

NANOTECHNOLOGY COOKBOOK

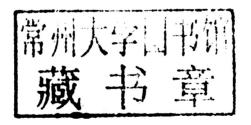
Practical, reliable and jargon-free experimental procedures

ANDREW M. COLLINS

Nanotechnology Cookbook

Practical, Reliable and Jargon-free Experimental Procedures

Andrew M. Collins School of Chemistry, University of Bristol





Elsevier

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

First edition 2012

Copyright © 2012 Elsevier Ltd. All rights reserved

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, without the prior written permission of the publisher

Permissions may be sought directly from Elsevier's Science & Technology Rights Department in Oxford, UK: phone (+44) (0) 1865 843830; fax (+44) (0) 1865 853333; email: permissions@elsevier.com. Alternatively you can submit your request online by visiting the Elsevier web site at http://elsevier.com/locate/permissions, and selecting Obtaining permission to use Elsevier material

Notice

No responsibility is assumed by the publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Because of rapid advances in the medical sciences, in particular, independent verification of diagnoses and drug dosages should be made

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

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

ISBN: 978-0-08-097172-8

For information on all Elsevier Publications visit our Web site: www.store.elsevier.com

Printed and bound in China

12 13 14 15 10 9 8 7 6 5 4 3 2 1

Working together to grow libraries in developing countries

www.elsevier.com | www.bookaid.org | www.sabre.org

ELSEVIER

Sabre Foundation

Nanotechnology Cookbook

Acknowledgements

A great many have contributed time and expertise to this project. Since I get a single page to thank everybody involved, I have instead opted to scatter the names of those patient and wonderful contributors throughout this book. I could not have done this without them. In particular the Bristol Centre for Functional Nanomaterials within the Nanoscience and Quantum Information Centre have been an invaluable source of knowledge and have helped me at every step.

I would like to thank the Elsevier team who have worked hard to make this book a physical reality.

Thanks to Stephen Mann for getting me into materials chemistry and nanotechnology and to his group who helped me at every opportunity.

Thanks to Simon Hall without whom this book would simply not have happened.

Thanks to Jon Jones and Sean Davis for their continued patience during the period I was writing.

Finally a big thanks to my Mum, Dad, brother Steve and my wife Gait who got me through a very long and busy year with their loving support.

Contents

ACK	nowledgements	vi
1.	Introduction	1
2.	Safety	3
	General Laboratory Procedure	3
	Personal Safety Equipment	
3.	Common Analytical Techniques for Nanoscale Materials	17
	Principles of Electron Microscopy	17
	Transmission Electron Microscopy	18
	Sample Preparation for TEM	19
	Scanning Electron Microscopy	20
	Sample Preparation in SEM Scanning Tunnelling Microscopy	21
	Atomic Force Microscopy	21 23
	Powder X-ray Diffraction	27
	UV-visible Spectroscopy	29
	Dynamic Light Scattering and Zeta Potential Measurement	30
	BET Surface Area Measurement	32
4.	Chemical Techniques	35
	The Sol-Gel Process	35
	Coating Nanomaterials Using the Sol Gel Method	49
	Using Sol Gel Dip Coating to Form Thin Films, Thin Porous Films and Replicas	61
	Replication of Oddly Shaped Morphologies Using Sol Gel Techniques Mesoporous Inorganic Powders	72
	Aerogels and Supercritical Drying	79 88
	Applications of Aerogels	89
	Monoliths and Glasses Containing Functional Biological Materials	95
	Growing Zinc Oxide Nanorods	104
	Cadmium Sulfide, Selenide and Telluride Quantum Dots	110
	Making Gold and Silver Colloids Ferrofluids	135
	Allotropes of Carbon	160 171
	Metal Organic Frameworks	187
5.	Physical Techniques	205
	Chemical Vapour Deposition	205
	Atomic Layer Deposition	211
		2.,

Index

	Photolithography Patterning	21
		214
	Soft Lithography, Pattern Replication and Contact Printing	223
	Making Wire Tips for Scanning Tunnelling Microscopy	233
5.	Biological Nanotechnology	255
	Cloning and Gene Expression to Produce Proteins in Escherichia Coli	255
	DNA Origami	283
	Keeping Bacteria Long Term in a Glycerol Stock	300
	Testing the Minimum Inhibitory Concentration of an Antibiotic	301

Contents

305

A companion site for the book is available at: http://www.elsevierdirect.com/companion.jsp?ISBN=9780080971728

Introduction

I am going to avoid beginning this book with a dry definition of nanotechnology in favour of conveying my excitement about the potential advances this field of study can provide. Nanoscale science and technology draws from a multitude of research interests and is not confined to any individual scientific discipline. The multi-platform approach to engineering at length that scales somewhere between the thickness of a hair down to a few atoms across requires a harmonious and collaborative approach from the 'pure' sciences (physics, biology and chemistry) and often this results in new ideas and avenues of investigation for the enquiring mind. The capacity to manipulate and control matter in ultra-small dimensions is more than just a technical challenge to be overcome for its own sake. Materials can begin to exhibit new properties when fashioned on the nanoscale which are unseen in the larger everyday bulk. Gaining new functionality from existing materials simply by virtue of the way in which they are structured is highly attractive and nanoscience opens up the opportunity to tailor-make a physical material through the hierarchy of atomic, chemical, crystal, micro, meso and macro composition. The terms 'top down' (starting with something large and making it smaller) and 'bottom up' (starting with the raw chemical, element or atom and working up from there) are often used as catch all terms for describing the manufacturing process of nanomaterials, but these phrases do not do justice to the plethora of cross-disciplinary techniques required to produce various nanostructured materials. It would not be correct to say that nanotechnology is a recent development. Products that utilise nanomaterials such as microchips, solar cells, sporting goods, clothes and medicines have already been available for decades in various guises. It would be more fitting to say that the concept of nanotechnology has recently risen to prominence in terms of academic development and public interest. Industry is investing heavily in this area with particular emphasis on electronic goods, information technology, materials, power storage, catalysis and energy generation. It is important to remember that nanotechnology is not limited to extremely small items, and many everyday scale items incorporate nanomaterials as part of a greater functional whole. Nanotechnology holds promise for major advances in drug delivery and the diagnosis and treatment of disease. In parallel with the purely scientific and commercial progress, the impact that nano-enabled products and medicines have on the environment and on our own bodies is being monitored so that the transition from the laboratory to the world at large can be made safely. To develop and study nanomaterials requires an interdisciplinary approach and many universities all over the world now run dedicated courses to train the next generation of nanoscale scientists.

Starting out in my own research on the nanoscale, I often found that I had to jump out of my role as a chemist and into the role of a biologist or physicist to get things done on a practical level. After speaking to other colleagues and students, I quickly discovered that I was not alone in having to get to grips with an alien technique or experimental procedure to compliment my practical work. Although learning new experimental approaches is fun, it can take precious time to come up to speed. Having someone by your side who knows what they are doing is the best way to learn something for the first time (for me at least), but this option is not always available. Similarly, a clear and well-written experimental section can be followed, but these often assume prior knowledge and it can be easy to omit a simple detail that could make all the difference to a given procedure working out as you hope it will. Personally, I always wanted a book at hand that would spell everything out for me step by step without having to dig through papers or knock on doors. Something like the teaching manual books that I followed as an undergraduate which broke each stage of a preparation down and explained why it was done. When I met Graham, the Elsevier acquisitions editor, in Texas two years ago, we discussed the possibility of a 'Cookbook' for nanomaterials and from then on I began to collect procedures and began to put this book together. Funnily enough, putting the book together involved large amounts of digging through papers and knocking on doors but then it is my hope that you, the reader, won't have to do as much of this yourself.

In this book I aim to provide you with some practical techniques drawn from the realms of physics, biology and chemistry as starting points for incorporating various aspects of nanotechnology, that you may otherwise be unfamiliar with, into your own research. I have tried to maintain a teaching manual approach to every synthesis in order to maintain clarity. In contrast to many textbooks, I have used a minimal approach to references to encourage a fresh direction of thought in how you move forward with your work. Each of the synthetic methods listed as recipes within this cookbook have been sorted into sections based on the classical

discipline from which they are derived. This is done only to give you a frame of reference for the kind of scientific setting in which you will most likely be attempting the experiment and does not infer that one type of procedure cannot be integrated with another. The hybridisation of scientific approaches can lead to discovery and I hope that you find this to be the case when undertaking any of the recipes outlined herein.

Andrew M. Collins January 2012

A Quick Definition

A nanometre is 1×10^{-9} m. To put this in perspective, the distance of a carbon—hydrogen bond is around 1 Å (or ~1 \times 10⁻¹⁰ m or ~100 pm). In broad terms, nanotechnology deals with the manipulation, fabrication and application of materials having at least one spatial dimension less than 100 nm (or 0.1 μ m) in size.

In all recipes the term 'water' is used to indicate deionised and distilled pure water unless otherwise stated.

Safety

This is the most important section of the book.

Many of the experiments in this book deal with chemical and biological hazards and hazardous reactions. If performed incorrectly or without adequate safety procedures and equipment, there is a real danger that the experimentalist or others around them will be injured or killed. The products of these experiments may be, in and of themselves, toxic and/or hazardous and should be contained or disposed of correctly after use.

The above statement may read as sensationalist scaremongering but is absolutely true. Accidents in the laboratory happen all the time (there are weekly bulletins posted by the American Chemical Society's Chemical and Engineering News). Even when everything appears to be correct with a reaction, there can still be factors beyond your control that result in dangerous problems. The reader should make their safety and the safety of others the main priority when undertaking any work. In this section we will explore some of the considerations surrounding the safety aspect of working with nanomaterials and some of the new protocols to help minimise the potential risks of working with them. Most of this section covers general best practice procedures and the reader should always default to local laboratory practices and regulations. Nanoscopic materials can behave in radically different ways from the bulk counterpart. This means that even materials considered Generally Recognised as Safe (GRAS status) in bulk cannot be considered so after formulation on the nanometre scale. Currently, no separate risk classification exists for nanomaterials and they are treated with the same risk management and disposal procedures that are in place for chemical and biological hazards. The field of nanotoxicology continues to grow and preliminary research shows that nanomaterials do behave in unique ways biologically. This is of some concern as products containing nanomaterials have already been in circulation for some years and the amount produced grows year on year. Some discussion of this is provided at the end of the section. Overall, working with nanomaterials means that you will be responsible for safely producing, handling and disposing of them with control of the associated immediate and long-term risks. This ethos of responsibility is encompassed by the phrase 'from the cradle, to the grave'.

GENERAL LABORATORY PROCEDURE

All laboratories should have a health and safety framework in place. This includes a hierarchy of people responsible for managing safe laboratory practice and its implementation. People trained as emergency first aiders should be on-site with a contact number on visible display in the laboratory. For every reaction you do, you should perform a risk assessment on it before starting. This is not only a legal requirement in most countries but will also allow you to think out the experiment and spot any potential accidents before they happen. A procedure for this is provided further on in this section. You should be aware of the following in any chemical or biological laboratory:

- Fire plan and fire extinguishers. In chemical laboratories, foam or carbon dioxide extinguishers are used. Water extinguishers are normally avoided as some reagents will catch fire on contact with water.
- The contact point for first aid and the location of the first aid kit.
- The emergency shower and emergency eyewash.
- Chemical spill kits. These kits are usually a large bucket of inert adsorbent granules. In the event of a spill, the granules can be used to soak up the liquid and collected to be disposed of.
- Reagent lists with the location of the chemicals or general reagent class listed on a map. This makes things easier to find day to day and also helps to keep track of dangerous and hazardous materials.
- A secure area for solvent storage (if solvents are used) that is adequately vented. Solvents are normally stored in cabinets built
 into fume hoods for this purpose.
- Solid and solvent waste disposal receptacles or procedures. Private companies will deal with the accumulated waste in the
 correct way. With the possible exception of washing glassware with water almost everything produced in a laboratory cannot
 and should not be poured down the sink.

- Dedicated glass bins and sharps bins. Both glass and needle waste cannot be mixed with regular waste for any reason.
- Never work alone in a laboratory. Some places have out of hours procedures, but these will always rely on having someone in the same room as you to summon aid in case of an accident.
- Hands must be washed before leaving the laboratory. Even if you have been wearing gloves.

Overall you should never tolerate unsafe practice in a laboratory. This may seem obvious, but it is easy for people to become complacent when they get comfortable with their work. One of the most effective methods of making the laboratory environment less accident-prone is to engender a culture of intolerance to lazy or unsafe practice. From a social point of view, people can sometimes be uncomfortable confronting others about this, but remember, the life you save may be your own. I have heard of a student who was too afraid of confronting a senior researcher about their use of hydrofluoric acid open on the bench instead of a fume hood. The matter was settled by an anonymous note delivered to an even more senior member of staff who then arranged to catch the offender red-handed in a surprise laboratory visit.

Even when every safety procedure is followed as carefully as possible, the unexpected can still happen. Below is a photo of a fume cupboard where a reaction under reflux suddenly 'ran away'. The uncontrolled reaction overpressured the glassware and released that pressure with enough force to shatter the front of the fume hood. In this case no one was hurt but it demonstrates that even with safeguards in place and an approved assessment of the risk, it can all go wrong. After a reaction has been safely conducted, you must still control where your products eventually end up. The photograph in fig. 2.1b shows a bin into which 'made safe' chemical waste had been deposited but unexpectedly caught fire overnight. Although independently the waste was benign, a chance combination must have spontaneously ignited. Once more, this type of accident is almost impossible to predict but does help to refine the procedures that will prevent incidents like it from happening again (Fig. 2.1).

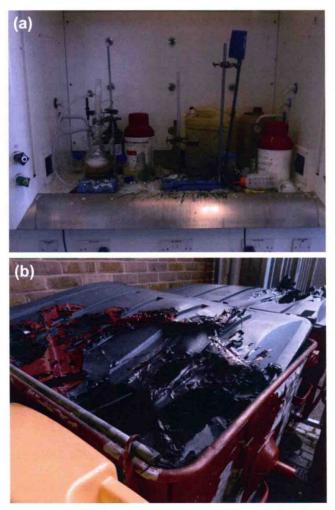


FIGURE 2.1 (a) A fume hood that has suffered catastrophic damage after a reaction has gone out of control and blown up. (b) The aftermath of a bin fire ignited by incompatible chemical waste.

PERSONAL SAFETY EQUIPMENT

There are some items that should be with you at all times when you are in a laboratory. A barrier in some form should be between you and whatever you are working with. Gloves and laboratory coats should remain in laboratory areas and never transferred into offices or group spaces:

- Safety spectacles. This is the number one item of equipment to protect you from losing your eyesight. Whenever you are in a laboratory, even if you are not working directly at a bench you should keep safety spectacles on at all times. Explosions in other areas of the laboratory can propel glass and other chemicals at high velocity and spectacles are the only thing that will save your sight. Something nasty could get in your eye at any time. Someone could drop a beaker of acid right next to you and it could splash in your face. You should feel naked without a pair on your face and resist the urge to place them on your head when working close up. Speaking as a former laboratory demonstrator, people will often take them off without thinking. You must notify the owner to immediately put them back on. Confront anyone not wearing safety spectacles in a laboratory and never let someone say 'it's OK, I'm not working with anything dangerous'.
- A laboratory coat. This is the first defence you have against spills on your clothes and can be quickly removed if it catches fire. Laboratory coats can be washed by specialist companies and should not be washed with normal clothes under any circumstances.
- Gloves. There are many different types of disposable gloves and, depending on the chemicals they will be exposed to, not all are suitable for all purposes. You must check that the gloves you are using are compatible with your experiment before starting! Nitrile gloves are commonly used around both chemical and biochemistry laboratories, but it is important to remember that these can be degraded by some chemicals and may offer only a partial barrier to the skin. Latex gloves used to be common but are no longer used as people can become sensitised to using them and they can cause a serious allergic response. A chart grading the protection offered from four common types of gloves against various solvents is provided below (Sourced from Ansell).

Chemical	Nitrile	Neoprene	Poly(vinyl chloride)	Natural rubber
Acetic acid (glacial)	G	Е	F	Е
Acetone	Nr	G	Nr	E
Ammonium hydroxide	E	E	E	E
Aqua regia	F	G	G	G
Benzene	P	Nr	Nr	Nr
Butanol	E	E	F	E
Chloroform	Nr	Nr	Nr	Nr
Dichloroethane	F	P	P	Nr
Dimethyl formamide	Nr	G	Nr	E
Dimethyl sulfoxide	E	E	Nr	E
Ethyl acetate	Nr	F	Nr	G
Ethyl ether	E	E	Nr	Nr
Formaldehyde	E	E	E	E
Hexane	E	E	Nr	Nr
Hydrochloric acid (10%)	E	E	E	E
Hydrofluoric acid (48%)	E	E	G	G
Hydrogen peroxide (30%)	E	E	E	E
Isopropanol	E	E	G	E
Methanol	Е	E	G	E
Methyl methacrylate	P	N	Nr	P
Methylene chloride	Nr	Nr	Nr	Nr
Nitric acid (70%)	Nr	G	F	Nr
Octanol	E	E	F	E
Phosphoric acid	E	E	G	G
Sodium hydroxide (50%)	E	E	G	E
Sulphuric acid (10%)	G	E	G	E
Sulphuric acid (95%)	Nr	F	G	Nr
Tetrahydrofuran	Nr	Nr	Nr	Nr
Toluene	F	Nr	Nr	Nr
Trichloroethylene	Nr	Nr	Nr	Nr
Triethanolamine	E	E	E	G

Risk Assessment

Most reagents and solvents used in a chemistry laboratory are in some way harmful. In a biological laboratory, there is the added risk of being exposed to an infection. A risk assessment must be performed before starting any new experimental procedure and checked with the person responsible for laboratory safety. Every chemical is labelled in some way to denote any potential hazards associated with it. All chemicals will also come with a Materials Safety Data Sheet (an MSDS) which will detail the associated hazards more explicitly. If you do not have the MSDS sheet, then these can be downloaded or obtained directly from the supplier. As of 2010, the European legislation regarding the labelling of chemicals has changed so that a globally standardised system of warning labels and hazard phrases is used (Health and Safety Executive, UK). This system is called Classification, Labels and Packaging (CLP) and replaces the older system of Chemicals Hazard Information and Packaging (CHIP). The CHIP system of classification is still more widely used and consists of Risk phrases and Prevention phrases which will be listed as R- and P-, respectively, followed by a number. The number relates to a particular hazard which can be read from a chart as given below. The new CLP system is similar but used the terms Hazard phrase and Safety phrase listed as H- and S-, respectively, followed by a number. The newer global hazard symbols under CLP classification are also included in the table.

These hazard/risk phrases will help you assess how dangerous it is to use a particular reagent and how to go about dealing with the risk it presents. When performing a risk assessment, write out the reaction you intend to do and list all of the chemicals involved. Check their risk phrases as given on the warning label (if any) and MSDS. List any potential hazards involved and how you will deal with them on a practical level. Also check the literature to see if any of the chemical combinations being used could fume, explode or do anything other than the expected reaction. A good place to start is to check in regularly updated handbooks like Brethericks 'Hazards in the Chemistry Laboratory' (Urben, 2006) and 'Hazardous Chemicals Handbook' (Carson and Mumford, 2002). Many of these risk phrases will denote a substance dangerous enough that you will need to perform a special COSHH (Control of Substances Hazardous to Health) assessment and get clearance from your safety officer before proceeding. *Include a procedure for what you will do if it becomes a worst case scenario (e.g., the reaction catches fire)*. A copy of the risk assessment should be kept with your safety officer and another copy should be placed in your laboratory book as a reference though it is also a legal requirement in most laboratories.

Symbol	Abbreviation	Hazard	Description
Explosive	Е	Explosive	Chemicals that explode.
Oxidising	O	Oxidising	Chemicals that react exothermically with other chemicals.
Flammable	F	Highly flammable	Chemicals that may catch fire in contact with air, only need brief contact with an ignition source, have a very low flash point or evolve highly flammable gases in contact with
	F+	Extremely flammable	water. Chemicals that have an extremely low flash point and boiling point, and gases that catch fire in contact with air.
	T+	Very toxic	Chemicals that at very low levels cause damage to health.

Toxic Category 1 or 2 carcinogen Category 1 or 2 mutagen Category 1 or 2 reproductive toxin Corrosive	Chemicals that at low levels cause damage to health. Chemicals that may cause cancer or increase its incidence. Chemicals that induce heritable genetic defects or increase their incidence. Chemicals that produce or increase the incidence of non-heritable effects in progeny and/or an impairment in reproductive functions or capacity. Chemicals that may destroy living tissue on
Category 1 or 2 mutagen Category 1 or 2 reproductive toxin	Chemicals that may cause cancer or increase its incidence. Chemicals that induce heritable genetic defects or increase their incidence. Chemicals that produce or increase the incidence of non-heritable effects in progeny and/or an impairment in reproductive functions or capacity. Chemicals that may destroy living tissue on
Category 1 or 2 reproductive toxin	defects or increase their incidence. Chemicals that produce or increase the incidence of non-heritable effects in progeny and/or an impairment in reproductive functions or capacity. Chemicals that may destroy living tissue on
toxin	incidence of non-heritable effects in progeny and/or an impairment in reproductive functions or capacity. Chemicals that may destroy living tissue on
Corrosive	Chemicals that may destroy living tissue on
	contact.
Category 3 carcinogen	Chemicals that may cause cancer or increase its incidence.
Category 3 mutagen	Chemicals that induce heritable genetic defects or increase their incidence.
Category 3 reproductive toxin	Chemicals that produce or increase the incidence of non-heritable effects in progeny and/or an impairment in reproductive functions or capacity.
Harmful Irritant	Chemicals that may cause damage to health. Chemicals that may cause inflammation to the skin or other mucous membranes.
Dangerous for the environment	Chemicals that may present an immediate or delayed danger to one or more components of the environment.
Compressed gas	Contains gas under pressure.
Lass serious harmful	Applies to many harmful substances
substances, irritants	normally marked with an X symbol.
Long-term damage	Includes respiratory sensitisers and carcinogens.

R1	Explosive when dry
R2	Risk of explosion by shock, friction, fire or other sources of ignition
R3	Extreme risk of explosion by shock, friction, fire or other sources of ignition
R4	Forms very sensitive, explosive metallic compounds
R5	Heating may cause an explosion
R6	Explosive with or without contact with air
R7	May cause fire
R8	Contact with combustible material may cause fire
R9	Explosive when mixed with combustible material
R10	Flammable
R11	Highly flammable
R12	Extremely flammable
R14	Reacts violently with water
R14/15	Reacts violently with water, liberating extremely flammable gases
R15	Contact with water liberates extremely flammable gases
R15/29	Contact with water liberates toxic, extremely flammable gases
R16	Explosive when mixed with oxidising substances
R17	Spontaneously flammable in air
R18	In use, may form flammable/explosive vapour—air mixture
R19	May form explosive peroxides
R20	Harmful by inhalation
R20/21	Harmful by inhalation and in contact with skin
R20/21/22	Harmful by inhalation, in contact with skin and if swallowed
R20/22	Harmful by inhalation and if swallowed
R21	Harmful in contact with skin
R21/22	Harmful in contact with skin and if swallowed
R22	Harmful if swallowed
R23	Toxic by inhalation
R23/24	Toxic by inhalation and in contact with skin
R23/24/25	Toxic by inhalation, in contact with skin and if swallowed
R23/25	Toxic by inhalation and if swallowed
R24	Toxic in contact with skin
R24/25	Toxic in contact with skin and if swallowed
R25	Toxic if swallowed
R26	Very toxic by inhalation
R26/27	Very toxic by inhalation and in contact with skin
R26/27/28	Very toxic by inhalation, in contact with skin and if swallowed
R26/28	Very toxic by inhalation and if swallowed
R27	Very toxic in contact with skin
R27/28	Very toxic in contact with skin and if swallowed
R28	Very toxic if swallowed
R29	Contact with water liberates toxic gas
R30	Can become highly flammable in use
R31	Contact with acids liberates toxic gas
R32	Contact with acids liberates very toxic gas
R33	Danger of cumulative effects
R34	Causes burns
R35	Causes severe burns
R36	Irritating to eyes
R36/37	Irritating to eyes and respiratory system
R36/37/38	Irritating to eyes, respiratory system and skin
R36/38	Irritating to eyes and skin
R37	Irritating to respiratory system
R37/38	Irritating to respiratory system and skin
R38	Irritating to skin

R39 Danger of very serious irreversible effects

R39/23 Toxic: danger of very serious irreversible effects through inhalation

R39/23/24 Toxic: danger of very serious irreversible effects through inhalation and in contact with skin

R39/23/24/25 Toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed

R39/23/25 Toxic: danger of very serious irreversible effects through inhalation and if swallowed

R39/24 Toxic: danger of very serious irreversible effects in contact with skin

R39/24/25 Toxic: danger of very serious irreversible effects in contact with skin and if swallowed

R39/25 Toxic: danger of very serious irreversible effects if swallowed

R39/26 Very Toxic: danger of very serious irreversible effects through inhalation

R39/26/27 Very Toxic: danger of very serious irreversible effects through inhalation and in contact with skin

R39/26/27/28 Very Toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed

R39/26/28 Very Toxic: danger of very serious irreversible effects through inhalation and if swallowed

R39/27 Very Toxic: danger of very serious irreversible effects in contact with skin

R39/27/28 Very Toxic: danger of very serious irreversible effects in contact with skin and if swallowed

R39/28 Very Toxic: danger of very serious irreversible effects if swallowed

R40 Limited evidence of a carcinogenic effect

R41 Risk of serious damage to eyes
R42 May cause sensitisation by inhalation
R43 May cause sensitisation by skin contact

R42/43 May cause sensitisation by inhalation and skin contact

R44 Risk of explosion if heated under confinement

R45 May cause cancer

R46 May cause heritable genetic damage

R48 Danger of serious damage to health by prolonged exposure

R48/20 Harmful: danger of serious damage to health by prolonged exposure through inhalation

R48/20/21 Harmful: danger of serious damage to health by prolonged exposure through inhalation and in contact with skin

R48/20/21/22 Harmful: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and

if swallowed

R48/20/22 Harmful: danger of serious damage to health by prolonged exposure through inhalation and if swallowed

R48/21 Harmful: danger of serious damage to health by prolonged exposure in contact with skin

R48/21/22 Harmful: danger of serious damage to health by prolonged exposure in contact with skin and if swallowed

R48/22 Harmful: danger of serious damage to health by prolonged exposure if swallowed Toxic: danger of serious damage to health by prolonged exposure through inhalation

R48/23/24 Toxic: danger of serious damage to health by prolonged exposure through inhalation and in contact with skin R48/23/24/25 Toxic: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if

swallowed

R48/23/25 Toxic: danger of serious damage to health by prolonged exposure through inhalation and if swallowed

R48/24 Toxic: danger of serious damage to health by prolonged exposure in contact with skin

R48/24/25 Toxic: danger of serious damage to health by prolonged exposure in contact with skin and if swallowed

R48/25 Toxic: danger of serious damage to health by prolonged exposure if swallowed

R49 May cause cancer by inhalation R50 Very toxic to aquatic organisms

R50/53 Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment

R51 Toxic to aquatic organisms

R51/53 Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment

R52 Harmful to aquatic organisms

R52/53 Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment

R53 May cause long-term adverse effects in the aquatic environment

R54 Toxic to flora R55 Toxic to fauna

R56 Toxic to soil organisms

R57 Toxic to bees

R58 May cause long-term adverse effects in the environment

R59 Dangerous for the ozone layer

R60	May impair fertility
R61	May cause harm to the unborn child
R62	Possible risk of impaired fertility
R63	Possible risk of harm to the unborn child
R64	May cause harm to breast-fed babies
R65	Harmful: may cause lung damage if swallowed
R66	Repeated exposure may cause skin dryness or cracking
R67	Vapours may cause drowsiness and dizziness
R68	Possible risk of irreversible effects
R68/20	Harmful: possible risk of irreversible effects through inhalation
R68/20/21	Harmful: possible risk of irreversible effects through inhalation and in contact with skin
R68/20/21/22	Harmful: possible risk of irreversible effects through inhalation, in contact with skin and if swallowed
R68/20/22	Harmful: possible risk of irreversible effects through inhalation and if swallowed
R68/21	Harmful: possible risk of irreversible effects in contact with skin
R68/21/22	Harmful: possible risk of irreversible effects in contact with skin and if swallowed
R68/22	Harmful: possible risk of irreversible effects if swallowed

Special Considerations for Chemical and Physical Laboratories

- When working in a chemistry laboratory assume that nothing is safe to touch without gloves on.
- Most experiments will be conducted inside a fume hood so that the risk of breathing in fumes or particulates is minimised. Ensure the fume hood you are working at is clearly labelled with your experiment and check with others who may use it that their experiments do not introduce risk or vice versa. It is not unknown for people to unknowingly use open flames next to beakers full of solvents. Many chemicals require special storage conditions under an inert gas or else require storage in a desiccator. Make sure chemicals are returned to their proper places after use.
- Sometimes reactions may need to be left running overnight. In this circumstance you must check that everything has been made
 failsafe as best as it can be before leaving it. A safety assessment must be performed before hand.
- Solvent waste is collected in marked containers and as much as possible similar solvents or type of waste should be kept together
 and not mixed. Solvent wash bottles of distilled water, methanol, ethanol, isopropanol and acetone are normally on hand. It is
 important that the solvents contained within the bottles do not get mixed up and are clearly marked. Acetone will dissolve many
 types of plastic and must not be poured down the sink. Have a dedicated solvent waste container for acetone.
- Lasers should be screened and shielded. Watches, computer screens and any similar reflective surface should be removed from
 the vicinity of the experiment involving the laser. Laser blocking eyewear should also be used as appropriate. Laser laboratories
 will have controls in place to prevent people walking in at the wrong time including lockable doors and 'laser in use' signs.

A Note on Acids and Bases

Chemical laboratories are the most likely environments to encounter strong acids and bases. Concentrated acids are highly corrosive and have a tendency to fume. They should be worked with exclusively in a fume cupboard. When diluting a strong acid solution, particularly H₂SO₄, the *acid should be added into the water* and not the other way around. The disassociation of the acid in the water is exothermic and if water is added into the acid then the solution can spit or splash. Some of the recipes in this book involve the use of hydrofluoric acid (HF) and this acid is extremely unpleasant. It rapidly destroys tissues and penetrates deep within the skin where it can also decalcify bone. Special measures are required for its use and these include the presence of a calcium gluconate gel when working with HF. This can be applied to areas of skin that have come into contact with HF to form an insoluble calcium fluoride. However, any casualty exposed to HF must be taken immediately to hospital. Wherever possible, avoid working with it.

Strong basic solutions are also corrosive to exposed tissue but you will not necessarily be able to feel it happening. Basic solutions attack the nerves first so that you will not be able to feel any pain. Areas of skin exposed to strongly basic solutions will feel slippery like a soap solution has been applied. This is in fact exactly what is happening, as the strongly basic solution will convert fatty tissues into surfactant molecules. Areas exposed to base should be rinsed with copious amounts of water immediately.

Special Considerations for Biological Laboratories

The risk an infectious agent presents falls into one of four biosafety levels with level one being relatively harmless up to level four which is the most dangerous (Health and Safety Executive, 2005). The recipes in this book do not go beyond biosafety level two and will involve genetic modifications of non-infectious organisms of minimal toxicity. Should you find yourself working with