friendly standard method selection.

Metrics for analytical reagents

Metrics systems like the ones mentioned above do take reagent and solvent environmental concerns into account in their algorithms, but they still need specialised evaluation methods. In order to optimise procedures, identify potentially dangerous compounds, and replace them, it is necessary to have access to substances that have been evaluated for their impact on the environment. The use of solvents is one of the most significant environmental issues in analytical chemistry. Solvents must be used with consideration for the environment as solventless techniques are not always feasible. To help with optimisation strategies related to solvents, pharmaceutical firms have created solvent selection guides. Environmental, health, and safety considerations form the basis of each of these solvent selection guidelines. We classify the solvent as "recom-mended," "recommended or problematic?", "problematic," "problematic or hazardous?", "hazardous" or "very hazardous" based on the evaluation findings. In most cases, the solvents that are "recommended" include water, alcohols, and even certain esters. Hydrocarbons, chlorinated solvents, and some ethers are toxic or very hazardous substances. Attempts are being made to merge them into a single manual and to choose solvents that are not as widely used. Using these solvent selection instructions has the benefit of producing results that are straightforward to understand. The most significant drawback is that these outcomes are only accessible for small volumes of solvents. The previously mentioned MCDA and grouping chemometric technique may also be used as a solvent selection aid. Based on their shared properties, 151 solvents were categorised into three groups for cluster analysis. One group was the least environmentally friendly, consisting of "nonpolar and volatile" solvents. The second group was in the middle, with "nonpolar and nonvolatile" solvents, and the third group had more environmentally friendly "polar" solvents. A comprehensive ranking was conducted using TOPSIS inside each category. The user may pick the solvents for the analysis and the assessment criteria, as well as specify their relative priority, making this the most flexible solvent selection guide compared to others. Because of this, it is possible to tailor the analysis parameters to the specific analytical issue. The rating, on the other hand, can only be done properly if the user knows what they're doing. The environmental friendliness of solvents employed in analysis is summarised in Fig. 4.

Good disposal techniques must be established for solvent waste. Using the life cycle analysis (LCA), we compared solvent distillation against incineration. The majority of the solvents used in the study benefit from distillation. Analytical chemistry solvents that are no longer needed, such as acetonitrile, tetrahydrofuran, acetone, acetic acid cyclohexane, or toluene, may be recovered by distillation. Benzene, methanol, pentane, hexane, and heptane are analytical solvents that should be burned off.

We created a methodology to rank the analytical procedures according to how much solvent they used. A technique for rating chemicals used in industry forms the basis of the instrument.40 After adding together all of the toxicological risks and exposure parameters, we get a score for each

solvent; a lower score indicates that the solvent is less harmful to the environment. This evaluation of solvents is based on the potential risks they pose. The procedural effect may be calculated using solvent scores by multiplying regarding the volume of the solvent, the millilitre being the most practical measure. This metrics system has a single flaw: it doesn't take into account the whole extent to which analytical approaches harm the environment. The analytical uses of conventional solvents were not the primary emphasis of previous methods of evaluation. Environmental persistence and particular range indicator findings reveal that commonly used analytical reagents are not very persistent.

Novel solvents, including bio-based ones, deep-eutectic solvents, ionic liquids, and others, are finding increasing use in analytical chemistry. Although ionic liquids have several uses in analytical chemistry, their primary use is in the extraction process.46 Green solvents is (or was?) the name given to them. Some of them were poisonous to people and aquatic creatures, casting doubt on their evergreen reputation. Multiple facets of ionic liquid applications were considered, allowing for the possibility of such findings. Solvents used in analytical applications should only be used after thorough evaluation investigations.

When compared to conventional solvents, bio-base solvents are more environmentally friendly, much like ionic liquids. It is possible to extract common laboratory solvents like methanol and acetone from lignocellulose. Case-by-case, based mostly on geographical location, LCA data reveal that the greenness of solvents generated from lignocellulose varies. The Soxhlet device was essential in the extraction of fatty acids and oils from limonene in analytical chemistry. Limonene is a renewable resource since it is a by-product of the citrus industry and is derived by azeotropic distillation. Limonene and hexane both had comparable extraction efficiencies. There is a claim that limonene is a more environmentally friendly solvent than hexane, although this claim is unsubstantiated by any criteria other than the fact that hexane is more poisonous. Although limonene is a more environmentally friendly alternative to hexane, solvent selection guidelines still list hexane as being non-green. It should be remembered that the renew-ability of the feedstock is not the only metric to evaluate the solvent's eco-friendliness; despite this, there have been several attempts to include bio-based solvents into extraction processes, such as analytical extraction. The fact that hexamethylenediamine may be made from both renewable and fossil fuels demonstrates that bio-based chemicals aren't always better for the environment. Regardless of the feedstock used—rice, maize, or potatoes—life cycle assessments reveal that the fossil fuel-based mode of production is more economic and ecologically beneficial than the bio-based technique.

The use of deep-eutectic solvents is another relatively new development in analytical chemistry. So far, they have been used in electrochemical processes and as solvents for extraction. They make it difficult to determine whether or not they are environmentally friendly since they include at least two compounds in different proportions.

The use of acids and bases as digestion aids and auxiliary chemicals is another facet of analytical reagents. When evaluating the environmentally friendlyness of acids and bases, somewhat different criteria are needed due to their distinct chemical characteristics. One more time, there was no

measurement system in place designed for use in analytical chemistry, however the acid and base selection recommendations provided by GlaxoSmithKline may provide some guidance on sourcing environmentally friendly alternatives. Environmental, safety, and health concerns, as well as those related to the disposal of hazardous by-products, form the basis of the assessment systems. The findings of the reagent evaluations utilised in analytical chemistry.

Using derivatisation agents is another part of analysis that has gone unnoticed by greenness evaluations. Similarly to green analytical chemistry, eight out of twelve principles suggest that derivatisation should be avoided. Some have sought to make analytical derivatisation more environmentally friendly by using derivatisation agents that are less harmful to the environment, switching to water instead of organic solvents, or enzymatic derivatisation.

Conclusions

There are currently no commonly used and internationally recognised metrics in green analytical chemistry. Although various green-ness criteria have been devised, they fall short of meeting the current demands. In addition to collecting sophisticated data on the environmental impacts of analytical procedures or reagents, these tests should be simple to do and understand. There are still significant gaps since the scientific area is quite young. It is necessary to establish standards for the evaluation of analytical reagents, analytical processes, and the overall environmental performance of analytical labs. The development of analytical chemistry-specific methods for solvent selection, digesting chemicals, and derivatisation agent evaluation is urgently required. When optimising the selection of solvents and reagents, it is important to keep in mind the potential environmental effects of analytical methods.

Before making any comments regarding how environmentally friendly they are, novel compounds that have recently been used in analytical chemistry, including ionic liquids, bio-based solvents, or deep eutectic solvents, need to be thoroughly evaluated. Analytical chemists have not yet made use of LCA for evaluation, however there are a few cases of its use in green chemistry. Applying LCA provides a comprehensive understanding of the process's environmental effect, as shown by the various instances. It seems that life cycle assessment (LCA) is the best method for evaluating the use of analytical reagents and methods.

***Department of Chemistry**
BBD Govt. College
Chimanpura, Shahpura

References

1. S. Armenta, S. Garrigues and M. de la Guardia, Trends Anal. Chem., 2008, 27, 497–511.
2. A. Rıos and M. Zougagh, Trends Anal. Chem., 2013, 43, 174– 188.
3. F. T. G. van den Brink, W. Olthuis, A. van den Berg and M. Odijk, Trends Anal. Chem., 2015, 70, 40–49.

4. F. Pena-Pereira, I. Lavilla and C. Bendicho, Trends Anal. Chem., 2010, 29, 617–628.
5. H. M. Mohamed, Trends Anal. Chem., 2015, 66, 176–192.
6. R. Je¸drkiewicz, A. Orłowski, J. Namie´snik and M. Tobiszewski, Talanta, 2016, 147, 282–288.
7. Y. Gaber, U. Tornvall, M. A. Kumar, M. A. Amin and R. Hatti-Kaul, Green Chem., 2011, 13, 2021–2025.
8. R. A. Sheldon, Green Chem., 2007, 9, 1273–1283.
9. M. J. Eckelman, J. B. Zimmerman and P. T. Anastas, J. Ind. Ecol., 2008, 12, 316–328.
10. X.-T. Sun, Q.-J. Tan, S.-X. Wang, J.-F. Shan and J.-L. Jiang, Anal. Methods, 2015, 7, 5428–5435.
11. M. Koel, Green Chem., 2016, 18, 923–931.
12. G. van der Vorst, H. Van Langenhove, F. De Paep, Aelterman, J. Dingenen and J. Dewulf, Green Chem., 2009, 11, 1007–1012.
13. D. J. C. Constable, A. D. Curzons and V. L. Cunningham, Green Chem., 2002, 4, 521–527.
14. J. Andraos, Org. Process Res. Dev., 2005, 9, 149–163.
15. T. V. T. Phan, C. Gallardo and J. Mane, Green Chem., 2015, 17, 2846–2852.
16. D. Cespi, E. S. Beach, T. E. Swarr, F. Passarini, I. Vassura, J. Dunn and P. T. Anastas, Green Chem., 2015, 17, 3390– 3400.
17. J. Andraos, Org. Process Res. Dev., 2005, 9, 404–431.
18. C. Turner, Pure Appl. Chem., 2013, 85, 2217–2229.
19. H. K. Lawrence, L. U. Gron and J. L. Young, Chem. Rev., 2007, 107, 2695–2708.
20. M. Tobiszewski, S. Tsakovski, V. Simeonov and J. Namie´snik, Green Chem., 2013, 15, 1615–1623.