Analysis of Chemical Warfare Degradation Products
Analysis of Chemical Warfare Degradation Products
Analysis of Chemical Warfare Degradation Products

Karolin K. Kroening
Renee N. Easter
Douglas D. Richardson
Stuart A. Willison
Joseph A. Caruso
About the Authors

Karolin K. Kroening, Ph.D.
University of Cincinnati, Cincinnati, OH, USA

Karolin received her Master’s degree in 2006 from the University of Bologna, Italy, for research based on hydroxyapatite/chitosan composites for bone substitution. At the University of Cincinnati her research focused on the identification and cytotoxicity of chemical warfare agent degradation products and protein phosphorylation studies on cerebral spinal fluid, a study that may help in the development of drugs for patients diseased with a hemorrhagic stroke. She obtained her Ph.D. in December 2010 and is currently working for Procter and Gamble in Cincinnati, OH.
Renee N. Easter
University of Cincinnati, Cincinnati, OH, USA

Renee Easter earned a B.S. from Xavier University, Cincinnati, in 2007 and is currently pursuing a Ph.D. in Analytical Chemistry from the University of Cincinnati. Her research has focused on metallomics approaches to identifying proteins associated with cerebral vasospasm, as well as using internal tags, such as sulfur and phosphorus for identification and quantification of oligonucleotides for siRNA drug applications.

Douglas D. Richardson, Ph.D.
Merck Research Labs, Rahway, NJ, USA

Doug earned his B.S. in Forensic Chemistry with a minor in Biological Sciences from Ohio University in 2003. Following graduation Doug pursued his Ph.D. in the laboratory of Joseph A. Caruso at The University of Cincinnati. His research centered around advancements in elemental speciation, coupling a variety of separation techniques with element specific detection. This research was the first to utilize chromatographic techniques with inductively coupled plasma mass spectrometry for the analysis of nerve agent degradation products. In 2007, Doug defended his dissertation, earning his Ph.D. in Analytical Chemistry. Doug currently supports the development of novel pharmaceuticals within Merck Research Labs.
Stuart Willison, Ph.D.
National Homeland Security Research Center at the US Environmental Protection Agency, Cincinnati, OH, USA

Stuart Willison received his Ph.D. in Chemistry from the University of Cincinnati. He is currently working for the National Homeland Security Research Center at the US Environmental Protection Agency in Cincinnati, OH. His work involves environmental restoration following homeland security events, such as providing support in the detection, response to, and remediation of an area from a terrorist attack or an environmental disaster. Research areas include water protection and indoor/outdoor decontamination as well as method development of chemical warfare agent degradation products in various environmental matrices.

Joseph A. Caruso, Professor
University of Cincinnati, Cincinnati, OH, USA

Joe Caruso holds a Ph.D. from Michigan State University. After a one-year postdoctoral fellowship at The University of Texas – Austin, he joined the University of Cincinnati Chemistry faculty and since then he has authored or co-authored 380 scientific publications and presented more than 325 invited lectures at universities, scientific meetings, government and industry laboratories. His current research interests are in: metallomics studies involving transgenic
plants and their phytoremediation mechanisms or enhancements; evaluating cell signaling changes through phospho- or metallo-proteomes as biomarkers in the CSF of certain stroke patients; investigating the metalloproteomes associated with viruses and their effect on viral capsid stability; and the effects on cell signaling changes when arsenic toxified cells are given selenium species as part of the nutrient mix.

Joe Caruso is a member of the American Chemical Society, Society for Applied Spectroscopy and a Fellow of the Royal Society of Chemistry (RSC). He is Chair of the RSC Metallomics Editorial Board. He has been honored many times including the 2000 Spectrochemical Analysis Award given by the Analytical Division of the American Chemical Society, the University of Cincinnati – Excellence in Doctoral Student Mentoring Award in 2006, and in 2007 he received the Rieveschl Award for Distinguished Scientific Research. His most recent award was to be elected Fellow of the Society of Applied Spectroscopy.
Contents

Preface xiii

1 Historical Milieu 1
   1.1 Organophosphorus Nerve Agents 2
   1.2 Blister Agents 5
   1.3 Sternutator Agents 11
   1.4 Chemical Weapons Convention (CWC) 13
       1.4.1 Schedule of Chemicals 14
       1.4.2 Destruction of Chemical Weapons 14
       References 16

2 Toxicity of Chemical Warfare Agents and their Degradation Products 19
   2.1 Organophosphorus Nerve Agent Toxicity 20
       2.1.1 Toxicity Mechanism – Acetylcholinesterase Inhibition 20
       2.1.2 Exposure 21
       2.1.3 Response, Treatment and Prevention 22
2.2 Toxicity of Nerve Agent Degradation Products

2.2.1 Toxicity of GA (Tabun) Degradation Products

2.2.2 Toxicity of GB (Sarin) Degradation Products

2.2.3 Toxicity of GD (Soman) Degradation Products

2.2.4 Toxicity of GF (Cyclosarin) Degradation Products

2.2.5 Toxicity of VX Degradation Products

2.3 Toxicity of Blister Agents

2.4 Toxicity of Sternutator Agents

2.4.1 Toxicity of Degradation Products of Sternutator Agents

References

3 Analysis of Chemical Warfare Agents

3.1 Introduction

3.2 Minimally Invasive Detection Techniques

3.3 Separation and Detection Techniques

3.3.1 Capillary Electrophoresis

3.3.2 Ion Mobility Spectrometry

3.3.3 Gas Chromatography (GC)/Gas Chromatography-Mass Spectrometry (GC-MS)

3.3.4 Liquid Chromatography (LC)/Liquid Chromatography-Mass Spectrometry (LC-MS)
CONTENTS

3.3.5 Desorption Electrospray Ionization and Direct Analysis in Real Time Mass Spectrometry 90

References 91

4 Chemical Warfare Agent Degradation Products 99

4.1 Analysis of Nerve Agent Degradation Products 100

4.1.1 Sample Preparation 101

4.1.2 Liquid–Liquid Extraction (Pre-concentration) 104

4.1.3 Solid Phase Extraction (SPE) 105

4.1.4 Solid Phase Microextraction (SPME) 106

4.1.5 Stir Bar Sorptive Extraction (SBSE) 106

4.1.6 Derivatization 107

4.2 Analytical Techniques 108

4.2.1 Gas Chromatography (GC) 109

4.2.2 Liquid Chromatography (LC) 110

4.2.3 Elemental Speciation 114

4.2.4 Ion Mobility 115

4.2.5 Capillary Electrophoresis 117

4.3 Analysis of Sulfur Mustard Degradation Products 117

4.4 Analysis of Sternutator Degradation Products 125

References 131

Appendix 135

Index 141
Preface

Lethal chemical warfare agents, including nerve agents and vesicants, still pose major threats to life around the world and our surrounding environment. Though their use has been forbidden by international conventions, nerve agents and vesicants are still produced and stockpiled by terrorist organizations. These agents degrade relatively easily. Therefore, it is understandably of great importance that these agents of interest and their degradation products are detected. Rapid and sensitive methods are required, in order to identify these warfare agents and their degradation products. This book describes the chemistry of nerve agents and vesicants, their decomposition and degradation products, in addition to their toxicity, and includes a list of appropriate detection and analysis techniques. Also included is a brief history of the research area, separation techniques, detection methods and detection limits together in a short, easy to read text, with an adequate number of tables and references for the reader who is looking for further detail.

The work to prepare this book was undertaken by the Caruso research group at the University of Cincinnati, including current and former graduate students, who, through their graduate studies, amassed a high degree of
knowledge regarding warfare agents and the analysis of their
degradation products through various analytical techniques.
While we do not pretend to portray all analytical techniques
and methods currently in use, for some may be proprietary
or classified, our hope is that those who are generally
interested in warfare agents will profit from this text.
This includes those wishing to learn about analysis, also
environmentalists, and more generally, those who have
interest in small molecule phosphorus, sulfur and arsenic
chemistry beyond warfare agents and their decomposition
products, as in pesticides or herbicides. Overall, we have
aspired to produce a product that will be of practical use as
well as a motivating factor for continued research interest in
this field.

Renee N. Easter
Karolin K. Kroening
1

Historical Milieu

1.1 Organophosphorus Nerve Agents 2
1.2 Blister Agents 5
1.3 Sternutator Agents 11
1.4 Chemical Weapons Convention (CWC) 13
   1.4.1 Schedule of Chemicals 14
   1.4.2 Destruction of Chemical Weapons 14
References 16