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Accurate Analysis of Chromium in Foodstuffs by Using Inductively Coupled Plasma Mass Spectrometry with a Collision-Reaction Interface

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Food is a common source of chromium (Cr) exposure. However, it is difficult to analyze Cr in complex food matrices by using inductively coupled plasma mass spectrometry (ICP-MS) because the major isotope, ^{52}Cr, is masked by interference generated by the sample matrix and the plasma gas. Among the systems available to minimize interference, the recently developed collision-reaction interface (CRI) has a different structure relative to that of other systems (*e.g.*, collision cell technology, octopole reaction system, and dynamic reaction cell) that were designed as a chamber between the skimmer cone and quadrupole. The CRI system introduces collision or reaction gas directly into the plasma region through a modified hole of skimmer cone. We evaluated the use of an CRI ICP-MS system to minimize polyatomic interference of ^{52}Cr and ^{53}Cr in various foodstuffs. The ^{52}Cr concentrations measured in the standard mode were 2–3 times higher than the certified values. This analytical method based on an ICP-MS system equipped with a CRI of helium gas was effective for Cr analysis in complex food matrices.

Key Words : Chromium, ICP-MS, Collision-reaction interface, Food

Introduction

Microanalysis continues to be a growing tool in the development of science and technology. Accurate microcontent analysis is an essential aspect of various fields such as the pharmaceutical, food and beverage, and environmental industries. Tracing of metals in diverse samples is generally performed by graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma optical emission spectrometry (ICP-OES), or inductively coupled plasma mass spectrometry (ICP-MS).[1] ICP-MS is a multi-element analytical machine in which samples are decomposed into ions in high-temperature plasma and analyzed based on their mass-to-charge ratios.[2,3] The sensitivity of ICP-MS is very high compared to that of other analytical methods; therefore, it is versatile and is widely used for identifying elements present in food samples and for determining their concentrations.[1-5] However, ICP-MS has disadvantages such as the polyatomic masking of specific ions, such as arsenic, selenium, and chromium (Cr), by residual carbon or high chloride concentrations in the sample matrix.[6] In general, interference in ICP-MS is derived from divalent and polyatomic ions from the plasma and from sample matrix components. Therefore, the removal of interference is important for the proper operation of ICP-MS systems.

Naturally occurring Cr is one of the most abundant elements in the earth's crust and has 3 stable isotopes: ^{52}Cr, ^{53}Cr, and ^{54}Cr. With regard to charge, the 3 main forms of Cr are Cr(0), Cr(III), and Cr(VI).[7,8] The general population is exposed to Cr by ingesting various foodstuffs and drinking water containing Cr.[7] Cr is an essential element for normal metabolism and is thus usually present in food in the trivalent form; however, the hexavalent form of Cr is toxic and is not normally found in food.[7,9] In humans and animals, Cr(III) is an essential nutrient that plays a role in the metabolism of glucose and protein.[10] However, the International Agency for Research on Cancer (IARC) has found that Cr(VI) compounds are carcinogenic in humans. Food is a common source of Cr exposure. Total Cr levels in most foods typically range from < 10 to 1,300 μg/kg, and the highest concentrations are found in meat, fish, fruits, and vegetables.[11] In animals, detrimental physiological effects resulting from the ingestion of Cr compounds are observed in the stomach and small intestines (irritation and ulcers) as well as the blood (anemia). The recommended daily intake proposed by the U.S. Food and Drug Administration (USDA) for Cr is 120 μg.[12] The total daily amount (mg/person/day) of Cr intake from typical Korean foods, on an average, was 0.089 in 2009.[13] A relatively high proportion of the Korean population consumes toxic Cr-containing seaweed, as Korea is surrounded by water on 3 sides.[13,14]

It is difficult to analyze Cr in complex food matrices by using ICP-MS because the major Cr isotope, ^{52}Cr, is masked by $^{40}\mathrm{Ar}^{12}\mathrm{C}^+$, $^{35}\mathrm{Cl}^{17}\mathrm{O}^+$, $^{38}\mathrm{Ar}^{14}\mathrm{N}^+$, $^{36}\mathrm{Ar}^{16}\mathrm{O}^+$, $^{37}\mathrm{Cl}^{15}\mathrm{N}^+$, $^{34}\mathrm{S}^{18}\mathrm{O}^+$, $^{36}\mathrm{S}^{16}\mathrm{O}^+$, and $^{35}\mathrm{Cl}^{16}\mathrm{OH}^+$ interference generated by the sample matrix and plasma gas.[5,15] Most major ICP-MS manufacturers are therefore making efforts to eliminate polyatomic interference.[2,4] Examples of these efforts include collision-reaction interface (CRI), collision/reaction cell (CRC) and octopole reaction system (ORS), collision cell technology (CCT), and dynamic reaction cell (DRC). The use of an inert gas such as He to decrease polyatomic interference through collision has been found to be a promising technique for samples with unknown matrix effects.[3] In the beginning stage, a collision chamber, a space located between the skimmer cone and the quadrupole analyzer, was proposed.[3,4] Its major purpose was to remove the interference ions using collision reaction.[16] Subsequently, other devices such as the DRC and the CRI were proposed.[17-19] The DRC is a chamber system that creates a limited bandpass to eliminate some ions made by secondary reactions.[17,18] Among the systems available to minimize interference, CRI has a different structure relative to the CCT, ORS, and DRC.[17-20] The CRI system introduces collision or reaction gas directly into the plasma region through a modified hole of skimmer cone.[19] Several studies have addressed the applications of CCT, ORS, and DRC for complex matrices, whereas for CRI, few reports are available because of the recent appearance of the CRI system in commercial markets.

The purpose of this study was to evaluate the use of a CRI ICP-MS to minimize the polyatomic masking of ^{52}Cr and ^{53}Cr in various foodstuffs for Cr determination. The results were also compared to those obtained in the ICP-MS standard mode.

Experimental

Instrumentation. Cr was analyzed using ICP-MS (Bruker 820-MS; Bruker Daltonics, Billerica, USA). The ICP-MS analysis method is an MS technique that involves the extraction of singly charged analyte ions generated *via* ICP. Details regarding the instrumental and operating conditions are described in Table 1.

Reagents. Electronic-grade (EP-S) nitric acid was purchased from Dongwoo Finechem (Seoul, Korea), and the Cr standard solution was purchased from SCP Science (Quebec, Canada). The standard concentrations were 0.625, 1.25, 2.5, 5.0, and 10 μg/L in 2% HNO_3. Three certified reference materials (CRMs) were purchased from the Korea Research Institute of Standards and Science (KRISS). These samples were 108-01-001 (rice), 108-04-001 (oyster), and 108-05-001 (water dropwort). The distilled water was purified through a purification system that provides conductivity above 18 MΩ/cm.

Sample Preparation. The 30 food items used in this study were purchased from large supermarkets and marketplaces. Foods were purchased such that general foods from all over the country were selected evenly, with no preference for foods from 1 specific place. The food list was generated using diet items selected from the food intake data obtained from the Korean National Health and Nutrition Survey (2009).

Samples for heavy metal analysis were digested using a microwave system (Ethos, Milestone, Sorisole, Italy): 0.5 g of a precisely measured homogenized sample was placed in a microwave pretreatment container, and 5 mL of nitric acid and 5 mL of distilled water (DW) were added. The gas generated was removed by opening the cap of the container inside a hood for 12 h, and the samples were digested using the microwave pretreatment equipment. The samples were digested for 30 min at 200 °C, and the temperature was decreased slowly to room temperature for 50 min. After the sample was digested completely, it was placed in a flask, and distilled water was added to obtain a set final volume.

Table 1. ICP-MS operating conditions

Parameter	ICP-MS
RF power	1400 W
Ar flow rate (L/min)	Plasma, 18.5 L/min; Auxiliary, 1.55 L/min; Nebulizer, 1.0 L/min
Sampling and skimmer cone	Nickel
Isotopes monitored	Cr^{52}, Cr^{53}, Cr^{52,53}
Pump rate	5 rpm
Stabilization delay	30 s
Acquisition time	Scan, 116 ms; minimum sampling time, 86.94 s
Scans/sample replicates	20/10
CRI mode	He, 120 mL/min

Results and Discussion

Analytical calibration curves showing the linearity of ^{52}Cr, ^{53}Cr, and ^{52,53}Cr in the standard and He-CRI modes have been provided in Figure 1. The correlation coefficients for the mean slope ranged from 0.9990 to 0.9999, and individual calibration coefficients were generally > 0.9990, which indicates excellent sensitivity and linearity. Therefore, a good standard calibration curve was obtained for all isotopes of Cr.

In the first evaluation of the use of the CRI for Cr measurement with ^{52}Cr, ^{53}Cr, and ^{52,53}Cr, 3 CRMs were analyzed after microwave digestion in the standard and He-CRI modes. The results are shown in Table 2. Most analyses of ^{52}Cr in the standard mode overestimated the Cr concentrations. The ^{52}Cr concentrations measured in the standard mode were 2–3 times higher than the certified values. The concentration of ^{53}Cr was relatively lower than that of ^{52}Cr in the standard mode, and the ^{53}Cr concentration in CRM 108-

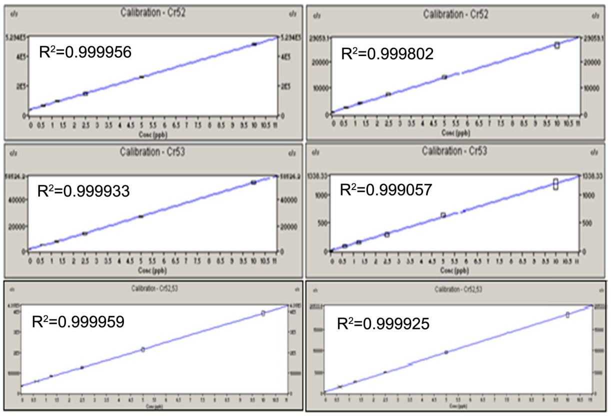

Figure 1. Calibration curves of ^{52}Cr, ^{53}Cr, and ^{52,53}Cr (left: non-CRI mode, right: He-CRI mode; n = 5).

Table 2. Chromium concentrations measured in 3 CRMs

CRM No.	Certified value (Cr mg/kg)	Standard mode (mg/kg)			He-CRI mode (mg/kg)		
		^{52}Cr	^{53}Cr	^{52,53}Cr	^{52}Cr	^{53}Cr	^{52,53}Cr
108-01-001 (rice)	0.16 ± 0.03	0.31 ± 0.05	0.17 ± 0.03	0.34 ± 0.15	0.15 ± 0.03	0.15 ± 0.02	0.15 ± 0.03
108-04-001 (oyster)	0.45 ± 0.07	1.25 ± 0.19	1.02 ± 0.15	1.17 ± 0.24	0.56 ± 0.11	0.49 ± 0.06	0.53 ± 0.13
108-05-001 (water dropwort)	(0.88)[a]	1.05 ± 0.12	0.98 ± 0.85	1.04 ± 0.11	0.96 ± 0.28	0.90 ± 0.16	0.96 ± 0.28

[a] Values in parentheses are not certified

01-001 was within the range of certified values. In the He-CRI mode, the levels of ^{52}Cr and ^{53}Cr were precisely measured. Analyses of ^{52}Cr and ^{53}Cr in this mode had higher accuracy than the analyses of ^{52}Cr and ^{53}Cr performed in the standard mode. Thus, the analytical method for Cr determination in complex food matrices based on ICP-MS equipped with a CRI of helium gas showed excellent performance. The analytical conditions chosen (^{52}Cr and ^{53}Cr in He-CRI mode) delivered accurate and precise concentration measurements relative to the reference values. The presence of high chloride concentrations in the samples could lead to pronounced masking of ^{53}Cr through $^{37}Cl^{16}O$.[8] The analytical method should therefore be selected on the basis of the components of the analyte.

Table 3 shows the mean concentrations of Cr isotopes (^{52}Cr, ^{53}Cr, and ^{52,53}Cr) in typical Korean foods for the different modes. The overall ^{52}Cr values in standard mode were high, *i.e.*, higher than those in CRI mode. The ^{52}Cr concentrations measured in the standard mode were 2–3 times higher than the values measured using the He-CRI mode, and there was probably extensive polyatomic masking of ^{52}Cr, *e.g.*, from $^{40}Ar^{12}C^+$, $^{35}Cl^{17}O^+$, $^{38}Ar^{14}N^+$, $^{36}Ar^{16}O^+$, $^{37}Cl^{15}N^+$, $^{34}S^{18}O^+$, $^{36}S^{16}O^+$, and $^{35}Cl^{16}OH^+$. In the standard mode, the measured level of ^{53}Cr was relatively lower than that of ^{52}Cr. In contrast, the concentration of ^{53}Cr was relatively higher than that of ^{52}Cr in the seasoning group in each mode. Similar results were obtained in the CRM tests, except in the seasoning group. The ^{52}Cr and ^{53}Cr content ranged from 78.6 to 810.6 and 57.8 to 1024.3 μg/kg, respectively, in the standard mode. In the He-CRI mode, the measured concentration of ^{52}Cr was similar to that of ^{53}Cr in many food samples. The ^{52}Cr content was reduced more than the ^{53}Cr content in the He-CRI mode. The ^{52}Cr and ^{53}Cr content ranged from 59.3 to 537.6 and 52.4 to 799.8 μg/kg, respectively, in the He-CRI mode.

It is difficult to analyze Cr in complex food matrices by using ICP-MS because the major isotope, ^{52}Cr, is masked by polyatomic interference generated by the sample matrix and the plasma gas.[4] We validated a method to remove the interference in Cr analysis by using an ICP-MS equipped with recently developed CRI technology in which the collision gas is near the plasma area, rather than near the quadrupole. In most commercial ICP-MS systems, the collision gas is near the quadrupole front.[17-19] Collision gases such as helium reduced polyatomic interference through a collision reaction. All polyatomic ions are larger than analyte ions of the same mass; therefore, they collide with the gas more often.[19]

Table 3. Chromium concentration in food groups according to modes

Group	Food	Standard mode (μg/kg)			He-CRI mode (μg/kg)		
		^{52}Cr	^{53}Cr	^{52,53}Cr	^{52}Cr	^{53}Cr	^{52,53}Cr
Cereals	Breads	201.6	223.0	197.3	145.8	111.5	100.6
	Cakes	316.1	187.7	295.7	164.1	157.8	163.4
	Rice	164.4	130.7	151.9	79.5	75.2	79.1
	Rice cake	103.2	104.3	103.4	80.1	81.6	80.2
Pulses	Soya milk	141.2	80.6	131.7	78.1	57.0	75.8
Vegetable	Kimchi	154.2	234.7	164.7	99.6	117.8	101.6
	Sesame leaf	96.1	87.4	92.3	71.4	54.2	69.5
	Garlic	151.7	128.8	142.8	79.3	79.6	79.3
	Onion	247.6	240.2	238.2	77.6	63.6	76.1
	Cucumber	78.6	57.8	76.7	61.9	52.4	60.8
	Green onion	106.8	81.1	102.6	81.4	67.4	79.9
Fruits	Persimmon	226.0	113.1	214.0	92.5	87.7	91.9
	Strawberry	99.6	99.0	93.9	78.4	73.7	77.9
	Banana	95.7	111.6	96.8	88.1	89.4	88.2
	Pear	120.4	93.7	112.8	72.6	57.0	70.9
	Peach	92.3	75.4	86.0	71.5	64.9	70.8
Fishes	Flatfish	167.5	165.7	167.1	65.9	62.6	65.5
	Canned tuna	215.1	161.6	205.5	118.6	117.6	118.5
	Oyster	212.4	274.3	214.2	166.6	174.3	167.4
Seaweed	Dried laver	759.4	820.2	765.9	331.4	321.3	330.3
	Sea mustard	242.0	399.9	258.8	102.2	125.9	104.8
Dairy product	Milk	125.1	108.2	118.8	83.2	71.7	82.0
	Yogurt	188.5	134.6	176.9	83.3	74.5	82.3
	Ice cream	536.4	444.2	473.3	313.2	286.5	310.4
Beverage	Beer	137.4	126.5	136.0	64.9	55.7	63.9
	Instant coffee	79.4	67.8	75.0	59.3	61.1	59.5
	Green tea	358.6	150.7	336.4	148.3	129.5	146.3
Seasoning	Vinegar	427.0	574.7	452.4	240.9	299.5	247.2
	Doenjang	810.6	1024.3	909.6	537.6	799.8	565.7
	Gochujang	556.1	704.3	583.4	375.8	580.9	397.8
	Soy sauce	173.9	809.8	286.2	150.5	416.5	179.1

These results show that it is difficult to obtain a relatively accurate value for the Cr concentration in the normal mode for many foods. The use of helium gas as a CRI reduced the interference caused by the sample matrix or plasma gas and produced lower measured concentrations for most food samples. Use of the CRC technique with ICP-MS should be considered for accurate analysis of Cr in foods. The real application of ICP-MS analysis highly depends on the various sample matrices.

Conclusion

Among the systems available to minimize for minimizing interference, the recently developed CRI has a different structure relative to that of CCT, ORS, and DRC systems that were designed with a chamber between the skimmer cone and quadrupole. The CRI system introduces collision or reaction gas directly into the plasma region through a modified hole of skimmer cone. Few reports on CRI ICP-MS systems are available because of the recent appearance of CRI systems in the commercial market. In this study, we performed Cr determination in various Korean foodstuffs by using an CRI ICP-MS. The Cr content obtained was compared to that obtained using the He-CRI and non-CRI modes. Most analyses of Cr in the standard mode produced an overestimation of Cr concentrations in foodstuffs. The chosen analytical conditions (^{52}Cr and ^{53}Cr in the He-CRI mode) delivered accurate and precise concentration measurements relative to the reference values. Thus, this analytical method based on a quadrupole ICP-MS with helium gas is effective for Cr determination in foodstuffs.

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