Exploiting the combination of NMR spectroscopy and mass spectrometry for the metabolic profiling of solid matrices

Linda Molteni[1], Alessandro Palmioli[1], Carlotta Ciaramelli[1], Maura Brioschi[1], Luca Moretti[1], Cristina Airoldi[1]
E-mail: l.molteni@campus.unimib.it
[1] Department of Biotechnology and Biosciences, University of Milano-Bicocca, Piazza della Scienza 2, 20126 Milano

Keywords: HR-MAS-NMR, HR-MS, metabolic profiling, solid matrices, food, flour

The metabolic profiling of biological samples provides crucial insights into several physiological and pathological processes. Due to high dynamic concentration ranges, extensive chemical diversity and different physical properties, the comprehensive characterization of complex samples may represent a true analytical challenge[1]. In this scenario, advanced analytical techniques, such as Nuclear Magnetic Resonance (NMR) spectroscopy and Liquid Chromatography coupled to High Resolution Mass Spectrometry (LC-HRMS), represent the “gold standard” for the in-depth characterization of sample mixtures. While both techniques show advantages and disadvantages, their combination represents a powerful option to maximise metabolic coverage and facilitate compound identification and quantification[1,2,3].

NMR- and LC-MS-based metabolic profiling of complex matrices, such as whole cells, biopsies, or food flours, is usually carried out at the liquid state after metabolite extraction. Such approaches involve time-consuming sample manipulation; also, since extraction efficiencies are strictly metabolite-dependent, both relative and absolute quantification may be affected. To tackle this problem, the application of NMR analysis under High-Resolution Magic Angle Spinning (HR-MAS) conditions and HR-MS employing the Atmospheric Solids Analysis Probe (ASAP) may be considered[4,5]; these techniques allow indeed the direct analysis of semi-solid and solid samples with minimal to no sample preparation.

Here, we report the application of both techniques to the analysis of metabolites contained in five different food flour samples (rice, quinoa, chickpeas, faba beans, and lentils). Data collected by extraction and analysis at the liquid state were compared with data provided under HR-MAS NMR and ASAP HR-MS conditions from both a qualitative and quantitative point of view. Once validated, this direct approach will be very useful for rapid anti-fraud checks of foodstuffs; also, it will increase the versatility and speed of NMR and MS analysis in resolving complex mixtures of organic compounds in a wide range of applications, minimizing solvent usage and environmental impact.

1. Marshall, D.D., Powers, R., 2017. Progress in Nuclear Magnetic Resonance Spectroscopy 100, 1–16.
2. Larive, C.K., Barding, G.A., Dinges, M.M., 2015. Anal. Chem. 87, 133–146.
3. Theodoridis, G.A., Gika, H.G., Want, E.J., Wilson, I.D., 2012. Analytica Chimica Acta 711, 7–16.
4. Corsaro, C., Cicero, N., Mallamace, D., Vasi, S., Naccari, C., Salvo, A., Giofrè, S.V., Dugo, G., 2016. Food Research International 89, 1085–1094.
5. Fussell, R.J., Chan, D., Sharman, M., 2010. TrAC Trends in Analytical Chemistry 29, 1326–1335.