From inorganic to speciation challenges: 2D to 3D applied to environmental and food applications. A long journey.

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Atomic spectrometry delivers a 1 D information that is the concentration of the analytes in the detector. However, inorganic constituents are very seldom present in the matrix as free ions. They are often engaged under different molecular structures, inorganic complex, organometallic moieties, belong to large biomolecules or have specific spatial arrangements when dealing with solids. So inorganic concentrations are not enough to understand processes, toxicity and impacts of elements in the environment, to the biota or to unravel industrial processes. There is the need for a second dimension of information with regards to inorganic detection. Indeed, by promoting the hyphenation to atomic detectors such as AAS and AFS, after cryofocusing, were where able to reach already detected chemical species of Sn, Hg, Pb, Se,.. below the ppt level or ng/L. The development of a new ethylation technic for the derivatization of selected metals and metalloids, allowed to promote the concepts of environmental speciation. This made the sample preparation simpler and quicker, by improving the sample preparation time from 24 hours down to 3 minutes when also using microwave assisted chemistry. When coupling this system to ICP/MS, the hyphenation of cryofocussing to plasma-based detection provided unprecedented sensitivities and allowed to unravel original and novel environmental pathways including the volatilization of metals and metalloids to the atmosphere. Then, the introduction of isotopically labelled compounds combined with the multichannel (multi-isotopic) possibilities of ICP/MS, opened also a new way to understand the reactivities during the sample preparation and implement some advanced correction techniques for fragile species undergoing interconversion during the sample preparation.

Another dimension was also added when coupling GC based techniques where hyphenated to Multi-collector ICP/MS. We were then in a position to merge the speciation information with isotopic detection. A new world. Indeed, the different species of the same elements do not have necessarily the same isotopic signature, promoting also a new array of fundamental environmental pathways and reactivity assessments. This road is still to be fully developed for improved environmental understanding. The fractionation of the elements gives us now a new reactivity understanding of the process that the elements have been undergoing. These information’s here also improve our global understanding of the reactivity of the elements of interest and their pathways in the environment.

Then, direct solid analysis was also developed in parallel with the first generation of Femto-second laser ablation systems. Hyphenating them to High resolution ICP/MS allowed to address new scientific questions.

In 2012, we were fortunate to be awarded the MARSS project (Center for Mass Spectrometry for Reactivity and Speciation Sciences). The originality of this unique platform is to go beyond the speciation concept that we know and

integrate speciation concepts from the isotopic level to 3D imaging in environment, life, material and industrial applications. 4 different mass spectrometry platforms were developed and are complementary within the concept of advanced speciation analysis. These platforms include an HR MC ICP-MS for high resolution and high sensitivity elemental and isotopic measurements and in hyphenation with separation techniques to advanced elemental speciation. The lager molecule identification was provided by the latest series of Orbitrap (LUMOS) providing unmatched high mass resolution. To reach the 3D dimension, a Nano SIMS contributes elemental and isotopic imaging at the nanometer scale which is indispensable within this concept for a localization of elemental species in biological cells or on small surfaces. Finally, a TOF-SIMS is for elemental and molecular analysis of the first single layers of atoms and molecules on surfaces. These combined new complementary platforms allowed: (i) novel speciation research pathways, (ii) new instrumentation developed with the manufacturer partners of the platform (Nu Instruments, CAMECA and THERMO).

We will ramble through the different instrumental developments made throughout these years with the only objective in mind: see better and understand the mechanisms involved in elements from the isotopic up the biomolecular level. We will present the key developments and highlight some of the latest developments.