KEMENTERIAN SAINS, TEKNOLOGI DAN INOVASI
MINISTRY OF SCIENCE, TECHNOLOGY AND INNOVATION

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DETERMINATION OF ARSENIC TOTAL IN RICE USING CONTINUOUS FLOW HYDRIDE GENERATION COUPLED WITH ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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- Introduction
- Literature review
- Material & Methodology
- Result and Discussion
- Conclusion

Introduction:

Rice *(Oryza sativa)* becomes one of arsenic exposure routes to human through the diet

Levels of As in rice and rice-based products start to receive attention due to its carcinogenic effect and other toxic properties

Why Rice?

Malaysian consumed 80 kg of rice per person in 2016

- 67 % Produced Locally

(Che Omar et al. 2019)

International Agency for Research on Cancer (IARC) classified arsenic as a Group 1 carcinogen; which human carcinogen ranges from the skin lesions such as hyperpigmentation to cancer of the brain

Introduction:

01

Sample Pre-treatment

- Grinded to powder by mill or blender
- Dry in oven

02

Extraction of As

- Microwave digestion is widely used : Allowed the used of small reagents volume, minimal loss of volatile analyte and shorter time for mineralization.
- Factor study : type of acid, volume of acid, microwave specified programme

03

Instrument used

- HG-AAS
- HG-AFS
- ICP-MS
- ETAAS

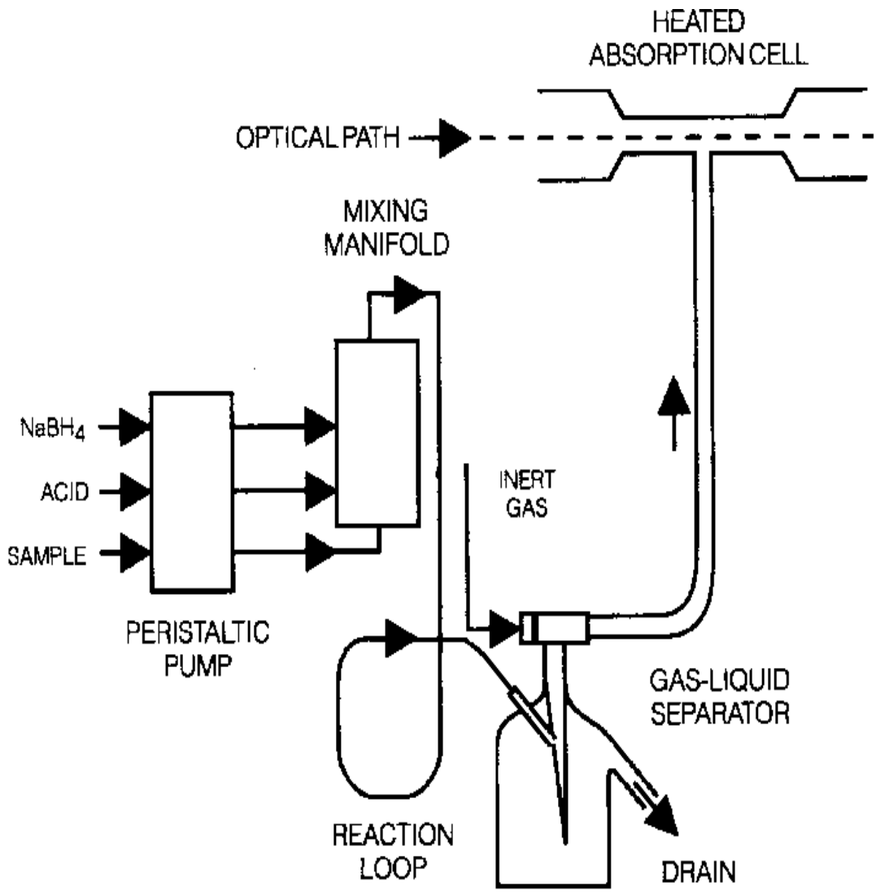
*The studied performed was included sample pre-treatment, differs technique for extraction of arsenic and various type of instrument used.

Introduction:

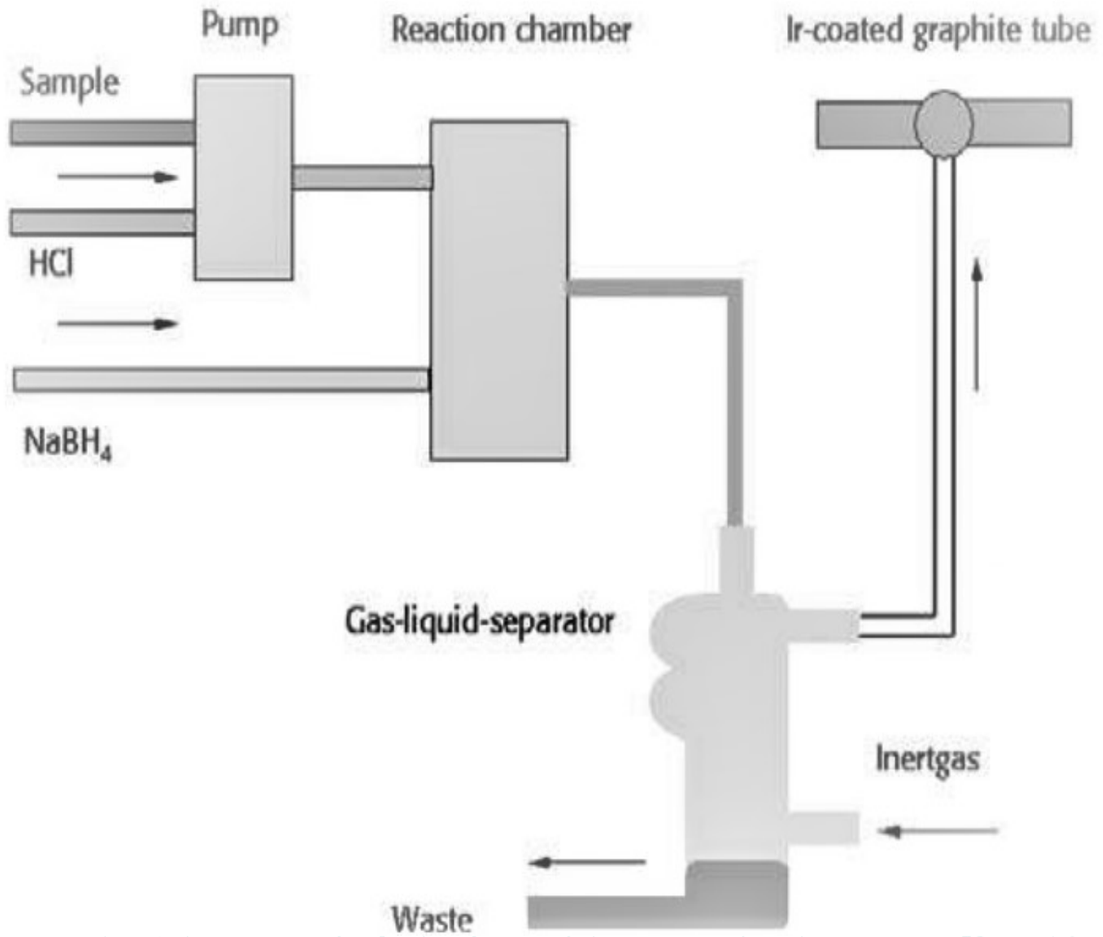
Table 1.1 Worldwide Regulations on inorganic arsenic and total arsenic in rice and rice-based products.

Guidelines	Food	iAs (mg/kg)	tAs (mg/kg)	Regulatory Authorities
Australia	Cereals		1	Food Standards Australia New Zealand
China	Paddy, brown rice, white rice	0.2		Ministry of Health
Codex Alimentarius	Rice, polished Rice, husked	0.2 0.35		FAO-WHO
European Union	Non-parboiled ,milled rice (polished or white rice) Parboiled rice Rice waffles, rice wafers, rice crackers and rice cakes Infants and young children.	0.2 0.25 0.3 0.1		European Food Safety Authority
Iran	Rice		0.15	Institute of Standard and Industrial Research of Iran
Malaysia	**Others** **Children and baby food**		**1** **0.1**	**Ministry of Health**
Singapore	Others food		1	Agro-Food and Veterinary Authority
United Kingdom	Rice-based products infants and young children	0.3 0.1		Food Standard Agency

Introduction:



HG-AAS



HG-ETAAS

Literature Review:

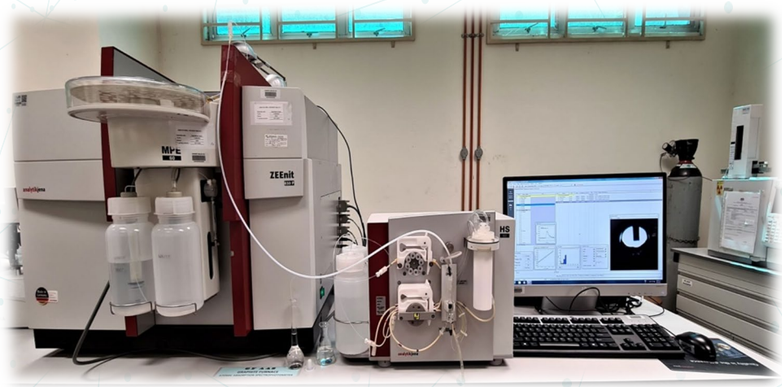
Summarized of analytical methods for arsenic total detection in rice (2010 -2020)

Sample preparation	Detection	Method performance	Reference
Dry ashing	FI-HG-AAS	LOD: 25 ng g^{-1} Recovery: 95.6% %RSD: 1.2 – 3.3	Ruangwises et al., 2012
Microwave digestion	ETAAS	LOD: 22.1 ng g^{-1} LOQ: 66.3 ng g^{-1} Recovery: 92-105 % RSD < 15%	Pasias,Thomaidis, & Piperaki, 2013, p. 5
Extraction with water bath 80 -90°C for 3 hours and centrifuge	HG-AAS	LOQ: 23 ng/g LOQ Liquid: 1.1 - 9.7 µg/L Recovery: 91 - 110%	Santos, et al., 2017
Microwave digestion	ICP-MS	LOD: 0.011 mg kg^{-1} LOQ: 0.038 mg kg^{-1} Recovery: 108%	Mataveli et al., 2016

Materials and Methodology:

Instrument Optimization → **Sample Preparation** → **Investigation : Influence of nitrate and nitrite ions on arsenic signal**

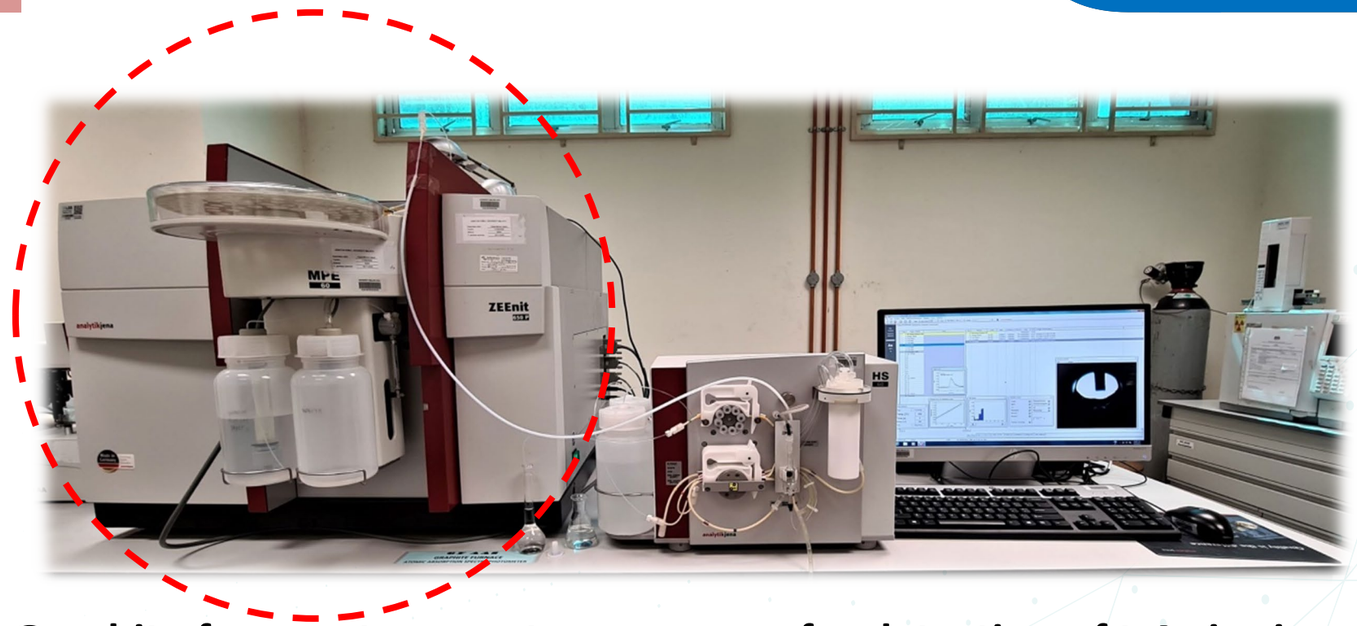
Sulfamic Acid addition → **Method validation** → **Application to real sample**



Instrumental Optimization:

GFAAS operating condition

System parameter	Setting
Sample type	Liquid
Tube type	Platform
Element	As
Light source	Hollow cathode lamp
Lamp current (mA)	5
Wavelength (nm)	193.7
Slit width (nm)	0.8
Measure time (s)	4.0
Background correction	Off
Replicate	3
Calibration mode	Linear



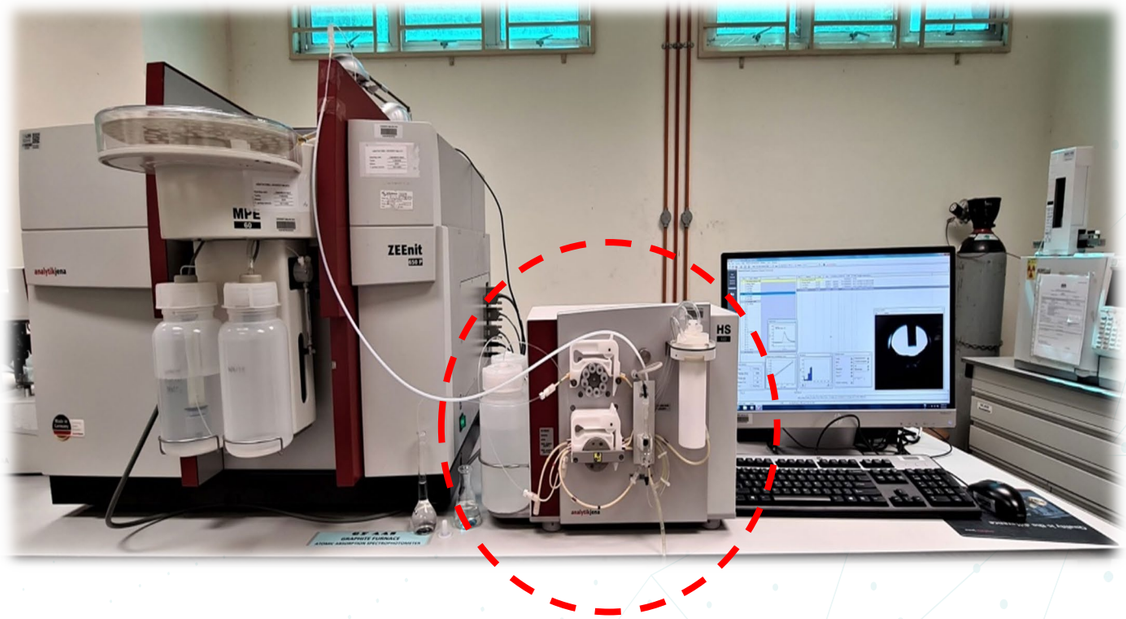
Graphite furnace temperature program for detection of t-As in rice

Step	Temp. [ºC]	Ramp. [ºC/s]	Hold [s]	Time [s]	Wash
Drying	300	300	2	2.9	Stop
Drying	305	50	20	20.1	Max
Pyrolysis	305	0	6	6.0	Stop
Atomization	2100	1000	5	6.8	Stop
Cleaning	2200	500	4	4.2	Max

Instrumental Optimization:

Hydride Generation Parameter

System parameter	Setting
Mode	Hydride (continuous)
Load time	14 s (6 L/h)
Reaction Time	35 s
Az wait time	10 s
Diluent	3.0 % HCl
Reductant	$NaBH_4$ (0.3% w/v) in NaOH (0.1% w/v)
Reducing agent	KI (5% w/v) in ascorbic acid (5% w/v)

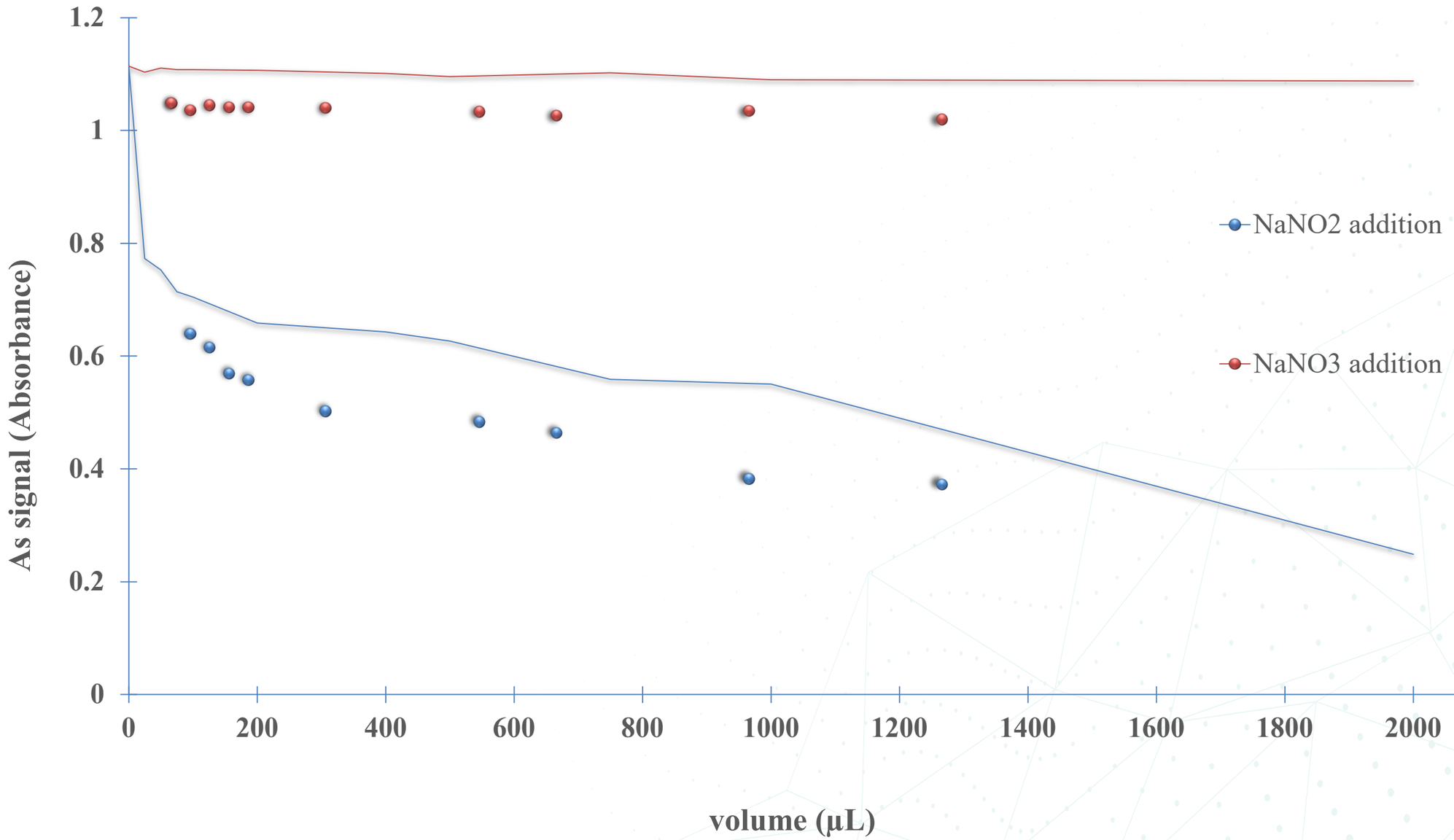


Optimize Microwave Digestion heating programme

Stage	Temp (°C)	Ramp (mm:ss)	Hold (mm:ss)	Pressure (psi)	Power (W)	Stirring
1	210	20:00	20:00	800	1000	0ff

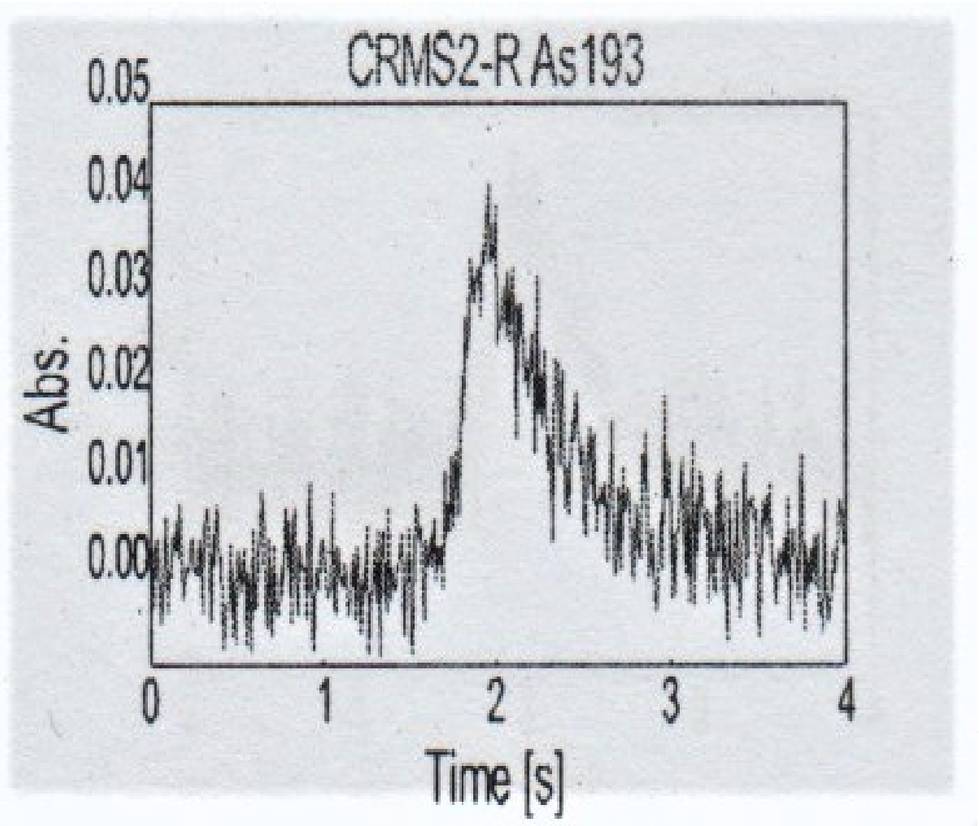
Result and discussion : Nitrate & Nitrite

Influence of nitrate and nitrite ions on arsenic signal.

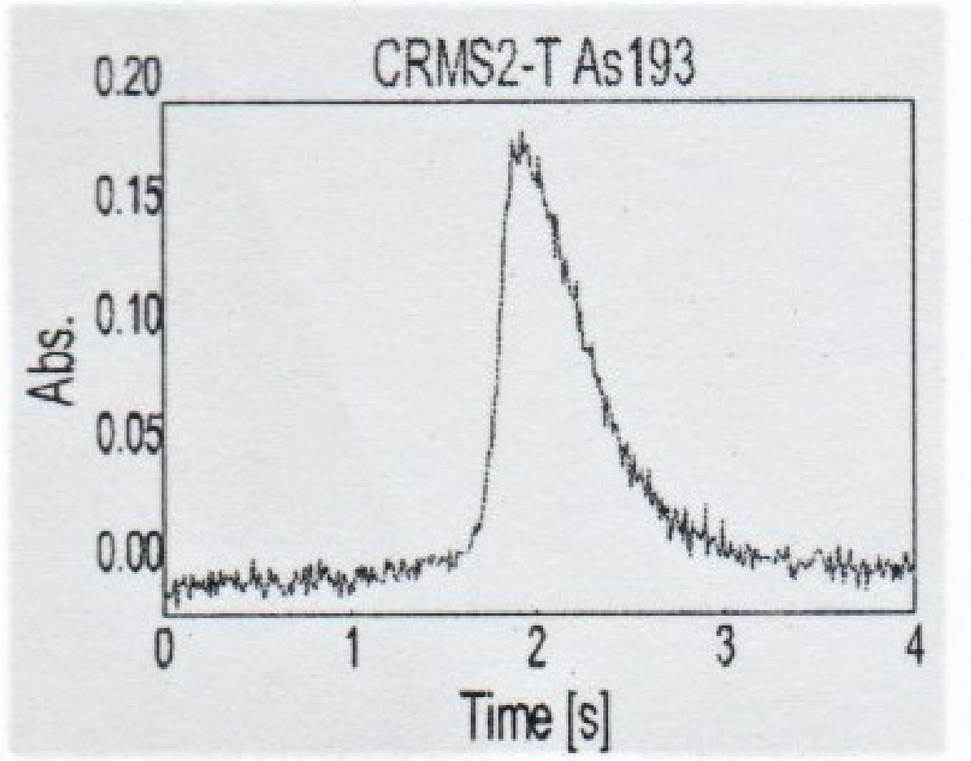


Result and discussion : Sulfamic Acid Addition

Signal of absorbance



- **without** addition of sulfamic acid



- with addition of sulfamic acid

Result and discussion : Summarized Method Validation

CRITERIA	VALUE
Linearity range (µg/L)	0.2 - 1.0
R^2	0.9978 - 0.9986
Mean Recovery of ERM-BC211	94.8 %
Method Performance	**ERM Application Note 1: - no significant different between the measurement result and the certified value at 95% confidence level.**
Matrix Spike (Mean Recovery) 50 µg/kg Low 100 µg/kg Medium 200 µg/kg High	 97.5 % 98.6 % 96.4 %
Limit of Detection (LOD)	2.14 ng/g
Limit of Quantification (LOQ)	5.48 ng/g

Result and discussion : Application to real samples

Sample Name	Sample type	Mean, µg/kg	Sd	%RSD	Comment	Origins
Brand A	White rice-polished	94.7	1.0	1.1	n = 3	Thailand
Brand B	White rice- polished	100.3	4.0	4.0	n = 3	Thailand

- Total As concentration in white rice from Thailand obtained was similar to those reported by Nishimura et al., 2010 (90 – 100 µg /kg).

Conclusion

Determination of arsenic total in rice using continuous flow hydride generation coupled with electrothermal atomic absorption spectrometry successfully developed

Good Method Performance achieved

- Nitrate showed no significant effect to As signal
- Nitrite proven significant effect to As signal
- Sulfamic acid managed to **successfully suppress signal interference**, thus enhance sensitivity of the method

Hyphenation between Hydride system with ETAAS produce lower LOD, better sensitivity when compared to previous literature.

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