

Gas chromatography-mass spectrometry screening persistent organic pollutant in environmental monitoring of vital activity objects

© Igor M. Fitsev,^{*+} Oksana V. Shlyamina, Aisylu Z. Mukharlyamova, Saniya L. Mokhtarova, Elvira R. Rakhmetova, Aigul G. Mukhammetshina, and Zhanna R. Nasybullina
FSBSI «Federal Center for Toxicological, Radiation and Biological Safety» (FSBSI «FCTRBS-RRVI»)
Nauchnyi Gorodok-2. Kazan. 420075. Russia. Republic of Tatarstan. E-mail: fitzev@mail.ru

*Supervising author; +Corresponding author

Keywords: Gas chromatography-mass spectrometry, screening, monitoring of vital activity objects, persistent organic pollutant, organochlorine pesticides, solid-phase extraction, extraction QuEChERS, chemical and biological risks.

Abstract

There are the results of the developed way of organochlorine pesticides (OCP) screening (OCP was classified by the Stockholm Convention (2001) as persistent organic pollutants (POP) by the gas chromatography–mass spectrometry (GC-MS)-detecting method for its simultaneous detection in vital activity objects (food, food raw material, food product, pathological animal material tissues, natural surface of waters) in this article. Preparation of the samples using solid-phase extraction (SPE) on cartridges «Diapak C18 Plus» or using the solid-phase extraction dispersion QuEChERS («quick», «easy», «affordable», «effective», «reliable», «safe») way (which contribute to high degree of detecting compound extraction) is preceding the GC/MS-detecting stage.

Among the detecting ones in conditions of GCMS screening OCP are explored compounds that are included in POP «dirty» dozen: α -, β -, γ -isomers of hexachlorocyclohexane (HCH) and its biotransformation product – pentachlorocyclohexene, hexachlorobenzene (HCB), heptachlor, aldrine (HHDN), 2,2-bis(4-chlorophenyl)-1-chloroethylene (p,p'-DDMU), 1,1-dichloro-2,2-Bis(p-chlorophenyl)ethylene (4,4'-DDE), 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (4,4'-DDD), 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (4,4'-DDT). The necessity of controlling the content of CO₃ (caused by its bioaccumulation in vital activity objects) takes part in trophic paths and caused by them violation of the normal microbiota of the human, agricultural animals and plants, connected with practical methods of realization chemical and biological risks monitoring are one of priority directions of the government policy in chemical and biological safety area.

The developed way of GC-MS-detecting range OCP is applied for monitoring in food, food raw material, food product, pathological animal material tissues, natural surface of waters. Quantitative detecting the OCP range on a level of GC-MS method sensitivity spend in selective ions (basic and confirmatory ions respectively) registration mode. This method characterizes by limit of detection that don't exceed maximum permissible level (MPL) content OCP in objects of environmental monitoring with a standard deviation 3-4%.

References

- [1] A.R. Makaeva, O.V. Shlyamina, I.M. Fitsev Monitoring the nutritional value and chemical safety of the main feeds of the Republic of Tatarstan based on the results of research carried out in 2019. *Butlerov communication*. 2020. Vol.62. No.4. P.123-128. DOI: 10.37952/ROI-jbc-01/20-62-4-123
- [2] Stockholm Convention on Persistent Organic Pollutants. Ratified by the Federal Law of June 27, 2011 N 164-FL. [Electronic resource]. URL: <http://docs.cntd.ru/document/901821036> (date of the application 10.06.2020).
- [3] Decree of the Government of the Russian Federation of May 18, 2002 N 320 «On the Signing of the Stockholm Convention on Persistent Organic Pollutants». [Electronic resource]. URL: <http://docs.cntd.ru/document/901818017> (date of the application 10.06.2020).
- [4] Federal Law No. 164-FZ of June 27, 2011 «On Ratification of the Stockholm Convention on Persistent Organic Pollutants». [Electronic resource]. URL: <http://docs.cntd.ru/document/902285927> (дата обращения 10.06.2020).
- [5] Decree of the President of the Russian Federation of March 11, 2019 No. 97 «On the Fundamentals of the State Policy of the Russian Federation in the Field of Chemical and Biological Safety for the Period until 2025 and Beyond». [Electronic resource]. URL: <https://www.garant.ru/products/ipo/prime/doc/72092478/> (date of the application 10.06.2020).

- [6] D. Tsipi, H. Botitsi, A. Economou. Mass spectrometry for the analysis of pesticide residues and their metabolites. *J Wiley & Sons Inc. New York NY*. **2015**. 288p.
- [7] M. Kochman, A. Gordin, P. Goldshlag, S.J. Lehotay, A. Amnirav. Fast, high-sensitivity, multipesticide analysis of complex mixtures with supersonic gas chromatography-mass spectrometry. *J Chromatogr A*. **2002**. Vol.974. No.1-2. P.185-212.
- [8] M.V.N. Rodrigues, F.G. R. Reyes, P.M. Magalhães, S. Rath. GC-MS determination of organochlorine pesticides in medicinal plants harvested in Brazil. *J. Braz. Chem. Soc.* **2007**. Vol.18. No.1. P.135-142.
- [9] V.C. Fernandes, V.F. Domingues, N. Mateus, C. Delerue-Matos. Organochlorine pesticide residues in strawberries from integrated pest management and organic farming. *J. Agric. Food Chem.* **2011**. Vol.59. No.14. P.7582-7591.
- [10] V.C. Fernandes, J.L. Vera, V.F. Domingues, L.M.S. Silva, N. Mateus, C. Delerue-Matos. Mass spectrometry parameters optimization for the 46 multiclass pesticides determination in strawberries with gas chromatography ion-trap tandem mass spectrometry. *J Amer. Soc Mass Spectrom.* **2012**. Vol.23. P.2187-2197.
- [11] N. Gurbuz, O. Arik, A. Baykal. Screening of pesticide residues in fresh vegetables and fruits by LC-MS/MS and GC-MS/MS. *Asian J. Chem.* **2014**. Vol.26. No.20. P.6975-6981.
- [12] I.M. Fitsev, A.Kh. Mukhametzyanov. On the trial operation of the chromatography-mass-spectrometric complex "Chromatek-Crystal" in the forensic center of the Ministry of Internal Affairs in the Republic of Tatarstan during the preparation and holding of the XXVII Games of the World Summer Universiade 2013 in Kazan. *Forensic examination*. **2016**. No.2(46). P.67-79. (russian)
- [13] B.I. Petrov. Liquid-liquid extraction: yesterday, today, tomorrow. *Bulletin of Altai State University. Chemical Sciences*. **2010**. Vol.67. No.3-1. P.184-191. (russian)
- [14] M.R. Hadjmohammadi, S.S. Ghoreishi. Determination of estrogens in water samples using dispersive liquid liquid microextraction and high performance liquid chromatography. *Acta Chim. Sloven.* **2011**. Vol.58. No.4. P.765-771.
- [15] P. Mogadati, J.B. Louis, J.D. Rosen. Multiresidue determination of pesticides in high-organic-content soils by solid-phase extraction and gas chromatography/mass spectrometry. *J. AOAC Int.* **1999**. Vol.82. No.1. P.705-715.
- [16] C. Gonzalvesa, M.F. Alpendurada. Solid-phase micro-extraction – gas chromatography – (tandem) mass- spectrometry as a tool for pesticide residue analysis in water samples at high sensitivity and selectivity with confirmation capabilities. *J. Chromatogr. A*. **2004**. Vol.1026. No.1-2. P.239-250.
- [17] K. Mastovska, K.J. Dorweiler, S.J. Lehotay, J.S. Wegscheid, A. Kelli, K.A. Szpylka. Pesticide multiresidue analysis in cereal grains using modified QuEChERS method combined with automated direct sample introduction GC-TOFMS and UPLC-MS/MS techniques. *J. Agric. Food Chem.* **2010**. Vol.58. No.10. P.5959-5972.
- [18] M. Pajewska-Szmyt, E. Sinkiewicz-Darol, U. Bernatowicz-Łojko, T. Kowalkowski, R. Gadzała-Kopciuch, B. Buszewski. QuEChERS extraction coupled to GC-MS for a fast determination of polychlorinated biphenyls in breast milk from Polish women. *Environm. Sci. Pollution Research*. **2019**. Vol.26. No.30. P.30988-30999.
- [19] *GOST R 8.736-2011*. State system for ensuring the uniformity of measurements (GSI). Multiple direct measurements. Methods for processing measurement results. Basic provisions. *Moscow: Standartinform*. **2013**. (russian)
- [20] *GOST 34100.1- 2017 / ISO / IEC Guide 98-1: 2009*. Measurement uncertainty. An introduction to guidelines for expressing measurement uncertainty. *Moscow: Standartinform*. **2018**. (russian)
- [21] Determination of residues of pesticides in food products, agricultural raw materials and environmental objects. Collection of guidelines. MUK 4.1.2162-4.1.2176-07 4.1. Control methods. Chemical factors. [Электронный ресурс]. URL: <http://docs.cntd.ru/document/1200079314> (date of the application 10.06.2020).
- [22] Hygienic standards for the content of pesticides in environmental objects (list): GN 1.2.3539-18. *Bulletin of normative and methodological documents of the State Sanitary and Epidemiological Supervision*. **2019**. Vol.3(77). P.7-103. (russian)