

PRACTICAL ASPECTS OF GAS CHROMATOGRAPHY/ MASS SPECTROMETRY

GORDON M. MESSAGE

A Wiley-Interscience Publication

JOHN WILEY & SONS

New York

Chichester

Brisbane

Toronto

Singapore

Copyright © 1984 by John Wiley & Sons, Inc.

All rights reserved. Published simultaneously in Canada.

Reproduction or translation of any part of this work beyond that permitted by Section 107 or 108 of the 1976 United States Copyright Act without the permission of the copyright owner is unlawful. Requests for permission or further information should be addressed to the Permissions Department, John Wiley & Sons, Inc.

Library of Congress Cataloging in Publication Data:

Message, Gordon M., 1950-

Practical aspects of gas chromatography/mass spectrometry.

"A Wiley Interscience publication."

Bibliography: p.

Includes index.

1. Gas chromatography. 2. Mass spectrometry.

I. Title

QD79.C45M46 1984 543'.0896 83-23475

ISBN 0-471-06277-4

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

**PRACTICAL ASPECTS
OF GAS
CHROMATOGRAPHY/
MASS SPECTROMETRY**

Gas chromatography is known as one of the separation sciences although the word chromatography literally means colored writing.

Mass spectrometry also implies separation, separation of the masses into different groups.

And yet the practice of GC/MS transcends boundaries of class or color. My experience in traveling the world visiting GC/MS users has been one of fellowship. This book is dedicated to those people who apply themselves and their instrumentation to make the world a better and safer place to live in.

PREFACE

The GC/MS instrument is a complex system and is becoming even more complex with the increasing use of computer control and data-handling facilities. Operation of the instrument requires a basic knowledge of a number of scientific disciplines that are often outside the experience and training of the instrument user. A greater understanding of the system will enable the average user to get better results with the instrument, and it is also likely to increase his or her chances of getting valid results on the first run. This latter point is of some significance where the available sample is very limited.

The use of the word *system* is important. Expertise in chromatography and mass spectrometry separately does not guarantee success with GC/MS. The instrument is a true combination of its separate parts. Each half has to work with the other and imposes constraints on the overall system design. It is also important to realize that once you have bought your instrument you are stuck with its features. Few people have the means, let alone the inclination, to design or redesign their equipment. Hence, a compromise must be reached between the operational requirements of each part of the system, so that the overall performance is optimized.

GC/MS operators are often experts in their own field of study, and the GC/MS system is one of the tools at their disposal. Naturally enough, they want to get the best results from the instrument. This book is not intended as a replacement for the manufacturers' handbooks and manuals but rather as a bridge between the technicalities of the instrument and the science of GC/MS.

This book is by no means a learned text. I have included very few references. However, I have included some suggestions for further reading in the Bibliography. To a scholar, the key words are obvious, and a search in a good library will be fruitful. To those using GC/MS instruments or specifying GC/MS methods, here is some food for thought, based on my experiences in laboratories around the world. Be warned, it is full of opinion. In the end you should make up your own mind about a technique or procedure, basing your decisions on facts and sound judgment. If I make you think about your methods, I will have succeeded. There is no single right way but certainly many wrong ways to operate a GC/MS system.

As I grew in experience at Finnigan Instruments, Ltd. I became more involved with customer training as well as routine service work. I was often struck by the

lack of knowledge about the instrument's "works." Not that I wish to imply that there was any unwillingness to learn. On the contrary, whenever I visited a laboratory someone would ask: "What does this bit do?" Or, "How does that work?" In most cases a long and involved explanation was not required. The questioner did not want to design a GC/MS system. Quite often this person would not even be going to use it; he/she worked next door, upstairs, or wherever and was just curious. In part, this book is for those questioners.

Right from the beginning of my activities in field service and customer training work, I enjoyed working as part of a team with my customers, learning from and with them. The first two laboratories where I installed GC/MS systems were in my opinion above average. They set a standard for me, a way of working, that I have always tried to maintain and pass on to others. I should like to take this opportunity to thank Don Kirkwood, Robin Law, and their colleagues at the MAFF Laboratories, Burnham-on-Crouch, and Tim Webber and his colleagues at Shell Research, Sittingbourne, for their help and encouragement in my GC/MS salad days.

Many people have helped in the preparation of this manuscript. I would like particularly to acknowledge the help and encouragement of the following. Frank Davis, International Service Manager, Finnigan-MAT encouraged me to start, saying it was a very worthwhile and personally rewarding project. Bill McFadden, also of Finnigan, advised me not to start, saying it would be many years of hard slog, but on seeing my determination went out of his way to help. (They were both right!) My colleagues at Finnigan Ltd. have been a continuing source of encouragement, in particular, John Wellby of Shell Research, who later joined us as Application Manager. John also became my neighbor, and we have worked together and talked over many ideas both in and out of work as a result. I should also like to thank Barbara Wellby, John's wife, for carefully reading through my manuscript.

Two major groups deserve special mention. These are the GC/MS manufacturers and their customers. With my association with Finnigan it is natural that there should be a lot of their material in this book, but all the other manufacturers approached were both encouraging and helpful and I thank them for this. Many GC/MS users, the customers, contributed material and ideas. I have tried to give credit where it is due and if I have left anyone out, I apologize.

Finally, I should like to stress that this work was a private venture and has only been possible with the help of my family. Not only has my wife, Jane, given me continuous support but she also acted as my secretary, handling a great deal of the paperwork. My mother-in-law, Min, did all the manuscript typing and her husband, Ron, with a lifetime of journalistic experience, gave me a lot of helpful advice. Simon and Emma, my children, allowed me to share the study with them. Their interest and enthusiasm toward my work have always been a great source of encouragement.

GORDON M. MESSAGE

*Leighton Buzzard, England
May 1984*

PRACTICAL ASPECTS
OF GAS
CHROMATOGRAPHY/
MASS SPECTROMETRY

CONTENTS

1. AN INTRODUCTION TO GC/MS SYSTEMS 1

PART 1 GC/MS SYSTEMS AND COMPONENTS

2. VACUUM SYSTEMS 9

Vacuum Terms 11

Vacuum Pressure Units and Typical System Parameters 13

Vacuum Components 14

Rotary Pumps 15

Diffusion Pumps 17

Diffusion Pump Fluids 18

Turbomolecular Pumps 19

Oil and Vapor Traps 21

Vacuum Gauges 22

Vacuum Seals 26

Valve Requirements in GC/MS 29

Other Pumping Arrangements 32

3. MASS SPECTROMETERS 33

Mass Spectrometer Terms and Abbreviations 33

Basic Mass Spectrometer Description 36

Ionizers 37

Electron Impact Sources 37

Chemical Ionization Sources 41

Other Ionizer Arrangements 54

Mass Analyzers	60
Magnetic Sector Mass Spectrometer	60
Double-Focusing Mass Spectrometers	70
Metastable Response in Sector Instruments	74
Quadrupole Mass Spectrometer	79
Multistage Mass Analyzers	89
Signal Detectors	93
Electron Multipliers	95
X-Ray Shield	97
Total Ionization Monitors	99
Negative Ion Detectors	100
4. GAS CHROMATOGRAPHY	103
Gas Chromatography Terms and Abbreviations	103
Theory of Gas-Liquid Chromatography	106
Gas Chromatography Hardware	108
Columns	109
Injectors	111
Gas Chromatography Detectors	116
Fittings and Gas Controllers	117
5. GC/MS INTERFACING	123
Separators	123
The Watson-Bieman Effusion Separator	124
The Jet Separator	124
The Membrane Separator	126
Solvent Diverters and Dump Valves	127
CI Interfaces	128
Capillary Column Interfaces	129
Transfer Lines and Fittings	131
Ferrules	133
Auxiliary Inlets	134
Direct Insertion Probes	134
Batch Inlets	137
Reference Inlets	137
LC Inlets	140

6. DATA SYSTEMS	141
GC/MS Data System Terms and Abbreviations	142
Basic Description of GC/MS Data Systems	146
Instrument Control	146
Data Acquisition	148
Data Storage	153
Data Manipulation and Display	158
Software	159
Additional Facilities	163
 PART 2 ROUTINE GC/MS OPERATION, TECHNIQUES, AND PROCEDURES	
 7. GAS CHROMATOGRAPHY METHODS AND TECHNIQUES RELEVANT TO GC/MS	 167
Choice of Column Phase	168
The Use of Packed Columns	168
Diverters	169
Temperature Considerations	170
Septum Bleed	171
The Use of Capillary Columns	171
Dead Volume	172
Capillary Injection Techniques	174
Injection Techniques	182
Syringe Handling	183
 8. MASS SPECTROMETER OPERATION	 187
Ionization Modes	187
Electron Impact Ionization	188
Chemical Ionization	189
Tuning and Calibration	194
Tuning the Mass Spectrometer	194
Calibrating the Mass Spectrometer	199
Calibration Compounds	204
Scanning	213

Resolution	218
Sector Instruments	218
Quadrupole Instruments	220
Data Acquisition with a Manual System	221
Ultraviolet Recording of Spectra	222
Hardware MID Acquisition	223
Data Acquisition With an Automated System	226
Zeroing	226
Integration Times	230
Noise Rejection	231
Accurate Mass Acquisition	231
Data Rates	232
Data Handling	233
Software	233
Quality of Data	236
Data Presentation	238
 9. LABORATORY PRACTICE	 239
Record Keeping	240
Data Storage	243
Operating Procedures	246
Sample Preparation	247
Auxiliary Inlets	248
Planning	249
Operators	250
 10. PREVENTIVE MAINTENANCE	 251
Safety	251
Instrument Care	252
System Checks	253
Spare Parts	254
Preparation and Care of Columns	255
Sylanizing Reagents	261
Interfaces	262
Analyzer Cleaning Techniques	263
Source Cleaning	264
Electropolishing	267

Plasma Ashing	271
Analyzer Cleaning	272
Multiplier Cleaning and Rejuvenation	272
Continuous Dynode Multiplier Cleaning	272
Box and Grid or Venetian Blind Rejuvenation	273
Continuous Dynode Multiplier Rejuvenation	274
Multiplier Gain Checks	274
Vacuum Systems Care	275
Rotary Pumps	276
Diffusion Pumps	277
Turbomolecular Pumps	279
Vacuum Seals	279
Peripheral Equipment Care	280

PART 3 TROUBLESHOOTING FAULTS ON GC/MS SYSTEMS

11. THE GC/MS INSTRUMENT UNDER FAULT CONDITIONS	285
Defining the Problem	286
Locating the Problem	286
Troubleshooting the Electronics System	287
Connectors and Cables	288
Power Supplies	289
Electronic Malfunctions	290
Calling in the Experts	291
In-House Experts	291
Professional Help	293
12. FAULT FINDING AND NONROUTINE MAINTENANCE	297
Vacuum System Problems	297
Air Leaks	297
Virtual Leaks	300
Pressure Limits	300
Contamination	301
Damaged GLT Lines	304
Chromatography and Interface Problems	305
Chromatographic Response	305

Fittings and Ferrules	307
Syringes	307
Blockages	309
Sensitivity	310
Mass Spectrometer Problems	313
Sensitivity	313
Charging Effects	315
Pressure Effects	316
Filament Problems	316
Resolution and Mass Peak Shape	317
Mass Discrimination	318
Data System Problems	320
Diagnostic Procedures	323
Hardware Checks	323
Disk and Tape Units	324
Pilot Error	325

PART 4 CHOOSING A GC/MS SYSTEM

13. INSTRUMENT SELECTION AND EVALUATION	329
Defining Requirements	330
The Present Need	330
Future Needs	333
Performance	333
Budgets	334
Evaluation of a GC/MS System	335
Test Samples	335
Demonstrations	336
Data System Considerations	338
Making Up Your Mind	340
Further Reading	342
Index	345

CHAPTER ONE

An Introduction to GC/MS Systems

The combination of the gas chromatograph with the mass spectrometer has resulted in an instrument of considerable importance in the field of chemical analysis and detection. Figure 1 shows two typical laboratory arrangements. It could be argued that the mass spectrometer is just one of a range of detectors available to the gas chromatograph user. On the other hand, some would say that the gas chromatograph is only one of many inlets that could be connected to the mass spectrometer. In truth, the synergy of this arrangement goes beyond the possibilities of the two separate instruments and almost warrants a new definition as an instrument in its own right. For this reason, and for convenience, the combined arrangement is referred to as a GC/MS system throughout this text.

The principal elements of a GC/MS system are shown in Figure 2. A computer system is included in the diagram, as well as its interface with the instrument operator. Depending on design, and certainly on manual systems, some or all of the computer control functions are undertaken by the operator directly. In any given system it is probably the mass spectrometer that sets the overriding design parameters.

An essential element in good mass spectrometer performance is a high-quality vacuum system. The pressure requirements vary with instrument type and application, but 1.3×10^{-3} Pa (10^{-5} torr) is a typical maximum, and often lower pressures are necessary. The gas chromatograph, by contrast, basically operates at or above atmospheric pressure, and so it is not surprising that some form of interface is required. This usually acts as a sample-enrichment device, extracting much of the carrier gas, although direct connection through tubing of a very fine bore is also possible. The latter arrangement simplifies interface design but places an increased burden on the mass spectrometer pumping system.

Interface design is discussed in detail in later chapters. All the enrichment

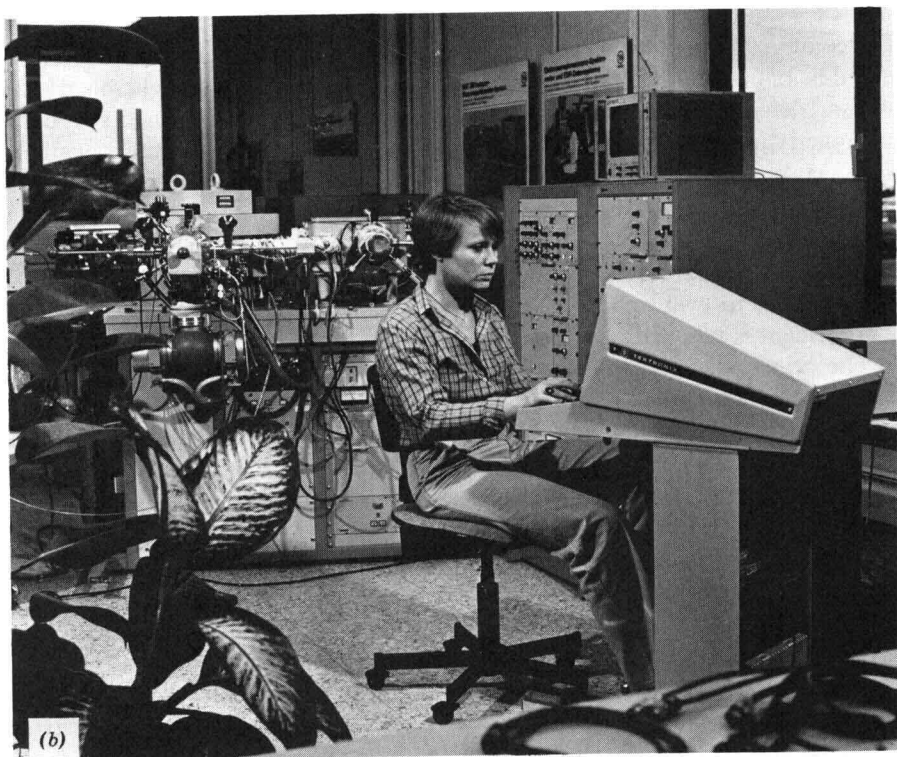
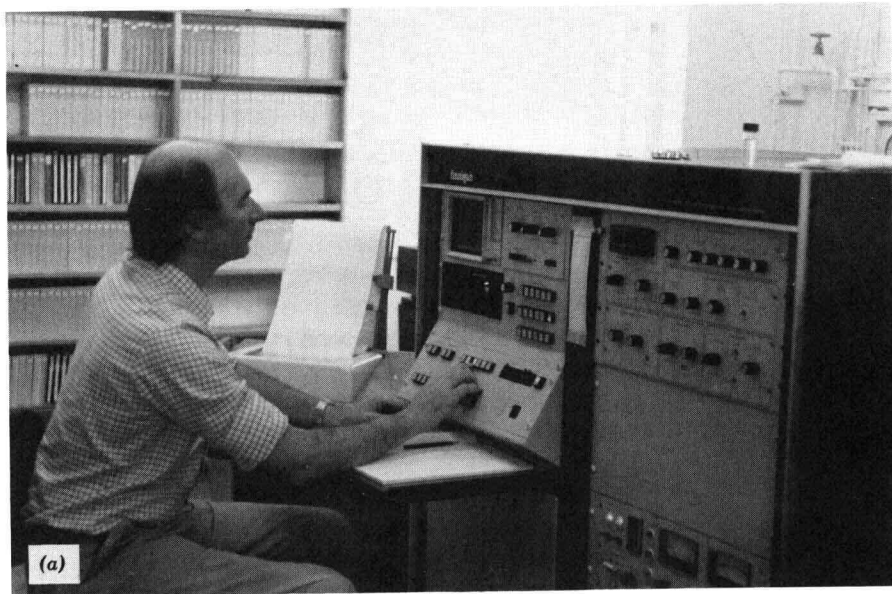


Figure 1. Typical GC/MS facilities. (a) A Finnigan 3200F with integral 6000 series data system. (Courtesy of Masspec Analytical Ltd.) (b) A MAT 212. The detachable GC is hiding in the trees to the left of the picture. (Finnigan-MAT, GmbH)

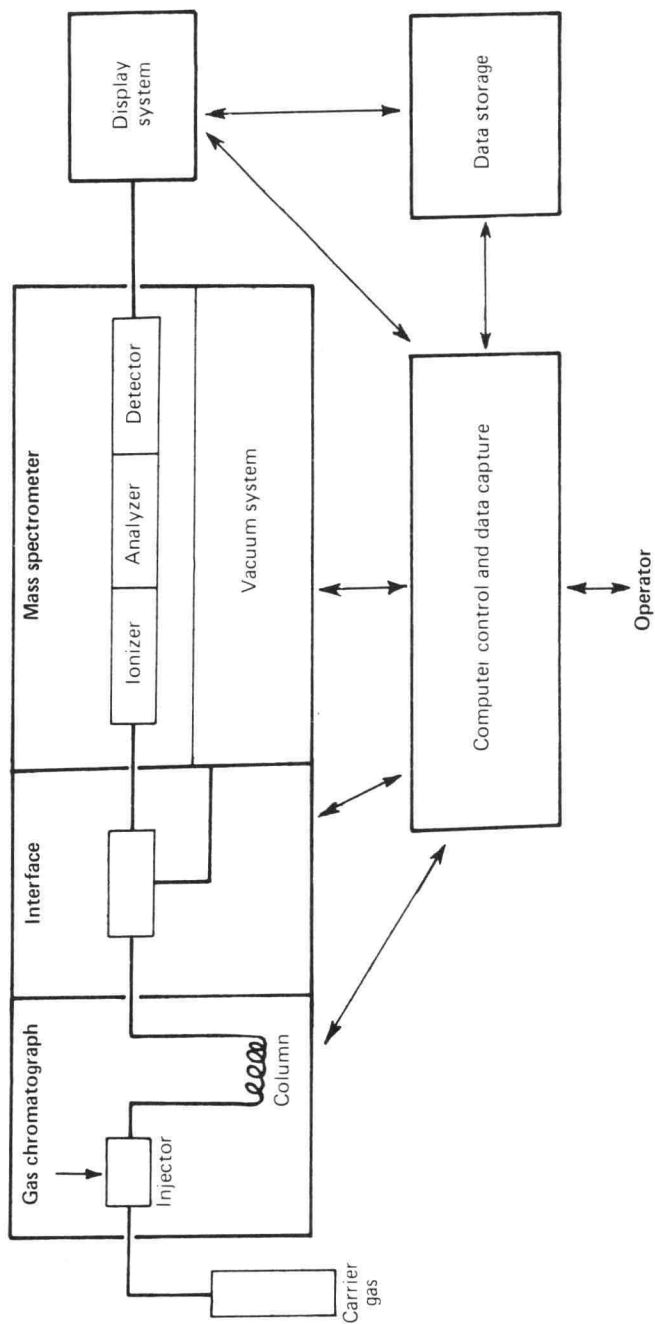


Figure 2. Block diagram of a typical GC/MS system.

types reflect the need to compromise between the amount of sample lost and the amount of carrier gas extracted. In general, they are more efficient with a light gas, and so helium is favored over nitrogen as the GC/MS carrier in most stand-alone gas chromatography work. As a result, many of the normal gas chromatograph parameters change when GC/MS systems are considered. Things are further complicated by the fact that the performance of the interface device is often dependent on the carrier gas flow rate and so it may be necessary to experiment with parameters to get the best from the system.

It is well to remember this last point. There may be a recommended or preferred value for a given parameter, but often significant improvements can be made by a deviation from the given value. In many applications it may not be worth the bother of experimentation, but occasionally it is vital to determine the limitations of the instrument parameters and the interactions between them.

While Part 1 (Chapters 2 to 6) concentrates on the theory of operation of each part of the GC/MS system, Part 2 (Chapters 7 to 10) reviews procedures and techniques in the light of this theory. Part 2 presents a number of ideas relating to instrument operation that are based on the author's experience of GC/MS laboratories around the world. It is important to realize that the methods and techniques presented here are not the only way to operate a GC/MS facility but are representative of the practices in successful laboratories. Applications are discussed primarily to illustrate topics rather than as the principal subject.

The increasing availability of sophisticated but low-cost computer systems has made possible a high level of instrument control and data handling. One might expect this to ease the GC/MS operator's burden. On the one hand, the data system can lead the user through the correct sequence of operations, even taking over some of the routine tasks. The computer can also provide a high level of system protection, self-checking, and control.

On the other hand, computer use opens up the way for complex control modes that were not practical before. Linked scans and automatic specific tuning are typical examples. Add to this the developments that have been made in data processing, such as precision mass assignment, data enhancement, and noise rejection, and the operator is faced with many new possibilities. Data outputs in the form of hard copies or video displays are also faster than could ever be achieved manually, assuming they could be achieved at all.

As a result it can be seen that computers make some routines possible and others easier. Unfortunately, it is all too easy to look at a beautifully drawn spectrum and believe it implicitly. The computer drew it, so it must be right! Sadly, this is not always the case, and once again it is those with a greater knowledge and understanding of their (even more complex) system that get the most reliable results. Hence Chapter 6 reviews the principles of computer operation that are applicable to GC/MS systems and throughout the text reference is made to data system methods as well as traditional manual approaches.

As instrument complexity increases, the likelihood of failure also increases. Failures can take many forms. They may be permanent and obvious, or they may be a nuisance but such that the instrument can still run. Worst of all, they may