ISO Fd Food ERA Chair

Safety Quality Traceability

Speciation of elements in foodstuffs

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SPECIATION OF Al IN FOODSTUFS

Al is not considered to be an essential element in human beings, but its toxic effects are well known, particularly in patients with chronic renal failure.

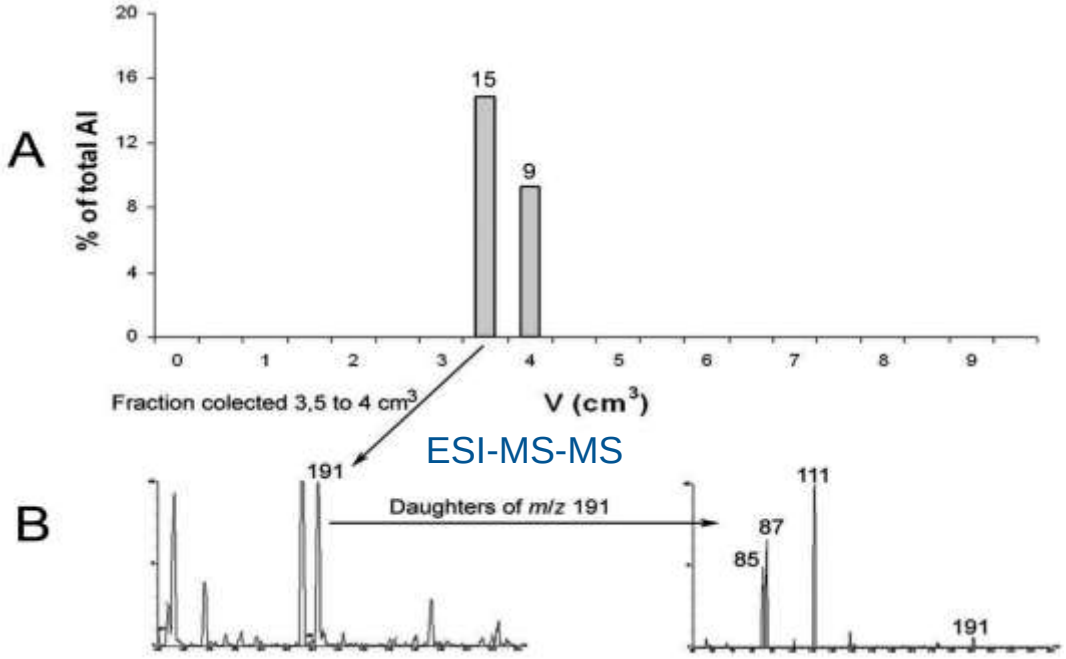
Concern over the possible relation between environmental Al exposure and Alzheimer's disease initiated investigations of the potential intake of Al into the human body, including foods.

The bioavaliability of Al from food depends on its chemical forms and the presence of Al binding ligands.

SPECIATION ANALYSIS IS NEEDED

Anion-exchange FPLC-ICP-AES

Golden Nepal black tea



Al-citrate, the bioavailable species, represents 20 - 35% of Al in infusions of black, green and red tea

Addition of lemon juice does not essentially increase the availability of Al from tea infusion

→ the part of Al-citrate remains practically the same.

Kralj B, Križaj I, Bukovec P, Slejko S, Milačič R, *Anal. Bioanal. Chem.,* 2005, 383, 467-475

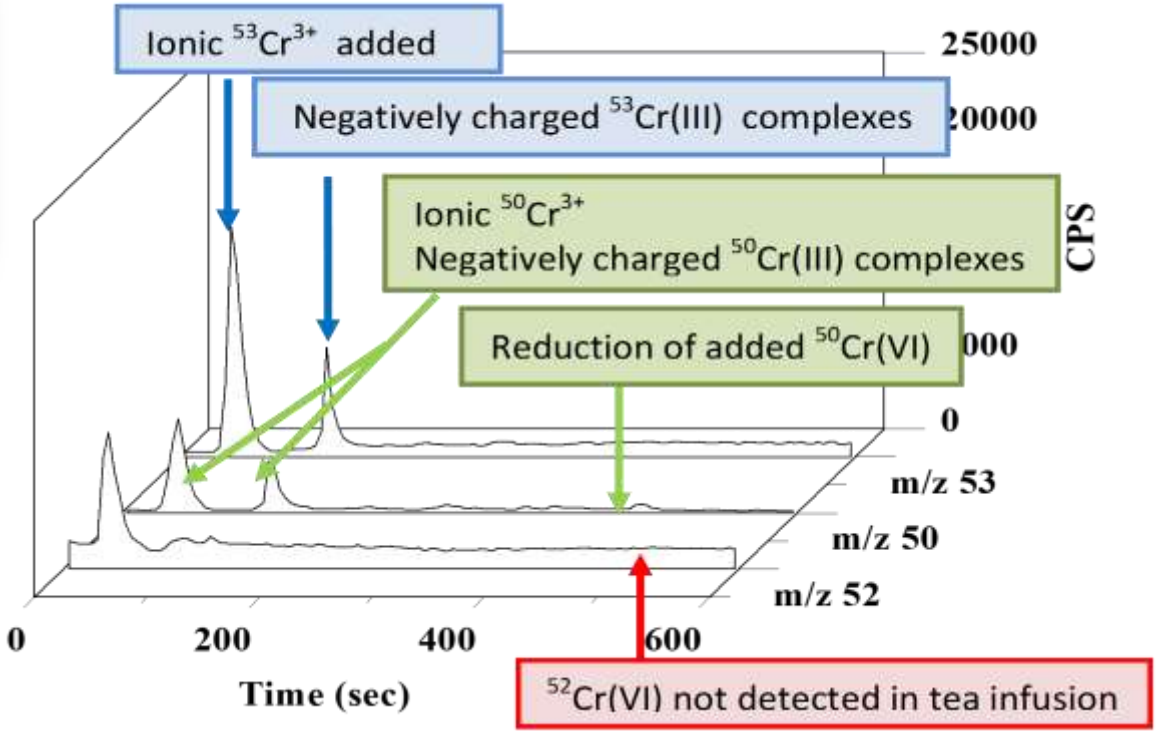
SPECIATION OF Cr IN FOODSTUFS

Cr(VI) is a common environmental contaminant. In the environment Cr(VI) is readily reduced to Cr(III) by organic matter.
Therefore, in biological samples Cr is exclusively present as Cr(III) except shortly after exposure.

Despite this known fact, several papers have been published in recent years on the presence of total Cr(VI) in tea leaves, bread samples and plants based on alkaline extraction and determination of Cr with ETAAS without performing any speciation analysis.

The use of enriched stable isotopes enables to follow species interconversions during the analytical procedure and to accurately quantify Cr(VI) content by speciated ID-ICP-MS.

Use of enriched isotopic spike solutions of $^{50}Cr(VI)$ and $^{53}Cr(III)$ in speciation of Cr by HPLC-ICP-MS in tea infusions and bread samples



Chromate cannot be present in tea infusions and bread

Novotnik B, Zuliani T, Ščančar J, Milačič R, *J. Anal. At. Spectrom.,* 2013, 28, 558-566

SPECIATION OF Zn IN HUMAN MILK

The importance of Zn for normal growth and development of infant has been well documented. Exclusive breastfeeding meets the nutrient needs for Zn, which is in human milk present in highly bioavailable form.

Numerous investigations demonstrated that Zn bioavailability in human milk is for infant much higher than in cow's milk. In human milk Zn is bound to proteins and low molecular mass (LMM) ligands. It was presumed that in the LMM fraction of human milk highly bioavailable species Zn-citrate prevails.

Literature data are controversial regarding the amount of Zn-citrate in human milk, since analytical procedures reported were not quantitative.

Monolithic chromatography with ICP-MS detection and ESI-MS-MS indentification was used to identify and quantify Zn-citrate as the Zn binding ligand.

Sample preparation in speciation of LMM-Zn species in human milk

Human milk sample

Removal of fat

Centrifugation
10 min, 4000 RPM

dilution 1:5

MW digestion

FAAS analysis

Identical values for total Zn concentration

Separation of LMM-Zn from HMM-Zn
Microultrafiltration MWCO 3000 Da, 15 min, 8100 RPM

CIM DEAE-1

FAAS detection:
20 - 25 % Zn in LMM milk fraction

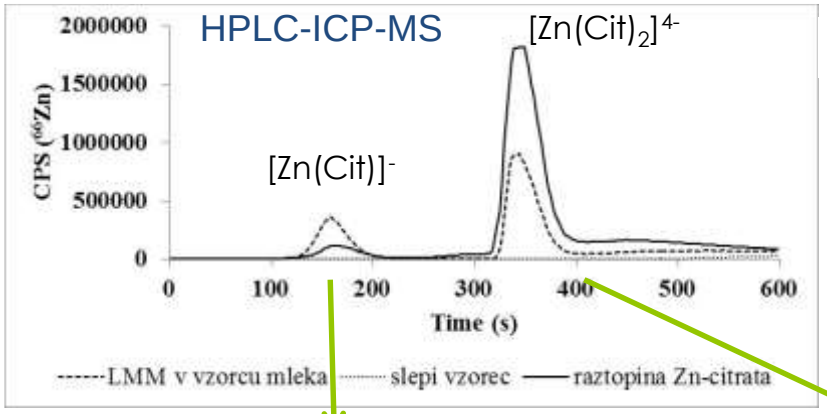
FAAS detection
1 mL fractions

ICP-MS detection

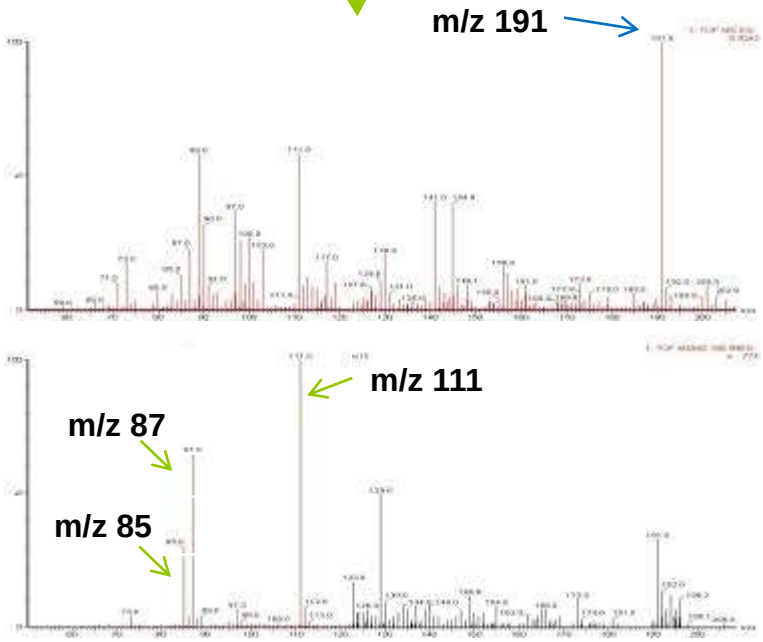
Fraction of 1st and 2nd chromatographic peak

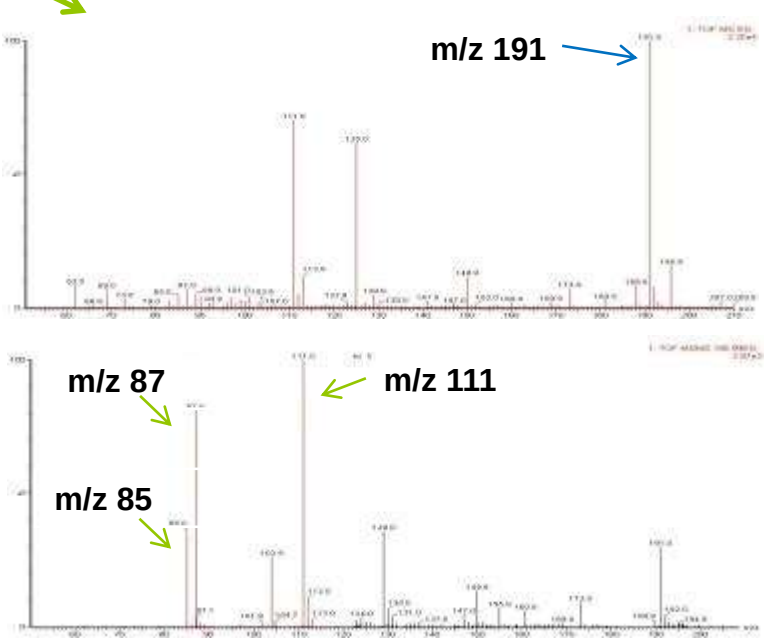
ESI-MS-MS analysis

Zn-citrate in human milk



~ 23 % of Zn is present in the LMM milk fraction as Zn-citrate, which is highly bioavailable species





Milačič R, Ajlec D, Zuliani T, Žigon D, Ščančar J, *Talanta*, 2012, 101, 203-210

SPECIATION OF Ni IN TEA INFUSIONS

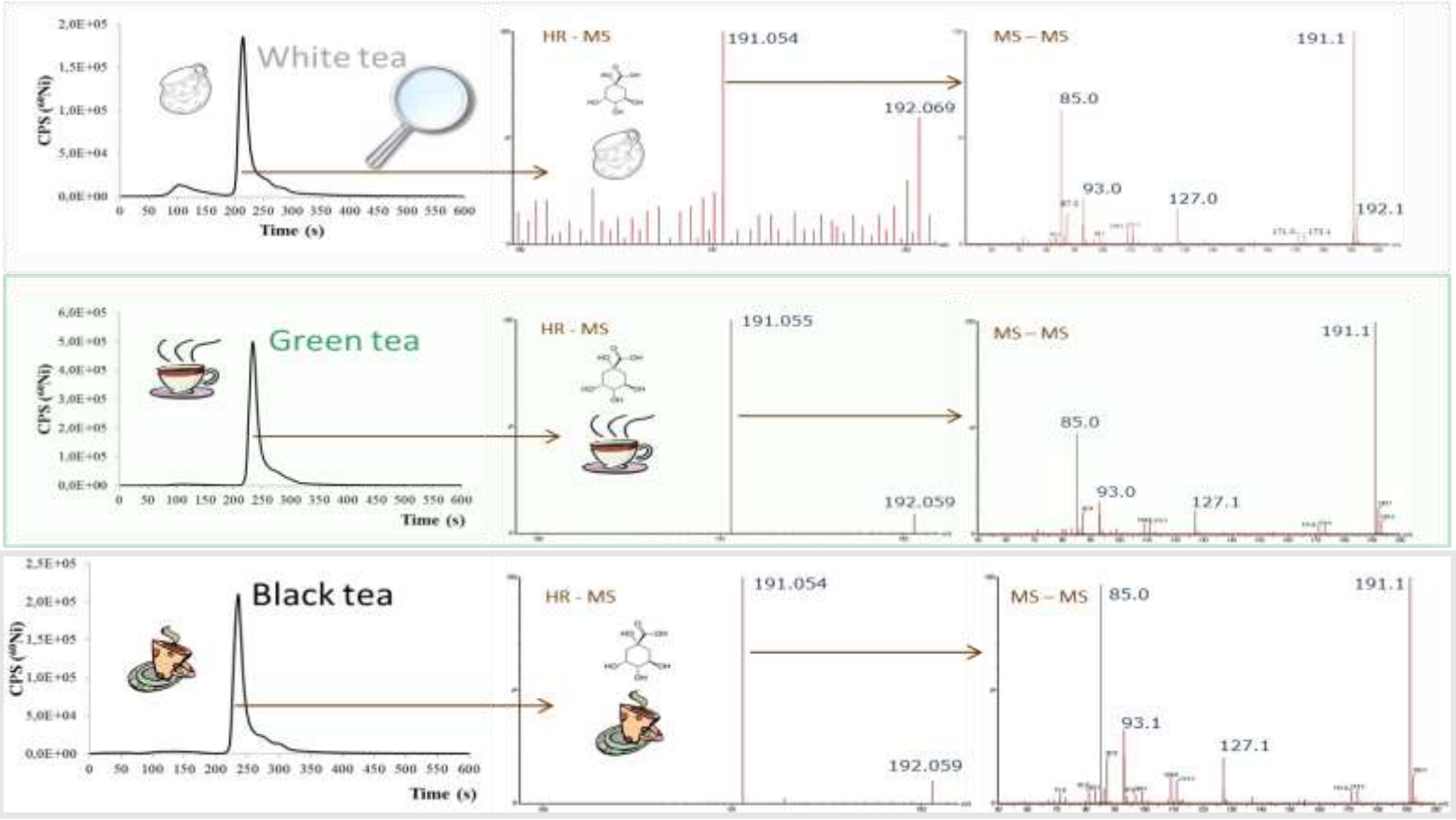
Ni and its compounds at the levels present in average daily diet are generally considered to be safe for consumption.

For individuals who already suffer from contact allergy to Ni and may develop systemic reactions from its dietary ingestion, dietary exposure to Ni must be kept under control.

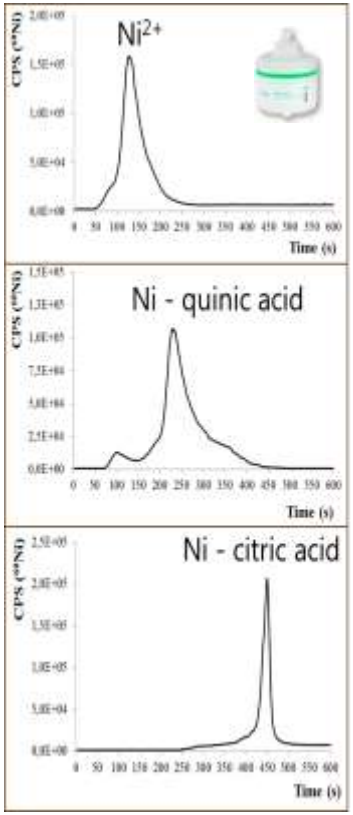
Tea is second, only to water, world's most popular beverage. Its consumption adds a part to daily intake of trace elements, including Ni. So far, little is known about chemical speciation of Ni in food and on the relationship between its speciation and bioavailability.

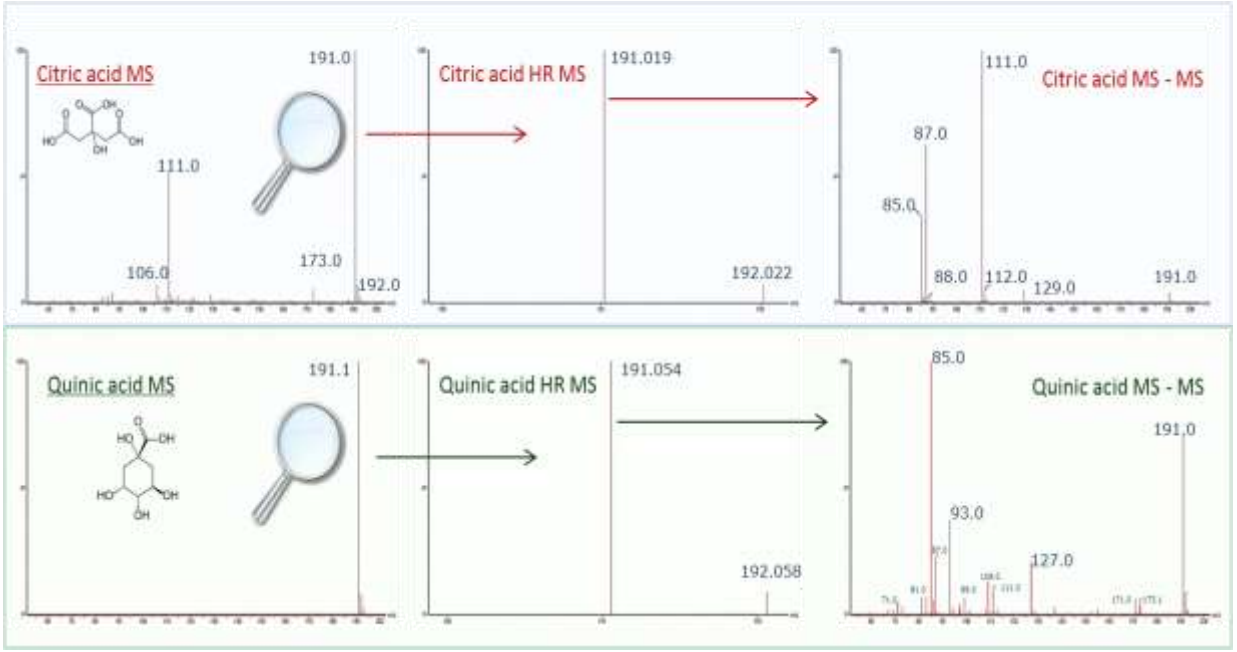
Ni speciation in samples of black, green, red and white tea (Camellia sinensis) as well as herbal tea infusions was carried out by monolithic chromatography with ICP-MS detection. Separated Ni species were identified by ESI-Q-TOF-MS.

Speciation of Ni in tea infusions by monolithic chromatography and mass spectrometry (1)



Speciation of Ni in tea infusions by monolithic chromatography and mass spectrometry (2)





HPLC and ESI-MS-MS analysis revealed that Ni in tea infusions is present as Ni-quinate.

Ščančar J, Zuliani T, Žigon D, Milačič R, A*nal. Bioanal. Chem.,* 2013, 405, 2041-2051

FUTURE WORK

- *Speciation of Zn in foodstufs of plant and animal origin*
- *Speciation of Ni in foodstufs of plant origin*
- *Speciation of organotin compounds in seafood*
- *Speciation of polybrominated diphenylethers in foodstufs*