Società Chimica Italiana
Divisione di Spettrometria di Massa

Università di Catania

Book of Abstracts

Different applications of the Liquid Chromatography coupled to Isotope Ratio Mass Spectrometry (LC-IRMS)

M. Perini[1], M. Pellegrini[2], S. Pianezze[1]

[1]Centro Trasferimento Tecnologico, Fondazione Edmund Mach, San Michele all'Adige (TN), Italy
[2]Thermo Fisher Scientific S.p.A, Rodano (MI) -Italy

Summary: *The liquid chromatography interface coupled with IRMS permits the compound-specific $\delta^{13}C$ analysis of non-volatile and water-soluble compounds in complex mixtures without resorting to derivatization. Applications in paleoarchaeology, nutrition and trophic, pediatrics, soil science and food genuineness are examined here by reporting the progress and the technical constraints.*

Keywords: *stable isotope ratio analysis, liquid chromatography*

1. Introduction

Isotope Ratio Mass Spectrometry (IRMS) is a mass spectrometry technique aiming to measure the relative stable isotopic abundances of the elements that comprise a specific material. The stable isotope ratios of carbon ($^{13}C/^{12}C$), hydrogen ($^{2}H/^{1}H$), oxygen ($^{18}O/^{16}O$), sulfur ($^{34}S/^{32}S$) and nitrogen ($^{15}N/^{14}N$) are usually measured to provide information about the geographical, chemical and biological origin of substances.
The IRMS can be coupled with different types of devices, in particular liquid (LC) or gas chromatographs (GC), so that the separation of the specific compounds in the studied matrices is performed before measuring the isotope ratio. The association between the liquid chromatography and the isotope ratio mass spectrometry (LC-IRMS), although more recent than the GC-IRMS, has an undisputed potential that will be here illustrated.

2. Results and Discussion

The three most commonly used liquid chromatographic techniques coupled with the IRMS are thereafter described. Ion exchange chromatography (technique 1) was used for the determination of the carbon isotope ratios of carbohydrates, amino sugars and amino acids. However, it is difficult to completely resolve the proteinogenic amino acids when adopting ion exchange as the only mechanism of separation. The resolution of many amino acids can be consistently improved by using a reversed phase (RP) column (technique 2). Almost all amino acids can be resolved by mixed mode chromatography (technique 3), i.e., the combination of RP and ion exchange interaction sites in the same stationary phase, which is today the most published method for LC-IRMS analysis of non-derivatized amino acids. The compounds that can be studied by applying this technique range from carbohydrates (in honey and sweet wine for the identification of sugar adulterations or for the study of human glucose metabolism and in the environmental field), to organic acids (such as citric acid fraudulently added in juices), to amino acids and polypeptides (for the separation and the measure of the ^{13}C isotope enrichment of non-derivatized amino acids in ecological, nutritional, trophic and pediatric studies) and to herbicides.
Recently, the application of high temperatures to the mobile and stationary phases (HT-LC-IRMS) was proposed as an alternative approach to increase the elution strength of aqueous eluents in reversed phase LC. This specific variant of the method has so far been applied to two matrices only: caffeine and pharmaceutical products.

3. Conclusions

The LC-IRMS is a powerful tool for the analysis of a wide variety of different matrices and can be applied to different research fields, as shown by several studies. Compound-specific isotopic analysis can be much more informative than the bulk one, and the technological advances that make it possible to isolate a specific compound before the isotopic analysis by an LC interface lead to the opening up of broad perspectives.
The LC technique proves to be an effective alternative approach to the GC technique, offering the advantage to avoid the derivatization of the sample, which can lead to unwanted fractionations.

References

1. M. Perini, L. Bontempo; Liquid Chromatography coupled to Isotope Ratio Mass Spectrometry (LC-IRMS): a review, *TrAC Trends in Analytical Chemistry*, 147 (2022), pp 1–11.

,

.