ARSENIC SPECIATION IN RICE: Exploring a method faster than FDA. Development and validation.

Melissa Verger,1 Lorena D. Tchorbadjian,2 Elena Darré,1* Raquel Huertas1.
1 Departamento de Espectrometría Atómica de Alimentos y Medio Ambiente. Laboratorio Tecnológico del Uruguay (LATU), Av. Italia 6201, Montevideo, Uruguay, www.latu.org.uy.
2 Latitud- Fundación LATU, Av.Italia 6201- Edificio Los Abetos, Montevideo, Uruguay, www.latitud.org.uy .
* mverger@latu.org.uy

INTRODUCTION

Due to the different toxicity of arsenic species (arsenite- As^{+3} > arsenate As^{+5} > dimethylarsenic acid- DMA> monomethylarsenic acid -MMA) and the prevalence of arsenic in rice crops, knowledge about the speciation of arsenic in rice is a mandatory requirement so as to offer an innocuous product to the population.

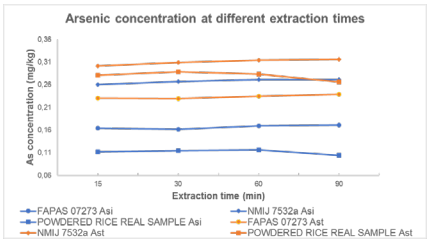
Since HPLC-ICP-MS is both a time consuming and expensive technique which requires trained analysts, arsenic speciation in rice continues to be a challenge in the laboratories of Latin America. Due to the above, obtaining faster, cheaper and accurate analytical methods is always a concern in our daily work. In that search we optimized speciation of arsenic in rice starting with FDA 4.11 method[1] and ended up obtaining an analytical method at least three times faster.

EXTRACTION OF ARSENIC SPECIES

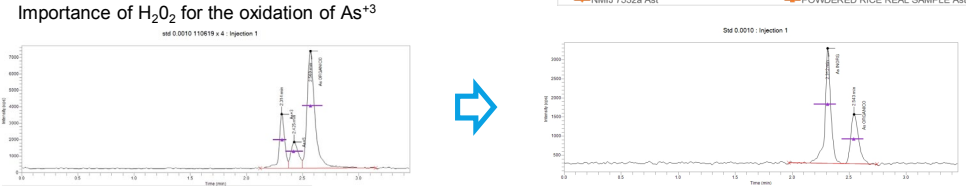
Development of the extraction process:

	FDA method [1]	Proposed Method [2]	Obtained Method
Sample taken	1g	0.5 g	1 g
Extracting solvent	10 mL HNO_3 0.28 M	2 mL de H_2O_2 0.20M + HNO_3 0.10 M	10 mL HNO_3 0.28 M
Temperature	95 ºC	100 ºC	95 ºC
Heating time	90′	15′	15′
Final volume	16.7 mL con H_2O and dilution 1/3 up to pH 6-8,5.	10 mL de H_2O	16.7 mL con H_2O_2 1M

Study of the optimal extraction time:



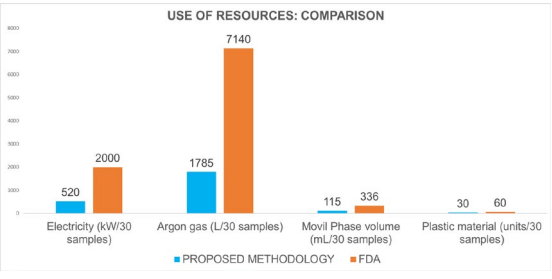
Importance of H_2O_2 for the oxidation of As^{+3}



DETERMINATION OF As SPECIES BY HPLC-ICPMS

	FDA 4.11:2012 [1]	PROPOSED METHODOLOGY [2]
Column	Hamilton PRP X-100, 5µm, 4.6x150 mm	GEMINI® 5 µm, C18,110 Å 250 x 4.6 mm
Movil Phase	$(NH_4)_2HPO_4$ 10 mM, pH (8.25 ± 0.05).	$(NH_4)_2HPO_4$ 1 mM:MeOH 0.05%, pH 2
Calibration curve:	Movil phase	HNO_3 0,28 M H_2O_2 1 M
Flow rate:	0.8 mL/min	Gradient flow: 2 min a 1.2 mL/ min; 1.5 min a 0.95 mL/min
Inyection volume:	50 µL	20 µL
Temperature	Ambient	35 ºC
Runtime	14 min	3.5 min
Retention time	As^{+3}- 2,3; DMA-2,9; MMA- 3,5; As^{+5}- 8,5	As_i-2,3; As_o- 2,5 (Rs: 1,54)

USE OF RESOURCES



RESULTS AND CONCLUSIONS

Accuracy and Precission					
Material	Specie	Declared Value (µg/kg)	n	Recovery (%) (x ± 2 RSD)	CV (%)
Nist 1568b- Rice Flour	As_i	92± 10	9	97,0 ± 14,1	7,1
	As_t	285±14		92,7 ± 9,9	4,9
Fapas 07273 Powdered Rice	As_i	162±5,2	15	100,4 ± 12,2	6,1
	As_t	220±4,6		106,8 ± 12,0	6
Spiked real sample	As_i	100	6	95,4± 19.5	9,7
	As_t	200		102,9± 9.8	4,9
Spiked real sample	As_i	200	6	96,0± 17,2	8,6
	As_t	400		104,3± 7,1	3,6

Detection Limit (DL)- Quantification limit (QL)			Uncertainty (k=2)		
Matrix	Calculated DL (µg/kg)	QL (µg/kg)	Level (µg/kg)	U As_i (%)	U As_t (%)
Powdered Rice (n:5)	As_i: 1,6	Asi: 4,8	50	21,7	23,4
Spiked blanc (n:7)	As_i: 3,5	Asi: 10,5	100	15.0	16,8
FAPAS 07289 Powdered Rice (n:6)	As_o: 0,60	As_o: 1,8	300	13,2	15,7
Spiked blanc (n:7)	As_o: 2,4e-05	Aso: 7,5e-05	Linearity: As_i 0,30-60 µg/L; As_o 0,30-20 µg/L.		

- A faster, cheaper, and more environmentally efficient method was obtained.
- Validation parameters show a better performance than FDA method in the determination of As_i and As_t in agreement with ISO 17025:2017.

REFERENCES

[1] Kubachka K., Shockey N., Hanley T., Conklin S., Heitkemper D., 4.11. FDA, (2012), available from: https://www.fda.gov/media/95197/download.
[2] Narukawa T., Chiba K., Sinaviwat S., Feldmann J.,(2017),Journal of Chromatography A, 1479, pag. 129-136.

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