WILSON & WILSON'S

COMPREHENSIVE ANALYTICAL CHEMISTRY

EDITED BY

D. BARCELÓ

VOLUME 61

ADVANCED TECHNIQUES IN GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GC-MS-MS AND GC-TOF-MS) FOR ENVIRONMENTAL CHEMISTRY

IMMA FERRER AND E. MICHAEL THURMAN

Advanced Techniques in Gas Chromatography–Mass Spectrometry (GC–MS–MS and GC–TOF–MS) for Environmental Chemistry

Comprehensive Analytical Chemistry

Volume 61

Edited by

Imma Ferrer and E. Michael Thurman
Center for Environmental Mass Spectrometry
Department of Environmental Engineering
University of Colorado
ECOT 441, 428 UCB
Boulder, CO 80309, USA

ELSEVIER
AMSTERDAM • BOSTON • HEIDELBERG • LONDON • NEW YORK • OXFORD
PARIS • SAN DIEGO • SAN FRANCISCO • SINGAPORE • SYDNEY • TOKYO

Elsevier
The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, UK
Radarweg 29, PO Box 211, 1000 AE Amsterdam, The Netherlands

British Library Cataloguing in Publication Data
A catalog record for this book is available from the British Library

Library of Congress Cataloging-in-Publication Data
A catalogue record for this book is available from the Library of Congress

ISBN: 978-0-444-62623-3
ISSN: 0166-526X

Transferred to Digital Printing in 2014

Advanced Techniques in Gas Chromatography–Mass Spectrometry (GC–MS–MS and GC–TOF–MS) for Environmental Chemistry

Comprehensive Analytical Chemistry

Volume 61

Contributors to Volume 61

Lissette Aguilar, Baylor University, Waco, Texas, USA

Olujide Akinbo, Butler University, Indianapolis, Indiana, USA

Sheher Bano Mohsin, Agilent Technologies, Schaumburg, Illinois, USA

Damià Barceló, Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, and Catalan Institute for Water Research (ICRA), Parc Científic i Tecnològic de la Universitat de Girona(Edifici H_2O), Girona, Spain

Enrique Barón, Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain

Michael J. Bartels, Dow Chemical, Midland Michigan, USA

Giancarlo Bianchi, Mass Spectrometry Laboratory, Environmental Health Sciences Department, IRCCS Istituto di Ricerche Farmacologiche "Mario Negri", Milano, Italy

Kathy Brzak, Dow Chemical, Midland Michigan, USA

Tomas Cajka, UC Davis Genome Center – Metabolomics, University of California, Davis, California, USA

Robert B. Cody, JEOL USA, Peabody, Massachusetts, USA

Andrea Colombo, Mass Spectrometry Laboratory, Environmental Health Sciences Department, IRCCS Istituto di Ricerche Farmacologiche "Mario Negri", Milano, Italy

Cayo Corcellas, Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain

Enrico Davoli, Mass Spectrometry Laboratory, Environmental Health Sciences Department, IRCCS Istituto di Ricerche Farmacologiche "Mario Negri", Milano, Italy

Michael P. Dolan, Dolan Integration Group, Boulder, Colorado, USA

Ethel Eljarrat, Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain

Imma Ferrer, Center for Environmental Mass Spectrometry, Department of Environmental Engineering, University of Colorado, Boulder, Colorado, USA

Vyacheslav N. Fishman, Dow Chemical, Midland Michigan, USA

Andrés Fernando Gallo Ortiz, Diagnosis and Control of Pollution Research Group (GDCON), Faculty of Engineering, Universitary Research Center (SIU), University of Antioquia (UdeA), Calle 70 No 52–21, Medellín, Colombia

Antonia Garrido Frenich, Department of Chemistry and Physics (Analytical Chemistry Area), Andalusian Center for the Assessment and Monitoring of Global Change (CAESCG), Agrifood Campus of International Excellence ceiA3, University of Almería, Almería, Spain

Michele Giavini, ARS Ambiente, Analysis, Research and Services for the Environment, Gallarate, Italy

Jeffrey R. Gilbert, Dow AgroSciences, Indianapolis, Indiana, USA

Jeffrie Godbey, Dow AgroSciences, Indianapolis, Indiana, USA

Jennifer N. Gushue, Agilent Technologies, Inc., Santa Clara, California, USA

Douglas G. Hayward, U.S. Food and Drug Administration, Center for Food Safety and Applied Nutrition, Office of Regulatory Science, College Park, Maryland, USA

Duvan Esteban Hoyos Ossa, Diagnosis and Control of Pollution Research Group (GDCON), Faculty of Engineering, Universitary Research Center (SIU), University of Antioquia (UdeA), Calle 70 No 52–21, Medellín, Colombia

Dimitra A. Lambropoulou, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece

Paul Lewer, Dow AgroSciences, Indianapolis, Indiana, USA

Viorica Lopez-Avila, Agilent Technologies, Santa Clara, California, USA

Anthony Macherone, Agilent Technologies, Inc., Wilmington, Delaware, and The Johns Hopkins School of Medicine, Baltimore, Maryland, USA

Dan Markham, Dow Chemical, Midland Michigan, USA

David McCaskill, Dow AgroSciences, Indianapolis, Indiana, USA

Shinichi Miki, MSI Tokyo Inc., Tokyo, Japan

Juan A. Padilla-Sánchez, Department of Chemistry and Physics (Analytical Chemistry Area), Andalusian Center for the Assessment and Monitoring of Global Change (CAESCG), Agrifood Campus of International Excellence ceiA3, University of Almería, Almería, Spain

Marinella Palmiotto, Mass Spectrometry Laboratory, Environmental Health Sciences Department, IRCCS Istituto di Ricerche Farmacologiche "Mario Negri", Milano, Italy

Gustavo Antonio Peñuela Mesa, Diagnosis and Control of Pollution Research Group (GDCON), Faculty of Engineering, Universitary Research Center (SIU), University of Antioquia (UdeA), Calle 70 No 52–21, Medellín, Colombia

Patricia Plaza-Bolaños, Department of Chemistry and Physics (Analytical Chemistry Area), Andalusian Center for the Assessment and Monitoring of Global Change (CAESCG), Agrifood Campus of International Excellence ceiA3, University of Almería, Almería, Spain

Andrés Ramírez Restrepo, Diagnosis and Control of Pollution Research Group (GDCON), Faculty of Engineering, Universitary Research Center (SIU), University of Antioquia (UdeA), Calle 70 No 52–21, Medellín, Colombia

Patrick J. Roach, Agilent Technologies, Santa Clara, California, USA

Eleanor Robinson, Baylor University, Waco, Texas, USA

Owen A. Sherwood, Dolan Integration Group, Boulder, Colorado, USA

Shuichi Shimma, National Cancer Center, Tokyo, Japan

Bikram Subedi, Baylor University, Waco, Texas, USA

E. Michael Thurman, Center for Environmental Mass Spectrometry, Department of Environmental Engineering, University of Colorado, Boulder, Colorado, USA

Michisato Toyoda, Project Research Center for Fundamental Sciences, Graduate School of Science, Osaka University, Toyonaka, Osaka, Japan

Patrick D. Travers, Dolan Integration Group, Boulder, Colorado, USA

Randall Urdahl, Agilent Technologies, Santa Clara, California, USA

Sascha Usenko, Baylor University, Waco, Texas, USA

Noelia M. Valera-Tarifa, Department of Chemistry and Physics (Analytical Chemistry Area), Andalusian Center for the Assessment and Monitoring of Global Change (CAESCG), Agrifood Campus of International Excellence ceiA3, University of Almería, Almería, Spain

Bill Winniford, Dow Chemical, Freeport, Texas, USA

Jon W. Wong, U.S. Food and Drug Administration, Center for Food Safety and Applied Nutrition, Office of Regulatory Science, College Park, Maryland, USA

Jeff H. Writer, Center for Environmental Mass Spectrometry, Department of Environmental Engineering, University of Colorado, Boulder, Colorado, USA

Paul Yang, Laboratory Services Branch, Ontario Ministry of the Environment, Ontario, Canada

Kai Zhang, U.S. Food and Drug Administration, Center for Food Safety and Applied Nutrition, Office of Regulatory Science, College Park, Maryland, USA

Series Editor's Preface

It is my pleasure to introduce this new volume on Advanced Techniques in Gas Chromatography-Mass Spectrometry (GC–MS–MS and GC–TOF–MS) for Environmental Chemistry, edited by Imma Ferrer and E. Mike Thurman. The reason for having such a book in the Comprehensive Analytical Chemistry series is quite obvious: I was able to convince both editors to do it. My plans to have it in the CAC series date back to my early days as Series Editor, some 15 years ago. I should add that it was not so difficult to convince Imma and Mike since both they are old friends of mine. I met Mike in person for the first time on the occasion of the 209th ACS National Meeting held in Anaheim, CA, in April 1995. Imma had just started to work in my group at that time and successfully defended her PhD thesis in December 1999.

This book can be considered complementary to other two related titles in the CAC series: Two Dimensional GC (Vol. 55) and TOF-MS in Food and Environmental Analysis (Vol. 58). It contains 20 chapters that cover a comprehensive variety of applications mainly in the environmental field but also in related matrices like food and biological samples. The various chapters contain details on the residue analysis of several groups of chemicals including pesticides, odour compounds, hormones, dioxins, PCBs, flame retardants and industrial applications using GC–MS–MS and/or GC–TOF–MS.

The book can be used as an academic text for postgraduate students and technicians, and as a reference for those working in chemical analytical laboratories who want to learn more about the applications of GC-tandem MS systems to environmental issues. Overall this book covers an important, routinely used and continuously improved technique in the field of Analytical Chemistry that has proven its usefulness for solving everyday problems in the analysis of organic chemical contaminants.

Finally I would like to thank both editors again and all the authors who have contributed to this book for their time and effort in preparing this excellent and useful book on GC-tandem MS techniques.

Prof. D. Barceló
Barcelona, Spain, July 18th 2013

Preface

Gas chromatography mass spectrometry (GC-MS) is not a forgotten field! Yes, it is true that LC-MS has been the preferred technique in environmental analyses over the past decade. Nonetheless, there have been major advances in the analysis of volatile and semi-volatile compounds by GC-MS. For example, there have been significant innovations in GC-MS instrumentation, such as the development of time-of-flight mass detectors (TOF) and two-dimensional gas chromatography (GC×GC) coupled to gas chromatographs. Furthermore, tandem mass spectrometry techniques (GC–MS–MS) are still commonly and successfully used for the achievement of high sensitivities.

Mainly, GC-MS techniques are used for the analysis of (i) volatile organic compounds that are analyzed by purge-and-trap techniques, (ii) semi-volatile compounds that don't ionize by LC-MS sources, and (iii) classic compounds (such as dioxins and chlorinated pesticides) where methodologies have been already well established and developed in the past. Today, even after developments for LC-MS ionization, these are still the main three areas for GC-MS applications. Furthermore, most environmental laboratories have people trained and qualified for GC-MS method development. Also, the inexpensive cost of this technique has made it easily available to all government, university, private, and industry labs. Standard methods by the Environmental Protection Agency (US EPA) have been the classic methods of choice by many scientists in the environmental field of research. Another fundamental aspect of GC-MS applications is the development of new sample preparation procedures, including extraction techniques and derivatization methods. This has opened a whole new area of remarkable applications in the field of environmental chemistry research.

Advances in high-resolution and accurate mass analysis by LC-MS have been recently carried over into the GC-MS instrumentation with time-of-flight mass spectrometry. This has only happened in the past 3–5 years, an important factor to take into account. These developments have resulted in innovative applications to environmental problems, as the reader will discover in this book.

The book consists of 20 chapters divided in two parts. The first one deals with both classic and advanced GC-MS and GC–MS–MS applications in the environmental field. The second part describes several applications using high-resolution and accurate mass GC-MS. The first part emphasizes basic features such as sample preparation for GC-MS analysis (Chapters 2, 5, and 8), development of multiresidue methods in food and water (Chapters 1, 3, and 7), analysis

of biological samples (Chapters 6 and 9), air samples (Chapter 4), and water samples (Chapters 9 and 10). The second part focuses on the use of high-resolution and time-of-flight GC-MS, describing and reviewing a whole variety of methodologies for the detection of environmental compounds. The basic principles for time-of-flight (TOF) analysis are described in detail in Chapters 11 and 12. New innovations such as the development of a miniaturized GC–TOF–MS system are illustrated in Chapter 13. Likewise, new developments in soft ionization sources are shown in Chapter 14. Several applications using high-resolution GC-MS techniques are described in Chapters 15 through 19. These applications include the analysis of stable isotopes in fracking waters, halogenated flame retardants, industrial compounds, persistent organic pollutants, and dioxins. Finally, Chapter 20 introduces a new idea called "exposomics" which discusses how GC–TOF–MS can be used to measure changes in specific individuals due to the exposure to a wide range of environmental contaminants. All classes of environmentally relevant compounds are represented in this book such as pesticides, odor-causing compounds, pharmaceuticals and personal care products, polychlorinated dibenzo-*p*-dioxins and furans, polychlorinated biphenyls, polyaromatic hydrocarbons, hormones, phytoestrogens, pyrethroids, hydrocarbon gases and their stable isotopes, halogenated flame retardants, and persistent organic pollutants.

As this is our third book together, we have the tradition of predicting future trends in environmental mass spectrometry: (i) GC-MS will continue to be a popular and highly used analytical technique for the identification of volatile and semi-volatile compounds, (ii) high-resolution and time-of-flight mass spectrometry will become more and more important for nontarget and unknown analyses, gaining terrain in many environmental labs, and (iii) development of new soft ionization techniques will be the key to more effective MS-MS analyses.

Finally, we would like to acknowledge our friend, colleague, and Series Editor, Damià Barceló, for giving us the opportunity to put this book together. As always, it has been an enjoyable endeavor to be part of. And we want to thank each of the individual authors for their outstanding contributions that made possible this state-of-the-art book on GC-MS applications for environmental chemistry.

Imma Ferrer and Mike Thurman
July 2013, Boulder, Colorado

Contents