Anal Bioanal Chem (2002) 373 : 123–124
DOI 10.1007/s00216-002-1304-0

EDITORIAL

Rita Cornelis

Speciation of trace elements: a way to a safer world

Published online: 1 May 2002

The concept of trace elements was introduced at the beginning of the twentieth century. Scientists knew that there were elements present at very low concentrations in all kinds of materials. They even assumed these to have a potential function in life or to influence the characteristics of materials. As they could hardly say which elements were involved, they surely were incapable of quantifying them. At the end of the twentieth century, analytical techniques had been developed to the point where picogram or lower amounts of nearly every element could be measured with good precision. Today, analysts are preoccupied with the species or chemical forms of the elements, as these determine most of their properties.

Chemical speciation and fractionation of elements now belong to the well-established chemical nomenclature as defined by IUPAC (International Union for Pure and Applied Chemistry) [1]. Chemical species denote the specific form of an element defined by its isotopic composition, electronic or oxidation state, and/or complex or molecular structure. It is, however, often not possible to determine the concentration of the different individual species that sum up the total concentration of an element in a given matrix (e.g. in metal-humic complexes or metal complexes in biological fluids), which means that it is impossible to determine the speciation. The practice is then to identify various classes of species of an element and to determine the sum of its concentrations in each class. Such fractionations can be based on many different properties of the chemical species, such as size, solubility, affinity, charge and hydrophobicity.

In recent years, trace element speciation has become an important concern in a wide variety of fields: food, environment, health, product-quality, etc. It is no longer a purely academic subject; various industrial sectors, government and legislative bodies are all involved [2]. Today it has become clear that mobility, bioavailability, storage, retention and toxicity of trace elements in living systems, food and the environment depends on the chemical form in which it enters the system and the final form in which it is present. The form, or species, clearly governs its biochemical and geochemical behaviour. Throughout the twenty-first century, analytical laboratories will be challenged to develop elemental speciation techniques for an ever-widening variety of species, at ever lower concentrations.

Synthesised substances of anthropogenic origin make up a major new category of species that must be investigated. The most ill famed are the organotin compounds, widely used as broad-spectrum biocides. It is well known that the abundance of these compounds in the aquatic environment has triggered a number of serious adverse effects in ecosystems. Although it has been hitherto claimed that organotin compounds in food pose only a negligible risk, it may be anticipated that the concentrations of these compounds in fish and seafood are on the increase [3]. There is no scientific basis for the statement that there is "only a negligible risk to humans". Convincing knowledge is completely lacking. The only sure thing is that before their introduction by man into the environment, their concentration was zero. The moral of this story is that, to ensure the quality of life, society has the duty to measure and follow the transformation of any compound that is released into the life cycle on a large scale.

It is also possible that an element is leached into the environment at low concentrations but on a large scale, in a form with low toxicity, similar or identical to that in which it occurs in nature. The element may subsequently be transformed into one or more toxic forms through the intermediary of living organisms at the bottom of the food chain, only to reach dangerously toxic levels in the top predators. The best example of this is mercury. Inorganic mercury is methylated through the action of enzymes and becomes highly toxic methyl mercury.

Although trace element species came into the limelight mainly because of the detrimental effect of impurities on the environment or the food chain, there can also be beneficial effects due to the presence of particular species of essential trace elements in food.

The connection between bioavailability and trace element species in food is being unravelled for a limited number of elements. The best documented of these is iron. A very puzzling element is selenium, as apparent from the number of research papers trying to identify a potent can-

R. Cornelis (✉)
Laboratory for Analytical Chemistry, University of Gent,
Proeftuinstraat 86, 9000 Gent, Belgium
e-mail: rita.cornelis@rug.ac.be

cer-protecting selenium compound. The most enigmatic element is chromium because of its alleged beneficial characteristics in sugar metabolism, referred to as the glucose tolerance factor of hitherto unknown composition. Last but not least, it is necessary to mention arsenic because of the baffling fact that a substantial number of arsenic species are non-toxic, contrary to the general belief that arsenic is a toxic element. There can be no doubt that the inorganic forms of arsenic (i.e. arsenite and arsenate) are toxic species. Humans, other mammals, fish, bivalves, algae – to name just some organisms – apply a detoxifying mechanism for inorganic arsenic through successive methylation steps. The resulting species are monomethylarsonic- and dimethylarsinic acid in mammals, additionally arsenobetaine and arsenocholine in fish and seafood and a variety of arsenosugars, especially in algae. These organic arsenic compounds are considered harmless, although doubts are arising concerning the biosynthesis of toxic intermediates in humans. The other question mark concerns the possible catabolism of the arsenosugars in the human gastro-intestinal tract into more toxic arsenic species. All this needs to be carefully studied. Moreover, legislation about the admissible amount of arsenic in food needs to be revised in view of the newly acquired knowledge of the very low (or non-existing) toxicity of organically bound arsenic species. Some products, such as fish gelatine, may have a total arsenic concentration exceeding the legal norm, but should not be prohibited because of the non-toxicity of the arsenic species that are present.

The least explored domain is without any doubt that of the trace element species in human beings, from the moment they are ingested, inhaled or absorbed through the skin to when they are incorporated in the body or excreted. A lot of fundamental research will be needed to understand the role of trace element species in the human body and to understand how they are essential, neutral or detrimental to human health. The importance of speciation in these matters has already been highlighted in a previous editorial, stressing the importance of learning more about the complexes of proteins and other macromolecules with trace elements [4]. Speciation of trace elements is the only rational approach to unravel the complex mechanisms of interactions between different components of elemental species at the root of beneficial and harmful effects in man.

Occupational hygiene and occupational medicine are very much aware of the importance of elemental speciation. The problem is very well documented in the nickel, chromium, platinum and semi-conductor industries. The chemical form of the element on the surface of the inhaled particulates in the workplace is decisive for the short-term and long-term injuries they may inflict.

Analytical method development for trace element speciation is by no means easy. The underlying reasons are many. As the total trace element concentrations are already very low (e.g. down to ng L^{-1} serum for vanadium), it goes without saying that the trace element concentration in, for example, a given bio-molecule will be even a hundred to a thousand times lower. This puts them out of scope of the existing analytical techniques for trace element measurements. The ultimate goal would be to devise "routine" analytical set-ups with detection limits three to six orders of magnitude lower than whatever has been achieved up till now.

However, the detection of the trace element species is only the last link in a chain of events. Prior to detection there are even bigger challenges, for example, with the sampling. How can a sample remain representative, as far as the trace element species is concerned, once it has been taken out of its natural surroundings? This applies to any type of sample: sediment, sludge, water, blood, urine, tissue, inhalable particulates, etc. Non-covalent bonds of the trace element to, for example, proteins, humic acids, sediments, will be very easily disrupted when the separation occurs in "denaturing" circumstances.

Besides the danger of disruption of the trace element species that is non-covalently bound to the molecules, there is also the opposite effect of capturing random trace element impurities by the ligands of molecules. They act as scavengers for trace element impurities in the reagents, the column fillings, the inner walls of the apparatus and a multitude of other "donors".

These considerations are generating so many difficulties, that it is time to think about alternative ways to perform speciation analysis. To date there are, unfortunately, very few hints as to where to look for them. Is in situ speciation possible in the body, plants or sediments? This is very desirable indeed and perhaps feasible for certain species if some specific microchips could be designed. This would require a very penetrating understanding of the kinetics of the trace element species, which would only be possible for those species that can be measured. How do we get out of this vicious circle?

References

1. Templeton DM, Ariese F, Cornelis R, Danielsson L-G, Muntau H, van Leeuwen HP, Lobinski R (2000) Pure Appl Chem 72:143
2. Ebdon L, Pitts L, Cornelis R, Crews H, Donard OXF, Quevauviller P (eds) (2001) Trace element speciation for environment, food and health. Royal Society of Chemistry
3. Belfroid AC, Purperhart M, Ariese F (2000) Mar Pollut Bull 40:226
4. Lobinski R (2001) Fresenius J Anal Chem 369:113

Rita Cornelis is Research Director at the Flemish National Fund for Scientific Research. Her research is centred around method development for the speciation of trace elements in biological materials, mainly clinical samples. The separation techniques used in her group are various forms of chromatography and gel-electrophoresis. Whenever applicable, method development is done using radiotracers. Detection of the cold trace element is achieved with spectrometry, and identification of the molecules with ES-MS-MS.