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Thema: Determination of inorganic arsenic in rice using the Wagtech Digital Arsenator

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List of abbreviations

AFS	atomic fluorescence spectrometer
c_{AFS}	concentration displayed at the AFS
$c_{Arsenator}$	concentration displayed at the Arsenator
c_{real}	real concentration
D_1	Dilution 1
D_2	Dilution 2
D.F.	Dilution Factor
DMAA	Dimethylarsenic acid
ICP-MS	Inductively coupled plasma mass spectrometry
m	mass [g]
MMAA	Monomethylarsenic acid
m_1	mass of 1 m nitric acid solution
m_r	mass of rice
m_{t1}	total mass of 1 m and 7 m HNO_3
m_{t2}	total mass of rice and used volume of 1 m nitric acid
m_{t3}	total mass of 1 m HNO_3 and H_2O
n.d.	non-determinable
ppb	part per billion
rpm	rounds per minute
V	volume [ml]
ρ	density [g/ml]
Ø	mean

1. Introduction

1.1 Background

Arsenic is one of the most toxic elements.[1] The society perception of the dangerousness of arsenic has changed a lot. In former times arsenic was a favoured poison to get rid of a husband/wife or a rival. Just add some arsenic to a meal or drink and this over a few weeks. Now the only thing to do was waiting. The death of this person was as sure as eggs is eggs. In these times it was not possible to diagnose the kind of poisoning because the equipment was not good and sensitive enough. So this kind of murder was really common. Today these problems do not exist any longer. It is now easier to identify which poison was used, how much of it and over which period of time.

As written before the perception has changed. While it was in these former times only in the heads of a few people, it is now in every one's mind. The reason is that in the last years many things were written and published about arsenic and its dangerousness. The most discussed topic was and still is the contamination of groundwater and drinking water with arsenic. Especially in countries like India and Bangladesh the problem of contaminated groundwater is very high (1). The sources of this high amount of arsenic in water are manifold. They are of a geological origin or caused by humans (2). Due to the fact that there is in some regions such a high amount of arsenic in water, it was necessary to create a device to determine these concentrations. Therefore field test kits were evolved. With them it is possible to determine the inorganic arsenic concentration in water and they are so small that they are perfect for rural areas. Even when everyone knows how much arsenic is in the groundwater it is still there and not disappeared. That is why it is necessary to find a way to minimize this arsenic concentration. During the last years there were a lot of considerations how to do this. In addition to precipitation processes (3) and adsorption processes (4) there are also possibilities to use ion exchange or membrane filtration (5).

While the water problem is discussed for now more than twenty years the food problem is more recent. Also in a lot of food products are elements like arsenic or mercury contained. In the last years the number of publications about arsenic in rice and rice products increased enormous. In some it is tested how much arsenic different rice samples contain (6) and in others if the way of cooking rice can reduce the amount of arsenic in it (7). Not only rice is a source of investigation but also other food products, e.g. wheat, tuna fish (8) are and will be analyzed.

[1] cf. European Union Law: Dangerous Substances Directive 67/548/EEC
cf. International Agency for Research on Cancer

1.2 Aim

As said before the contamination of food and water with arsenic is a common discussed topic. Because rice is one of the main food products for millions of people it is necessary to find a way to determine the arsenic concentration in it. There are different ways to do so. The topic of this Bachelor Thesis was to see if it is possible to detect inorganic arsenic in rice by using the Wagtech Digital Arsenator. If this method should work then it would be a great thing. In this case it would not be necessary to use an ICP-MS and the experiments could be done in the field. The Wagtech Digital Arsenator was used because it is the only field kit with a digital system in addition to a colour chart card.

2. The basics

2.1 Arsenic

2.1.1 General information

Arsenic is the 33rd element in the periodic table with the symbol As. It stands in the same main group as nitrogen, phosphorus, antimony and bismuth. Arsenic is a metalloid which occurs in many minerals or also as an elemental crystal. The molecular weight is 74,92 g/mol. It is a solid element with a density of 5,72 g/cm^3. While gray arsenic is the most common allotrope there are also a yellow and a black form. These three forms have different properties. As said it occurs in many minerals like realgar (As_4S_4), arsenopyrite (FeAsS) and orpiment (As_2S_3). It was used in medicine in former times and still is a part of it (9).

2.1.2 Species of Arsenic

There are two different forms of arsenic - the inorganic and the organic form.

2.1.2.1 Inorganic arsenic

Inorganic arsenic is more toxic than the organic one (10). It can occur as oxides, sulphides, halides and also forms with metals. Two other really well known forms of inorganic arsenic are arsine gas (AsH_3) and arsenic acid (H_3AsO_4). In the following are a few examples for each group listed.

Oxides:

- arsenic trioxide As_2O_3
- arsenic pentoxide As_2O_5

Sulphides:

- arsenic trisulfide As_2S_3
- realgar As_4S_4

Halides:

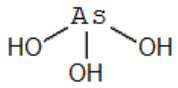
- arsenic trifluoride AsF_3
- arsenic trichloride $AsCl_3$
- arsenic pentafluoride AsF_5

Metal forms:

- calcium arsenate $Ca_3(AsO_4)_2$
- lead arsenate $PbHAsO_4$

In rice also forms of inorganic arsenic are found. These forms are arsenic acid (H_3AsO_4) and arsenous acid (H_3AsO_3). The figure below will show the structure of these two forms.

arsenous acid



arsenic acid

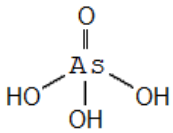
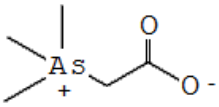


Figure 1: Structure of arsenous acid and arsenic acid

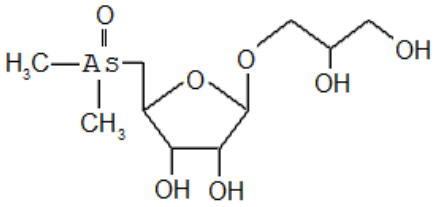
2.1.2.2 Organic arsenic

Organic arsenics have a bond between arsenic and carbon. This bond is really strong and cleaving it is not so easy. To cleave the arsenic-carbon bond a strong oxidant and ultraviolet light is necessary. There are a lot of examples for organic arsenics. On the one hand there are compounds like arsenobetaine, arsenosugar and arsenolipids which are often found in marine food like fish and seaweed (11). On the other hand there are also compounds like dimethylarsinic acid (DMAA), monomethylarsonic acid (MMAA) and phenylarsonic acid. Although all of this organic arsenic compounds are in some way toxic the most toxic one is DMAA. As said in 2.1.2.1 there is inorganic arsenic found in rice, but there are also organic arsenic forms found (12). These forms are DMAA and MMAA with the amount off MMAA being really small. In the two figures on the next page the structure of all these compounds is shown.

Arsenobetaine

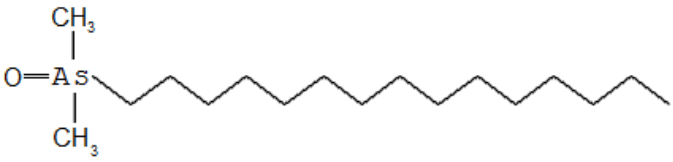


Arsenosugar



glycerol arsinoylriboside

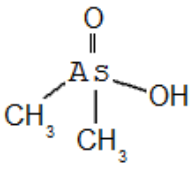
Arsenolipids



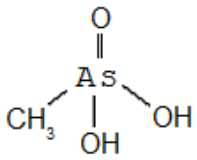
1-dimethylarsinoylpentadecane

Figure 2: Structure of Arsenobetaine, Arsenosugar and Arsenolipids

Dimethylarsenic acid



Monomethylarsenic acid



Phenylarsonic acid

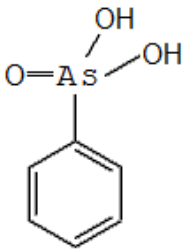


Figure 3: Structure of DMAA, MMAA and phenylarsonic acid

2.2 Atomic Fluorescence Spectrometer (AFS)

2.2.1 Base of atomic fluorescence spectroscopy

Atomic fluorescence spectroscopy is a type of electromagnetic spectroscopy. This type has aspects of both absorption and emission.

The principle of atomic fluorescence spectroscopy is simple. All needed elements are shown in the next figure.

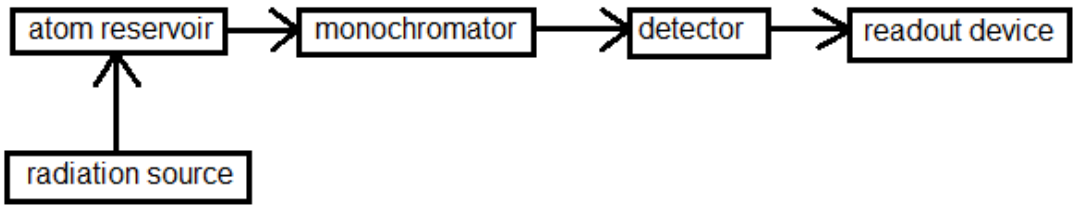


Figure 4: Scheme of the atomic fluorescence spectrometer elements

The reason of atomic fluorescence spectroscopy is that an atom changes its energy levels. As known an atom has different energy levels. Under normal circum stances it is settled in the ground state. But when the atom is exposed to a radiation source, e.g. a hollow cathode lamp it will be excited to a higher energy level by absorption the electromagnetic radiation. When this excited atom relaxes back to the ground state it is accompanied by a radiation which is called atomic fluorescence emission. This whole procedure is illustrated in a so called Jablonski diagram.

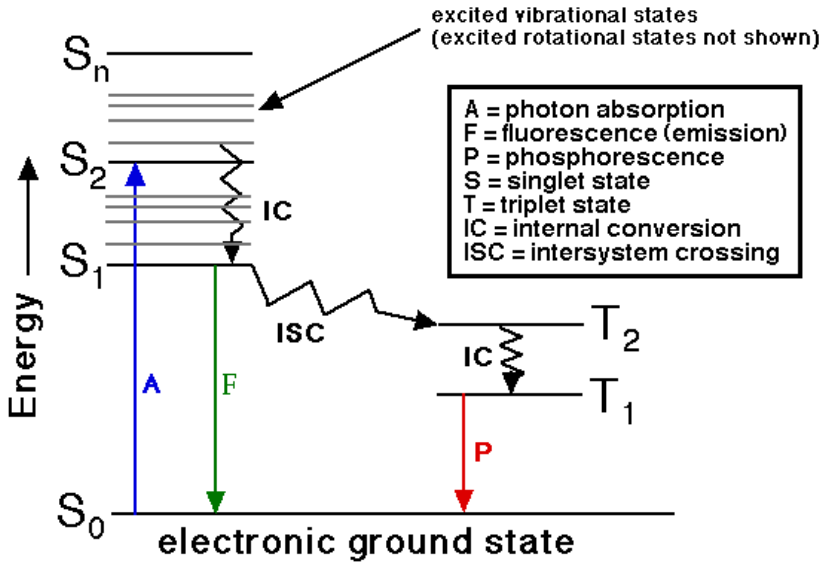


Figure 5: Scheme of a Jablonski diagram (13)

After explaining how fluorescence is formed now the process of atomic fluorescence spectroscopy will be described. First the sample also called analyte is brought into an atom reservoir. Here the sample will be transformed into gaseous atoms. There are different ways to do so. These ways will be described in the next passage. The gaseous atoms will then be excited to higher energy levels. The reason is the absorption of the electromagnetic radiation of the radiation source. The transmitted atomic fluorescence emission will then be dispersed and after passing a monochromator recorded by a detector. The collected data will then be sent to a readout device which in most of the cases is a computer with suitable software to analyse all the data immediately.

2.2.2 Elements of an atomic fluorescence spectrometer

2.2.2.1 Radiation source

The radiation source is the most important element in an atomic fluorescence spectrometer. There are two different possibilities available: a continuous source and a monochromatic or line source. Continuous sources will be used for multielement analysis but their problem is the low radiant density. Monochromatic sources are not suitable for multielement analysis but instead their radiance is high. Examples are a tungsten lamp or a deuterium lamp for continuous sources and a hollow cathode lamp or an electrodeless discharge lamp for monochromatic sources. The most commonly used lamp is a hollow cathode lamp. Until today there are 60 different element hollow cathode lamps available. The figure below shows the scheme of such a hollow cathode lamp.

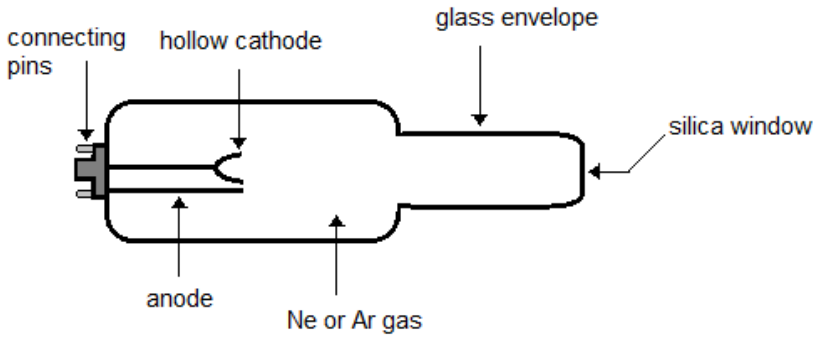


Figure 6: Scheme of a hollow cathode lamp

2.2.2.2 Atom reservoir

As said in 2.2.1 there are different ways to transform liquid samples into gaseous atoms. The possibilities are flame, electrothermal, glow discharge, cold vapour and hydride atomisation. Every kind of atomisation is different. On the one hand the used technique is different and on the other hand not all techniques are suitable for each element. If mercury is the element which should be analysed, then only cold vapour atomisation is suitable. For hydride forming elements like arsenic, selenium, bismuth and antimony only hydride atomisation is the real deal. When using flame atomisation the nebulised sample will be atomised directly by the flame. In contrast cold vapour atomisation do not need a flame or any other thermal source. Here the dissolved mercury will be reduced to elemental mercury by a reaction with tin(II)-chloride. This mercury vapour will then be transported to a quartz cell by a carrier gas like argon. There the atoms will be excited by a suitable source. Like said before if hydride atomisation is used a hydride forming element is necessary. To generate this volatile hydride the sample has to be reacting with sodium borohydride and an acid e.g. hydrochloric acid. A carrier gas is transporting the formed hydride to a flame where it will be atomised and following excited by a suitable source. Electrothermal atomisation is also not using a flame. Rather a graphite tube containing the sample will be heated by a controlled temperature programme up to atomisation.

2.2.2.3 Monochromator

A monochromator is a device that separates one wavelength or one emission line from a wider range of them. This is necessary because polychromatic light cannot be detected. As shown in figure 7 the polychromatic light passes the entrance slit and is reflected from a spherical mirror. At the grating the light is diffracted and then the dispersed light is reflected from another spherical mirror to the exit slit. It is only for one wavelength possible to pass the exit slide. Not every atomic fluorescence spectrometer includes a monochromator.

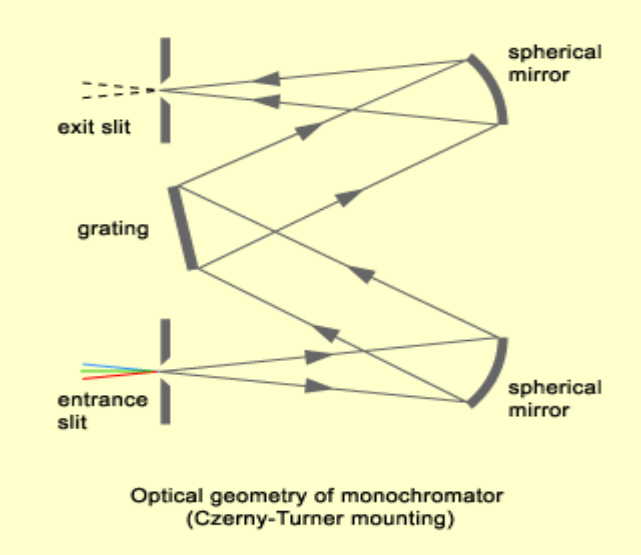


Figure 7: Scheme of a monochromator (14)

2.2.2.4 Detector

A detector is a device that converts the given wavelength of the monochromator to an electronic signal. This signal can then be read by an electronic instrument like a computer. The most common detector is a photomultiplier. As it is shown in figure 8 the photon strikes the photocathode and an electron is ejected. This electron is accelerated to the first dynode. There it collides with other electrons and they will be accelerating to the next dynode. This happens eight times before all electrons reach the anode where the current will be measured.

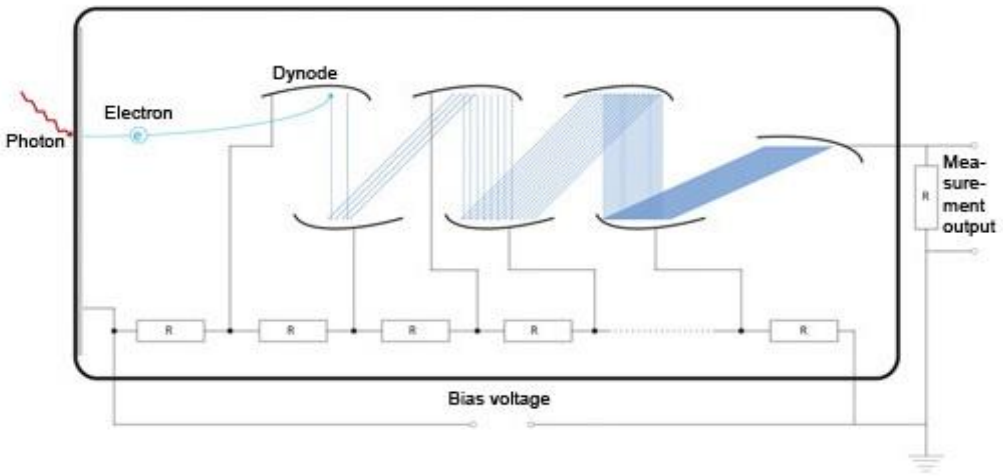
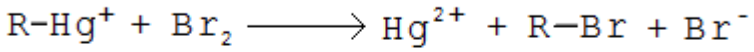


Figure 8: Scheme how a photomultiplier works (15)

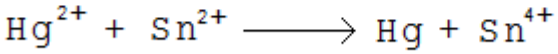
2.2.3 Chemical reactions

The chemical reactions for the AFS will be described in this chapter. On the one hand the chemistry behind cold vapour atomisation will be characterised and on the other hand the chemistry behind hydride generation.

As said in 2.2.2.2 cold vapour atomisation is used for mercury. There are two steps to form mercury vapour. First the samples, which are often forms of organic mercury will be oxidised to inorganic mercury. Then all inorganic mercury will be reduced to elemental mercury by using tin(II)-chloride.

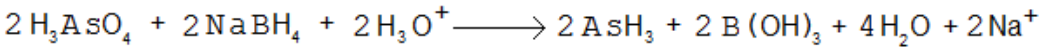


$$R\text{-}Hg^{+} + Br_2 \longrightarrow Hg^{2+} + R\text{-}Br + Br^{-}$$



$$Hg^{2+} + Sn^{2+} \longrightarrow Hg + Sn^{4+}$$

Hydride atomisation is only possible when using hydride forming elements. The reaction below shows how the volatile hydride is formed. Sodium borohydride is used as a reductant and the acid is necessary to create an acidic media.



$$2\,H_3AsO_4 + 2\,NaBH_4 + 2\,H_3O^{+} \longrightarrow 2\,AsH_3 + 2\,B(OH)_3 + 4\,H_2O + 2\,Na^{+}$$

In both cases the formed product –arsine gas or elemental mercury- will be transported by a carrier gas (Argon) to the next step of atomic fluorescence spectroscopy. The figure below shows a typical atomic fluorescence spectrum.

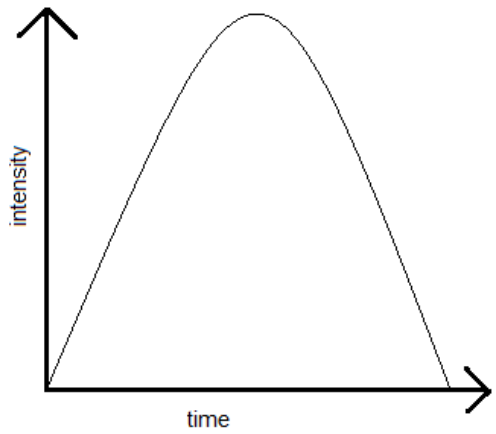


Figure 9: Scheme of an atomic fluorescence spectrum

2.3 Wagtech Digital Arsenator

2.3.1 Overview of different field kits

As mentioned before there was an increase of designing and developing field test kits because of the high arsenic amount in groundwater. These test kits are perfect for rural areas because they are small, not so heavy and they present the results in 20 to 30 minutes. In the last years a lot of companies developed such field kits. The earlier kits had some problems with their low sensitivity (16) and their release of the toxic arsine gas (17). Although these problems are mostly solved the utility of such field test kits is still hotly debated. While some are still discussing the reliability (16) other are convinced that such kits are perfect for detecting arsenic in tube wells (18). In the table below some of the most common field test kits are listed.

Table 1: Overview of different field test kits

Field test kit	Concentration range	Reaction time
Wagtech Digital Arsenator	Digital system: 2 ppb – 100 ppb Colour chart: 10 ppb – 500 ppb	20 min
Hach EZ Arsenic High Range Test Kit	Colour chart: 0 ppb – 4000 ppb	20 min
Hach Arsenic Low Range Test Kit	Colour chart: 0 ppb – 500 ppb	30 min
Arsenic Quick Test Kit	Colour chart: 0 ppb – 500 ppb	12 min
Arsenic Quick II Water Test Kit	Colour chart: 1 ppb – 160 ppb	14 min
Merck Test Kit	Colour chart: 0 ppb – 3000 ppb	30 min

2.3.2 The Basics

As shown in the last passage there are a lot of field test kits which can be used to determine inorganic arsenic in water samples. For this thesis the Wagtech Digital Arsenator was used. The reason was that this kit is the only one with a digital system.

2.3.2.1 Elements of the Wagtech Digital Arsenator

The Wagtech Digital Arsenator- from this point on only called Arsenator- is a field test kit produced in the United Kingdom. All components are placed in a practical case which is optimal for doing field analysis. The picture below shows how this field test kit look like.

Figure 10: The Wagtech Digital Arsenator (19)

The Arsenator contains all important elements and reagents. On the one hand there are all elements which are needed for the reaction. These are an Erlenmeyer flask, a tri-filter arsenic gas trap, arsenic collection filter holders plus filters, arsine gas removal filter holders plus filters, hydrogen sulphide removal filters and the two different reagents - sulphamic acid powder and sodium borohydride tablets. On the other hand there are the evaluation units. These are the portable Digital Arsenator System and the colour comparison chart. Also included are a dilution tube, waste disposal bags, gloves and tweezers.

2.3.2.2 Mode of operation

The use of the Arseantor is simple and will be described in detail in the following. The first step is to insert the filters in the correct filter holders. Here the arsenic collection filters, which consist of mercury dibromide, will be inserted in the black arsenic collection filter holder, the arsine gas removal filters will be inserted in the red arsine gas removal filter holders and the wool will be inserted in the hydrogen sulphide removal filter. Then the black filter holder has to be pocketed in the Digital Arsenator System to zero it. In the meantime the red filter holder and the hydrogen sulphide removal filter have to be pocketed in the tri-filter arsenic gas trap. The sample will then be filled in the flask and a bag of reagent A1 –sulphamic acid powder- will be added. The next step is the removal of the black filter holder from the digital system and the insertion of it in the gas trap. Now the sodium borohydride has to be added and closing the flask has to be done immediately. After 20 minutes reaction time the last step is to remove the black filter holder and to insert it again in the digital system. This system will show now the concentration of arsenic in the sample. If the display indicates more than 100 ppb the colour chart will give an idea of the arsenic amount and the sample has to be diluted for a second test. The image below gives a look of the flask where the reaction takes place.

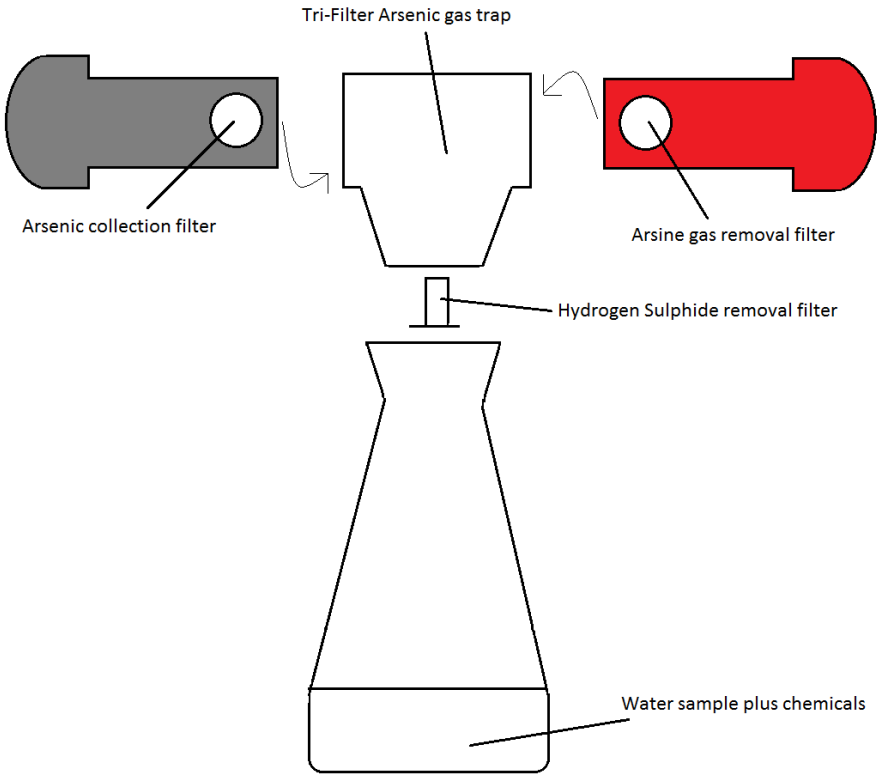


Figure 11: Scheme of the reaction chamber

2.3.3 Chemical reactions

The reactions at the Arsenator will be explained following. Actually there are two reactions taking place. The first reaction is the forming of arsenic hydride. It is the same reaction as for the AFS. The inorganic arsenic like As^{III} and As^{V} will be transformed into arsine gas AsH_3 with the help of sodium borohydride and an acid.

$$2\,H_3AsO_4 + 2\,NaBH_4 + 2\,H_3O^+ \longrightarrow 2\,AsH_3 + 2\,B(OH)_3 + 4\,H_2O + 2\,Na^+$$

The second reaction is the so called Gutzeit-method. This method is known for many years and almost all of the arsenic detecting field kits are based on this method. The formed arsine gas will react with the mercury dibromide to a yellow complex. Unfortunately it is still not completely clear how this complex is formed and what the structure is. The company Wagtech WTD, who invented the Arsenator, gives a possible structure of this complex.

$$AsH_3 + HgBr_2 \longrightarrow H_2As{-}HgBr + HBr$$

3. Experimental

After picturing all the bases followed the experimental part will be described.

3.1 Equipment and chemicals

For the experiments six different rice samples were used. These rice samples were bought in several shops and were grinded to the same size.

The samples were:

- Tilda Long Grain Rice (Sample 8)
- Morrison's Organic Long Grain Brown Rice (Sample 2)
- Tilda Thai Jasmine Rice (Sample 3)
- Asda Carnaroli Rice (Sample 9)
- Uncle Benz Whole Grain Rice (Sample 10)
- Organic Long Grain Rice (Sample 1)

The grinded rice samples were filled in bags and labelled.

3.1.1 Atomic fluorescence spectrometer

The AFS which was used for the control experiments is the PSA 10.005 Millennium Excalibur System from the firm PS Analytical. The used software installed on the computer is the Millennium software.

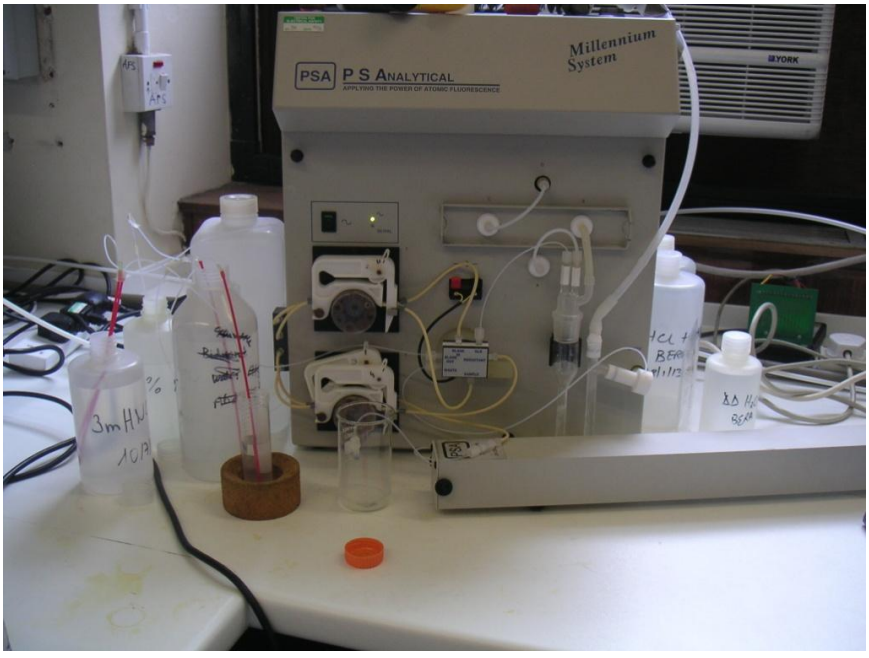


Figure 12: The PSA 10.005 Millennium Excalibur System

In the table below the most important parameter for using the AFS are shown.

Table 2: Instrumentation parameters for AFS

Lamp Current	27,5 mA
Boost lamp current	34,9 mA
Reductant flow rate ($NaBH_4$)	4,5 ml/min
Acid/blank flow rate (HNO_3)	2,1 ml/min
Analysis gas	Argon (40 psi)
Dryer gas	Compressed air

The used chemicals are:

- Sodium hydroxide [Laboratory reagent grade; Fisher Chemical]
- Sodium borohydride [powder; 99%; ACROS Organics]
- Nitric acid [S.G. 1,42 (70%); Analytical reagent grade; Fisher Chemical]
- Hydrogen peroxide [100 volumes; >30%; Laboratory reagent grade; Fisher Chemical]

3.1.2 Arsenator

The used Arsenator was the Wagtech Digital Arsenator from the firm Wagtech WTD. As mentioned in 2.3.2.1 all needed chemicals for the reaction are contained in the practical case. In addition to the contained chemicals two more chemicals are needed.

Figure 13: The Wagtech Digital Arsenator (19)

In the following all needed chemicals are listed:

- Sodium borohydride [< 10%; Wagtech WTD]
- Sulphamic acid [Palintest Ltd]
- Nitric acid [S.G. 1,42 (70%); Analytical reagent grade; Fisher Chemical]
- Hydrogen peroxide [100 volumes; >30%; Laboratory reagent grade; Fisher Chemical]

For both methods nitric acid and hydrogen peroxide were used to extract the arsenic from the rice samples. Also beaker glasses, Petri dishes, spatulas, a hot plate and a thermometer were used for the extraction process. In the next chapter the different ways of the extraction process will be described.

3.2 Extraction method

It was searched for the perfect extraction method. After studying different papers (7), (20) it was decided to use two different concentrations of nitric acid and a mix of nitric acid and hydrogen peroxide.

3.2.1 Using nitric acid

The two used concentrations of nitric acid were 1 molar HNO_3 and 7 molar HNO_3. These two concentrations were chosen to see if there will be a significant difference in the amount of arsenic. The whole extraction process took two days. In the following the process will be described.

The six different rice samples were weighed in 50 ml test tubes. Following 10 to 15 ml HNO_3 were added. The volume of nitric acid depends on the mass of the rice samples. The samples stood over night at room temperature with a not completely closed lid. Picture a) shows one of the samples after standing over night. The next day the rice samples were filled in a beaker glass and a defined volume of nitric acid was added. After covering the beaker glass with a Petri dish it was cooked on a hotplate, see picture b). While cooking the temperature was measured several times. All rice samples were cooked at 80°C for a minimum of 20 minutes. The solution had to undergo a colour change from white to yellow and at the end it had to be a clear yellow solution, see pictures c) to e). During cooking brown vapours (nitrous fumes) had to appear. After cooking all solutions had to cool down to room temperature. The next step was then the centrifugation. All solutions were centrifuged two times for 10 minutes at 3300 rpm.

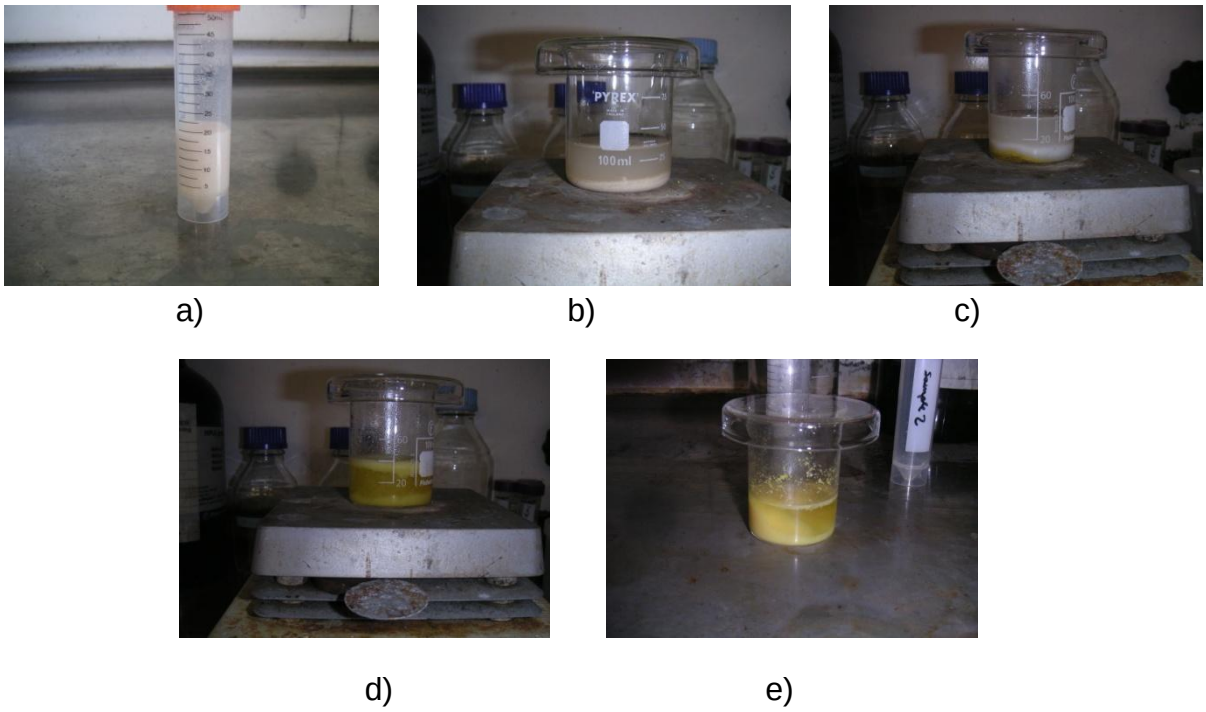


Figure 14: Extraction process a) rice sample stood over night; b) sample plus HNO_3 covered with a Petri dish on a hot plate; c) first sign of colour change; d) complete yellow solution; e) sample is cooling down after cooking

3.2.2 Using nitric acid and hydrogen peroxide

When using nitric acid and hydrogen peroxide the procedure is almost the same as for nitric acid. Also here the samples were weighed in 50 ml test tubes. Then 10 to 15 ml nitric acid was added. The samples stood over night at room temperature. The next day the samples were also filled in beaker glasses. In contrast to using only nitric acid now the same volumes of nitric acid and hydrogen peroxide were added. After covering the beaker glasses with Petri dishes everything was cooked on a hot-plate. All samples were cooked at 100°C for minimum 20 minutes. Also at this experiments there had to be a clear solution after cooking. After cooling down the samples were centrifuged two times for 10 minutes at 3300 rpm.

3.3 Subsequent treatment

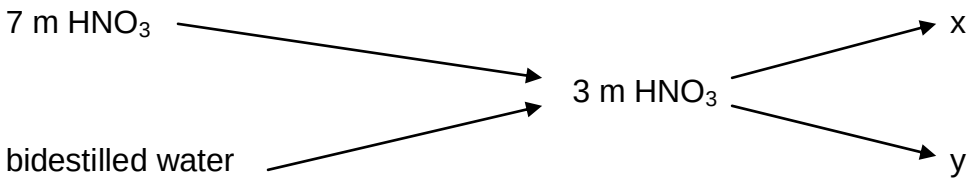
After centrifuging the samples had to be prepared for the AFS and the Arsenator. In the following the way of doing so will be explained.

3.3.1 Atomic fluorescence spectrometer

To use the AFS there are a few more steps necessary. On the one hand the sample has to be prepared and on the other hand the needed reductant and acid has to be prepared as well. The used reductant is sodium borohydride ($NaBH_4$). To produce 500 ml of it 2 g of sodium hydroxide were filled in a plastic bottle with a few ml of bidestilled water. The solution was stirred for two min. Then 5 g of sodium boro-hydride and the rest of bidestilled water were added. It had to be stirred again. The sodium hydroxide was used to stabilize the sodium borohydride. After preparing the reductant the acid had to be prepared. It was decided to use a 3 m nitric acid as acid/blank. To produce 500 ml of this acid 95,1 ml of 7 molar HNO_3 were mixed with 404,9 ml bidestilled water. Now the samples had to be changed to 3 molar. For this a defined volume of the solution was mixed with bidestilled water or 7 molar nitric acid. The following calculations show the used volumes of acid and water.

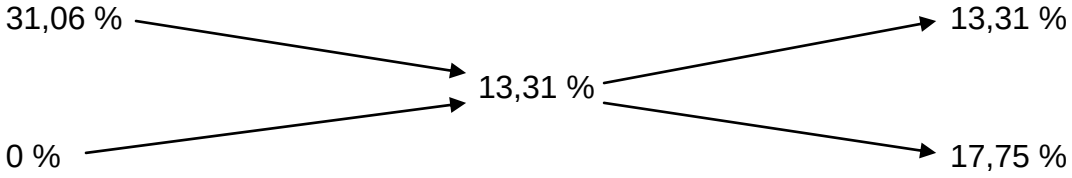
Table 3: Properties of the used chemicals

	Concentration [%]	Density [g/ml]
1 m HNO3	4,44	1,02225
3 m HNO3	13,31	1,0725
7 m HNO3	31,06	1,1867
bidistilled water	0	0,9982



x = l bidest water – 3 m HNO_3 l

y = l 7 m HNO_3 – 3 m HNO_3 l



$$V = \frac{m}{\rho}$$

x = 13,31 g

$$V_{7\ m\ HNO3} = \frac{x}{\rho}$$

$$V_{7\ m} = \frac{13{,}31\ g}{1{,}1867\ g/ml}$$

$V_{7\ m}$ = 11,21 ml

y = 17,75 g

$$V_{water} = \frac{y}{\rho}$$

$$V_{water} = \frac{17{,}75\ g}{0{,}9982\ g/ml}$$

V_{water} = 17,78 ml

Because only 15 ml of solution was needed the calculated volumes had to be calculated again.

$$V_{7\ m,new} = \frac{V_{7\ m}}{V_{total}} \cdot V$$

$$V_{7\ m,new} = \frac{11{,}21\ ml}{28{,}99\ ml} \cdot 15\ ml$$

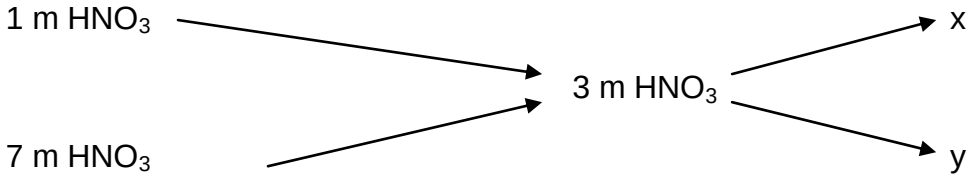
$V_{7\ m,new}$ = 5,80 ml

$$V_{water,new} = \frac{V_{water}}{V_{total}} \cdot V$$

$$V_{water,new} = \frac{17{,}78\ ml}{28{,}99\ ml} \cdot 15\ ml$$

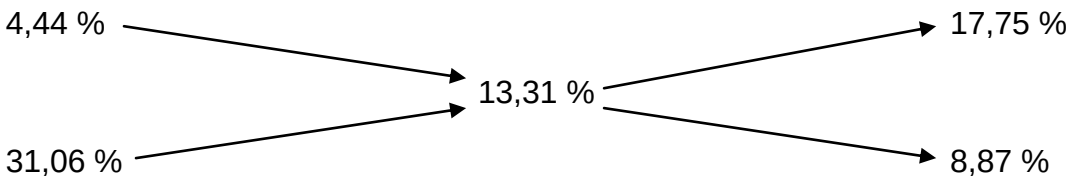
$V_{water,new}$ = 9,20 ml

The same procedure to calculate the needed volume was used for 1 m nitric acid.



x = I 7 m HNO_3 – 3 m HNO_3 I

y = I 1 m HNO_3 – 3 m HNO_3 I



$$V = \frac{m}{\rho}$$

x = 17,75 g

$$V_{1\ m\ HNO3} = \frac{x}{\rho}$$

$$V_{1\ m} = \frac{17{,}75\ g}{1{,}02225\ g/ml}$$

$V_{1\ m}$ = 17,36 ml

y = 8,87 g

$$V_{7\ m\ HNO3} = \frac{y}{\rho}$$

$$V_{7\ m} = \frac{8{,}87\ g}{1{,}1867\ g/ml}$$

$V_{7\ m}$ = 7,47 ml

Because only 15 ml of solution was needed the calculated volumes had to be calculated again.

$$V_{1\ m,new} = \frac{V_{1\ m}}{V_{total}} \cdot V$$

$$V_{1\ m,new} = \frac{17{,}36\ ml}{24{,}83\ ml} \cdot 15\ ml$$

$V_{1\ m,new}$ = 10,49 ml

$$V_{7\ m,new} = \frac{V_{water}}{V_{total}} \cdot V$$

$$V_{7\ m,new} = \frac{7{,}47\ ml}{24{,}83\ ml} \cdot 15\ ml$$

$V_{7\ m,new}$ = 4,51 ml

In addition the standards for the calibration had to be prepared. For them a defined volume of an inorganic arsenic stock solution was mixed with the 3 molar nitric acid. After this the analysis at the AFS could start. First the flow rates were measured and then the calibration. Then also all samples were measured. In the next chapter the results will be shown.

3.3.2 Arsenator

As said before the cooked solutions had to be prepared using them for the Arsenator. Because it is necessary to use 50 ml of a solution for the Arsenator all samples had to be diluted to 50 ml. Of every cooked solution ten ml were filled in test tubes. The tubes were then filled up to 50 ml with bidestilled water. These solutions were used for the Arsenator. In 2.3.2.2 it is described how to use this kit.

4. Results and analysis

In the following chapter all results will be shown. Furthermore all results will be evaluated.

4.1 Atomic fluorescence spectrometer

Actually the use of the AFS was not scheduled. Unfortunately there were a few problems when using the Arsenator. Therefore it was decided to use the AFS to see if the used extraction methods were working.

First of all the results of using 1 molar nitric acid will be shown and explained.

As said before it is necessary to do a calibration at the AFS otherwise it is not possible to get to know how much arsenic is in the samples. The chart below shows the calibration curve for the 1 molar samples. All relevant data is displayed in table 1 and 2 in appendix 1.

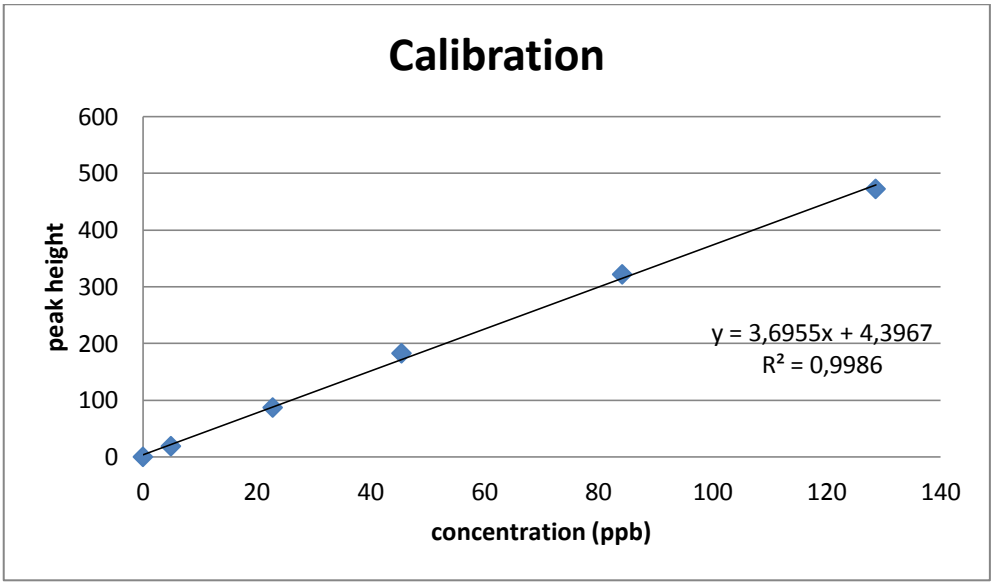


Figure 15: Calibration curve for samples extracted with 1 m nitric acid

With the help of this calibration curve it was possible to calculate the amount of arsenic in the different rice samples. The calculation was done by the millennium software on the computer. The next table will show the results from the AFS.

Table 4: Concentrations of the rice samples displayed at the computer (1 m HNO_3)

Sample	Concentrations [ppb]			
	Trial 1	Trial 2	Trial 3	Mean [Ø]
S1	14,5383	14,3129	13,5010	14,1174
S2	12,7459	10,8668	10,8075	11,4734
S3	8,5072	8,2175	8,2070	8,3106
S8	5,1488	6,3539	5,0533	5,5186
S9	6,8103	7,4003	7,1298	7,1135
S10	11,6908	11,2988	8,9358	10,6418

These results are not the real concentrations of arsenic in the different rice samples. The real amount of arsenic has to be calculated with all the dilutions. The used formulas to calculate the real concentration of arsenic are shown below. As an example the real concentration of rice sample 1 will be calculated. All used masses and volumes are displayed in table 3 and 4 in appendix 1.

D.F. – Dilution Factor

$$D.F. = \frac{1}{D_1 \cdot D_2}$$

D_1 – Dilution 1

D_2 – Dilution 2

$$D_1 = \frac{m_1}{m_{t1}}$$

m_1 – mass of 1 m nitric acid solution

m_{t1} – total mass of 1 m and 7 m HNO_3

$$D_2 = \frac{m_r}{m_{t2}}$$

m_r– mass of rice

m_{t2}– total mass of rice and used volume of 1 m nitric acid

$$c_{real} = D.F. \cdot c_{AFS}$$

c_{real} - real concentration

c_{AFS} – concentration displayed at the AFS

$$D_1 = \frac{m_1}{m_{t1}}$$

$$D_1 = \frac{10{,}9385\ g}{16{,}1939\ g}$$

$$\underline{D_1 = 0{,}6755}$$

$$D_2 = \frac{m_r}{m_{t2}}$$

$$D_2 = \frac{4{,}6045\ g}{38{,}7477\ g}$$

$$\underline{D_2 = 0{,}1188}$$

$$D.F. = \frac{1}{D_1 \cdot D_2}$$

$$D.F. = \frac{1}{0{,}6755 \cdot 0{,}1188}$$

D.F. = 12,4582

c_{real} = D.F. · c_{AFS}

c_{real} = 12,4582 · 14,1174 ppb

c_{real} = 175,8780 ppb

In the table below the real concentrations of all rice samples will be shown as well as the concentrations of all samples measured with the ICP-MS. The results of the ICP-MS were not measured by me. They were measured during another experiment by Andrea Raab.

Table 5: Rice sample concentrations measured with AFS (1 m HNO_3) and ICP-MS

Sample	Real concentration [ppb] measured with AFS				Concentration [ppb] measured with ICP-MS
	Trial 1	Trial 2	Trial 3	Mean Ø	
S1	181,1215	178,3141	168,1983	175,8780	95,8
S2	135,3604	115,4048	114,7750	121,8467	149,9
S3	84,9115	82,0198	81,9148	82,9487	106,7
S8	44,5732	55,0060	43,7464	47,7752	138,7
S9	73,0774	79,4082	76,5049	76,3302	129,4
S10	196,7254	190,1282	150,3655	179,0730	182,4

When comparing the concentrations measured with the AFS and the ICP-MS then a difference is clearly apparent. On the one hand there is one sample with a higher concentration of inorganic arsenic when measured with the AFS. On the other hand the concentrations of the other 5 samples are lower when measured with the AFS. In figure 15 these differences are shown. A reason for these lower results could be the reaction of DMAA with the sodium borohydride. As said in 2.1.2.2 rice contains also DMAA. This DMAA can react with sodium borohydride to dimethyl arsine. This dimethyl arsine is also volatile but will not be detected by the AFS. These results show that the extraction method with 1 molar nitric acid is working. Inorganic arsenic will be extracted from the rice and can then form the needed arsenic hydride for the AFS.

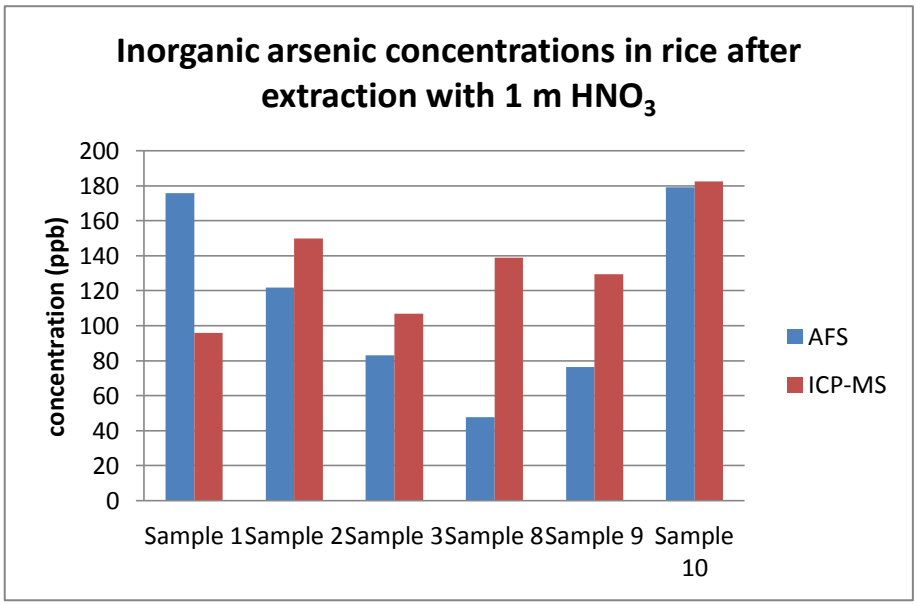


Figure 16: Comparison of inorganic arsenic concentrations in different rice samples by using 1 molar HNO_3 as an extracting agent

After evaluating the results when using 1 molar nitric acid now the results of using 7 molar nitric acid will be discussed. As for the 1 molar HNO_3 also for the 7 molar HNO_3 a calibration was done. The chart below will show the calibration curve and all used data is written in table 1 and 2 in appendix 2.

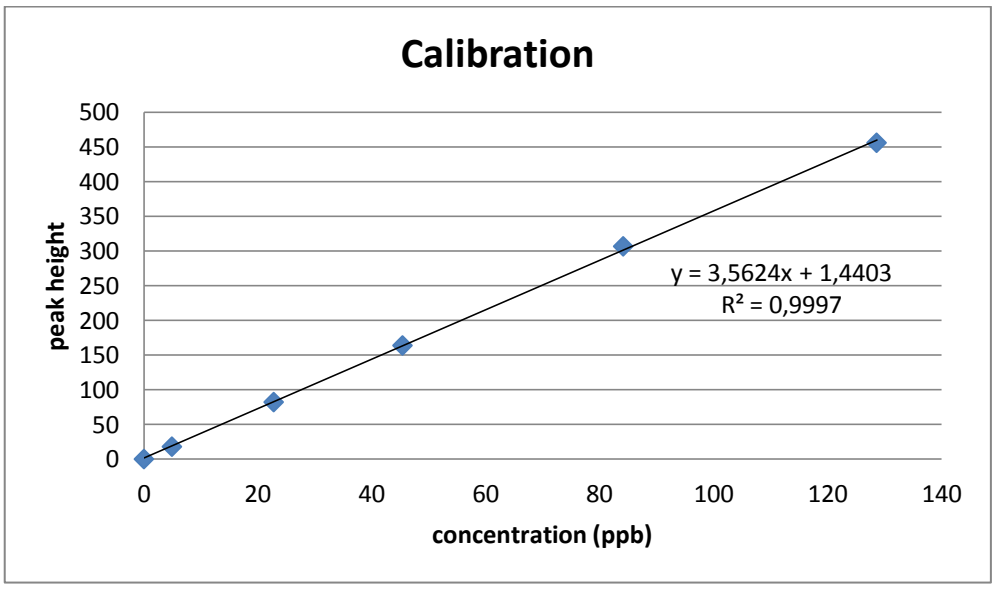


Figure 17: Calibration curve for samples extracted with 7 m nitric acid

As for 1 m nitric acid also for 7 m nitric acid the calibration curve can be used to calculate the amount of inorganic arsenic in all samples. The table on the next page will show the results of the AFS.

Table 6: Concentrations of the rice samples displayed at the computer (7 m HNO_3)

Sample	Concentrations [ppb]			
	Trial 1	Trial 2	Trial 3	Mean [Ø]
S1	5,7066	5,6123	7,1558	6,1583
S2	9,4915	9,7160	10,9695	10,0590
S3	7,8604	7,7303	8,0810	7,8906
S8	5,1414	5,5653	5,6565	5,4544
S9	10,2748	10,2495	10,4654	10,3299
S10	8,3942	9,3227	8,8142	8,8437

These results are not the exact concentrations of inorganic arsenic in the samples therefore they have to be calculated again. The used formulas for doing so are the same as for 1 molar nitric acid. The table below shows the new calculated concentrations of all samples. The used masses and volumes are displayed in table 3 and 4 in appendix 2.

Table 7: Rice sample concentrations measured with AFS (7 m HNO_3) and ICP-MS

Sample	Real concentration [ppb] measured with AFS				Concentration [ppb] measured with ICP-MS
	Trial 1	Trial 2	Trial 3	Mean Ø	
S1	111,7266	109,8796	140,0993	120,5685	95,8
S2	160,7762	164,5784	185,8115	170,3887	149,9
S3	122,7677	120,7357	126,2133	123,2389	106,7
S8	65,5699	70,9755	72,1385	69,5613	138,7
S9	169,5835	169,1656	172,7297	170,4929	129,4
S10	257,6810	286,1817	270,5723	271,4783	182,4

When comparing the results of both, the AFS- and the ICP-MS- method, then a difference is clearly apparent. On the one hand these concentrations show that an extraction with a 7 molar nitric acid is working. But on the other hand this 7 molar nitric acid causes problems. A problem is the possible detection of organic arsenic like DMAA. 7 molar nitric acid is a really strong acid and could cleave the carbon- arsenic-bonds in DMAA. After cleaving these bonds it is possible to detect it with the AFS. Consequently the amount of displayed inorganic arsenic is higher than the actually amount of inorganic arsenic in the samples. Another problem is possible species transformation which also changes the concentration of inorganic arsenic. Figure 17 will show these differences in a more visual way.

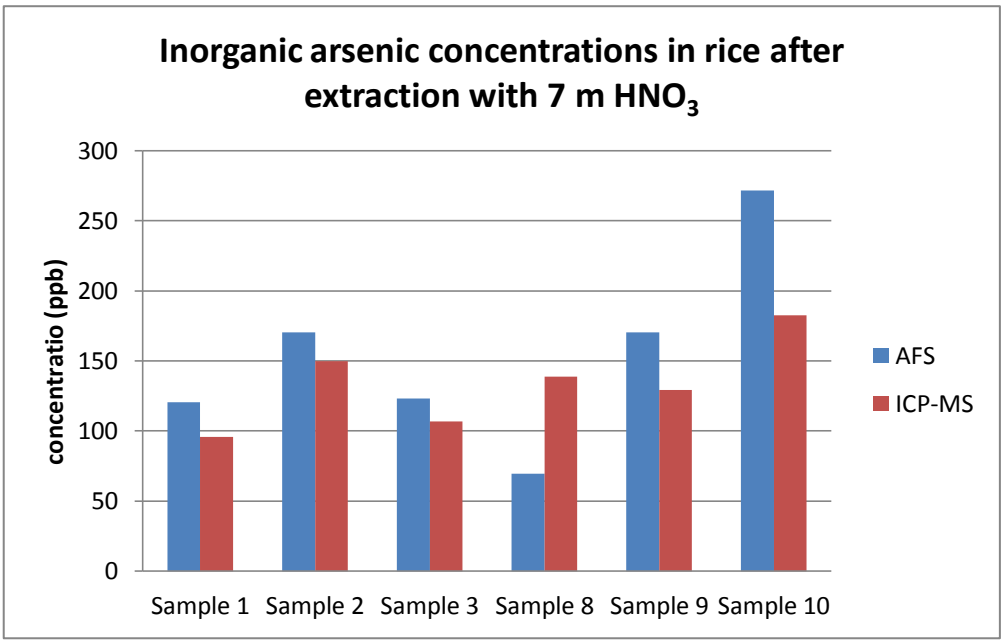


Figure 18: Comparison of inorganic arsenic concentrations in different rice samples by using 7 molar HNO_3 as an extracting agent

Now the results of using 7 molar nitric acid and hydrogen peroxide as an extracting agent will be discussed. In this case only three of six samples were used. The reason was that the mass of these three not used samples was not enough to do another measurement. The used samples were sample 3, sample 9 and sample 10. As for the other two extraction methods also here a calibration was necessary to calculate the amount of arsenic in all three samples. All relevant data is displayed in table 1 and 2 in appendix 3.

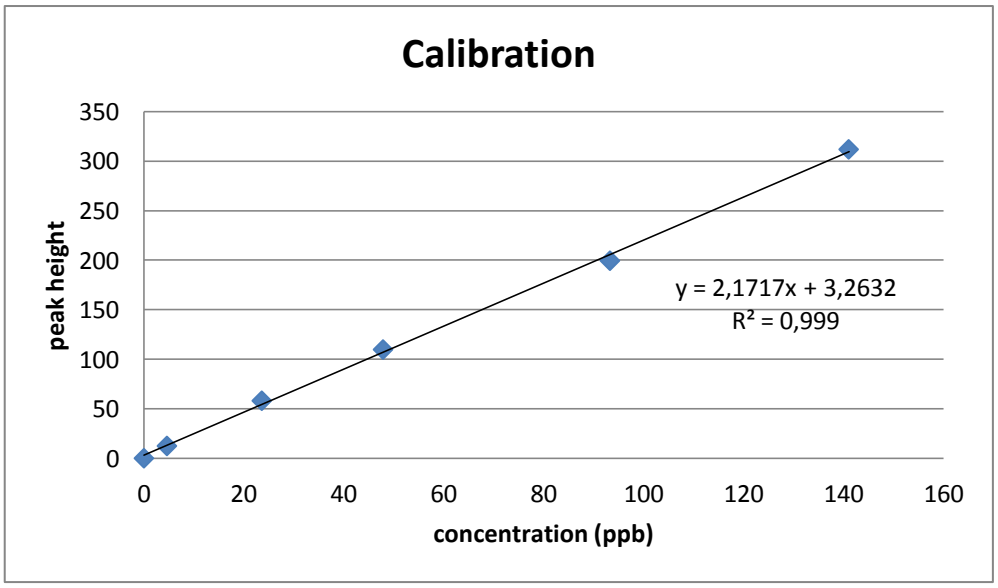


Figure 19: Calibration curve for samples extracted with 7 m nitric acid and 30 % hydrogen peroxide

The next table shows the displayed results from the AFS.

Table 8: Concentrations of the rice samples displayed at the computer (7 m HNO_3 and H_2O_2)

Sample	Concentrations [ppb]			
	Trial 1	Trial 2	Trial 3	Mean [Ø]
S3	4,4546	7,3309	3,1944	4,9933
S9	3,8579	3,7064	3,3054	3,6232
S10	4,3738	4,0907	4,0353	4,1666

As for the others also here a new calculation is necessary to get the real amount of arsenic. The formulas are the same as for the previous two methods. All used masses and volumes are displayed in table 3 and 4 in appendix 3. The following table shows the exact concentrations.

Table 9: Rice sample concentrations measured with AFS (7 m HNO_3 and H_2O_2) and ICP-MS

Sample	Real concentration [ppb] measured with AFS				Concentration [ppb] measured with ICP-MS
	Trial 1	Trial 2	Trial 3	Mean Ø	
S3	96,3718	158,599	69,109	108,027	106,7
S9	93,197	89,536	79,848	87,527	129,4
S10	184,355	172,421	170,087	175,621	182,4

The concentrations between both measure methods are apparent. But here the differences between AFS and ICP-MS are not so huge. One explanation for the lower concentration could be that not all hydrogen peroxide was boiled off. The rest of this hydrogen peroxide reacts then with the sodium borohydride and therefore not enough sodium borohydride is left to form arsine gas. The reaction equation below explains what exactly happens with the sodium borohydride. Figure 20 will show the results in a more visual way.

$$NaBH_4 + 4\,H_2O_2 \longrightarrow NaOH + B(OH)_3 + 4\,H_2O$$

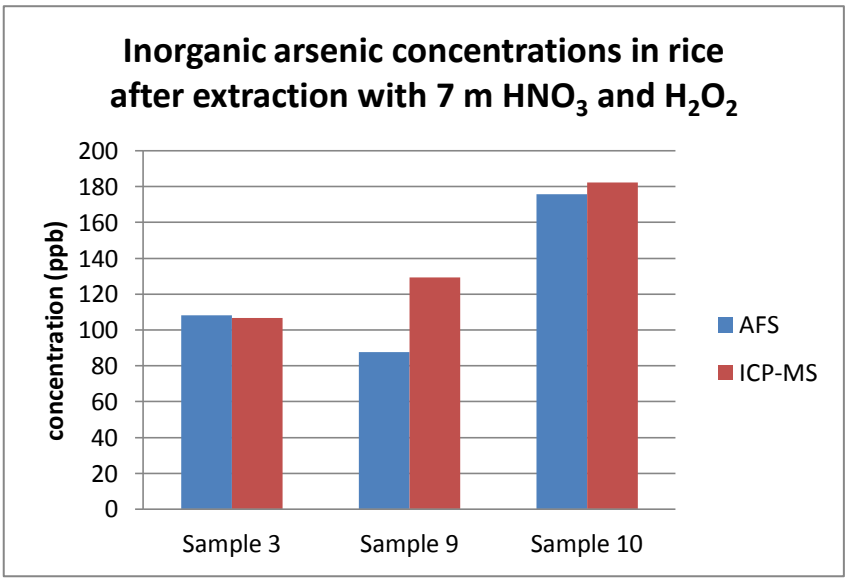


Figure 20: Comparison of inorganic arsenic concentrations in different rice samples by using 7 m HNO_3 and 30 % H_2O_2 as an extracting agent

4.2 Arsenator

The use of the Arsenator was the main task. Unfortunately there were a few problems. The biggest problem was that the colour change of the mercury dibromide paper was hardly visible. The reason for this was that not enough digest was used and so the amount of arsenic was too low for the Arsenator. Actually at the beginning it was calculated how much grams of rice and how much volume of extracting agent are necessary to get a result with the Arsenator. The necessary amount of rice was used, but unfortunately not the calculated volume of extracting agent. The steps of calculating both will be described below.

Hypothesis:

1 g rice contains 150 ng arsenic per g rice. The Arsenator limit of detection is 10 µg/l, which is the same as 10 ng/l. Because 50 ml solution is necessary the limit of detection amount of arsenic is 500 ng. This means that at least 4 g of rice are needed.

10 ng/ml · 50 ml= 500 ng As

4 g · 150 ng/g = 600 ng As

Before using the Arsenator a calibration had to be done. For this different concentrations were measured three times and the mean was calculated. With the help of this calibration curve all sample results could be calculated exactly enough. In appendix 4 table 1 and 2 all used data is shown. The figure below will show the calibration curve for the Arsenator.

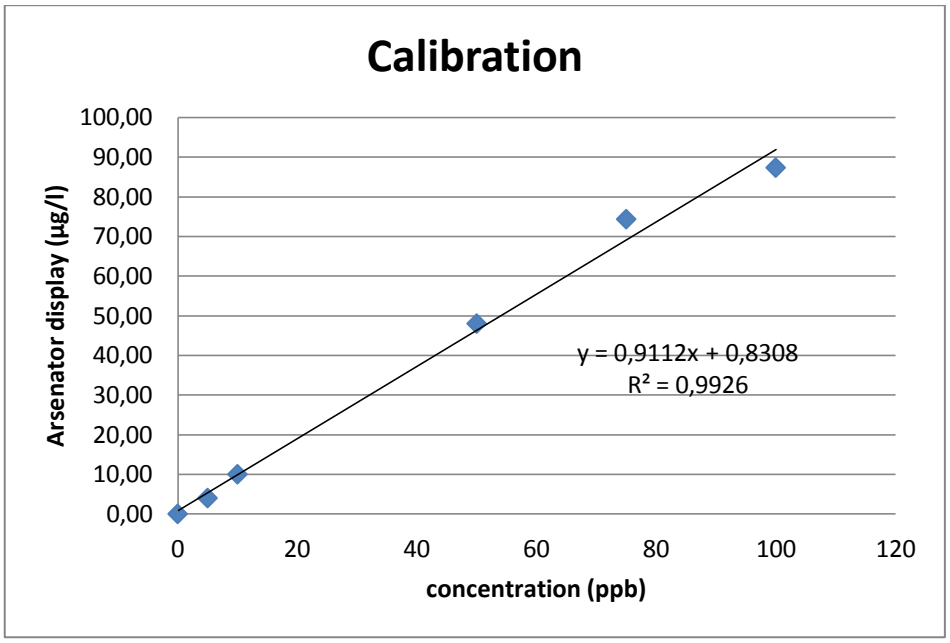


Figure 21: Calibration of the Wagtech Digital Arsenator

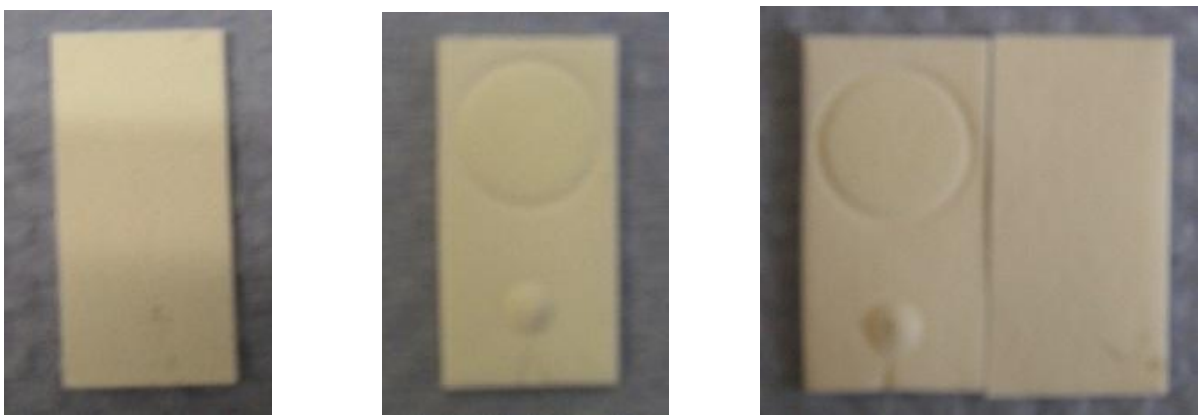
This calibration curve will be used to calculate the right concentrations of all samples. The displayed data will be converted in the right concentrations with the linear equation y = 0,9112x + 0,8308. The new value has to be calculated again due to the dilution. The procedure of doing so will be described later.

First the results of using a one molar nitric acid will be shown and discussed. As said before 10 ml of the digest were filled up to 50 ml with bidestilled water. This 50 ml were then used for the Arsenator. The results were too low for the detection system of the Arsenator. The table below shows the displayed results.

Table 10: Concentrations of the rice samples displayed at the Arsenator (1 m HNO_3)

samples	Concentrations [ppb]		
	Trial 1	Trial 2	Trial 3
S1	1	4	n.d.
S2	n.d.	n.d.	n.d.
S3	n.d.	n.d.	n.d.
S8	n.d.	n.d.	n.d.
S9	n.d.	n.d.	n.d.
S10	n.d.	n.d.	n.d.

The n.d. means non-determinable. Actually all non-determinable results in the table were displayed as 0 ppb. Although the digital system displayed 0 ppb there was a light colour change visible. The next pictures will show the colour change.



a) b) c)

Figure 22: Filter papers: a) unused mercury dibromide filter paper; b) used mercury filter paper with colour change; c) comparison of both filter papers: on the left the used one and on the right the unused one

As said a few sentences before the displayed concentrations are not the real ones. Therefore a new calculation has to be done. Following all steps of doing so will be described. As an example the trial 2 of sample 1 will be calculated. All used masses and volumes are displayed in appendix 5.

$$D.F. = \frac{1}{D_1 \cdot D_2}$$

D.F. – Dilution Factor

D_1 – Dilution 1

D_2 – Dilution 2

$$D_1 = \frac{m_1}{m_{t3}}$$

m_1 – mass of 1 m nitric acid solution

m_{t3} – total mass of 1 m HNO_3 and H_2O

$$D_2 = \frac{m_r}{m_{t2}}$$

m_r– mass of rice

m_{t2}– total mass of rice and used volume of 1 m nitric acid

$$c_{real} = D.F. \cdot c_{Arsenator}$$

c_{real} - real concentration

$c_{Arsenator}$ – concentration displayed at the Arsenator

$D_1 = \frac{m_1}{m_{t3}}$

$D_1 = \frac{10{,}9193\ g}{50{,}7967\ g}$

$\underline{D_1 = 0{,}2150}$

$D_2 = \frac{m_r}{m_{t2}}$

$D_2 = \frac{6{,}0111\ g}{39{,}1320\ g}$

$\underline{D_2 = 0{,}1536}$

$D.F. = \frac{1}{D_1 \cdot D_2}$

$D.F. = \frac{1}{0{,}2150 \cdot 0{,}1536}$

$\underline{D.F. = 30{,}2844}$

$y = 0{,}9112x + 0{,}8308$

$x = \frac{y - 0{,}8308}{0{,}9112}$

$x = \frac{4 - 0{,}8308}{0{,}9112}$

$\underline{x = 3{,}478}$

$c_{real} = D.F. \cdot c_{Arsenator}$

$c_{real} = 30{,}2844 \cdot 3{,}478$ ppb

$\underline{c_{real} = 105{,}3306\ ppb}$

For the other samples the procedure is the same. The real concentrations will be shown in the next table. For the non-determinable values the concentrations will be displayed as 0 ppb.

Table 11: Rice sample concentrations measured with the Arsenator (1 m HNO_3) and ICP-MS

Sample	Real concentration [ppb] measured with the Arsenator			Concentration [ppb] measured with ICP-MS
	Trial 1	Trial 2	Trial 3	
S1	7,1975	105,3306	0	95,8
S2	0	0	0	149,9
S3	0	0	0	106,7
S8	0	0	0	138,7
S9	0	0	0	129,4
S10	0	0	0	182,4

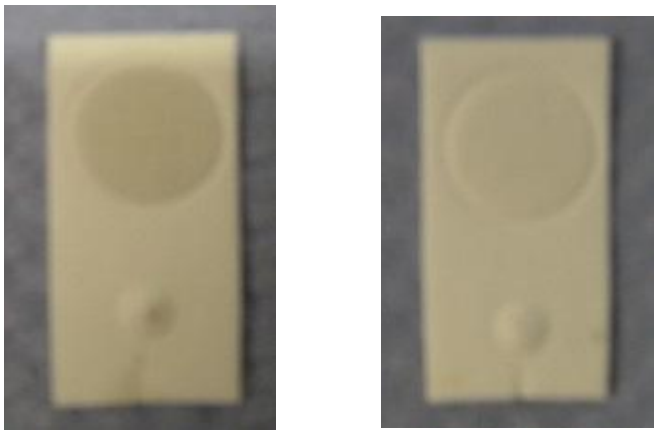
These results show that the amount of arsenic was not high enough to be detected by the Arsenator. The use of only 10 ml solution was consequently not enough.

After discussing the results using the 1 molar nitric acid now the results using the 7 molar nitric acid will be discussed. Also here only 10 ml of the cooked solution were used and filled up to 50 ml with bidestilled water. The real concentrations were also here to low for the Arsenator. The following table will show the displayed data.

Table 12: Concentrations of the rice samples displayed at the Arsenator (7 m HNO_3)

samples	Concentrations [ppb]		
	Trial 1	Trial 2	Trial 3
S1	> 100	> 100	n.d.
S2	> 100	5	n.d.
S3	n.d.	n.d.	n.d.
S8	n.d.	3	n.d.
S9	n.d.	62	4
S10	5	93	n.d.

Five results indicate a problem. In these cases the digital system displayed three times a value greater than 100 and two times also a too high value. The problem with all these results was that instead of a yellow colour a gray colour appeared. The pictures below show this gray colour.



a) b)

Figure 23: Filter papers: a) mercury dibromide filter paper with dark gray colour (> 100 displayed); b) mercury dibromide filter paper with bright gray colour (93 displayed)

This colour change means that a side reaction took place. Because the digital system of the Arsenator is based on photodetection it displayed a value even when it was the wrong colour change. Therefore these high results were specified as 0 ppb. To calculate the real concentrations the same equations as for 1 molar nitric acid were used. All relevant data is displayed in appendix 6. These new calculated concentrations will be presented in the next table.

Table 13: Rice sample concentrations measured with the Arsenator (7 m HNO_3) and ICP-MS

Sample	Real concentration [ppb] measured with the Arsenator			Concentration [ppb] measured with ICP-MS
	Trial 1	Trial 2	Trial 3	
S1	0	0	0	95,8
S2	0	167,539	0	149,9
S3	0	0	0	106,7
S8	0	67,106	0	138,7
S9	0	0	122,194	129,4
S10	235,538	0	0	182,4

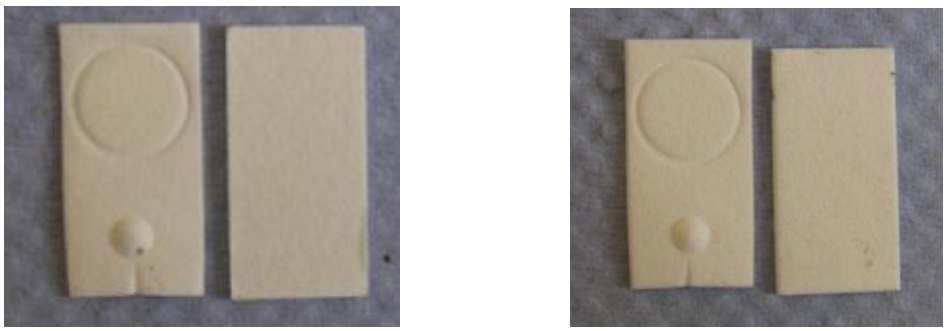
On the one hand the amount of arsenic was too low to be detected by the digital system of the Arsenator. But on the other hand there were also some side reactions due to the strong acidity of the seven molar nitric acid. These side reactions cause to the gray colour.

Now the results of using seven molar nitric acid and 30% hydrogen peroxide will be discussed. As for the AFS also here only three samples were used. These samples are sample 3, sample 9 and sample 10. The results for them are worse than the other ones were. The table below will show this.

Table 14: Concentrations of the rice samples displayed at the Arsenator (7 m HNO_3 + H_2O_2)

samples	Concentrations [ppb]		
	Trial 1	Trial 2	Trial 3
S3	n.d.	n.d.	n.d.
S9	n.d.	n.d.	n.d.
S10	n.d.	n.d.	n.d.

Because all samples displayed 0 ppb a calculation of the real concentrations is not possible. While the mercury dibromide filters from the other experiments with the one and seven molar nitric acid show at least a light colour change here all filters had no colour change. The pictures on the next page will show this.



a) b)

Figure 24: Filter papers: a) and b) two different samples but both lead to no colour change (on the left used mercury dibromide filter paper, on the right unused mercury dibromide filter paper)

The reasons for this were mentioned before. On the one hand only 10 ml cooked solution was used instead of 50 ml. And on the other hand the used hydrogen peroxide was not completely boiled off.

5. Conclusion

All these experiments show one thing really clear. It is possible to determine inorganic arsenic in rice with the Wagtech Digital Arsenator. But there are still some problems which have to be solved before this kit can be used officially for such analysis. The problems are the way of extracting the arsenic out of rice and the use of the right amount of solution for the Arsenator. The results from the AFS show that the extraction with nitric acid is working. But more improvements have to be done. Both used concentrations are too high for an extraction. They can cause to species transformation and cleave the carbon-arsenic bond. Thereby the received data are higher than the actual amount of arsenic in rice.

So the next steps will be manifold. One step will be to use a lower concentration of nitric acid. In most papers a nitric acid concentration of 0,29 mol/l for rice extraction is used. Thus a try with this concentration will be a good beginning. Another step should be the use of the calculated volume of cooked solution for the Arsenator. The use of only 10 ml was insufficient. Therefore the experiments should be done again with the one and seven molar nitric acid. But this time the full amount of calculated solution should be used. Perhaps then there will be some better results for the Arsenator. Using the lower acid concentration for the Arsenator should also be one next step. The use of nitric acid and hydrogen peroxide should be done again. But the next time it has to be ensured that all hydrogen peroxide is boiled off. Another point is that the ratio of nitric acid and hydrogen peroxide should be changed to see if this will have an influence on the results.

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AFS

Appendix 1:

1 molar HNO_3

Table 1: Concentrations of the calibration solutions

supposed concentration [ppb]	mass of vial [g]	mass of vial + As^{III} [g]	mass of vial + As^{III} + 3 m HNO_3 [g]	real concentration [ppb]
0	14,5102	14,5102	69,0331	0
5	14,8157	14,8617	66,8636	4,907
25	14,4878	14,7127	69,3060	22,778
50	14,6010	15,0289	66,9272	45,402
100	14,5608	15,3896	69,2443	84,148
150	14,1680	15,3880	66,8223	128,640

Table 2: AFS calibration results

	Concentration [ppb]	Peak height	Peak area
Trial 1	0,000000	0,111499	-31,938606
Trial 2	0,000000	0,165252	2,995574
Trial 3	0,000000	0,151033	-6,354260
Mean Ø	0,000000	0,142595	-11,765763
Trial 1	4,910000	18,803331	594,085632
Trial 2	4,910000	19,347065	603,615601
Trial 3	4,910000	18,662487	606,124817
Mean Ø	4,910000	18,937628	601,275391
Trial 1	22,780001	82,905373	2768,107666
Trial 2	22,780001	88,065170	2851,869385
Trial 3	22,780001	90,190056	2867,074219
Mean Ø	22,780001	87,053528	2829,017334
Trial 1	45,400002	180,889618	56447,312012
Trial 2	45,400002	187,597717	5745,025879
Trial 3	45,400002	179,419907	5675,187012
Mean Ø	45,400002	182,635742	5689,175293
Trial 1	84,150002	324,033875	10417,306641
Trial 2	84,150002	313,928894	10358,206055
Trial 3	84,150002	327,310455	10591,763672
Mean Ø	84,150002	321,757721	10455,758789
Trial 1	128,639999	468,194214	15708,525391
Trial 2	128,639999	467,170135	15482,373047
Trial 3	128,639999	481,622131	15754,327148
Mean Ø	128,639999	472,328827	15648,409180

Table 3: Masses of all rice samples and used volumes of nitric acid

sample	mass of vial [g]	mass of vial + rice [g]	mass of rice [g]	added ml HNO_3 (total) [ml]	mass of added ml HNO_3 [g]
S1	14,4111	19,0156	4,6045	33,4	34,1432
S2	14,4004	19,3934	4,9930	30,4	31,0764
S3	14,4733	20,4818	6,0085	33,1	33,8365
S8	14,4280	23,0204	8,5924	42,8	43,7523
S9	14,4564	19,4547	4,9983	30,6	31,2809
S10	14,4212	17,2193	2,7981	28,1	28,7252

Table 4: Masses of the used 1 m nitric acid solutions

sample	mass of vial [g]	mass of vial + 7m HNO_3 [g]	mass of vial + 7m HNO_3 + 1 m HNO_3 [g]	mass of 1m HNO_3 [g]
S1	14,4686	19,7240	30,6625	10,9385
S2	14,5177	19,7464	30,8692	11,1228
S3	14,4476	19,5247	29,5759	10,0512
S8	14,6199	19,2670	30,3036	11,0366
S9	14,4027	19,6986	30,7696	11,0710
S10	14,6225	19,9918	30,8687	10,8769

Appendix 2:

7 molar HNO_3

Table 1: Concentrations of the calibration solutions

supposed concentration [ppb]	mass of vial [g]	mass of vial + As^{III} [g]	mass of vial + As^{III} + 3 m HNO_3 [g]	real concentration [ppb]
0	14,5102	14,5102	69,0331	0
5	14,8157	14,8617	66,8636	4,907
25	14,4878	14,7127	69,3060	22,778
50	14,6010	15,0289	66,9272	45,402
100	14,5608	15,3896	69,2443	84,148
150	14,1680	15,3880	66,8223	128,640

Table 2: AFS calibration results

	Concentration [ppb]	Peak height	Peak area
Trial 1	0,000000	0,296707	-14,007535
Trial 2	0,000000	0,136177	-30,558414
Trial 3	0,000000	0,184993	2,018410
Mean Ø	0,000000	0,205959	-14,182513
Trial 1	4,910000	18,103336	573,951599
Trial 2	4,910000	17,493647	583,145996
Trial 3	4,910000	18,571360	605,145813
Mean Ø	4,910000	18,056116	587,414490
Trial 1	22,780001	81,465691	2649,504395
Trial 2	22,780001	83,288567	2721,328613
Trial 3	22,780001	82,074509	2689,540039
Mean Ø	22,780001	82,276253	2686,791016
Trial 1	45,400002	161,862564	5388,355957
Trial 2	45,400002	164,029160	5441,169434
Trial 3	45,400002	165,655533	5410,062500
Mean Ø	45,400002	163,849091	5413,195801
Trial 1	84,150002	306,217377	10035,296875
Trial 2	84,150002	310,679810	10038,293945
Trial 3	84,150002	303,229126	10152,550781
Mean Ø	84,150002	306,708771	10075,379883
Trial 1	128,639999	457,989655	15143,905273
Trial 2	128,639999	462,597748	15407,070313
Trial 3	128,639999	447,314240	15037,963867
Mean Ø	128,639999	455,967194	15196,313477

Table 3: Masses of all rice samples and used volumes of nitric acid

sample	mass of vial [g]	mass of vial + rice [g]	mass of rice [g]	added ml HNO_3 (total) [ml]	mass of added ml HNO_3 [g]
S1	14,5623	19,1549	4,5926	30	35,601
S2	14,7192	19,7154	4,9962	26,8	31,804
S3	14,4009	20,3992	5,9983	26,4	31,329
S8	14,3823	22,9759	8,5936	33,2	39,398
S9	14,3715	19,3734	5,0019	25,4	30,142
S10	14,4117	17,2144	2,8027	25,2	29,905

Table 4: Masses of the used 7 m nitric acid solutions

sample	mass of vial [g]	mass of vial + 7m HNO_3 [g]	mass of vial + 7m HNO_3 + H_2O [g]	mass of 7m HNO_3 [g]
S1	14,5599	21,3902	29,8397	6,8303
S2	14,4177	21,0338	29,6331	6,6161
S3	14,5679	20,2042	28,7140	5,6363
S8	15,0344	21,6579	30,1601	6,6235
S9	14,6183	20,9349	29,4563	6,3166
S10	14,6463	19,9515	28,6014	5,3052

Appendix 3:

7 molar HNO_3 and 30% H_2O_2

Table 1: Concentrations of the calibration solutions

supposed concentration [ppb]	mass of vial [g]	mass of vial + As^{III} [g]	mass of vial + As^{III} + 3 m HNO_3 [g]	real concentration [ppb]
0	14,1802	14,1802	66,8965	0
5	14,6047	14,6508	68,2450	4,604
25	14,6878	14,9266	68,9263	23,586
50	14,3878	14,8794	69,4140	47,859
100	14,5501	15,5070	69,5022	93,283
150	14,5644	15,9945	68,8746	141,061

Table 2: AFS calibration results

	Concentration [ppb]	Peak height	Peak area
Trial 1	0,000000	0,485549	-17,257668
Trial 2	0,000000	0,358855	-0,517796
Trial 3	0,000000	0,584246	8,792795
Mean Ø	0,000000	0,476217	-2,994223
Trial 1	4,600000	12,681646	389,392181
Trial 2	4,600000	13,655176	442,083649
Trial 3	4,600000	12,270844	382,815399
Mean Ø	4,600000	12,869222	404,763763
Trial 1	23,590000	58,156578	1773,045776
Trial 2	23,590000	60,289692	1877,664063
Trial 3	23,590000	56,966896	1718,158936
Mean Ø	23,590000	58,471054	1789,623047
Trial 1	47,860001	110,023773	3521,534424
Trial 2	47,860001	117,634117	3792,256348
Trial 3	47,860001	102,693420	3297,021973
Mean Ø	47,860001	110,117096	3536,937744
Trial 1	93,279999	200,376312	6393,741699
Trial 2	93,279999	200,508514	6665,862305
Trial 3	93,279999	198,170090	6527,811035
Mean Ø	93,279999	199,684982	6529,138672
Trial 1	141,059998	296,028961	9142,693359
Trial 2	141,059998	326,665833	9811,566406
Trial 3	141,059998	313,367920	10072,311523
Mean Ø	141,059998	312,020905	9675,523438

Table 3: Masses of all rice samples and used volumes of nitric acid

sample	mass of vial [g]	mass of vial + rice [g]	mass of rice [g]	added ml HNO_3 (total) [ml]	mass of added ml HNO_3 [g]	added ml H_2O_2 [ml]	mass of added ml H_2O_2 [g]
S3	14,4882	20,4758	5,9876	27,2	32,278	15	16,65
S9	14,5752	19,5757	5,0005	26,1	30,973	15,2	16,872
S10	14,3808	17,1823	2,8015	26,5	31,448	15	16,65

Table 4: Masses of the used mixed solutions

sample	mass of vial [g]	mass of vial + mixed solution [g]	mass of vial + mixed solution + H_2O [g]	mass of mixed solution [g]
S3	14,5715	21,1638	30,1217	6,5923
S9	14,5083	21,4725	30,4276	6,9642
S10	14,5001	21,2477	30,1542	6,7476

Arsenator

Appendix 4:

Calibration Arsenator

Table 1: Concentrations of the calibration solutions

Standards [ppb]	mass of vial [g]	mass of vial + As^{III} [g]	mass of vial + As^{III} + H_2O [g]	real concentration [ppb]
0	14,4508	14,4508	63,9538	0
0	14,3599	14,3599	63,4450	0
0	14,5738	14,5738	62,9404	0
5	14,7584	14,8043	63,8314	5,193
5	14,5455	14,5910	64,3045	5,077
5	14,8299	14,8759	62,5935	5,347
10	14,6182	14,7122	62,6098	10,875
10	14,6039	14,6861	62,2348	9,943
10	14,4556	14,5464	63,8993	10,196
50	14,6658	15,1970	63,7625	60,070
50	14,5497	15,0736	63,9641	58,863
50	14,6035	15,0567	61,9275	53,169
75	14,5286	15,2833	63,9935	84,708
75	14,6434	15,3885	64,3082	83,294
75	14,7188	15,3903	64,6179	74,714
100	14,1368	15,1085	61,4980	113,909
100	14,5372	15,4095	64,4547	97,020
100	14,7155	15,6123	64,1045	100,813

Table 2: Displayed concentrations at the Arsenator

standards [ppb]	Arsenator display			Mean
	trial 1	trial 2	trial 3	
0	0	0	0	0,00
5	5	3	4	4,00
10	12	10	8	10,00
50	50	49	45	48,00
75	80	78	65	74,33
100	84	91	87	87,33

Appendix 5:

1 molar HNO_3

Trial 1

Table 1: Masses of all rice samples and used volumes of nitric acid

sample	mass of vial [g]	mass of vial + rice [g]	mass of rice [g]	added ml HNO_3 (total) [ml]	mass of added ml HNO_3 [g]
S1	14,4111	19,0156	4,6045	33,4	34,1432
S2	14,4004	19,3934	4,9930	30,4	31,0764
S3	14,4733	20,4818	6,0085	33,1	33,8365
S8	14,4280	23,0204	8,5924	42,8	43,7523
S9	14,4564	19,4547	4,9983	30,6	31,2809
S10	14,4212	17,2193	2,7981	28,1	28,7252

Table 2: Masses of the used 1 m nitric acid solutions

sample	mass of vial [g]	mass of vial + 10 ml solution [g]	mass of vial + solution + H_2O [g]	mass of solution [g]
S1	14,6027	25,1264	63,0759	10,5237
S2	14,4455	25,1454	65,1356	10,6999
S3	14,5181	25,1552	63,3686	10,6371
S8	14,5570	25,0477	64,4411	10,4907
S9	14,6207	25,3212	63,5912	10,7005
S10	14,5639	24,9172	64,8029	10,3533

Trial 2

Table 3: Masses of all rice samples and used volumes of nitric acid

sample	mass of vial [g]	mass of vial + rice [g]	mass of rice [g]	added ml HNO_3 (total) [ml]	mass of added ml HNO_3 [g]
S1	14,4402	20,4513	6,0111	32,4	33,1209
S2	14,5472	19,5248	4,9776	31,4	32,0987
S3	14,3657	20,3566	5,9909	31,2	31,8942
S8	14,4280	23,0204	8,5924	42,8	43,7523
S9	14,4260	19,4180	4,9920	30,5	31,1786
S10	14,4068	17,1917	2,7849	31,9	32,6098

Table 4: Masses of the used 1 m nitric acid solutions

sample	mass of vial [g]	mass of vial + 10 ml solution [g]	mass of vial + solution + H_2O [g]	mass of solution [g]
S1	14,4821	25,4014	65,2788	10,9193
S2	14,4103	25,0362	64,8779	10,6259
S3	14,4793	25,1431	65,1691	10,6638
S8	14,3753	22,4197	65,1133	8,0444
S9	14,5839	24,7818	65,1493	10,1979
S10	14,5267	22,2692	64,9907	7,7425

Trial 3

Table 5: Masses of all rice samples and used volumes of nitric acid

sample	mass of vial [g]	mass of vial + rice [g]	mass of rice [g]	added ml HNO_3 (total) [ml]	mass of added ml HNO_3 [g]
S1	14,4402	20,4513	6,0111	32,4	33,1209
S2	14,5472	19,5248	4,9776	31,4	32,0987
S3	14,3657	20,3566	5,9909	31,2	31,8942
S8	14,4280	23,0204	8,5924	42,8	43,7523
S9	14,4260	19,4180	4,9920	30,5	31,1786
S10	14,4068	17,1917	2,7849	31,9	32,6098

Table 6: Masses of the used 1 m nitric acid solutions

sample	mass of vial [g]	mass of vial + 10 ml solution [g]	mass of vial + solution + H_2O [g]	mass of solution [g]
S1	14,4834	25,0358	65,1674	10,5524
S2	14,5658	24,8923	64,5313	10,3265
S3	14,3669	24,5434	64,4183	10,1765
S8	14,4985	21,0960	64,2211	6,5975
S9	14,0843	24,5589	62,8820	10,4746
S10	14,6796	23,0407	64,8667	8,3611

Appendix 6:

7 molar HNO_3

Trial 1

Table 1: Masses of all rice samples and used volumes of nitric acid

sample	mass of vial [g]	mass of vial + rice [g]	mass of rice [g]	added ml HNO_3 (total) [ml]	mass of added ml HNO_3 [g]
S1	14,5623	19,1549	4,5926	30	35,6010
S2	14,7192	19,7154	4,9962	26,8	31,8036
S3	14,4009	20,3992	5,9983	26,4	31,3289
S8	14,3823	22,9759	8,5936	33,2	39,3984
S9	14,3715	19,3734	5,0019	25,4	30,1422
S10	14,4117	17,2144	2,8027	25,2	29,9048

Table 2: Masses of the used 7 m nitric acid solutions

sample	mass of vial [g]	mass of vial + 10 ml solution [g]	mass of vial + solution + H_2O [g]	mass of solution [g]
S1	14,4500	26,2832	65,8152	11,8332
S2	14,3922	26,1750	66,3576	11,7828
S3	14,4795	24,2593	65,9240	9,7798
S8	14,5966	26,2317	64,3724	11,6351
S9	14,4699	24,3038	65,9173	9,8339
S10	14,3956	26,1674	66,3226	11,7718

Trial 2

Table 3: Masses of all rice samples and used volumes of nitric acid

sample	mass of vial [g]	mass of vial + rice [g]	mass of rice [g]	added ml HNO_3 (total) [ml]	mass of added ml HNO_3 [g]
S1	14,5033	19,0907	4,5874	30,5	36,1944
S2	14,4029	19,3935	4,9906	31	36,7877
S3	14,4074	20,4061	5,9987	29,7	35,2450
S8	14,4371	23,0251	8,588	40,2	47,7053
S9	14,4767	19,4718	4,9951	30,3	35,9570
S10	14,4723	17,2693	2,797	30,5	36,1944

Table 4: Masses of the used 7 m nitric acid solutions

sample	mass of vial [g]	mass of vial + 10 ml solution [g]	mass of vial + solution + H_2O [g]	mass of solution [g]
S1	14,5591	26,6106	66,8985	12,0515
S2	14,5246	26,5106	66,9514	11,9860
S3	14,5346	26,4453	66,7116	11,9107
S8	14,379	26,3113	65,6958	11,9333
S9	14,5345	26,4695	66,0623	11,9350
S10	14,5439	26,367	66,0874	11,8231

Trial 3

Table 5: Masses of all rice samples and used volumes of nitric acid

sample	mass of vial [g]	mass of vial + rice [g]	mass of rice [g]	added ml HNO_3 (total) [ml]	mass of added ml HNO_3 [g]
S1	14,5033	19,0907	4,5874	30,5	36,1944
S2	14,4029	19,3935	4,9906	31	36,7877
S3	14,4074	20,4061	5,9987	29,7	35,2450
S8	14,4371	23,0251	8,588	40,2	47,7053
S9	14,4767	19,4718	4,9951	30,3	35,9570
S10	14,4723	17,2693	2,797	30,5	36,1944

Table 6: Masses of the used 7 m nitric acid solutions

sample	mass of vial [g]	mass of vial + 10 ml solution [g]	mass of vial + solution + H_2O [g]	mass of solution [g]
S1	14,4368	20,402	65,4614	5,9652
S2	14,476	26,2658	66,4442	11,7898
S3	14,4951	25,5208	66,0018	11,0257
S8	14,7393	26,4633	64,6558	11,7240
S9	14,6065	26,2782	64,6235	11,6717
S10	14,6855	20,2425	65,4278	5,5570

Appendix 7:

7 molar HNO_3 and 30% H_2O_2

Table 3: Masses of all rice samples and used volumes of nitric acid

sample	mass of vial [g]	mass of vial + rice [g]	mass of rice [g]	added ml HNO_3 (total) [ml]	mass of added ml HNO_3 [g]	added ml H_2O_2 [ml]	mass of added ml H_2O_2 [g]
S3	14,7164	20,7024	5,986	25,6	30,380	15,1	16,761
S9	14,4848	19,4755	4,9907	25,4	30,142	15	16,650
S10	14,4941	17,2749	2,7808	24,9	29,549	14,9	16,539

Trial 1

Table 4: Masses of the used mixed solutions

sample	mass of vial [g]	mass of vial + mixed solution [g]	mass of vial + mixed solution + H_2O [g]	mass of mixed solution [g]
S3	14,5598	21,9944	65,4666	7,4346
S9	14,4285	22,8480	65,5539	8,4195
S10	14,4150	21,7811	65,2582	7,3661

Trial 2

Table 4: Masses of the used mixed solutions

sample	mass of vial [g]	mass of vial + mixed solution [g]	mass of vial + mixed solution + H_2O [g]	mass of mixed solution [g]
S3	14,5804	22,1455	65,2155	7,5651
S9	14,4259	22,9252	65,2732	8,4993
S10	14,4312	21,9656	65,2142	7,5344

Trial 3

Table 4: Masses of the used mixed solutions

sample	mass of vial [g]	mass of vial + mixed solution [g]	mass of vial + mixed solution + H_2O [g]	mass of mixed solution [g]
S3	14,4929	22,0960	65,1165	7,6031
S9	14,5325	22,9805	65,1672	8,4480
S10	14,6524	22,0614	65,5042	7,4090

STATUTORY DECLARATION

according to the bachelor thesis

written by

Nadine Weis

I declare that I have developed and written the enclosed thesis entitled

“Determination of inorganic arsenic in rice using the Wagtech Digital Arsenator”

entirely by myself and have not used sources or means without declaration in the text.
Any thoughts or quotations which were inferred from these sources are clearly marked as such.

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