

# Inorganic arsenic - SPE HG-AAS method for RICE tested in-house and collaboratively

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*Publication date:*
2013

*Document Version*
Publisher's PDF, also known as Version of record

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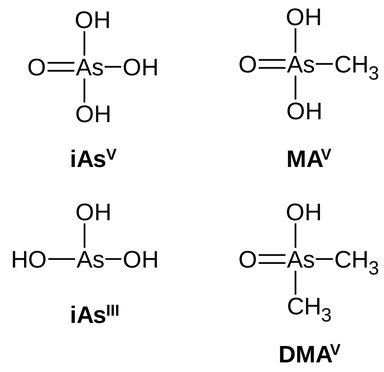
# INORGANIC ARSENIC

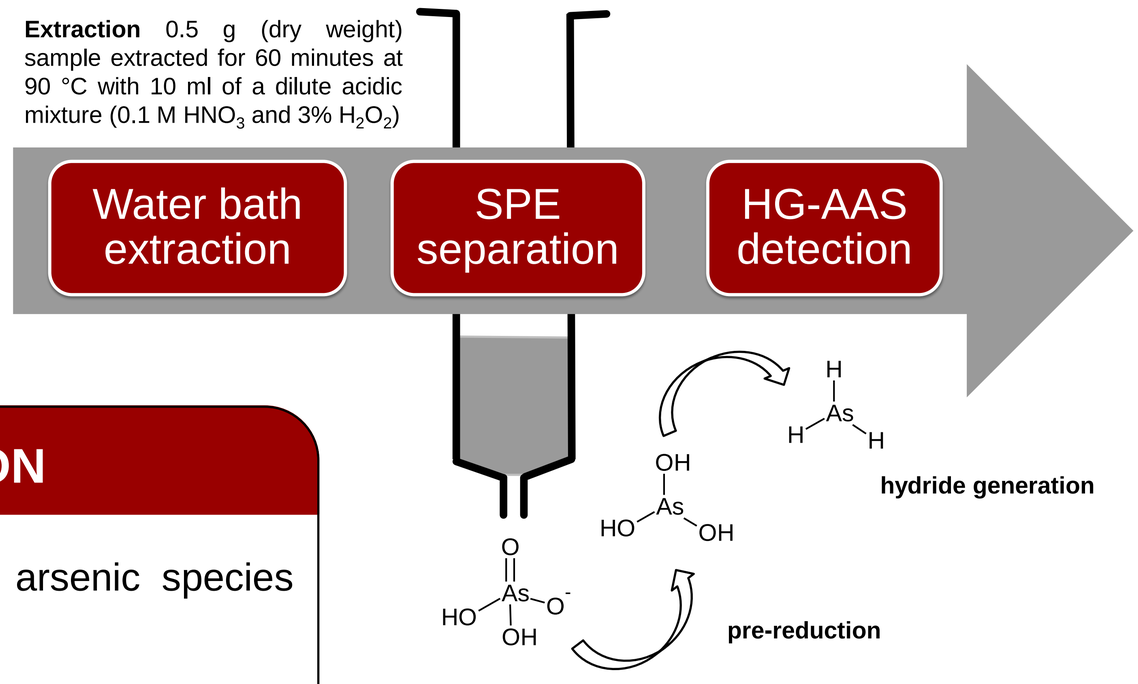
## **SPE HG-AAS** METHOD FOR **RICE** TESTED IN-HOUSE AND COLLABORATIVELY

## INTRODUCTION

Internationally accepted validated method(s) are needed for establishment of a maximum level (ML) for inorganic arsenic (iAs) in rice as recently emphasised by the European Food Safety Authority (2009), the World Health Organization (2011) and Codex Alimentarius (2012).

Rice contains most often three forms of the trace element arsenic; iAs and the methylated species monomethylarsonic acid ($MA^V$) and dimethylarsinic acid ($DMA^V$). Dietary intake of iAs is of special concern due to its carcinogenicity to humans, whereas DMA and MA are generally considered of less toxicological importance.




## SPE SEPARATION

- The charge of the arsenic species depends on pH
- pH 5-7 → $iAs^V$ is negatively charged
- SPE → strong anion exchange
- Sequential elution:

**1.** Pre-condition of SPE, MeOH
**2.** Equilibrate SPE, 35 mM $(NH4)_2CO_3$, 0.05 M $HNO_3$, 1.5% $H_2O_2$
**3.** Load buffered sample: pH 5.0-7.5
**4.** Wash SPE, 0.5 M $CH_3COOH$
**5.** Elute SPE, 0.4 M $HNO_3$

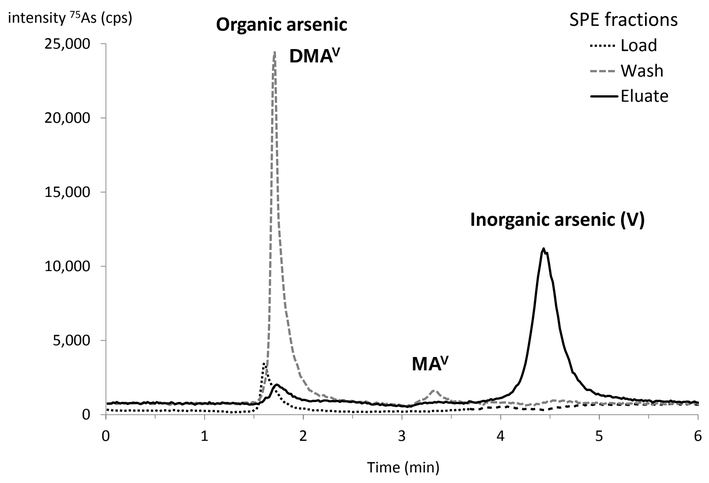



**Figure 1**. Overlaid HPLC-ICP-MS chromatogram of 3 SPE fractions (load, wash and eluate) of a rice sample (NIST1568a) containing both inorganic and organoarsenic species.

## DETECTION

### HG-AAS

- Pre-reduction of eluate ($As^V$ → $As^{III}$) using KI, HCl and ascorbic acid
- Hydride generation using HCl, NaOH and $NaBH_4$
- HG-AAS settings - heated cell (900°C), As lamp (193.7 nm wave length, 0.5 nm slit width)


**Figure 2**. The Atomic Absorption Spectrometer (ICE-3300) coupled with a Hydride Generation system (VP100) and an electrically heated quartz cell (all from Thermo Scientific).

### SPE HG-AAS versus HPLC-ICP-MS

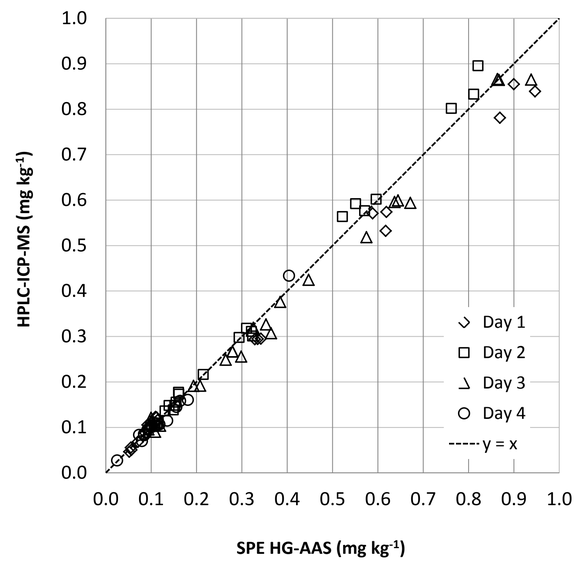



**Figure 3.** Determination of inorganic arsenic by two different methods; HPLC-ICP-MS and SPE-HG-AAS. In total results for 84 spiked and natural incurred rice samples analysed on four different days. The correlation is y=x (99% confidence interval - regression analysis by Excel 2010).

## CONCLUSION

The presented SPE HG-AAS method enables selective determination of inorganic arsenic in rice by use of inexpensive instrumentation (HG-AAS) and is a **candidate method for future control** of the inorganic arsenic content in rice and rice products.

## VALIDATION RESULTS

The developed method was subjected to an **in-house validation study**, which gave satisfying figures of merit (Table 1). The LOD (0.02 mg·kg$^{-1}$) was below the proposed maximum levels (0.2-0.3 mg·kg$^{-1}$).

**Table 1.** In-house validation results

| | Spiked rice samples | | | Rice reference materials | |
|---|---|---|---|---|---|
| | Low | Medium | High | IMEP-107 | NIST1568a |
| **Target level (mg·kg$^{-1}$)** | 0.30 | 0.55 | 0.80 | 0.107* | 0.096* |
| **Observations (N)** | 9 | 9 | 9 | 8 | 7** |
| **Mean recovery (%)** | 105 | 106 | 106 | 101 | 103 |
| **Repeatability RSD$_{ir}$ (%)** | 5 | 3 | 4 | 6 | 5 |
| **Reproducibility RSD$_{IR}$ (%)** | 7 | 9 | 8 | 7 | 7 |

*) Consensus mean values: IMEP-107 (de la Calle MB et al., 2011 TrAC 30:641–651) and NIST1568a (Raab A et al., 2009 J Environ Monit 11:41–44).
**) One outlier result discarded (0.048 mg·kg$^{-1}$).

The SPE method was furthermore **collaboratively tested** among 10 laboratories on a wholemeal rice meal sample with a satisfactory HorRat value of 1.6.

**References**
- Codex (2012) Proposed draft maximum levels for arsenic in rice (at step 3).
- European Food Safety Authority (2009) EFSA Journal 7(10), 1351:1-199
- Rasmussen et al (2013), ABC, doi 10.1007/s00216-013-6936-8
- World Health Organization (2011) WHO Technical Report Series 959

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The present work was funded by the European Community's Seventh Framework Programme (*FP7/2007-2013)* under *grant agreement* n° 211326 project: CONffIDENCE; www.conffidence.eu