

## Green Analytical Chemistry: Social dimension and teaching

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### Abstract

Green Analytical Chemistry (GAC) is the idea which every analytical chemist should be familiar of. Due to continuous improvement in the subject both from the aspects of theory and experimentation, the dynamic way analytical chemistry studies are evolving in the frame of chemistry degrees should not be surprising. Recently, many efforts have been made in order to include Green Chemistry principles to Education, also in the field of analytical chemistry, where twelve GAC principles play a main role. The understanding and awareness of these principles and other evolving related concepts requires special teaching of GAC as a part of curriculum at undergraduate and graduate levels. This article is focused on the main concepts and challenges of teaching GAC and also presents the current accomplishment in this field. In addition, teaching social responsibility in GAC is discussed. Several case studies are also presented as an example for the learners.

### Keywords

Green Analytical Chemistry; teaching methods; social responsibility; educational materials; GAC metrix

### 1. Green Analytical Chemistry: history, principles and recent trends

40 The interest and concern for the sustainable environment is constantly increasing,  
41 thus, it becomes important to examine the activities of those chemists and chemical engineers  
42 which may meaningfully impact on the environment, both at the laboratory and the industrial  
43 scale [1]. Introduction of the green chemistry idea is associated to the dissemination of the  
44 principles of the sustainable development and the highly visible tendency to implementation  
45 of these principles in laboratories and chemical plants. In fact, the principles of green  
46 chemistry have been adopted in the specific fields of chemistry and thereafter, several other  
47 sets of principles have been issued such as Principles of Green Chemical Technology, 12  
48 principles of Green Engineering and 12 principles of Green Analytical Chemistry [2].

49 The adverse effects of the application of analytical procedures may cause damage to  
50 the environment and serious risks for operators. Therefore, for these reasons, it is essential to  
51 think about the effects as well as consequences of actions taken by the researchers/users of  
52 analytical methods. Respecting the viewpoint of people who take care of the environment also  
53 considering economic aspects of analytical methodologies, the special attention should be  
54 paid to the inherent risk of some samples type, aliquot of reagents and solvents used, the  
55 consumption of energy related with advanced instrumentation and, without a doubt, resulting  
56 laboratory wastes and emissions coming from the numerous steps of analytical methodologies  
57 [3]. Such a responsibility among the analytical chemists' society appeared long before the  
58 introduction of the term Green Analytical Chemistry. Several innovative advances in the  
59 sample preparation as well as measurement and data handling were introduced in the middle  
60 of the 1970s. It needs to be mentioned that the methodological milestones (Figure 1) which  
61 were conceived to increase the green character of the analytical procedures were mainly  
62 achieved before formulation of GAC concepts [4]. One of the most important idea was to  
63 apply the term "clean waste" instead of word "waste", suggesting an alternative method  
64 which includes an additional chemical effort to minimize the environmental impact of FIA  
65 determinations. That was the beginning of the clean analytical chemistry concept. In 1995, the  
66 opportunities proposed by the degradation processes contribution and flow injection analysis  
67 to enhance analytical methods were confirmed. In the same year, the manuscript entitled:  
68 "Towards environmentally conscientious Analytical Chemistry through miniaturization  
69 containment and reagent replacement" was published and it is said that this was the first  
70 declaration of the principles of what is today called Green Analytical Chemistry [5]. In  
71 another work [6], a term "waste minimization" was introduced and recommended to the  
72 analytical practice. Although a term Green Analytical Chemistry was not applied in this work,  
73 it is recognized as the pioneer works of GAC because the green idea was inherently present.  
74 Since that time, the development of green analytical practices has accelerated and improved  
75 as for the introduction of methodologies and instrumentations as it can be seen in Figure 1.

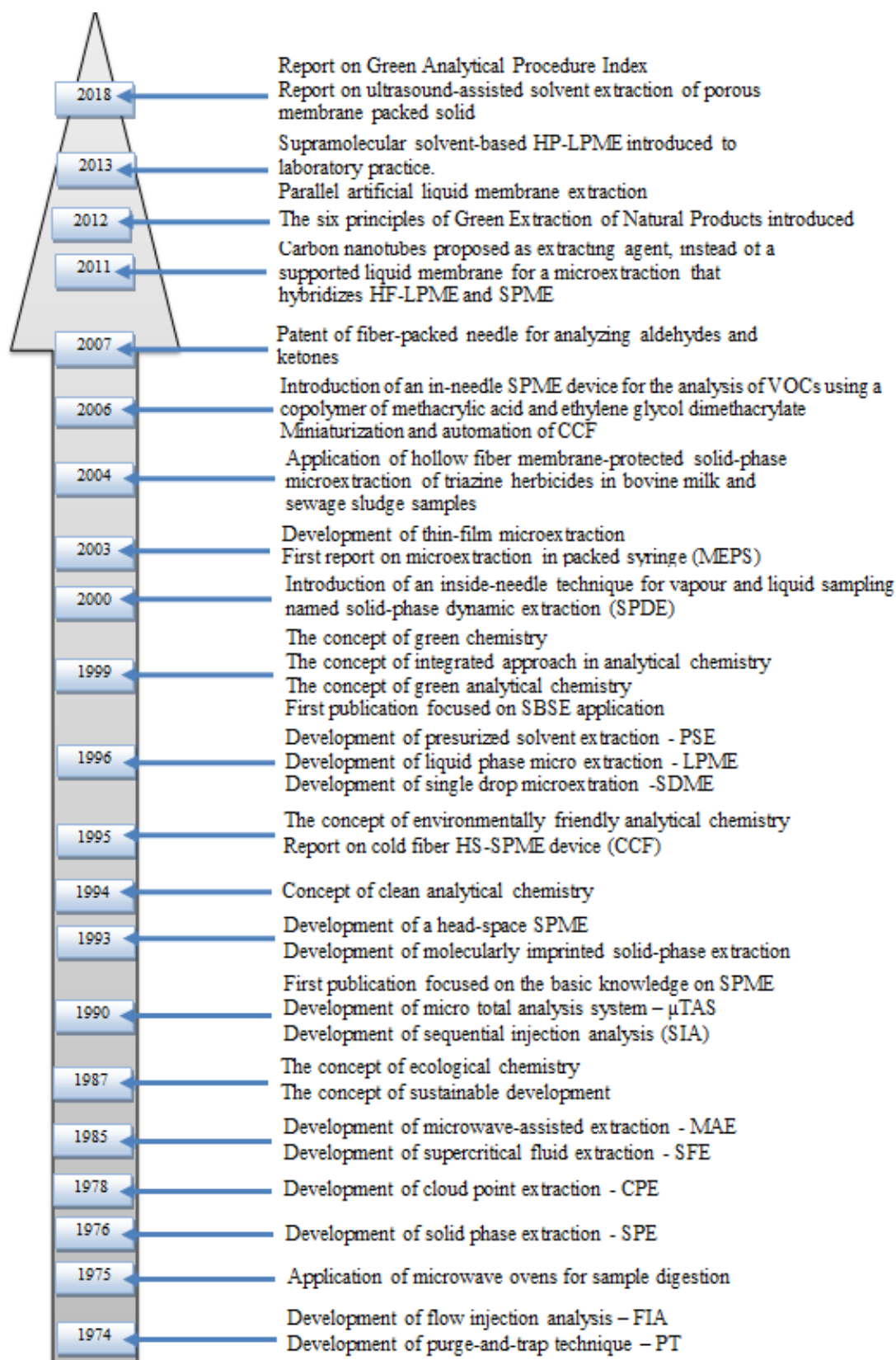


Figure 1. Milestones of Green Analytical Chemistry [7-12]

Nowadays, Green Analytical Chemistry is the idea which every analytical chemist should know. Thus, it is not surprising that analytical chemistry studies in the frame of chemistry degrees around the world have evolved in different ways [13]. This is mainly due to the



82 development in analytical chemistry field but also due to the on-going trend to be more and  
83 more eco-friendly which is many often pointed out during the chemical study. However,  
84 teaching analytical chemistry today is, in general opinion, maintaining the past advances in  
85 order to improve the main analytical figures of merit of the available and common approaches  
86 and also to improve them [13]. From the other side, it is required to adequately response to the  
87 questions and problems associated with our social compromise with the safety of operators  
88 and the environment. Hence, teaching analytical chemistry should include the way of thinking  
89 about the analytical problems as well as their solutions in terms of sustainability, considering  
90 and paying attention to both, the well known past knowledge of analytical figures of merit  
91 related to different approaches, and ways to reduce the use of persistent, bioaccumulative,  
92 toxic, hazardous or corrosive solvents and the resulting waste generation [13].

93 Recently, many efforts have been made in order to include Green Chemistry principles  
94 to Education, also in the field of analytical chemistry, where twelve Green Analytical  
95 Chemistry principles play a main role. Education in GAC would balance both ethical and  
96 chemical aspects. Hence, the concept is to convince the students on the fact that chemistry is  
97 not only a risk for the planet, indeed it has great promises for human health care as well as  
98 sustainable environment. Now it is teachers' obligation to transmit this kind of knowledge.

## 100 2. Teaching Social Responsibility in Green Analytical Chemistry

101  
102 Social responsibility is undoubtedly one of the pillars of modern chemistry [14], and in  
103 particular of analytical chemistry [15]. This is because, in principle, every area of life today  
104 depends on data obtained and transmitted via (bio)chemical research. These areas include  
105 health, culture, transport, industry, energy, new technologies and building, which are of  
106 strategic importance to our ever-expanding globalized states and societies [16]. Analytical  
107 chemistry should be socially responsible, because the data and knowledge that it provides  
108 affects every element of the reality that surrounds us.

109 The 20<sup>th</sup> century was undoubtedly the age of chemistry, which contributed enormously  
110 to raising living standards, the industrialization of societies, and the economic development of  
111 states. However, this did not come without a cost. The degradation of the natural environment  
112 as well as biological, physical pollution and aesthetic damage, these all called for an  
113 alternative development policy [17]. The concept of sustainable development, initiated at the  
114 turn of the 1980s and 1990s, was a proposal aimed at striking a balance between the  
115 continuous improvement of the quality of life and the exploitation of finite natural resources.  
116 At the beginning of the 21st century, sustainable development became one of the leading  
117 paradigms of contemporary chemical education [18].

118 The corporate and scientific social responsibility and the idea of sustainable  
119 development is a topic which has been present in the public discourse for a long time.  
120 However, until now both have been treated either as a way of justifying application for funds  
121 for research and development, or as a fig leaf of social involvement of public institutions or  
122 enterprises [19]. The situation is similar in the chemical industry, which increasingly treats  
123 both issues strategically — as the foundation of its operations and the basis of research and  
124 commercial projects [20]. There are two basic benefits arising from the application of social  
125 responsibility and sustainable development in the chemical industry: socialization and  
126 rationalization. Grounding analytical chemistry in both concepts can increase the efficiency of  
127 the industry itself, and at the same time have a positive impact on society, which is the most  
128 important beneficiary for the chemical branch.

### 130 2.1. *The humanistic coefficient: the rationalization and socialization of analytical chemistry*

132 The socialization of the chemical industry means enabling and facilitating the  
133 participation of internal and external stakeholders in the creation, implementation and  
134 evaluation of chemical policy, both on a macro (e.g. state or union of states) and micro (e.g.  
135 companies or regions) scale. The internal stakeholders in the chemical industry are primarily  
136 the managers, employees, customers, suppliers, regulators and partners of chemical  
137 companies. The external stakeholders are institutions within the broad environment of the  
138 chemical industry, including in particular public administration, universities, think tanks or  
139 non-governmental organizations (NGOs). Rationalization, in turn, means using the potential  
140 of knowledge management, both in the form of interdisciplinary analytical teams and the use  
141 of operational databases. This is important especially in the area of analytical chemistry, for  
142 which the metrological quality of data and information is of premium value.

143 The socialization of analytical chemistry provides an insight into the activities of  
144 chemists from the viewpoint of their key beneficiary (society) and main stakeholders, while  
145 rationalization facilitates the solving of social problems, both in the area of costs generated by  
146 chemical production and problems related to the distribution of information. The  
147 implementation of the principle of rationalization and socialization of analytical chemistry is  
148 important primarily because the data, information and knowledge contained in analytical  
149 reports form the basis for political decisions that make a profound impact on our lives [21].

150 Rationalization and socialization can be referred to two types of associations  
151 (connotations) of the social responsibility of analytical chemistry: internal and external [22].  
152 Rationalization refers in particular to the internal connotations (and stakeholders) associated  
153 with the generation and acquisition of the highest quality of (bio)chemical data, while  
154 socialization is mainly concerning the process of packaging and transferring information and  
155 knowledge to external stakeholders, both commercial customers and public policy makers.  
156 However, it is worth emphasizing that rationalization and socialization should characterize all  
157 entities and processes involved in chemical activities. Their differentiation and connection  
158 with a different type of stakeholder is purely analytical (*nomen omen*).

## 159 160 2.2. Green analytical chemistry as a tool for teaching and promoting social responsibility 161

162 The concept of green chemistry is the synthesis of socialization, rationality,  
163 responsibility and sustainability in the chemical industry [23]. It is a response to the  
164 unprecedented development of the chemical industry, generating high social and ecological  
165 costs. The enormous number of chemicals that cause damage to the natural environment on an  
166 exceptional scale requires thought and specific repair programs. However, as widely known, it  
167 is easier, faster and cheaper to prevent rather than to repair. The paradox of chemistry, which  
168 undoubtedly contributed to raising living standards, is that it is not well-viewed today —  
169 instead, it stands for contamination, artificiality and the very opposition of nature [13]. Green  
170 chemistry can contribute to not only reducing or preventing environmental risks and disasters,  
171 but also to improving the social (including media) image of the chemical industry.

172 Green chemistry is an appropriate platform for teaching and promoting social  
173 responsibility because it is a social movement itself [24]. It can be treated initially as a  
174 bottom-up and later an institutionalized way for the representatives of the chemical industry to  
175 organize themselves in order to implement socio-technological change expressed in an  
176 innovative approach to chemistry as a forefront of sustainable development. Green chemists  
177 have treated themselves as advocates of a healthier, safer and more sustainable society,  
178 without any political inclinations, but with a clear desire to convince the intellectual elites and  
179 technocrats to their ideas. They also realized how important role education could play in the  
180 dissemination of this new idea.

181 Social responsibility should form one of the strategic currents that run through  
182 chemistry teaching, especially analytical chemistry. Nothing is better suited to achieve this  
183 goal than the concept of green chemistry [25]. If we want the responsible and socially  
184 sensitive analytical chemists who would take care of the metrological quality of data and  
185 information, we have to educate them from the very beginning — from pre-school, through  
186 school and ending at university. This should be done not by creating separate chapters in  
187 chemistry textbooks or by arranging guest lectures by humanists, but by integrating chemical  
188 instrumentation and nomenclature with social and ethical themes [26]. Green chemistry offers  
189 the most effective tools for linking chemistry with topics such as health, development and  
190 social justice at every level of school and academic education.

191 The need to take social responsibility into account in chemistry education is confirmed  
192 by a study conducted on a sample of 6,100 students, in which it turned out that Science,  
193 Technology, Engineering and Mathematics (STEM) students treat the development of their  
194 own career as a goal more important than social development [27]. It is possible that no one  
195 ever opened their laboratories to the world; no one made them aware that they are agents of  
196 change. Chemists will become socially sensitive if they are consequently encouraged to be  
197 conscious and responsible. They can be inspired by engagement in solving specific problems  
198 — e.g. during group activities, and in particular by linking chemistry education with everyday  
199 life, with interesting human stories, with real-life examples, with something that involves  
200 them [28].

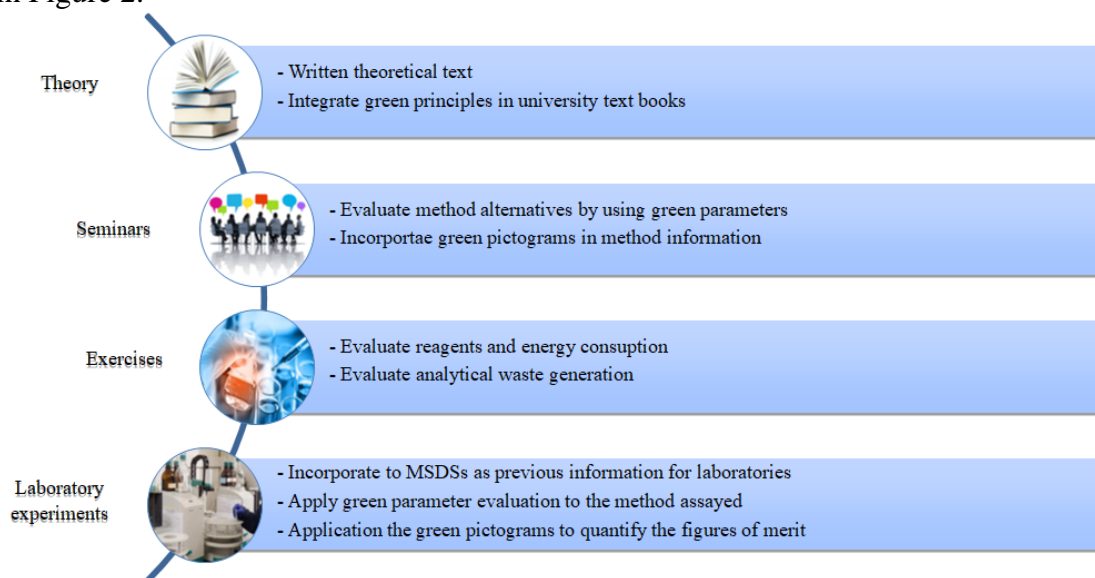
201 Social responsibility, sustainable development, justice, honesty and transparency  
202 should not be enclosed in the conceptual ghetto of incomprehensible theories, but become the  
203 very foundation of education preparing for chemistry in practice — a compass that will not  
204 only help navigate in an increasingly complex world, but also indicate a direction worth  
205 taking.

### 207 **3. Teaching Green Analytical Chemistry: challenges**

208  
209 Without a doubt the teaching and practice of analytical chemistry reflects the  
210 measurement science development over the time. Both, qualitative as well as quantitative  
211 measurements can be track down to “old” prebiblical times, and have been significant  
212 throughout the human history, while nowadays, they are the key to the modern society  
213 functioning [22]. This is mainly because the environment is more and more polluted and its  
214 monitoring is undoubtedly indispensable. From the other side, analytical chemistry involves  
215 highly toxic reagent consumption and waste generation introducing a “brick” to pollute the  
216 environment. Thus, in recent years, many efforts have been made in order to incorporate GAC  
217 principles to analytical practice, but this brings new challenges, including the Education and  
218 teaching of Green Analytical Chemistry.

219 It needs to be stated that teaching GAC cannot mean that some lessons concerning  
220 the side effects of old, existed methods will be added, but all the matter must be changed and  
221 modified by adding the environmental ethical compromise, from the beginning to the end of  
222 the analytical process [13]. Thus, greening teaching practices must engage a powerful  
223 theoretical effort together with a modification in analytical practices. This should be started  
224 from the seminars as well as practical work recommended to students. In addition,  
225 incorporating decontamination steps in the analytical laboratory experiments should be  
226 carried out [29]. All of these mean that the challenge today is to establish new objectives  
227 without devoting the existed ones and it must convert all teaching practices from the subject  
228 and content of the theoretical lessons to the laboratory practices [13]. In addition to this issue,  
229 a huge challenge is to create such a team of teachers able to make a huge pedagogical effort  
230 which must be made in all different aspects. Some of them are the integration of GAC

231 theoretical principles in the university textbooks as well as the generalized application of  
 232 material safety data sheets (MSDS) on both the laboratory notebook documents and as  
 233 complementary data from protocols of analytical method [13]. Moreover, the introduction of  
 234 green parameters and pictograms used for evaluation of alternative methodologies to solve the  
 235 same analytical problem could be helpful in forming a new mentality in young students.  
 236 Aspects worth considering for greening Analytical Chemistry teaching practices are presented  
 237 in Figure 2.



238 Figure 2. Aspects to be considered for greening Analytical Chemistry teaching practices  
 239  
 240

### 241 3.1. Awareness in the field of green analytical chemistry

242  
 243 Presently, personal health and environment protection are given more consideration in the  
 244 field of chemistry, especially in more economically developed countries. The needed  
 245 awareness in the field of green analytical chemistry should be perceived multidimensional.  
 246 There is the need to turn laboratory practices into more environmentally friendly. In addition,  
 247 it is an urgent international necessity to reduce pollution problems and become more eco-  
 248 friendly not only in the laboratory but also in everyday life. The need to increase the  
 249 environmental awareness especially in low-income societies emerges from the current public  
 250 idea of responsible and respectful citizenship concerning environmental issues. The education  
 251 towards sustainable development and in-depth understanding of Principles of Green  
 252 Chemistry becomes a primary and central goal [2].

253 Moreover, one should realize the deficiencies not only in the educational sphere, but also in  
 254 the research and literary fields. If the analytical procedure is called “green” basing only on  
 255 one of the Twelve Principles of Green Analytical Chemistry, it is a meaningful gap in the  
 256 research area. Such a narrow vision of a green analytical chemistry may cause confusion.  
 257 Proper understanding of chemical principles and methodologies are fundamental for human  
 258 and environmental health. Future chemists must become aware of the importance of  
 259 sustainable strategies in chemical research and industry [30].

260 The design of chemical product such as new analytical methodology defines the level  
 261 of the impact on the ecological environment. Therefore, future analytical chemists first need  
 262 to learn how to take a full account of the methodology optimization development, waste  
 263 recycling, including other required chemical product aspects. Secondly, after methodology  
 264 products have been developed and the application has been scrapped, consider the proper  
 265 methods to deal with the final waste [2].

266 The challenge students need to face is the compromise between the base of 12 principles  
267 of GAC (operator, sample, reagent, instrument, method waste) and the performance  
268 parameters (accuracy, precision, sensitivity). Decreasing in performance parameters may  
269 consequently lead to miniaturizing instruments or declining in sample numbers, reagents,  
270 energy and waste. In practice, representativeness, accuracy, selectivity, sensitivity and  
271 precision will drop if the sample size in the sampling process is being reduced. However,  
272 there are different solutions noteworthy for students facing the need of compromise between  
273 improving green aspects of analytical methods and increasing value of the analysis [31]:  
274

- 275 - “Modifying *in situ* measurements to improve calibration by running standards between  
276 sample
- 277 - Using chemometrics and statistics for the reduction of the amount of sample
- 278 - Using integrated analytical systems for the improvement of the analytical efficiency
- 279 - Using chemometric data treatment to allow the development of solvent-free methods  
280 based on direct measurements without any sample pretreatment (i.e; near-  
281 infrared/mid-infrared/Raman spectrometry, UV-Vis spectroscopy, fluorescence,  
282 nuclear magnetic resonance techniques” .

283 The application of the above-mentioned methods may reduce the time of analysis as well as  
284 the use of reagents and solvents in the same time avoiding the pretreatment of samples.

285 Following two principles of GAC; automation and real-time analysis for pollution prevention,  
286 students should be aware of multiply advantages in miniaturization of analytical instruments;  
287 portability of instruments in on-site analysis. Moreover, miniaturization ensures improvement  
288 of sensitivity and the speed of separation as well as reduced waste production and energy  
289 consumption, lower costs allowing at-line, quick analysis or less consumables and space. In  
290 addition, the number of samples in miniaturized system (a lab on a chip) is smaller than when  
291 traditional analysis takes place, which is important in such areas as biomedical science or  
292 forensic. The miniaturized separation system usage is greener than conventional methods  
293 [31].

### 294 295 3.2. Educational materials for teaching 296

297 The challenge in education in the analytical chemistry discipline would be to reach a  
298 compromise between the growing environmental friendliness of analytical methods and  
299 improving quality of the results as well as to assess whether applied methods are green.  
300 Another encounter considers education aids such as reliable and well-written material. In  
301 contrast to green chemistry, in green analytical chemistry there are not many literature items,  
302 especially when it comes to typical student materials, i.e. scripts. However, there are more and  
303 more books [32-40]. In addition to the books published, several publishers published special  
304 editions related to green analytical chemistry in their journals. For example, Elsevier in  
305 Trends in Analytical Chemistry had a special issue entitled: Green Extraction Techniques  
306 [32].

307 Primarily, students should be taught the principles of green analytical chemistry. Noteworthy  
308 is the fact that it is impossible to formulate universals for all potential applications, however  
309 clear guidelines would provide students with GAC framework essential for better  
310 understanding [41]. Gałuszka et al. [41] using four of the principles provided in 1998 by  
311 Anastas and Warner revise and supplement the 12 principles of green chemistry to achieve  
312 full possible application in analytical chemistry.

313 As stressed previously, the necessity of effective green analytical chemistry teaching  
314 requires not only relevant students’ materials but also the use of modern memorizing methods, which



315 aid information retention or retrieval memory. Thus, below presented mnemonic  
316 SIGNIFICANCE (Figure 3) which includes the 12 Principles of GAC seems useful for  
317 students. Furthermore, an important element that will help in understanding and assessing  
318 whether the methods evaluated are green, would be green analytical metrics, which are  
319 discussed in more detail in the next section.



320

321 Figure 3. The principles of green analytical chemistry expressed as the mnemonic  
322 SIGNIFICANCE based on the idea published in [41].

323

324 In addition, the six principles of green extraction of natural products has been introduced in  
325 2012 as a new idea to meet the challenges of the 21<sup>st</sup> century, to protect the environment and  
326 consumers, and in the meantime enhance competition of industries to be more innovative,  
327 ecologic and economic. Within this green extraction concept, an extract should be obtained in  
328 such a way to have the lowest possible impact on the environment (less energy and solvent  
329 consumption, *etc.*), and whose eventual recycling would have been planned for (co-products,  
330 biodegradability, *etc.*) [12].

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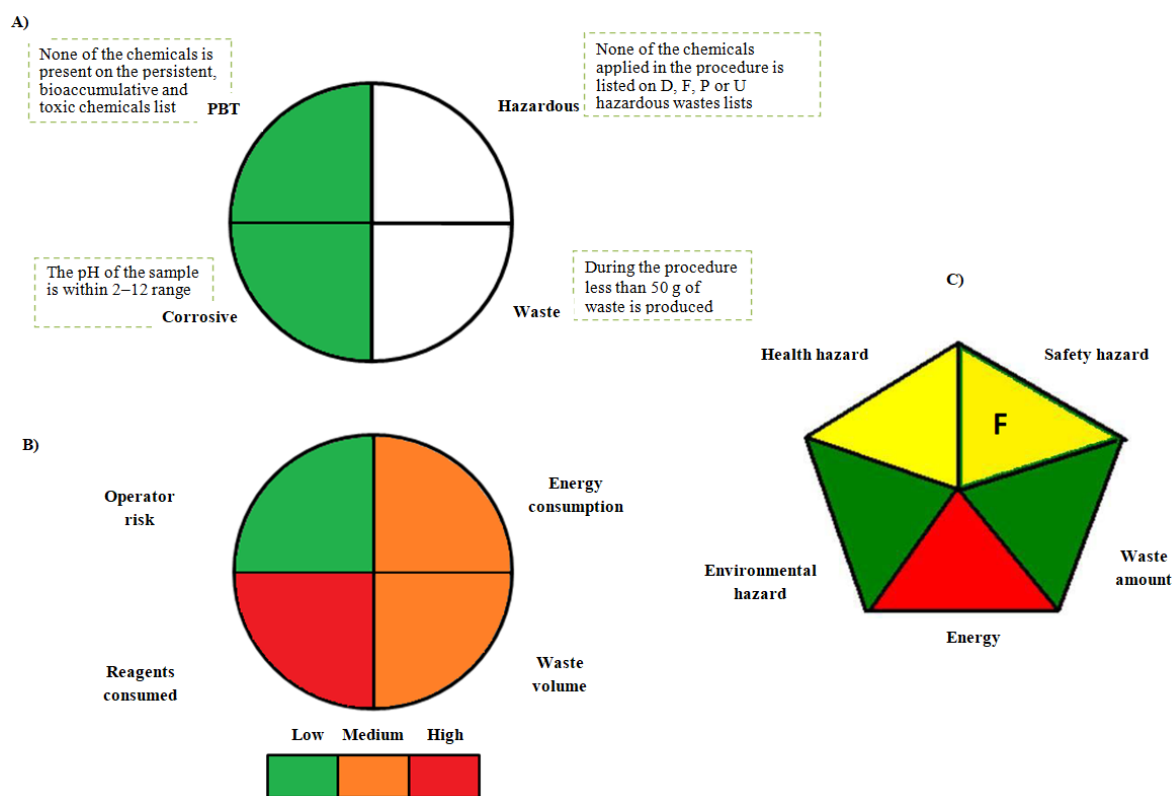
### 332 3.3. Metrics for assessing green analytical procedures

333

334 Nowadays, many analytical chemists who publish work focused on the newly  
335 developed methodology, claim in their work that this new procedure is green, however, very  
336 often no evaluation of the greenest (e.g. in the form of applied metrics of greenness, and  
337 comparisons with previously developed analytical or standard procedures) is performed. This  
338 is also educational challenge, how to prove students that the communicates of methodology  
339 greenness are many often based on the authors' impressions or uncertain assumptions and  
340 such proceeding is wrong [42]. There are several literature examples where this kind of  
341 thinking is wrong. Thus, calculations that give an answer for question whether an analytical  
342 procedure can be considered green, should be carried out by utilizing the tools that serve such  
343 assessment [7] and such proceedings should be learned from the earliest steps of the analytical  
344 chemists. However, it may provoke to ask another question: how to measure the greenness of

345 analytical methods? Without a doubt, it can be stated that one of the main problems of GAC is  
 346 that there are no well-established methods of “greenness” assessment [42], while in general,  
 347 green chemistry has several existed metrics systems [43]. The most popular metrics in green  
 348 chemistry are environmental impact factor, atom economy, and reaction mass efficiency.  
 349 These are mainly used to evaluate the green character of chemical reactions, applicable in  
 350 organic synthesis. But also other tools were introduced for the fragrance or pharmaceutical  
 351 industries [44, 45]. Because these tools are associated to the mass of the reaction product, it is  
 352 not possible to use them in the field of green analytical chemistry.

353 Only few published and universal methods for assessment of the green character of  
 354 analytical procedures exist and these should be presented to students as an option to choose  
 355 during these researches. One of the oldest tool that can be applied to evaluate the greenness of  
 356 analytical methodologies is National Environmental Methods Index (NEMI) [36]. In this tool,  
 357 analytical methodologies are assessed by applying the pictogram - greenness profile symbol -  
 358 divided into four fields (Figure 4A), however, each part mirrors different aspect of the  
 359 described analytical methodology and the field is filled green if certain requirements are met.  
 360



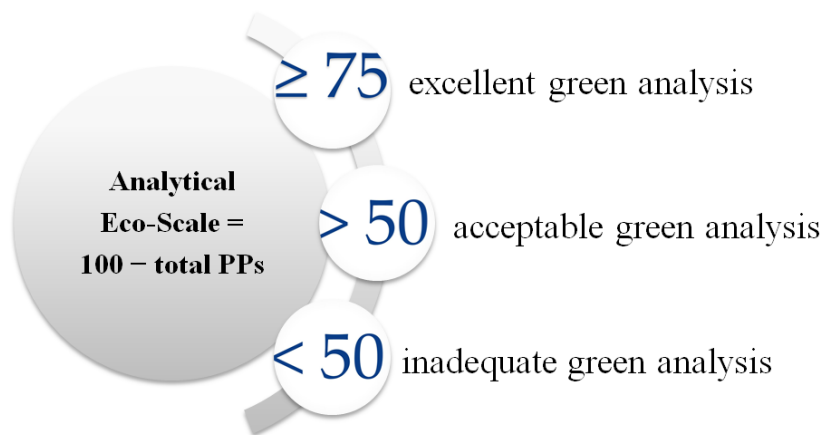
361  
 362 Figure 4. Assessment of analytical procedure by A) NEMI tool and B) additional pictogram  
 363 proposed by Guardia et al. [36], pictogram proposed by Raynie et al. [46]

364 The NEMI as a greenness assessment tool is easy to read by potential procedure users,  
 365 however, it presents only general information about an environmental impact of the evaluated  
 366 methodologies. Moreover, the NEMI pictogram cannot be considered as being semi-  
 367 quantitative because this symbol presents each threat either below or above a certain value. In  
 368 addition, preparation of a pictogram is time consuming because each compound has to be  
 369 checked, especially if many, non-typical chemicals are used in the procedure. Each compound  
 370 has to be checked if it is inherent on at least one of the lists as EPA's TRI list [47] and  
 371 Resource Conservation and Recovery Acts lists [48]. However, all of the proposed pictograms  
 372 are time consuming, thus, this drawback is common to all. Therefore, in order to ameliorate  
 373 the NEMI tool, Guardia et al. [36] suggested a supplementary pictogram (Figure 4B) to  
 374 classify, applying a color scale, three levels of assessment of procedures for how green they

375 are. Based on the same principle of the green symbols, a circle with four fields could be  
376 applied to quantify-from red to orange and green-the high, medium, or low risk engaged for  
377 operators and the levels of solvents as well as reagent and energy consumption and wastes.  
378 This alteration makes the NEMI procedure evaluation more quantitative.

379 Another tool for evaluating chemical methods including analytical methodologies  
380 relative to features of green chemistry has been introduced by Raynie et al. [46]. In this tool,  
381 the evaluation classify the risk potential into five categories as follows: health, safety,  
382 environmental, energy, and waste, based on toxicity, bioaccumulation, reactivity, waste  
383 generation, corrosivity, safety, energy consumption, and related factors (Figure 4C). Assessed  
384 procedures obtain a 1-3 score for each attribute applying available chemical data. All of the  
385 criteria are presented on pentagram and marked green, yellow or red depending on the impact  
386 on the environment [46]. The visual presentation of this tool permits individual researchers to  
387 make their own value verdicts about conflicting green criteria, thus, this tool is most precious  
388 in comparing procedures.

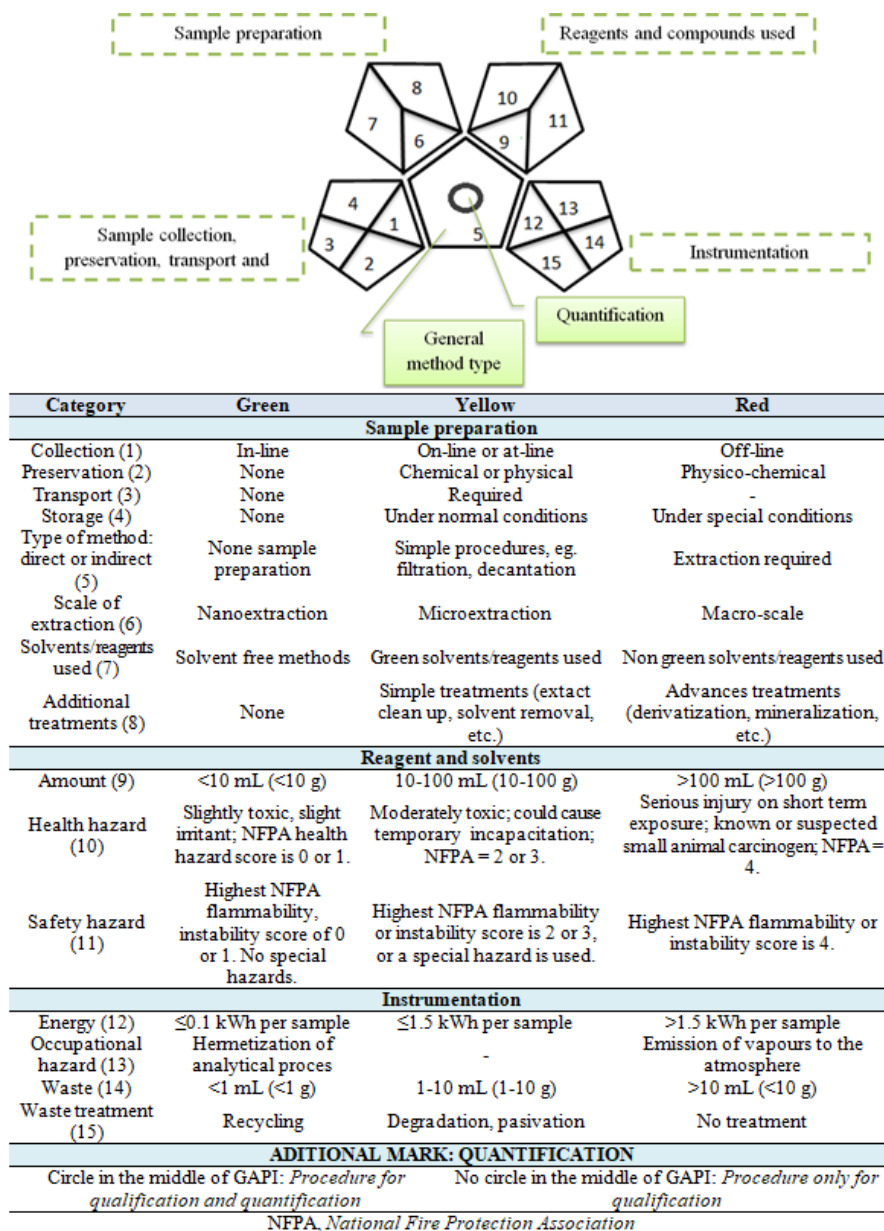
389 Another comprehensive tool for semi-quantitative evaluation of analytical procedures  
390 that can be used by the students as well as researchers is Analytical Eco-Scale introduced by  
391 Namieśnik et al. [49]. This tool can be used for comparison and assortment of the greenest  
392 alternative, but also it provides possibility to assess the green character of the new or modified  
393 methods to be evaluated. The idea of Analytical Eco-Scale is based on the definition of the  
394 ideal green analysis, which can be characterized, by reduction or elimination of reagents as  
395 well as energy consumption, and no generation of waste. The basis for the Analytical Eco-  
396 Scale concept is that the ideal green analysis has a value of 100 points. Each of the analytical  
397 methodology parameters including reagents and solvents amount, hazards, waste and energy,  
398 penalty points (PPs) are assigned if it departs from ideal green analysis. Due to the fact that  
399 the impact of hazardous substances depends also on their amount, it was proposed that the  
400 total PPs should be calculated by multiplying the sub-total PPs for a given hazard and amount  
401 [49]. The sum of PPs for the whole methodology should be included in the Eco-Scale  
402 calculation, in accordance with to the formula presented in Figure 5.  
403



404 Figure 5. Equation for the calculation of Analytical Eco-Scale and its description  
405  
406

407 In 2018, Płotka-Wasyłka introduced to analytical practice a new tool called Green Analytical  
408 procedure Index (GAPI) [7]. The GAPI tool uses a pictogram to classify the greenness of each  
409 analytical procedure stage, applying a color scale, with three levels of evaluation for each  
410 stage. A GAPI symbol consists of five pentagrams and can be used to assess and quantify-  
411 from green through yellow to red-the low, medium and high environmental impact engaged  
412 for each stage of the analytical procedure. Similar as in NEMI, each part of GAPI pictogram  
413 reflects a different aspect of the described analytical methodology and the field is filled green

414 if certain requirements are met. Description of Green Analytical Procedure Index parameters  
 415 used for the assessment of procedure as well as GAPI symbol are presented in Figure 6.  
 416



417  
 418 Figure 6. Green Analytical Procedure Index symbol and parameters description  
 419

420 The GAPI tool is a good semi-quantitative tool for educational purposes and laboratory  
 421 practice. It is characterized by several advantages: has well-defined evaluation criteria, is very  
 422 simple and fast to apply, and can be used to any known and new methodologies. The GAPI  
 423 symbol not only supplies an immediately noticeable perspective to the user and reader but  
 424 also provides exhaustive information on assessed methodologies [7].  
 425

#### 426 4. Main concepts for teaching GAC

427 Making analytical chemistry more benign is the basic approach that combines old and  
 428 new concepts of analytical chemistry and as such, it should be transmitted into the teaching of  
 429 green analytical chemistry.

430 Being benign implies the consideration of the key words concerning the sustainable  
431 development context: safety, reduced energy consumption and decontamination of waste.  
432 Considering this, it seems quite clear: The environmental mentality in analytical chemistry is  
433 a recent compromise of chemistry but it should be carefully considered in order to assure the  
434 sustainable development of our discipline [50]. Changing chemistry according to the  
435 principles of green chemistry through introductory chemistry courses, we can change the  
436 mentality of those who practice chemistry, students and citizens.

437 An important goal in teaching analytical chemistry is to change the attitude of  
438 chemistry student, also change the attitude of future generations about chemistry and its  
439 impact on the environment, and eventually leads to the sustainable development through  
440 green chemistry. The basic concepts for teaching green analytical chemistry are related to the  
441 well-known principles of green analytical chemistry [41, 51].

442 For a long time, some of the principles of green chemistry have been included in teaching  
443 analytical chemistry since they are essential for safety and lab costs: natural reagents, non or  
444 less-toxic solvents, drop reactions or work with a small amount of sample mass and reagents.  
445 This will enhance the safety of students, but also reduce waste and costs of purchasing new  
446 chemicals. Also, these efforts were not mandatory and they only depended on ethic  
447 preferences of teachers and lab staff.

448 In achieving this goal, additional efforts should be made to educate teachers about  
449 transmitting sustainability messages in analytical chemistry teaching. To chemistry students  
450 or related professions it should be quite clear that the principles of green analytical chemistry  
451 should be a daily thinking styles of solving analytical problems, some kind of obligations and  
452 in no case a matter of choice.

453 As pointed out in recent paper [2], the main concepts for teaching green analytical chemistry  
454 should be:

- 455 i) application of less toxic solvents and reagents; As an alternative to the process of  
456 greening the analytical methods, the consumption of reagents and solvents, as well as  
457 the sample mass can be reduced. This will finally contribute to the environmentally  
458 acceptable approach and result in laboratory costs and waste amount reduction.  
459 Initially it is good to reduce the consumption of toxic reagents and solvents or replace  
460 them with less toxic, but the ultimate goal could be the use of completely benign ones  
461 as the reagents from nature.
- 462 ii) reduction and on-line decontamination of waste; It is very important to seek for new  
463 online decontamination options that involve recovery or detoxification of wastes. The  
464 benefits of such a procedure are numerous but most evident improvements are in the  
465 economical and environmental aspects.
- 466 iii) lower power consumption; Modern analytical methods imply the use of the new  
467 instrument techniques, often in-field measurement or the use of portable instruments  
468 which reduce the time of analysis, lowers both lab costs and power consumption.
- 469 iv) integration of analytical procedure; According to a modern approach of analytical  
470 chemistry, all of the analytical steps become one analytical problem that needs to be  
471 solved integrally.
- 472 v) automation, miniaturization; The last but, apparently, the most important concepts,  
473 atomization and miniaturization are directly related to all other concepts, permitting  
474 dramatic reduction in the consumption of reagents and waste generation [41].

475  
476 Obviously, the new concepts in teaching green analytical chemistry include the greening of  
477 analytical methods and also the development of new green methodologies. Depending on the  
478 analytical procedure, sampling, sample processing and the use of reagents, it implies the use  
479 of hazardous and harmful chemicals, and eventually the generation of hazardous waste, rarely

480 in large quantities. Safety concerns regarding to the lab and waste have become the reason for  
481 developing new ideas of improving the safety in a laboratory and reducing successfully the  
482 amount of waste or decontaminating it. Hazard and waste become recognized as design flaws  
483 or, more positively, as opportunities for innovation. Experiments can be performed in  
484 laboratories that are more comfortable and alluring as well as more economical to maintain  
485 [25].

486 Analytical chemistry gives the opportunity for innovations in both teachings and science, in  
487 the context of waste treatment or by using new reagents, for example, natural reagents that  
488 increase students` understanding and sensitivity to the environmental consequences of their  
489 scientific choices [25, 52].

490 The possibility of automation in the process of developing the method is always an added  
491 value and implies the possibility of integration of the entire analytical procedure, beginning  
492 from the sampling, then reagent delivery, detection and direct decontamination of waste.

493 Very often, flow injection analysis (FIA), sequential injection analysis (SIA), or other  
494 techniques based on similar principles are a very powerful tool in the efforts of automation or  
495 minimization of the methods, to green the existing method significantly [53].

496 It is very important to emphasize the advantages of using these systems: wide potential of  
497 application, reduction of solvent and reagents consumption and sample size, increase of  
498 sample throughput, the ability to use different detectors, improved sensitivity and other basic  
499 analytical features of the method. Considering that the most of these devices can be found in  
500 laboratories or obtained at an acceptable price, this analytical tool becomes a very interesting  
501 and inventive tool in teaching green analytical chemistry.

502 In all these efforts to include a new approach in the teaching of green analytical chemistry, the  
503 importance of analytical features of the methods should not be neglected. Green analytical  
504 chemistry concepts are not introduced in order to replace the existing ones. New concepts,  
505 rather, can be considered complementary to the existing concepts and can be studied through  
506 the curriculum by giving them the same attention. Green analytical chemistry is also a tool for  
507 obtaining information of analytes of different origin, taking into account the safety in the  
508 laboratory and with minimal environmental impact, but without scarifying the analytical  
509 requirements: sensitivity, selectivity, robustness, accuracy and precision.

510 However, at the end we will ask:

- 511 i) What do new concepts in teaching green analytical chemistry bring to the  
512 teachers? Much effort in mastering new teaching skills.
- 513 ii) What do students get? - Interesting and innovative approach to chemistry with the  
514 ability of critical thinking about experimental design. They will learn the  
515 development of new environmental friendly analytical methods. Students will  
516 become better chemists and more responsible citizens because they will learn to  
517 solve the problem not always in an easier way, but in a more socially responsible  
518 way. They will learn to manage the risks and find a compromise between the  
519 demands of the profession, the economy and the environment.
- 520 iii) What about chemistry? Chemistry will become more acceptable to students. They  
521 will understand the content of the course in depth and consequently, the public  
522 perception of all the benefits that analytical chemistry brings will change on  
523 positive. Much more students will find a science discipline - chemistry - as  
524 enjoyable and worth selecting for their future profession.

526 A Table 4 summarizes relevant information in terms of green analytical chemistry of works  
527 discussed in this section.

528

529 **Table 1.** Basic concepts and improvements in the teaching of green analytical chemistry

530

Concepts in teaching GAC	Recommendation	Improvements	The main goal
Less toxic or innocuous solvents and reagents	Application of reagents from nature and benign solvents	Save costs; More comfortable and safer lab	
Reduction of waste	On-line decontamination or less reagents and solvents	Better economical and environmental aspects	
Lower power consumption	New instrument techniques; In-field measurements portable instruments	Reduce the time of analysis, Lower lab costs; Lower power consumption	
Integration of analytical procedure	All analytical steps become one analytical problem	Integral approach to learning and problem-solving models	Safety lab and more socially responsible analytical chemist
Automation, miniaturization	Application of methods based on flow injections and similar techniques	Less reagents and waste, enhanced analytical features	
Analytical figure of merit	Should not be neglected	New green analytical method with enhanced analytical features	

531

## 532 **5. Case studies**

533 Changing the mentality of future chemists and chemical engineers is already  
534 beginning through the introductory courses of green chemistry. The most important  
535 responsibility is for the instructors who need to make additional effort and apply the proposed  
536 concepts in teaching analytical chemistry to the classroom and, even more importantly, in the  
537 lab.

538 There are texts that help teachers to understand the basic principles of green chemistry  
539 and how to introduce them into the teaching process. However, lab manuals for green  
540 analytical chemistry are seldom available. There are also a few scientific papers  
541 problematizing the teaching green analytical chemistry in specialized Educational journals.

542 There is a growing need to expand the range of pedagogical materials from the same  
543 chemical subdisciplines most notably to the analytical/environmental and physical chemistry  
544 [54].

545 Numerous studies are available that provide direct green analytical methods. Special  
546 authors were referring to the NEMI bases that make green methods easier to identify by  
547 giving analytical teachers and chemists the opportunity and responsibility to select low  
548 environmental impact processes.

549 S. Dutta and A. K. Das [55] have suggested fifteen Green Analytical Chemistry  
550 experiments, which can be practiced by the graduate students of chemistry. In this work the  
551 conventional method was described and a green laboratory proposal was offered with  
552 additional comments. These experiments cover some of the most significant achievements in  
553 the application of green analytical chemistry: solvent free, pressurized-solvent extractions,  
554 microwave-assisted treatments, ultrasound-assisted leaching, solid phase extractions, green  
555 spectrometry and so on. Thus, students become familiar with basic principles of analytical,  
556 environmental and green chemistry through real world application [55].

557 In the early days of green analytical chemistry education, at Hendrix College a  
558 laboratory was developed for teaching green analytical chemistry as an introductory course to  
559 students by using simple, outcome-based assessment tools, guiding three basic criteria:  
560 experiments should both apply and teach the principles of green chemistry, train students in  
561 analytical techniques, and use environmental samples. In the lab they use modified standard  
562 UV-Vis molecular and flame atomic absorption spectroscopy protocols to analyze the iron.  
563 These experiments allow them to maintain a green laboratory while engaging student interest  
564 through parallels to more toxic materials. Although the introductory program cannot create  
565 experts, students will be "green" educated to continue and choose their professional and  
566 personal lives that in accordance with their green ethics, will have a significant and positive  
567 impact on the environment [56, 57].

568 There are many examples of using simple herbal extracts for chemical analysis. These  
569 processes are safe for undergraduate and high school students. Using available materials in  
570 conducting research, as well as taking into account personal experiences of students, may  
571 maximize student participation and increase interest in initiating research. The use of low  
572 quality herbal extracts in chemical analysis is a green chemistry approach and does not have  
573 to sacrifice the quality of chemical education. There are three good examples of green  
574 analytical methods in teaching through the categorization of problem based learning, and  
575 method development-based learning. Students study green chemistry through these  
576 categorizations using herbal extracts as natural reagents, with careful guidance and design of  
577 research projects. Students' experience; participation in the conferences and publications was  
578 achieved with a minimum budget [52].

579 There are also educational papers that describe the application of green extraction  
580 methods in the analysis of environmental samples. For example, there was a designed  
581 experiment to introduce students into the philosophy of green analytical chemistry by using  
582 solvent microextraction techniques (SME) in determination of phosphorus in water, an  
583 environmentally friendly alternative to solvent extraction. Students are involved in the  
584 development of a miniaturized methodology with the assessment of the main experimental  
585 parameters that affect the extraction process using univariate optimization, preparation of the  
586 phosphorus calibration curve, and determination of the corresponding figures of merit [58].

587 Buckley et al. [59] have shown that a classic example of green chemistry can be  
588 introduced in the undergraduate analytical chemistry laboratory. This experiment is divided  
589 into two major parts: liquid CO<sub>2</sub> extraction of D-limonene from orange rind and quantitative  
590 analysis of extract by gas chromatography (GC-FID). The procedure established natural  
591 product extraction, calibration curves, and internal standards while simultaneously



592 demonstrating alternative solvent selection for pollution prevention and increased chemical  
593 safety. Undergraduate students have applied some of the important principles of green  
594 chemistry including pollution prevention, energy efficiency, renewable raw materials, safer  
595 solvents, design for degradation, and safer chemistry for accident prevention [59].

596 The extraction of heavy metals from environmental samples using micelle-mediated  
597 extraction has been used as a pilot lab in an advanced undergraduate analytical chemistry  
598 laboratory. The aim of this study was to introduce students with basic principles of green  
599 analytical chemistry and environmental through a "real world" application. Extraction of  
600 heavy metals from surface waters and wastewater was carried out using an environmentally  
601 benign preconcentrating technique. Atomic absorption spectrometry (AAS) was used for  
602 metal identification. The analytical procedure consisted of; preparation of calibration curve,  
603 analysis of water samples, evaluation of the matrix effect, analysis of several spiked samples  
604 and analysis of reference sample. This study has provided students with hands-on experience  
605 in environmental analysis that uses an alternative technique instead of hazardous and volume-  
606 consuming organic solvent methods. New method demonstrates minimization of laboratory  
607 wastes and the replacement of the remaining small volume of wastes with less hazardous  
608 surfactants, which is beneficial for both laboratory personnel and the environment [60].

609 The experiment of extraction and antibacterial properties of thyme leaf (*Tymus*  
610 *vulgaris*) extracts was carried out in teaching undergraduate analytical chemistry.  
611 Approximately 600 students in advanced general chemistry and quantitative analysis classes  
612 at UC Berkeley have successfully conducted this experiment. Students developed critical  
613 reasoning, analytical skills (solid–liquid extraction, chromatography basics, TLC and HPLC  
614 of thyme extract) and met microbiology techniques (Kirby–Bauer disk diffusion). The main  
615 goal of the experiment was to incorporate green analytical chemistry into the curriculum.  
616 Several important principles of green chemistry have been applied such as use of renewable  
617 feedstocks, design for degradation, use safe solvents and auxiliaries and prevention [61].

618 Microwave extraction is a research topic that has affected several areas, especially in  
619 green analytical chemistry. Chemat et al. [62] have developed a new green procedure in  
620 teaching green analytical chemistry, using microwave energy as energy source, to teach the  
621 fundamental concepts of extraction of essential oils from orange peel. Qualitative and  
622 quantitative analysis has been performed by using gas chromatography (GC-FID and GC-  
623 MS). Green extraction method has been conducted by using Dean-Stark glassware and a  
624 Vigreux column inside a microwave oven without adding water and solvents. The advantages  
625 of using microwave energy for extraction of essential oils would be: reduced equipment size,  
626 energy efficiency, elimination of process steps and organic solvents, faster process and  
627 increase production. This experiment gives students fundamental and sustainable principles of  
628 green analytical chemistry [62].

629 The analysis of whiskey by dispersive liquid–liquid microextraction coupled with gas  
630 chromatography-mass spectrometry (GC-MS) helped the students to developed hands-on  
631 skills of green chemistry extraction on “real-world” samples [63]. The pedagogical  
632 importance of this procedure was in the exploration of the power of MS and the post  
633 processing software to determine compounds in the whiskey samples. In this experiment,  
634 students have determined the content of individual components in whiskey based on literature  
635 data. In addition, students have critically analysed the results obtained, acquired MS database  
636 skills as well as searching scientific literature for the given problem. This has reduced the  
637 longevity of the process and the consumption of energy and chemicals [63].

638 One can note that in the some above reported experiments, as analytic technique used  
639 for quantification, is spectrometry. Nevertheless, the main role in “greening” this experiment  
640 has some other aspects of procedure.

641 Based on reports from some authors [64] it may be the easiest way to develop and  
642 apply a green analytical method based on spectrometry. Spectroscopy methods require, in  
643 general, low amounts of reagents, a reduced treatment of samples, and are suitable to be easily  
644 mechanized, thus reducing the operator and environment risks and scaling down the  
645 consuming of hazardous products [65]. According to this, it has been expected that we have  
646 more educational green analytical chemistry papers that discuss the appliance of the green  
647 spectrometry in teaching.

648 However, the experiment that can be employed to introduce green analytical chemistry  
649 principles to undergraduate students is proposed by Hg determination in milk by AFS and the  
650 online passivisation of analytical wastes. The method was designed to feature two key  
651 requisites of a green analytical method: use of less toxic reagents and waste management [29].

652 In addition, electrochemical devices offer unique opportunities for addressing the  
653 challenges of green analytical chemistry, namely providing effective process monitoring  
654 while minimizing its environmental impact [66]. There is a research showing that using ion-  
655 selective electrode as an alternative way of the greening process of in-line electrochemical  
656 procedure, like the Just-Dip-It approach that almost fulfills the 12 principles of GAC [67].

657 It was reported on the application of microcell for electrochemistry in the undergraduate  
658 analytical laboratory with the aim of reducing hazardous waste [68]. Based on this, it seems  
659 interesting to use a construction of glucose biosensor in undergraduate analytical chemistry  
660 laboratory that allows analysis in a drop. These experiments offer high educational content  
661 related to biosensor principles and new contemporary trends in analytical chemistry [69].

662 Quantitative analysis by voltammetry is proposed for undergraduate chemistry  
663 students for understanding the fundamentals and the analytical applications of  
664 electrochemistry. This experiment presents new educational values regarding the replacement  
665 of classical methods with a "greener" electrochemistry by substituting the mercury electrodes  
666 with bismuth-coated screen-printed electrodes in the determination of quinine in tonic water.  
667 In addition, students are exposed to some of the essential problems of experimental analytical  
668 chemistry and a real-world sample, which makes the experiment more interesting [70].

669 Green or greener principles can be skillfully applied in teaching with flow analysis  
670 methods. Simple handling, versatile tools for automation of wet chemistry procedures is a  
671 special way that can enhance green chemistry experiment or any other experiment can make  
672 „greener“.

673 An experiment that comprises a flow-injection spectrophotometric method for the  
674 determination of creatinine is described for introducing the green analytical chemistry to  
675 undergraduate students. This procedure allows a reduction of reagent consumption by 60%  
676 compared to the corresponding batch procedure. Creatinine is determined in real or synthetic  
677 urine samples by UV-Vis spectrophotometry. Subsequently, the wastes are photochemically  
678 degraded by UV radiation. This approach highlights two key requisites of an ideal green  
679 analytical method: minimization of reagent consumption and waste management [71].

680 The spectrophotometric method based on sequential injection analysis (SIA), aiming  
681 at determining Fe ions by the application of the natural reagent, is suggested for the courses of  
682 analytical chemistry in undergraduate studies. The students have goal to design SIA method  
683 through experiments optimization and finally take advantage of this method in the analysis of  
684 real samples. SIA is the second generation of flow systems and offers good analytical  
685 characteristics due to their simplicity, high analytical frequency and capacity to reduce  
686 reagent consumption when compared with FIA or batch procedure. This method is interesting  
687 for students, inexpensive and meets basic principles of green analytical chemistry [72].

688 In this review, some interesting experiments were described, for which their authors  
689 selected the keyword "green analytical chemistry". All the examples, mainly for graduate and  
690 undergraduate studies, reported above are the result of the commitment of scientists and

691 teachers in the field of analytical chemistry with the aim of enriching existing or introducing  
692 new content into the curricula of green analytical chemistry. Experiments meet some of the  
693 basic principles of green analytical chemistry: contribute to the reduction of the sample and  
694 the consumption of reagents and solvents, the replacement of toxic chemicals, the new  
695 „green“ treatment of sample, the treatment or waste reduction and energy saving.  
696

## 697 **6. Summary**

698 Nowadays, chemistry curricula as well as the education of chemistry teachers should more  
699 accurately reflect to the significance of education and sustainable development, but should  
700 also support and promote the development of human identity, which is undoubtedly correlated  
701 with the environment. This is also correct for Analytical Chemistry. Obviously, the new  
702 concepts in teaching green analytical chemistry include the greening of analytical methods  
703 and the development of new green methodologies. Teaching analytical chemistry should  
704 include the way of thinking about the analytical problems as well as their solutions in terms of  
705 sustainability. Few aspects should be emphasized; the classical figures of merit well known  
706 from the past and evaluating the persistent, bioaccumulative and toxic characteristics of some  
707 solvents and reagents, the application of hazardous or corrosive agents or solvents and the  
708 analytical wastes generation.

709 Although, there are texts that help teachers to understand the basic principles of green  
710 chemistry, discussing the way of introducing them into the teaching process, lab manuals for  
711 green analytical chemistry are seldom available. In addition, a few scientific papers  
712 problematize the teaching green analytical chemistry in specialized educational journals.  
713 Thus, there is a growing need to expand the range of pedagogical materials from the same  
714 chemical subdisciplines most notably to the analytical/environmental and physical chemistry.  
715 Therefore, we believe that this manuscript is of high importance and can help readers in the  
716 future practice.

717

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