



XA0103436

## **Trace Metal Speciation: Finally, Correctly Addressing Trace Metal Issues**

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*Status of trace metal speciation analysis* : The concept of trace metal or metalloid "speciation " has seen considerable evolution of its appreciation amongst the inorganic analytical chemistry community during the last 20 years. Together with the progress of analytical instrumentation and analytical schemes, the perception of issues related to species identification will bring a new insight into the use and applicability of trace metal species determination. Increasing numbers of inorganic analysts have become aware of this analytical approach.

If everyone now agrees of the importance of the chemical formulation concept, one can wonder why this analytical approach is so limited within the analytical inorganic community to date. There are certainly a number of different reasons for this state of affairs. There is no order of priority between the different factors given below and they have certainly combined to limit the widespread determination of metal species content and the use of speciation information.

One of the first reason is the lack of availability of commercial instrumentation. *Figure 1* displays the current status of commercial instrumentation developments and compares the evolution of the inorganic field against that of the organic field. Both analytical domains have developed in different directions. The organic field has always been directly orientated towards the molecular identification of the analyte of interest. It has immediately taken advantage of the rapid developments of both liquid and gas separation sciences. Initial analytical efforts were directed towards structural identification rather than being aimed at complete analyte recovery and sensitivity issues. The instrumental translation of these analytical efforts have resulted in the optimisation of mature hyphenation systems between separative methods and refined mass detectors. On the other hand, the inorganic field developed the necessary methodologies to ensure complete matrix dissolution in order to optimise atomisation procedures and make the best of atomic spectrometry techniques for quantitation. In the inorganic field, analytical efforts have been directed towards achieving high analyte recovery factors and improvement of detection limits. The analytical trends have seen the development of atomic absorption instrumentation reach maturity and slowly become eclipsed by the gradual rise of multi-elemental detection techniques based on inductively coupled plasma ionisation sources incorporating atomic emission or mass spectrometric detectors. Most recent instrumental efforts address improved detection limits, fast data acquisition and reduction of interferences generated in the plasma by the use of collisions cells or high resolution scanning mode on the mass analyser.

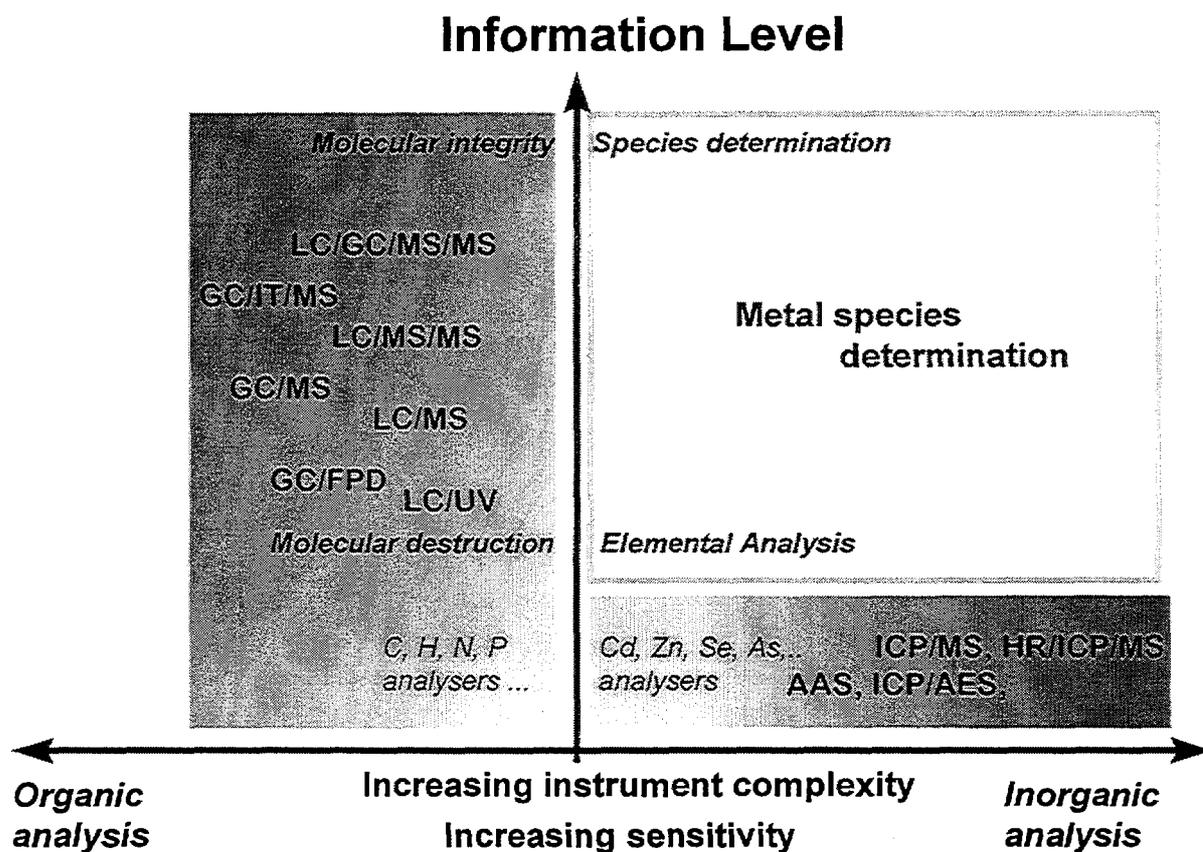


Figure 1 : Status of metal species determination in the field of analytical instrumentation.

These developments have required constant spectroscopical, physical improvements of the detectors and have left aside the need for metal species preservation at the detection stage. Issues to be addressed through metal determinations have been forgotten compared to the increasing attention paid to improved instrumental performances. This fact has biased our appreciation of metal related problems since all analytical determinations in inorganic analysis required the complete destruction of the metal species of interest to only select the bare metal atom for detection and quantitation in the spectrometer. All scientific and legislative issues have then been adapted to this instrumental approach despite the “inaccuracy” of the problem being considered. However, if we were to translate the inorganic analysis considerations in terms of the analytical strategies used in the organic analysis domain, it would be the equivalent of trying to evaluate the dispersion of organophosphorus pesticides in a field by determining the total amount of phosphorus in a sample!

However evolution towards metal speciation is not easy since the analytical market is well established and renewing itself with more sensitive equipment. Regulations follow this trends and are logically relying on the most common information available delivered by inorganic instrumentation. This feed back loop has slowly created the gap between rational decision making based on metal species determination and a simplified approach using total metal determination. Finally, speciation analysis not only requires good mastery of the spectroscopy and its fundamental physics, but it also requires controlled, reliable and reproducible chemistry which is a fundamental pre-requisite prior to spectroscopic detection. This part of the whole analytical process is more complex to control and has also prevented routine developments.

A less obvious negative reason can certainly be associated with the poor appreciation of the toxicity of some metal species due to the scarcity of the data available. Indeed organometallic species of Hg are far more toxic than their inorganic counterparts. Cr (VI) is a well established carcinogenic agent whereas Cr(III) is sometimes supplemented in food. Trialkyltin compounds can be considered to be some of the most toxic biocidal agents ever synthesised and directly released in the environment.

Inorganic tin is non toxic and is present in the tin can containing food. Legislative attitudes to controlling tin in foodstuffs are ambiguous because of the difficulty of obtaining reliable information due to the lack of routine instrumentation. This ambiguous position is reflected in a recent EC regulation. EC regulation 76/464 recommends the control of a list of 132 substances in industrial effluents. If organic compounds are most of the time listed with their full chemical formulation, recommendations towards metal species are either very vague (e.g. Arsenic and its inorganic forms, Mercury and its organic derivatives, Cadmium and its compounds etc) or are too accurate and lists the full formulation with the counter ion. This is the case for organotin compounds. This accuracy is misplaced since most metal species determination methods use a derivatisation stage for gas chromatographic separation methods and therefore use the substitution of the counter ion. Very few routine laboratories can offer the full service for the complete control of the 132 substances in the industrial effluents.

**Environmental issues :** Environmental research has clearly established now that metal and metalloids occur in the environment under a large array of chemical species. They seldom occur at low concentrations as free metal ions and are most of the time engaged in most complex formulation as inorganic salts, oxyhydroxydes or charged or neutral organometallic entities. They can also be found integrated into larger molecular structures (amino-acids, proteins, metalloenzymes,) belonging most often to the biological world.

All these different chemical species are in continuous chemical evolution and kinetic interchanges between the different compartments of the ecosystems. It has been now well established that the chemical species of a metal closely regulate its basic physico-chemical properties (liquid/solid and liquid to gas partitioning) and hence, its mode of bioaccumulation in the food chain. They also regulate the toxicity of the chemical species to the biota directly. This knowledge is the result of the continuous evolution of the biogeochemical approaches developed by environmental geochemists and biogeochemists with very crude analytical tools and solid chemical reasoning.

In the early 1950's, aquatic geochemists first made the distinction between "dissolved metal" and "particulate metal" fractions in order to improve transport models in waterways. A simple filtering membrane of 0.45  $\mu\text{m}$  and a clean filtration unit allowed the two different phases to be discriminated between. The simultaneous and rapid development of electrochemistry allowed free and complexed metal species in water to be distinguished between bringing them the first analytical "speciation" schemes. The early developments were backed with inorganic equilibrium simulation calculations. The first global speciation approach was published in the 1970's by Florence and Batley in a paper where they carefully differentiated between different metal fractions in water by using preconcentration Chelex 100 protocols, irradiation, or not, of the fraction collected and final detection by electrochemistry or atomic absorption. At the same time, the first instrumental hyphenation between a gas chromatograph and a flame atomic absorption spectrometer was achieved by Kolb *et al* to determine alkyllead compounds in gasoline.

Later, the sequential extraction scheme proposed by Tessier *et al* was announced to open improved understanding of the metal partitioning in the different mineral phases of environmental particulate material. Most of the developments mentioned previously have

now been seriously reconsidered, but they are all a vital testimony of the efforts made by the environmental scientific community to improve the knowledge of the metal and metalloids species migration in the environment.

Analytical instrumentation has followed the changes of metal speciation schemes and the advent of improved hyphenation techniques between separative methods and atomic spectrometry detectors have allowed the chemical formulation of the analyte of interest among its matrix to be directly addressed (*Figure 2*). They have contributed to shift the “concept of metal speciation” rather vague and involving the application of different chemical schemes address the “operationally defined” partitioning of metal and metalloids within the different fractions of the matrix to the direct metal and metalloid “chemical species” identification procedure. The term “speciation” still comprise different analytical strategies used and does not offer the full potential offered now by modern analytical instrumentation. It should and can now be replaced by “chemical species determination”. The IUPAC commission is also making progresses in this direction. It has not fully stated of the exact content of the term “speciation” but is referring to it as : 1) the distribution of an element between its different chemical formulations and 2) the analytical efforts deployed to determine the chemical formulation of an element.

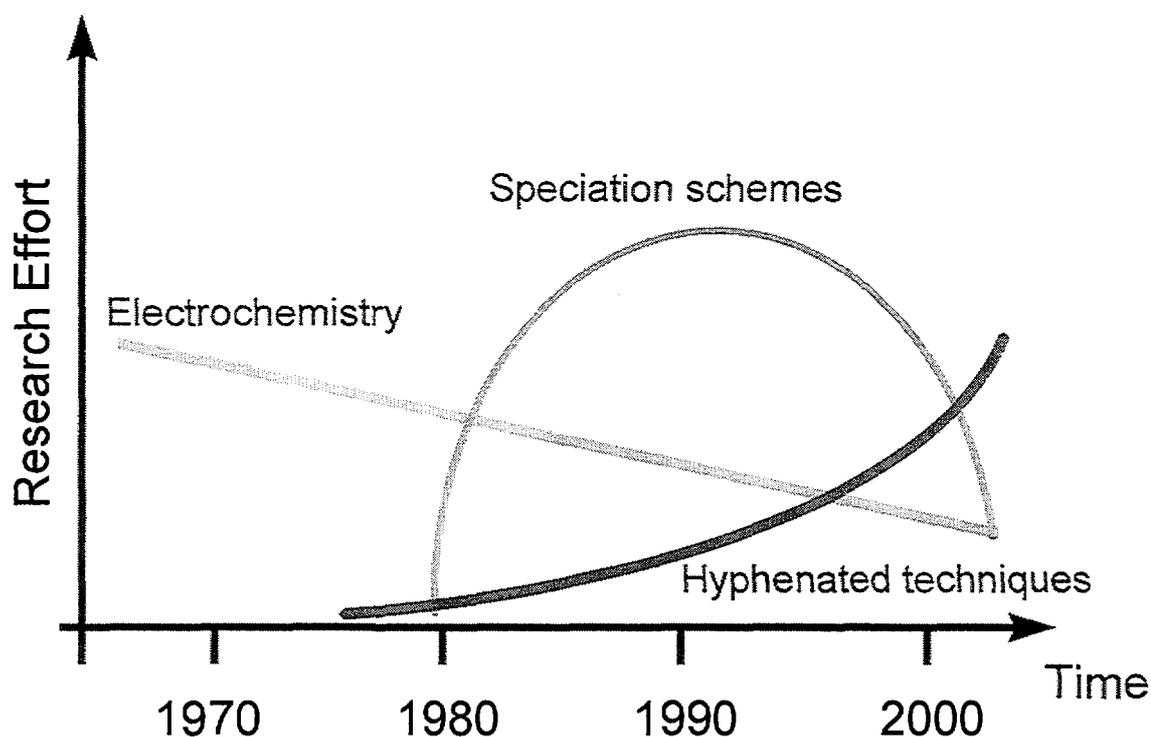


Figure 2 : Evolution of “speciation” trends.

**Analytical developments :** If trace metal analysis has always involved different steps that are critical all along the analytical chain such as sample collection, preservation and preparation prior to detection in the atomic spectrograph, these states have gained further importance when dealing with metal species determination.

**Conclusion :** Further to the analytical progress to be expected in the future, this analytical approach will redesign our understanding of the fate and impact of metals in the ecosystem. Analytical instrumentation will always remain as one of the vital pathways to correctly assess and control quality criteria of our environment (Figure 3). In the future, one must expect that in many fields, the term “speciation” will be replaced by “Risk assessment” for an improved and more rational control of our environment. Also, the need for commercial analytical instrumentation is urgent.

We can consider that major analytical solutions for traces metal speciation are now scientifically mature and that most of the efforts required to make speciation information applicable to detailed quality of life improvements will simplify the existing procedures and

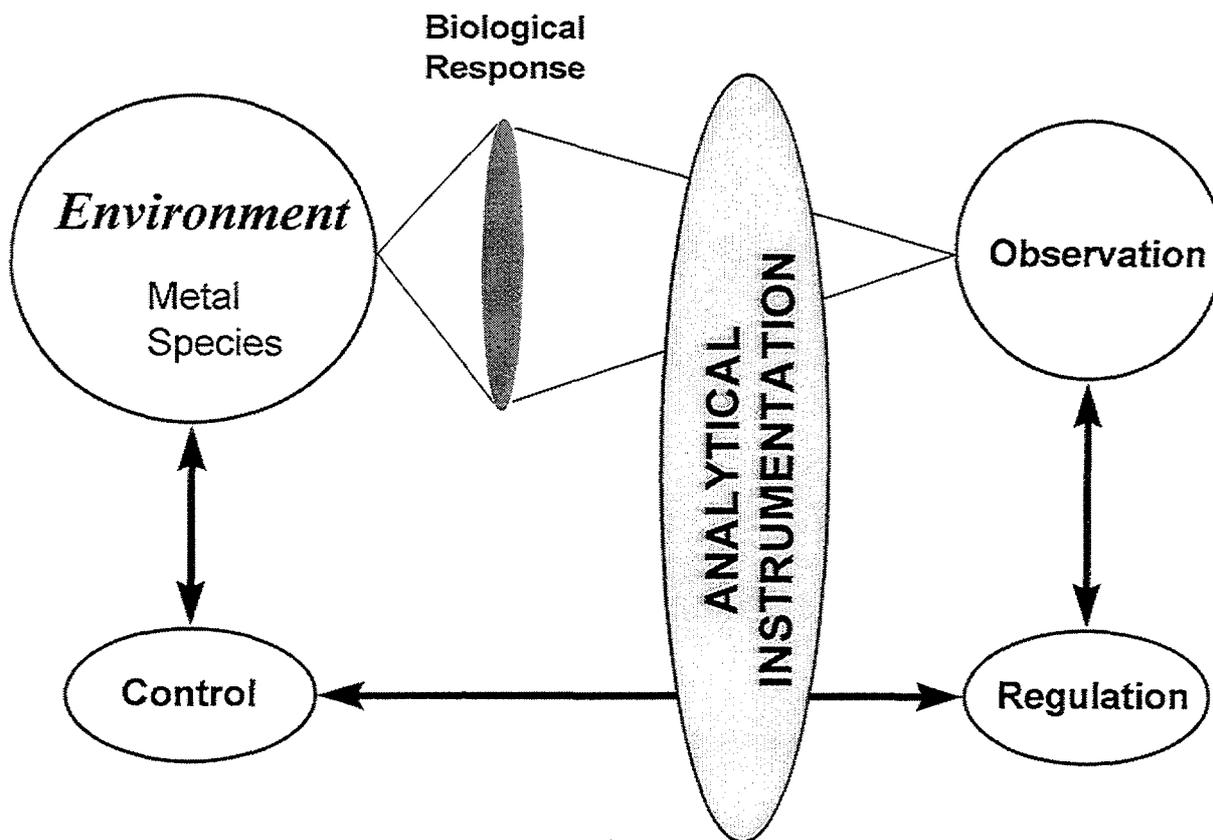


Figure 3 : Analytical instrumentation and environmental quality

introduce cost effective analytical instrumentation. This trend is already foreshadowed in the market place since several companies are currently considering the introduction of instrumentation specifically designed for metal species determination. The introduction to the market of reliable commercial instrumentation will allow a vast community to redevelop and reconsider many analytical developments. These branching developments are needed to find innovative solutions, confirm the existing knowledge or reveal profound artefacts in the field of trace metal species determination

These developments will render total metal determination obsolete and will help to establish a sound knowledge base in this complex field of analytical instrumentation. Their applications will slowly change our perception of the world we live in by defining more rational

approaches to the problems which confront us all and enable improved decision making scenarios.