Arsenic in Rice and Rice Products and it's effect on human health

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10007

M.Sc. Part II - Semester 4

Research Project

CERTIFICATE

This is to certify that **HONEY SANJAY DUMRALIA**, a student of **M.Sc. II** year has successfully completed the research project in analytical chemistry on the topic "**ARSENIC IN RICE AND RICE PRODUCTS AND IT'S EFFECT ON HUMAN HEALTH**" under the guidance of **Dr. Jaya Gade & Dr. Sulekha Gotmare** in partial fulfillment of M.Sc. analytical chemistry programme during the year **2020-21.**

This project is absolutely genuine does not indulge in plagiarism of any kind.

Signature of Guide   Signature of HOD

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Arsenic content in rice and rice products and its harmful effect on human body.

By - Miss Honey Dumralia, Student of M.Sc. Part II, Analytical Chemistry, S.N.D.T Women's university, Santa Cruz (West), Mumbai - 400 049

Abstract : Inorganic arsenic intake is likely to affect long-term health. High concentrations are found in some rice-based foods and drinks widely used in infants and young children. In order to reduce exposure, we recommend avoidance of rice drinks for infants and young children.

For all of the rice products, strict regulation should be enforced regarding arsenic content. Moreover, infants and young children should consume a balanced diet including a variety of grains as carbohydrate sources. Although rice protein-based infant formulas are an option for infants with cows' milk protein allergy, the inorganic arsenic content should be declared and the potential risks should be considered when using these products.

INTRODUCTION

Metal contamination in foods is a global health concern. Metallic contaminants including arsenic, cadmium, lead and mercury exist naturally in the earth's crust can be found at various levels in the environment and subsequently enter the food chain. Each of these contaminants also form compounds with other organic entities, which vary in chemical properties and levels of toxicity to humans when ingested. Long term use of contaminated water for irrigation can cause accumulation of these metals in soil which can be trans located to food crops and thus enter the food chain. Awareness with regard to heavy metal contamination in food has increased world wide.

Chemical exposure incidents in communities need utmost attention to curb metal toxicity. Internationally, to protect against high exposures of metal contaminant, the Codex Alimentary Commission has set limits for these metals in food commodities. At the national level, FSSAI has also prescribed maximum limits for metal contaminants in various foodstuffs. This guidance note briefly describes sources, exposure pathways, toxicity and measures that could be undertaken by the stakeholders in assuring safe food to the consumers.

KEY TAKEAWAYS :

Metal contaminants or heavy metals are present in different environmental matrices in various concentrations.

Contamination of toxic metals/metalloid in food is a major route of exposure for the general population. It may also occur through inhalation of polluted air as dust fumes, or through occupational exposure at workplace.

Metal contaminants also enter food chain through contaminated soil, sea food, and water.

The main threats to human health are associated with the exposure to lead, cadmium, mercury and arsenic.

Food Safety and Standards (Contaminants, Toxins and Residues) Regulation, 2011, has specified maximum limits of metal contaminants in different food categories

Guidance to industry and other relevant stakeholders on heavy metal exposure, its deleterious effects and proper management is needed.

-- Metals such as lead, arsenic, cadmium, mercury find their way in foods. At high levels, these metals can be toxic, but eliminating them entirely from our food supply is not always possible because these metals are found in the air, water and soil and then taken up by plants as they grow

There is a global health concern associated with metal contamination because of their toxicity even at low concentrations. Heavy metals can contaminate food commodities as a result of anthropocentric activities such as mining, smelting, use of phosphate fertilizers, industry or car exhausts which have resulted in their diffusion and accumulation in the food. The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic.

Metal contaminants of concern in human diet :-

Concerns regarding toxicity of metals exist primarily due to their bioaccumulation in the tissues of the body where they are taken up and stored faster than they are excreted. Secondly, their presence in the body disrupts normal cellular processes, leading to toxicity in a number of organs. Four heavy metals, namely lead, arsenic, cadmium and mercury, are of particular concern in food. Ingestion of such metals from food and water is a major route of exposure for the general population. In order to protect human health it is necessary to control the levels of these toxic metals in foodstuffs.

Exposure pathways of heavy metals :-

Human exposure to metals occur through consumption of contaminated food stuffs, sea foods, and drinking water, through inhalation of polluted air as dust fumes, or through occupational exposure at workplace. These metals can be taken up through several routes. The chain of contamination usually follows from industry, to the atmosphere, soil, water, foods and then human. Some heavy metals such as lead, cadmium, mercury, arsenic can enter the body through the gastrointestinal route that is, through the oral ingestion after consuming food including fruits, vegetables, drinking water or other beverages. Some metals can enter the body by inhalation while others such as lead can be absorbed even through the skin.

Arsenic:-

People are exposed to elevated levels of inorganic arsenic through various sources. The greatest threat to public health from arsenic originates from contaminated groundwater. Rice plants take up more arsenic, approx. 10 folds, as compared to other cereal crops.

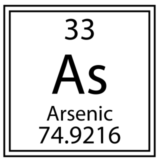
Arsenic-contaminated water used for irrigation and food preparation is the source of the high arsenic content detected in cultivated grains and vegetables and in cooked food. Terrestrial foods typically contain low levels of arsenic but arsenic in rice is elevated when grown on arsenic-rich groundwater and soil, arsenical pesticides, phosphate fertilizer, processing industries, and through pollution from mining activities.

Toxicity of Arsenic:-

People affected with arsenicosis generally show symptoms of skin lesions like pigmentation, keratosis or melanosis which could range anywhere between moderate to severe. Symptoms of early acute toxicity include muscular pain, nausea, vomiting and rice-watery stool diarrhea. Severe toxicity is known to cause kidney failure, seizures and finally death due to shock.

Literature Survey

What Is Arsenic?



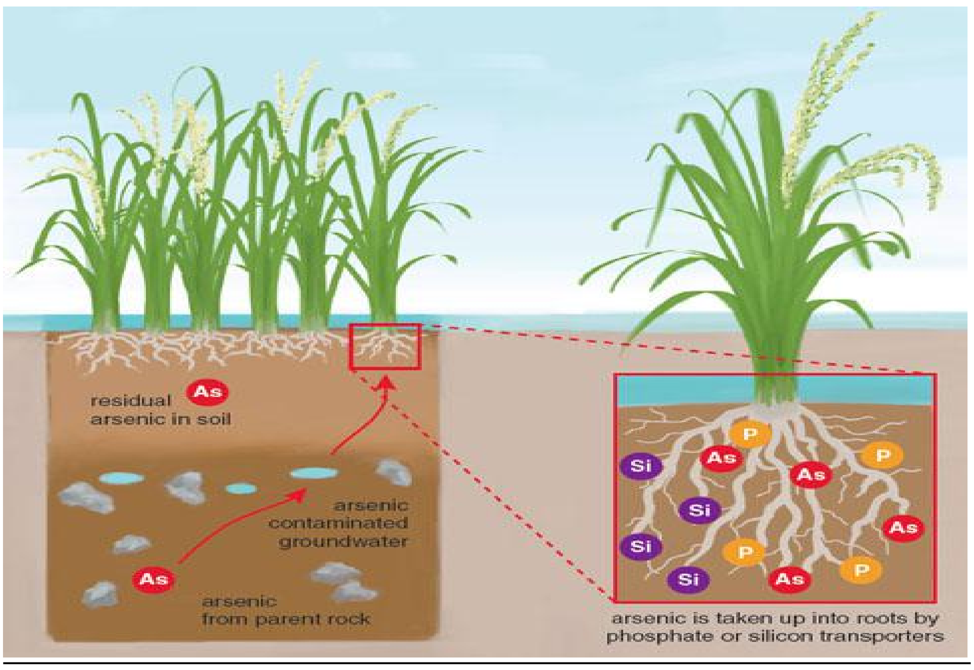
Arsenic is a toxic trace element, denoted by the symbol As. It is not usually found on its own. Rather, it is bound with other elements in chemical compounds. These compounds can be divided into two broad categories:

1. *Organic arsenic*: mainly found in plant and animal tissues.
2. *Inorganic arsenic*: found in rocks and soil or dissolved in water. This is the more toxic form.

Both forms are naturally present in the environment, but their levels have been increasing due to pollution.

For a number of reasons, rice may accumulate a significant amount of inorganic arsenic (the more toxic form) from the environment.

Why Is Arsenic Found in Rice?



Arsenic naturally occurs in water, soil and rocks, but its levels may be higher in some areas than others. It readily enters the food chain and may accumulate in significant amounts in both animals and plants, some of which are eaten by humans.

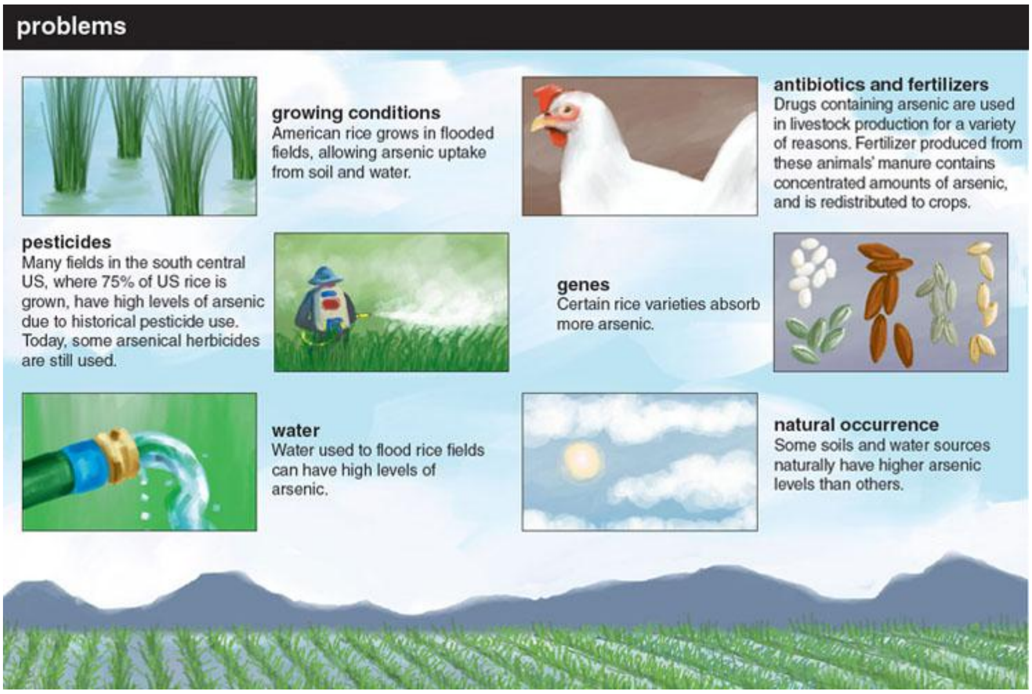
As a result of human activities, arsenic pollution has been rising. The main sources of arsenic pollution include certain pesticides and herbicides, wood preservatives, phosphate fertilizers, industrial waste, mining activities, coal burning and smelting. Arsenic often drains into groundwater, which is heavily polluted in certain parts of the world. From groundwater, arsenic finds its way into wells and other water supplies that may be used for crop irrigation and cooking.

Paddy rice is particularly susceptible to arsenic contamination, for three reasons: It is grown in flooded fields (paddy fields) that require high quantities of irrigation water. In many areas, this irrigation water is contaminated with arsenic. Arsenic may accumulate in the soil of paddy fields, worsening the problem.

Rice absorbs more arsenic from water and soil compared to other common food crops. Using contaminated water for cooking is another concern, because rice grains easily absorb arsenic from cooking water when they are boiled.

Rice Rhizosphere

BOTTOM LINE: The toxic symptoms of dietary arsenic usually take a long time to develop. Long-term ingestion may increase the risk of various health problems, including cancer, heart disease, type 2 diabetes and decreased intelligence.



The arsenic content in rice varies depending on the type of the rice cultivar, the place where it was cultivated, and how it was processed; brown rice contains higher concentrations than white rice. Moreover,

changes in arsenic content may occur during the preparation of food in which cooking water seems to be of special importance; cooking rice in uncontaminated water can reduce the arsenic content of the rice.

Most of the inorganic arsenic in rice is concentrated in the bran layers that contain 10 to 20 times higher concentrations than whole grain. Therefore, the risk from consumption of products made from rice bran such as rice drinks is much higher than that from raw, but polished (white) rice. Moreover, rice bran is often added to products such as rice crackers or rice cereals to increase the fiber content or used directly as a health food supplement.

Type of Rice which contains least amount of arsenic

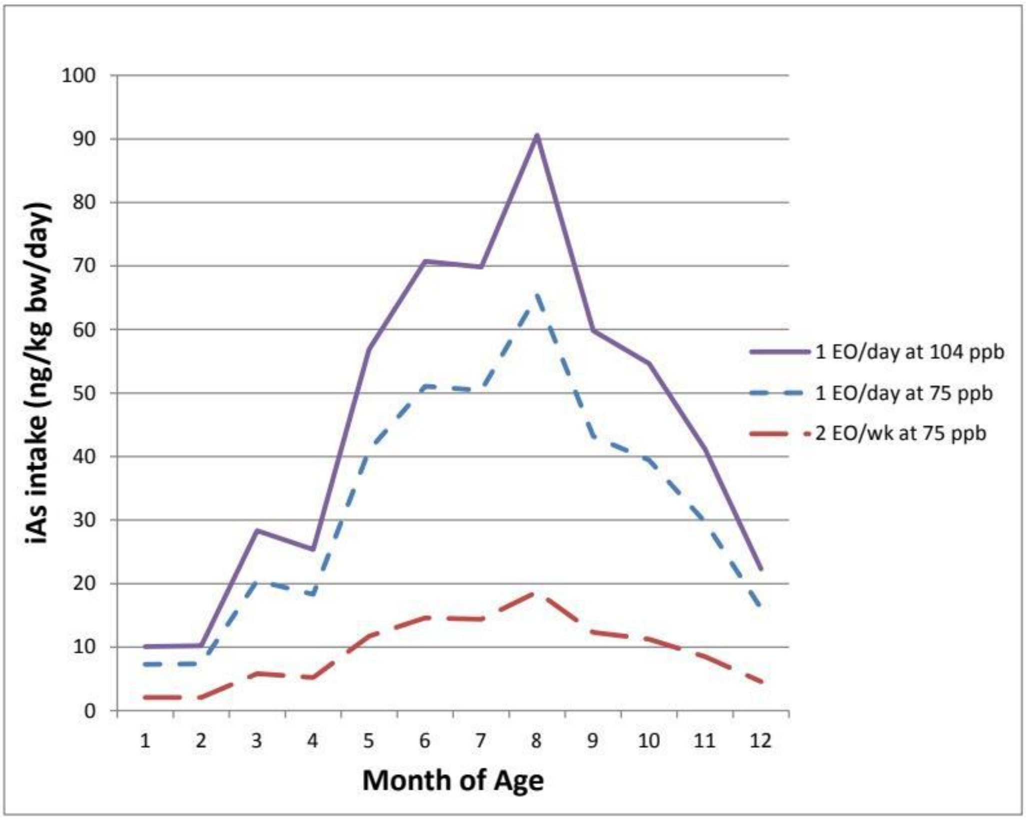


Figure 6.3. Hypothetical Variation in Daily Inorganic Arsenic (iAs) Intake from Infant White-Rice Cereal, Based on the iAs Concentration and Number of Cereal-Eating Occasions (EO)

Basmati rice is lower in arsenic than other kinds of rice.

Brown rice usually contains more arsenic than white rice because it is found in the husk, which isn't removed in brown rice. (That said, remember that brown rice has more nutrients.)

Whether rice is grown organically or conventionally does not have an impact on arsenic levels.

Rice cakes and crackers can contain levels higher than in cooked rice.

The levels of arsenic found in rice milk are way more than the amounts that is generally allowed in drinking water

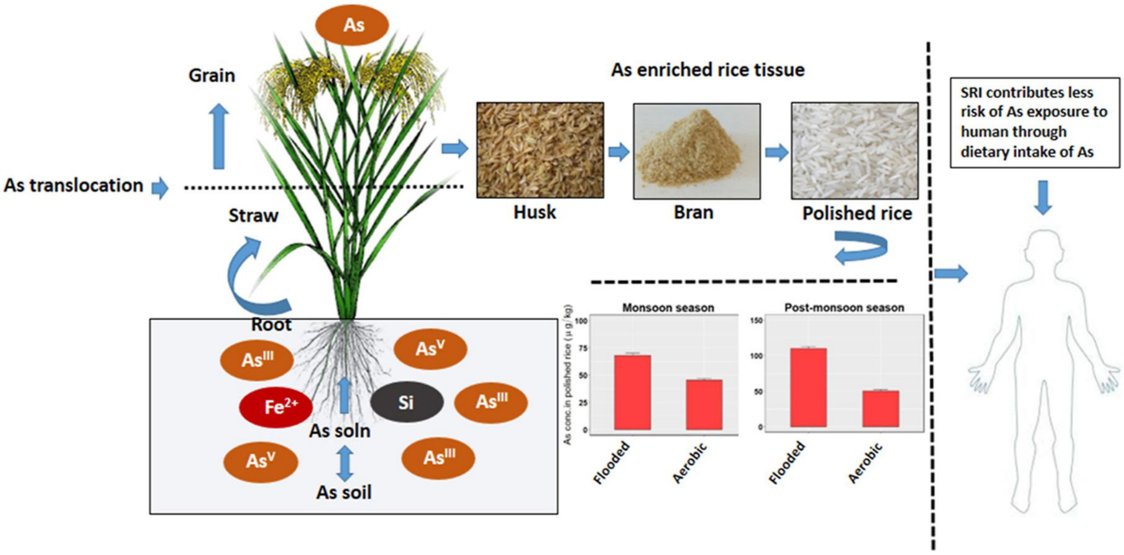
Is Arsenic in Rice a Concern?

Yes. There is no doubt about it, arsenic in rice is a problem. This may pose a health risk to those who eat rice every day in considerable amounts. This mainly applies to people in Asia or people with Asian-based diets. Other groups who may eat a lot of rice products include young children and those on a milk-free or gluten-free diet. Rice-based infant formulas, rice crackers, pudding and rice milk sometimes make up a large portion of these diets.

Young children are especially vulnerable because of their small body size. Therefore, feeding them rice cereals every day may not be such a good idea. Of additional concern is brown rice syrup, a rice-derived sweetener that may be high in arsenic. It is often used in baby formulas.

Of course, not all rice contains high arsenic levels, but determining the arsenic content of a particular rice product may be difficult (or impossible) without actually measuring it in a lab. BOTTOM LINE: Arsenic contamination is a serious concern for the millions of people who rely on rice as their staple food. Young children are also at risk if rice-based products make up a large part of their diet.

Health Effects of Arsenic

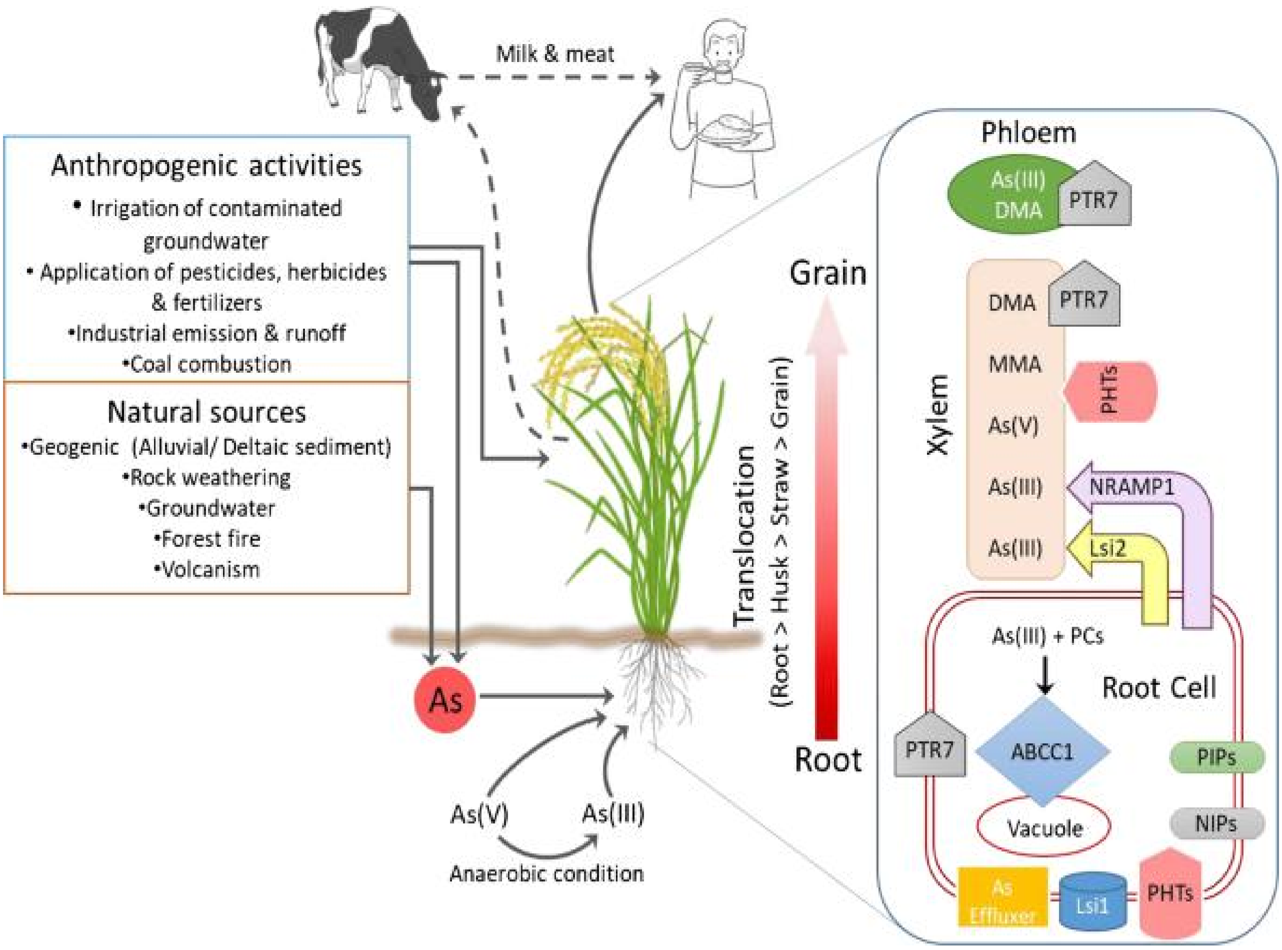


High doses of arsenic are acutely toxic, causing various adverse symptoms and even death. Dietary arsenic is generally present in low amounts, and does not cause any immediate symptoms of poisoning. However, long-term ingestion of inorganic arsenic may cause various health problems and increase the risk of chronic diseases.

These include:

- Various types of cancer.
- Narrowing or blockage of blood vessels (vascular disease).
- High blood pressure (hypertension)
- Heart disease
- Type 2 diabetes
- In addition, arsenic is toxic to nerve cells and may affect brain function. In children and teenagers, arsenic exposure has been associated with:
- Impaired concentration, learning and memory

- Reduced intelligence and social competence.
- Some of these impairments may have taken place before birth. Several studies indicate that high arsenic intake among pregnant women has adverse effects on the fetus, increasing the risk of birth defects and hindering development.



How to Reduce Arsenic in Rice?

The arsenic content of rice can be reduced by washing and cooking the rice with clean water that is low in arsenic. This is effective for both white and brown rice, potentially reducing the arsenic content by up to 57%. However, if the cooking water is high in arsenic, it may have the opposite effect and raise the arsenic content significantly.

The following tips should help reduce the arsenic content of your rice:

- Use plenty of water when cooking.
- Soaking rice in large bowl with water

- Soak your rice overnight – this opens up the grain and allows the arsenic to escape.
- Drain the rice and rinse thoroughly with fresh water.
- Draining rice and rinsing with water.

- For every part rice add 5 parts water and cook until the rice is tender – do not allow it to boil dry.
- Drain the rice and rinse again with hot water to get rid of the last of the cooking water
- Wash the rice before cooking. This method may remove 10–28% of the arsenic.
- Brown rice contains higher amounts of arsenic than white rice. If you eat large amounts of rice, the white variety may be a better choice.
- Choose aromatic rice, such as basmati or jasmine.
- Choose rice from the Himalayan region, including North India, North Pakistan and Nepal.
- If possible, avoid rice that is grown during the dry season. The use of arsenic contaminated water is more common during that time.
- The last and most important piece of advice concerns your diet as a whole. Make sure to diversify your diet by eating many different foods. Your diet should never be dominated by one type of food. Not only does this ensure that you are getting all the nutrients you need, it also prevents you from getting too much of one thing.
- You can follow a few simple cooking methods tips to reduce the arsenic content of rice. Also keep in mind that some types of rice, such as basmati and jasmine, are lower in arsenic.

Regulatory status:-

Regulations have been established in many countries for metal contaminants in foods. Internationally, Codex Alimentarius Commission has set limits for metal contaminants in foods under the "General standard for contaminants and toxins in food and feed (CXS

193-1995)" which serves as the reference standard for international trade in food. Provisions under Food Safety and Standards Act, 2006 The maximum limits for metal contaminants are prescribed under Food Safety and Standards (Contaminants, Toxins and Residues) Regulations, 2011 (FSSR). These Regulations are available on FSSAI website (www.fssai.gov.in). The regulations establish maximum levels (MLS) for various metal contaminants in a range of foodstuffs. Maximum limits of some of the major food categories covered above are reproduced below:

Name of metal contaminant	Article of food	Parts per million by weight
Lead	Brassica vegetable excluding Kale, Leafy vegetables (excluding spinach)	0.3
	Bulb vegetables, Fruiting vegetables, cucurbits and Root & tuber vegetables	0.1
	Foods not specified	2.5
Arsenic	Foods not specified	1.1
Cadmium	Rice Polished	0.4
	Brassica, Bulb and fruiting vegetables, cucurbits	0.05
	Leafy vegetables	0.2
	Other foods	1.5
Mercury	Fish	0.5
	Predatory Fish (Tuna, Marlin, Sword Fish, Elasmobranch)	1.0
	Non predatory fish, Cephalopods, crustaceans, molluscus	0.5
	Other Foods	1.0

*For specific limits please refer the Regulations.

Test methods for determination of metal contaminants in food 15. Various analytical methods are employed in analysis of metal contaminants in food. The analytical methods include Atomic Absorption Spectrometer, Inductively Coupled Plasma Optical Emission Spectrometer, Spectrophotometer, cliometric method, and titrimetric method. The detailed methodology for sample preparation, extraction, and analysis is provided in the Manual of methods of analysis of foods- Metals.

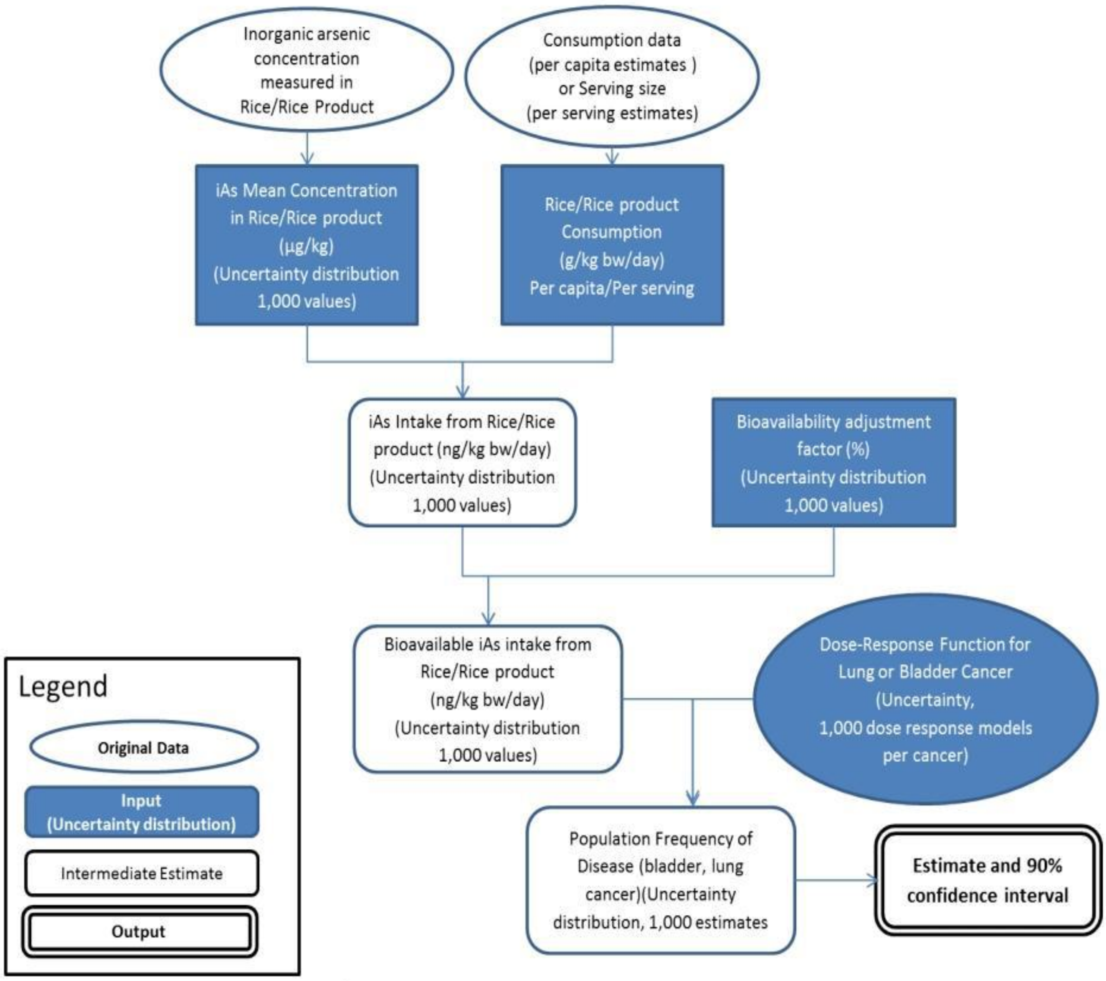


Figure 5.1 Interrelationship of the Risk Assessment Model Components

Arsenic limits allowed in rice by governmental bodies:-

The arsenic content of raw rice varies from 0.1 to 0.4 mg of inorganic arsenic/kg of dry mass. Rice has a much higher arsenic level than that in other grains such as wheat and barley, for which the reported total arsenic content is 0.03 to 0.08 mg/kg. Moreover, the quantity of inorganic arsenic in cereals based on grains other than rice was less than detection levels.

As stated in the EFSA report, ‘‘rice grains’’ and ‘‘rice based products’’ in the EU market contain very high mean levels of total arsenic, ranging from 0.14 and 0.17 mg/kg.

Table 4.13. Mean Inorganic Arsenic Exposure from Rice per Eating Occasion: Males and Females, 0 – 50 years

Rice Type	Mean Inorganic Arsenic Concentration[a] ppb[b]	Mean rice intake[c] g/kg bw/eating occasion	Mean inorganic arsenic exposure[d] ng/kg bw/eating occasion
Brown Basmati	133.3	0.866	115.5
Brown Jasmine	142.4	0.866	123.4
Brown Instant/pre-cooked	72.0	0.866	62.3
Brown Parboiled	191.3	0.866	165.7
Brown Long/med/short grain,	156.5	0.866	135.5
White Basmati	62.3	1.094	68.2
White Jasmine	75.1	1.094	82.1
White Instant/pre-cooked	57.6	1.094	63.0
White Parboiled	112.4	1.094	123.0
White Long grain, regular	102.0	1.094	111.5
White Medium grain, regular	81.5	1.094	89.2
White Short grain, regular	78.9	1.094	86.3

Consumption in Infants and Children:-

Table 7.1. Lifetime Risk for Different Exposure Periods and Exposure Estimates

Exposure Period	Exposure Estimate	Food Products	Cancer Risk (cases/million) (CI90%)
Infancy (< 1 yr)	Average per capita	All rice and rice products incl infant rice cereal	2.3 (0, 4.6)
Childhood (0 – 6 yrs)	Average per capita	All rice and rice products	9.1 (0, 19)
Lifetime (0 – 50 yrs)	Average per capita	All rice and rice products	39 (0, 79)
Infancy (< 1 yr)	Per daily serving	Infant cereal (white rice)	2.8(0, 5.7)
Childhood (0 – 6 yrs)	Per daily serving	White long grain rice	33 (0, 67)
Lifetime (0 – 50 yrs)	Per daily serving	White long grain rice	136 (0, 278)

Rice consumption differs between ethnic groups. Traditionally in European adults, an average of 9 g of rice is consumed per day, leading to an additional exposure to inorganic arsenic of 0.015mg/kg body weight, whereas in the Asian diet, rice consumption is approximately 300 g per day leading to an extra exposure of 0.5mg/kg body weight; however, the risk of exposure to inorganic arsenic from rice is not limited to Asian communities; infants and young children have 2 to 3 times higher inorganic arsenic exposure than adults.It has been reported that infants fed with breast milk consume the lowest levels of arsenic.

CASE STUDY

Case Study 1 :-

INDIA TV

Washington, Sep 20: The US Food and Drug Administration (USFDA) has found arsenic content in about 30 samples of Indian basmati rice in its preliminary analysis.

PTIPTI

Updated on: September 21, 2012 12:15 IST

The regulator would issue advisory to consumers only after completing its entire study. However, exporters from India said that basmati rice was free from arsenic content as shipments are made only after complying with required tests.

Arsenic is a chemical matter present in the environment from both natural and human sources. It is found in water, air, food and soil in organic and inorganic form.

As of now, the USFDA has collected 200 samples of rice and rice products available in American market from different countries including India. "The FDA is in the process of collecting and analysing a total of approximately 1,200 samples to examine the issue thoroughly. This data collection will be completed by the end of 2012. Once the data collection is completed, FDA will analyse these results and determine whether or not to issue additional recommendations," the USFDA said in a release.

Of 200 samples released yesterday, as many as 34 samples were from Indian origin basmati rice. Of that, 31 samples contained inorganic arsenic content in the range of 1.8 to 6.5 microgram per serving.

When asked about the preliminary findings of the USFDA, All India Rice Exporters Association former President Vijay Sethia said, "Indian basmati rice is free from arsenic content as we export only after testing water and rice."

India, the world's largest producer and exporter, ships about 2 million tonne basmati rice a year. In its statement, the USFDA said that the analysis of 200 initial samples found average levels of inorganic arsenic for the various rice and rice products in the range of 3.5 to 6.7 micrograms per serving. "Based on the currently available data and scientific literature, the FDA does not have an

adequate scientific basis to recommend changes by consumers regarding their consumption of rice and rice products," it added.
For the time being, the regulator has advised consumers to have a balanced diet with wide variety of grains.

USFDA Deputy Commissioner Michael Taylor said, "The FDA's ongoing data collection and other assessments will give us a solid scientific basis for determining what action levels and/or other steps are needed to reduce exposure to arsenic in rice and rice products."

Case Study 2:-

Should I worry about arsenic in my rice?

By Dr Michael Mosley

BBC News

Published10 February 2017

Does rice really contain harmful quantities of arsenic? Dr Michael Mosley of Trust Me, I'm A Doctor investigates.

Many of us are regular consumers of rice - UK consumption is on the rise, and in 2015 we ate 150m kg of the stuff. But there have been reports about rice containing inorganic arsenic - a known poison - so should we be worried?

Arsenic occurs naturally in soil, and inorganic arsenic is classified as a category one carcinogen by the EU, meaning that it's known to cause cancer in humans.

The consequences of arsenic poisoning have been seen most dramatically in Bangladesh, where populations have been exposed to contaminated drinking water.

The result has been described as a "slow burning epidemic" of cancers, heart disease and developmental problems.

Because arsenic exists in soil, small amounts can get into food, though in general these levels are so low that they're not a cause for concern.

Rice however, is different from other crops, because it's grown under flooded conditions. This makes the arsenic locked in the soil more readily available, meaning that more can be absorbed into the rice grains.

'Dose dependent'

This is why rice contains about 10-20 times more arsenic than other cereal crops. But are these levels high enough to do us any real harm?

"The only thing I can really equate it to is smoking," says Prof Andy Meharg of Queen's University Belfast, who has been studying arsenic for decades. "If you take one or two cigarettes per day, your risks are going to be a lot less than if you're smoking 30 or 40 cigarettes a day. It's dose-dependent - the more you eat, the higher your risk is."

He believes that the current legislation isn't strict enough, and that more needs to be done to protect those who eat a lot of rice.

Eating a couple of portions of rice a week isn't putting an adult like me at high risk, but Prof Meharg is concerned about children and babies.

"We know that low levels of arsenic impact immune development, they impact growth development, they impact IQ development," he says.

Because of this, the legislation is stricter around products specifically marketed at children - but many other rice products that they may also eat, such as puffed rice cereals, can contain adult levels of arsenic.

It sounds quite scary, even if you don't eat lots of rice, but there's an easy solution - a way to cook rice that dramatically reduces the arsenic content.

Now, some ways of cooking rice reduce arsenic levels more than others. We carried out some tests with Prof Meharg and found the best technique is to soak the rice overnight before cooking it in a 5:1 water-to-rice ratio.

That cuts arsenic levels by 80%, compared to the common approach of using two parts water to one part rice and letting all the water soak in. Using lots of water - the 5:1 ratio - without pre-soaking also reduced arsenic levels, but not by as much as the pre-soaking levels.

So, while I would now think twice about feeding young children too much rice or rice products, I'm not going to stop eating rice myself. I

will, however, be cooking it in more water and, when I remember, leave it to soak overnight.

Case Study 3:

Arsenic in Rice: A Cause for Concern

Iva Hojsak, Christian Braegger, Jiri Bronsky, Cristina Campoy, Virginie Colomb, Tamas Decsi, Magnus Domello, Mary Fewtrell, Natas Fidler Mis, Walter Mihatsch, Christian Molgaard, and Johannes van Goudoever, for the ESPGHAN Committee on Nutrition - January2015

Inorganic arsenic intake is likely to affect long-term health. High concentrations are found in some rice-based foods and drinks widely used in infants and young children. In order to reduce exposure, we recommend avoidance of rice drinks for infants and young children. For all of the rice products, strict regulation should be enforced regarding arsenic content. Moreover, infants and young children should consume a balanced diet including a variety of grains as carbohydrate sources. Although rice protein–based infant formulas are an option for infants with cows' milk protein allergy, the inorganic arsenic content should be declared and the potential risks should be considered when using these products.

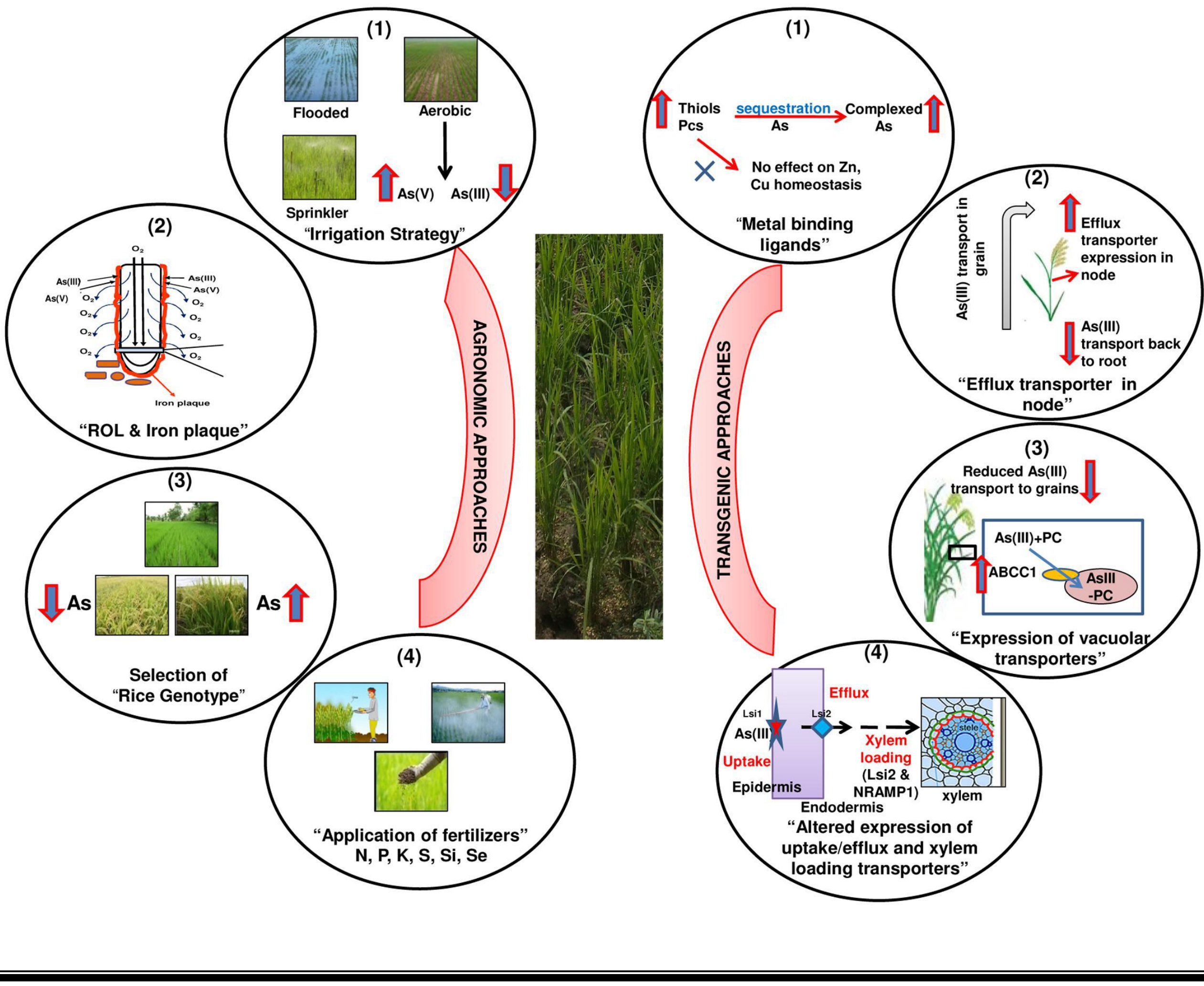
Case Study 4:

Simple Cooking Method Flushes Arsenic out of Rice

Preparing rice in a coffee machine can halve levels of the naturally occurring but toxic substance

By Emily Sohn, Nature magazine on July 27, 2015

Cooking rice by repeatedly flushing it through with fresh hot water can remove much of the grain’s stored arsenic, researchers have found—a tip that could lessen levels of the toxic substance in one of the world’s most popular foods.



Billions of people eat rice daily, but it contributes more arsenic to the human diet than any other food. Conventionally grown in flooded paddies, rice takes up more arsenic (which occurs naturally in water and soil as part of an inorganic compound) than do other grains. High levels of arsenic in food have been linked to different types of cancer, and other health problems.

Andrew Meharg, a plant and soil scientist at Queen’s University Belfast, UK, wondered whether cooking the grain in a different way might help to lessen the health risk. The standard method for making rice—boiling it in a pot until it soaks up all the liquid—binds into place any arsenic contained in the rice and the cooking water.

Percolation is key:- On the basis of earlier work, Meharg and his colleagues knew that arsenic levels drop when rice is thoroughly rinsed and then cooked in an excessive amount of water. The method helps even when the cooking water contains arsenic.

Meharg and colleagues found that using this method with increasing proportions of water removed progressively more arsenic—up to a 57 percent reduction with a ratio of 12 parts water to one part rice. That result confirmed that the arsenic is "mobile" in liquid water, and thus can be removed.

The team then cooked rice in an apparatus that continually condenses steam to produce a fresh supply of distilled hot water, and in an ordinary coffee percolator with a filter, which allows cooking water to drip out of the rice. Testing the rice before and after cooking showed that coffee-pot percolation removed about half the arsenic, and that the lab apparatus removed around 60–70 percent. In some cases, the technique removed as much as 85 percent of the substance, depending on the type of rice used. The findings are reported in PLoS ONE.

Short-term fix:- Meharg does not expect people to start cooking rice in their coffee machines. “We just took something that’s in everybody’s kitchen and applied it to show a principle,” he says. He sees the research as a proof of concept that could feed the development of simple, inexpensive rice cookers that lower arsenic concentrations.

The risk of arsenic poisoning is greatest for consumers who eat rice several times a day. In Bangladesh, where rice is a staple and the water is also naturally high in arsenic, people are particularly vulnerable. Parboiling facilities in the country process rice by pre-cooking, drying and husking the grain. These processes offer the opportunity to intervene on a commercial scale with cookers that would reduce arsenic levels—something that Meharg plans to do.

The same technique could also help companies elsewhere to lower arsenic levels in baby cereals and other products that use pre-cooked rice. Rice-based baby foods often contain high levels of arsenic, a double-whammy for small children, who consume proportionately more of the substance for their body size.

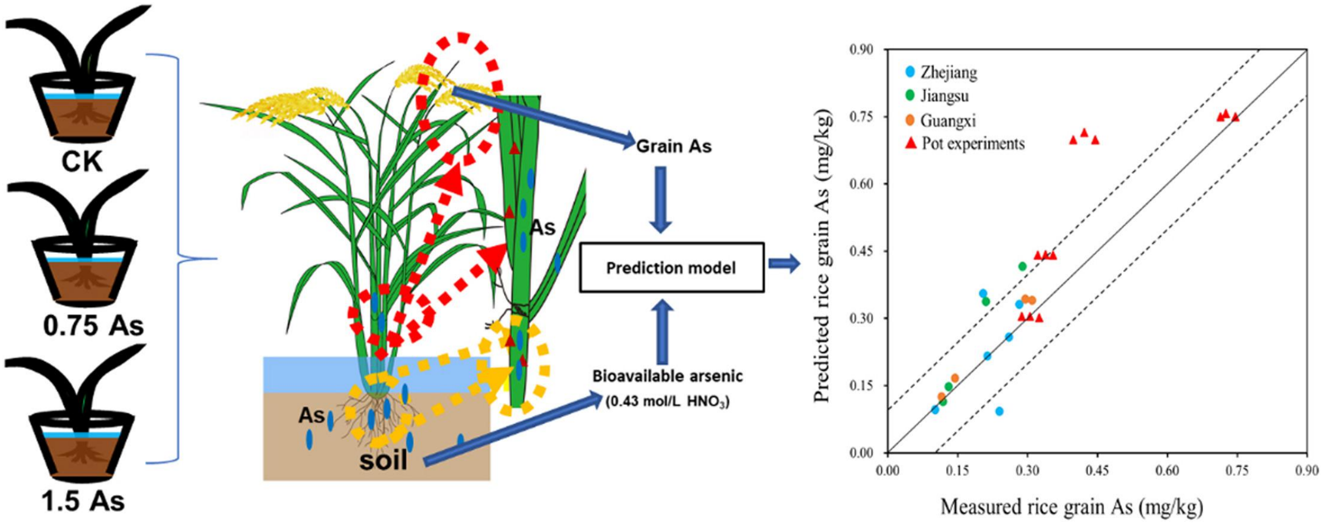
In the long term, the best strategies for removing arsenic from rice will come from ongoing efforts to breed low-arsenic strains and alter growing techniques, says Margaret Karagas, an epidemiologist at Dartmouth College in Hanover, N.H. But, she says, “This paper is really interesting because it is offering a short-term solution to the problem. It’s giving people an opportunity to reduce the arsenic burden of their rice.”

Experimentation

1. Analytical Analysis

Determinations of iAs (inorganic arsenic) in general includes two steps: separation of different As species, followed by quantification. As can be analysed by inductively coupled plasma mass spectrometry (ICP-MS), graphite furnace atomic absorption spectrometry (GF-AAS), hydride generation atomic absorption spectrometry or hydride generation atomic fluorescence spectrometry Among these, ICP-MS typically has the lowest limit of detection (LOD); however, the cost is relatively high. HG-AFS, by contrast, can also achieve low LOD at lower cost. Thus, this affordable HG-AFS method was selected in this study.

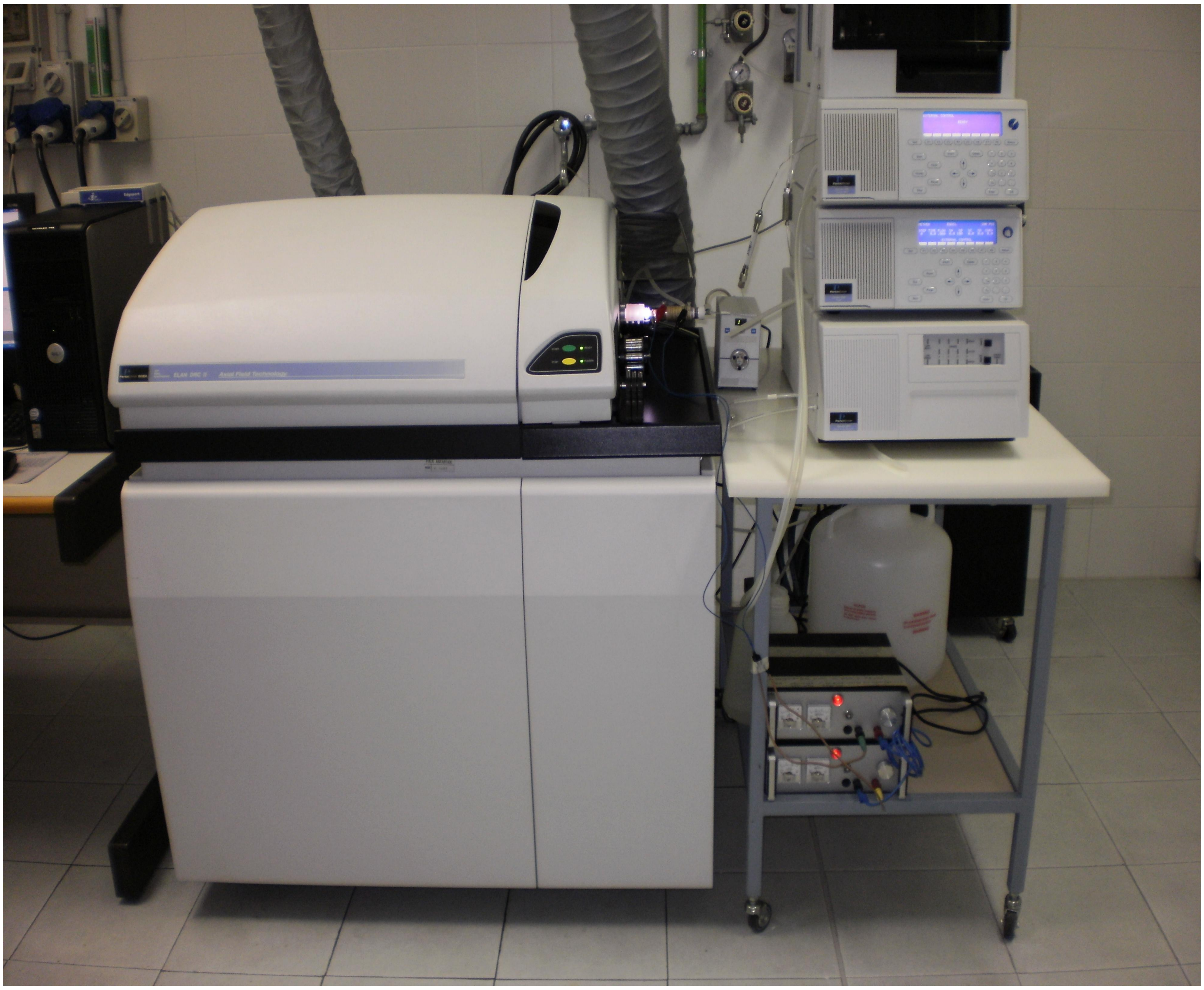
Separation of iAs from organic forms and matrix components is critical; chromatography is widely used for this purpose, HPLC-ICPMS is the golden standard. In addition, gas chromatography (GC) and capillary electrolysis (CE) have been used. To simplify the process and reduce costs, non-chromatographic method may be a promising alternative. iAs was directly determined in rice grains by selective hydride generation at high acidity (4.8 mol/L HCl), which was 50 times more efficient than DMA. Solvent extraction has recently been investigated for the separation of As species, but the method uses toxic chemicals and is time-consuming. Solid phase extraction (SPE) can also be used to separate the target. As species with a variety of sorbents and can be operated in parallel to enhance the sample throughput. Recently, a silica-based SAX sorbent was used to separate iAs from organic forms through adjustment of the pH based on dissociation constants, which proved highly sensitive for iAs quantification. This method can be used to separate As^{5+} from organic As; accordingly, As^{3+} was oxidized to As^{5+} prior to separation. As^{3+} also forms covalent molecular $AsCl_3$ in concentrated HCl. The aim of this study was to develop a new method for separating iAs from other forms using polystyrene resin as SPE sorbent and utilizing the characteristics of $AsCl^3$, followed by HG-AFS determination. This method is suitable for routine use because of low cost and simplicity.



2. Experimental method

2.1 Reagents and standards

Arsenite (As^{3+}), arsenate (As_{5+}), Monomethylarsonic Acid (MMA), and Dimethylarsinic Acid (DMA), Deionized water $(NH_4)_2HPO_4$, KBH_4, HCl, and HNO_3. methanol (HPLC grade). solid phase column KOH and thiourea (analytical reagent grade) The Rice flour and Rice samples were purchased from a supermarket. All samples were stored at 4 ºC until analysis.



2.2 Instrumentation

HG-AFS was equipped with an As-boosted hollow cathode lamp (193.7 nm). HPLC-HG-AFS with an anion exchange column (PRP-X 100, 250 mm × 4.1 mm i.d., 10 μm) was used to separate As species with 15 mmol/L $(NH_4)_2HPO_4$ (pH = 6.0, 1 mL/min flow rate) as the mobile phase and 7% HCl and 1.5% KBH4 as the carrier solution and reductant, respectively.

ICP-MS was coupled with HPLC systems , and the HPLC-ICP-MS instrument was used to verify the results of SPE-GH-AFS. The column used was an anion exchange column (PRP-X 100), and 15 mmol/L (NH4)2HPO4 (pH 6.0, 1 mL/min flow rate) was used as the mobile phase. The ICP-MS operating parameters were as follows: incident RF power at 1300 W, cooling Ar gas flow rate at 13 L/min, nebulizer Ar gas flow rate at 0.9 L/min, and auxiliary Ar gas flow rate at 1 mL/min. The ICP-MS was used in the collision-reaction cell with the kinetic energy discrimination (CCT-KED) mode using H_2 – He as the collision cell gas (5 mL/min) to reduce $^{40}Ar^{35}Cl^{+}$ interference with As.

2.3 Determination of iAs

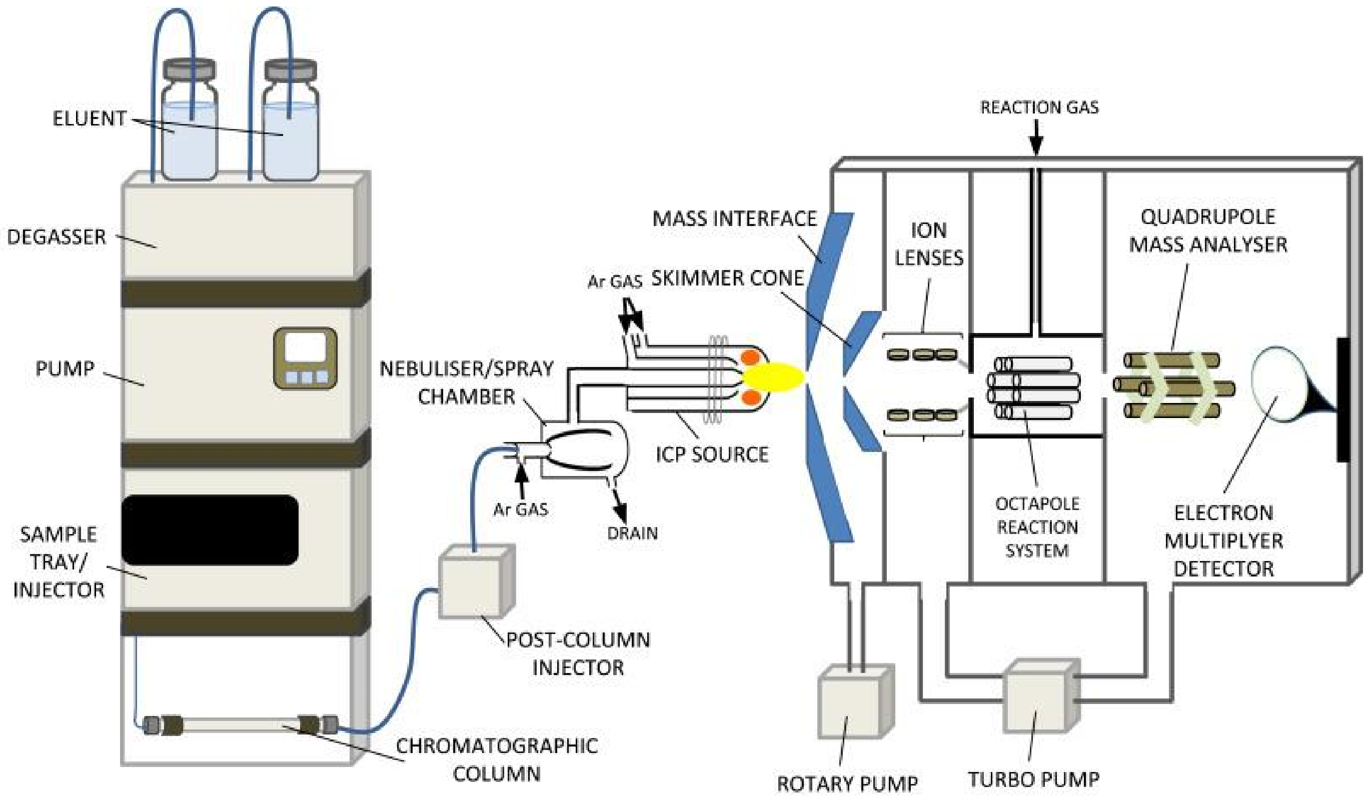
2.3.1 *Arsenic extraction*

Sample powders (1.000±0.001 g) was placed in a 50-mL polypropylene tube with 20 mL of 0.02 mol/L HNO_3. After mixing thoroughly with a vortex mixer, the tube was held in a water bath at 90 ºC for 60 min and then centrifuged at 3300g for 10 min. Finally, the supernatant was filtered through a 0.22-μm membrane, and the solution was analysed by SPE-HG-AFS and HPLC-ICPMS.

2.3.2 *SPE-HG-AFS analysis*

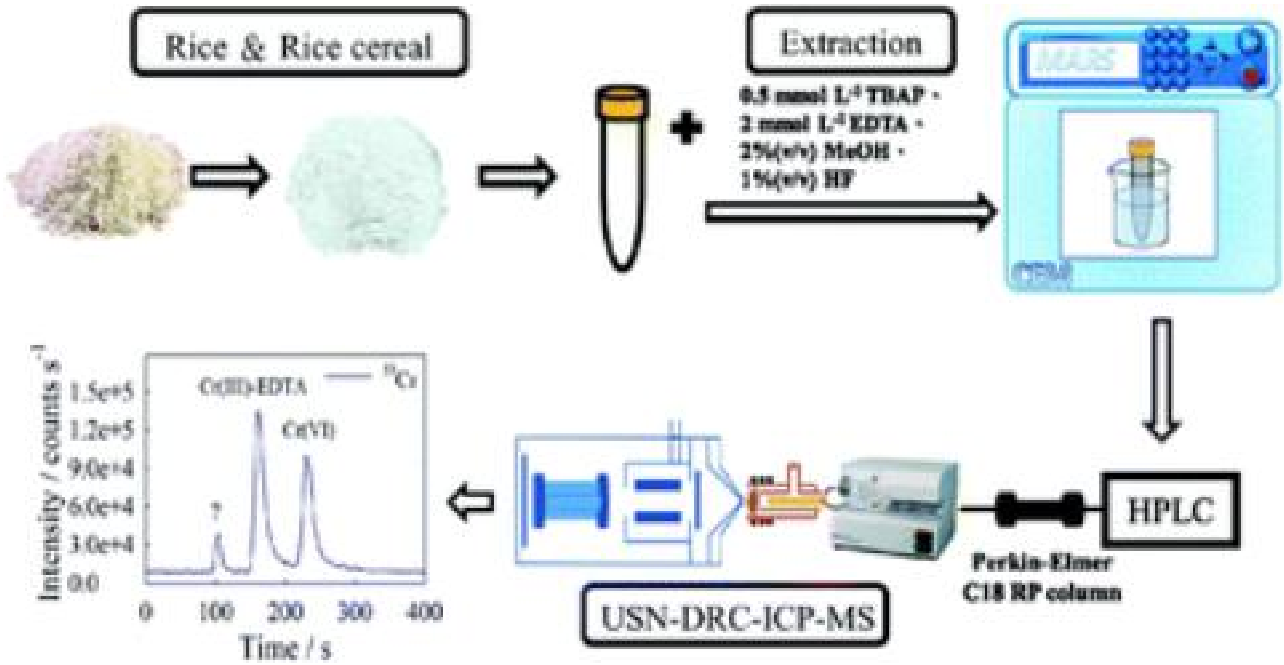
Sample solutions were adjusted to 10.0 mol/L HCl and 0.2% thiourea, and held for 30 min. The cartridges were activated prior to installation using 3 mL of methanol and 3 mL of water. After rinsing the cartridges with 2 mL of 10 mol/L HCl, sample solutions were pumped through the cartridge at 0.5 mL/min to sequester As^{3+} . The cartridges were then rinsed with 2 mL of 10 mol/L HCl and eluted with 2 mL of water. The solutions were vortex mixed and analysed

by HG-AFS. For the comparison method, the extracted solution was directly analysed by HPLC-ICP-MS.



2.4 Determination of total As

Total As in the CRMs and the rice flour samples were determined by HG-AFS after microwave digestion. Smples (0.500±0.001 g) were placed in digestion vessels, and added with 8 mL of HNO3 and 2 mL of H2O2. The vessels were placed on the hot block and kept at 130 ℃ for 2 h, and then heated at 145 ℃ until roughly 1 mL volume remained. After cooling, the digests were transferred to 50 mL volumetric flasks and diluted to mark with 0.5% thiourea. Following 15s vortex mixing, the solutions were measured by HG-AFS.



2.5 Method validation

Stock solutions of four As species were prepared at 0.1–50 µg/L. The linear regression equations and the correlation coefficients were obtained from the peak area ratios vs. concentration plot.

2.6 Statistical analysis

Experimental data were evaluated using the statistical software. Statistically significant differences were assessed using Duncan’s multiple range test, with $p \leq 0.05$ being considered significant.

3. Results and discussion

3.1 Extraction of As species from rice samples

Extraction of As species from rice samples should avoid the transformation of organic As to iAs and should simultaneously attain good extraction efficiency; therefore, the choice of the extractant is a critical factor in method development. The most commonly used extractants include dilute acid solutions, enzymes, water, and methanol solutions. The cost of enzymes was relatively high and methanol should be removed before analysis by HG-AFS because it affects the intensity of HG-AFS. Acid extraction with HCl, HNO3, trifluoroacetic acid (TFA), etc. is common due to high efficiency and low cost. Therefore, to select the most efficient extractant among the acids, the extraction efficiencies (ratio of all species to total As) of 0.02 and 0.1 mol/L TFA, 0.02 and 0.1 mol/L HNO_3, and 0.02 and 0.1 mol/L HCl were calculated by comparing the As species analysed by HPLC-ICPMS to total As by HG-AFS. Extraction efficiencies are also influenced by the rice species and variety. We minimized matrix effects by mixing rice samples; therefore, we similarly prepared a mixed rice sample by mixing sample Nos. 2, 4, and 5. Among the extractants, HNO_3 and TFA achieved higher extraction efficiencies than HCl, possibly due to Cl- competing with H_2AsO_4 - for amine groups. Therefore, 0.02 mol/L HNO3 was selected as the optimal extractant. As^{5+} in the extract should be reduced to As^{3+} first by iodide, L-cysteine, or thiourea. Among these, thiourea was selected because it acts both as a reducing agent for As^{5+} and a masking reagent to eliminate interferences from transition metals. The effect of the thiourea concentration was investigated over the range

0.1–0.6% (m/v), and 0.2% thiourea in 10 mol/L HCl was found to be effective within 20 min.

3.2 Solid phase extraction

In a previous study, iAs in rice was separated from other As species by using a silica-based SAX sorbent. Based on dissociation constants, only As^{5+} was retained on ion exchange sorbents at certain pH. A novel method for separating iAs from other species by SPE was developed based on the properties of covalent $AsCl_3$, which can be selectively extracted by the solvent with high recovery and can also be retained by a non-polar resin. Therefore, the PS solid phase

column was adopted. Retention of three species of As (As^{3+}, DMA, and MMA) on the PS resin at various HCl concentrations was evaluated. A series of solutions containing 50 μg/L As^{3+} , DMA, or MMA was prepared at different HCl concentrations. After elution, the eluates were analysed by HPLC-HG-AFS and the recoveries of the three As species at different HCl concentrations were calculated. As^{3+} recovery increased with increasing HCl concentration, reaching a plateau at 10 mol/L HCl; DMA and MMA, on the other hand, did not retain at any HCl concentration. Clearly, retention of As^{3+} was the result of the PS resin attracting the molecular covalent compound, because formation of molecular AsCl3 was enhanced at higher HCl concentrations. For maximum recovery, 10 mol/L HCl was chosen.

In the presence of certain elements, such as Sb^{3+}, DMA are also retained on the PS resins leading to substantial interfere. In order to wash out other As species and interfering ions, and to maintain retention of molecular $AsCl_3$ on the PS, the columns were washed with 1 mL of 10 mol/L HCl. AsCl3 retained on the PS sorbent was eluted by hydrolysis. The elution solution should promote As^{3+}

desorption from the PS resin by facilitating the following hydrolysis reaction.

$$AsCl_3 + 3H_2O = AsO_3\ 3- + 3Cl- + 6H+$$

From the above equation, it is obvious that water or OH containing eluents could promote AsCl3 hydrolysis. Therefore, the recoveries of different volumes of water and 0.1% NaOH (m/v) were studied; At 1 mL, 0.1% NaOH achieved higher elution efficiency (68.9% ± 4.0%) than water (59.3% ± 5.8). At 3 mL, however, water (98.2% ± 4.0%) and 0.1% NaOH (98.1% ± 2.4%) showed identical recoveries; therefore, water was chosen as the most suitable eluent for its simplicity and low cost.

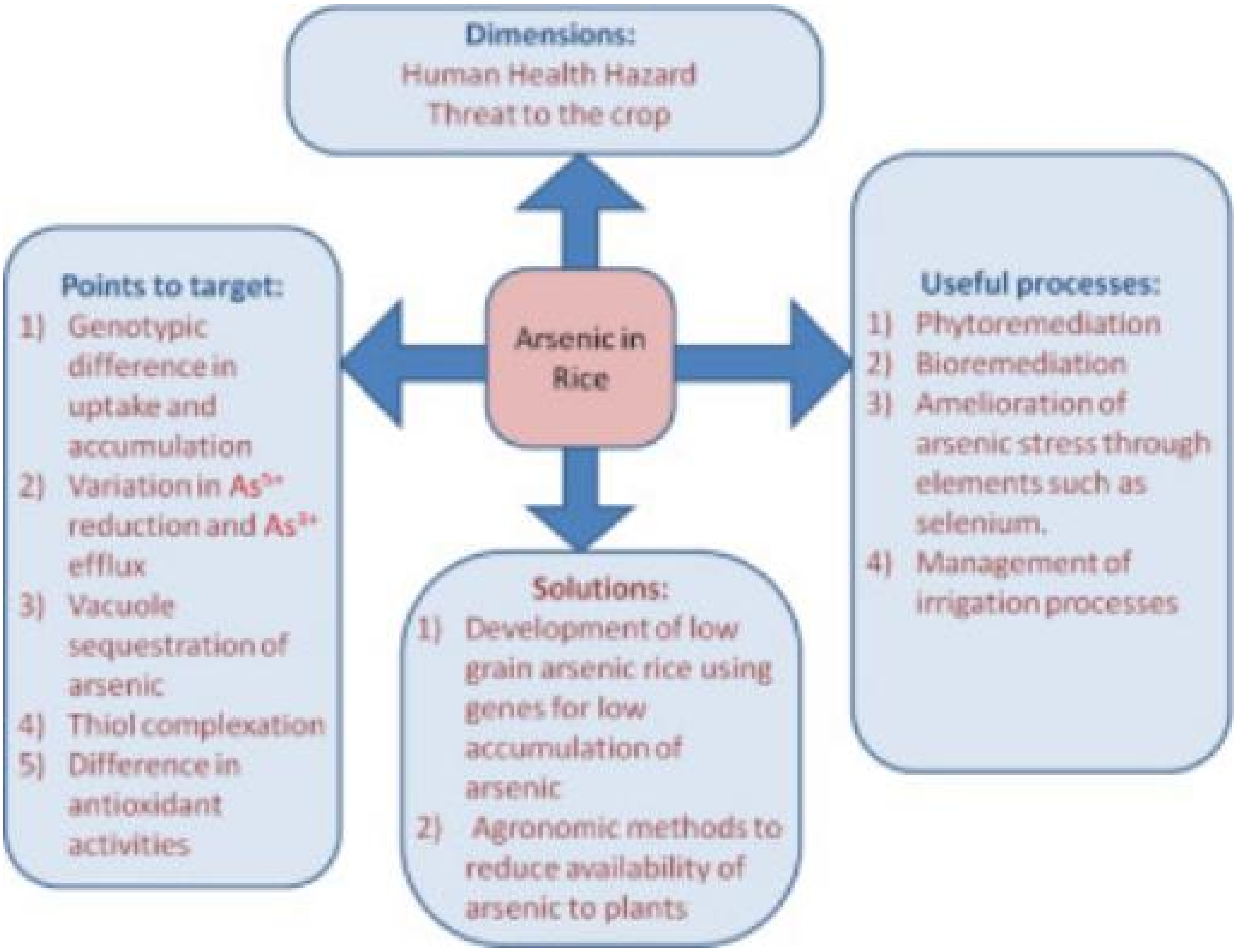
3.3 Hydride generation atomic fluorescence spectrometry

The HG procedure was critical for the determination of As, HCl and KBH_4 were used for reducing As^{3+} to arsine and producing H_2 to sustain a flame. The volume and concentration of HCl and KBH_4

were critical for the AFS intensity and stability. Based on the recommended volume by the manufacturer: 3.7 mL of HCl and 2.3 mL of KBH_4 for 1 mL of sample, the effects of HCl and KBH_4 concentrations were studied. 1.4% KBH_4 and 7% HCl were considered optimal.

3.4 Method validation

The calibration curve for As^{3+} had a linear range from 0.5 to 50 µg/L with a high correlation coefficient (R = 0.9997). Based on the signals of 11 reagent blanks, the limit of detection (LOD) was 1.1 µg/kg (3σ) and the limit of quantification (LOQ) was 3.6 µg/kg (10σ). Recoveries of iAs, determined from three rice samples spiked with iAs (As^{3+}:As^{5+} = 1:1), DMA, and MMA, were 90.3–102.6% with RSDs (n = 3) of 3.1–6.3%. The CRMs and seven rice samples were analysed. The results obtained by the present and conventional methods were in good agreement and were not significantly different (95% confidence level, paired t-test), thus verifying the high specificity and accuracy of the developed SPE HG-AFS method.



Conclusion

SPE coupled with the HG-AFS method for the determination of iAs achieved good selectivity with a low LOD. Operation of this method is relatively simple and can be conducted in parallel to improve

throughout. With results closely agreed with those of the conventional methods, this method is applicable to routine As speciation in rice.

We determined that the new literature published after we completed our risk assessment supports the findings in our risk assessment. A large amount of literature has been published on possible modes of action for inorganic arsenic and several promising biomarkers for arsenic exposure and effects have been described. However, none of this research is sufficiently developed to be useful in quantitative risk assessment. Since these are all areas of considerable research, the FDA Arsenic Risk Assessment Team will continue to monitor closely the emerging literature.

References

- EFSA European Food Safety Authority. Scientific Opinion on Arsenic in Food. Available http://www.efsa.europa.eu/en/efsajournal/doc/1351.pdf

- Consumer Reports. 2012. Arsenic in your food. http://www.consumerreports.org/cro/magazine/2012/11/arsenic-in-your-food/index.htm

- Food and Drug Administration (FDA). 2013. Arsenic in rice and rice products. http://www.fda.gov/food/foodborneillnes

- https://www.researchgate.net/publication/298724405_Analytical_Strategies_for_the_Determination_of_Arsenic_in_Rice

- https://www.indiatvnews.com/business/india/30-indian-basmati-rice-samples-contain-arsenic-usfda-2921.html

- https://www.bbc.com/news/health-38910848

- https://pubmed.ncbi.nlm.nih.gov/25536328/

- https://www.scientificamerican.com/article/simple-cooking-method-flushes-arsenic-out-of-rice/

- https://www.healthline.com/nutrition/arsenic-in-rice#TOC_TITLE_HDR_5

- https://www.sciencedirect.com/science/article/pii/S0160412018331283

- https://www.treehugger.com/how-cook-rice-remove-most-arsenic-4858788

- Fowler, B., Alexander, J. and Oskarsson, A. (2015). Handbook of Toxicology of Metals. 4th ed.

- WHO (2018) Arsenic, WORLD Health Organization, Geneva

- Should I worry about arsenic in my rice?- By Dr Michael Mosley BBC Published10 February 2017

- Washington, Sep 20: The US Food and Drug Administration (USFDA) has found arsenic content in about 30 samples of Indian basmati rice in its

  preliminary analysis. By - IndiaTV, Updated on: September 21, 2012 12:15 IST

- Simple Cooking Method Flushes Arsenic out of Rice,Preparing rice in a coffee machine can halve levels of the naturally occurring but toxic substance - By Emily Sohn, Nature magazine on July 27, 2015

- Regulations are available on FSSAI website (www.fssai.gov.in)

- Hite AH. Arsenic and rice: a call for regulation. Nutrition 2013

- European Food Safety Authority Panel on Contaminants in the Food Chain (CONTAM). Scientific opinion on arsenic in food. EFSA J

- Navas-Acien A, Francesconi KA, Silbergeld EK, et al. Seafood intake and urine concentrations of total arsenic, dimethylarsinate and arseno betaine in the US population. Environ

- Sun GX. Williams PN. Carey AM, et al. Inorganic arsenic in rice bran and its products are an order of magnitude higher than in bulk grain.

- Meharg AA. Williams PN, Adomako E, et al. Geographical variation in total and inorganic arsenic content of polished (white) rice. Environ Sci Technol 2009

- World Health Organization. Safety Evaluation of Certain Contaminants in Food. WHO Food Additives Series No. 63. Geneva: World Health Organization

- Agency for Toxic Substances and Disease Registry (ATSDR). Toxico logical Profile for Arsenic. Atlanta, GA: U.S. Department of Health and Human Services; 2007