Determination of arsenic in food and beverages with pure oxygen reactive gas using the Thermo Scientific iCAP RQ ICP-MS

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Keywords

Arsenic, interference removal, oxygen, reaction gases, fruit juices, rice

Goal

To demonstrate the interference free analysis of arsenic in rice and fruit juice after conversion of As into $^{75}As^{16}O^+$ with pure oxygen reactive gas using the Thermo Scientific iCAP RQ ICP-MS.

Introduction

Arsenic is a chemical element present in the environment that may come from both natural and anthropogenic sources, for example erosion of arsenic-containing rocks, volcanic eruptions, or contamination from mining and smelting ores. It has also historically been added to pesticides, the use of which has since been discontinued but could still lead to significant concentrations of arsenic found in the environment.

Although highly toxic, typically, the low levels of arsenic in food do not cause immediate health problems for the average person; however, chronic exposure seriously increases the risk of adverse effects. Long-term exposure to arsenic is known to cause lung, kidney, skin and bladder cancers and it also interferes with different hormones that regulate metabolic functions and the immune system. Additionally, arsenic may be present in various chemical forms, or species, which differ in their toxicity or bioavailability. Whereas fish and seafood, for example, may contain elevated levels of organic arsenic species, which are generally considered harmless, soil grown food such as fruit and their products mainly contain inorganic arsenic, which is highly toxic. Rice in particular, is well known for its potential to accumulate high levels of this element.

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As a sample may contain diverse forms of arsenic, speciation analysis should be used to correctly assess the potential toxicity of the sample. However, when the probability of organic forms of arsenic existing in the sample is sufficiently low (e.g. in fruit juices and rice products), determination of the total content yields valuable information, as any arsenic present can be assumed to be in the inorganic form; therefore, highly toxic and the worst-case scenario.

Scientists have been measuring total arsenic concentrations in food matrices for a long time. As an authority, the Food and Drug Administration (FDA) has been doing it effectively through its 'Total Diet Study Program' since 1991. The agency monitors a range of toxic elements, including arsenic, in a variety of domestic and imported foods under the Toxic Elements Program, with emphasis placed on foods that children are likely to eat or drink, such as juices. Maximum Contaminant Levels (MCLs) issued by different authorities are displayed in Table 1.

Table 1. Maximum Contaminant Levels for arsenic in rice and fruit juice as published by different regulatory bodies (**EU:** European Union, **FSSAI:** Food Safety and Standards Authority of India, **US FDA:** United States Food and Drug Administration).

Elements	Rice (ppm)		Fruit Juice (ppm)		
	EU	FSSAI	EU	FSSAI	US FDA
Arsenic	-	1.1	-	0.2	0.01

Arsenic (As), with its high first ionization potential (9.82 eV), is one of the most difficult elements to measure accurately by ICP-MS. Furthermore, there is only one stable isotope available for analysis ($^{75}As^+$), which is heavily interfered through polyatomic interferences such as $^{40}Ar^{35}Cl^+$ and $^{40}Ca^{35}Cl^+$. Typically, collision/reaction cell (CRC) systems are used to eliminate those polyatomic interferences effectively. Two different approaches are commonly applied, either the use of an inert reaction gas and kinetic energy discrimination (KED), or the use of reactive gases, such as oxygen or hydrogen, to form product ions that can be detected free from interferences.

Whereas the KED approach is a generic approach suitable for a wide range of polyatomic interferences, the use of reactive gases is far more specific since only a small number of analytes may undergo reactions with a given gas. However, unwanted reactions of other elements present in the sample may lead to the formation of new interferences. Nevertheless, in some cases the use of reactive gases may lead to improved detection limits.

Sample Preparation

Approximately 0.2 g of a homogeneous, finely ground rice sample and approximately 0.5 g of mixed fruit juice were digested with 3 mL concentrated nitric acid, 0.5 mL hydrochloric acid and 0.5 mL hydrogen peroxide (all reagents obtained from Fisher Scientific) using a microwave digestion system (Anton Paar Multiwave PRO, Anton Paar, Germany). The microwave program used is shown in Figure 1. After cooling, clear transparent solutions were obtained and were made up with ultrapure water to a final volume of 20 mL before analysis. A preparation blank was prepared by performing the complete sample preparation procedure without any sample.
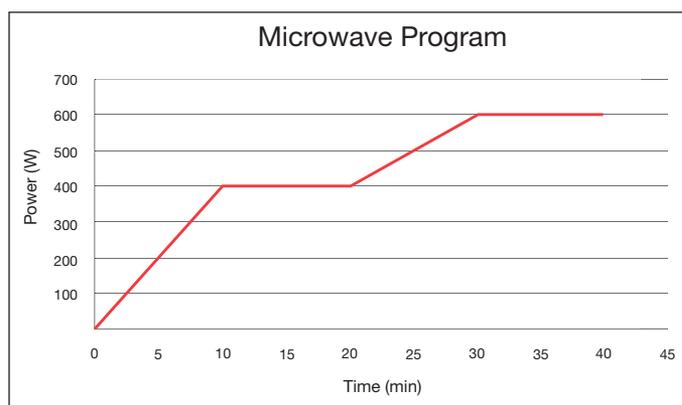
Figure 1. Microwave program used for the digestion of rice and fruit juice samples.

Instrumentation

All measurements were performed using a Thermo Scientific™ iCAP™ RQ ICP-MS. The instrument was operated using the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution (ISDS) Software, which allows complete compliance with the requirements of Part 11 of Title 21 of the Code of Federal Regulations (21 CFR Part 11). The instrument was tuned daily for optimized sensitivity. Tuning of the CCT mode using oxygen as the reaction gas was accomplished using the autotune routines included in the software. The typical operation parameters of the instrument are shown in Table 2. Calibration for fully quantitative analysis of arsenic was accomplished using a single element standard. The calibrated range typically covered concentrations between 0.01 to 10 ng·mL^{-1} using eight calibration solutions.

Table 2. Typical instrumental parameters.

Parameter	Value	
Nebulizer	PFA-ST nebulizer, pumped at 40 rpm	
Spraychamber	Quartz cyclonic spraychamber cooled at 2.7 °C	
Injector	2.5 mm id, Quartz	
Interface	High Sensitivity insert (2.8 mm), Ni cones	
RF Power	1550 W	
Nebulizer Gas Flow	1.17 L·min^{-1}	
QCell Settings	He KED	CCT-O$_2$
Gas Flow	100% helium @ 4.8 mL·min^{-1}	100% oxygen @ 0.82 mL·min^{-1}
QCell Bias	-18 V	-6 V
Quadrupole Bias	-21 V	-12 V
Scan Settings	0.1 s dwell time per analyte, 10 sweeps	

Due to the high level of chlorine in the sample matrix (contribution from HCl used for digestion and from Cl naturally present in mixed fruit juice), the accurate analysis of arsenic is not possible without the use of CRC. In this case, the use of oxygen as a reaction gas and the subsequent analysis of $^{75}As^{16}O^+$ has been selected to demonstrate the effective removal of polyatomic interferences such as $^{40}Ar^{35}Cl^+$ and $^{40}Ca^{35}Cl^+$.

Results

Figure 2 shows the calibration graphs obtained for arsenic in KED mode at *m/z* 75 and CCT mode using oxygen as the reaction gas and converting $^{75}As^+$ into $^{75}As^{16}O^+$. Although the use of an inert gas such as He and KED is also an effective way to eliminate polyatomic interferences, the use of oxygen and a mass shift reaction leads to an improved detection sensitivity and lower blank equivalent concentrations (BEC) and instrumental limits of detection (IDL) (Table 3).
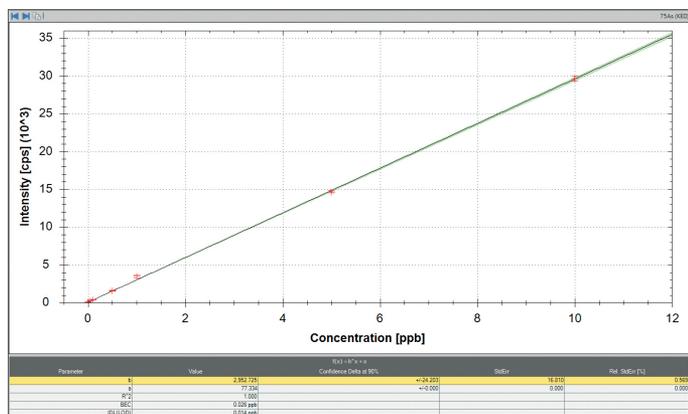
Table 3. Figures of merit for arsenic detection in He KED and CCT mode.

	He KED	CCT-O$_2$
Sensitivity (cps·µg·L^{-1})	2953	7612
BEC (ng·L^{-1})	26	3
IDL (ng·L^{-1})	14	2

Both samples (rice and fruit juice) were prepared in triplicate and subsequently analyzed for arsenic. The results showed that the detected levels were below 1 µg·L^{-1} for both sample types, and therefore below regulatory thresholds.

The accuracy and precision of the method was checked by analyzing a sample spiked with a known concentration of arsenic (using a certified single element standard) before sample preparation using microwave digestion. The spike levels prepared were 0.25 µg·L^{-1} for rice and 0.5 µg·L^{-1} for fruit juice. The spike recovery was determined in triplicate and Table 4 shows good agreement with the expected values. The precision observed for the three replicates showed variation of less than 2% RSD. The data accuracy also indicates that the proposed sample preparation strategy using microwave digestion fully decomposes the organic components of the sample matrices (i.e. starch in rice and sugar in fruit juices) that would otherwise lead to false positive results through the well-known carbon signal enhancement effect on As.

Table 4. Results of spike recovery experiments for rice and fruit juice.

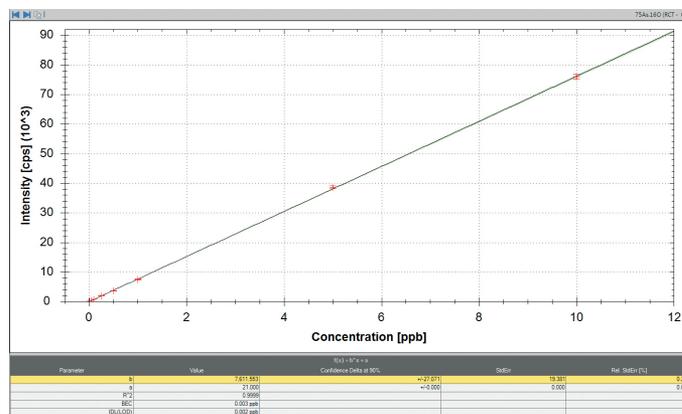| Replicate No.	Rice (µg·L^{-1})	Fruit Juice (µg·L^{-1})
1	0.240	0.479
2	0.247	0.490
3	0.247	0.491
Average	0.245	0.487
Recovery [%]	98%	97%
Std. Deviation	0.004	0.007
% RSD	1.65	1.37

Figure 2. Calibration curves for arsenic using KED mode (left) and CCT mode with oxygen reaction gas (right).

Conclusion

The iCAP RQ ICP-MS is a powerful tool for the determination of trace elements in a wide range of samples. In addition to the use of He and KED as a generic tool for the comprehensive removal of polyatomic interferences, the instrument is also fully capable of using reactive gases such as oxygen and subsequent mass shift reactions of target ions into products that can be determined free from interferences. As shown in this note, the use of such approaches may lead to improved detection sensitivity, BEC and LOD values and setting up the measurement mode for analysis is straightforward using the provided autotune routines in the Thermo Scientific™ Qtegra™ ISDS Software.

The data obtained clearly indicates that the polyatomic interferences of $^{40}Ar^{35}Cl^+$ and $^{40}Ca^{35}Cl^+$ have been fully eliminated using oxygen as reaction gas, which produces a mass shift reaction to convert $^{75}As^+$ into $^{75}As^{16}O^+$, for interference free analysis at *m/z* 91. This provides accurate and reliable data for analysis of arsenic in food and beverage samples.

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