CONCORSO PER L'ASSEGNAZIONE DI BORSE DI STUDIO DI DOTTORATO DI RICERCA

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TITOLO DEL PROGETTO: Liquid Electron Ionisation ("LEI") and Chemical Ionisation ("CI") technology to address capability gaps in active ingredient ("AI") measurement to support crop protection development and registration
RICERCA PROPOSTA - Abstract: Explore the impact of key factors on matrix and detection interference at the point of analysis by employment of a new LEI technology adapted for addressing matrix interference to improve detection measurement, quantitation reproducibility with minimum sample manipulation prior to measurement at the point of analysis. Employing LC with LEI source coupled to high resolution and triple quadrupole GC mass spectrometry - According to M4C2 guidelines of PNRR and D.M. 117, the research project proposed by the undersigned Tommaso Grazioso is based on the use of chromatographic and micro-extraction techniques for the analysis of target active ingredients (AI) in environmental matrices in collaboration with Syngenta. The development of new and effective micro-extraction techniques for the sample preparation is important to promote the innovation and technological transfer according to the green chemistry principles in order to reduce the consumptions and the quantity of wastes produced with the analytical methods currently used in analysis laboratory, at the same time micro-extraction techniques represent a valid alternative by the point of view of the cost and time required per analysis. Green Chemistry is an important branch of Chemistry because in this historic period the respect and preservation of the environment is of crucial importance, in the field of Green Analytical Chemistry further research is needed to develop new analytical methods with a lower environmental impact through a lower consumption of organic solvents and reducing the number of steps in the sample preparation, micro-extraction represents one of the most interesting possibilities by this point of view and it's continuously in development through the use of new materials and methods. The analysis of pollutants in environmental matrices, but also biological fluids and food matrices, is fundamental for gaining a better knowledge about the distribution of the pollutants in the environment in order to evaluate the hydrogeologic risk due to the climate change, to monitor the presence of new emerging pollutants and to plan reclamation and isolation strategies of the polluted sites to minimize the risk of citizens and workers associated with the exposure to pathogens. The development and optimization of Liquid Electron Ionisation (LEI) and Chemical Ionisation (CI) can represent also an important technological development in the field of hyphenated techniques of chromatography and mass spectrometry and also for the direct coupling of micro-extraction to mass spectrometry for the analysis of complex matrices as those inherent to this research project. Liquid Electron Ionisation has the great advantage, with respect to Ambient Pressure Ionization systems like ESI, of giving the possibility to induce in-source fragmentation, the fragmentation pattern obtained from EI is a distinctive characteristic of the analytes and can be used to perform the identification of unknown analytes in real samples, while using Ambient Pressure Ionization systems structural information can be obtained only through the use of High Resolution Mass Spectrometry (HRMS) or tandem mass spectrometry (MS/MS)(Marittimo et al., 2022). An example of the instrumental set up for the coupling of Microfluidic Open Interface (MOI) with LEI-MS/MS systems is reported in Figure 1.

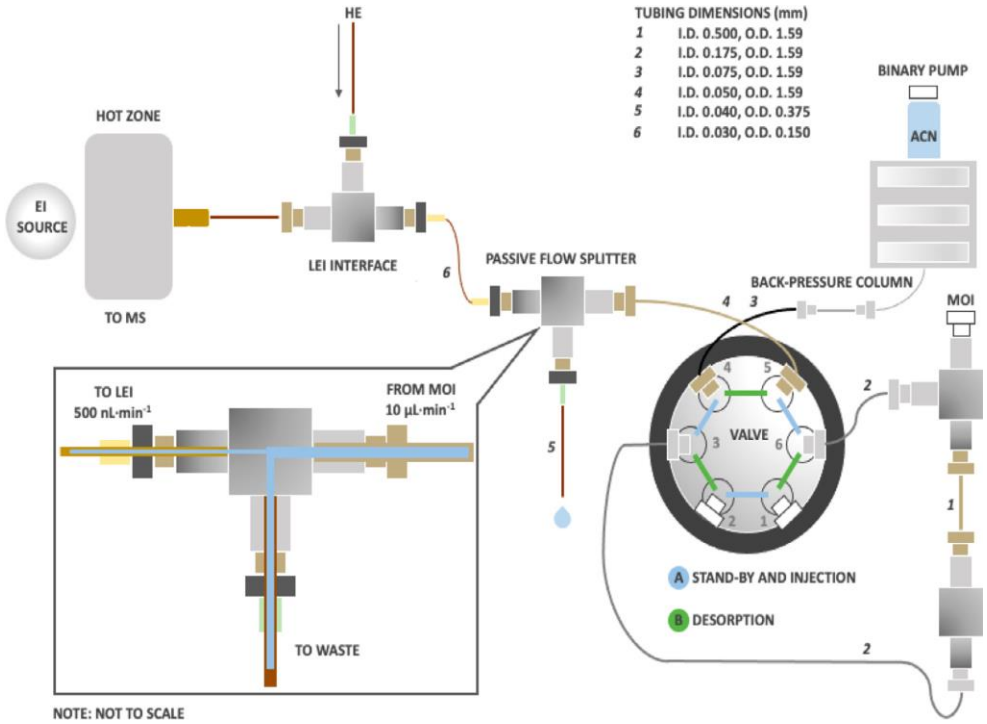

Figure 1. Scheme of the MOI-PFS-LEI-MS/MS system. (Marittimo et al., 2022)

In the three years of research planned for this program, the purpose of the undersigned is to work on the development of LEI-based methods for the analysis of the selected active ingredients through the optimization of the instrumental set up and parameters and optimizing the micro-extraction and its coupling with the analytical instrument. About the micro-extraction step for the sample preparation, several methods will be tested (e.g. SPME fibers with different extraction phases to evaluate the extraction efficiency of the different coatings, but also other micro-extraction techniques could be employed to improve the extraction efficiency) in order to develop a method that has low matrix effects and a sensitivity in line with the recommended detection levels. This can be done through the use of a well-suited extraction phase for the extraction of the active ingredients and optimizing all the extraction parameters. The developed methods at the University of Urbino will also be evaluated during the 6-18 months collaboration with Syngenta at Jealott's Hill International Research Centre, Berkshire, UK.

Bibliography

Marittimo, N., Famiglini, G., Palma, P., Arigò, A., & Cappiello, A. (2022). Enhanced microfluidic open interface for the direct coupling of solid phase microextraction with liquid electron ionization-tandem mass spectrometry. *Journal of Chromatography A*, *1681*. https://doi.org/10.1016/j.chroma.2022.463479