Quantitative Analysis of Chromium and Arsenic Species in Food and Food Packaging using LC-ICPMS

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1. Overview

Food safety is one of the major concerns of the European population and the European Commission is aiming to assure a high level of food safety and animal & plant health within the EU through the farm-to-fork principle. This implements effective control systems for harmful substances such as pesticides, mycotoxins and heavy metals. Nowadays in food control the speciation analysis has become an important tool for the determination of elements like cadmium, chromium, mercury, tin, and arsenic where simply the measurement of the total amount of the element is not sufficient.

Figure 1: Inductively Coupled Plasma Mass Spectrometer ICPMS-2030 (Shimadzu) connected to the Prominence Inert LC System (Shimadzu)

2. Non intentionally added Substances

The idea is to have a clear identification and quantification of the different species for a better understanding of toxicological impacts on human health, animal health and the environment. In case of arsenic for example the inorganic species arsenite and arsenate have a bigger toxicological relevance than the organic species. For chromium in food packaging the hexavalent species needs to be determined as it is recognized as a human carcinogen and the speciation analysis needs to be performed using the combination of HPLC and ICPMS as applie in figure 1.

Further application example is the arsenic speciation in rice, which is getting more relevant because of the tendency that an increasing amount of people follow gluten free diets (even without having celiac disease) and different products of rice like rice flour are a common substitute of wheat products. As rice is well known to bioaccumulate certain toxic elements like arsenic, special attention has to be paid to avoid any negative consequences for the human health [1].

3. Chromium Speciation in Food Packaging

As early as 1998, the European Union has adopted the Ordinance on the Avoidance and Recovery of Packaging Wastes (VerpackV) and amended it in the most recent version of 2014 [2]. The VerpackV regulates the concentration of harmful substances, such as heavy metals that may be present in packaging materials. Accordingly, packaging or its components may only be put into circulation if the cumulative concentration of lead, cadmium, mercury and chromium VI does not exceed 100 milligrams per kilogram.

The ICPMS-2030 has been used in basic Minitorch setup, enabling drastically lower flow rates of Argon. Even for higher matrix samples the total consumption is below 10 l/min. At the same time the Argon purity requirements for the ICPMS-2030 are on a very low level (min. Argon 3.5 = 99.95 %). The basic method parameters are summarized in table 1 for ICPMS and in table 2 for LC.

Parameter	Setting
RF generator power	1.2 kW
Plasma gas	8 l/min
Auxilliary gas	1,1 l/min
Carrier gas	0.75 l/min
Nebulizer	coaxial
Sampling depth	4.5 mm
Spray Chamber temperature	4 °C
Collision Cell Gas flow (Helium)	4.4 ml/min
Cell Voltage	-10 V
Energy Filter	5.5 V

Table 1: ICPMS 2030 measurement parameters

Parameter	Setting
Mobile phase	30Mm Ammonium Nitrate(V) pH=7,1
Column	Hamilton PRP-X100, 250x4,1mm, 10µm
Sample injection volume	495 µL

Table 2: HPLC measurement parameters

Applying the instrumental parameters for ICPMS-2030 as listed in table 1 and those for HPLC in table 2, excellent sensitivity within low ppt concentration range can be obtained combined with a good calibration curve linearity for both Cr(III) and Cr(VI) (r > 0.9999, as shown in figure 2).

The system configuration consisting of ICPMS-2030 connected to the Prominence Inert LC System is an ideal tool for determination of the hexavalent chromium according to the requirements of the Ordinance on the Avoidance and Recovery of Packaging Wastes (VerpackV).

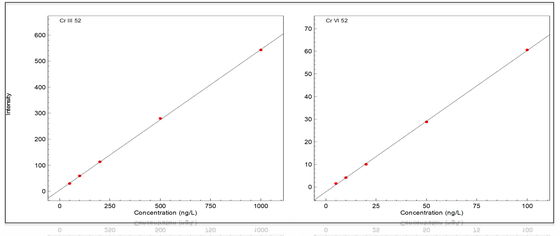

Figure 2: Calibration curve of Cr(III) and Cr(VI)

4. Arsenic Speciation in Rice

In case of food safety, the checking of rice for contaminants is getting more and more important. Over the past 10 years, the global rice consumption is increasing and compared to other leading food crops, global rice production accounted 78% for human consumption, whereat the rate is much lower for wheat (64%) or maize (14%) [3].

Especially when rice is getting the main food source like for some Asian countries or in low-income countries, to ban contaminants or to keep them on a minimum level should be a major goal. The European commission has fixed the maximum levels of inorganic arsenic in Non-parboiled milled rice at 0.2 µg/Kg and rice for the production of food for infants and young children at 0.1 µg/Kg [4].

Parameter	Setting
RF generator power	1.2 kW
Plasma gas	8 l/min
Auxilliary gas	1,1 l/min
Carrier gas	0.6 l/min
Nebulizer	coaxial
Sampling depth	5.0 mm
Spray Chamber temperature	5 °C
Collision Cell Gas flow (Helium)	6.0 ml/min
Cell Voltage	-21 V
Energy Filter	7.0 V

Table 3: ICPMS 2030 measurement parameters

With the described parameters in table 3 and table 4, ion pair chromatography is applied. Different species like As(V), As(III) and dimethylarsenic acid (DMAA) are well separated within 5 minutes (Figure 3).

Parameter	Setting
Mobile phase	10mM Sodium 1-butanesulfonate 4mM Tetramethylammonium hydroxide 4mM Malonic acid (pH=3) 0.05% Methanol
Column	Shiseido Capcell Pak C18 MG S5
Sample injection volume	20 µL

Table 4: Prominence Inert LC Method Parameters

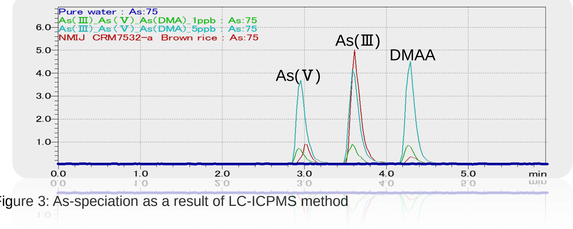

Figure 3: As-speciation as a result of LC-ICPMS method

For checking the method correctness, certified reference material was analysed and the recovery rate is on a very good level (table 5).

Results in [mg/kg]		As(Ⅲ)	As(Ⅴ)	DMAA
White Rice	Measurement Result (n=3)	0.0649	0.0203	0.0138
	Total Inorganic Arsenic	0.0852		-
	NMIJ Certified Value	0.0841 As(Ⅲ)+ As(Ⅴ)		0.0133
Brown Rice	Measurement Result (n=3)	0.251	0.0511	0.0186
	Total Inorganic Arsenic	0.302		-
	NMIJ Certified Value	0.298 As(Ⅲ)+ As(Ⅴ)		0.0186
	RSD(%) (n=6)	1.1		2.6

Tab. 5: Measurement results of certified reference material White Rice: Certified Standard Material (NMIJ CRM 7503-a) Brown Rice: Certified Standard Substance (NMIJ CRM 7532-a)

5. Conclusion

LC-ICPMS is an ideal tool for chromium and arsenic speciation in food and food packaging. Easy method development, routine measurement plus result overview – all is combined in a single software platform and allows the highest level of compliance for food and food safety.