

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.

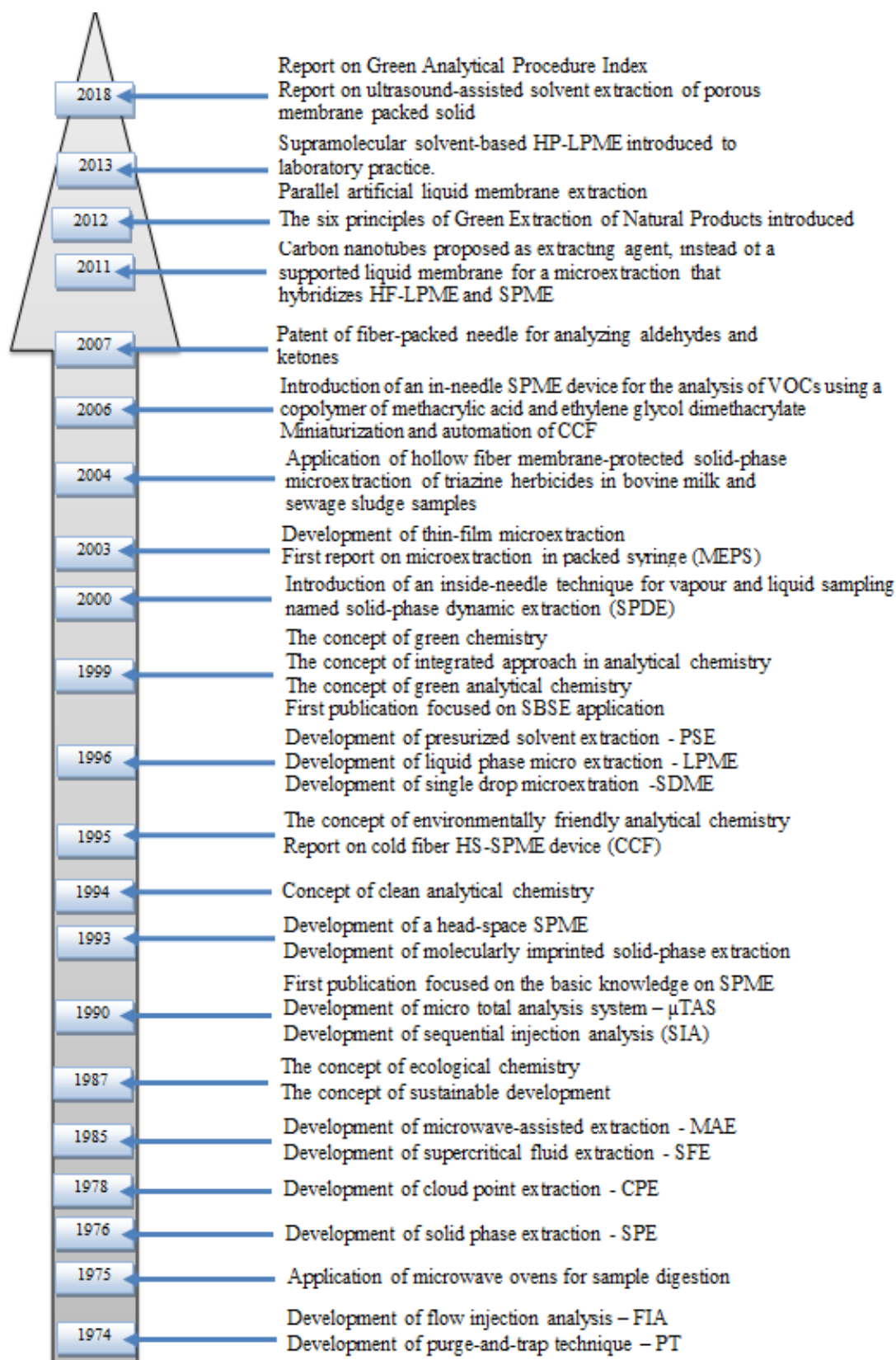


Figure 1. Milestones of Green Analytical Chemistry [7-12]

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 20th 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].

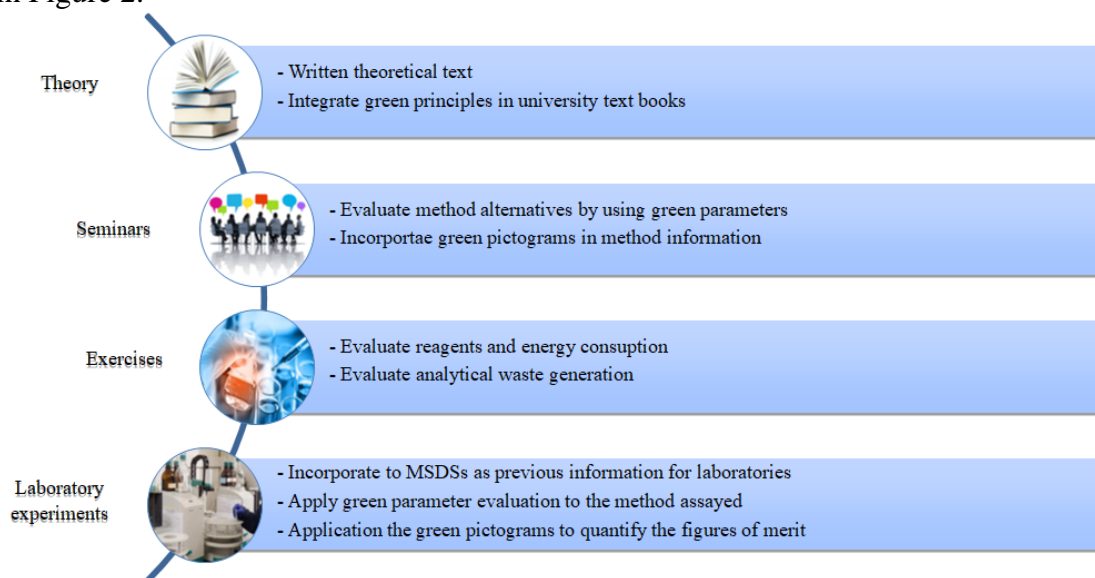
201 Social responsibility, sustainable development, justice, honesty and transparency
202 should not be enclosed in the conceptual ghetto of incomprehensible theories, but become the
203 very foundation of education preparing for chemistry in practice — a compass that will not
204 only help navigate 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
 239 Figure 2. Aspects to be considered for greening Analytical Chemistry teaching practices
 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 21st 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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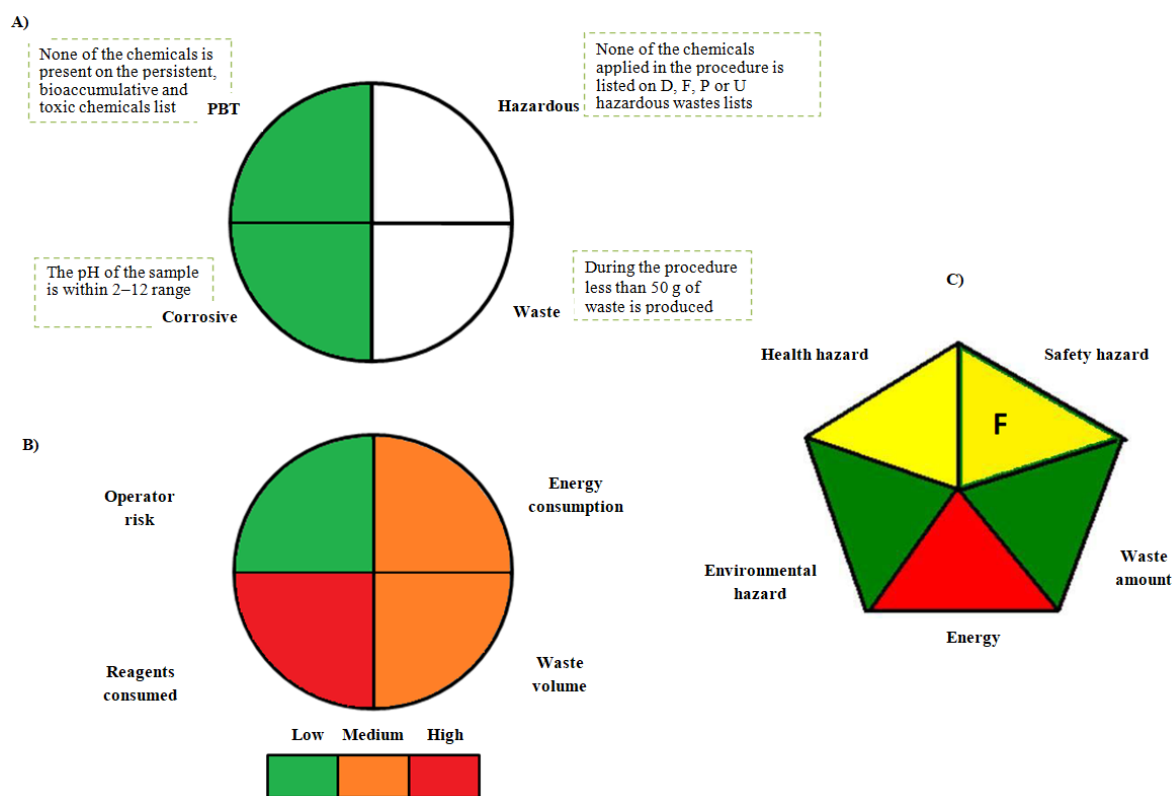
332 3.3. Metrics for assessing green analytical procedures

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



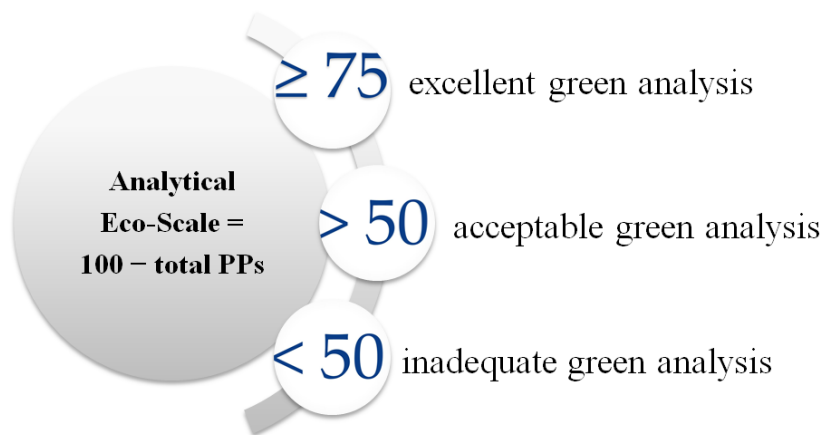
361
 362 Figure 4. Assessment of analytical procedure by A) NEMI tool and B) additional pictogram
 363 proposed by Guardia et al. [36], pictogram proposed by Raynie et al. [46]

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.

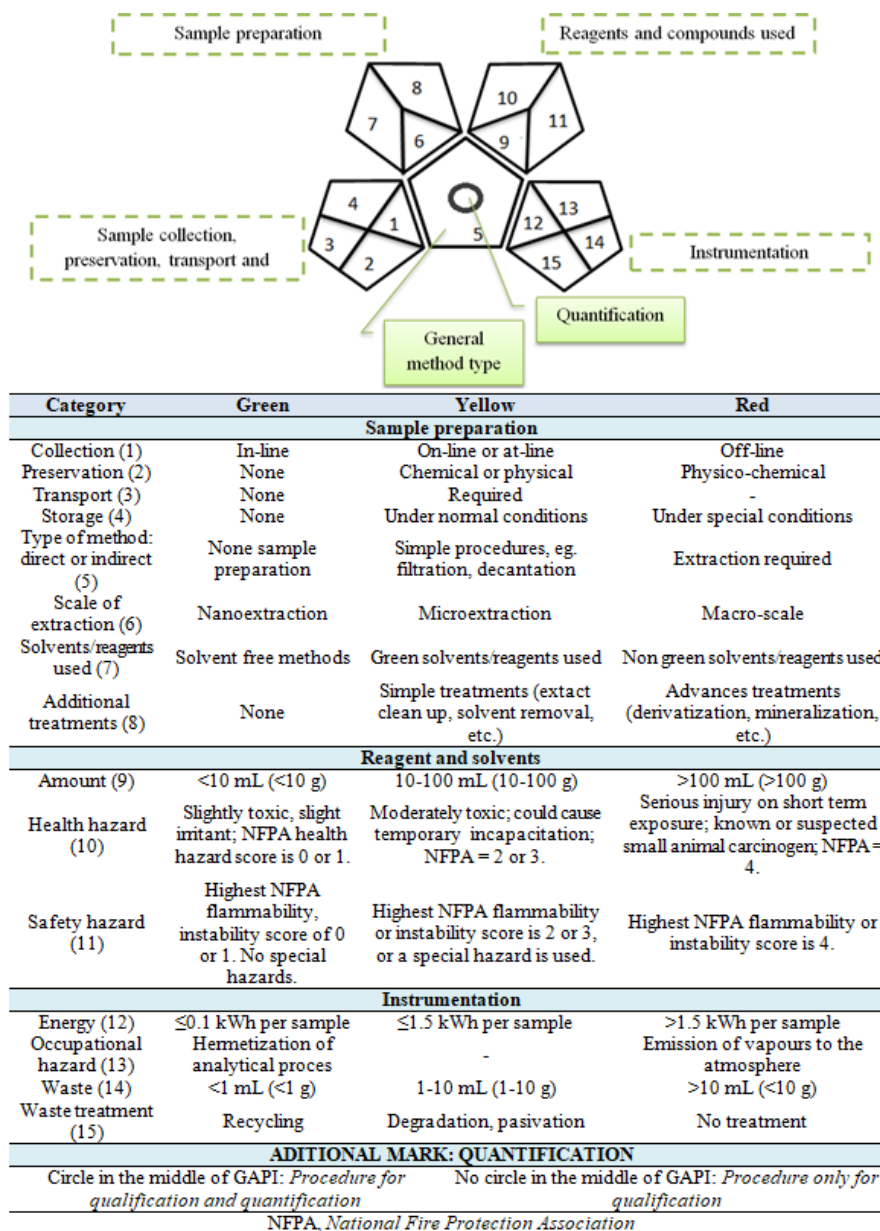
389 Another comprehensive tool for semi-quantitative evaluation of analytical procedures
390 that can be used by the students as well as researchers is Analytical Eco-Scale introduced by
391 Namieśnik et al. [49]. This tool can be used for comparison and assortment of the greenest
392 alternative, but 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 CO₂ 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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