

Application Handbook Thermal Analysis

热分析应用手册系列丛书

Cyril Darribère →

..... 唐远旺 →



逸出气体分析

Evolved gas analysis

东华大学出版社

热分析应用手册

Application Handbook

Thermal Analysis

逸出气体分析 Evolved Gas Analysis

Cyril Darribère 著

唐远旺 译

本应用手册提供各种精选的应用实例。实验是由瑞士梅特勒-托利多热分析实验室采用在每个应用实例中描述的特定仪器十分认真地完成的,并以最新知识为依据对结果进行评估。

然而,这并非意味着读者无需用自己的适合样品的方法、仪器和用途进行亲自测试。由于对实例的效仿和应用是无法控制的,所以我们当然无法承担任何责任。

使用化学品、溶剂和气体时,必须遵循常规安全规范和制造商或供应商提供的使用指南。

This application handbook presents selected application examples. The experiments were conducted with the utmost care using the instruments specified in the description of each application at METTLER TOLEDO Thermal Analysis Lab in Switzerland. The results have been evaluated according to the current state of our knowledge.

This does not however absolve you from personally testing the suitability of the examples for your own methods, instruments and purposes. Since the transfer and use of an application is beyond our control, we cannot of course accept any responsibility.

When chemicals, solvents and gases are used, general safety rules and the instructions given by the manufacturer or supplier must be observed.

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序

热分析是测量物质升降温时,在转变或反应过程发生的各种变化。严格来讲,热分析观测的是物质受热过程的表现变化(现象),即质量、热学量、力学量、电学量、磁学量、光学量等的变化,而追根溯源则需追究其结构上的本质变化,辅以结构分析的手段(即与热分析联用的技术)来分析逸出分解产物和样品的结构变化,这就是联用技术必要性的根本所在。

联用技术有同时联用技术(诸如 TG-DTA、TG-DSC 等)和串接联用技术(连续跟踪逸出的气体组成与温度或时间的关系,如 TG/MS、TG/FTIR 等)、间歇联用技术(每隔一定时间或温度间隔取样分析,如 TG/GC 等)之分。对于串接和间歇联用技术,新版国标 GB/T 6425-2008《热分析术语》提出采用斜线“/”连接两种技术,以便强调它们在时间上的前后关系,但基于充分尊重原文表达的考虑,译文未予改动。

本书主要介绍瑞士梅特勒-托利多公司利用热重法与质谱法、热重法与傅立叶变换红外光谱法联用的应用实例,以示示范。有关热重法与气相色谱法的联用,读者可参阅已故蔡根才教授的著述(详见:分析化学手册 第8分册 热分析.北京:化学工业出版社,2000:29-39)。

《热分析应用手册》是系统介绍热分析在诸多领域应用的一项系统工程,《热重法-逸出气分析》是其中的一个分册。这套丛书汇集梅特勒-托利多公司瑞士总部和梅特勒-托利多(中国)公司科技人员的智慧而潜心编著的。

该分册的作者 Cyril Darribère 是梅特勒-托利多瑞士总部热分析实验室的资深工程师。译者唐远旺 2006年毕业于北京化工大学材料科学与工程系,工学硕士。毕业后加入梅特勒-托利多(中国),一直从事热分析仪器的技术与应用工作。

本书的酝酿和出版正值我国改革开放 30 年,我国在世界的影响全面提升。这一时期我国科技人员在国际期刊发表的论文数量迅速提高。曾有报道,2004 年,中国科学院发表 SCI 论文较 1998 年增长 115%,总量已约为德国马普学会的 2 倍;在国际各领域居前 20 位学术刊物上发表的高质量论文数量,已占全国同期总量的一半以上(见:科学时报,2009 年 7 月 3 日第 2 版)。

本书的一个明显特点是以中英文对照的形式出版,这就为熟悉英语论文的写作方法提供了一种借鉴。

相信这套丛书的出版,将会对我国热分析技术的普及与提高,起到重要的推动作用。

刘振海

2009 年 10 月 于长春

著者序

过去的几十年,由于人们对材料质量的要求日益提高,使得材料的发展及其表征愈加专业化。此外,由于共混物、复合材料、新稳定剂和添加剂的广泛使用使得化学体系更加复杂。人们对材料科学的巨大兴趣产生了用专业分析工具表征无机和有机分子组分的需求。将成熟的分离和识别技术结合到一套仪器系统中是一项特别重要的发展。这大大提高了所获得的专业信息量,并缩短了分析时间。

这本手册着重阐述 TGA-FTIR 和 TGA-MS 两种联用技术。手册的第一部分讲述这两种技术的基本原理,也包括一些实际内容和图谱解析的介绍。第二部分讨论在我们实验室用 TGA-FTIR 和 TGA-MS 做的 15 项不同的应用,以及两个相对较少使用的 TMA 和 MS 联用技术的应用。

我要感谢在瑞士 Schwerzenbach 的市场支持团队材料表征组同事的有益讨论,还要感谢 Helga Judex 女士的排版设计以及 Dudley May 的校对工作。

Cyril Darribère

Preface

Over the past decades, the development and characterization of materials has become increasingly specialized due to the ever-increasing demands placed on quality. In addition, the widespread use of products such as blends, composites, new stabilizers and additives has resulted in relatively complex chemical systems. The great interest in material sciences has created a need for specific analytical tools to characterize the constituent inorganic and organic molecules. One particularly important development has been to combine well-established separation and identification techniques into one instrument system. This drastically increases the amount of specific information that can be obtained and shortens analysis times.

This booklet provides an insight into two such so-called hyphenated techniques, TGA-FTIR and TGA-MS. The first part of the booklet focuses on basic principles and describes the techniques. It also includes a practical section and an introduction to the interpretation of spectra. The second part discusses some 15 different applications performed in our applications laboratory using TGA-MS and/or TGA-FTIR. Two additional applications illustrate the use of the rather unusual combination of TMA with MS.

I would like to thank the Materials Characterization Section of the Market Support Group in Schwerzenbach, Switzerland for their helpful discussions, Mrs. Helga Judex for preparing the layout and Dudley May for checking the text.

Cyril Darribère

出版前言

《热分析应用手册系列丛书》是由梅特勒-托利多瑞士热分析实验室专家撰写的系列手册,包括《热分析基础》、《热塑性聚合物》、《热固性树脂》、《弹性体》、《食品》、《药物》、《无机物》、《化学品》和《逸出气体分析》等分册。

本套书既注重实用性,又注重学术性。它们可以作为应用手册查询,也可以作为实验指南,如帮助选择合适的热分析测试技术和方法、制备和处理样品、设定实验参数等。手册中的所有应用实例均经过认真挑选,实验方法经精心设计,测试曲线重复可靠,数据处理严格谨慎、对实验结果的解释和对实验结论的推导科学合理。

本套手册面向所有用到热分析和对热分析感兴趣的教授、科学家、工程师和学生(特别是研究生)及其他科技工作者,适合所有热分析仪器的直接使用者。

本书是《热分析应用手册系列丛书》之《逸出气体分析》分册。

与其它分册一样,本书以中英文对照方式出版,读者可以阅读中文,同时可对照原著。无论对热分析工作者,还是热分析学习者,应该都有帮助和裨益。

这里要特别感谢刘振海教授,他仔细审阅了本书全部书稿,并亲自进行修改,使本书的质量得到了很大提高。

东华大学出版社的编辑对本书的出版付出了辛勤的劳动,在此表示感谢。

陆立明

2009年10月,上海

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缩写和简称 Abbreviations and Acronyms

	化学品 Chemicals
BHET	对苯二甲酸乙二醇酯 bis-Hydroxyethyl terephthalate
BR	丁二烯橡胶 Butadiene rubber
EG	乙二醇 Ethylene glycol
ETFE	乙烯-四氟乙烯共聚物 Ethylene tetrafluoroethylene
MF	三聚氰胺甲醛 Melamine formaldehyde
NBR	丁腈橡胶 Acrylonitrile butadiene rubber
NR	天然异戊二烯橡胶 Natural isoprene rubber
PDMS	聚二甲基硅氧烷 Poly(dimethylsiloxane)
PET	聚对苯二甲酸乙二醇酯 Poly(ethylene terephthalate)
PVC	聚氯乙烯 Poly(vinyl chloride)
TPA	对苯二甲酸 Terephthalic acid

	技术/物理量 Techniques / Quantities
DTG	微商热重法 Derivative thermogravimetry
EGA	逸出气分析 Evolved gas analysis
EGP	逸出气剖面图 Evolved gas profile
FGP	官能团剖面图 Functional group profile
FTIR	傅立叶变换红外光谱法 Fourier transform infrared
GS	格莱姆—施密特 Gram-Schmidt
IR	红外线 Infrared
MID	多离子检测 Multiple ion detection
MS	质谱法/光谱仪 Mass spectrometry / spectrometer
MW	分子量[g/mol] Molecular weight [g/mol]
m/z	离子质荷比 Mass-to-charge ratio of the ion
SDTA	单-差热分析 Single differential thermal analysis
SEM	二次电子倍增管 Secondary electron multiplier
SIM	选择离子监控 Selected ion monitoring
TGA	热重分析/热重分析仪 Thermogravimetry analysis / analyzer
TMA	热机械分析/热机械分析仪 Thermomechanical analysis / analyzer
z	电量与单电荷电量的倍数(n. e) Number of charges times the charge on one electron (n. e)

TGA-EGA 概述 Introduction to TGA-EGA

逸出气分析(EGA)是描述热分析过程中分析样品释放出的挥发性组分或气体的术语。

热重分析(TGA)是一种在特定气氛中测试样品质量随温度(动态)或时间(等温)变化的定量技术。同步 SDTA(单一差热分析)信号提供了额外的热效应信息,例如挥发、吸热和放热化学反应以及相转变。

然而 TGA 本身并不是识别技术。它不能鉴别或表征热重测试过程中逸出气体产物的性质。TGA 与质谱仪(MS)或傅立叶变换红外光谱仪(FTIR)的结合使这种分析成为可能。这两种技术提供了非常有用的信息,获得的数据可以直接与测试的质量损失关联起来。

定义 Definition

根据 ICTAC(国际热分析和量热学协会)的提法,逸出气分析(EGA)被定义为“在程序控温和特定气氛中监控样品逸出的气体或蒸气的性质和/或量随时间或温度变化的技术。这种技术包括一个炉子和一个气体分析器或检测器。通常情况下,一般使用质谱法(MS)或傅立叶变换红外光谱法(FTIR)对逸出气体进行分析。”

Evolved gas analysis, EGA, is the term used to describe the analysis of gases or volatile components that are evolved from a sample undergoing thermal analysis.

Thermogravimetric analysis (TGA) is a quantitative technique used to measure the change in weight of a sample as a function of temperature (dynamically) or time (isothermally) under a controlled atmosphere. The simultaneously recorded SDTA signal (single differential thermal analysis) provides additional information on thermal effects such as evaporation, endothermic and exothermic chemical reactions, and phase transitions.

TGA alone, however, is not an identification technique. It cannot identify or characterize the nature of the gaseous products evolved during a thermogravimetric measurement. The combination of TGA with a mass spectrometer (MS) or a Fourier transform infrared (FTIR) spectrometer however makes this possible. The two techniques provide complimentary information and the data obtained can be correlated directly with the measured weight losses.

According to ICTAC (International Confederation of Thermal Analysis and Calorimetry), Evolved Gas Analysis (EGA) is defined as “a technique in which the nature and/or the amount of gas or vapor evolved from a sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed (...). This technique involves a furnace and a gas analyzer or detector. Most commonly, the evolved gases are analyzed using mass spectrometry (MS) or Fourier transform infrared spectroscopy (FTIR)”.

结果解释 Interpretation of results

对于联用的仪器(即 TGA 和 MS 或 TGA 和 FTIR)来说时间是共同

Time is the parameter common to the instruments making up the combination (i. e. TGA and MS, or TGA and FTIR). An

的参数。对于测试的解析,首先需要详细研究 TGA 曲线。除了质量损失台阶的定量分析外,DTG 曲线(即 TGA 曲线的一阶微商曲线)可使从 TGA 获得的数据与从波谱仪获得的数据相关联。当样品发生质量变化时,DTG 曲线的峰值(失重速率最大)应与气体分析仪测试的信号强度曲线的最大值非常相近。最好能够配备 MS 和 FTIR 气相波谱数据库。

interpretation of a measurement first of all requires a detailed study of the TGA curve. In addition to the quantification of the weight loss steps, the DTG curve, i. e. the first derivative of the TGA curve, allows the data obtained from the TGA to be correlated with that from the spectrometer. When the sample undergoes a change in weight, a peak maximum in the DTG curve (max. rate of change of weight) should correspond closely to a maximum in the signal intensity curve measured by the gas analyzer. Ideally, both MS and FTIR require the support of vapor phase spectral databases.

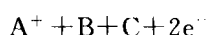
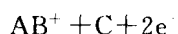
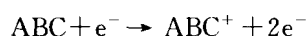
测试原理 Measurement principles

质谱是一种检测和鉴别微量气体物质的非常灵敏的方法。这种技术可以量化原子和分子,提供化合物化学和结构的信息(官能团和侧链)。

通常在联用的质谱中,样品分子通过一个离子源进入质谱,在离子源中样品分子被高能电子束(通常约 70 eV)轰击。这个能量比有机物质的离子化势能和键强度大。这实际上足够从分子上移动一个(或更多)电子,形成正电荷分子离子。多余的能量还能够引起分子大量的分裂,通过复杂的途径形成许多不同的正电荷碎片离子。然而,形成的碎片离子直接与所研究的分子的结构相关。例如:

Mass spectrometry is an extremely sensitive method for the detection and identification of traces of gaseous substances. The technique can quantify atoms or molecules and provide chemical and structural information (functional groups and side chains) on the compounds analyzed.

In the mass spectrometers typically used for hyphenated techniques, sample molecules enter the mass spectrometer through an ion source where they are bombarded with a beam of high-energy electrons (usually about 70 eV). This energy is greater than the ionization potentials and bond strengths of organic substances. It is in fact sufficient to remove one (or more) electrons from molecules to form positively charged molecular ions. The excess energy also causes extensive fragmentation of the molecule with the formation of many different positively charged fragment ions according to complex pathways. The fragment ions formed are, however, directly related to the structure of the molecule under investigation, e. g.



...

质谱根据质荷比 m/z 将离子进行分离。对于联用技术我们通常只关心单电荷分子和碎片离子。由于种种原因,与传统的磁场扇形分析器相比,在过去的 25 年中四极杆质谱仪已经被广泛用于仪器联用。四极杆质谱仪由两对平行的杆电极组成,它们介于离子源和检测器之间。四个杆彼此相对安装,成对相连(见图示)。质量分离是通过连续的静电场和高频交互电场实现的。通过系统传送的离子在 SEM 检测器中进行记录。稳定提高(扫描)电场强度使得更高

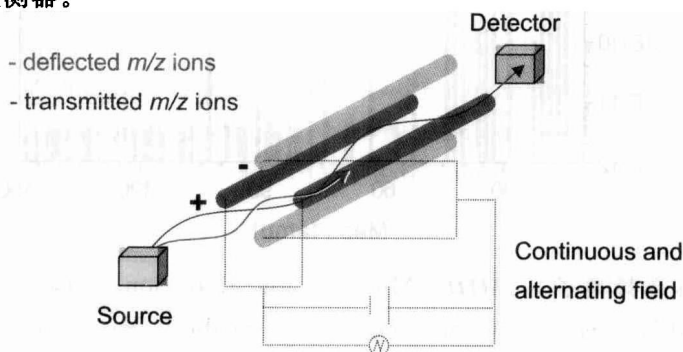
The mass spectrometer separates the ions according to their mass-to-charge ratio m/z . With hyphenated techniques we are normally only interested in the singly charged molecule and fragment ions. For a number of reasons, quadrupole mass spectrometers have been widely used over the past twenty-five years in preference to conventional magnetic field sector analyzers in instrument combinations. A quadrupole mass analyzer consists of two pairs of parallel rod electrodes located between an ion source and a detector. The four rods are mounted opposite to each another and are connected in pairs (see diagram). Mass separation is achieved by the combination of a continuous electrostatic field and a high-frequency alternating field. The ions transmitted through the system are recorded at the SEM detector. Steadily increasing (scanning) the field strength causes ions of increasing m/z value to arrive at the detector

m/z 值的离子到达检测器,从而产生质量谱。

质谱仪在高真空下条件下(典型值为 10^{-5} mbar)操作。这对于在从离子源到检测器的路径上防止离子与残余气体分子发生碰撞是必要的,否则将阻止它们到达检测器。

and thereby produce a mass spectrum.

Mass spectrometers operate under high vacuum (typically 10^{-5} mbar). This is necessary to prevent ions colliding with residual gas molecules along their path from the ion source to the detector, which would prevent them from reaching the detector.



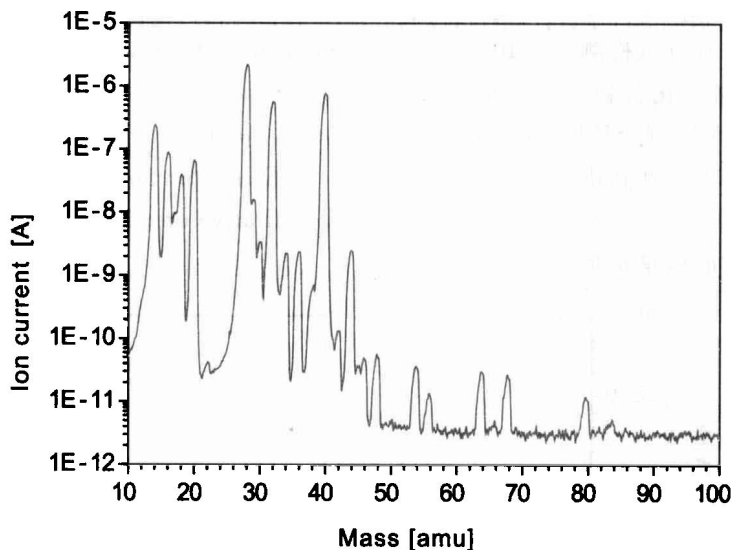
四极杆质量过滤器原理图

Schematic diagram of a quadrupole mass filter

测试模式 Measurement modes

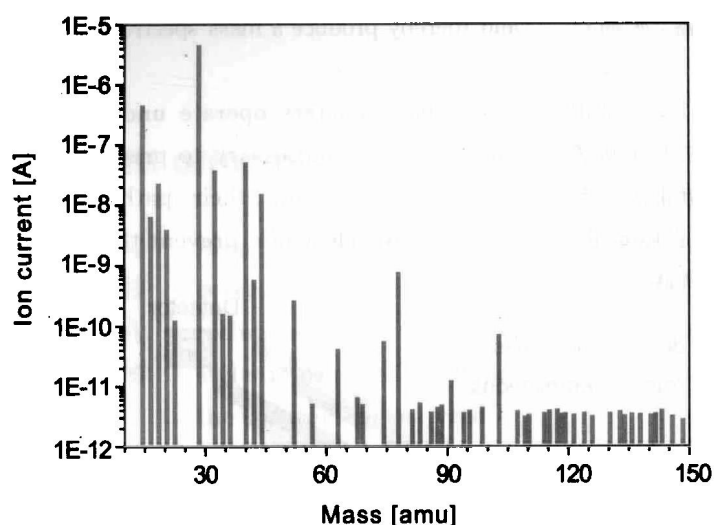
模拟扫描图:连续测试离子电流与质荷比(即单电荷离子的质量)的函数关系。由强度和碎片离子的质量提供所研究材料性质的信息。

Scan analog: The ion current is continuously measured as a function of the mass-to-charge ratio (i. e. for singly charged ions, the mass). The intensity and mass of the fragment ions provide information on the nature of the material under investigation.



柱状扫描图:只显示那些信号强度超过某一特定值(即在某个阈值之上)的质量。所以 m/z 的增量是不连续的。这样的图谱可以被转换成时间强度曲线。

Scan paragraph: Only those masses are displayed whose signal intensity exceeds a particular value (i. e. that are above a certain threshold). The increment in m/z is therefore not continuous. The spectrum can be transformed into time-dependent intensities curves.

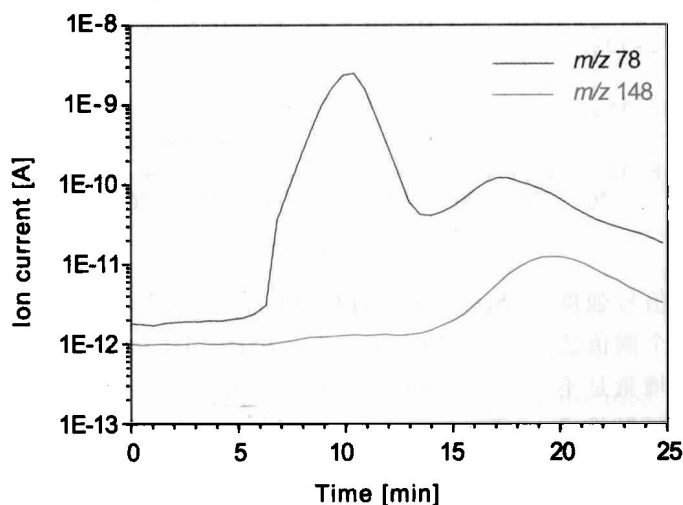


MID: 多离子检测(也称选择离子监测, SIM)可以连续监测特定 m/z 值离子的强度, 例如下图所示的 m/z 为 78 和 148 的图谱。

在这种技术中, 并不扫描总质量谱, 只选择一些特定 m/z 值的离子进行分析, 仪器在选择离子之间快速切换, 直到测试结束。分析仪在给定的 m/z 值保持的时间(所谓的停留时间)大大增加。这反过来提高了到达监测器的离子的数量, 从而明显提高了灵敏度。所以, 虽然使用全扫描四极杆质谱通常可以检测亚纳克(10^{-10} 到 10^{-9} g)量的化合物, 但是在合适的情况下 MID 或 SIM 可以降低这个限制, 能够检测到皮克(10^{-12} 到 10^{-11})的范围。MID 经常应用到化合物的混合物的微量定量或定性分析中。

MID: Multiple Ion Detection (also known as Selected Ion Monitoring, SIM) enables you to continuously monitor the intensity of ions at defined m/z values, e. g. as shown in the following diagram at m/z 78 and 148.

In this technique the whole mass spectrum is not scanned, only a selected number of ions with particular m/z values are analyzed and the instrument rapidly switches between the selected ions until the measurements are completed. The amount of time (the so-called dwell time) that the analyzer remains at a given m/z value is thereby greatly increased. This in turn increases the fraction of these ions that reach the detector and results in a major improvement in sensitivity. Thus while subnanogram (10^{-10} to 10^{-9} g) quantities of compounds can normally be detected using full-scan quadrupole mass spectra, MID or SIM can in favorable cases lower the limit of detection to the picogram (10^{-12} to 10^{-11} g) range. MID is often applied to mixtures of compounds where sensitive quantitative or qualitative analysis is required.



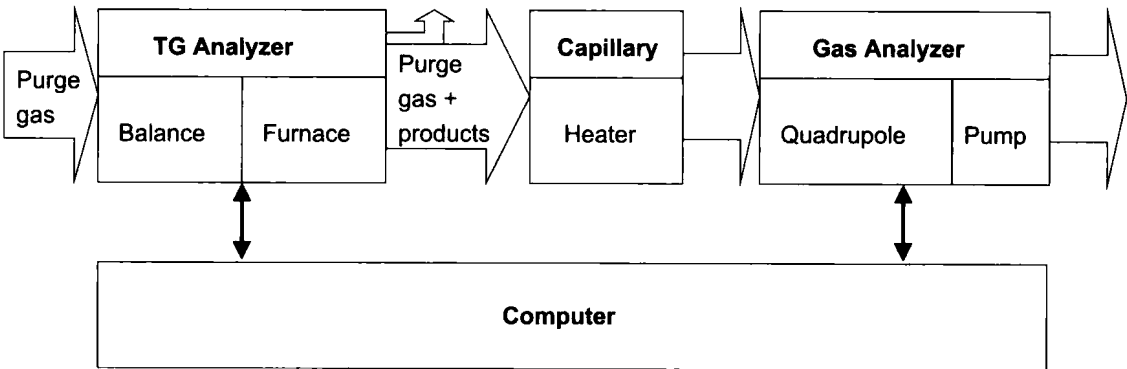
一个质量谱由大量的不同强度的信号组成,这些信号对应于分子离子和不同离子片段的丰度,所以它是所研究的特定物质所独有的。一些重要的元素有多种同位素,都有较大的丰度(例如:C、Si、Cl、Br)。这些同位素峰也被记录,经常会产生有价值的额外信息。遗憾的是,通常情况下,用于联用技术的质谱仪的分辨能力不足以分辨具有相同 m/z 比的离子(例如: N^{2+} 和 CO^+ , 二者都显示 m/z 为 28)。

A mass spectrum consists of a large number of signals of different intensity corresponding to the abundance of the molecular ion and the different fragment ions. It is therefore characteristic of the particular substance under investigation. Some important elements have more than one isotope with significant abundance (e. g. C, Si, Cl, Br). These isotope peaks are also recorded and often yield valuable additional information. Unfortunately, in general, the resolving power of the spectrometers used for hyphenated techniques is not sufficient to distinguish between ions of the same nominal m/z ratio (e. g. N^{2+} and CO^+ , both appear at m/z 28).

TGA-MS 系统 TGA-MS system

TGA/SDTA851[®] 通过一根石英毛细管与 MS 相连,石英毛细管被包在一根加热的传输线中。因为 MS 在高真空的条件下操作,所以从 TGA 中逸出的气体只有约 1% 通过质谱仪(否则会失去真空条件)。然而这么少的量已经足够了,因为 MS 的灵敏度是非常高的。从 TGA 中出来的余下气体被排出(到一根收集管)。传输毛细管通常保持在约 200℃,以防气体产物冷凝。TGA(通常为大气压)和 MS(高真空, $p < 10^{-5}$ mbar)之间的压力降使气体从 TGA 流向 MS。

The TGA/SDTA851[®] is coupled to the MS via a fused silica capillary enclosed in a heated transfer line. Since the MS operates at high vacuum, only about 1% of the effluent gas from the TGA is allowed to pass to the mass spectrometer (otherwise the vacuum would collapse). This small amount is however perfectly adequate because the sensitivity of the MS is extremely high. The remaining gas from the TGA is vented (to a collection tube). The transfer capillary is usually maintained at about 200°C to prevent condensation of the gaseous products. The pressure drop between the TGA (usually atmospheric pressure) and the MS (under high vacuum, $p < 10^{-5}$ mbar) causes the effluent from the TGA to be sucked into the MS.



TGA-MS 系统的块状图
Block diagram of a TGA-MS system

解析程序 Interpretation procedure

如上所述,质谱经常被表示为柱状图,横坐标为 m/z 比,纵坐标是每一种离子的强度。此外,也可将经过选择的具有特定 m/z 比的碎片离子的信号强度(MID/SIM)表示成时间的函数(这有助于与 TGA 曲线或 DTG 曲线的关联)。当然最重要的是谱图上的质量是正确的,仅仅是一个质量单位的错误将严重影响解析。

下面的指导原则对于质谱的解析是有用的:

1. 峰的丰度(强度)经常指明化合物为芳族的(稳定的分子离子, M^+) 还是脂肪族的。
2. 具有最高 m/z 的碎片离子通常对应于离子化的分子,即分子离子,这样 m/z 等于 M (化合物的分子量)。从分子离子中失去中性碎片产生的离子峰汇总在下表中:

As mentioned above, a mass spectrum is often displayed as a bargraph, where the abscissa is the m/z ratio and the ordinate is the intensity of each ion. In addition, the signal intensities of selected fragment ions with particular m/z ratios (MID/SIM) can be also displayed as function of time (this aids correlation with a TGA or DTG curve). It is of course of the utmost importance that the masses assigned in the spectrum are correct—an error of just one mass unit would seriously confuse the interpretation.

The following guidelines are useful for the interpretation of mass spectra:

1. The abundance (intensity) of peaks often indicates whether the compound is aromatic (stable molecular ion, M^+) or aliphatic.
2. The fragment ion with the highest m/z generally corresponds to the ionized molecule, i. e. the molecular ion so that m/z is equal to M , the molecular weight of the compound. The ion peaks resulting from the loss of neutral fragments from the molecular ion peak are summarized in the following table:

从分子离子中失去中性碎片 Loss of neutral fragment from molecular ion	常见的中性碎片 Common neutral fragments
M-15	• CH ₃
M-16	• NH ₂
M-17	• OH
M-26	• CN
M-27	• HC=CH ₂
M-28	CO, C ₂ H ₄
M-29	• CH ₂ CH ₃ , • CHO
M-30	NO, NH ₂ CH ₂ •
M-31	• OCH ₃ , • CH ₂ OH
M-35	• Cl
M-41	CH ₂ =CHCH ₂ •
M-43	CH ₃ C • =O
M-45	• OCH ₂ CH ₃
M-49	• CH ₂ Cl
M-91	C ₆ H ₅ -C • H ₂

3. 如果一个化合物仅仅包含 C、H、O、S 和 Si, 那么它的分子离子的标称 m/z 比是偶数; 如果一个化合物包含的氮原子为偶数, 那么它的分子离子的 m/z 是一个偶数(氮原则)。

4. 同位素(两个原子的原子数相同, 但原子质量不同)的相对强度是非常有价值的。例如: ^{12}C 和其同位素 ^{13}C 的相对丰度是 100:1.1。如果一个化合物含有 n 个碳原子, 且分子离子峰被归一化为 100, 那么 $M+1$ 同位素峰为 1.1 的 n 倍。由此, 如果不发生干扰, 一个未知分子中 C 原子数量的最大值可以被计算。

5. 同位素效应对于鉴别含有氯和溴的化合物非常有用。氯有同位素 ^{35}Cl 和 ^{37}Cl , 它们在自然界中的相对丰度为 75% 和 25% (3:1), 这意味着任何含有一个氯原子的化合物, 例如一氯甲烷, 相隔两个质量单位显示一对峰, 峰高比为 3:1。

6. 在一个质谱中, 一个峰的 m/z 比值并不能绝对鉴别一个分子或碎片离子, 例如: m/z 18。水的分子量为 18, 但是离子化也能产生具有相同标称 m/z 比的离子, 例如铵离子 $[\text{NH}_4]^+$ 。这就需要更多的信息, 例如: 后面的情况应该有对应于 N^+ 和 $[\text{NH}]^+$ 的 m/z 14 和 15 (氮原子量为 14) 的峰。

7. 下面的物质对可以用于检查, 避免混淆。这也意味着应该仔细地选择吹扫气体:

m/z 17: OH and NH_3

m/z 28: N_2 and CO

m/z 29: $^{14}\text{N}^{15}\text{N}$ 和 C_2H_5 (乙醇)

m/z 36: ^{36}Ar and HCl

m/z 44: CO_2 and N_2O

8. 未知化合物的质谱由许多不同 m/z 比的峰组成, 这些峰来源于初始分子的分裂。分裂的过程可以被归类为直接分裂 ($\text{ABCD}^+ \rightarrow \text{AB}^+ + \text{CD}$) 或者重排 ($\text{ABCD}^+ \rightarrow \text{AD}^+ + \text{B} = \text{C}$)。When an

3. If a compound contains only C, H, O, S and Si, the nominal m/z ratio of its molecular ion will be an even number; if a compound contains an even number of nitrogen atoms, the m/z of its molecular ion is an even number (nitrogen rule).

4. The relative intensities of isotopes (two atoms having the same atomic number but different atomic masses) can be very informative. For example, the relative abundance of ^{12}C compared to its isotope ^{13}C is 100:1.1. If a compound contains n carbon atoms and the molecular ion peak is normalized to 100, then the $M+1$ isotope peak is n times 1.1. It follows from this, that if no interferences occur, the maximum number of C atoms that an unknown molecule can contain can be calculated.

5. Isotopic effects are very helpful for identifying compounds containing chlorine and bromine. Chlorine has isotopes of ^{35}Cl and ^{37}Cl . Their relative natural abundances are 75% and 25% (3:1). This means that any compound containing one chlorine atom, e. g. chloromethane, shows a pair of peaks separated by two mass units with a 3:1 peak height ratio.

6. The m/z ratio of a peak in a spectrum does not exclusively identify a molecule or fragment ion, e. g. m/z 18. Water has a molecular weight of 18, but ionization can also produce ions that have the same nominal m/z ratio, e. g. the ammonium ion $[\text{NH}_4]^+$. Further information is required, e. g. in the latter case there should be peaks at m/z 14 and 15 corresponding to N^+ and $[\text{NH}]^+$ (atomic mass of nitrogen is 14).

7. The following pairs should be checked to avoid possible confusion in interpretation. This also means that careful consideration should be given to the choice of the purge gas:

m/z 17: OH and NH_3

m/z 28: N_2 and CO

m/z 29: $^{14}\text{N}^{15}\text{N}$ and C_2H_5 (alcohol)

m/z 36: ^{36}Ar and HCl

m/z 44: CO_2 and N_2O

8. The mass spectrum of an unknown compound consists of a number of peaks of different m/z ratios arising from the fragmentation of the initial molecule. The fragmentation processes can be classified as direct cleavage ($\text{ABCD}^+ \rightarrow \text{AB}^+ + \text{CD}$) or rearrangement ($\text{ABCD}^+ \rightarrow \text{AD}^+ + \text{B} = \text{C}$). When an