

# 23. BÖLÜM

## Mikroekstraksiyon Yöntemleri

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### Giriş

Madde kullanımı ile mücadelede, bireyleri madde kullanımından uzak tutmayı hedefleyen stratejiler gündemdedir. Bu maddeleri kullananların saptanması, dolayısıyla kullanıcıların toksikolojik analizleri büyük öneme sahiptir. Analitik kimya alanında olduğu gibi, adli toksikoloji alanında da son yıllarda bilim insanları; hassas, doğru ve güvenilir enstrümantasyon teknikleri üzerine yoğunlaşmıştır. Yeni teknolojik gelişmeler, birçok maddenin saç, ter ve ağız sıvısı gibi alternatif biyolojik materyallerde eser miktarlarını bile saptamaya olanak sağlamaktadır. Ayrıca daha az örnek hacmi kullanılmasına olanak sağlayan hassas enstrümantasyon teknikleri, adli toksikoloji alanında aynı örnekten birçok inceleme yapılmasına izin vermektedir. Son derece hassas ve spesifik analitik enstrümantasyonun geliştirilmesine rağmen, karmaşık matrislerden ilgili bileşiklerin ekstraksiyonu ve/veya konsantrasyonu için genellikle numune ön işlemleri gereklidir.

Numune hazırlama aşaması, biyoanalizde en çok zaman alan adımdır ve analit kayıplarından kaynaklanan hatalara da yatkındır. Numune hazırlama, testin performansını bozabilecek nihai matris kaynaklı etkileşimleri ortadan

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## Sonuç

Bu kitap bölümünde madde analizlerinde güncel yaklaşımlardan biri olan mikroekstraksiyon yöntemleri, avantajları ve dezavantajları ile detaylı olarak ele alınmıştır. Teknolojik gelişmeler doğrultusunda kullanım alanı genişleyen mikroekstraksiyon yöntemlerinin, adli toksikoloji alanında da kullanımı yaygınlaşmaya başlamıştır. Maddelerin biyolojik örneklerde; doğru, hızlı, hassas ve güvenilir analizine olanak sağlayan bu yöntemler, organik çözücü tüketimini en aza indirmekte, örnek hazırlama aşamasını basitleştirmekte ve zamandan kazanıma yarayan otomasyon sistemine olanak sağlamaktadır. Malzeme biliminde meydana gelen gelişmeler doğrultusunda minyatürize edilmiş bu yöntemler sürekli olarak güncellenmektedir.

## KAYNAKLAR

1. Samanidou V, Kovatsi L, Fragou D, et al. Novel strategies for sample preparation in forensic toxicology. *Bioanalysis*. Bioanalysis; 2011;3(17): 2019–2046. doi:10.4155/bio.11.168
2. Jalili V, Barkhordari A, Ghiasvand A. Bioanalytical Applications of Microextraction Techniques: A Review of Reviews. *Chromatographia* 2020 83:5. Springer; 2020;83(5): 567–577. doi:10.1007/S10337-020-03884-1
3. Pawliszyn J. *SPME method development*. In *Solid Phase Microextraction: Theory and Practice*. Wiley-VCH, New York; 1997. 97–139 p.
4. Ouyang G, Pawliszyn J. Recent developments in SPME for on-site analysis and monitoring. *TrAC - Trends in Analytical Chemistry*. Elsevier; 2006;25(7): 692–703. doi:10.1016/j.trac.2006.05.005
5. Ouyang G, Pawliszyn J. SPME in environmental analysis. *Analytical and Bioanalytical Chemistry*. Springer; 2006;386(4): 1059–1073. doi:10.1007/s00216-006-0460-z
6. Tang B, Isacson U. Analysis of mono- and polycyclic aromatic hydrocarbons using solid-phase microextraction: State-of-the-art. *Energy and Fuels*. American Chemical Society; 2008;22(3): 1425–1438. doi:10.1021/ef7007166
7. Jeleń HH, Dziadas M, Majcher M. Different headspace solid phase microextraction - Gas chromatography/mass spectrometry approaches to haloanisoles analysis in wine. *Journal of Chromatography A*. Elsevier; 2013;1313: 185–193. doi:10.1016/j.chroma.2013.07.080
8. Câmara JS, Arminda Alves M, Marques JC. Development of headspace solid-phase microextraction-gas chromatography-mass spectrometry methodology for analysis of terpenoids in Madeira wines. *Analytica Chimica Acta*. Elsevier; 2006;555(2): 191–200. doi:10.1016/j.aca.2005.09.001
9. Wardencki W, Michulec M, Curyło J. A review of theoretical and practical aspects of solid-phase microextraction in food analysis. *International Journal of Food Science and Technology*. John Wiley & Sons, Ltd; 2004;39(7): 703–717. doi:10.1111/j.1365-2621.2004.00839.x
10. Pragst F. Application of solid-phase microextraction in analytical toxicology. *Analytical and Bioanalytical Chemistry*. Anal Bioanal Chem; 2007;388(7): 1393–1414. doi:10.1007/s00216-007-1289-9

11. Agius R, Nadulski T, Kahl HG, et al. Validation of a headspace solid-phase microextraction-GC-MS/MS for the determination of ethyl glucuronide in hair according to forensic guidelines. *Forensic Science International*. Elsevier; 2010;196(1-3): 3-9. doi:10.1016/j.forsci-int.2009.07.023
12. Duff MC, Crump SL, Ray RJ, et al. Solid phase microextraction sampling of high explosive residues in the presence of radionuclides and radionuclide surrogate metals. *Journal of Radioanalytical and Nuclear Chemistry*. Springer; 2008;275(3): 579-593. doi:10.1007/s10967-007-7116-0
13. Lai H, Guerra P, Joshi M, et al. Analysis of volatile components of drugs and explosives by solid phase microextraction-ion mobility spectrometry. *Journal of Separation Science*. J Sep Sci; 2008;31(2): 402-412. doi:10.1002/jssc.200700292
14. Alizadeh N, Mohammadi A, Tabrizchi M. Rapid screening of methamphetamines in human serum by headspace solid-phase microextraction using a dodecylsulfate-doped polypyrrole film coupled to ion mobility spectrometry. *Journal of Chromatography A*. Elsevier; 2008;1183(1-2): 21-28. doi:10.1016/j.chroma.2008.01.020
15. Musteata FM, Pawliszyn J. In vivo sampling with solid phase microextraction. *Journal of Biochemical and Biophysical Methods*. Elsevier; 2007;70(2): 181-193. doi:10.1016/j.jbbm.2006.07.006
16. Musteata FM, Pawliszyn J. Bioanalytical applications of solid-phase microextraction. *TrAC - Trends in Analytical Chemistry*. Elsevier; 2007;26(1): 36-45. doi:10.1016/j.trac.2006.11.003
17. G K, S M, AW F, et al. Simultaneous detection of monomers associated with resin-based dental composites using SPME and HPLC. *Dental materials journal*. Dent Mater J; 2021; doi:10.4012/DMJ.2020-240
18. Jalili V, Barkhordari A, Ghiasvand A. A comprehensive look at solid-phase microextraction technique: A review of reviews. *Microchemical Journal*. Elsevier; 2020;152: 104319. doi:10.1016/J.MICROC.2019.104319
19. Bojko B, Bogusiewicz J, Burlikowska K, et al. SPME Probes: A Novel Chemical Biopsy Tool for Spatially Resolved Profiling of Human Brain Tissue in vivo. 2021; doi:10.21203/RS.3.RS-668958/V1
20. Ramos L. Critical overview of selected contemporary sample preparation techniques. *Journal of Chromatography A*. 2012;1221: 84-98. doi:10.1016/j.chroma.2011.11.011
21. Filipiak W, Bojko B. SPME in clinical, pharmaceutical, and biotechnological research – How far are we from daily practice? *TrAC Trends in Analytical Chemistry*. Elsevier; 2019;115: 203-213. doi:10.1016/J.TRAC.2019.02.029
22. Zhang W, Cao J, Li Z, et al. HS-SPME and GC/MS volatile component analysis of Yinghong No. 9 dark tea during the pile fermentation process. *Food Chemistry*. Elsevier; 2021;357: 129654. doi:10.1016/J.FOODCHEM.2021.129654
23. Pawliszyn J. *Handbook of Solid Phase Microextraction*. [Online] Handbook of Solid Phase Microextraction. Elsevier Inc.; 2012. doi:10.1016/C2011-0-04297-7
24. Harris A, Wheeler J. GC-MS of Ignitable Liquids Using Solvent-Desorbed SPME for Automated Analysis. *Journal of Forensic Science*. ASTM International; 2003;48(1): 1-6. doi:10.1520/JFS2002067
25. Zhao Y, Cai L, Jing Z, et al. Determination of aliphatic amines using N-succinimidyl benzoate as a new derivatization reagent in gas chromatography combined with solid-phase microextraction. *Journal of chromatography. A*. J Chromatogr A; 2003;1021(1-2): 175-181. doi:10.1016/J.CHROMA.2003.09.025

26. MT S, WF N. In-situ derivatisation of degradation products of chemical warfare agents in water by solid-phase microextraction and gas chromatographic-mass spectrometric analysis. *Journal of chromatography. A. J Chromatogr A*; 1999;832(1-2): 173-182. doi:10.1016/S0021-9673(98)00990-X
27. Jacek A. Koziel †, Japheth Noah and, Pawliszyn\* J. Field Sampling and Determination of Formaldehyde in Indoor Air with Solid-Phase Microextraction and On-Fiber Derivatization. *Environmental Science and Technology*. American Chemical Society ; 2001;35(7): 1481-1486. doi:10.1021/ES001653I
28. R A, A P, L O, et al. Determination of linear alkylbenzenesulfonates in aqueous matrices by ion-pair solid-phase microextraction-in-port derivatization-gas chromatography-mass spectrometry. *Journal of chromatography. A. J Chromatogr A*; 2003;999(1-2): 51-60. doi:10.1016/S0021-9673(03)00493-X
29. Pan L, Pawliszyn J. Derivatization/Solid-Phase Microextraction: New Approach to Polar Analytes. *Anal. Chem.* 1997;69: 196-205. <https://pubs.acs.org/sharingguidelines>
30. Spietelun A, Pilarczyk M, Kloskowski A, et al. Current trends in solid-phase microextraction (SPME) fibre coatings. *Chemical Society Reviews*. 2010;39(11): 4524-4537. doi:10.1039/c003335a
31. Sigma Aldrich. *Sigma Aldrich*. [Online] <https://www.sigmaaldrich.com/catalog>
32. Lashgari M, Yamini Y. An overview of the most common lab-made coating materials in solid phase microextraction. *Talanta*. Elsevier; 2019;191: 283-306. doi:10.1016/J.TALANTA.2018.08.077
33. Mpupa A, Selahle SK, Mizaikoff B, et al. Recent Advances in Solid-Phase Extraction (SPE) Based on Molecularly Imprinted Polymers (MIPs) for Analysis of Hormones. *Chemosensors*. MDPI AG; 2021;9(7): 151. doi:10.3390/CHEMOSENSORS9070151
34. Haggi A, Dalali N, Abolghasemi MM. Selectively Determination Trace Amounts of Polycyclic Aromatic Hydrocarbons from Water and Wastewater Matrices Using Graphitic Carbon Nitride/Layered Double Hydroxide Nanocomposite on Porous Anodized Aluminum Wire as SPME Fiber. <https://doi.org/10.1080/10406638.2021.1886122>. Taylor & Francis; 2021; doi:10.1080/10406638.2021.1886122
35. Sereshti H, Karami F, Nouri N, et al. Electrochemically controlled solid phase microextraction based on a conductive polyaniline-graphene oxide nanocomposite for extraction of tetracyclines in milk and water. *Journal of the Science of Food and Agriculture*. John Wiley & Sons, Ltd; 2021;101(6): 2304-2311. doi:10.1002/JSEA.10851
36. Feng J, Feng J, Ji X, et al. Recent advances of covalent organic frameworks for solid-phase microextraction. *TrAC Trends in Analytical Chemistry*. Elsevier; 2021;137: 116208. doi:10.1016/J.TRAC.2021.116208
37. Tashakkori P, Tağaç AA, Merdivan M. Fabrication of montmorillonite/ionic liquid composite coated solid-phase microextraction fibers for determination of phenolic compounds in fruit juices by gas chromatography and liquid chromatography. *Journal of Chromatography A*. Elsevier; 2021;1635: 461741. doi:10.1016/J.CHROMA.2020.461741
38. Ghasemi E, Farahani H. Head space solid phase microextraction based on nano-structured lead dioxide: Application to the speciation of volatile organoselenium in environmental and biological samples. *Journal of Chromatography A*. Elsevier; 2012;1258: 16-20. doi:10.1016/J.CHROMA.2012.08.027
39. Gholivand MB, Piryaei M, Abolghasemi MM. Anodized aluminum wire as a solid-phase microextraction fiber for rapid determination of volatile constituents in medicinal plant. *Analytica Chimica Acta*. Elsevier; 2011;701(1): 1-5. doi:10.1016/J.ACA.2011.05.046

40. Mehdinia A, Aziz-Zanjani MO. Recent advances in nanomaterials utilized in fiber coatings for solid-phase microextraction. *TrAC - Trends in Analytical Chemistry*. Elsevier B.V.; 2013;42: 205–215. doi:10.1016/j.trac.2012.09.013
41. Riahi-Zanjani B, Balali-Mood M, Asoodeh A, et al. Developing a new sensitive solid-phase microextraction fiber based on carbon nanotubes for preconcentration of morphine. *Applied Nanoscience (Switzerland)*. Springer Nature; 2018;8(8): 2047–2056. doi:10.1007/s13204-018-0882-x
42. Latrous El Atrache L, Hachani M, Kefi BB. Carbon nanotubes as solid-phase extraction sorbents for the extraction of carbamate insecticides from environmental waters. *International Journal of Environmental Science and Technology*. Center for Environmental and Energy Research and Studies; 2016;13(1): 201–208. doi:10.1007/s13762-015-0861-7
43. Augusto F, Carasek E, Silva RGC, et al. New sorbents for extraction and microextraction techniques. *Journal of Chromatography A*. J Chromatogr A; 2010;1217(16): 2533–2542. doi:10.1016/j.chroma.2009.12.033
44. Ghaemi F, Amiri A, Yunus R. Methods for coating solid-phase microextraction fibers with carbon nanotubes. *TrAC Trends in Analytical Chemistry*. Elsevier; 2014;59: 133–143. doi:10.1016/J.TRAC.2014.04.011
45. Koziel J, Odziemkowski M, Pawliszyn J. Sampling and analysis of airborne particulate matter and aerosols using in-needle trap and SPME fiber devices. *Analytical Chemistry*. Anal Chem; 2001;73(1): 47–54. doi:10.1021/AC000835S
46. Baysal E, Uzun UC, Ertas FN, et al. Development of a new needle trap-based method for the determination of some volatile organic compounds in the indoor environment. *Chemosphere*. Pergamon; 2021;277: 130251. doi:10.1016/J.CHEMOSPHERE.2021.130251
47. Asl-Hariri S, Gómez-Ríos GA, Gionfriddo E, et al. Development of Needle Trap Technology for On-Site Determinations: Active and Passive Sampling. *Analytical Chemistry*. American Chemical Society; 2014;86(12): 5889–5897. doi:10.1021/AC500801V
48. Kędziora-Koch K, Wasiak W. Needle-based extraction techniques with protected sorbent as powerful sample preparation tools to gas chromatographic analysis: Trends in application. *Journal of chromatography. A*. J Chromatogr A; 2018;1565: 1–18. doi:10.1016/J.CHROMA.2018.06.046
49. Ziegler M, Schmarr H-G. Comparison of Solid-Phase Microextraction Using Classical Fibers Versus Mini-Arrows Applying Multiple Headspace Extraction and Various Agitation Techniques. *Chromatographia 2018 82:2*. Springer; 2018;82(2): 635–640. doi:10.1007/S10337-018-3659-1
50. Herrington JS, Gómez-Ríos GA, Myers C, et al. Hunting Molecules in Complex Matrices with SPME Arrows: A Review. *Separations 2020, Vol. 7, Page 12*. Multidisciplinary Digital Publishing Institute; 2020;7(1): 12. doi:10.3390/SEPARATIONS7010012
51. Lisanti MT, Laboyrie J, Marchand-Marion S, et al. Minty aroma compounds in red wine: Development of a novel automated HS-SPME-arrow and gas chromatography-tandem mass spectrometry quantification method. *Food Chemistry*. Elsevier; 2021;361: 130029. doi:10.1016/J.FOODCHEM.2021.130029
52. Eisert R, Pawliszyn J. Automated In-Tube Solid-Phase Microextraction Coupled to High-Performance Liquid Chromatography. *Analytical Chemistry*. American Chemical Society; 1997;69(16): 3140–3147. doi:10.1021/AC970319A
53. Y M-M, C M-L, J V-A, et al. Advantages of monolithic over particulate columns for multiresidue analysis of organic pollutants by in-tube solid-phase microextraction coupled to capillary liquid chromatography. *Journal of chromatography. A*. J Chromatogr A; 2011;1218(37): 6256–6262. doi:10.1016/J.CHROMA.2011.07.026

54. Song X, Wu J, Pang J, et al. Task specific monolith for magnetic field-reinforced in-tube solid phase microextraction of mercury species in waters prior to online HPLC quantification. *Journal of hazardous materials*. J Hazard Mater; 2021;411. doi:10.1016/J.JHAZMAT.2021.125141
55. Fernández-Amado M, Prieto-Blanco MC, López-Mahía P, et al. Strengths and weaknesses of in-tube solid-phase microextraction: A scoping review. *Analytica Chimica Acta*. Elsevier; 2016;906: 41–57. doi:10.1016/J.ACA.2015.12.007
56. Mirnaghi FS, Hein D, Pawliszyn J. Thin-Film Microextraction Coupled with Mass Spectrometry and Liquid Chromatography–Mass Spectrometry. *Chromatographia* 2013 76:19. Springer; 2013;76(19): 1215–1223. doi:10.1007/S10337-013-2443-5
57. Olcer YA, Tascon M, Eroglu AE, et al. Thin film microextraction: Towards faster and more sensitive microextraction. *TrAC - Trends in Analytical Chemistry*. Elsevier B.V.; 2019;113: 93–101. doi:10.1016/J.TRAC.2019.01.022
58. Racamonde I, Rodil R, Quintana JB, et al. Fabric phase sorptive extraction: A new sorptive microextraction technique for the determination of non-steroidal anti-inflammatory drugs from environmental water samples. *Analytica Chimica Acta*. Elsevier; 2015;865(1): 22–30. doi:10.1016/J.ACA.2015.01.036
59. Aznar M, Alfaro P, Nerin C, et al. Fabric phase sorptive extraction: An innovative sample preparation approach applied to the analysis of specific migration from food packaging. *Analytica Chimica Acta*. Elsevier; 2016;936: 97–107. doi:10.1016/J.ACA.2016.06.049
60. Kabir A, Mesa R, Jurmain J, et al. Fabric Phase Sorptive Extraction Explained. *Separations* 2017, Vol. 4, Page 21. Multidisciplinary Digital Publishing Institute; 2017;4(2): 21. doi:10.3390/SEPARATIONS4020021
61. Liu S, Dasgupta PK. Liquid Droplet. A Renewable Gas Sampling Interface. *Analytical Chemistry*. American Chemical Society; 2002;67(13): 2042–2049. doi:10.1021/AC00109A023
62. Jeannot MA, Przyjazny A, Kokosa JM. Single drop microextraction—Development, applications and future trends. *Journal of Chromatography A*. Elsevier; 2010;1217(16): 2326–2336. doi:10.1016/J.CHROMA.2009.10.089
63. S P-B, KE R. Liquid-liquid-liquid microextraction for sample preparation of biological fluids prior to capillary electrophoresis. *Analytical chemistry*. Anal Chem; 1999;71(14): 2650–2656. doi:10.1021/AC990055N
64. Rasmussen KE, Pedersen-Bjergaard S. Developments in hollow fibre-based, liquid-phase microextraction. *TrAC Trends in Analytical Chemistry*. Elsevier; 2004;23(1): 1–10. doi:10.1016/S0165-9936(04)00105-0
65. Liu W, Wei Z, Zhang Q, et al. Novel multifunctional acceptor phase additive of water-miscible ionic liquid in hollow-fiber protected liquid phase microextraction. *Talanta*. Talanta; 2012;88: 43–49. doi:10.1016/J.TALANTA.2011.08.017
66. P F, C G, MT P, et al. A rapid ultrasound-assisted dispersive liquid-liquid microextraction followed by ultra-performance liquid chromatography for the simultaneous determination of seven benzodiazepines in human plasma samples. *Analytica chimica acta*. Anal Chim Acta; 2013;767(1): 88–96. doi:10.1016/J.ACA.2013.01.016
67. Zuloaga O, Olivares M, Navarro P, et al. Dispersive liquid-liquid microextraction: trends in the analysis of biological samples. *Bioanalysis*. Bioanalysis; 2015;7(17): 2211–2225. doi:10.4155/BIO.15.141
68. Huang S, Chen G, Ye N, et al. Solid-phase microextraction: An appealing alternative for the determination of endogenous substances - A review. *Analytica Chimica Acta*. Elsevier B.V.; 2019;1077: 67–86. doi:10.1016/J.ACA.2019.05.054

69. S A, M K. Recent progress, challenges and trends in trace determination of drug analysis using molecularly imprinted solid-phase microextraction technology. *Talanta*. Talanta; 2017;164: 612–625. doi:10.1016/J.TALANTA.2016.11.007
70. MM M, R S, F B, et al. Solid phase microextraction and related techniques for drugs in biological samples. *Journal of analytical methods in chemistry*. J Anal Methods Chem; 2014;2014. doi:10.1155/2014/921350
71. Kataoka H, Saito K. Recent advances in SPME techniques in biomedical analysis. *Journal of pharmaceutical and biomedical analysis*. J Pharm Biomed Anal; 2011;54(5): 926–950. doi:10.1016/J.JPBA.2010.12.010
72. Jalili V, Barkhordari A, Norouzian Baghani A. The role of microextraction techniques in occupational exposure assessment. A review. *Microchemical Journal*. Elsevier; 2019;150: 104086. doi:10.1016/J.MICROC.2019.104086
73. Seidi S, Rezazadeh M, Yamini Y. Pharmaceutical applications of liquid-phase microextraction. *TrAC Trends in Analytical Chemistry*. Elsevier; 2018;108: 296–305. doi:10.1016/J.TRAC.2018.09.014
74. FR M, MA K. Pharmaceutical and biomedical applications of dispersive liquid-liquid microextraction. *Journal of chromatography. B, Analytical technologies in the biomedical and life sciences*. J Chromatogr B Analyt Technol Biomed Life Sci; 2017;1061–1062: 382–391. doi:10.1016/J.JCHROMB.2017.07.055
75. Tabani H, Nojavan S, Alexovič M, et al. Recent developments in green membrane-based extraction techniques for pharmaceutical and biomedical analysis. *Journal of Pharmaceutical and Biomedical Analysis*. Elsevier; 2018;160: 244–267. doi:10.1016/J.JPBA.2018.08.002
76. Saraji M, Khaje N. Recent advances in liquid microextraction techniques coupled with MS for determination of small-molecule drugs in biological samples. *Bioanalysis*. Bioanalysis; 2012;4(6): 725–739. doi:10.4155/BIO.12.26