DETERMINATION OF ARSENIC IN JUICES USING ICP-MS/MS

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Abstract

Reports from the USA media have called the attention towards a possible contamination of apple juices by arsenic. The study here described presents the development of an analytical procedure using inductively coupled plasma tandem mass spectrometry (ICP-MS/MS) for determination of As in apple and orange juices commercialized in Tetra Pack® containers. Suitable recoveries were reached when using the octopole reaction system (ORS^3). The reaction with O_2 and consequent monitoring of $^{75}As^{16}O^+$ significantly improved the accuracy of the analysis reaching a limit of detection of 0.013 µg/L. Thus, ICP-MS/MS operated in reaction mode was an effective instrumental strategy for determination of trace concentrations of As free of isobaric interference caused by argon chloride ion.

Introduction

The Food and Drug Administration (FDA) started in 2011 a quantitative evaluation of the presence of As in apple juices, adopting in 2013 the maximum tolerable limit of 10 µg/L of inorganic As in apple juice[1]. In 2013, the Brazilian Health Surveillance Agency (ANVISA) has decreased the maximum allowed concentration of As in fruit juices from 0.5 to 0.1 mg/L [2]. The ICP-MS with a tandem configuration, thus called ICP-MS/MS or ICP-QQQ, combines two quadrupole mass analyzers and a collision/reaction cell (ORS^3) and it may be operated either in single quadrupole mode or in mass-shift mode by selecting different m/z for Q1 e Q2. The operation in mass-shift mode allows controlling the ions that are introduced into the ORS^3 and the formed species that will be detected in Q2. Critical spectral interferences are solved by using mass-shift mode strategy[3].

Results and Discussion

Eighteen samples of fruit juices from 13 producers in three Brazilian states (SP, MG and PR) were analyzed. Aliquots of 4.0 mL of juice samples, in triplicate, were microwave-assisted digested in 5.0 mL of HNO_3 2 mol/L and 3.0 mL of 30 % H_2O_2 m/m. The determined concentrations of As in juices using single quadrupole mode was higher than those measured using mass-shift MS/MS mode for all samples.

Table 1. Recoveries of addition and recovery experiments for As (mean ± standard deviation, n = 3) in single and MS/MS *mass-shift modes*.

Added (µg/L)	*Single Mode* $^{75}As^+$ (µg/L)	Rec(%)	*Mass-shift Mode* $^{75}As^{16}O^+$ (µg/L)	Rec(%)
DA	0.103 ± 0.003		0.050 ± 0.004	
+ 0.015	0.125 ± 0.004	151	0.065 ± 0.003	104
+ 0.03	0.151 ± 0.045	161	0.083 ± 0.002	109
+ 0.07	0.217 ± 0.058	164	0.125 ± 0.002	107

LOD *Single mode*: 0.006 µg/L; LOD MS/MS mode: 0.013 µg/L

Table 2. Determination of As (mean ± standard deviation, n = 3) in samples using MS/MS *mass-shift mode*.

Sample	Concentration µg/L	Sample	Concentration µg/L
FO	1.452 ± 0.016	MA	0.818 ± 0.143
GO	0.928 ± 0.009	AO	0.975 ± 0.038
HO	0.469 ± 0.063	GA	0.629 ± 0.029
DO	0.465 ± 0.018	JA	0.486 ± 0.048
JO	0.353 ± 0.073	DA	0.429 ± 0.012
CO	0.232 ± 0.004	LA	0.567 ± 0.047
EO	0.190 ± 0.031	NA*	1.247 ± 0.076
AO	0.175 ± 0.012	BA*	0.127 ± 0.010
NO*	0.407 ± 0.058	BO*	0.126 ± 0.006

O: Orange; A: Apple; * Soy juice; LOD: 0.013 µg/L

Conclusions

The use of ICP-MS/MS with ORS^3 pressurized with O_2 was effective for eliminating spectral interferences on the determination of As. Adopting this strategy, $^{75}As^{16}O^+$ was accurately determined in apple and orange juices and all samples contained As concentrations lower than those established by Brazilian legislation.

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