石油组分高分辨质谱分析进展与展望

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摘要 石油是一种复杂体系, 研究石油分子组成是分析化学领域的经典难题. 近年来, 傅里叶变换离子回旋共振质谱技术(Fourier transform ion cyclotron resonance mass spectrometry, FT-ICR MS)的发展, 为从分子水平认识石油组成提供了机会, 引起了石油化学界的高度关注, 并被期待能在石油、石化领域的相关研究中实现重大突破. 本文从质谱分辨率和电离技术方面介绍了石油样品的分析需求, 总结了近几年基于 FT-ICR MS 技术对石油分子组成的研究进展, 分析了其在应用中存在的关键技术问题及下一步研究方向, 并对 FT-ICR MS 的发展前景给予展望.

关键词

石油
FT-ICR
质谱
石油组学
分子组成

1 引言

石油组成十分复杂, 色谱技术无法实现石油中重质组分单体化合物的完全分离, 通过质谱分析分子组成是认识石油复杂体系的最有效方法. 石油中普遍存在含硫化合物, 含硫化合物和其邻近质量的烃类化合物(C_3/S_4)相差 3.4 mDa. 如此小的质量差异, 在质量数 500 附近要求质谱分辨率为 15 万以上. 这一要求远超过了早期高分辨质谱的能力范围, 因此, 提高质谱分辨率是石油分析的最大挑战. 20 世纪 90 年代, 傅里叶变换离子回旋共振质谱仪(Fourier transform ion cyclotron resonance mass spectrometry, FT-ICR MS)已具有超过传统磁质谱的分辨率, Hsu 等^[1]最早利用磁场强度为 3 T 的商业 FT-ICR MS 分析石油组分, 尽管分辨率远达不到要求, 但实验结果证明, FT-ICR MS 具有较大的发展潜力. 之后, FT-ICR MS 的发明人 Marshall^[2]与 Rodgers^[3]开始将石油分析作为 FT-ICR MS 的一个重要应用方向, 不断将最新的 FT-ICR MS 仪器用于石油样品分析. Qian 与其合作^[4, 5], 在 9.4 T 磁场强度的 FT-ICR MS 上利用电喷

雾电离(electrospray ionization, ESI)技术分析了重质石油组分(简称重质油, 指密度或黏度较大的原油, 或指石油中的高沸点难挥发组分)中的极性杂原子化合物. 2001 年发表在 *Energy and Fuels* 杂志上的两篇论文^[4, 5]可以作为对石油组成认识的重要里程碑, 真正从分子水平揭示了石油的化学组成, 形成了基于高分辨质谱分析的“石油组学”概念与方法^[6, 7], 并推动了石油分子组成研究的新一轮热潮.

本文根据石油样品的分析需求, 介绍了 FT-ICR MS 在石油样品分析方面的应用, 并分析了其发展前景.

2 质谱分辨率

石油的元素组成主要包括 C、H、O、N 和 S 5 种元素, 一旦测得某种化合物的精确质量, 很容易计算其元素组成. 精确质量测定在许多质谱仪上均可实现, 甚至在四极杆质谱仪上也可借助同位素峰相对丰度测得精确的质量数值, 但是获得精确质量的前提是保证不同质量峰的相互分离, 即仪器的分辨

率必须足够高. 以分辨 C_3/SH_4 元素组成差异为例, 在 m/z 400 处实现分离需要的最低分辨率为 12 万, 该分辨能力通常被认为是分析石油组分的最基本要求. 实际上, 石油质谱峰中还存在更接近的质量峰对, 如分辨 $O_3H_3/C_2N^{13}C$ (1.7 mDa) 需要提高一倍分辨率, 而 $^{13}CSH/C_4$ 之间质量差仅为 1.1 mDa, 在 m/z 400 处的分辨率要求为 36 万.

图 1 所示为负离子 ESI 模式下得到的石油组分 m/z 521 处 FT-ICR MS 质谱图, 放大窗口中显示的 4 个质谱峰之间质量差约为 1.1 mDa. 通过质量校准, 3#峰被指定为 $[^{13}CC_{34}H_{55}NS-H]^-$, 但是存在一个明显的质量偏差, 理论计算这个峰可以是两个质谱峰的重叠, 即与 $[^{13}CC_{28}H_{56}NO_5Na-H]^-$ 共存. 如果这种离子对存在, 其质量差小于 0.1 mDa, 仅为电子质量的 1/5, 则这一分辨能力也是理论上完全分离 C、H、O、N 和 S 几种元素及其同位素形成的各种化合物的最高要求^[8]. 分辨此离子对的质谱分辨率大于 500 万. 可见在存在其他元素情况下, 目前质谱仪的质量分辨率还远未达到完全分辨石油组分的要求.

新型离子回旋池延长了离子回旋时间, 在磁场

强度不变的情况下, 大幅度提高了质量分辨率^[9, 10], 尽管对实际石油样品无法像单离子检测时达到的最大分辨率, 但目前已经商业化的 FT-ICR MS 仪器可以在 7.0 T 磁场强度下实现传统检测池在 9.4 T 磁场强度下的分辨能力^[11]. 美国高磁场国家实验室和西北太平洋实验室同时开发的 21 T 超强磁场强度下的新型 FT-ICR MS 仪器即将投入使用, 将为石油样品分析提供更有力的技术支持.

3 电离技术

石油样品分析早期最常用的是电子轰击(electron impact, EI)和场电离(field ionization/desorption, FI/FD), 但这两种电离技术在 FT-ICR MS 上均未得到好的应用. 石油样品组成本身已十分复杂, 如果使用 EI 电离, 大量碎片离子混合在一起, 则无法解释原始分子组成信息. FI/FD 电离源是理想的电离烃类化合物的软电离方法. Smith 等^[12]将连续进样 FD 电离源应用于 FT-ICR MS, 但由于电离效率低及难以控制等问题并没有后续应用的报道^[13]. 埃克森美孚公

图 1 重质油 FT-ICR MS 质谱图. 样品来源: 委内瑞拉重质原油渣油超临界萃取 2#窄馏分. Bruker 公司 Solarix FT-ICR MS, 磁场强度为 12 T, 动态协调回旋池(dynamically harmonized FT-ICR cell). 负离子 ESI

司、中国石油大学(北京)重质油国家重点实验室以及中国石化石油化工科学研究院与德国 Linden 公司合作, 通过提高离子源真空度和改变离子传输通道等方法, 分别尝试将 FD 电离源应用于 FT-ICR MS, 但效果均不理想, 其主要问题包括正构烷烃电离效率低以及产生脱氢离子等。目前, FT-ICR MS 上最常用的电离源是 ESI 和大气压光致电离(atmospheric-pressure photoionization, APPI)。ESI 选择性地电离极性杂原子化合物, ESI 结合 FT-ICR MS 成功解决了石油中极性大分子化合物分析的传统难题^[4, 5]。APPI 既能电离极性化合物, 也能电离大部分烃类化合物, 因此也是一种比较理想的石油样品电离技术^[14]。APPI 能够电离更多类型的化合物, 对应的离子类型也比较复杂, 产生的质谱峰数量可以达到 ESI 的 5 倍^[15]。质谱峰数量的增加对质谱分辨率提出了更高的要求, 因此, 对于一般的 FT-ICR MS 仪器, APPI 电离的相对通用性并不一定是优点。石油分子间存在缔合作用^[16], 只有在非常低的进样浓度下才能避免产生缔合离子, 然而样品浓度很低时离子强度也很低; 另一方面, 检测池的空间有限, 需要维持较低的离子浓度以消除不同离子间的电荷效应对质量分析的影响, FT-ICR MS 通常采用多次检测信号叠加的方法提高检测信噪比和检测动态范围。信号叠加需要保持稳定的信号性, 而基质辅助激光解析(matrix-assisted laser desorption/ionization, MALDI)及实时直接电离(direct analysis in real time, DART)等电离方法由于难以产生稳定的离子流, 因此难以应用于石油样品的高分辨质谱分析。为了解决非极性化合物的电离, 可以通过化学衍生化方法将非极性化合物转化为可在 ESI 中分析的极性化合物, 如可将含硫化合物转化为甲基铈盐或硫的氧化物^[17, 18]、可将饱和烃通过钨离子催化氧化转化为醇^[19]。激光诱导声波解吸化学电离(laser-induced acoustic desorption/chemical ionization, LIAD/CI)和银离子加合激光电离(laser desorption silver cationization, LDI-Ag)对非极性烃类化合物也可获得较好的电离效果^[13, 20, 21]。

4 主要进展

Marshall 课题组是 FT-ICR MS 技术和石油组学研究的引领者, 该课题组针对 FT-ICR MS 仪器在离子累积和高浓度离子检测方面进行了专门设计, 对

于石油样品分析, 其性能远高于同等磁场强度下同一时期的商业化仪器。埃克森美孚公司 Qian 等^[4, 5, 22, 23]和韩国庆北大学 Kim 研究组^[24-27]在石油样品的 FT-ICR MS 方面均做了开创性工作; 英国帝国大学 Barrow 研究组^[28-30]和德国慕尼黑大学 Andersson 研究组^[18, 31-33]分别在石油酸和含硫化合物分析方面做出了重大贡献; 2010 年以来, 中国石油大学(北京)重质油国家重点实验室成为该领域研究最活跃的实验室之一^[17, 19, 34-46]。

高分辨 FT-ICR MS 的应用真正实现了从分子水平认识重质油化学组成, 验证了一些基于宏观性质推测的石油化学组成问题, 形成了一些新认识: (1) 石油分子的小分子特征。石油重质组分, 尤其是沥青质的分子量问题是石油化学界长期争议的话题, 越来越多的质谱分析结果证明, 一些难挥发石油组分的分子量并不是很大^[47], 只是分子间的相互作用使其宏观性质表现出一些大分子特征^[48]; (2) 杂原子化合物的类型分布。杂原子化合物的组成十分复杂, 已鉴定出超过 30 种不同类型的杂原子化合物, 硫、氮、氧杂原子化合物相互重叠, 无法按照单元素进行简单分类^[4, 5, 42, 49, 50]; (3) 杂原子化合物在重质油中的含量很高。烃类化合物是石油的主要成分, 这一认识对重质油来讲不一定正确, 杂原子化合物可能成为主要成分^[35, 51]; (4) 新型生物标志化合物的鉴定。依靠新型电离技术的特殊选择性及 FT-ICR MS 可以准确确定分子元素组成的特点, 传统分析无法检测的一些大分子极性化合物被发现和鉴定, 如具有生物构型的酚类^[39]、羧酸^[37]、含硫化合物^[52]和金属卟啉类化合物^[22, 53], 这些生物标志化合物具有潜在的地球化学意义。

5 定量分析问题

针对石油工业的应用需求分析, 分子组成可以为石油地球化学研究提供石油生源、沉积环境、成熟度、运移、生物降解等方面的重要信息, 解决石油勘探和开发中的问题; 另一方面, 详细的分子组成可以解释石油加工过程的化学反应机理, 通过建立转化模型实现“分子炼油”的理论设想。在分析石油分子组成方面, FT-ICR MS 已经表现出不可替代的作用。近年来, 大型石油公司和相关研究机构竞相装备高性能的 FT-ICR MS 仪器, 但是缺乏成功的实际应用。

地球化学和石油化工领域的应用均需要提供定量数据, 然而目前没有理想的基于 FT-ICR MS 分析石油组成的定量分析方法。

定量分析首先要求数据的可重复性。ESI、APPI 尽管可以产生连续稳定的离子流, 然而重现性并不理想, 尤其是 ESI 电离存在较强的电离抑制效应。质谱仪器检测池在高磁场和高真空条件下工作, 离子从产生到检测池必须经过较长的传输过程, 商业化 FT-ICR MS 仪器在离子传输方面的设计远不如其他商用型质谱仪器成熟, 存在较强的质量歧视效应; 另一方面, 检测器对较宽质量范围高浓度离子的同时检测存在一定困难, 也导致质量歧视问题。

对于挥发性组分, 电离选择性和质量歧视可以通过气相色谱分析结果进行验证。最新实验结果表明^[54], 石油中的含氮、氧化合物在 ESI 电离源中存在较宽的线性响应浓度范围, 同一类型化合物分子间电离抑制效应并不明显, 定量数据与气相色谱得到的结果具有可比性。对于质量歧视问题, 可以通过分段优化分析条件, 合成宽程谱图的方法消除其影响。在 FT-ICR MS 上建立定量分析方法存在着很大困难, 然而这是必须解决的问题, 因为短期内其他质谱技术在分辨率方面还无法满足石油分析的需要。

6 展望

石油工业体量巨大, 微小的技术进步可能带来巨大的经济效益, 从分子水平认识和利用这一资源已经成为业界共识。一旦解决了定量分析问题, FT-ICR MS 必将为石油、石化行业的科学研究与生产过程提供重要的技术支撑。新型商业 FT-ICR MS 已经针对石油分析进行了较多的优化设计, 除了新型检测器的应用, 在离子传输方面也做了很大改进, 质量歧视问题也在很大程度上得到了改善, 仪器更加容易控制, 为获得可重复数据提供了条件。数据采集采用阈值限制有效过滤噪音干扰, 设定自动分段采集功能可以直接实现不同谱图叠加直接解决宽范围的质量歧视。

FT-ICR MS 一直被认为是质谱仪器中的高端产品, 昂贵的价格影响其推广应用, 而有限的市场又使生产商难以降低成本。近年来, 高端 FT-ICR MS 被更多行业所关注, 市场扩大必将推动这一技术的快速发展。另一方面, 飞行时间和电场轨道阱质谱在分辨率方面不断提高, 已能够满足一些石油馏分油样品的分析需求, 这些技术将来或者能够代替 FT-ICR MS, 至少在技术上形成竞争, 有助于促进 FT-ICR MS 走向成熟。

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Progress and prospect on petroleum analysis by Fourier transform ion cyclotron resonance mass spectrometry

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Abstract: Petroleum is an ultra-complex hydrocarbon system. Characterization of petroleum has been challenging for the analytical chemistry community. The recent development of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) enables the characterization of petroleum molecular composition. This new technique provides new insights on petroleum chemistry which can result in technological breakthroughs in petroleum and petrochemical industries. In this paper, the mass resolving power and ionization techniques required in mass spectrometry for petroleum analysis are summarized, the advances in FT-ICR MS for petroleum analysis are discussed, and the technique challenges and the further research issues are discussed. What's more, the prospective of using FT-ICR MS technique for petroleum characterization and its application to petroleum research are also included.

Keywords: petroleum, FT-ICR, mass spectrometry, petroleomics, molecular composition