ЕҢБЕК ҚЫЗЫЛ ТУ ОРДЕНДІ
«Ә. Б. БЕКТҰРОВ АТЫНДАҒЫ
ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»
АКЦИОНЕРЛІК ҚОҒАМЫ

ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

CHEMICAL JOURNAL of KAZAKHSTAN

АКЦИОНЕРНОЕ ОБЩЕСТВО
ОРДЕНА ТРУДОВОГО КРАСНОГО ЗНАМЕНИ
«ИНСТИТУТ ХИМИЧЕСКИХ НАУК
им. А. Б. БЕКТУРОВА»

3 (67)

ИЮЛЬ – СЕНТЯБРЬ 2019 г.

ИЗДАЕТСЯ С ОКТЯБРЯ 2003 ГОДА

ВЫХОДИТ 4 РАЗА В ГОД

АЛМАТЫ
2019

УДК 547.673

T. V. KHARLAMOVA

JSC «A. Bekturov Institute of Chemical Sciences», Almaty, Republic of Kazakhstan

"GREEN" DIRECTIONS MICROWAVE EXTRACTION IN CHEMISTRY OF NATURAL COMPOUNDS
Report 1. Methods for assessing the environmental performance of analytical procedures

Abstract. Over the past decades, areas related to the improvement of complex processing of vegetable raw materials and the creation of highly efficient methods for the isolation of biologically active substances (BAS), one of the approaches of which is microwave extraction (microwave-assisted extraction (MAE)), have received intensive development. At present, microwave extraction is one of the areas of analytical "green" chemistry, which quickly gained the position of one of the most effective methods for isolating compounds. The tendency of its development is the development and introduction of innovative approaches to reduce or eliminate the use of hazardous and toxic chemicals that comply with the principles of "green chemistry". To properly measure the effects of chemical processes on the environment, their special assessment is necessary. The review examines a variety of methods used to assess environmental friendliness, developed metrics of green analytical chemistry, including the NEMI labeling and Eco-Scale analytical. The question of assessing the environmental performance of analytical procedures for the microwave extraction of natural compounds is considered.

Keywords: natural compounds, microwave extraction, environmental assessment methods.

Introduction. Microwave extraction is currently one of the areas of analytical chemistry, which quickly gained the position of one of the most effective and modern methods to increase the efficiency of extraction of biologically active compounds from vegetable raw materials. Over the past decades, MAE methods have been investigated and implemented that allow to carry out the process with power, pressure, temperature control, as well as new modified microwave extraction methods that combine extraction with ultrasonic treatment, allow MAE without the use of organic solvents and other technologies. The tendency of its development is the development and introduction of innovative approaches to reduce or eliminate the use of hazardous and toxic chemicals that comply with the principles of "green chemistry" [1-5].

Green chemistry approaches are based on using cleaner and less polluting processes, reducing or completely eliminating the use of hazardous chemicals, preventing pollution at the initial stages of process planning and responsibility for the products produced [6]. Most efforts to make chemical processes more environmentally friendly emphasize the need for safer, less toxic, and more benign solvents, or the elimination of solvents, as well as a reduction in the use of reagents and auxiliaries. Other actions include reducing energy consumption through the use of milder conditions, preference for substrates based on renewable sources.

One of the problems in "green" chemistry is the assessment of environmental friendliness of chemical processes. It is well known that processes that cannot be measured cannot be controlled. Control in "green" chemistry should be understood as the ability to choose the most "green" option. Currently, when assessing the impact of chemical processes on the environment, various factors are used. The purpose of this article is to examine the various approaches to assessing the environmental performance of analytical procedures at MAE.

Green Analytical Chemistry has its own achievements in measuring environmental impact. The analytical process differs from industrial processes mainly in scale. Unlike industrial emissions, analytical processes cause diffuse pollution. On the one hand, emissions from analytical laboratories are low, but on the other hand, they are more dispersed than industrial emissions, which makes them more difficult to control.

There are only a few published and universal methods for assessing the environmental performance of analytical procedures [7]. To assess the environmental profile of the analytical methodology, various environmental impact assessment systems have been developed, for example, the National Environment Methods Index (NEMI) [8], Eco-Scale [9,10], Rayne and Driver profile [11]. In the case of microwave extraction, the environmental assessment can be considered on the basis of the use of hazardous reagents, the amount of waste, safety, energy consumption and environmental impact.

The first of these is the National Environment Methods Index (NEMI) [7, 8]. First released in 2002, the National Environmental Method Index (NEMI) (www.nemi.gov/) is a searchable database of environmental methods, protocols, statistical and analytical methods and procedures that allows scientists and managers to find and compare at all stages of the monitoring process, which results in a very easy-to-read pictograph showing whether hazardous and corrosive reagents are used or the procedure generates a significant amount of waste.

Pictograms NEMI is a circle consisting of four fields. Each field reflects different aspects of the analytical methodology and is filled with green if certain requirements are met. The first requirement is that none of the chemicals are on the list of persistent, bioaccumulative and toxic chemicals. The second of the requirements is that none of the chemicals in the applicable procedure are listed in the D, F, P or U hazardous waste lists (Resource Conservation and Recovery Act (RCRAs)) (https://www.epa.gov/). The third requirement is that the pH of the sample is in the range of 2–12 to avoid severe corrosion during the entire analytical process. The fourth and final requirement is that less than 50 g of waste is produced during the procedure.

If the above requirements are met, the corresponding part of the NEMI icon is colored green. An example of the NEMI icon is shown in figure 1.

Evaluation of an analytical procedure using NEMI is problematic, as it involves an excessive search for each reagent used, which must be present in lists with toxic, dangerous or persistent chemicals.

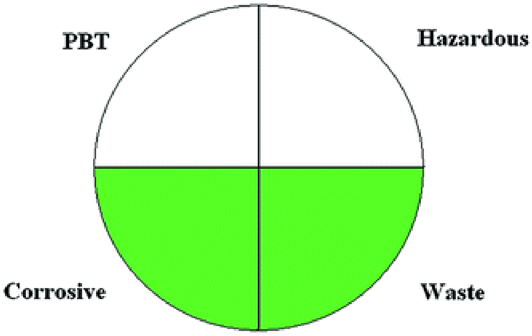


Figure 1 – The example of the assessment score with the NEMI procedure

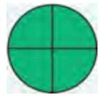
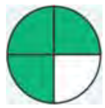
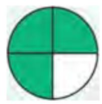
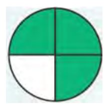
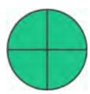
Thus, table 1 presents some examples of the use of the NEMI icon in MAE. The main advantage of NEMI as an environmental assessment tool is that it is easy to read and obtain general information about the environmental impact of the procedure. The two main disadvantages of NEMI marking are that the information obtained is fairly general, and filling in the NEMI character is time consuming. The symbol indicates that each threat is below or above a certain value and cannot be considered to be semiquantitative. The second drawback is associated with the tedious preparation of the symbol, especially if the procedure uses a lot of non-standard chemicals. Improvement of the NEMI icon has been proposed by De la Guardia M. and Armenta S. [24]. These authors proposed that each of the fields be colored using a three-color scale – red for a non-environmentally friendly analysis, yellow for a moderate, and green for an environmentally friendly analysis. This modification makes the assessment of the NEMI procedure more visual.

The second assessment procedure is an analytical eco-scale [9,10]. It includes more environmental impact assessment parameters than in the case of the NEMI exhibition sites. The eco-scale assessment procedure is based on penalty points deducted from 100 points. Penalty points are given for each type of reagent and the amount that can cause environmental problems, hazards associated with the use of chemicals, high energy consumption, occupational hazards and the way in which analytical waste is treated (and, more importantly, their absence). A summary of the procedural penalties is presented in table 2. The final result of the analytical eco-scale is a number that differs from 100 (“perfect green analysis”) in the number of penalty points. The closer the value is to 100, the “greener” the analysis will be [25].

Penalty points for each reagent are calculated by multiplying the hazard quantity of the pictogram by the degree of danger (‘warning’ multiplying by 1 and ‘danger’ multiplying by 2). Since hazard pictograms are placed on reagent containers, the hazards associated with their use are easily calculated.

Examples of the calculation of penalty points for used reagents are presented in table 3.

Table 1 – Examples of the use of microwaves
for more environmentally friendly extraction and its NEMI profile

Extractions method	Solvent	Raw material	Ana-lyzed deri-vatives	Extraction	NEMI profile	Ref.
1	2	3	4	5	6	7
MAE	Water	Medi-cinal Herb	Meta-bolites	0.5 g of sample 20 mL ultra-pure water T=100 °C, t=20 min, 600 W		12
MWE, Microwave assisted water extraction	Water	Green tea	Poly-phenols	6.0 g of sample 120 mL water T=80-100 °C, t=60 min, 600 W		13
MAAEE, Microwave assisted aqueous enzymatic extraction	Enzyme mixture: cellulose, proteinase, pectinase (1:1:1 w/w/w)	Isatis indigo-tica seeds	Oil	140 mL of water at pH 5 (adjusted with citric acid) Enzyme concentration 1.82% w/w 20 g of sample, T=43 °C, t=83 min, 375 W		14
Microwave assisted micellar extraction	Nonionic surfactant	Medi-cinal plants	Alka-loids	2 g of sample 40 mL of 5 % v/v acidified Genapol X-080 (Oligoethylene glycol monoalkyl ether) T=100 °C, t=10 min		15
Ionic liquid-based ultrasonic /microwave-assisted extraction	Ionic liquid (IL)	Rhubarb	Anthra-quino-nes	1 g of sample, 15 mL 80 % v/v ethanol 2.0 M [C_4MIM][Br] T=120 °C, t=6 min, 1200 W		16

Continuation table 1

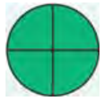
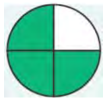
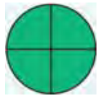
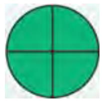
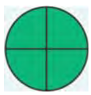
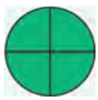
1	2	3	4	5	6	7
Ionic liquids-based microwave-assisted environmentally friendly extraction	IL	Medi-cinal plants	Alka-loids	1 g of sample, 12 mL IL 0.8 M [C_8MIM][Br] MAE at atmospheric pressure T=2 h soaking time, t=8 min, 385 W		17
Microwave-assisted ionic liquid extraction	IL	Medi-cinal plants	Poly-phenolic com-pounds	1 g of sample 20 mL of ILs ([C_4MIM]$_2$[SO_4] and other ILs) T=70 °C, t=10 min		18
MAE	IL	Ligus-ticum chuan-xiong Hort	Lacto-nes	0.5 g sample 5 mL ILs, N,N-dimethyl-N-(2-hydro-xyethoxyethyl)ammonium propionate) (DMHEEAP) and N,N-dimethyl(cyano-ethyl)ammonium propionate (DMCEAP) T=160 °C, t=1-5 min		19
MAE	Deep eutectic solvents	Camel-lia sinensis leaves	Cate-chins	1 g sample 35 mL of Choline chloride and lactic acid T=66 °C, t=8 min		20
MAE	Deep eutectic solvents	Grape skin	Plant pheno-lics	0.1 g of sample DES: Choline chloride: oxalic acid (ChOa, 1:1) T=50-90 °C, t=5-90 min		21
MAE	Deep eutectic solvents	Radix Scutel-lariae	Flavo-noids	2 g sample 30 mL of solvents (60% ethanol and NADESs) T= 55 °C, t=10 min, 500 W		22
MAE	Polyols-based deep eutectic solvents	Pyrola incar-nata Fisch.	Phenolic compou nds	1 g sample 30% of water in ChCl/1,4-Butanediol (1/4) T=70 °C, t= 20 min and liq./solid ratio 10 mL/g		23

Table 2 – Penalty points applied for the calculation of final analytical Eco-Scale score [25]

		Sub-Total Panalty Points	Total Panalty Points
Amount		Reagents	Amount Panalty Points × Hazard Panalty Points
	< 10 mL (<10 g)	1	
	10-100 mL (10-100 g)	2	
	> 100 mL (>100 g)	3	
Hazard	None	0	
	Less severe hasard	1	
	More severe hasard	2	
Energy		Instruments	
	< 0.1 kWh per sample		0
	< 1.5 kWh per sample		1
	> 1.5 kWh per sample		2
Occupational hazard	Hermetization of analytical process		0
	Emission of vapors to the atmosphere		3
Waste	None		0
	< 1 mL (< 1 g)		1
	1-10 mL (1-10 g)		3
	> 10 mL (>10 g)		5
	Recycling		0
	Degradation		1
	Passivation		2
	No treatment		3

Table 3 – Solvents, its pictograms and penalty points

Solvents	Pictograms	Signal	Penalty points
dichloromethane		warning	2
chloroform		danger	2
acetonitrile		danger	4
acetonitrile		danger	4
acetone		danger	4
ethyl acetate		danger	4
isopropanol		danger	4
diethyl ether		danger	4
benzene		danger	6
methanol		danger	6
toluene		danger	6
isooctane		danger	8
hexane		danger	8

The advantages of the analytical eco-scale include the ease of calculating points, the ease of comparing analytical procedures and the inclusion of various aspects of environmental impact. On the other hand, there is no information on the structure of hazards. The result of the Eco-Scale calculation does not indicate the reasons for the environmental impact of the used solvents and other reagents, production risk or generation of waste. Compared to the NEMI label, the analytical eco-scale provides information on the environmental impact in more quantitative terms.

Raynie D., Driver J.L. [9] proposed a new tool for evaluating chemical methods related to green chemistry. The assessment classifies potential risks in five categories – health, safety, energy, environment, and waste – depending on toxicity, bioaccumulation, reactivity, waste generation, corrosivity, safety, energy consumption, and related factors. This is shown schematically in figure 2.

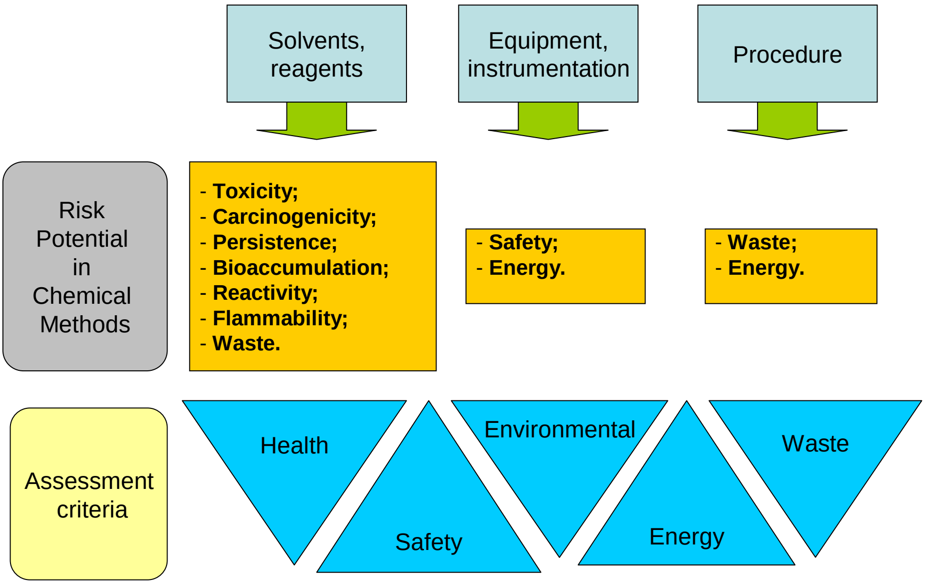


Figure 2 – Classification of potential risks and evaluation criteria in model Raynie D., Driver J.L. [9]

Chemical methods receive 1-3 points for each attribute, using readily available chemical data. A visual representation of the assessment tool allows individual researchers to independently evaluate conflicting green criteria.

For example, if a method produces little waste, but the waste is very toxic, individual flexibility allows you to compare the method with another, which generates large quantities of less hazardous waste. Therefore, this assessment tool is most valuable when comparing procedures.

The resulting assessment criteria icon in the Raynie D. model, Driver J.L. presented in figure 3 [9].

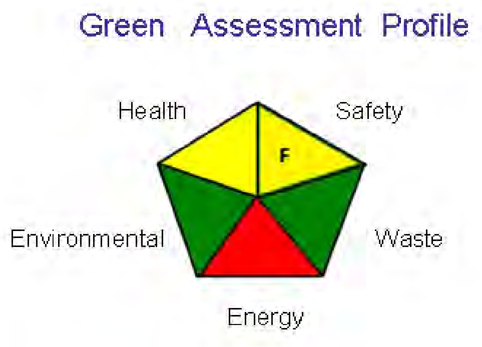


Figure 3 – Evaluation Criteria in the model of Raynie D. and Driver J.L. [9]

Acknowledgements. *The work was supported by the Ministry of Education and Science of the Republic of Kazakhstan on the program № BR05234667/PCF «Physicochemical bases of creation of inorganic, organic, polymer compounds, systems and materials with the pre-set properties» and on the project «The search for new medicinal substances on the basis of available synthetic analogues of natural derivatives of anthraquinone» (IRN: AP05131788).*

REFERENCES

[1] Anastas P. T., Warner J. C. Green Chemistry: Theory and Practice. Oxford University Press: New York, 1998.

[2] Sheldon R.A. Fundametals of green chemistry: Efficiency in reaction design // Chemical Society Reviews. 2012. Vol. 41, N 4. P. 1437-1451.

[3] Armenta S., Esteve-Turrillas F.A., Garrigues S., Guardia M. Chapter One: Green Analytical Chemistry: The Role of Green Extraction Techniques.// Comprehensive Analytical Chemistry. 2017. Vol. 76. P. 1-25.

[4] Tobiszewski M., Namieśnik J. Greener organic solvents in analytical chemistry // Current Opinion in Green and Sustainable Chemistry. 2017. Vol. 5. P. 1-4

[5] Armenta S., Garrigues S., Guardia M. The role of green extraction techniques in Green Analytical Chemistry // TrAC Trends in Analytical Chemistry. 2015. Vol. 71. P. 2-8.

[6] Bourne R.A., Poliakoff M. Green chemistry: what is the way forward? // Mendeleev Communication. 2011. Vol. 21, Issue 5. P. 235-238

[7] Tobiszewski M. Metrics for green analytical chemistry // Anal. Methods. 2016. Vol. 8. P. 2993-2999.

[8] Keith L.H., Gron L.U., Young J.L. Green analytical methodologies // Chem. Rev. 2007. Vol. 107. P. 2695-2708.

[9] Gałuszka A., Konieczka P., Migaszewski Z.M., Konieczka P., Namieśnik J. Analytical eco-scale for assessing the greenness of analytical procedures // TrAC Trends Anal. Chem. 2012. Vol. 37. P. 61-72.

[10] Aken K.V., Strekowski L., Patiny L. Ecoscale, a semi-quantitative tool to select an organic preparation based on economical and ecological parameters // Beilstein J. Org Chem. 2006. Vol. 2. P. 1-7

[11] Raynie D., Driver J.L. Green Assessment of Chemical Methods // 13th Annual Green Conference. June 23-25, 2009, College Park, Maryland, USA. Available from URL: http://acs.confex.com/acs/green09/recordingredirect.cgi/id/457. (Accessed 18.03.19).

[12] Tan S.N., Yong J.W.H., Teo C.C., Ge L., Chan Y.W., Hew C.S. Determination of metabolitesin Uncaria sinensis by HPLC and GC-MS after green solvent microwave-assisted extraction // Talanta. 2011. Vol. 83. P. 891-898.

[13] Nkhili E., Tomao V., El Hajji H., El Boustani E.-S., Chemat F., Dangles O. Microwave assisted water extraction of green tea polyphenols // Phytochem. Anal. 2009. Vol. 20. P. 408-415.

[14] Gai Q.-Y., Jiao J., Mu P.-S., Wang W., Luo M., Li C.-Y. Microwave-assisted aqueous enzymatic extraction of oil from Isatis indigotica seeds and its evaluation of physicochemical properties, fatty acid compositions and antioxidant activities // Ind. Crops Prod. 2013. Vol. 45. P. 303-311.

[15] Sun C., Liu H. Application of non-ionic surfactant in the microwave-assisted extraction of alkaloids from Rhizoma Coptidis // Anal. Chim. Acta. 2008. Vol. 612. P. 160-164.

[16] Lu C., Wang H., Lv W., Ma C., Xu P., Zhu J. Ionic liquid-based ultrasonic/microwave-assisted extraction combined with UPLC for the determination of anthraquinones in rhubarb // Chromatographia. 2011. Vol. 74. P. 139-144.

[17] Wang S., Yang L., Zu Y., Zhao C., Sun X., Zhang L. Design and performance evaluation of ionic-liquids-based microwave-assisted environmentally friendly extraction technique for camptothecin and 10-hydroxycamptothecin from Samara of Camptotheca acuminate // Ind. Eng. Chem. Res. 2011. Vol. 50. P. 13620-13627.

[18] Du F.-Y., Xiao X.-H., Luo X.-J., Li G.-K. Application of ionic liquids in the microwave-assisted extraction of polyphenolic compounds from medicinal plants // Talanta. 2009. Vol. 78. P. 1177-1184.

[19] Yansheng C., Zhida Z., Changping L., Qingshan L., Peifang Y., Welz-Biermann U. Microwave-assisted extraction of lactones from Ligusticum chuanxiong Hort. using protic ionic liquids // Green Chem. 2011. Vol. 13. P. 666-670.

[20] Li J., Han Z., Zou Y., Yu B. Efficient extraction of major catechins in Camellia sinensis leaves using green choline chloride-based deep eutectic solvents // RSC Adv. 2015. Vol. 5. P. 93937-93944.

[21] Cvjetko Bubalo M., Curko N´., Tomaˇsevi´c M., Kovaˇcevi´c Gani´c K., Radojˇci´c Redovnikovi´c I. Green extraction of grape skin phenolics by using deep eutectic solvents // Food Chem. 2016. Vol. 200. P. 159-166.

[22] Wei Z.-F., Wang X.-Q., Peng X., Wang W., Zhao C.-J., Zu Y.-G., et al., Fast and green extraction and separation of main bioactive flavonoids from Radix Scutellariae // Ind. Crops Prod. 2015. Vol. 63. P. 175-181.

[23] Yao X.-H., Zhang D.-Y., Duan M.-H., Cui Q., Xu W.-J., Luo M., et al., Preparation and determination of phenolic compounds from Pyrola incarnata Fisch. with a green polyols based-deep eutectic solvent // Sep. Purif. Technol. 2015. Vol. 149. P. 116-123.

[24] De la Guardia M., Armenta S. Green Analytical Chemistry: Theory and Practise; Elsevier: Amsterdam, The Netherlands, 2011.

[25] Tobiszewski M., Marć M., Gałuszka A., Namieśnik J. Green Chemistry Metrics with Special Reference to Green Analytical Chemistry // Molecules. 2015. Vol. 20. P. 10928-10946; doi:10.3390/molecules200610928

Резюме

Т. В. Харламова

ТАБИҒИ ҚОСЫЛЫСТАР ХИМИЯСЫНДАҒЫ
МИКРОТОЛҚЫНДЫ ЭКСТРАКЦИЯЛАУДЫҢ
«ЖАСЫЛ» БАҒЫТТОРЫ
1-ші хабарлама. Аналитикалық процедурлардың
экологиялығын бағалау әдістері

Шолуда қолданылып жүрген экологиялығын бағалау, NEMI маркирлеу және Eco-Scale аналиттеу әдістері қарастарылған. Табиғи қосылыстарды микротолқынды экстракциялаудығы аналитикалық процедурлардың экологиялығын бағалау мәселері қарастырылған

Түйін сөздер: табиғи қосылыстар, микротолқынды экстракция, экологиялығын бағалау әдістері.

Резюме

Т. В. Харламова

«ЗЕЛЕНЫЕ» НАПРАВЛЕНИЯ
МИКРОВОЛНОВОЙ ЭКСТРАКЦИИ
В ХИМИИ ПРИРОДНЫХ СОЕДИНЕНИЙ
Сообщение 1. Методы оценки экологичности аналитических процедур

В обзоре рассматриваются методы, используемые для оценки экологичности, включая маркировку NEMI и аналитическую Eco-Scale. Рассмотрен вопрос оценки экологичности аналитических процедур при микроволновой экстракции природных соединений.

Ключевые слова: природные соединения, микроволновая экстракция, методы оценки экологичности.