

The Ultraviolet Disinfection Handbook

James R. Bolton, PhD
Christine A. Cotton, PE



**American Water Works
Association**

The Authoritative Resource on Safe Water®

*Advocacy
Communications
Conferences
Education and Training
Science and Technology
Sections*



Documents
Document Sharing Hub

The Ultraviolet Disinfection Handbook

The Ultraviolet Disinfection Handbook

James R. Bolton, PhD
Christine A. Cotton, PE

First Edition



**American Water Works
Association**

Copyright © 2008 American Water Works Association.
All rights reserved.
Printed in the United States of America.

Project Manager/Senior Technical Editor: Melissa Valentine
Production: Glacier Publishing Services, Inc.

No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopy, recording, or any information or retrieval system, except in the form of brief excerpts or quotations for review purposes, without the written permission of the publisher.

Disclaimer

This book is provided for informational purposes only, with the understanding that the publisher and authors are not thereby engaged in rendering engineering or other professional services. The authors and publisher make no claim as to the accuracy of the book's contents, or their applicability to any particular circumstance. The authors and publisher accept no liability to any person for the information or advice provided in this book, or for loss or damages incurred by any person as a result of reliance on its contents. The reader is urged to consult with an appropriate licensed professional before taking any action or making any interpretation that is within the realm of a licensed professional practice.

Library of Congress Cataloging-in-Publication Data

Bolton, James R., 1937-

The ultraviolet disinfection handbook / James R. Bolton, Christine Cotton. -- 1st ed.
p. cm.

Includes bibliographical references and index.

ISBN 978-1-58321-584-5

I. Water--Purification--Ultraviolet treatment--Handbooks, manuals, etc. I. Cotton, Christine A.
II. Title.

TD460.B65 2008
628.1'62--dc22

2008014266

ISBN 1-58321-584-0



**American Water Works
Association**

6666 West Quincy Avenue
Denver, CO 80235-3098
303.794.7711

Contents

	List of Figures	ix
	List of Tables	xi
	Preface	xiii
	Acknowledgments	xv
Chapter 1	Introduction	1
	What is Ultraviolet Disinfection?	1
	How Does UV Disinfection Compare to Chemical Disinfection?	1
	History of Ultraviolet Disinfection	2
	Government Regulations	5
	Advantages and Disadvantages of UV Disinfection	6
	References	8
Chapter 2	Fundamentals of UV Light and Photochemistry	11
	Light and Photons	11
	UV Light Spectral Ranges	12
	Emission, Transmission, and Absorption of Light	13
	What Happens When UV Light Reaches Its Intended Target	19
	Laws of Photochemistry	19
	Advanced Oxidation Technologies	21
	References	22
Chapter 3	Mechanism of UV Disinfection	25
	Inactivation Mechanisms	25
	Reactivation Mechanisms	29
	UV Sensitivity of Microorganisms	31
	UV Dose (Fluence) in a UV Reactor	37
	References	39
Chapter 4	UV Disinfection Regulations Summary	41
	Regulatory Background	41
	Long-Term 2 Enhanced Surface Water Treatment Rule	43
	Ground Water Rule	45
	References	46
Chapter 5	UV Disinfection Equipment	49
	Types of Available UV Equipment	49
	UV Lamps	51
	UV Sensors	58



	Sleeves	59
	Ancillary Components	60
	Full-Scale Operating UV Disinfection Systems	60
	References	60
Chapter 6	Validation of UV Reactor Performance	63
	Regulatory Requirements	63
	Biodosimetry Process	64
	Overview of USEPA Recommended Approach	65
	Modeling UV Dose (Fluence) Distributions	71
	Validation Effects on UV Facility Design	74
	References	75
Chapter 7	Effects of Water Quality on UV Disinfection	77
	UV Transmittance	77
	Fouling	80
	Turbidity	81
	Upstream Treatment	82
	Algae	83
	Chlorine Reduction	83
	By-products From UV Treatment	84
	Site-Specific and Operational Issues	84
	References	85
Chapter 8	Potential Locations for UV Disinfection Facilities	87
	Filtered Water Systems	87
	Unfiltered Systems Applications	90
	Uncovered Reservoir Applications	90
	Groundwater Applications	91
	Small Systems	91
	Reuse Applications	91
	Reference	92
Chapter 9	UV Facility Design Issues	93
	Disinfection Goals	93
	Key Design Criteria	94
	Hydraulics	97
	Electric Power Systems	100
	Site Constraints/Layout	101
	Cost Estimation	102
	Design Tools Available	102
	Modeling to Assist Design	103
	References	103

Chapter 10	Start-up, Operations and Maintenance	105
	Operational Requirements	105
	Steps for Facility Start-up	106
	Routine Operations and Maintenance Tasks	108
	Monitoring	110
	Monitoring and Recording Frequencies	114
	Reporting Requirements	116
	Troubleshooting	116
	Reference	116
Chapter 11	Safety and Handling of UV Equipment	119
	UV Light Exposure	119
	Electrical Safety	120
	Burn Safety	120
	Lamp Break Issues	120
	Operator Health and Safety—Mercury Exposure Limits	121
	Mercury Release Response	121
	References	124
Chapter 12	Issues for a Water Utility Manager	125
	Using an Engineering Consulting Firm or <i>Go-it-Alone?</i>	125
	Information Needs	125
	Information to Provide and Questions for a Potential Engineering Consulting Firm	126
	Questions for a Potential UV Equipment Manufacturer	126
	Government Regulations	127
	Reference	127
Appendix A	Terms, Units, Symbols, and Definitions	133
	Index	139
	About the Authors	149

Figures

1-1	UV disinfection plant installed in 1910 in Marseilles, France	3
2-1	Spectral ranges of UV, visible, and IR light	12
2-2	Reflection and refraction as a light beam passes from medium 1 with refractive index n_1 to medium 2 with refractive index n_2	14
3-1	Specific absorption cross section versus wavelength for proteins and nucleotides within the cell of a microorganism	26
3-2	Absorption spectra of nucleotides and of DNA	27
3-3	Photochemical dimerization of two thymine bases	28
3-4	Double-stranded DNA chain showing how the formation of thymine dimers disrupts the structure of the chain	28
3-5	Action spectra (relative response versus wavelength) for DNA, MS2 coliphage, <i>Cryptosporidium</i> , and <i>E. coli</i>	29
3-6	<i>Home-made</i> collimated beam apparatus and commercial collimated beam apparatus	32
3-7	UV dose–response curves for <i>B. subtilis</i> and the virus MS2 coliphage	33
3-8	Two possible UV dose distributions	38
5-1	An example of an open-channel UV disinfection system	50
5-2	Closed-pipe UV reactor types	51
5-3	Picture of a standard LP mercury lamp	53
5-4	Relative emittance of the various lines from an LP mercury lamp	53
5-5	Relative lamp UV light output of an LP lamp versus the ambient temperature	54
5-6	Relative UVC output from an LP UV lamp in a quartz sleeve as a function of the water temperature	54
5-7	Picture of an amalgam lamp	55
5-8	Picture of a 2.5 kW MP UV lamp	56
5-9	Relative spectral emittance from LP and MP lamps	56
5-10	Pictures of UV sensors	58
5-11	Pictures of quartz cleaning systems	59
5-12	Trojan Technologies UV disinfection system installed in Victoria, B.C., Canada	61



5-13	Wedeco K-series UV disinfection system installed in Clayton County, Ga.	61
5-14	Calgon Carbon UV disinfection system installed in Edmonton, Alta., Canada	62
5-15	Hanovia photon UV disinfection system installed at Silver Spring Mineral Bottling Co., Folkestone, UK	62
6-1	Biodosimetry process	66
6-2	UV dose–response curves for male-specific-2 bacteriophage and <i>Cryptosporidium</i>	67
6-3	Ideal UV reactor UV dose distribution	68
6-4	Theoretical UV dose distribution	69
7-1	Dependence of the relative average irradiance and the UV dose versus the UVT in an ideal UV reactor	79
7-2	Absorbance spectrum of a typical drinking water	80
7-3	Effect of different environmental particles on UV performance	82
7-4	Effect of ozonation on the UV absorbance where the ozone is quenched or has decayed prior to the UV disinfection unit	83
8-1	Combined filter effluent location in a WTP	88
8-2	Individual filter effluent retrofit example	88
8-3	Example location of UV facility downstream of the clearwell	88
9-1	UV reactor validation options and how they affect installation hydraulics	99
10-1	Monitoring of UV sensor calibration flow chart	113
10-2	Low UV intensity or low validated UV dose decision chart	117
10-3	Low UVT decision chart	118
A-1	The concepts of irradiance and fluence rate	134

Tables

1-1	LT2ESWTR bin classification for filtered public water systems	7
2-1	Comparison of terms, units, and symbols in use in various jurisdictions	18
3-1a	Bench-scale UV dose (fluence) at 254 nm required for 4-log (99.99%) inactivation of various bacteria	35
3-1b	Bench-scale UV dose (fluence) at 254 nm required for 4-log (99.99%) inactivation of various viruses	36
3-1c	Bench-scale UV dose (fluence) at 254 nm required for 4-log (99.99%) inactivation of various protozoa	37
4-1	Summary of microbial and disinfection by-product rules	42
4-2	UV dose requirements	44
5-1	Classification of UV lamps	52
5-2	Emission wavelengths for some common excilamps	57
5-3	Comparison of the characteristics of UV lamps used for UV disinfection of drinking water	57
6-1	Calculated RED based on ideal UV dose distribution and UV dose–response curves	68
6-2	Calculated RED based on nonideal UV dose distribution and UV dose–response curves	70
6-3	Summary of USEPA recommendations for hydraulic configurations for validation testing and the UV facility	74
6-4	Comparison of off-site and on-site validation	76
7-1	Summary of the molar absorption coefficients at 254 nm for components that may be present in drinking water	78
8-1	Comparison of possible postfiltration UV facility locations	89
9-1	Potential method to determine design flow	97
9-2	Power quality triggers for UV reactors	97
9-3	Design tools available	103
10-1	Recommended operations and maintenance tasks	109
10-2	Recommended monitoring and recording frequencies for required monitoring parameters	115



10-3	Recommended monitoring and recording frequencies for recommended monitoring parameters	115
11-1	Summary of on-line lamp break causes and prevention methods	122
11-2	Health and safety standards for mercury compounds in air	123
11-3	Mercury sampling locations	123
12-1	Possible content for UV equipment specifications	127
A-1	Physical constants of interest in ultraviolet technologies	133

Preface

Until recently, the use of ultraviolet light (UV) to disinfect water was dismissed in North America¹ because of the (erroneous) perception that UV could not protect against harmful protozoa, such as *Cryptosporidium parvum* and *Giardia lamblia*. That situation changed dramatically in 1998 when it became clear that UV could inactivate protozoa at very low UV doses. This has led to an explosion of interest in UV disinfection to the point that now the US Environmental Protection Agency recommends the use of UV disinfection in the new Long Term 2 Enhanced Surface Water Treatment Rules.

This handbook is designed to provide a practical introduction to the subject of UV disinfection and UV reactors. It is not a monograph; hence, the literature coverage is not comprehensive, although essential references are given.

No background is assumed except that of general science, such as that given in undergraduate science and engineering degree programs. This handbook should be of value to engineering and scientific consultants, water treatment operators and managers, students and faculty members in science and engineering programs that deal with water treatment, and staff in government regulatory offices.

Careful attention was paid to terminology, units, and definitions. An appendix provides a convenient summary.

1 The use of UV to disinfect water (largely groundwater) has been prevalent in Europe for over 40 years.

Acknowledgments

The authors of this book gratefully acknowledge Malcolm Pirnie, Inc. for supporting Christine Cotton, James Collins, and Laurel Passantino (Malcolm Pirnie, Inc. employees) in the writing of this book. James Collins and Laurel Passantino helped write chapters and complete edits from reviewers; without them, this book would not be possible.

The authors appreciatively acknowledge the US Environmental Protection Agency for allowing use of the *Ultraviolet Disinfection Guidance Manual* (UVDGM) text, figures, and tables; in many cases, these were used verbatim from the UVDGM.

The writing of this book would not have been possible without the help of many friends and colleagues who read and commented on various chapters. We are particularly grateful to Karl Linden (University of Colorado at Boulder), Jim Malley (University of New Hampshire), and Paul Swaim (CH2M Hill), who provided insightful comments that significantly improved this book. We have incorporated their comments wherever possible. We are also thankful to Thomas Oppenländer, who provided a critical read.

Christine Cotton would like to dedicate this book to her husband (Brian), her son (Ethan), and her daughter (Amelia). The book would not have been possible without their endless and tireless support and love. Also, Christine would like to thank her late father and her mother, for their love and support. Jim Bolton would like to thank his wife, Ingrid Crowther, for her unwavering support and encouragement during the writing of this book.

Introduction

WHAT IS ULTRAVIOLET DISINFECTION?

Ultraviolet (UV) lamps emit light in the 200–400 nm wavelength range (see Chapter 2 for more details on the nature of UV light). The 200–300 nm range is often called *germicidal* because this UV light is absorbed by the DNA and RNA of microorganisms. The absorption of UV photons causes changes in the structure of the DNA and RNA, rendering the microorganisms incapable of replicating. Because they cannot multiply, they cannot cause disease, even though technically they are still metabolically *alive*.¹ The degree of microorganism inactivation is determined by the UV dose (or fluence)² applied. More details on the mechanism of UV disinfection are given in Chapter 3.

UV light is usually delivered to drinking water as it flows through a UV reactor (Chapter 5 gives more description of the design of UV reactors). The UV equipment (including one or more UV reactors) is typically applied to filtered water and is often installed after the filter effluent piping recombining before the clearwell. It is very important that the operators are able to control the UV output in the reactor so that at least a minimum UV dose is applied at all times.

UV disinfection is a physical disinfection process. No chemicals are added and there is no residual effect once the water leaves the UV reactor.

HOW DOES UV DISINFECTION COMPARE TO CHEMICAL DISINFECTION?

Chemical disinfection is achieved by adding chemicals, such as chlorine, chloramines, chlorine dioxide, or ozone to the water and maintaining a chemical dose level for a sufficiently long period of time to achieve adequate disinfection. These chemical disinfection processes work quite well with bacteria and viruses, but most have limited efficacy with protozoa, such as *Cryptosporidium* and *Giardia*. Also, most of these chemical disinfectants produce disinfection by-products, which have regulatory limits.

1 It is for this reason that the word *kill* should not be used in regard to UV disinfection.

2 The correct term is *fluence*; however, the term *UV dose* is widely used, particularly in North America. Thus, in this handbook, the term *UV dose* is used in most places in this book. Nevertheless, see the discussion in Chapter 2.

UV disinfection does not significantly change the water quality and thus does not produce significant levels of regulated disinfection by-products (DBPs). Also, recent research (see following section) has demonstrated that UV light is effective for almost all bacteria, viruses, and protozoa. In contrast to chlorine-based chemical disinfectants, there is no residual disinfection capacity with UV disinfection. Thus, chlorine or chloramines are often used following UV disinfection to provide a disinfectant residual in the distribution system.

HISTORY OF ULTRAVIOLET DISINFECTION ³

UV light has had a long and fascinating history in connection with its effects on microorganisms. The following is a brief chronology:

- 1801: Johann Ritter, a pharmacist in Silesia (now in Poland) discovered UV light by demonstrating that silver chloride is decomposed most efficiently by the invisible rays beyond the violet.
- 1842: Becquerel and Draper showed independently that a gelatin solution containing silver iodide darkened when exposed to sunlight (Hockberger 2002). This was the first indication of the spectral extent of UV light.
- 1877: Downes and Blunt (1877) observed that test tubes filled with a broth containing bacteria, when exposed to sunlight, eventually became sterile.
- 1878: Downes and Blunt (1878) further observed that, by using color filters, it is the blue and violet end of the spectrum that is responsible for the inactivation of bacteria.
- ~1900: The Danish physician Niels Finsen, considered the founder of modern phototherapy, discovered a UV treatment for *lupus vulgaris*, a form of skin tuberculosis. For this discovery, he received the Nobel Prize in Physiology or Medicine in 1904.
- 1903: Bernard and Morgan found that the most sensitive wavelengths for the inactivation of bacteria are around 250 nm (see Lorch 1987).
- 1904–1905: Hertel showed that UV light from arc lamps was far more powerful than sunlight in its effect on microorganisms. He showed that the order of efficacy was UVC > UVB > UVA light (see Chapter 2 for a definition of these UV ranges).
- 1904: The glassblower Richard Küch at Heraeus in Germany successfully learned how to blow quartz and was able to fabricate the first quartz enclosed mercury lamp.

³ Hockberger (2002) published a review of the history of UV light and UV disinfection prior to 1920. Sommer et al. (2002) provided a history of UV disinfection in Europe. Whitby and Scheible (2004) published a review of the history of UV in wastewater disinfection.

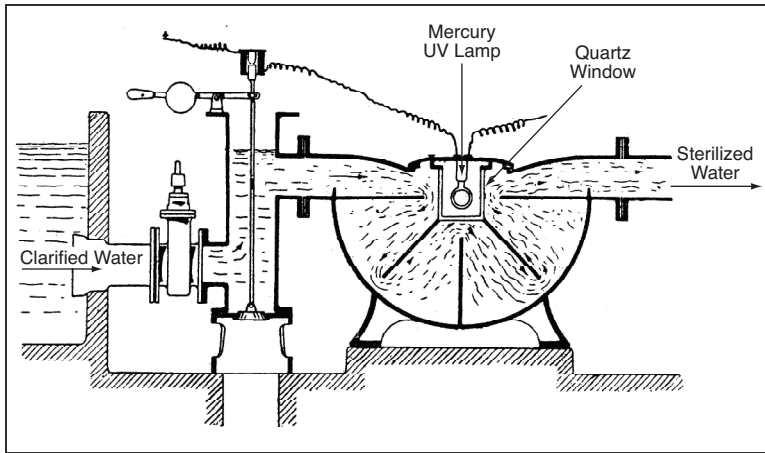


Figure 1-1 UV disinfection plant installed in 1910 in Marseilles, France (Henri et al. 1910a)

- Henri et al. (1910a,b) described the first commercial UV facility that used UV light to disinfect water in Marseilles, France. A diagram of this plant is shown in Figure 1-1. However, because of problems with technical failures, unreliable UV lamps, and instability of the electrical power supply, the system was shut down a short time after it was started.
- 1914: Henri and Moycho (1914) found that 280 nm is the most lethal of the wavelengths emitted from mercury arc lamps. (It is now known that the 254 nm emission is more effective.)
- 1920s: Chlorine disinfection was introduced. This technology was much cheaper than UV disinfection, so the latter went out of favor until the 1950s.
- 1938: Westinghouse introduced the first fluorescent gas discharge lamp.
- 1929, 1930: Gates (1929, 1930) was the first to carry out detailed investigations of the action spectrum of *E. coli*; he showed that the optimal wavelength for inactivation was about 260 nm.
- 1949: Kelner (1949a,b) was the first to discover *photoreactivation*. He found that bacteria stored for some time after UV exposure were able to recover; however, the effect was quite variable. On further investigation, he found that exposure of bacteria, previously inactivated by UV light, to visible or near UV light greatly enhanced the ability of the bacteria to recover.
- 1955: The first modern installations of UV disinfection systems using low-pressure UV lamps in water treatment plants occurred in Switzerland and Austria.

- 1960: Beukers and Berends (1960) irradiated frozen thymine solutions with UV light and were able to isolate thymine dimers. This was the basis of the currently accepted concept that UV inactivation is initiated by the formation of thymine dimers from adjacent thymines on a DNA strand.
- 1975: UV disinfection was introduced in Norway as a result of concern with the disinfection by-products from the use of chlorine disinfection.
- 1978: A full-scale UV system was successfully demonstrated at the N.W. Bergen wastewater treatment plant, Walwick, N.J. (Scheible and Bassell 1981).
- By 1985: There were over 1,500 UV installations in Europe. Most were for the treatment of groundwater and bank-filtered water.
- Malley et al. (1996) found that regulated DBP formation was not affected by UV disinfection at UV doses lower than 400 mJ cm^{-2} .
- Prior to 1998: In North America, until the late 1990s, there was little drinking water application of UV disinfection except in small groundwater systems. This was the result of a perception that UV disinfection was not effective for the treatment of protozoa, such as *Cryptosporidium* or *Giardia*.
- 1998: Bolton et al. (1998) found that UV was very effective against *Cryptosporidium* (and later *Giardia*), contrary to the perception at that time that UV disinfection was not effective. Their paper, presented at the Annual Conference of the American Water Works Association (AWWA), changed this perception.⁴ They showed that earlier research on these protozoa was flawed and that if one used an assay that focused on the ability of these protozoa to infect hosts (i.e., neonatal mice), UV was found to be extremely effective in inactivating these organisms. This indicated that UV disinfection could be used as a broad spectrum disinfectant capable of inactivating almost all viruses, bacteria, and protozoa. Therefore, since 1999 there has been a remarkable increase in interest in UV disinfection for treating drinking water.
- 2001: Sommer et al. (2002) reported that the number of UV installations in Europe had risen to over 6,000, with most treating groundwater.
- 2003: USEPA issued the first draft Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR), which included UV disinfection as a treatment technique. The USEPA also issued a draft *Ultraviolet Disinfection Guidance Manual* (UVDGM). This stimulated the installation of large UV disinfection systems throughout North America.
- 2006: USEPA issued the final versions of the LT2ESWTR (USEPA 2006a) and the UVDGM (USEPA 2006b).

⁴ This paper was subsequently published (largely unchanged) in the *Jour. AWWA* (Bukhari et al. 1999).

GOVERNMENT REGULATIONS

Several countries have now established regulations for UV disinfection.⁵ In 1996, Austria was the first country to introduce UV regulations [initially as guidelines but later enacted as binding regulations (ÖNORM 2001)] by requiring that UV reactors be certified, using biosimetry testing (involving challenging a UV reactor with a nonpathogenic microorganism) to deliver a UV dose (fluence) of at least 40 mJ cm^{-2} (400 J m^{-2}) using a specific challenge microorganism. The first Austrian UV regulations were restricted to UV reactors containing LP UV lamps but were later extended to UV reactors containing medium-pressure (MP) UV lamps (ÖNORM 2003).

Germany followed a year later with the Deutscher Verein des Gas- und Wasserfaches (DVGW) Standard (DVGW 1997). This standard is similar to that in Austria, in that it also requires a minimum UV dose of at least 40 mJ cm^{-2} (400 J m^{-2}) using a specific challenge microorganism. This standard was later revised (DVGW 2006) so that the German and Austrian standards are now almost equivalent.

The US Environmental Protection Agency (USEPA) has established several rules to address various issues of water treatment. The impacts on UV disinfection are as follows:

- Surface Water Treatment Rule (SWTR) (USEPA 1989).

These rules were based on the perception that UV disinfection is not effective in the treatment of *Giardia* but that it is effective for virus inactivation. These rules included UV dose tables for virus inactivation.

- A group of regulations collectively called the “Stage 1 Disinfectants and Disinfection By-products Rule” (USEPA 1998).

These rules did not consider UV light as a disinfectant technology largely because of the perception that UV disinfection was not effective in the treatment of protozoa (e.g., *Cryptosporidium* or *Giardia*), and UV disinfection does not leave a disinfectant residual.

- LT2ESWTR (USEPA 2006a). This rule lays out specific UV dose tables for *Cryptosporidium*, *Giardia*, and viruses. For UV disinfection applications, the companion *Ultraviolet Disinfection Guidance Manual* (USEPA 2006b) is a valuable source of UV information. This rule reversed the previous perception that UV disinfection was not highly effective for protozoa. In addition, this rule reversed the previous perception that it was highly effective for virus inactivation and requires a UV dose of 186 mJ cm^{-2} for 4-log virus inactivation.
- Stage 2 Disinfectants and Disinfection By-products Rule (Stage 2 DBPR) (USEPA 2006c).

⁵ Sommer et al. (2002) review the history of UV regulations, particularly those in Europe.

- Ground Water Rule (GWR) (USEPA 2006d).

This rule identifies UV disinfection as a promising technology for virus inactivation, although the UV dose levels for 4-log virus inactivation are much higher than what can currently be validated. Until validation procedures are available to validate the higher UV doses required for virus inactivation, UV disinfection can be used in series or in combination with other treatment techniques to meet the virus inactivation requirements. However, recent research studies show that validation of UV reactors for virus inactivation will be possible on a wide-scale in the next few years (See Chapter 4 for details).

In the LT2ESWTR and Stage 2 DBPR, UV disinfection is classified as one of the microbial options and is a *best available technology* because of the focus on *Cryptosporidium*. Thus, the USEPA has come full circle from rejecting UV disinfection as a viable treatment technology for protozoa to currently highlighting that it is a *best available* disinfection treatment technology. An important innovation in these rules is the classification of water utilities into *bins* according to the level of *Cryptosporidium* oocysts found in their source waters (Table 1-1). Water utilities in Bin 1, with source waters with relatively low levels are considered *safe* and do not require additional treatment, whereas water utilities in higher bins and *Cryptosporidium* levels have to introduce additional treatment. The various treatment technologies are gathered together into a *toolbox*, and each is assigned a log reduction credit. Therefore, utilities can combine treatment technologies to achieve the level of treatment required for their bin. UV disinfection becomes an attractive treatment option for water utilities with a high level of *Cryptosporidium* in their water, and accordingly these utilities are in bins 3 or 4.

The UV regulations are discussed in more detail in Chapter 4.

ADVANTAGES AND DISADVANTAGES OF UV DISINFECTION

There are many advantages and disadvantages for UV disinfection, as described in the following section.

Advantages

1. It is a very effective disinfection technology for *Cryptosporidium* and *Giardia*.
2. It does not significantly alter the water quality; that is, no change in total organic carbon (TOC), pH, corrosivity, DBP formation potential, or turbidity.
3. The technology is relatively inexpensive with low capital and operating costs, compared to other disinfection options for protozoa.
4. It is relatively easy to operate (i.e., turn up or turn down) the UV equipment based on changes in water flow, water quality, etc.
5. The UV equipment has a relatively small *footprint* and is usually amenable to retrofit into existing water treatment plants.

Table 1-1 LT2ESWTR bin classification for filtered public water systems (PWSs) (USEPA 2006a)

<i>Cryptosporidium</i> Concentration (oocysts/L)	Bin Classification	Additional Treatment Required			
		Conventional Filtration Treat- ment (includes softening)	Direct Filtration	Slow Sand or Diatomaceous Earth Filtration	Alternative Filtration Technologies
< 0.075	Bin 1	No additional treatment	No additional treatment	No additional treatment	No additional treatment
≥ 0.075 and < 1.0	Bin 2	1-log treatment*	1.5-log treatment*	1-log treatment*	As determined by the state* [‡]
≥ 1.0 and < 3.0	Bin 3	2-log treatment [†]	2.5-log treatment [†]	2-log treatment [†]	As determined by the state [†] [§]
≥ 3.0	Bin 4	2.5-log treatment [†]	3-log treatment [†]	2.5-log treatment [†]	As determined by the state [†] ^{**}

* PWSs may use any technology or combination of technologies from the microbial toolbox.

† PWSs must achieve at least 1 log of the required treatment using ozone, chlorine dioxide, UV light, membranes, bag/cartridge filters, or bank filtration.

‡ Total *Cryptosporidium* treatment must be at least 4.0 log.

§ Total *Cryptosporidium* treatment must be at least 5.0 log.

** Total *Cryptosporidium* treatment must be at least 5.5 log.

6. No chemicals are needed for UV disinfection.

7. Disinfection is very fast. Contact times are in the range of a few seconds.

Disadvantages

1. There is no residual disinfection capacity. Therefore, some level of chlorine or chloramines is usually added to maintain a disinfection residual in the distribution system.
2. At present, it is not possible to continuously monitor the UV dose, so operators have to rely on secondary measurements (sensor readings, UV transmittance, water flow rates, etc.).
3. Most UV reactors contain mercury lamps, so breakage of UV lamps represents a possible mercury hazard. However, calculations (USEPA 2006b) appear to show that even if the mercury in a lamp were to enter the water completely, the mercury level in the distributed water would still be well below maximum contaminant levels. More research is required to address this issue.
4. The electric power supply to the utility could be subject to interruptions, which could cause UV lamps to extinguish for time periods of 1–5 min. This could result in some water not being treated unless the water is diverted to waste.

5. There are times when water could be underdisinfected because of power interruptions or lamp warm-up. These situations are considered by the USEPA as *off-specification events* because the UV system would be operating outside of the verified limits of performance.

REFERENCES

- Beukers, R., and W. Berends. 1960. Isolation and Identification of the Irradiation Product of Thymine. *Biochim. Biophys. Acta*, 41: 550–551.
- Bolton, J.R., B. Dussert, Z. Bukhari, T.M. Hargy, and J.L. Clancy. 1998. Inactivation of *Cryptosporidium parvum* by Medium-Pressure Ultraviolet Light in Finished Drinking Water. In *Proc. of the AWWA Annual Conference*. Denver, Colo.: AWWA.
- Bukhari, Z., T.M. Hargy, J.R. Bolton, B. Dussert, and J.L. Clancy. 1999. Medium-Pressure UV Light for Oocyst Inactivation. *Jour. AWWA*, 91(3):86–94.
- Downes, A., and T.P. Blunt. 1877. Researches on the Effect of Light Upon Bacteria and Other Organisms. *Proc. Res. Soc. London*, 26: 488–500.
- . 1878. On the Influence of Light Upon Protoplasm. *Proc. Res. Soc. London*, 28: 199–213.
- DVGW (Deutscher Verein Gas- und Wasserfaches). 1997. UV-Desinfektionsanlagen für die Trinkwasserversorgung—Anforderungen und Prüfung (UV Systems for Disinfection in Drinking Water Supplies—Requirements and Testing). Technical Standard W294, October, 1997. Bonn, Germany: DVGW (German Association on Gas and Water).
- . 2006. *UV Devices for Disinfection in Drinking Water Supply: Part 1: Requirements on Properties, Function and Operation; Part 2: Testing of Properties, Function and Disinfection Effectiveness; Part 3: Ports and Sensors for the Radiometric Monitoring of UV Disinfection Devices—Requirements, Testing and Calibration*. Deutscher Verein des Gas- und Wasserfaches (German Association for Gas and Water), Bonn, Germany. [Online] Available only in German: http://www.wvgw.de/index.php?id=451&submit_gesamtsuche=&tx_indexedsearch%5Bsword%5D=W+294.
- Gates, F.L. 1929. A Study of the Bactericidal Action of Ultraviolet Light II: The Effect of Various Environmental Factors and Conditions. *Jour. Gen. Physiol.*, 13: 249–260.
- . 1930. A Study of the Bactericidal Action of Ultraviolet Light III: The Absorption of Ultraviolet Light by Bacteria. *Jour. Gen. Physiol.*, 14: 31–42.
- Henri, V., and V. Moycho. 1914. Actions des Rayons Ultraviolets Monochromatique dur les Tissus. Mesure de L'Energie de Rayonnement Correspondant au Coup de Soleil. *Compt. rend. Hebd. Seances Acad. Sci.*, 158: 1509–1511.
- Henri, V., A. Helbronner, and M. de Recklinghausen. 1910a. Nouvelles Recherches sur la Sterilization de Grandes Quantités d'Eau par les Rayons Ultraviolets. *Compt. rend. Acad. Sci.*, 151: 677–683.
- . 1910b. Sterilization de Grandes Quantités d'Eau par les Rayons Ultraviolets. *Compt. Rend. Acad. Sci.*, 150: 932–934.
- Hockberger, P.E. 2002. A History of Ultraviolet Photobiology for Humans, Animals and Microorganisms. *Photochem. Photobiol.*, 76(6):561–579.
- Kelner, A. 1949a. Effect of Visible Light on the Recovery of *Streptomyces griseus condidia* From Ultraviolet Irradiation Injury. *Proc. Natl. Acad. Sci. US*, 35(2):73–79.

- . 1949b. Photoreactivation of Ultraviolet-Irradiated *Escherichia coli*, With Special Reference to the Dose–Reduction Principle and to Ultraviolet-Induced Mutation. *Jour. Bacteriol.*, 58: 511–522.
- Lorch, W. 1987. *Handbook of Water Purification*. 2nd ed. Chichester, UK: Ellis Horwood.
- Malley, J.P., J.P. Shaw, and J.R. Ropp. 1996. *Evaluation of By-products Produced by Treatment of Groundwaters With Ultraviolet Irradiation*. Denver, Colo.: Awwa Research Foundation.
- ÖNORM (Österreichisches Normungsinstitut). 2001. Austrian National Standard: ÖNORM M 5873-1 E. 2001. Plants for Disinfection of Water Using Ultraviolet Radiation: Requirements and Testing, Part 1: Low Pressure Mercury Lamp Plants. Vienna, Austria: ÖNORM (Austrian Standards Institute); www.on-norm.at.
- . 2003. Austrian National Standard: ÖNORM M 5873-2 E. 2003. Plants for Disinfection of Water Using Ultraviolet Radiation: Requirements and Testing, Part 2: Medium Pressure Mercury Lamp Plants. Vienna, Austria: ÖNORM; www.on-norm.at.
- Scheible, O.K., and C.D. Bassell. 1981. Ultraviolet Disinfection of a Secondary Wastewater Treatment Plant Effluent. *EPA Report No. EPA-600/S2-B1-152*, Cincinnati, Ohio: US Environmental Protection Agency.
- Sommer, R., A. Cabaj, G. Hirschmann, W. Pribil, and T. Haidler. 2002. UV Disinfection of Drinking Water in Europe: Application and Regulation. In *Proc. of the First Asia Regional Conference on Ultraviolet Technology for Water, Wastewater, and Environmental Applications*. Scottsdale, Ariz.: International Ultraviolet Association. CDROM.
- USEPA (US Environmental Protection Agency). 1989. Surface Water Treatment Rule [Online]. Available: <http://www.epa.gov/ogwdw/therule.html#Surface>.
- . 1998. Stage 1 Disinfectants and Disinfection Byproduct Rule [Online]. Available: <http://www.epa.gov/ogwdw/mdbp/dbp1.html>.
- . 2006a. Long Term 2 Enhanced Surface Water Treatment Rule (LT2) [Online]. Available: <http://www.epa.gov/safewater/disinfection/lt2/index.html>.
- . 2006b. *Ultraviolet Disinfection Guidance Manual for the Final Long Term 2 Enhanced Surface Water Treatment Rule* [Online]. Available: http://www.epa.gov/safewater/disinfection/lt2/pdfs/guide_lt2_uvguidance.pdf.
- . 2006c. Stage 2 Disinfectants and Disinfection Byproducts Rule (Stage 2 DBP Rule) [Online]. Available: <http://www.epa.gov/safewater/disinfection/stage2/index.html>.
- . 2006d. Ground Water Rule (GWR) [Online]. Available: <http://www.epa.gov/safewater/disinfection/gwr/index.html>.
- Whitby, G.E., and O.K. Scheible. 2004. The History of UV and Wastewater. *IUVA News*, 6(3):15–26.

Fundamentals of UV Light and Photochemistry¹

UV disinfection arises from a photochemical process, in which UV light² is absorbed by DNA or RNA (see Appendix A for definitions) in the microorganism, causing a disruption in the structure of the nucleic acid. Therefore, an understanding of UV disinfection requires some background in the fundamentals of UV light, photochemistry, and photobiology. This chapter is designed to help the reader understand these fundamental concepts, which are discussed in general terms. Terms and symbols will often be introduced without explanation. Specific definitions of terms, symbols, and units are given in Appendix A.

Light is important to almost all life forms. Humans *see* only a very small fraction of the *colors* of light. This book primarily addresses the light with wavelengths *beyond the violet* end of the rainbow or the *ultraviolet*. There are several references for information on light and its measurement; for example, a free handbook is available from International Light (Ryer 1997).

LIGHT AND PHOTONS

Light is a form of electromagnetic energy that extends from radio waves to cosmic rays over at least 16 orders of magnitude in wavelength. Light has both particle and wave properties. It is transmitted in discrete packets of energy (photons) and yet has a frequency and wavelength. The connection between these two properties is embodied in the Planck Law of Radiation

$$u = h\nu = hc/\lambda = hc\bar{\nu} \quad (\text{Eq. 2-1a})$$

$$U = N_A h\nu = hcN_A/\lambda = hcN_A\bar{\nu} \quad (\text{Eq. 2-1b})$$

1 Some of this chapter has been adapted from Bolton (2001).

2 Physicists prefer to use the term *ultraviolet radiation*, reserving the term *light* for *visible light*. The authors prefer to use a broader definition of *light* to include the UV, visible, and infrared (IR) spectral regions because of the negative public connotation for the term *radiation*.

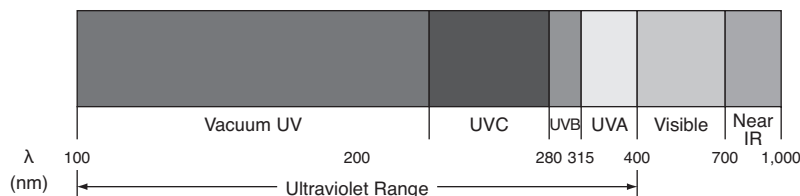


Figure 2-1 Spectral ranges of UV, visible, and IR light. The ultraviolet range is 100–400 nm.

where u is the *energy* (J) of one photon, ν is the *frequency* (s^{-1}), λ is the *wavelength* (m), $\bar{\nu}$ is the *wavenumber* (m^{-1}), c is the *speed of light* ($2.9979 \times 10^8 \text{ m s}^{-1}$) in a vacuum, h is the *Planck constant* ($6.6261 \times 10^{-34} \text{ J s}$), N_A is the *Avogadro number* ($6.02214 \times 10^{23} \text{ mol}^{-1}$) and U is the *energy per einstein*.³ The units here have been given in the standard *Système Internationale* (SI) forms (see Appendix A); however, for applications in UV light and photochemistry, λ is usually given in nanometers (nm) and $\bar{\nu}$ in cm^{-1} , with appropriate numerical factors to make Equation 2-1b come out to joules (J einstein^{-1}).

The absorption of photons by a molecule raises that molecule to an excited state from which a chemical reaction may occur. (This process is called *photochemistry*. See the following section.)

UV LIGHT SPECTRAL RANGES

The usual wavelength range in photochemistry is 100–1,000 nm. Light photons with wavelengths longer than 1,000 nm have a photon energy too small to cause chemical change when absorbed. Photons with wavelengths shorter than 100 nm have so much energy that molecules are ionized, producing electrons and reactive radicals (e.g., $\cdot\text{OH}$), which cause molecular disruptions characteristic of the effects of radiation from radioactive sources. The total photochemical wavelength range is divided into bands with specific names as given in Figure 2-1.

Little photochemistry occurs in the *near infrared* (700–1,000 nm), except for some photosynthetic bacteria, which are capable of storing solar energy at wavelengths out to 980 nm. The *visible* range (400–700 nm) is completely active for photosynthesis in green plants and algae. Also, many dyes undergo photochemical transformations in the visible range or sensitize reactions in other molecules.

Most studies in photochemistry involve the *ultraviolet* ranges (100–400 nm). This region is divided into four subranges connected with the human skin's sensitivity to UV light. The UVA range (315–400 nm) causes changes in the skin that lead to suntanning. The UVB range (280–315 nm) can cause sunburning and eventually can induce skin cancer. The UVC range (200–280 nm) is absorbed by RNA, DNA, and proteins and can lead to cell mutations, cancer, or cell death. In regard to humans, UVC must be treated

³ An *einstein* is one mole (6.0221367×10^{23}) of photons.

with appropriate care. UVC is absorbed strongly in the surface layer of skin cells, which are sloughed off almost daily. Therefore, moderate exposures can be tolerated. However, UVC exposure to the eyes is more dangerous because it can cause the formation of cataracts (Wieringa 2006).

The UVC range is sometimes called the *germicidal range* because it is very effective for inactivating bacteria and viruses. The *vacuum ultraviolet* (VUV) range is absorbed by almost all substances (including liquid water and oxygen in air). Therefore, it can only be transmitted in a vacuum.

EMISSION, TRANSMISSION, AND ABSORPTION OF LIGHT

Various aspects of light are discussed in the context of *emission* from a UV lamp, *transmission* through a medium (air, water, etc.), and absorption by a target molecule.

Light Emission

The emission of light from a UV lamp depends on a number of factors, such as the electrical power input, the radiant power efficiency, the dimensions of the lamp, and the characteristics of a quartz sleeve (if present). The *brightness* of the lamp is described by the *emittance* (W m^{-2}), which is the radiant power emitted per unit area from a small area of the lamp.

Light Transmission and Absorption

Light is transmitted at a speed of $2.994 \times 10^8 \text{ m s}^{-1}$ in a vacuum but slows down when entering any finite medium. The ratio of the speed of light in a vacuum to that in a given medium is called the *refractive index*, the value of which in a vacuum is 1.000 [the refractive index of air is very close to unity (1.0003)]. When light passes from one medium of refractive index n_1 to another with refractive index n_2 ($n_2 > n_1$), two effects occur:

1. Some of the light is reflected back from the interface⁴ such that the angle of reflection (θ_r) is equal to the angle of incidence (θ_i). For light directly incident on a surface, the reflection coefficient is given by

$$R = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2} \quad (\text{Eq. 2-2})$$

If the two media are air and water, $R = 0.025$.

2. Light entering the new medium is *refracted* so that its direction is changed; that is, the angle to the normal of the surface (θ_2) is less than the angle of incidence

⁴ This is the familiar phenomenon of seeing the *reflection* of a mountain on the surface of a lake. The amount of reflection depends on the angle of incidence, with more light being reflected for more oblique angles.

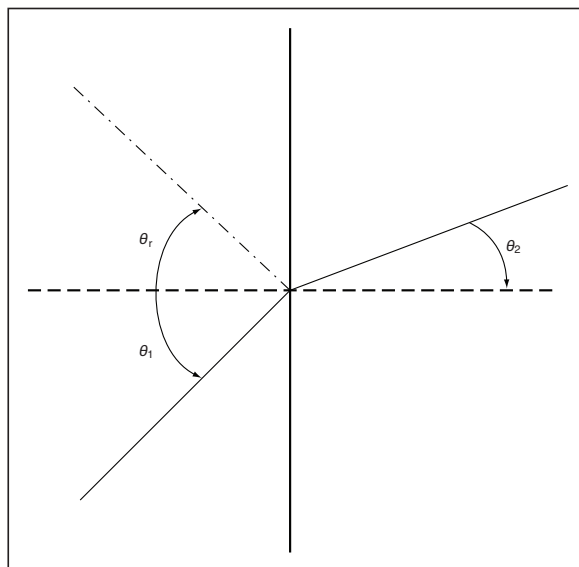


Figure 2-2 Reflection and refraction as a light beam passes from medium 1 with refractive index n_1 to medium 2 with refractive index n_2 . The dotted line represents the reflected light. θ_i is the angle of incidence, $\theta_r (= \theta_i)$ is the angle of reflection and $\theta_2 (< \theta_i)$ is the angle of refraction.

(θ_i). The magnitude of these two effects increases as $n_2 - n_1$ becomes larger. These effects are illustrated in Figure 2-2.⁵

If there are absorbing substances in the medium, the light is attenuated as it passes through according to the Beer-Lambert law.

$$\frac{E^t}{E^0} = 10^{-A} = T \quad (\text{Eq. 2-3a})$$

or

$$A = \log \left(\frac{E^0}{E^t} \right) = -\log(T) = al \quad (\text{Eq. 2-3b})$$

E^t and E^0 are the transmitted and incident irradiances⁶ as a beam passes through a medium over a path length l ; A is the *absorbance* (unitless) and the fraction T is the *transmittance*

⁵ For a quantitative discussion of reflection and refraction, see Bolton (2001).

⁶ The UVDGM (USEPA 2006) uses UV intensity (symbol I) in place of irradiance.

(unitless).⁷ A is directly proportional to the path length l , that is, $A = al$, where a is the *absorption coefficient* (cm^{-1}). It is important to understand that Eqs. 2-3 apply only for a beam of light with a narrow range of wavelengths. In fact, a plot of A versus wavelength is called the *absorption or absorbance spectrum*, and a plot of T versus wavelength is called the *transmittance spectrum*.

Eqs. 2-3 assume that no scattering occurs in the beam. If scattering by particles is present, the situation is more complex because some of the light is scattered at oblique angles and some may be absorbed by the particles.

The absorbance is related to the concentrations of absorbing components by

$$A = \sum_i \varepsilon_i c_i l \quad (\text{Eq. 2-4})$$

where ε_i is the *molar absorption coefficient* ($\text{M}^{-1} \text{cm}^{-1}$) for component i at wavelength λ ; c_i is the *concentration* (M) of component i in the solution; and l is the path length (cm). Remember that ε and hence A are wavelength dependent. Eq. 2-4 is employed in measurements of absorbance that are often used to determine concentrations.

Often the transmittance of UV light in the medium (e.g., drinking water) is described by the UV transmittance (UVT), which is defined as the percent transmittance in the medium when the path length is 1 cm and the wavelength is 254 nm. That is

$$\text{UVT} = 100T = 100 \times 10^{-A_{254}} \quad (\text{Eq. 2-5})$$

where A_{254} is the absorbance⁸ at 254 nm in a 1.0 cm path length. The UVT⁹ of a drinking water is the most important water quality factor as regards the disinfection efficiency of a UV reactor.

Absorbance and transmittance are measured with a spectrophotometer, which measures the irradiance of UV light as it passes through a quartz cell containing the solution of interest (e.g., a drinking water sample). Because a small fraction of the UV beam is reflected from the quartz surfaces, a *blank* measurement must be made with only pure solvent (e.g., distilled water) in the quartz cell. Thus, in practice the ratio $\frac{E^e}{E^0}$ in Eq. 2-3a is the ratio of the detector level for the cell with the solution of interest to that for the cell containing pure solvent. The *transmittance* is displayed (or plotted) as this ratio itself. In the case of *absorbance*, the spectrophotometer performs the negative logarithm of this ratio. Because many UV reactors use low-pressure lamps, which primarily

7 Often the transmittance is expressed as the *percent transmittance* ($\%T$), which usually implies a 1-cm path length.

8 This is really an *absorption coefficient* because the path length is defined as 1 cm.

9 Here the UVT is used, as defined by USEPA (2006), namely, the percent transmittance when the path length is 1 cm.

emit at 254 nm, the measurement of the absorbance at 254 nm (A_{254}) has become a standard water quality parameter, even when medium-pressure UV lamps are used. There exists a standard method for A_{254} (APHA et al. 1998). This method is typically used for SUVA measurement and includes lab filtration of the sample before analysis, which is *not* recommended when assessing A_{254} for UV disinfection purposes.

Most drinking waters have UVT values between 75–95 percent or more. This means that E^t is almost the same as E^0 . Significant errors can occur if one uses a 1.0-cm path length cell. To minimize these errors for highly transmitting waters, it is advisable to use a 5.0 cm or 10.0 cm cell. A_{254} is the measured absorbance divided by the path length.

Light Impinging on a Target

When the light arrives at a final target (e.g., a surface or a microorganism), one must consider the light's *intensity*. Unfortunately, the word *intensity* can mean many things, and so it is best to use this term in a qualitative sense, such as to observe that sunlight is *more intense* than moonlight. The UVDGM (USEPA 2006) has chosen to use the term *intensity* or *UV intensity* to mean irradiance or fluence rate.

Irradiance

When quantitative analyses are made, the geometry of the target becomes important. In the case of a flat surface target, the term *irradiance* (W m^{-2})¹⁰ (symbol E) is used. Irradiance is defined as:

The UV power incident on an infinitesimally small area dA of a flat surface from all upward directions divided by dA .

Thus, irradiance is appropriate when the UV shines on a large, nearly flat surface, such as in the UV curing of inks and coatings or in collimated beam experiments (see Chapter 3).

Fluence Rate

In the case of a tiny spherical or almost spherical target, such as a microorganism, the term *fluence rate* (W m^{-2}) (symbol E_0) is used. Fluence rate is defined as:

The UV power incident on an infinitesimally small sphere of cross-sectional area dA divided by dA .

It should be noted that irradiance and fluence rate have the same units (W m^{-2} or mW cm^{-2}); the only difference is the geometry of the target and the incident UV light.

In many situations (e.g., in a collimated beam), fluence rate and irradiance are almost the same. Because the term *irradiance* is commonly used in the water treatment industry, in this handbook, that term will usually be used, even though the term *fluence*

¹⁰ In North America and some other countries, irradiance is measured as mW cm^{-2} . Note that $1 \text{ mW cm}^{-2} = 10 \text{ W m}^{-2}$.

rate might be more appropriate. However, in modeling studies, where the details of the light distribution are important, the term *fluence rate* should be used.

UV Dose or Fluence

When the fluence rate is integrated over time, one obtains the *fluence* or commonly called the *UV dose* (J m^{-2}) (symbol F).¹¹ That is

$$F = \int E_0 dt \quad (\text{Eq. 2-6a})$$

If the fluence rate is constant in time

$$F = E_0 t \quad (\text{Eq. 2-6b})$$

Fraction of UV Light Absorbed

Because photochemistry is initiated only by the photons that are absorbed by the medium, it is important to determine the fraction of light absorbed from an incident beam.

It should be noted that all of the equations related to the Beer-Lambert law apply only for monochromatic light or for a narrow band of wavelengths where the absorption coefficient does not change significantly with wavelength. For monochromatic or narrow-band light in the absence of reflection, the fraction of light absorbed f_λ in the medium is given by

$$f_\lambda = (1 - T_\lambda) = (1 - 10^{-A_\lambda}) \quad (\text{Eq. 2-7a})$$

In the case of a single microorganism, where the path length is about $1 \mu\text{m}$ or less, the absolute absorbance is very small (0.02 or less). Therefore, the fraction of UV light absorbed is only 1–2 percent or less. In this case, Eq. 2-7a may be expanded as a Taylor series to obtain

$$f_\lambda \cong \ln(10)A_\lambda \quad (\text{Eq. 2-7b})$$

Under these conditions ($A_\lambda < 0.1$), the fraction of UV light absorbed is directly proportional to the absorbance.

When the light source spans over a broad range of wavelengths, one can determine the total fraction of light absorbed f_{total} by dividing the spectral band of interest (e.g., 200–300 nm) into several narrow bands (e.g., 5 nm in width). f_{total} is then determined as a weighted average from Eq. 2-8

¹¹ Again, in North America and some other countries, fluence or UV dose is measured as mJ cm^{-2} . Note that $1 \text{ mJ cm}^{-2} = 10 \text{ J m}^{-2}$. The UVDGM (USEPA 2006) uses the term *UV dose* (symbol D) to mean fluence.

$$f_{\text{total}} = \frac{\sum_{i=0}^n w_i (1 - 10^{-A_{i\lambda}})}{\sum_{i=0}^n w_i}$$

(Eq. 2-8)

where $A_{i\lambda}$ is the absorbance in band i and w_i is a weighting factor proportional to the relative emittance of the light source in band i .

Terms, Units, and Symbols

Unfortunately, when it comes to terms, units, and symbols for UV light parameters, there exists considerable confusion around the world. The International Union of Pure and Applied Chemistry (IUPAC) has put forward a rational set of terms, definitions, units, and symbols (Braslavsky 2007); however, the engineering and science community has been slow to adopt these recommendations. In particular, the UVDGM (USEPA 2006) has gone *on its own* to present an independent set. Table 2-1 compares the various common uses of terms, units, and symbols so that the reader can make appropriate conversions. There has been debate on the definitions of UV intensity and UV irradiance, and it is recommended that the reader use the terms described in this book. Also, the UVDGM does not distinguish the concepts of irradiance and fluence rate, as discussed in this chapter.

Table 2-1 Comparison of terms, units, and symbols in use in various jurisdictions

Term	Jurisdiction		
	IUPAC	USEPA* and North America	Europe and Other Parts of the World
Intensity	Irradiance [†] $E \text{ (W m}^{-2}\text{)}$	Intensity [‡] $I \text{ (mW cm}^{-2}\text{)}^{\S}$	Irradiance $E \text{ (W m}^{-2}\text{)}$
Intensity	Fluence Rate [†] $E_0 \text{ (W m}^{-2}\text{)}$	Not defined	Fluence Rate $E_0 \text{ (W m}^{-2}\text{)}$ or Irradiance $E \text{ (W m}^{-2}\text{)}$
UV dose	Fluence [†] $F \text{ (J m}^{-2}\text{)}$	UV dose $D \text{ (mJ cm}^{-2}\text{)}^{\S}$	Fluence or UV dose $H_0 \text{ (J m}^{-2}\text{)}$

* As specified in the UVDGM (USEPA 2006).
† As defined in this chapter.
‡ In the UVDGM, sometimes intensity means irradiance, but at other times, it appears to mean fluence rate. Unfortunately, the UVDGM does not clearly distinguish the concepts of “irradiance” and “fluence rate” as defined in this chapter.
§ 1 mW cm⁻² = 10 W m⁻²; 1 mJ cm⁻² = 10 J m⁻².

Furthermore, the UVDGM uses UV dose rather than fluence because of the drinking water community's familiarity with the concept of *dose*. However, dose is almost always used in other contexts to mean total absorption of radiant energy. Other scientific communities (Braslavsky 2007) recommended the term *fluence*, rather than *UV dose*. Nevertheless, because UV dose is widely used, particularly in North America, UV dose is used in this handbook, but sometimes fluence is added in brackets.

In this handbook, both the IUPAC and the UVDGM terms, units, and symbols are used wherever possible. Appendix A gives amore complete set of terms, units, and symbols.

WHAT HAPPENS WHEN UV LIGHT REACHES ITS INTENDED TARGET

When UV light reaches its intended target, part of it will be absorbed by molecules in the target (e.g., by DNA in a microorganism). The absorbed photon energy causes the molecule to rise in energy from its initial *ground state* to an *excited state*. At this point, several processes can occur:

1. The molecule returns to its ground state with emission of a photon—this is called *fluorescence*.
2. The excited state can convert to another (usually longer lived) excited state from which photon emission can occur—this is called *intersystem crossing* followed by *phosphorescence*.
3. The molecule can return to the ground state with the excess energy being lost as heat into the medium—this is called *internal conversion*.
4. The molecule can undergo a chemical transformation (rearrangement or fission)—this is the nature of *photochemistry*.

The fraction of excited states that result in photochemistry (the rate of step 4 over the sum of the rates of steps 1–4) is called the *Quantum Yield* (symbol Φ) defined as

$$\Phi = \frac{\text{moles of product formed or reactant removed}}{\text{einsteins of photons absorbed}} \quad (\text{Eq. 2-9})$$

Note that the denominator is photons *absorbed*, not incident. Recall that an einstein is one mole (6.023×10^{23}) of photons.

LAWS OF PHOTOCHEMISTRY ¹²

The possible photochemical reaction by molecules is governed by several laws of photochemistry.

¹² An excellent textbook on photochemistry is that by Wayne (1988).

First Law of Photochemistry

The first law of photochemistry, also known as the Grotthuss-Draper law,¹³ states that

Light must be absorbed by a chemical substance in order for a photochemical reaction to take place.

This means that molecules that do not absorb light of a particular wavelength will not undergo a photochemical reaction when exposed to light at that wavelength. For example, when one puts on sunscreen on the skin, no sunburn occurs because the damaging UV light is absorbed by the components in the sunscreen. Very little UV penetrates the skin, so no sunburn occurs.

Second Law of Photochemistry

For each photon of light absorbed by a chemical system, only one molecule is activated for a photochemical reaction.

This law means that each photon of light can (at most) cause the photochemical reaction of only one light-absorbing molecule. A related law states that the total amount of photoreaction that occurs is directly proportional to the product of the absorbed photon flow and the time of illumination. In other words, more light produces more photoproduct.¹⁴ This is the reason that UV dose or fluence is so important in the UV disinfection of microorganisms. The UV dose or fluence is directly proportional to the *total* number of UV photons absorbed by a given microorganism.

Third Law of Photochemistry¹⁵

The energy of an absorbed photon must be equal to or greater than the weakest bond in the molecule.

A photochemical reaction usually involves the breaking of one or more bonds in the molecule and possible reformation of new bonds. Thus, the law of conservation of energy requires that the energy of the absorbed photon must be at least as large as that of the weakest bond broken. For example, when considering the photolysis of nitric oxide (NO₂), the brown gas that is seen so often in the smog over many cities in the summer, absorption of light can cause the N–O bond to break in NO₂. However, this

13 In 1841, John William Draper developed this law. It came to be known as the Grotthuss-Draper law (his name is linked with Grotthuss, who apparently promulgated the same idea in 1817).

14 This law breaks down for very high photon flows, such as that from a very powerful laser. Under such conditions, the concentration of excited states is high enough so that excited states themselves can absorb a photon, and so multiphoton absorption is possible. This condition is almost never encountered in UV disinfection reactors.

15 This law applies only for photochemical reactions that involve splitting of the molecule into two fragments. Photo-rearrangement reactions are not subject to this restriction.

bond has a high energy, so that even though NO_2 absorbs light out to 700 nm, only UV light with wavelengths less than about 390 nm can lead to the photochemical breakup of NO_2 . Light of longer wavelengths is absorbed, but the excited state simply returns to the ground state, releasing the energy as heat.

A corollary of the first and third laws is that for a molecule with a very weak bond, a photochemical reaction is only possible if there is significant absorption, even though by the third law, breaking of a bond is theoretically possible. For example, the O–O bond in H_2O_2 is quite weak, such that (theoretically) photochemical fission into two $\cdot\text{OH}$ radicals could occur at wavelengths as long as about 560 nm. However, H_2O_2 does not absorb significantly for wavelengths >300 nm. So in practice, the photolysis of H_2O_2 only occurs below 300 nm. This is the basis of the UV/ H_2O_2 advanced oxidation process (see next section), which is becoming of considerable importance in the treatment of trace contaminants (e.g., herbicides and pesticides) in drinking water sources.

ADVANCED OXIDATION TECHNOLOGIES

Advanced Oxidation Technologies (AOTs) are those that utilize powerful oxidizing intermediates (e.g., the hydroxyl radical $\cdot\text{OH}$) to oxidize primarily organic pollutants from contaminated air and water. The term *advanced* is used because the chemical oxidation reactions involved are essentially the same (except billions of times faster) as those that take place very slowly if these organic pollutants are dispersed into the environment. Some of the commercially viable AOTs use UV and visible light to generate $\cdot\text{OH}$ radicals. Other non-UV based AOTs also exist, such as the $\text{O}_3/\text{H}_2\text{O}_2$ process. A very useful free handbook on AOTs is available (AOT 1998). Two other reviews may be consulted for further coverage (Bolton and Cater 1994, Legrini et al. 1993). Finally, books by Oppenländer (2003) and Parsons (2004) provide an excellent overviews of AOTs.

Treatment with AOTs leads not only to the destruction of the target pollutants but also, given sufficient treatment time and energy, to the complete mineralization (i.e., the only products are CO_2 , H_2O , and mineral acids for any Cl, N, S, etc. present in the pollutants) of the pollutants and their by-products. AOTs have proven to be very effective in treating a wide variety of organic contaminants, such as trichloroethylene, perchloroethylene, 1,4-dioxane, methyl-*tert*-butyl ether (MTBE), acetone, phenols, N-nitrosodimethylamine (NDMA), BTEX (benzene, toluene, ethylbenzene and xylenes found in waters contaminated with gasoline), and many other contaminants in groundwaters and industrial effluents.

One of the most popular and effective AOTs is the UV/ H_2O_2 process, which is based on the direct photolysis of added hydrogen peroxide:



The quantum yield for generation of $\cdot\text{OH}$ radicals is 1.0, and most organic pollutants can be degraded rapidly. Because the molar absorption coefficients of H_2O_2 are low, sufficient H_2O_2 must be added (usually >5 mg/L) so that a significant fraction of the UV

between 200 and 300 nm is absorbed. Medium-pressure UV lamps that emit strongly below 250 nm take advantage of the fact that the molar absorption coefficient of H_2O_2 is much larger in that wavelength region. However, low-pressure and low-pressure, high-output lamps have a higher overall efficiency and have a distinct advantage if the water strongly absorbs UV in the 200–250 nm region. If the alkalinity is very high (for pH > 7), neither process may be effective because bicarbonate and particularly carbonate scavenge $\cdot\text{OH}$ radicals.

Many water utilities are now considering the UV/ H_2O_2 process (as well as other AOTs such as the $\text{O}_3/\text{H}_2\text{O}_2$ process) to treat low levels of contaminants, such as pesticides, herbicides, endocrine disruption compounds, pharmaceutical products, and many others. The largest such facility is an installation at the Orange County Water District's groundwater replenishment system, which is designed to treat low levels of NDMA and herbicides.

The UV/ H_2O_2 AOT differs from UV disinfection in that it requires the addition of H_2O_2 and UV doses at least 10–50 times those required for UV disinfection. For example, the UV dose applied in these installations is about 800 mJ cm^{-2} , which is about 20 times the UV dose required for inactivation of virtually all pathogens. Thus, any drinking water treatment plant that installs a UV/ H_2O_2 AOT system will automatically achieve high levels of pathogen inactivation. The UV/ H_2O_2 AOT is also used to treat seasonal taste-and-odor problems in drinking water.

REFERENCES

- AOT. 1998. *Advanced Oxidation Technologies—A Handbook*. Pittsburgh: Calgon Carbon Corporation.
- APHA, AWWA, and WEF (American Public Health Association, American Water Works Association, and Water Environment Federation). 1998. *Standard Methods for the Examination of Water and Wastewater*. 20th ed. Washington, D.C.: APHA.
- Bolton, J.R. 2001. *Ultraviolet Applications Handbook*. 2nd ed. Edmonton, Alta., Canada: Bolton Photosciences Inc.
- Bolton, J.R., and S.R. Cater. 1994. Homogeneous Photodegradation of Pollutants in Contaminated Water: An Introduction. In *Aquatic and Surface Photochemistry*. Edited by G.R. Helz, R.G. Zepp, and D.G. Crosby. Boca Raton, Fla.: Lewis.
- Braslavsky, S.E. 2007. Glossary of Terms Used in Photochemistry, Third Edition. *Pure Appl. Chem.*, 79(3):293–465.
- Legrini, O., E. Oliveros, and A.M. Braun. 1993. Photochemical Processes for Water Treatment. *Chem. Rev.*, 93: 671–698.
- Oppenländer, T. 2003. *Photochemical Purification of Water and Air: Advanced Oxidation Processes (AOPs)—Principles, Reaction Mechanisms, Reactor Concepts*. New York: Wiley.
- Parsons, S., ed. 2004. *Advanced Oxidation Processes for Water and Wastewater Treatment*. London: IWA Publishing.
- Ryer, A. 1997. *The Light Measurement Handbook* [Online]. Available: International Light. <http://www.intl-lighttech.com/services/light-measurement-handbook>.

-
- USEPA. 2006. *Ultraviolet Disinfection Guidance Manual for the Final Long Term 2 Enhanced Surface Water Treatment Rule* [Online]. Available: http://www.epa.gov/safewater/disinfection/lt2/pdfs/guide_lt2_uvguidance.pdf.
- Wayne, R.P. 1988. *Principles and Applications of Photochemistry*. Oxford, UK: Oxford University Press.
- Wieringa, F.P. 2006. Five Frequently Asked Questions About UV Safety. *IUVA News* 8(2):29–32.

Mechanism of UV Disinfection

This chapter explores the process of how absorbed UV photons inactivate microorganisms so effectively. It is important to use the term *inactivate*, rather than *kill* because microorganisms inactivated by UV light are typically still metabolically *alive*.

The process starts with the absorption of UV photons in a given microorganism (First Law of Photochemistry, Chapter 2). Absorption of UV light by proteins in the outer cell membranes with high UV doses (fluences) ultimately leads to the disruption of these membranes and hence, the death of the cell arising from leakage of the protoplasm. However, at much lower UV dose (fluence) levels, absorption of UV photons by DNA (or RNA in some viruses) can disrupt the ability of the microorganism to replicate. *Cells that cannot replicate cannot cause infection.*

Most government regulations require that UV equipment inactivate microorganisms to a specific level. For example, Austria and Germany require four orders of magnitude, that is, 4 log (or 99.99 percent) inactivation for all microorganisms. This means that only one microorganism in 10,000 will remain viable. Chapter 4 provides an overview of UV disinfection regulations.

INACTIVATION MECHANISMS

Absorption of UV Light by Cell Components

As UV light (200–300 nm) passes through a microorganism, it is absorbed by various components in the cell, but only proteins and the nucleotides comprising DNA and RNA absorb a significant amount of UV light in this wavelength range. The relative absorbance of proteins versus that of nucleotides in a microorganism is shown in Figure 3-1. It is clear that below 230 nm, the proteins absorb most of the UV light; however, above 230 nm, absorption is dominated by the nucleotides. It should also be noted: the only amino acids that absorb significantly above 210 nm are the aromatic amino acids: tryptophan, phenylalanine, and tyrosine. These three amino acids have a small absorption peak at around 280 nm, with tryptophan being the strongest absorber at 280 nm. For UV disinfection of drinking water, the water itself strongly absorbs light below 230 nm, which makes these wavelengths unavailable to inactivate the microorganisms.

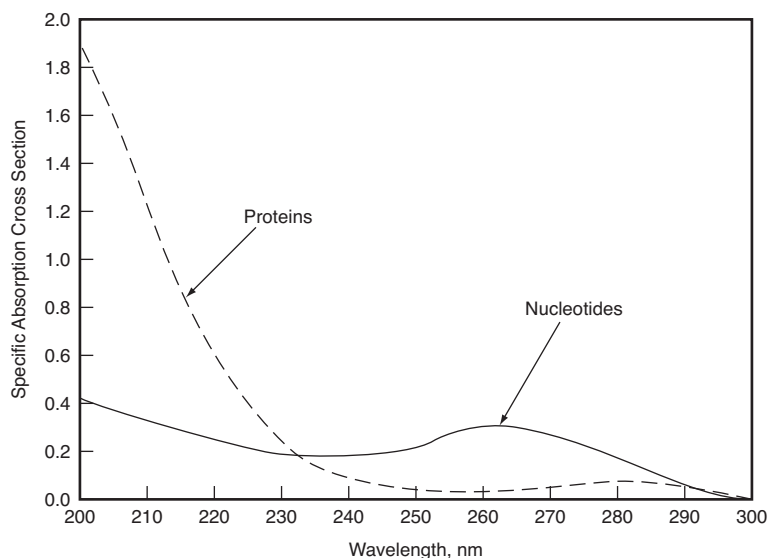


Figure 3-1 Specific absorption cross section versus wavelength for proteins and nucleotides within the cell of a microorganism. Here the dry weight percentages are protein (70%), nucleotides (20%), and other components (10%) (e.g., lipids).

Another factor to consider is that the overall absorbance of a microorganism is rarely more than 0.02 and usually much less because the optical path length in a cell is so small ($< 1 \mu\text{m}$). Thus, less than 5 percent (usually $< 1\text{--}2$ percent) of the UV incident on a microorganism is absorbed. Under these conditions, all absorbers behave independently. That is, it is not possible for the protein in the outer membrane of a cell to act as a *filter* to shield the UV light from the nucleus in the center of the cell.

Although UV light can be absorbed by proteins (mostly in the outer cell membranes), very high UV doses (fluences) are required, compared to those necessary to disrupt the DNA and RNA. Thus, the important fact is that almost all UV inactivation arises from UV absorption by nucleotides. Therefore, to understand the mechanism of UV inactivation of microorganisms, the structure and photochemistry of DNA and RNA need to be examined.

Structure and Photochemistry of DNA and RNA

DNA is the fundamental template for life. It is a polymer of nucleotides in a double-stranded helix linked by a sequence of four constituent bases (adenine, cytosine, guanine, and thymine), which constitute the genetic code. These form base pairs (adenine with thymine and cytosine with guanine) held together by hydrogen bonds. This is the glue that binds the two strands of DNA.

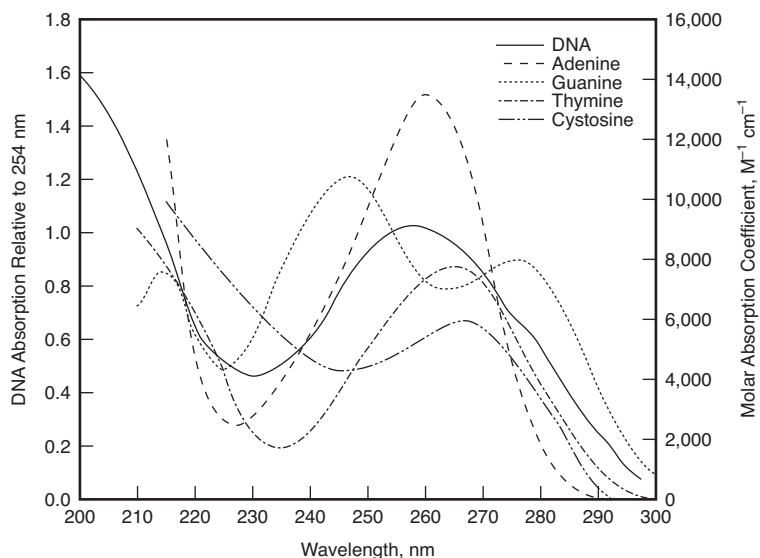


Figure 3-2 Absorption spectra of nucleotides and of DNA

RNA has several roles in a cell. Messenger RNA (mRNA) is transcribed from DNA and carries the genetic information from DNA to the ribosomes where proteins are synthesized. Transfer RNA (tRNA) binds with specific amino acids and carries them to the ribosomes for protein synthesis. RNA has four types of nucleotides: adenine, cytosine, and guanine, but uracil replaces thymine.

Most bacteria and protozoa contain DNA in the cell nucleus. Viruses are subcellular entities that can only reproduce by infecting specific host cells. They consist of a DNA or RNA nucleotide helix with a protein outer shell. The DNA or RNA in viruses can be single stranded or double stranded.

All of the nucleotides in DNA or RNA absorb UV light between 200–300 nm (see Figure 3-2). Of the four essential nucleotides in DNA, thymine undergoes a unique photochemical reaction (see Figure 3-3).¹ If two thymine bases are adjacent to each other, absorption of a UV photon by one of the thymines leads to a chemical bond between the two thymine molecules (called a *thymine dimer*).

The formation of thymine dimers (and other similar dimers) disrupts the structure of the DNA, so that if a critical number of dimers is formed,² the DNA cannot replicate. This prevents infection and is the fundamental mechanism of UV disinfection. Figure 3-4

- ¹ Cytosine also forms dimers; however, the quantum yield is much lower than that of thymine.
- ² Oguma et al. (2002) has shown that the generation of approximately 100 thymine dimers is sufficient to inactivate the entire DNA chain.

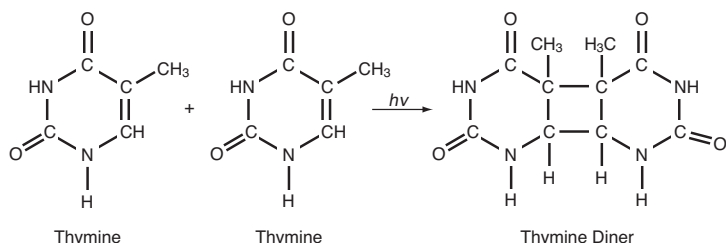


Figure 3-3 Photochemical dimerization of two thymine bases

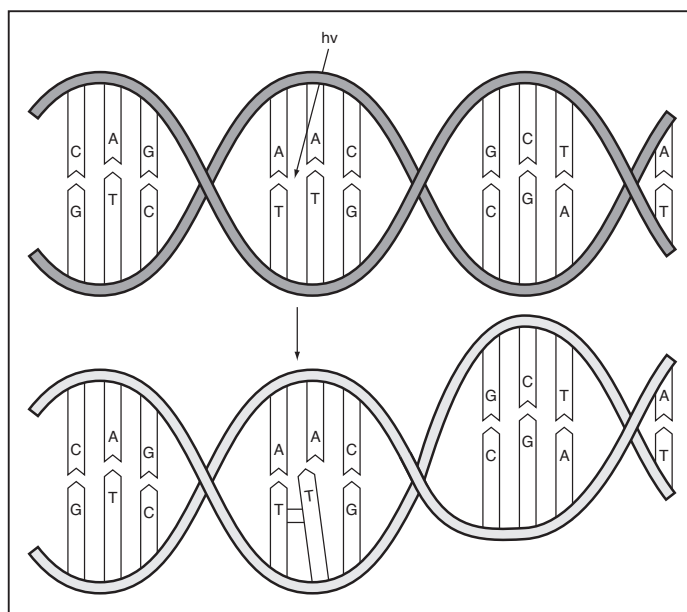


Figure 3-4 Double-stranded DNA chain showing how the formation of thymine dimers disrupts the structure of the chain (A = adenine; G = guanine; T = thymine; C = cytosine)

illustrates the disruption of a DNA chain. For viruses that contain only RNA, a similar photochemical dimerization reaction takes place between two uracil bases.

Viruses can be single- or double-stranded DNA or RNA. There does not appear to be any relation between the *strandedness* or the presence of DNA or RNA with the UV sensitivity of the virus.

Action Spectra and the Germicidal Factor

The relative inactivation response of a microorganism to UV light is determined by the ability of the UV light to be absorbed, causing inactivation of the organism through

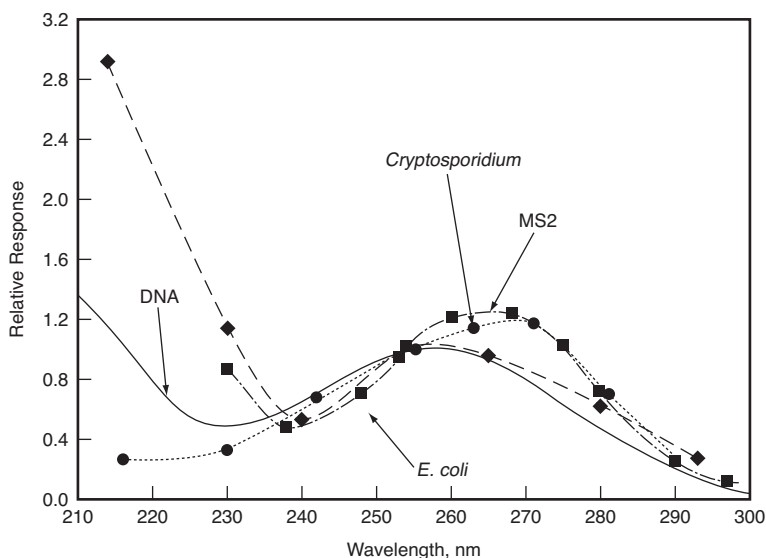


Figure 3-5 Action spectra (relative response versus wavelength) for DNA (—) (von Sonntag and Schuchmann 1992); MS2 coliphage (-----) (Mamane-Gravetz et al. 2005); *Cryptosporidium* (—■—) (Linden et al. 2001); and *E. coli* (---◆---) (Gates 1930)

photochemical reactions, such as the dimerization of adjacent thymine pairs in the DNA chains. This relative response is called the *inactivation action spectrum*. Figure 3-5 shows the action spectra of some microorganisms, along with the relative spectrum of DNA. It should be noted that the maximum germicidal effectiveness occurs around 260 nm. The differences in the action spectra probably arise from different compositions of nucleotides in their DNA and RNA.

In many models of the influence of UV light on microorganisms, it is necessary to include the relative germicidal effectiveness of the UV light at various wavelengths. This is particularly true for polychromatic light sources, such as medium-pressure UV lamps. For this purpose, the *germicidal factor* (GF) has been introduced, such that the $GF = 1.000$ at 254 nm, the principal wavelength emitted by a low-pressure UV lamp. If the action spectrum for a microorganism is available, it can be normalized to 1.000 at 254 nm. However, in most cases, the action spectra are not known; then the relative absorption spectrum of DNA is often used as the GF. The use of the GF is particularly important for UV equipment using UV lamps emitting polychromatic UV light (e.g., medium-pressure lamps).

REACTIVATION MECHANISMS

Some microorganisms (particularly bacteria) have mechanisms that can repair or bypass thymine dimer lesions in the DNA chain during the replication process. Some viruses are able to reactivate by using the reactivation enzymes of their host. *Giardia* and

Cryptosporidium have not yet been shown to reactivate such that they regain infectivity (Linden et al. 2002, Shin et al. 2001, and Oguma et al. 2001). These mechanisms are divided into *dark* and *light* mechanisms. The latter are called *photoreactivation* and are activated by near UV and short-wavelength visible light. Harm (1980) has a good discussion of reactivation mechanisms, which is summarized in the following section.

Dark Reactivation Mechanisms

Most bacteria have some reactivation potential in the dark. Various mechanisms have been proposed by which a microorganism can repair DNA damage in the dark:³

- *Replacement of UV-damaged nucleotides.* In this case, the UV photoproduct (e.g., thymine dimer) and a sequence of adjacent nucleotides are removed from the DNA and a corresponding sequence is resynthesized.
- *Combination of undamaged regions in replicating DNA molecules.* Undamaged regions of DNA are replicated and reconstituted, so that an intact, double-stranded DNA, identical with the original undamaged DNA, is formed. This is possible because the complete information for a DNA molecule exists totally in each single strand. Thus, one strand can function even if the other strand is damaged.

Photoreactivation Mechanisms

It is possible to have *light-induced reversal of the UV damage*. This is also called *photoenzymatic repair*. This mechanism is the most prevalent reactivation mechanism and was discovered independently in bacteria by Kelner (1949a,b) and in bacteriophages by Dulbecco (1949, 1950). Here, a special light-activated enzyme, *photolase*, splits the thymine dimers, restoring the original structure on the DNA.

This process is triggered by the absorption of UVA light and is thus called *photoreactivation*. This repair mechanism can be overcome, but this requires a higher UV dose (fluence). This is typically not of concern in water treatment systems that are totally covered; however, if water is stored in open ponds or reservoirs exposed to sunlight, photoreactivation must be considered. Photoreactivation may be particularly important for the UV treatment of wastewater, where the effluent is discharged into a river or lake. On the other hand, drinking water is rarely exposed to sunlight, and photoreactivation is unlikely.

If a residual disinfectant (e.g., chlorine or chloramines) is maintained in the distribution system, photoreactivation is not a concern because reactivated microorganisms will be inactivated by the residual disinfectant.

³ The meaning of the term *dark* in this context means mechanisms that do not require light activation.

UV SENSITIVITY OF MICROORGANISMS

Microorganisms exhibit a wide variation in their sensitivity to UV light. The measurement of the UV sensitivity of microorganisms at a specific wavelength, or narrow band of wavelengths, is performed through the determination of a UV dose (fluence)–response curve.

Collimated Beam Tests

The UV sensitivity of microorganisms is determined using a *collimated beam test*, where a sample suspension of the microorganisms⁴ is exposed to UV light (usually in an open petri dish) in a collimated beam apparatus where the sample is exposed to beams of UV light that are almost parallel.⁵ Figure 3-6 illustrates two types of collimated beam apparatus. Such an apparatus can be constructed from commonly available materials or purchased from a vendor.

In a properly conducted determination of the UV dose (fluence)–response curve for a microorganism,⁶ where the sample is well stirred and proper corrections are made, an accurate determination of the average irradiance (fluence rate) E_{avg} in the water suspension can be made from the incident irradiance as determined using a calibrated radiometer. The product of E_{avg} and the exposure time in seconds gives the delivered UV dose (fluence) F . For each exposure time, the sample suspension is sent to a microbiological laboratory where the concentration of viable organisms is determined. A detailed operating protocol for such measurements has been specified by Bolton and Linden (2003), and Excel spreadsheets are available on the IUVA web site (www.iuva.org; for members) or from Jim Bolton (jbolton@boltonuv.com).

UV Dose (Fluence)–Response Curves

Figure 3-7 shows an example of a UV dose (fluence)–response curve. The UV dose (fluence)–response curve can exhibit up to three phases. For many bacteria, there exists a *shoulder* phase, such as that seen for *B. subtilis* (see Figure 3-7), where $\log(N/N_0)$ changes only slowly with the UV dose (fluence) at the beginning. This is followed by a *semilog* phase, where $\log(N/N_0)$ decreases linearly with UV dose (fluence). Finally, there may exist a *saturation* phase, in which $\log(N/N_0)$ changes only slowly with UV dose (fluence).

⁴ Hereinafter, this will be referred to as the *suspension*.

⁵ The term *collimated beam apparatus* is widely used, but it is important to realize that the beam is not truly collimated, in the sense that all rays are parallel. The beam does diverge, and thus there is a need for a divergence factor. Often the term *quasi* collimated beam is used to reflect this reality.

⁶ Unfortunately, until recently most response curves were based on the incident irradiance, rather than the average irradiance in the microorganism suspension. Thus a significant part of the published literature should be considered as upper limits because the irradiance has been overestimated.

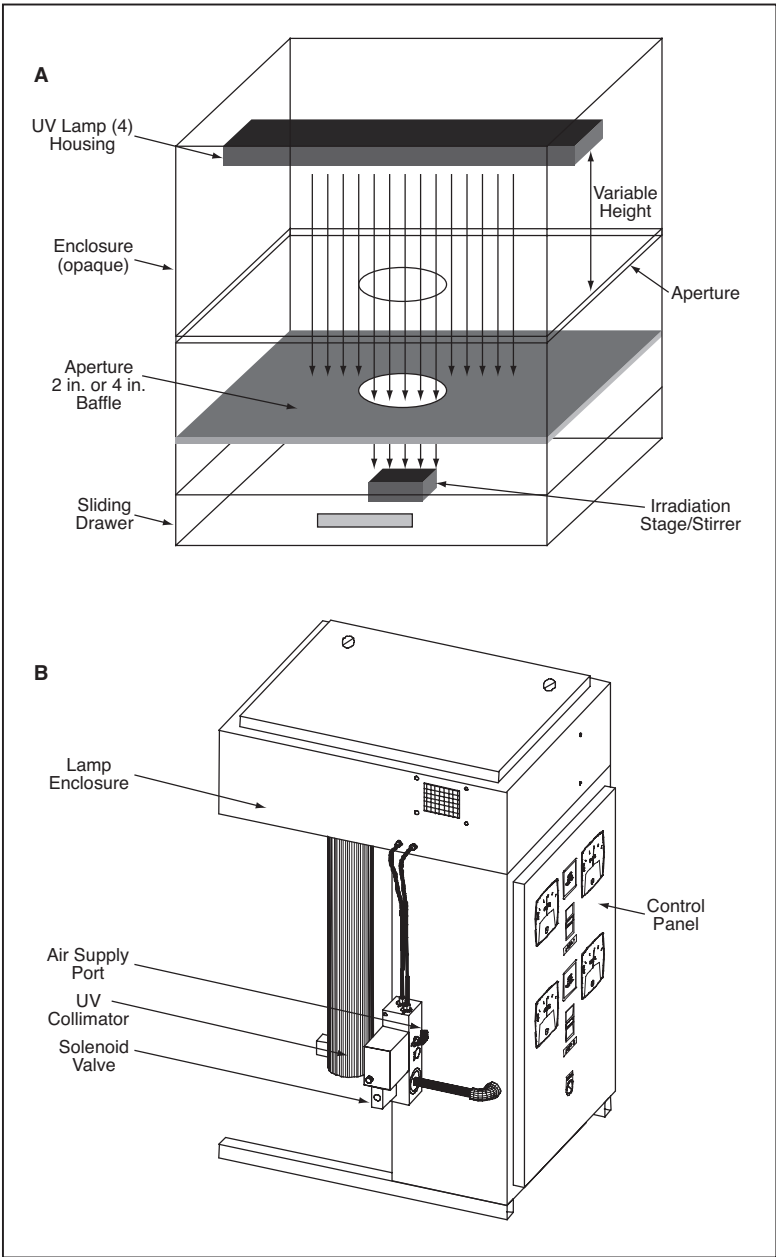


Figure 3-6 (A) Home-made collimated beam apparatus (courtesy of Prof. Linden, private communication); (B) Commercial collimated beam apparatus (courtesy Calgon Carbon Corporation, Pittsburgh, Pa.)

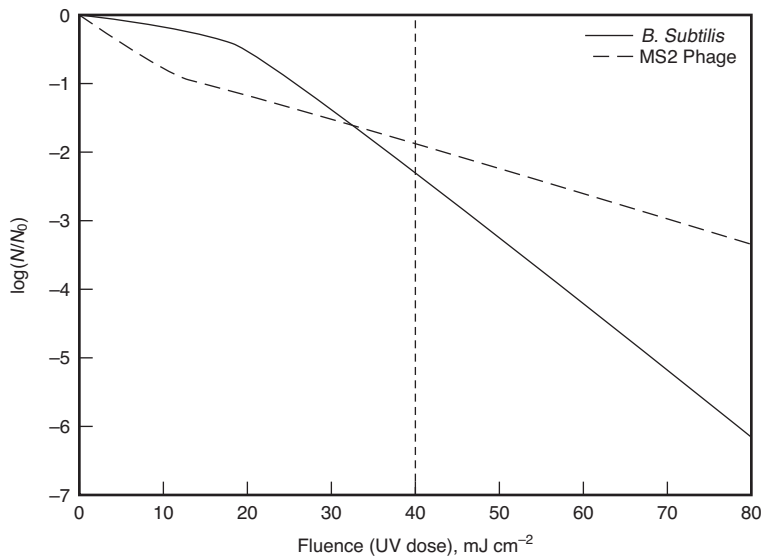


Figure 3-7 UV dose–response curves for *B. subtilis* and the virus MS2 coliphage

The *shoulder* phase is thought to be associated with DNA repair mechanisms, or it may arise from the requirement of several *hits* (DNA damage sites) before a microorganism becomes inactivated (Roessler and Severin 1996). The saturation phase may arise from several causes, such as microorganisms clumping or associating with particles (this is particularly prevalent in wastewater systems).

The *semilog* phase is characterized by the rate equation

$$\log\left(\frac{N}{N_0}\right) = -kF \quad (\text{Eq. 3-1})$$

where k is a standard fluence-based rate constant [$\text{cm}^2 \text{mJ}^{-1}$ or $\text{m}^2 \text{J}^{-1}$] that is characteristic of the microorganism, and F is the UV dose (fluence). Other more sophisticated equations have been developed to model the other two phases (Roessler and Severin 1996).

Relative UV Sensitivity of Pathogenic Microorganisms

The UV sensitivity of pathogenic microorganisms varies considerably. The currently accepted order is

$$\begin{array}{c} \text{bacteria} \approx \text{protozoa} > \text{most viruses} > \text{bacteria spores} > \text{adenovirus} > \text{algae} \\ \text{(most sensitive)} \quad \text{-----} \quad \text{(least sensitive)} \end{array} \quad (\text{Eq. 3-2})$$