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2 Andruch V., Green analytical chemistry as an integral part of sustainable education development, Sustainable 3 Opinion in Green and Chemistry Current Vol. 31. (2021).100508. 4 DOI: 10.1016/j.cogsc.2021.100508 5 6 © 2021. This manuscript version made available under the CC-BY-NC-ND 4.0 is 7 license http://creativecommons.org/licenses/by-nc-nd/4.0/ 8 9 10 Green analytical chemistry as an integral part of sustainable education development 11 Justyna Płotka-Wasylka<sup>1,\*</sup>, Heba M. Mohamed<sup>2</sup>, Aleksandra Kurowska-Susdorf<sup>3</sup>, Rajkumar Dewani<sup>4</sup>, 12 Michel Y. Fares<sup>5</sup>, Vasil Andruch<sup>6</sup> 13 14 <sup>1</sup> Department of Analytical Chemistry, Faculty of Chemistry, Gdańsk University of Technology, 80-233 15 Gdańsk, Poland 16 <sup>2</sup> Analytical Chemistry Department, Faculty of Pharmacy, Cairo University, Cairo, 11562 Egypt 17 18 <sup>3</sup> The Naval Academy, Faculty of Humanities and Social Sciences, 81-127 Gdynia, Poland 19 <sup>4</sup> Leather Research Centre, PCSIR, D/102, South Avenue, S.I.T.E, Karachi-75700, Pakistan 20 <sup>5</sup> Pharmaceutical Chemistry Department, Faculty of Pharmacy, Nahda University, Sharq El-Nile, 62511 21 Beni-Suef, Egypt 22 <sup>6</sup> Department of Analytical Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, SK-23 04154, Košice, Slovakia 24 25 Abstract 26

Postprint of: Płotka-Wasylka J., Mohamed H. M., Kurowska-Susdorf A., Dewani R., Fares M. Y.,

Green chemistry is an important way of thinking in the field of chemistry and aims to conduct processes 27 in accordance with the principles of sustainable development. It is the application of a wide range of 28 principles that minimize the impact of both chemical processes and products on the environment. And 29 what about analytical chemistry? Without a doubt, analytical chemistry plays an important role in the 30 sustainable development of the planet. However, this only applies if analytical procedures are of high quality (sensitive, precise and accurate) and also in line with the principles of environmental 31 32 sustainability. This essay presents a brief discussion of the evolution of green chemistry and its 33 multidimensional impacts, including the "industry" of analytical chemistry as well as academic education 34 and research. We emphasize the difference between the term "sustainability" and "greenness". 35 Therefore, at least basic information on sustainability in analytical chemistry is provided. We hope that 36 our considerations will inspire analytical chemists and will contribute to the further development of 37 both green analytical chemistry and sustainable analytical chemistry.

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# 39 Keywords

40 Analytical chemistry; sustainability; green analytical chemistry; education; research

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# 43 1. Introduction

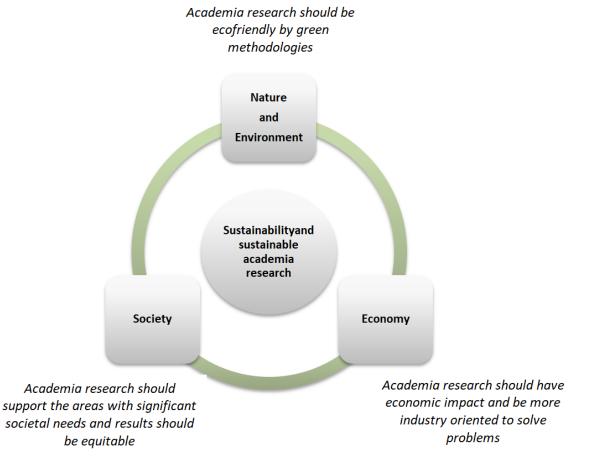
The principles of green chemistry are widely used in industrial management, government policy, educational practice and technological development around the world. The main aim of the so-called

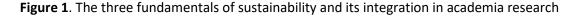
circular economy is to balance economic growth, resources sustainability and environmental protection. 46 47 Green chemistry, which in fact leads to a change in attitudes and behavior in the chemical industry, can 48 be considered an important tool for achieving sustainability [1]. In addition, it has a major impact on the 49 emergence and development of new ways of thinking in specific areas of chemistry, including analytical 50 chemistry, where the term Green Analytical Chemistry (GAC) is used. In our opinion, the most difficult 51 task is to find the right way to evaluate the greenness of an analytical procedure, as many different 52 parameters must be taken into account [2]. There are some published methods for evaluating the 53 greenness of various analytical methods [3, 4, 5]. However, we must keep in mind that the terms 54 "sustainability" and "greenness" are not the same. It is well known that for development to be truly 55 sustainable, three interrelated areas - the environment, the economy and society - need to be 56 considered, while the philosophy of green analytical chemistry deals primarily with only the first of these 57 areas. We hope that our philosophical considerations inspire analytical chemists around the world to 58 reflect on this difference.

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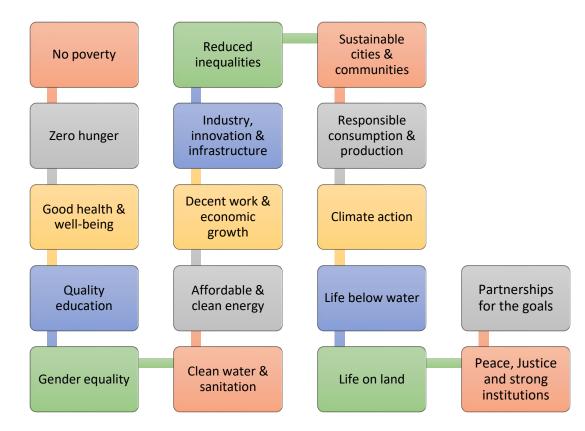
### 60 2. Brief history of sustainable development

61 Sustainable development is now commonplace and connects almost all areas of human activity. 62 However, it is difficult to say exactly when the concept of sustainability emerged. Probably the earliest reported findings date to the ideas of economist Thomas Robert Malthus from the 17<sup>th</sup> century [6]. The 63 64 first famous international conference on the side effects of rapid industrial growth and economic 65 development took place in New York in 1949 [7]. Later, in 1970, US President Richard M. Nixon laid the 66 foundations of the Environmental Protection Agency (EPA) [8]. Environmental concerns became part of the few international agendas as well as commissions [9, 10, 11]. The three pillars of sustainable 67 68 development are shown in Figure 1.





In nineties, also happened a lot in this area, for example publication of the Pollution Prevention Act, [8], activation of the program called the Alternative Synthetic Pathways for Pollution Prevention [12], performing a meetings such as "Earth Summit". All of these efforts were reflected in the comprehensive "Agenda 21" [13]. Recently, 17 points designated as "Sustainable Development Goals" (SDG) were published (Figure 2) [14].



81 Figure 2. Sustainable development goals

The global acceptance of sustainability eventually led to the development of emerging areas at that time, such as "Green Chemistry". In this are such researchers should be known

Anastas and Warner who outlined the main principles of green chemistry through which the goals of sustainability can be achieved. Green chemistry was defined as "The design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances" [16]. Since this time many implementations have placed [17, 18].

Among the pragmatic developments in this area were the replacement of toxic solvents, such as chlorofluorocarbons (CFCs). Alternative green solvents included the reintroduction of aqueous systems, ethanol, rediscovered CO<sub>2</sub> and various combinations [19]. Some processes that were discovered earlier are now associated with green processes, such catalysis, which was reported as early as 1830, or ionic liquids, which were discovered in 1914 by Paul Walden. They are particularly interesting, as they can be tailored to specific needs [20].

# 3. Green analytical chemistry

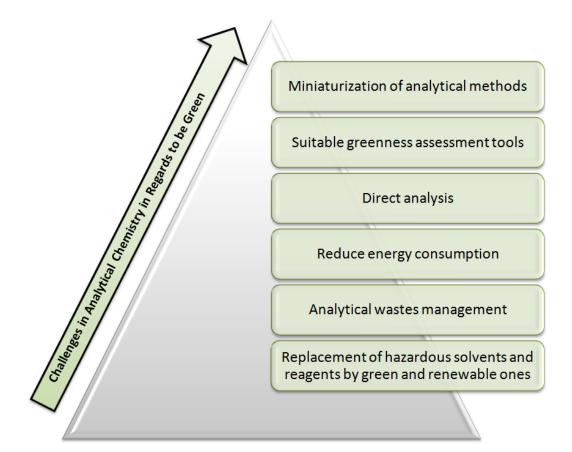
Green analytical chemistry goes hand in hand with sustainable development and corresponds to the "triple bottom line" of sustainability – the economic, social and environmental – to improve the quality of human life [21],[22]. The principles of GAC emphasize the necessity of safer, less toxic and more benign solvents or the elimination of solvents, as well as reducing energy consumption, avoiding derivatization and favoring substances based on renewable sources [23,24]. The correct application of GAC provides many benefits in various aspects of sustainability. However, we have to believe that GAC is

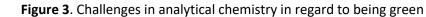
a way, not the goal. It is a multistep approach that should result in an analytical procedure that meetsboth the GAC criteria and the performance criteria required by the customer [16].

One reason for the success of GAC in applications laboratories as well as at the academic level, in general, is that green methods are less costly than classical methods [25]. Being less expensive, ecofriendlier and safer makes them the current trend in developing or modifying analytical methods whether in academic or industrial level laboratories.

108 The trend of GAC leads to significant challenges due to differences in the validation priorities of 109 analytical methods such as sensitivity, selectivity, accuracy, precision, and robustness, which are the 110 most important factors in this regard. In contrast, the time, cost (including purchase, operation, training 111 and space) and an analytical procedure's environmental safety are secondary [26]. Analytical chemists around the world are therefore trying to find a balance between the parameters of validation of 112 113 analytical methods and their sustainability. The need to compromise between improving the quality of 114 the analysis and bettering the environmental aspects of analytical methods is becoming the most crucial 115 obstacle to the future implementation of GAC [27]. These challenges can be summarized in the points 116 presented in Figure 3.

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In addition to working on the environmental aspects of the new technology and laboratory approaches within the principles of GAC, an educational approach is also important. Health and safety

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are becoming a priority. The Green Analytical Chemistry paradigm is based on old practices, however
 with an added value of environmental responsibility to make chemical practices more eco-friendly in
 line with social demands [28].

The main educational task is to transmit a clear message to society that would shed light on chemistry as a fundamental part of the solution to pollution problems and not just part of the problem [28]. The modification of the analytical chemistry paradigm means complementing the basic analytical properties with the incorporation of the "green" parameters. The renewed paradigm of Green Analytical Chemistry Accuracy still respects representativeness, traceability, sensitivity and selectivity however with a greater care of the environment, safety of operators, the greater reduction of reagents, energy, solvents and decontamination of analytical wastes

133 Sustainable education in academia has a challenge before it: to transform teaching practices, 134 starting from the content of theoretical lessons to laboratory practices [28]. Teaching green analytical 135 chemistry is a challenge today for building a better future for tomorrow. This involves the development 136 of new analytical methodologies, techniques and technologies that can help future chemists and 137 chemical engineers to research, develop and minimize the environmental impacts of their work [29]. 138 Ecological practices in the teaching of analytical chemistry must be based primarily on an awareness of 139 the twelve principles of green analytical chemistry [29]. The result of such training should be a new 140 generation of chemists who consider the importance of an environmentally friendly approach to 141 maintaining the sustainable development of society [28, 30]. Effective teaching and education includes 142 the use of modern memorizing and problem solving methods during seminars as well as students having 143 access to the relevant materials for self-study. Green analytical metrics would help in understanding and 144 assessing whether the methods being evaluated are green or not [29]. The effect of such teaching could 145 be a new generation of chemists who are aware of the need for ethical compromise between the 146 environment and society [28].

#### 148 4. Sustainable analytical chemistry

Analytical chemistry should be eco-friendly and safer to the analyst as discussed in GAC principles. It is not about to monitor the waste and pollutants but rather to green methodologies. This is achieved by waste minimization through; miniaturization, using green solvents or solventless methods, minimizing energy consumption, avoiding the use of auxiliary reagents and chemicals.

For analytical chemistry to be described as sustainable, it should consider the three pillars for sustainable development – the environment, the economy and social dimensions and needs (Figure 1) [1]. Many academic institutions lack a structured framework to bridge basic research and viable products. Academic research needs to be more practical; it needs to seek solutions to industrial problems and not only target conceptual research but also aim to have an economic impact.

Research in academia should foster the use of new extraction techniques to make sample preparation steps greener; these are the most crucial and challenging steps in reducing the environmental footprint of analytical techniques. In academic research, there is currently an increasing demand towards replacing traditional analytical methods with portable and miniaturized sensors with more interest in microfluidics and lab-on-a-chip applications. These smart and powerful analytical tools can fulfill all the pillars of sustainability. Wider attention is being paid on wearable non-invasive sensors

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as a promising tool for diagnostics and remote follow-up of patients. Electrochemical sensors provide rapid measurements of different analytes in different matrices, and they are at the same time userfriendly [31,32]. Furthermore, improvements in spectroscopy have made it possible for researchers and scientists to develop *in situ* and in-the-field analysis techniques. For example, NMR spectroscopy can be used to monitor flowing material. Low-field NMR techniques can be used to measure moisture, fat, and/or fluorine contents in food analysis without pretreatment, separation or purification steps [33].

171 As was previously mentioned, analytical methods in academic research should be cost-effective [34, 172 35]; this often leads to the designing of energy-efficient methodologies, analytical tools and high-173 throughput analysis whenever possible. Portable and disposable devices can be a cost-effective 174 alternative, since sampling is minimized; they can also be available in the field of measurements, which 175 in turn would result in minimum transportation cost [31,32]. Still, portable cost-effective instruments 176 have some drawbacks in terms of methodology selectivity and limit of detection, but more advanced 177 technologies could improve their performance, which could become a hot research area in academia. 178 Moreover, academic research should make the best use of applications and smart devices, such as smart 179 phones [36], smart watches, scanners and 3D printers, which can extract data and analytes without 180 adding extra cost. Some researchers are now using household coffee machines for extraction, as it 181 requires lesser volume of solvents and consumes less time for getting satisfactory recovery compared to 182 the traditional laboratory extractors. Classic espresso machines have been reported by researchers to 183 successfully isolate bioactive compounds, for instance, eugenol from cloves [37]. Isolation of polycyclic 184 aromatic hydrocarbons (PAHs) from soil and sediments [38] was reported using hard-cap espresso 185 machines, where the solid sample placed inside a sealed capsule undergo pressurized extraction.

186 The societal responsibility in analytical chemistry covers two major aspects; first, analytical chemistry 187 should support the areas where there is a significant societal need, this will not only support the needs 188 but also will create new job opportunities, improved use of renewable materials and energy efficiency. 189 Secondly, analytical chemistry is to introduce methodologies that are of high quality and have reliable 190 results with minimum impact on the analysts' health and environment. Additionally, the social aspects 191 of green chemistry have to involve the transmission of information to society in a comprehensible and 192 contextualized way. In another meaning, analytical procedures, the analytical devices, and results are 193 easily accessible for all in need. To align with this pillar, academia research should tackle the society 194 needs and to ensure the use of simple analytics that anyone could easily perform anywhere. Handy 195 smart devices should be explored, for example, smartphones and digital cameras, to run chemical 196 analysis for routine tests. The use of smartphones or applications can make the analytical methods far 197 more accessible, cheaper, and do not require trained personnel for operation. Some studies have 198 reported smartphone-based sensors and other wearable noninvasive sensors with different detection 199 modes for measurements in different matrices such as food, saliva, blood, and others [32]. Further 200 investigation is required in academia research to invest more in using smartphone wearable sensors and 201 tattoos as cost-effective and available point-of-care diagnostic tools, fully integrating and analyzing the 202 data without the need for additional devices in health care, environmental and food research.

#### 5. Conclusions and future trends

Although it is true that the waste generated in analytical laboratories is sometimes larger and more hazardous than the sample analyzed, it is also likely that the amount of hazardous waste generated in

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analytical laboratories in academic research is significantly less than in industrial laboratories.
Nevertheless, it is a great pity that analytical procedures often contribute to further pollution of the
environment by the production of hazardous waste. Green analytical chemistry can therefore be seen as
an important area of green chemistry that needs to be given due attention.

211 Of the twelve principles of green chemistry defined at the beginning of this century, analytical 212 chemistry is primarily concerned with the eleventh principle: "Analytical methodologies need to be 213 further developed to allow for real-time, in-process monitoring and control prior to the formation of 214 hazardous substances". This principle concerns and emphasizes the use of analytical chemistry in 215 industry to improve the analytical control of technological processes, so that analytical results can be 216 used to manage technological processes online and in real time. Probably, this has largely been 217 achieved, although a large space for further development in this area certainly exists. On the other 218 hand, this principle did not deal with so-called laboratory analytical chemistry.

If we look at the path of green analytical chemistry, we can observe two trends: On one hand, analytical equipment manufacturers are offering increasingly sophisticated instruments that allow the determination of an increasing number of target analytes with lower and lower detection limits in diverse samples. Of course, this is most often accompanied by an increase in price (investment costs) as well as increased operating costs, in addition to increased requirements for skilled laboratory staff.

On the other hand, we are also seeing a tendency to miniaturize, automate and simplify devices so that they are more affordable and do not require highly qualified personnel, so that even a non-expert can use them. This approach is very suitable for field work and routine environmental analyses, etc.

Analysis is a multistep process consisting of several consecutive steps, starting with sampling and including sample processing, the subsequent measurement itself as well as the cleaning of laboratory equipment.

An analytical laboratory cannot influence the greenness of some of these steps, such as the sampling process, the transport of the sample to the laboratory or the storage of the sample during transport. The measurement itself depends mainly on the available equipment, customer requirements and the standard protocols used. Therefore, we should focus on assessing the greenness of the analytical procedure itself and not on the greenness of the whole process of analysis as such.

Sample pretreatment can be made greener, for example, by reducing the volume of organic solvents used or by replacing hazardous reagents with less hazardous ones. As a result, in the last two decades, we have witnessed the introduction of new solvents, such as SHS and DES, into analytical procedures, and we have also seen the emergence of new so-called microextraction techniques that use significantly smaller volumes of solvents (less than one hundred microliters) or some that can be called virtually solvent-free techniques.

Taking all of this into account, we cannot forget why the ideology of Green Chemistry was introduced. It aims to conduct laboratory work based on the principles of sustainable development. It is well known that for a development to be truly sustainable, all three areas – the environment, the economy and society – need to be considered, while the philosophy of green analytical chemistry mainly describes the first factor. Thus, being more than just "green", which means to cover the requirements of these three areas, is recommended. Therefore, if you have called your methodology "green", please apply the available metrics, such as GAPI or AGREE, to ensure development towards environmental sustainability. In addition, during the creation of a new project, think about the needs of the global

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society. Be an explorer of human needs; be useful to people. Remember that your work in the area of analytical chemistry does not have to be merely a simple tool for other chemists to use, but a continuously developing research area with large implications for the future good.

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# 259 Authors' contribution

260 The idea of this work was proposed by Justyna Płotka-Wasylka who also suggested the content of the 261 manuscript and contributed in manuscript preparation mainly in write up of the abstract, introduction, 262 and conclusion and formatting of the rest of the manuscript. Aleksandra Kurowska-Susdorf wrote the 263 part connected with the education of sustainability. Heba M. Mohamad wrote the section 4: sustainable 264 analytical chemistry. Rajkumar Dewani wrote the part connected with history of sustainable 265 development and evolution of green chemistry and its multidimensional impacts. Michel Y. Fares wrote 266 the parts related with challenges in analytical chemistry in regard to being green. Vasil Andruch 267 contributed in overall manuscript preparation mainly in write up of the conclusion and future 268 perspectives and formatting of the rest of the manuscript.

# 270 Declaration of interests

The authors declare that they have no known competing financial interests or personal relationshipsthat could have appeared to influence the work reported in this paper.

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