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### A Comparison of Recent Analytical Methods for Analysis of Arsenic

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#### ABSTRACT

Arsenic is one of the known toxic elements to human's life. Never the less, the level of toxicity relies on the classification of chemical species of arsenic as organic or inorganic which being a big concern in industrial and environmental chemistry. different separation methods as HPLC or IC has been coupled to either ICP-MS or ICP-OES in order to increase sensitivity of determining As(III) and As(V), while for determining As(III) and total As need a chemical reduction of As(V) before utilise voltammetry .with the aim of having best technique to trace elements levels especially toxic elements , some aspects must to be advanced such as reducing chemical and physical interferences , high sensitivity , low LOD and LOQ , less time consuming , more accurate than conventional techniques and less cost equipment. Other methods as bio-components, ETAA, (INAA) and AAS have been showing promising future for analysis techniques.

#### Introduction

Arsenic has come from the Persian word zarnikh, meaning "yellow." Symbol As is referred to Arsenic with atomic number 33 and it is ubiquitous heavy metal which make it the most effective element in human history more than any other toxic Compound or element. About its abundance, in the human system is the 12th, in sea water is the 14th and in the earth's crust is the 20th. [Yusuf, S., Krahenbuhl,(2012). Improving NNA accuracy for the measurement of arsenic in the characterization of heterogeneous catalysts using a TRIGA reactor. *Journal Of Radioanalytical And Nuclear Chemistry*]

Naturally, arsenic is existed in both inorganic and organic forms and the degree of arsenic toxicity classified whether the chemical species are inorganic or organic because the inorganic species as arsenate As (V) more toxic than organic species as mono-methyl arsenic acid, although volatile As compounds are the most toxic As species. As a result of arsenic toxicity and high abundance, determining arsenic in human consumption (food, oil and water) is becoming important issue [Higashidani, N., Kaneta,(2014). Speciation of arsenic in a thermoacidophilic iron-oxidizing archaeon, *Acidianus brierleyi*, and its culture medium by ICP-OES combined with flow injection pretreatment using an anion-exchange mini-column.]

Natural environment has arsenic biogeochemical cycle and volatile arsenic is playing an important role in the cycle due to its capability to produce atmospheric As 8 times more than continental dust. volatile As has 3 oxidation states and with the absence of UV, the stable compounds of volatile As have high mobility which make them cross long distance in the air. [ deGois, J., Lucena, I., Cezario, P., da Silva, A., Lima, I., & Luna, A. (2018). A high-throughput method for multi-element determination in green coffee beans using diluted nitric acid and ultrasound energy. *Analytical Methods*]

#### OXIDATION STATES AND ISOTOPES OF ARSENIC

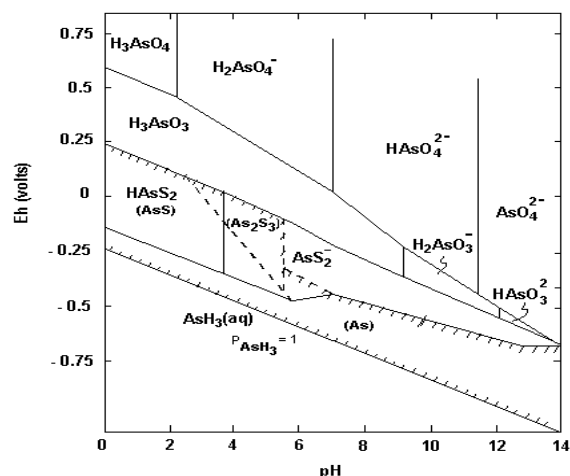


Figure (1) demonstrates the Eh-PH diagram for arsenic at 25 C°

Naturally, arsenic is considered as mono-isotopic element  $^{75}\text{As}$ . Never the less, at least 30 radioisotopes are synthesized from 60 to 92 atomic mass. The most stable isotope is  $^{73}\text{As}$  due to its half-life of 80 days, whereas other isotopes have short half-lives roughly less than one day [ $^{74}\text{As}$  ( $t_{1/2}=17.77$  hours),  $^{76}\text{As}$  ( $t_{1/2}=1.0942$  23 hours), and  $^{77}\text{As}$  ( $t_{1/2}=38.83$  hours)] apart from  $^{71}\text{As}$  ( $t_{1/2}=65.30$  hours)]. [ Malhotra, R. (1999). Estimation of trace impurities in reactor-grade uranium using ICP-AES. ]

#### ARSENIC COMPOUNDS

Arsenic oxidizes converted to arsenic trioxide by heating arsenic oxidizes in the air, arsenic trioxide can be performed. Some arsenic compounds is converted to a gaseous form by heating at atmospheric pressure.

arsenic has three common oxidation states (-3 in the arsenide, as alloy-like inter-metallic compounds and +3 in the arsenates.

As (III) is characteristically pyramidal owing to the effect of the lone pair of electrons.

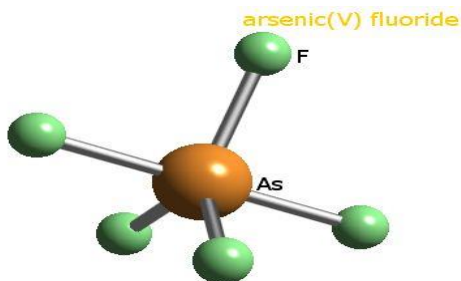


Figure (2) shows the shape of As<sub>5</sub> in space

### INORGANO-ARSENIC

Dissolving As<sub>2</sub>O<sub>3</sub> ("white arsenic") and As<sub>2</sub>O<sub>5</sub> in water solution can form weak acids as arsenous acid As(OH)<sub>3</sub> or (Arsenic(V) acid). All arsenic tri-halides are known apart from the astatide which is unknown.

### ORGANO-ARSENIC

Organo-arsenic can be performed by methylation of arsenic trioxide, while Minerals consider as the main source of arsenic which has formula {MAS and MAS<sub>2</sub> (M = Fe, Ni, Co)}. The proportional of Arsenic about 1.5 ppm (0.00015%) of the Earth's crust, 1–10 ppm in Soil and only 1.6 ppb in Seawater according to the British Geological Survey and the United States Geological Survey "almost 50% of world white arsenic was produced by China In 2005 with, followed by Chile, Peru, and Morocco". [Okibe, N., & Sasaki, K. (2014). Speciation of arsenic in a thermo-acidophilic iron-oxidizing archaeon, *Acidianus brierleyi*, and its culture medium by inductively coupled plasma-optical emission spectroscopy combined with flow injection pretreatment using an anion-exchange mini-column.]

### CLASSIFICATION OF ARSENIC

Arsenic and its species are classified as toxic and harmful compounds in the environment. according to "The International Agency for Research on Cancer (IARC) that arsenic and arsenic compounds recognizes as group 1 carcinogens", while the EU consider arsenic pent-oxide, arsenic trioxide and arsenate salts as group 1 carcinogens [Lienemann, M, (2018). Towards patterned bioelectronics: facilitated immobilization of exoelectrogenic *Escherichia coli* with heterologous pili. *Microbial Biotechnology*]

### APPLICATIONS OF ARSENIC

- *Agricultural*

Arsenic and its compounds, especially calcium arsenate, copper(II) acetoarsenite and lead hydrogen arsenate has been used in producing agricultural pesticides, treating herbicides, insecticides and wood products.

- *Medical use*

Arsenic compounds are used as respiratory metabolites by a few kinds of bacteria. Experimentally, tiny quantities of arsenic are an essential dietary element in the chicken, hamster, goat, rat, and humans. On the other hand, multi-cellular life might be poisoned by As because of its presence in higher level than needed. [Sterba, G. Steinhauser and F. Grass, 2012, *Journal of Radioanalytical and Nuclear Chemistry*]

### LEVEL OF ARSENIC IN DIFFERENT SAMPLES

Arsenic is a widespread element existing commonly in natural waters, air, rocks, organisms and soils drinking groundwater (pollute water) from wells is naturally the main source of inorganic arsenic species. Health issues are a most important concern for whole world, especially in SE Asia where arsenic-induced cancers cause death to thousands of people. In the earth's crust contain roughly 3 mg/kg of arsenic while seawater has approximately 1–2 mg/L (Cullen and Reimer, 1989). On the other hand, irrigation and drinking water and variety of vegetables and cereals have been recorded higher concentration of arsenic more than permissible limits in different parts of the world. Recently, arsenic has been reaching high levels in the environment which aroused great attention because of its dangerous influence on life species including humans.

### ANALYTICAL METHODS WHICH HAVE BEEN USED FOR DETERMINATION OF ARSENIC

One of the techniques which has been used widely for the detection of arsenic is Inductively Coupled Plasma (ICP) which depends on determining the typical wavelength of a specific light which resulting from the metal. This technique has some advantages as the capability of detecting all elements apart of argon, less time consuming (30 second), simple, and also, it can measure different concentrations of components due to its limit of detection LOD 1-100 mg/L. Nevertheless, unstable elements require special facilities to deal with the radioactive emission of the plasma. Moreover, halogens need special optics due to their very short wavelength. [Zaib, M., Saeed, A., Hussain, (2014). Voltammetric detection of As(III) with *Porphyridium cruentum* based modified carbon paste electrode-biosensor. *Biosensors And Bioelectronics*].

ICP-MS methods is widely applied because of the solution ranges from ppm to ppt. accuracy and precision can be achieved at 1-10% for the most elements. In addition, ICP-MS is used to determine elements in geological, food, physiological and environment samples. [van der Meer, J. (2004). Development of a Set

of Simple Bacterial Biosensors for Quantitative and Rapid Measurements of Arsenite and Arsenate in Potable Water. *Environmental Science & Technology*]

Another technique that has been used frequently to analyse arsenic is Neutron Activation Analysis (NAA) which based on nuclear reaction. No pre-treated to the sample, but it is wrapped up first then irradiated inside a reactor. The analyte turn out to be radioactive when nuclei of the atoms of the element interact with the neutrons which produce radioisotopes and then decay by releasing gamma rays. [2, 7, 25]. One of the good points of this method is no matrix effect due to the majority of the samples are transparent in gamma ray and neutron. In addition, accurate consequence is provided for high amount without any dissolution or digestion. however, this method suffer from some disadvantages as low sensitivity due to the need of high flux neutron source and it cannot provide information on some of light elements as C or B [Danso, K., Adusei-Fosu, K., & Klu, G. (2012). Analysis of mineral nutrients status using Instrumental Neutron Activation Analysis. *Journal Of Radioanalytical And Nuclear Chemistry*].

XRF method is a common analytical techniques which is used to determine elements in different types of samples that include geological, foodstuff, biological and environmental samples, with limit of detection (10\_100 ppm). Due to the need of homogeneity, the sample is prepared rapidly and easily. On the other hand, some elements as Be cannot be determined by XRF. Flow injection analysis (FIA) is depending on injecting a liquid sample throughout a moving transporter stream of non-volatile liquid and it is suitable for determining a wide range of elements by using a number of electro-chemical and photometric detector. This method has low LOD and LOQ and high sensitivity but it is consuming a high amount of reagent and high equipment cost [5]. Atomic absorption spectroscopy is one of most applicable techniques because it has many advantages which increase the ability of determining the majority of the elements such as simultaneous analysis of elements which reduce analysis time. Moreover, it is simple and fast techniques and it has high sensitivity, low LOD and LOQ and it can identify elements from 185 nm to 900 nm (wavelength). Nevertheless, it cannot applied to organic species, it is consuming a big amount of sample and it is analysis samples in solutions only. [Lienemann, M., TerAvest, M., Pitkänen, J.,(2018). Towards patterned bioelectronics: facilitated immobilization of exoelectrogenic *Escherichia coli* with heterologous pili. *Microbial Biotechnology*]

#### PIE CHART OF RECENT PAPERS

The proportion of variety methods which have been used to analysis arsenic from 2013 to 2015 according to Huddersfield university website.

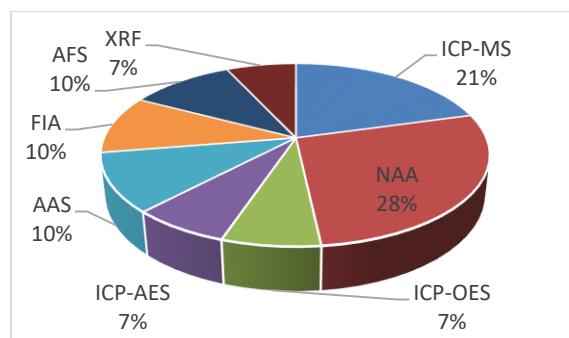


Figure (3) illustrates the proportional of different methods in 40 papers from 2013 to 2015.

It can be seen that from the pie chart that NAA is the most used method with the highest percentage 28% while ICP-MS came second with 21% following by FIA, AFS and AAS with same percentage 10%. On the other hand, ICP-AES, XRF and ICP-OES have the lowest percentage with 7% for each one.

#### RECENT DEVELOPMENTS IN ANALYSING TECHNIQUES

Recently, a number of techniques have been developed for the determination of arsenic. Most of the analysing methods are useful and reliable to measure arsenic at extremely low concentrations. however, these methods have some major disadvantages as high-cost instrumentation, field applicability, necessity of highly skilled technician, processing the sample chemically, etc.so, Biosensors is the best alternative method which used to determine arsenic due to its sensitivity, specificity, simplicity, lower cost, better limit of detection, fast response time, ease of use, portability, and capability to furnish continuous real-time signals. The sample does not need pre-treatment or expert handling. Also, the extent of bio-available toxicity of arsenic can be measured as the bio-components used in the system are part of the living world. [Danso, K. Adusei-Fosu and G. Klu, 2012, *Journal of Radioanalytical and Nuclear Chemistry*]

Arsenic owning it's important because of its present in nature and its high toxicity to living creatures. Biosensor can quantify and qualify arsenic beside various elements in water, soil, agriculture and food samples. Biosensor is based on whole cell bio-sensitive of arsenic. Due to advent bio-molecular biosensor, lower limit of detection and incubation period have been overcoming. Interference of phosphate, silicate and iron that could result in dissociation of As from all complexes can be reduced by adding EDTA which leading to an accurate estimating of As in water. Similarly to that, E-coli DH5 $\alpha$  containing LuxAB gene with limit of detection 7  $\mu\text{g/L}$ . E-coli strain one of the most sensitive micro-organisms to As with limit of detection 7.5  $\mu\text{g/L}$ . By aptamer-target technology, lower limit of detection (sub-ppm levels) has been provided which establishing a futuristic pathway for specific

target biosensor developments. E-coli MC 1061 has limit of detection 6 ng /g. biosensor technique is more efficient than chemical extracting to assessing the bioavailability of arsenic. [Fifield, F., &Kealey, D. (2000). Principles and practice of analytical chemistry. Oxford: Blackwell Science]

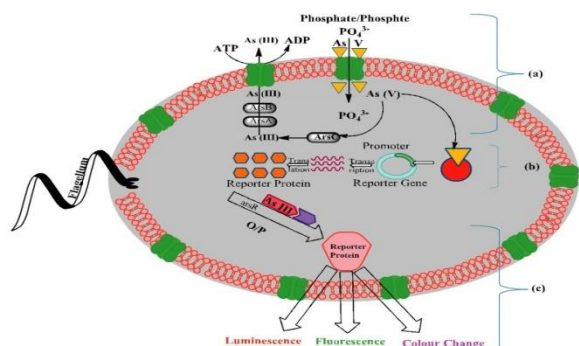


Figure (4) shows whole-cell-based biosensor for (a) Arsenic [As(V) and As(III)] transport by phosphate channel (b) Working mechanism of signal transducer for arsenic biosensor, and (c) Detection of As(III) by luminescence.

Arsenic biosensor has been divided into two types:

A- Cell-free-based biosensors which have three categories \

- 1- Protein-based biosensor
- 2- DNA-based biosensor
- 3- Aptame-based biosensor

B- Whole-cell-based biosensors which include\

- 1- Luciferase-based biosensor
- 2- lacZ-based biosensor
- 3- GFP-based biosensor
- 4- Other alternate approaches

Here is a brief explanation of one of these techniques (protein-based biosensors): specific protein is playing as a sensitive material to As. this mechanism based on HSAB principle (soft acid arsenic has affinity for binding sulphur in the protein. sulphur of cystine is susceptible to be oxidase in the presence of As).in order to prevent interference of positively charged ions the amino acid carry out positively charged substituent at PH = 7. Catalytic action of acetylcholine-terase produce formation of radix activity product thio-choline which provide signal for As estimation. (As concentration proportional to the decrease of thio-choline oxidation). It has a detection limit of 5 µg/L. [Sterba, G. Steinhauser and F. Grass, 2012, Journal of Radioanalytical and Nuclear Chemistry]

*USING ETAAS TO INVESTIGATE THE USE OF IS METHOD COMBINED WITH PERMANENT CHEMICAL MODIFICATION FOR DETERMINING AS IN AN ENVIRONMENTAL SAMPLE.*

Electro-thermal atomic absorption spectrometry (ETAAS) has been broadly used for determining of As

levels in a variety of difficult matrices due to its exceptional detection limit with lowest sample consumption. ETAAS provides accurate measurement more than other modern methods. Never the less, it has been suffered from high background level, the interaction between heated carbon with arsenic during the atomization process and the possibility of volatilisation losses of arsenic in pyrolysis step. The use of several permanent or non-permanent chemical modifier is proposed to overcome these difficulties. Alternative quantification technique in combination with permanent chemical modifier has been introduced in order to solve such as problems.

Internal standard is a simple and effective method to compensate for systematic and random errors in AAS analysis. The method is based on addition a constant amount of Bismuth and tellurium to standard solutions and matrix sample. The ratio of (analyte signal / internal standard signal) is independent of perturbation source. However, the main issue is the unavailability of multi-channel instrument and how internal standard can be chosen properly?

Bismuth and tellurium have been evaluated as internal standards which used in order to reduce matrix effects on determining arsenic directly in sediments. also, Co is referred as an internal standard in the presence of Zr and Ir as a chemical modifier which provide lower detection limit and compensate systematic and random errors and improve precision and accuracy (LOD 30ng/g , LOQ 100 ng/g) comparing to addition standard. In addition to the advantages of internal standard is increasing the life time of graphite tube up to 40%. [Lienemann, M., TerAvest, M., Pitkänen, J., Stuns, I., Penttilä, M., Ajo-Franklin, C., & Jäntti, J. (2018). Towards patterned bioelectronics: facilitated immobilization of exoelectrogenic Escherichia coli with heterologous pili. Microbial Biotechnology]

*ANALYSING RICE SAMPLE BY INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY (ICP-OES)*

A semi-aquatic grass plant (rice) is a primary food for 3billion people around the world. As a result of exposing to both water and soil, rice can contain various elements. studies have shown that the various species of rice might contain toxic and essential elements such as As, Cr, Pb, Se and V which occur due to using fertilizers and chemicals or aerial deposition, industrial disposal etc. many of these elements like As, Cr, Hg, Pb and Ni or their chemical forms are harmful to life creatures. This aspect lead to the need for determining rice contains to avoid potentially problematic of toxic elements, various methods have been used tracing acid digestion: flame atomic absorption spectrophotometry (AAS) ,graphite furnace AAS (GFAAS), inductively coupled plasma (ICP) optical emission spectrometry (OES),ICP mass spectrometry (MS) and/or total reflection X-ray fluorescence.

Digestion steps altogether could be eliminated by direct solid analysis, along with unavoidable dilution as well as analyte loss and time-consuming. For analysing the rice containment, (SS) has been combined with GFAAS (solid sampling is the former and graphite furnace flame atomic absorption spectrophotometry is the latter), instrumental neutron activation analysis (INAA), laser-induced breakdown spectroscopy (LIBS) and micro-X-ray fluorescence. Never the less, INAA and micro-X-ray fluorescence techniques are not broadly available due to the high cost and time consuming.

Also, GFAAS is not appropriate and LIBS is not mechanized to the concurrent determination of several elements. on the other hand , one automated technique that is quick and simple, although it has not been applied yet to the direct analysis of rice, is SS–ETV–ICP-OES(SS electro-thermal vaporization (ETV) coupled to inductively coupled plasma optical emission spectrometry), with efficiency sample introduction roughly close to 80%. This is a massive improvement compared to what has been achieved with a usual nebulization system. in addition, for the reason that only a few mg of sample are normally loaded onto graphite boats which then positioned in the furnace, when only a small sample size is available , many experiments can still be conducted SS–ETV–ICP-OES should be applicable to quick, sensitive and precise multi-elemental determination of toxic and essential elements in powdered rice.

Much sharper analyte signal peak is resulted by a cooling step directly before and after the vaporization step in the ETV temperature program. Secondly, the linearity of calibration curves which obtained with a rising amount of rice flour (CRM) has been significantly improved by the point-by- point internal standardization with an Ar emission line. Also, using a little amount of CCl<sub>2</sub>F<sub>2</sub> to change analytes into more volatile chlorides and fluorides had a very valuable effect. The range of detection limits from 0.01 to 6 ng /g in the solid which based on the element and wavelength selected under the optimized conditions. To illustrate the accuracy of the technique for the analysis of rice samples, by comparing with an independent method (acid digestion) followed by analysis by ICP-MS. The non-linearity prompted by matrix effects in the analyte mass response curve could correct by using Ar<sub>2</sub> + as internal standard in ICP-MS. SS–ETV–ICP-OES can become an essential tool for danger assessment of food safety due its quick and accurate direct quantify of multi-elemental analysis of solid food. [Penttilä, M., Ajo-Franklin, C., & Jäntti, J. (2018). Towards patterned bioelectronics: facilitated immobilization of exo-electrogenic *Escherichia coli* with heterologous pili. *Microbial Biotechnology*.]

#### THE USE OF SINGLE REACTION CHAMBER IN ICP-OES FOR TRACE ELEMENTS IN AGRICULTURE SAMPLE (NUT)

Sample preparation in some cases preferred techniques which using concentrated acids and microwave heating.

Particularly for organic matrices, using conc HNO<sub>3</sub> acid towards alter samples in a suitable solution to determined elements by plasma-based techniques. Though, using low and medium pressure microwave systems are not oxidizing several organic compounds fully. The analytical response of a few emission lines can be affected by residual carbon content throughout element determination by ICP-OES .according to Aline L.H. Muller "the emission intensity of ionic lines is not affected while the emission intensity of atomic lines with higher excitation energies can be increased (up to 30%)".

Agriculture sample as nuts content polyunsaturated fatty acids (difficult matrix) which make it barely oxidized by HNO<sub>3</sub>, even though a complete digestion only can be achieved by using higher temperatures than 180 °C and concentrated HNO<sub>3</sub>. The dry ashing method is the most common and simple method, that achieve digests with very low RCC .nevertheless, some issues as losses of volatile elements and the risk of contamination at sample breakdown step.

A developed method as MIC (Microwave induced combustion) can be advised as suitable for digesting organic samples completely with RCC lower than 1%. However, pressure overload of microwave system can be prevented by digesting only 0.5 g of sample. Also, pressurization with oxygen required a special vessel. FMIC (focused microwave-induced combustion) was lately proposed to improve the introducing sample mass in the combustion system [20]. This method has increased digestion of the sample up to 3 g and lower LODs has been allowed by using diluted HNO<sub>3</sub> as an absorbing solution.

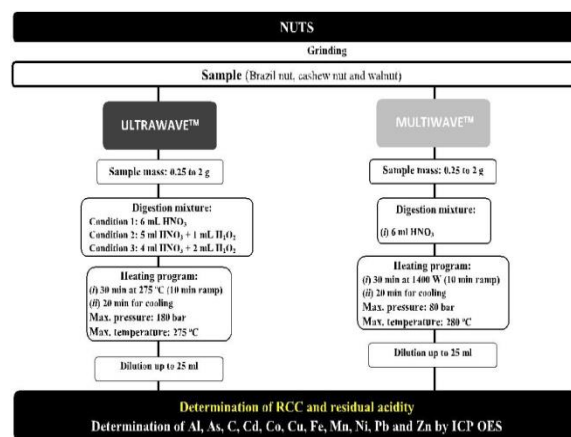


Figure 5 shows the conditions of using Ultra-Wave and Multi-wave methods.

However, the FMIC method is not usually available. alternatively, focused microwave systems is used in wet digestion method which increase the applicable amount of the sample to digested up to 10 g without overpressure, although, the main dark-point is relying on the use of sulfuric acid to progress the breakdown temperature in atmospheric pressure and physical interferences .also, sulfate may form insoluble

compounds with some elements. A new system called SRC (single reaction chamber, Ultra-Wave™ system) has been proposed recently, which allows higher temperature and pressure up to 300 °C and 199 bar. Ultra-Wave™ system is using N<sub>2</sub> to cool the chamber in order to prevent boiling and spitting, and dispose of any chance of cross-contamination. The digestion efficiency Ultra-Wave™ system is assessed by the determination of residual acidity and RCC in final digests. [Barreca, C. Lino and F. Di Gaudio., 2018, Essential micronutrient and toxic trace element concentrations in gluten containing and gluten-free foods, *microchemical journal*.]

*ANOTHER DEVELOPMENT IN ICP-MS FOR ANALYSING ENVIRONMENTAL SAMPLE CONTAINING (AS):*

Inductively coupled plasma mass spectrometry (ICP-MS) is a sensitive and great multi-element analysis technique. Never the less, suitable sample preparation strategies have to be adopted before analysis. In general, preparing a sample for ICP-MS analysis includes acid digestion methods, which consuming a lot of time, and increasing the chance of losing volatile elements due to the need of using inorganic acids and reagents and the threat of sample contamination. Additionally, the major drawbacks of digestion methods are using expensive microwave ovens for analytical work, the chance of irregular explosions due to operating digestion short lifetime vessels at high pressures. So as to avoid these troubles, ultrasound-assisted extraction method has been recommended for determining elements (75As, 52Cr, 63Cu, 60Ni103Rh, 118Sn, and 66Zn) by ICP-MS in environmental samples.

It's called a green analytical procedure because of lower energy requirements and consuming a small amount of solvent. by using ultrasound-assisted extraction method many processes are eliminated, less solvents and acids are used, decrease the chance of losing analyte and less cost equipments which make tracing and determining As in environmental sample fast, more accurate with (LOD 15 µg/g, LOQ 0.4µg/g, range of linearity 0.05-100 ng/ml) and less expensive than with conventional ICP-MS. [M. Frena, D. Quadros, 2014, A high-throughput method for multi-element determination in green coffee beans using diluted nitric acid and ultrasound energy, *Madureira, Microchemical Journal*]

*CONCURRENT DETERMINATION OF HYDRIDE-FORMING AND NON-HYDRIDE-FORMING ELEMENTS IN AN ENVIRONMENTAL SAMPLE BY ATOMIC FLUORESCENCE SPECTROMETRY (AFS)*

Most of the samples must be determined every day which make concurrent high throughput and sensitive determination of several elements never become greater. Atomic fluorescence spectrometry (AFS), mass spectrometry (ICP-MS) and inductively coupled plasma

optical emission spectrometry (ICP-OES) can be used to achieve the function of high throughput determination due to their potential of simultaneous multi-element analysis. Nevertheless, because of both low content and the serious interference from the sample matrix, the determination of several elements in an environmental sample by these methods is difficult. Therefore, they need improve their sensitivity and throughput. Chemical vapour generation CVG provides many exceptional advantages as lower matrix and spectral interferences, higher efficiency of sample introduction and better sensitivity and selectivity comparing with conventional pneumatic nebulisation (PN).

The most commonly CVG technique used is Hydride generation (HG) not only used for classic hydride creating elements (As, Bi, Hg, Ge, Sn, and Zn), it include many transition and noble elements. Never the less, the efficiency of HG is too low to be analytically valuable. Furthermore, different hydride might form elements have different optimum experimental circumstances for hydride generation. Consequently, concurrent multi-element analysis which using HG is quite restricted. Which lead to developing sample introduction for simultaneous determination of hydride-forming and non-hydride-forming elements. A multi-mode sample introduction spray chamber (MSIS) has been developed to could introduce analyte to an atomizer with CVG or PN independently, or simultaneously, thus achieving multi-element determination of non-hydride-forming and hydride forming elements.

On the other hand, the sensitivity has not yet been improved for the determination of non-hydride-forming elements for that reason, developing a technique for concurrently sensitive determination of both hydride-forming elements and non-hydride- elements is an attractive idea. Many unique advantages have been presented by CVG as eliminating the need for fresh tetra-hydro borate solution and reducing H<sub>2</sub> production. Consequently, by using PVG as an alternative to HG, the instability of plasma which occurring from H<sub>2</sub> can be considerably reduced. (DM-CVG) system that integrates HG and PVG can achieve concurrent multi-element analysis of hydride-forming and non-hydride-forming elements by AFS which also provide less matrix and spectral interferences and high sensitivity for trace elemental analysis. [D. Skoog, F. Holler and T. Nieman, 1998, *Principles of instrumental analysis*, Saunders College Pub., Philadelphia., Book]

**Conclusions**

One of the known toxic element to humans is arsenic. Never the less, the level of toxicity relies on the classification of chemical species of arsenic as organic or inorganic. the organic species for example mono-methyl arsenic acid and di-methyl arsenic acid are less toxic than the inorganic species such as arsenide As(III) and arsenate As(V) (arsenide As(III) is the most toxic,

arsenate As(V) comes after and then organic varieties. for that reason, the classification of the As types, especially of the inorganic species, is an important concern in industrial and environmental chemistry. The mainly species of inorganic As are As(III), As(V), and total As. different separation methods as HPLC (high-performance liquid chromatography) or IC (ion chromatography) has been coupled to either ICP-MS or ICP-OES in order to increase sensitivity of determining As(III) and As(V), while for determining As(III) and total As need a chemical reduction of As(V) before utilise voltammetry .

The most commonly technique has been used to determine As is flow-injection pre-treatment system coupled with inductively coupled plasma optical emission spectrometry (ICP-MS) because it is a simple, sensitive, accurate method especially for river water or environmental sample containing As(III) and As(V)

species. On the other hand, atomic fluorescence spectrometry (AFS) is the most efficient technique for determining arsenic due to high sensitivity, low detection limit to ng/g, high accuracy measurements and less matrix and spectral interferences. in order to have best technique to trace elements levels especially toxic elements , some aspects must to be advanced such as reducing chemical and physical interferences , high sensitivity , low LOD and LOQ , less time consuming , more accurate than conventional techniques and less cost equipment. Other methods as bio-components , ETAA , Instrumental neutron activation analysis (INAA) and AAS have been showing promising future for analysis techniques and each one of them has several advantages and they need to overcome their negative side to have the best techniques for determining elements easy, fast and accurate

## Acknowledgements

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