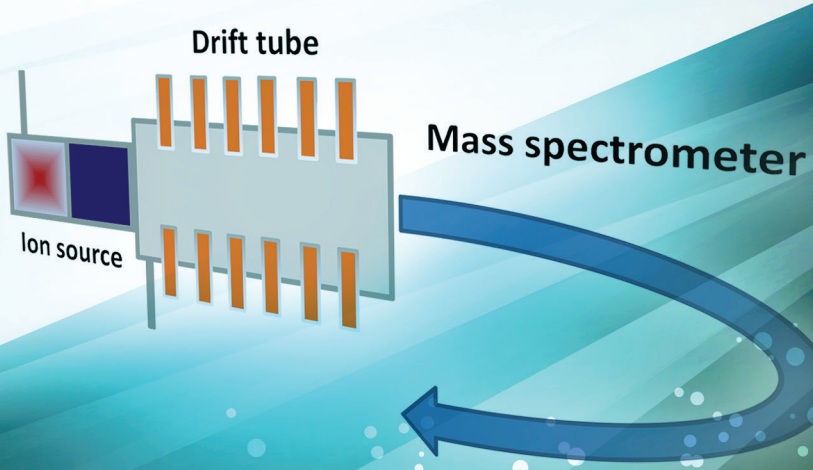
Proton Transfer Reaction Mass Spectrometry

Principles and Applications

Andrew M. Ellis
Christopher A. Mayhew



WILEY

Proton Transfer Reaction Mass Spectrometry

Proton Transfer Reaction Mass Spectrometry

Principles and Applications

ANDREW M. ELLIS

Department of Chemistry, University of Leicester, UK

CHRISTOPHER A. MAYHEW

School of Physics & Astronomy, University of Birmingham, UK

WILEY

This edition first published 2014

Registered office
John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

Library of Congress Cataloging-in-Publication Data

Ellis, Andrew M. (Andrew Michael), 1963–
Proton transfer reaction mass spectrometry : principles and applications / Andrew M. Ellis, Christopher A. Mayhew.
pages cm.
Includes index.
ISBN 978-1-4051-7668-2 (cloth)
1. Proton transfer reactions. 2. Mass spectrometry. I. Mayhew, Christopher A. II. Title.
QD501.E545 2014
539′.60287–dc23

2013028864

A catalogue record for this book is available from the British Library.

Set in 10/12pt Times by Aptara Inc., New Delhi, India.

Contents

Nothing tends so much to the advancement of knowledge as the application of a new instrument.
Sir Humphry Davy

Preface

Proton transfer reaction mass spectrometry (PTR-MS) is widely used for the detection of volatile organic compounds in air. The historical development of this technique can be traced back to measurements of the rates of ion–molecule reactions in the 1960s and 1970s using flow tube methods. The technology introduced for measuring the kinetics of these reactions morphed into the analytical technique we now know as PTR-MS in the mid-1990s. The seminal work in this area was performed by Werner Lindinger and his team at the University of Innsbruck.

Remarkably, the development of PTR-MS by the Innsbruck group very nearly did not happen! Early requests for funding of this work were rejected by various research agencies, as the acknowledgements in some of the early PTR-MS research papers forcibly testify. It was only through Lindinger's perseverance, support from Fa. Nestle (Nestec Ltd, Switzerland) and initial funding from the "*Gesellschaft für Strahlenforschung*" (GSF, Neuherberg, BRD), that made it possible for the developmental work on PTR-MS to be pursued. With limited resources, and together with Armin Hansel, Alfons Jordan and other colleagues, PTR-MS as we know it today began to emerge. This developmental work was followed up with pioneering applications in the environmental sciences, food science and medicine, all in collaboration with colleagues at Innsbruck and external establishments. By the time of his untimely death in 2001, Werner Lindinger had demonstrated the applicability of PTR-MS as an analytical tool for monitoring trace gases in several different environments and had established a spin-out company for the commercial exploitation of this novel technology.

The initial growth of PTR-MS research was so fast that by the beginning of the twenty-first century it warranted its own international conference. The first took place in 2003 in Innsbruck and it has now become a regular event taking place every two years, usually in Obergurgl, Austria. These conferences are a testament to the growth of PTR-MS as an analytical technique, with new applications being regularly reported and new researchers from many disciplines becoming involved in this exciting technology. The various books of abstracts for these conferences provide a unique summary of the activities pursued and the diverse range of applications, as well as an illustration of how fast the technology is evolving. For the interested reader, these books of abstracts are available as downloadable pdf files and they provide a valuable resource which is impossible to duplicate in this book.

PTR-MS has become a remarkably versatile tool, with applications in many areas of science and technology. A review of the research literature at the time of writing indicates that approximately 50% of all reported activities are based on studying VOCs (anthropogenic and biogenic) in the environment, and in particular for atmospheric science. Approximately 30% of publications are based in the area of food science/technology while another major field of application is to be found in the health sciences, representing approximately 15%

of PTR-MS publications to date. The remaining 5% of publications deal with a multitude of topics.

The diverse range of applications inevitably means that the users of PTR-MS come from a variety of backgrounds. While we suspect that the majority of users are likely to have received strong training in the chemical sciences, others may be drawn into the field from, for example, the environmental, biological or medical sciences. To learn about PTR-MS, one can turn to the research literature and consult the original publications that describe key developments in the technique or focus on a certain application. Equally, there are several excellent reviews on PTR-MS available in the published research literature. However, the research literature can be a rather terse and fragmented source of information, geared as it is towards specialists in the subject field. Furthermore, there have been several important new developments in PTR-MS in recent years, especially with regard to instrumentation. It would therefore seem timely to gather much of this information in one place.

Given the diverse user community and the increasing maturity of PTR-MS as a technique for gas monitoring and gas analysis, it is surprising that no book dedicated to PTR-MS has been published. Here we have attempted to fill this hole. Our primary aim has been to produce a book that is particularly targeted at those who are relatively new to PTR-MS, although more seasoned investigators may also benefit in some ways from its content. Broadly speaking, this book is divided into two parts. In the first part, which consists of Chapters 1–4, we describe the underlying principles of the PTR-MS technique, including the relevant ion–molecule chemistry, thermodynamics and reaction kinetics. Details are provided on practical aspects of PTR-MS, including a discussion of ion sources, drift tubes and mass spectrometers. As we proceed on this journey we give, where appropriate, some brief historical narrative.

The second part of the book, which spans Chapters 5–9, turns its attention to some of the many applications of PTR-MS. Here we want to demonstrate the scope and benefits, as well as the limitations, of PTR-MS. Our aim here has been to give a thorough but not exhaustive coverage of applied PTR-MS. We particularly want to try and show that PTR-MS, while already in widespread use, is rapidly finding new avenues where it can be applied. Four key areas of application will be described, namely environmental science, topics associated with food/drinks, medicine and homeland security, and each of these receives a dedicated chapter (Chapters 5–8). A short chapter (Chapter 9) will also deal with the applications of PTR-MS in liquid analysis. Chapters 5–9 build upon the material presented in Chapters 1–4 and are essentially self-contained reviews of the specific topics mentioned above. Consequently, the reader can dip into those that are of particular interest to him/her and if desired can safely ignore those of more peripheral interest.

Overall, we have tried to pitch the content of the book at a level which can be followed by an advanced undergraduate or early stage graduate student with a decent background in chemistry, and in particular physical chemistry. However, we also hope that people approaching PTR-MS from other disciplines who have a more modest knowledge of physical chemistry can follow much of the text. Our overarching aim has been to provide the reader, particularly one who is relatively new to PTR-MS, with a level of understanding of the technique which will then allow them to approach the research literature in this field with confidence. If we have come anywhere near this aim, then we will be delighted.

We need to thank several people for assisting with the preparation of the manuscript including Dr Peter Watts, Professor Paul Monks, Dr Franco Biasioli, Dr Philipp Sulzer,

Dr Valerie Gros, Dr Jens Herbig, Dr Margaret O'Hara, Dr Robert Blake, Dr Wilfried Szymczak, Shane Barber, Vicky Orson-Wright and Kathleen Hynes. We are also grateful to the publisher, and in particular our primary contact at Wiley, Sarah Tilley, for patience as each revised deadline came and went! Most of all, we are grateful for the enduring support and patience of our families while this book was being written.

Andrew M. Ellis
Christopher A. Mayhew
April 2013

Section 1

Principles

1
Background

1.1 Volatile Organic Compounds in the Earth's Atmosphere

Air usually contains many volatile organic compounds (VOCs).[1] These VOCs can derive from numerous sources, including emissions from plants and animals, as well as man-made sources such as motor vehicles and factories. The air we breathe consists mainly of inorganic gases: predominantly nitrogen and oxygen, but there are also other inorganic gases at lower concentrations, such as argon, water and carbon dioxide (see Table 1.1). By comparison the quantity of organic compounds in air is extremely small, of which the most abundant organic gas by far, methane, forms only around 1 part per million by volume (ppmv). At much lower concentrations still are other organic compounds such as methanol, acetone and isoprene. The exact quantities of these and other VOCs can vary depending on where any measurement is made. However, given that such compounds are usually present at extremely low levels (often referred to as *trace* levels) relative to the inorganic compounds in air, with even the more abundant VOCs often being in the low parts per billion by volume (ppbv) range,[2] it would seem safe to assume that VOCs are of negligible importance in almost any context. This assumption is incorrect.

There are many reasons why it is important to know the identities and the quantities of VOCs in the Earth's atmosphere. One of the major motivations is the desire to understand the impact of human activities on the natural atmosphere. Broadly speaking, the sources of VOCs in air can be divided into two groups: natural sources, also known as *biogenic* emissions, and man-made sources, known as *anthropogenic* emissions [2–4].

After methane the principal biogenic compounds are isoprene and monoterpenes. It is the release of monoterpenes that is responsible for the characteristic smell of forests, particularly

[1] The distinction is sometimes made between volatile and semi-volatile organic compounds but no such distinction is employed in this book.

[2] A billion here refers to a multiplier of 10^9, so 1 ppbv is one part in 10^9 by volume. For an ideal gas this implies one gas atom/molecule out of a total of 10^9 atoms/molecules.

Proton Transfer Reaction Mass Spectrometry: Principles and Applications, First Edition. Andrew M. Ellis and Christopher A. Mayhew.

Table 1.1 *The most abundant gaseous constituents of air and their typical mixing ratios*

Gas[a]	Mixing ratio[b] (ppmv)
Nitrogen	781 000
Oxygen	209 000
Argon	9 300
Carbon dioxide	387
Neon	18
Helium	5.2
Methane	1.7
Hydrogen	0.53

Source: Numerical data extracted from Reference 1.
[a]The amount of water vapour (not shown in the table) strongly varies depending on the humidity and can range from near-zero up to 40 000 ppmv (i.e. 4% of atmospheric gas).
[b]Mixing ratio (volume fraction) expressed in parts per million by volume (ppmv).

pine forests. Much of the emission of these compounds is linked to the photosynthesis cycle in plants, but there are other reasons for their emission, including as a defence mechanism against insect damage. However, many other compounds, including oxygenated VOCs such as alcohols, aldehydes and ketones, can be emitted from plants in response to various stimuli. In addition to their obvious biological interest, the emission of biogenic VOCs is extremely important in atmospheric chemistry. Biogenic emission is the dominant source of VOCs in the Earth's atmosphere and many of these compounds play an important role in atmospheric oxidation processes leading, among other things, to the formation of ozone.

Anthropogenic VOCs can disturb the natural atmospheric oxidation processes. Sources range from fossil fuel emissions to industrial solvent emissions and biomass burning. Significant compounds can include a variety of hydrocarbons, both aliphatic and aromatic, as well as oxygenated compounds. One of the well-known detrimental aspects of anthropogenic VOC emission is the production of photochemical smog, which forms when there are excessive levels of both nitrogen oxides and VOCs in combination with sunlight. The relatively high levels of ozone and particulate matter that this produces can make breathing difficult for many people and in worst-case scenarios can lead to serious injury or even death through respiratory diseases, such as chronic asthma. More generally, many anthropogenic VOCs may be highly toxic, carcinogenic and/or mutagenic, and emissions in the urban environment, in factories, or perhaps even in the home are of considerable concern.

Given the importance of VOCs in the environment, a variety of techniques have been developed for their measurement. The ideal technique does not currently exist, and thus one must assess the pros and cons of each available method in order to decide which is the most suitable for a given application. For example, the requirement might be to determine the amount of one or more compounds in the atmosphere on a large scale, perhaps over a region, a country or even a continent. In such circumstances, one must look towards techniques like satellite observation, which can explore large areas very rapidly, albeit only for a relatively small number of compounds. Aircraft measurements offer a compromise, where small-scale instruments can be carried over large ranges, but with

limited coverage. On the more local scale, there is a greater variety of instrumentation that can be deployed, ranging from differential optical absorption spectroscopy (DOAS) to even more local techniques such as gas chromatography (GC), ion mobility spectrometry (IMS) and proton transfer reaction mass spectrometry (PTR-MS), all of which essentially sample air in the immediate vicinity of the instrument. However, in addition to spatial distribution, time-resolved VOC measurements may also be important to the atmospheric scientist. Are measurements every hour satisfactory, or might information be required every minute of every day? In some circumstances, it is important to be able to follow transitory events and thus a slow measurement technique may be of little or no use.

The focus in this book is on one particular technique, PTR-MS, which is widely used for measuring trace-level VOCs. Along with other applications, we aim to show that this is an important and versatile technique for atmospheric scientists. It provides a means of making local measurements with good sensitivity and at relatively high speeds. However, in this chapter we shall also describe complementary techniques, most notably gas chromatography–mass spectrometry (GC–MS), and competitor techniques such as selected ion flow tube mass spectrometry (SIFT-MS), to give some context. In each case, we will provide an assessment of the major strengths and weaknesses of each technique.

1.2 Volatile Organic Compounds in Other Environments

Instruments that can identify and quantify trace levels of VOCs have many potentially important applications beyond atmospheric science. For example, VOC emissions from foods and drinks are critical in our perception of their taste and smell. Food manufacturers are keen to understand the factors that contribute to flavour perception, and correlating VOC measurements with human trials of sensory perception is an important way of doing this. VOC emissions from foods and drinks can also be an indicator of quality. In particular, the onset of serious degradation may be characterized by the excessive emission of one or more VOCs, and these marker compounds therefore offer the key to an automated indication of food and drink decay. This is an area of investigation that is still very much in its infancy, but which may have very considerable implications for the food and drinks industries.

Another area where VOC measurements are still in their infancy is in the diagnosis of diseases through the measurement of the VOC composition of human breath. Breath is a mixture dominated by the common inorganic constituents of air, but it also contains a small fraction of VOCs in the ppbv to pptv (parts per trillion by volume) range. VOCs can be produced anywhere in the body and may be transported via the bloodstream to the lungs, where they are exhaled in breath. It has long been known by the medical community that a characteristic smell on the breath of a patient can sometimes indicate a specific medical condition. However, until recently no technique was available which could reliably and quickly assess the identities and quantities of the many VOCs present in human breath. That barrier is beginning to disappear and with it comes the prospect of using breath analysis as a serious means of non-invasive screening for specific diseases.

The above list of applications is by no means complete, and there are many other areas of science and technology that might benefit from rapid and sensitive VOC measurements, such as botany, forensic science and security screening. Some of these topics are considered in detail in the later chapters of this book (Chapters 5–9). In this short overview, we hope to

have convinced the reader that trace VOC measurements are beneficial across a wide range of science and industry.

1.3 Techniques for VOC Measurements

It is not the aim of this book to provide an exhaustive account of analytical techniques that can be used to determine trace levels of VOCs in the gas phase. Our focus is, of course, on PTR-MS. However, like any measurement technique, PTR-MS has its strengths and weaknesses and it is important to put these into context by making a comparison with other types of instrumentation. As we will see, important criteria to be considered by any potential user include sensitivity, linearity of response, accuracy, specificity and speed of measurement, together with the cost and size of the instrumentation. Some of the major alternatives to PTR-MS for trace VOC measurements are described in this section.

We start with a description of what is currently the single most important and widely used technique for VOC gas analysis, *gas chromatography*. We will then turn our attention to techniques that typically show a much faster response, starting with *ion mobility spectrometry* and its variants. *Flowing afterglow* and *selected ion flow tube* studies of ion–molecule reactions are then considered, since these set the scene for the two main direct mass spectrometry techniques for quantifying gaseous VOCs, PTR-MS and SIFT-MS. The chapter closes with an introductory account of both PTR-MS and a comparison of PTR-MS with SIFT-MS.

1.3.1 Gas Chromatography

Gas chromatography (GC) is, in many respects, the 'gold standard' for trace gas analysis. The basic principle behind GC is that the constituents of a flowing gas mixture (the *mobile* phase) can be separated by passage over a suitable liquid or solid (the *stationary* phase). Partitioning between the mobile and stationary phases can lead to different *retention times* for different compounds due to differences in the way each compound in the gas interacts with the stationary phase. It is this difference in retention times that underlies GC.

In the early days of GC, the stationary phase was a particulate solid and would be packed into a tube known as a *column*. Nowadays much narrower diameter columns, known as *capillary columns*, are prevalent and the stationary phase is frequently a thin layer (typically 1 μm thick) of viscous liquid coated on the inside of the column wall. The columns are coiled and are normally very long, with lengths up to 60 m not being uncommon. As illustrated in Figure 1.1, the analyte mixture is injected into a flowing carrier gas, usually helium, upstream of the column and then proceeds through the column and onwards to a detector at the end of the instrument. The column is located within an oven to maintain a well-regulated temperature for the elution process. Whatever type of column is used, the aim is to ensure that the gas constituents are able to interact intimately and frequently with the stationary phase as they make their way through the column, with those interacting most strongly taking the longest time to reach the detector. Consequently, a plot of detector signal versus time should give a series of peaks at retention times that are characteristic for specific compounds. Such a plot is known as a gas chromatogram.

There are a number of important issues to consider in the practical application of GC for air analysis. First and foremost is the sensitivity, which is insufficient to measure the very

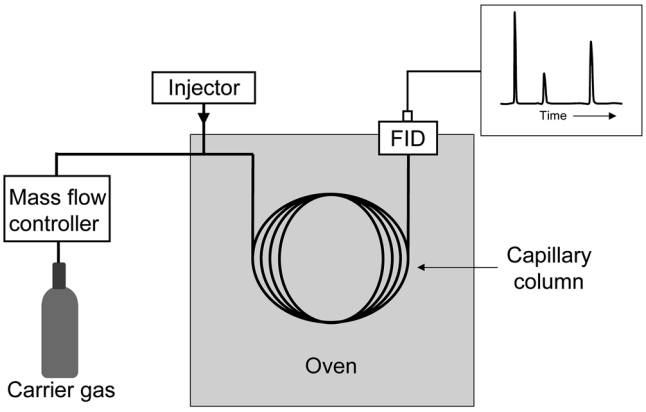


Figure 1.1 *Schematic diagram of a GC instrument with an FID. An analyte gas is injected into a flow of inert carrier gas at the injector. The gradual separation of compounds in the column leads to elution of distinct compounds at different (retention) times, as measured by the FID, leading to a chromatogram such as that shown in the upper right of the diagram.*

small quantities of VOCs in a single syringe injection of air. Instead a pre-concentration process is required, in which the desired analyte gas is accumulated over a period of time in an appropriate vessel before rapid release in a concentrated burst into the GC column. One way of doing this is to collect the analyte in a cryogenic trap. This will not condense the common constituents of air, such as O_2 and N_2, but will condense organic compounds. If this approach is adopted, a suitable collection container is required. One possibility is a stainless steel canister, but the inside surfaces must be coated with some relatively inert material, such as Teflon or silica, to minimize the possibility of surface-catalysed reactions. Once sufficient material is in the trap, it can be released by flash heating, which can be done electrically or by simply immersing the trap in hot water. Relatively simple cryogenic traps are rarely used for pre-concentration, partly because they are indiscriminate and thus collect all condensable materials, including water. Furthermore, it is relatively inconvenient to rely on a cryogenic approach, particularly if measurements are made in environments well away from standard laboratory facilities. As an alternative, traps consisting of suitable adsorbent materials, such as a carbon-based material (e.g. charcoal) or a polymer, can be employed. An example of the latter is a material known as Tenax, which works well for trapping compounds such as aromatics and terpenes and is widely used.

Another important issue is the column. The length of the column is one significant factor, since a longer column should improve the separation, but the choice of the stationary phase is critical. No single stationary phase is suitable for all types of compounds. For example, a stationary phase composed of a non-polar substance is best for separating hydrocarbons, particularly volatile hydrocarbons, whereas a polar stationary phase is essential for oxygenated VOCs such as alcohols, aldehydes and ketones. There are many types of stationary phases available and an important aspect of GC is selecting the right one for the particular application.

Water from the analyte is a major problem in GC work, not least because it interferes with the performance of the column. Consequently, efforts are made to remove as much

water as possible before it reaches the column. Cold traps or traps packed with drying agents can be used for this purpose, but one must always take care to ensure that these traps do not also remove the organic constituents of the analyte gas.

There are several types of detectors that can be coupled to a gas chromatograph. One example is the flame ionization detector (FID), where, as the name implies, the effluent flows through a flame as it leaves the column, which generates ions as one of the products. These ions are then detected via an electrical current monitor. When coupled with suitable pre-concentration of the analyte, GC-FID can approach compound detection sensitivities as low as a few pptv. However, the FID works best for compounds such as hydrocarbons and is therefore not a universal detector. Other types of well-known GC detectors include the electron capture detector (ECD) and the thermal conductivity detector (TCD), and as with FID these alternatives also have their strengths and weaknesses but we will not discuss these in this book.

Unfortunately, compound resolution is not as easy as the discussion above implies. Many distinct compounds are difficult to separate fully on a column. Even if the compounds can be separated, the FID, ECD or TCD does not provide any compound identification: it merely registers the fact that a compound is leaving the column at a given moment in time. As implied earlier, compounds can sometimes be identified on the basis of the time taken to leave the column, that is, from their retention times. The retention time of a particular compound can be pre-determined by adding that specific compound to the GC instrument in a calibration procedure. Of course, there is the possibility, particularly with complex mixtures, that two or more compounds may have very similar retention times and therefore cannot be distinguished in this way. Furthermore, a calibration approach will only work if you already have a pretty good idea of what might be present in the analyte.

To get around these limitations, the FID, ECD or TCD can be replaced with a mass spectrometer equipped with an electron impact ionization source. In most cases, the mass spectrometer is of the quadrupole variety (see Chapter 3 for further details). The instrument works by recording a whole series of mass spectra, one after the other, as the analyte elutes through the column. In this way, important analytical information is obtained from both the retention time and the mass spectrum. The mass spectrum recorded for a particular GC peak can be compared with those stored in a library on the control computer, which usually allows compound identification. GC–MS is an extremely valuable analytical tool, but it suffers from a lower detection sensitivity than GC-FID because of the scanning time of the mass spectrometer, and so for air analysis it is often used more for compound identification than for quantification.

From the description above, some of the limitations with GC and its variants become clear. It is not a universal technique, since the choice of trap and column will affect the sensitivity and accuracy towards certain classes of compounds. In particular, oxygenated VOCs are more of a problem than hydrocarbons for GC analysis. The principal problem with oxygenated VOCs in GC stems from their polarity, which requires polar or semipolar column materials to achieve sufficient compound separation. Unfortunately, these columns also easily degrade when they come into contact with water, and therefore stringent efforts must be made to avoid any moisture. A particularly serious matter in GC analysis is the speed of measurement which, because of the need for sample collection and also some degree of pre-concentration, is often limited to a single measurement every few minutes, at

best. Consequently, if rapidly evolving gas systems are being explored, GC techniques are not suitable.

Despite these limitations, GC remains the analysis technique of choice for many applications. It frequently achieves good compound separation, has good sensitivity, is reasonably cheap, is very well established and is reliable. Furthermore, developments such as two-dimensional GC techniques offer new scope [5]. The two-dimensional GC technique employs two columns in series but the two columns have different separation characteristics. This allows resolution of a much wider range of compounds than standard GC and has the potential to allow the exploration of very complex VOC environments in great detail.

1.3.2 Ion Mobility Spectrometry

Ion mobility spectrometry (IMS) has become a widely used analytical technique in the past two decades. It has found particular popularity in military and security circles because relatively cheap, simple, robust and compact IMS devices can be constructed which are capable of rapidly detecting a wide range of VOCs with high sensitivity. Figure 1.2 shows the basic structure of an IMS instrument. The analyte gas is injected and subjected to ionization at one end of the instrument and an ion detector is located at the other end. The tube in-between contains a series of electrodes which generate an electric field along its axis, drawing ions towards the detector. A tube equipped with these electrodes is called a *drift tube* and the underlying principle of IMS is the separation of ions according to their *mobilities* through a gas, which is usually air at atmospheric pressure.

We can draw a very loose analogy with GC in that the ions in IMS act like the mobile phase and the neutral gas as the stationary phase. The mobility quantifies the ease with

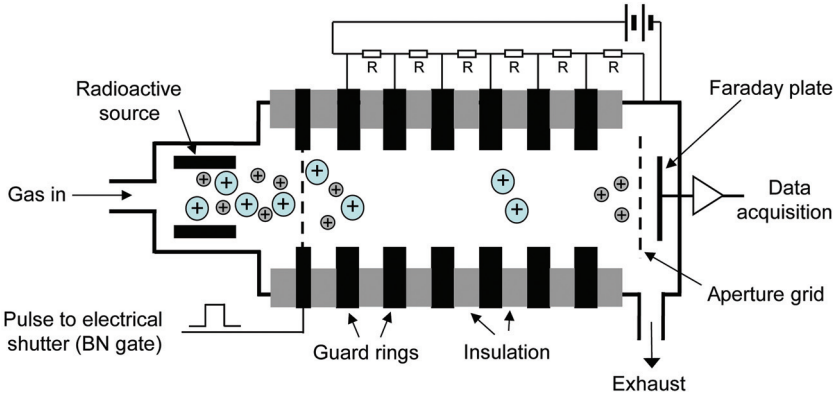


Figure 1.2 *Typical arrangement for a conventional ion mobility spectrometer. Ions are produced in the upstream region (left-hand side of the figure), in this case via a radioactive source, and are then drawn from left to right by an electric field applied through a series of electrodes (the 'guard rings'). Ions are injected in pulses using an electrical shutter (a Bradbury–Nielson (BN) gate) and the time taken to reach the detector is then determined. The ion detector in the figure is a simple Faraday plate (see Section 3.6).*

which a particular ion can move through a specified buffer gas at a given temperature and pressure when drawn along by an electric field of known magnitude. Light ions will tend to have higher mobilities than heavy ions, and thus the mobility through a gas serves to discriminate ions according to their masses. However, the size and structures of the ions are also important, since they will affect the collision cross section between neutral gas molecules and the ions. Consequently, large ions will tend to have smaller mobilities than small ions, but there is clearly room for some subtleties here because the collision cross section is also influenced by intermolecular forces, which in turn can depend on factors such as the charge distribution in the ion. Thus, while the mobilities of ions through the neutral gas may not always be easily predictable, they do offer a means of separating different types of ions on the basis of the time they take to pass through the buffer gas.

A radioactive strip is commonly employed in IMS to create ions, although other sources are also in use including photoionization and corona discharge sources, with the latter becoming increasingly popular for commercial instruments. In positive ion mode, the presence of water vapour in the background gas leads to the formation of hydrated hydronium ions, $H_3O^+(H_2O)_n$, where $n = 0, 1, 2$, etc.[3] These ions are the initiators of ionization in the analyte gas molecules and they do this by transferring charge to organic gases (M) by reactions of the type

$$H_3O^+(H_2O)_n + M \rightarrow (H_2O)_m MH^+ + (n + 1 - m)H_2O \tag{1.1}$$

To separate the different types of ions, a short burst of ions must be injected into the drift tube. This is achieved via a fast-acting electronic shutter, which is actually an ion deflection device known as a Bradbury–Nielsen gate. Injection of this pulse of ions has the effect of starting a clock and the arrival of ions at the detector is then measured relative to this starting time. Although there have been a number of different designs, the basic constituents of most drift tubes are a series of metal electrodes of circular cross section (sometimes called guard rings) interspersed by insulators. The electrical potential along the tube is chosen so as to draw the reagent and product ions towards the detector (see Figure 1.2). If the drift tube was operated under high vacuum conditions, such that ion–molecule collisions were essentially eliminated, then the speed of the ions would increase continuously as they travelled from one end of the drift tube to the other. However, IMS devices are not operated under high vacuum conditions and therefore collisions with the background gas results in the ions quickly reaching a constant, terminal velocity, the so-called drift velocity, which depends on the factors mentioned earlier and is directly proportional to the electric field strength.

The ion signal is measured as a function of time and should therefore consist of a series of peaks corresponding to ions with different mobilities arising from different chemical compounds in the analyte. Drift tube transit times depend on the length of the tube but are typically on the order of several tens of milliseconds. By comparison, the injection time for ions is <1 ms, and until all of the ions in the injected bunch reach the end of the drift tube, a second bunch of ions cannot be injected. Consequently, the *duty cycle*, which is a measure of the fraction of ions that reach the detector out of the total number of ions that could reach the detector if the experiment was not pulsed, is rather low and is typically 1%. This is an important factor in limiting the sensitivity of IMS. Nevertheless, detection of compounds

[3] The mechanism by which hydrated hydronium ions form in a radioactive or electrical discharge source is described in Chapter 3.

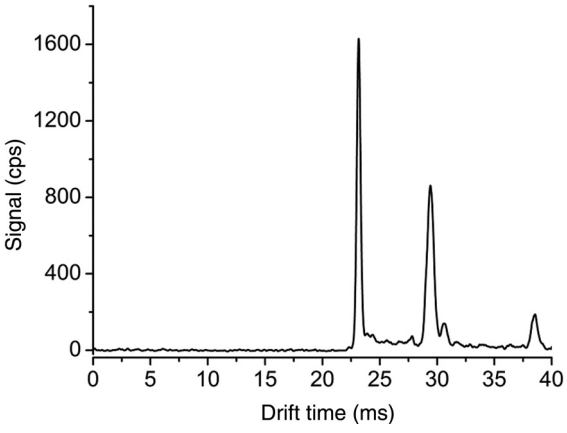


Figure 1.3 *An example of an ion mobility spectrum. In this example, the IMS was operated in positive ion mode using air as the buffer gas. Di(propylene glycol) methyl ether (DPGME), which is a commercial solvent, was introduced into the reaction region of the drift tube. Moving from left to right the first peak corresponds to the reagent ions* $H_3O^+(H_2O)_n$*, while the second and third peaks correspond to* $DPGME(H_2O)_nH^+$ *and* $(DPGME)_2(H_2O)_nH^+$*, respectively. On the vertical axis cps = ion counts per second.*

present in quantities as low as 1 ppbv or so can be reached, which is often adequate for many applications such as security and military uses. An illustrative ion mobility spectrum is shown in Figure 1.3.

The main drawback with IMS is its inherently poor selectivity. As with GC, many compounds cannot be fully separated by IMS, and even if they are separated it may not be easy to establish their identities. To try and rectify this, IMS has been coupled with mass spectrometry [6], but this comes at the expense of increased cost, complexity and size of the instrument. A notable development is Hadamard transform IMS [7, 8], which promises to resolve the problem of the low duty cycle of conventional IMS and should therefore result eventually in a significantly improved sensitivity, although again this delivers a more complex instrument.

1.3.3 The Flowing Afterglow Technique

PTR-MS has its origins in the development of the flowing afterglow (FA) method for the study of ion–molecule reaction kinetics. This so-called ion-swarm technique was introduced in the 1960s by Ferguson and co-workers and it revolutionized the study of ion–molecule reaction kinetics and thermodynamics [9, 10].

Figure 1.4 shows a schematic of the apparatus. The main feature is a flow tube,[4] which provides the means of extracting kinetic information from relatively fast reactions. The idea here is that reactions between some atomic or molecular ion, X^+, and neutral molecules, which we designate as Y, are explored. The production of reagent ions, X^+, is a two-stage

[4] A flow tube is distinct from a drift tube in that the transport mechanism in the former is gas flow driven by a pressure difference between the two ends of the tube, that is, no electric field is involved in transporting ions.

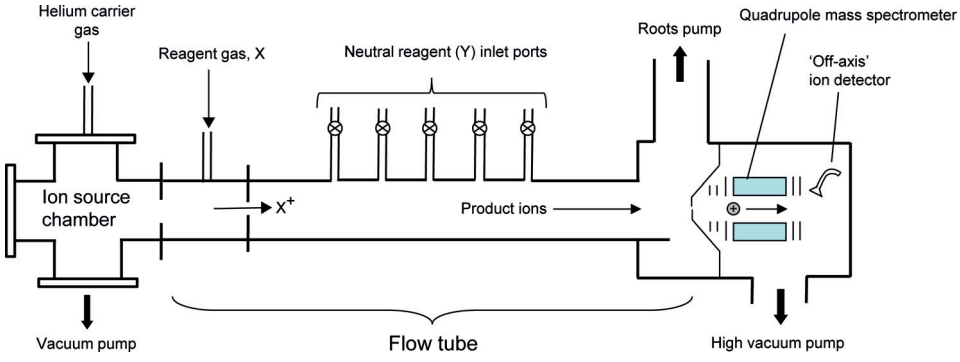


Figure 1.4 *Schematic of a flowing afterglow apparatus. With the apparatus shown reagent Y can be added at any one of the inlet ports positioned along the flow tube. An off-axis ion detector, as shown in the figure, is often used in quadrupole mass spectrometers to minimize noise from radiation and excited neutral molecules generated upstream in the ion source and in the flow tube. Ions are deflected towards the detector by electrodes (not shown).*

process. First, ions are created in an inert buffer gas, which is usually helium. This is normally achieved either by an electron impact using a heated filament electron source or via an electrical discharge. These ions are then carried along a flow tube by the flowing buffer gas (again usually helium) and further downstream they are mixed with gas X. Gas X can be ionized, typically by charge transfer from He^+, but also by Penning ionization from metastable electronic excited states of helium that are also produced in the initial ionization region. The advantage of keeping the gas X away from the initial point of ionization is that it helps to minimize the formation of unwanted fragment ions, which would be more of a problem if gas X was exposed directly to a highly energetic electrical discharge or direct electron bombardment.

A bright glow extends along the upstream part of the flow tube due to the light emitted by electronically excited constituents of the discharged gas. The extensive glow of this plasma is the origin of the name *flowing afterglow*. An essential feature of the FA technique is that it attempts to explore ion–molecule reactions at thermal energies. This is achieved by using a large excess of buffer gas and ensuring that the reactant ions are formed well upstream of the point where the neutral reagent gas, Y, is added. The flow tube is usually fairly long, a typical length being 1 m, and with gas flow speeds in the region of 100 m s^{-1}. This means that the ions have a period of several milliseconds to thermalize prior to reaction, although cases are still known where thermalization is incomplete due to slow collisional energy transfer from electronically excited and vibrationally excited states [11].

The neutral reactant gas, Y, is added at a specific entrance port along the flow tube. The pressure in the flow tube is maintained at approximately 1 mbar. After mixing with the buffer gas and reactant ions, a portion of the flow tube effluent passes through a small orifice at the end of the flow tube and enters a mass spectrometer, which is usually a quadrupole mass spectrometer (see Chapter 3). Reaction essentially stops as the mixture passes through the orifice since this mass spectrometer chamber must be operated at a low pressure ($\leq 10^{-4}$ mbar), and therefore further reactive collisions virtually cease. One way of determining the reaction kinetics is to vary the flow rate of the incoming neutral gas while monitoring the ion current of the reactant ions with the mass spectrometer. As the