INTRODUCTION TECHNIQUES TO MICROWAVE PLASMA TORCHES (MPT) FOR THE DETERMINATION OF ARSENIC.
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ABSTRACT

Arsenic is a ubiquitous trace element, and its environmental chemistry is complicated as a result of the widely different properties of generally occurring arsenic compounds. The extensive use of arsenic compounds in insecticides, herbicides, food additives and as wood preservatives has been heavily reduced, but unfortunately the emission of arsenic from metal melting, glass manufacturing, sulphuric acid production, waste incineration and fossil fuel driven power stations is still considerable. Many arsenic compounds are known to be toxic, and, accordingly, the exposure of man and animals to arsenic remains of international concern. Arsenic contamination of drinking water supplies is a world problem, for arsenic it is generally accepted that arsenic (V) species are less toxic than arsenic (III) species. In view of this difference between the oxidation states, and in order to follow the pathways of the conversion of arsenic compounds within the compartments of the environment, it is increasingly important to determine the concentration of the individual chemical species as well as the total concentration of arsenic in the environment. There the concentration of arsenic in waters may range from ng/ml to µg/ml levels. The health-based standard, or primary maximum contamination level (MCL), for arsenic in drinking water as recently set by the U.S. Environmental Protection Agency (EPA) and by the World Health Organization (WHO) is as low as 0.01 µg/ml. accordingly, the development of reliable methods for the determination of arsenic in a simple and reproducible way is always challenging.

INTRODUCTION

Atomic spectrometry is one of the most popular and widely used instrumental methodologies in the laboratory today. Atomic absorption instruments, as well as plasma emission spectrometers, can be found in nearly all commercial, industrial, and private laboratories. In this study a newly developed analytical source, namely the microwave plasma torch has been used in atomic emission spectrometry for the determination of arsenic because of its advantages including low operating costs and also because of its simple and robust structure. The use of instrument with a tunable as well as a fixed torch construction and the different features of microwave induces plasmas are going to be studied in this work. (Prokisch et al, 1999)
From the properties of the chemical compounds, it is known that a number of elements easily can be converted into their stable, gaseous hydrides when they are brought together with a strong reducing agent. These hydrides can then be thermally reduced to the free metal. This is the base of the classic Marsh test for arsenic, where the hydride is formed through reduction with hydrogen developed when highly reactive metals are brought into strong acid solutions. As chemical analyses advanced and more reagents became available to the analytical laboratory, strongly reducing (and safe) reagents became available through which both the reproducibility and the overall sensitivity of hydride generation could be improved. The most popular reducing agent used in the determination of arsenic is sodium tetrahydroborate (NaBH₄) reagent, which releases hydrogen when brought together with acids and allows arsine (AsH₃) generation. Many researchers describe a batch mode hydride generation system or a continuous hydride generation system where a solution of NaBH₄ is used and couple it to atomic emission spectrometry. In this study, a determination of As(V) and As(III) will be performed in a continuous flow hydride generation system coupled to microwave plasma torch atomic emission spectrometry. Therefore, a solution containing As(III) and As(V) was introduced into the arsine generator where only As(III) reacts to form arsine. For the determination of As(V) the solution is then reduced with a pre-reducing agent prior to the hydride generation step. After reduction with the NaBH₄ solution, the total As(III) and As(V) concentration can be determined, whereas from the difference the concentration of As(V) can be calculated. Alternately, electrochemical hydride generation can be used for the generation of arsenic hydride. Electrochemical processes are of increasing importance as they allow it
to avoid the use of freshly prepared reducing reagents. The general requirements of designing a cell for electrochemical hydride generation include the use of a simple modular design, a good efficiency of hydride generation, reliable operation with low maintenance, and easy scale-down. The optimization of cell design is a step-by-step procedure. Indeed, the construction and development of different electrochemical hydride generators coupled to microwave plasma torch atomic emission spectrometry for the determination of arsenic is necessary. (Engel et al, 1998)

For a number of applications the power of detection of the hydride generation techniques developed certainly will not be efficient. It is known that for this purpose preconcentration procedures easily can be worked out. For this aim, the optimized miniaturized electrochemical hydride generation set-up was combined to hot trapping in a palladium coated graphite furnace prior to releasing the analyzed in microwave plasma torch atomic emission spectrometry.

In this work it will be studied how the amount of palladium solution and the temperature of the trapping influence the emission signal of arsenic. With the analytical procedures developed it will be shown that in real samples arsenic reliably can be determined. In this respect analytical results for spring waters from Hungary and river sediment samples from Germany will be reported. In real samples the arsenic concentrations may be very low it was necessary to optimize the methods used so as to reach the lowest limit of detection possible. Further a good performance in terms of long-range signal stability for arsenic was required in order to make possible to implement the miniaturized electrochemical hydride generation microwave plasma torch atomic emission spectrometry, combined with in-situ trapping, as a routine technique.
This work represents an experimental study of the coupling of different sample introduction techniques to microwave plasma torches (MPT) operated with argon and helium for the determination of arsenic.

**Literature Reference Information About Arsenic in Environmental**

Arsenic occurs in all soils and in water throughout the world, as well as in food, particularly in sea food. Further it is found in ores and together with many minerals. In nature one finds inorganic and organic arsenic compounds like realger (As$_2$S$_2$), orpiment (As$_2$S$_3$), arsenolite (As$_2$O$_3$), mispickel (FeS$_2$ + FeAs$_2$) and arsenopyrites (FeAs$_2$) but no arsine (AsH$_3$). Arsenic itself often is prepared as a by product in the production of copper, lead, zinc, tin and gold from ores. During the melting operation, it is obtained as arsenic trioxide As$_2$O$_3$, which is the industrial and commercial form of arsenic and is used to manufacture most of the other arsenic compound. The naturally occurring arsenic trioxide is arsenolite. (Leonard, 1990)

1. **Physical and Chemical Properties**

Arsenic (atomic number 33, atomic mass 74.9216) is an element in the main group VA of the periodic table, where it is located between phosphorous and antimony. The mass numbers of its isotopes range from 68 to 80, but only the natural isotope 75 is stable. Arsenic may be found as a metal, which is widely distributed in the earth’s crust, namely as gray arsenic. As a nonmetal it occurs as yellow arsenic. Both forms of elemental arsenic exit at room temperature. Gray arsenic normally is the stable form and it can be produced by reduction of As$_2$O$_3$ with carbon. Its density is 5.73 g/cm$^3$, its melting point at 36.5 bar pressure is 814°C, its specific heat at 28°C is 0.0772, and its vapor pressure at 604°C is 1 bar. It normally sublimes. Metallic arsenic is not soluble in common solvents.
Yellow arsenic has a density of 2.03 g/cm$^3$ at 18°C and is unstable. The nonmetallic form of arsenic can be produced by a sudden cooling of arsenic vapor, and it consists of tetra atomic molecules, As$_4$. In its yellow form arsenic is more volatile than in the gray form. Arsenic and its compounds occur in crystalline, amorphous or vitreous forms and usually can be found in trace quantities in all kinds of rocks, soils, waters and even in air (Leonard, 1990).

Elemental arsenic is not soluble in water. The salts of arsenic widely differ with respect to their solubilities in water, which depend on the pH and the ionic environment. In its compounds arsenic can have four valence states, namely $-3$, 0, $+3$ and $+5$. In its $-3$ state arsenic can be present as poisonous compound arsenic trihydride (arsine, AsH$_3$). It is a colorless, extremely poisonous, neutral gas with a characteristic and disagreeable garlic odor. Its melting and boiling points are -117°C and -55°C, respectively. This hydride is a powerful reducing agent, even for fairly weak oxidizing agents. Arsine is used in the determination of arsenic with several methods in both atomic and molecular spectrometry (Bombach et al., 1999). Under moderately reducing conditions, arsenic mainly occurs in the trivalent state, whereas in oxygenated environments As(V) thermodynamically is more favored. Because of its ability to form complexes with certain co-enzymes, As(III) is more toxic to animals and plants than As(V). Therefore, the speciation of arsenic is important for understanding both the biological and the geochemical behavior of this element (Wrobel et al., 2002).

2. Sources and Occurrence of Arsenic in the Environment

The most common mineral of arsenic is arsenopyrite. The natural occurring arsenic accounts for about one-third of the atmospheric flow of
arsenic. It has been estimated that the atmospheric flow of arsenic amounts to about 73,540 tonnes/year of which 60% is of natural origin and the rest items from anthropogenic sources. Volcanic action is a further most important natural source of arsenic, and on a local scale it even may be the dominant atmospheric source (Bombach et al, 1994).

Inorganic arsenic of geological origin is found in groundwater, which often are used as drinking water in several parts of the world, for example in Bangladesh. Organic arsenic compounds such as arsenocholine, tetramethylarsonium salts, arnosugars and arsenic-containing lipids are mainly found in marine organisms. Elemental arsenic can be produced by a reduction of arsenic trioxide (As$_2$O$_3$) with charcoal. As$_2$O$_3$ is produced as a byproduct in metal melting processes. Mining, melting of non-ferrous metals and burning of fossil fuels are the major industrial processes that contribute to anthropogenic arsenic emissions in air, water and soil. Historically, the use of arsenic-containing pesticides has caused a lot of contamination of agricultural land with arsenic. Further, the use of arsenic for the preservation of timber also has led to contamination of the environment. More than 200 minerals, of which about 60% are arsenate, 20% sulfides and sulfosalts and the remaining 20% include arsenides, arsenites, oxides and elemental arsenic. The most common arsenic mineral is arsenopyrite (FeAsS) and arsenic is found together with many types of mineral deposits especially with those that stem from sulfide mineralization.

The mean total arsenic concentrations in air from remote and rural areas range from 0.02 to 4 ng/m$^3$ where in urban areas it range from 3 to about 200 ng/m$^3$. Much higher concentrations (> 1000 ng/m$^3$), however, have been found in the vicinity of industrial sources, although in some areas his is decreasing
because of pollution abatement measures. Concentrations of arsenic in open ocean seawater are typically 1-2 µg/L. Arsenic is widely distributed in surface freshwaters, and concentrations in rivers and lakes are generally below 10 µg/L, although individual samples near anthropogenic sources may have arsenic concentrations up to 5 mg/L. Arsenic levels in groundwater at the average about 1-2 µg/L except in areas with volcanic rocks and sulfide mineral deposits, where arsenic concentration can be up to 3 mg/L. In sediments the mean arsenic concentrations range from 5 to 3000 mg/kg, and higher levels are found in areas with contamination. Background concentrations in soil range from 1 to 40 mg/kg, while mean values often around 5 mg/kg. Elevated levels of natural arsenic in soils may be due to associations with geological substrates such as sulfide ores. In anthropogenically contaminated soils concentrations of arsenic may be up to several grams per 100 mL. Marine organisms normally contain arsenic between < 1 to more than 100 mg/kg. This is predominantly present as organic arsenic species such as arsenosugars (macroalgae) and arsenobetaine (in invertebrates and fish).

The concentration of arsenic in various types of igneous rocks range from < 1 to 15 mg As/kg, and the value is about 2 mg As/kg. Similar concentrations (< 1-20 mg As/kg) are found in sandstone and limestone. Significantly higher concentrations of up to 900 mg As/kg are found in argillaceous sedimentary rocks including shales, mudstone and slates. Up to 200 mg As/kg can be present in phosphate rocks. Concentrations of arsenic in open ocean water are typically 1-2 µg/L. The concentrations of arsenic in unpolluted surface water and groundwater are typically in the range of 1-10 µg/L. Elevated concentrations in surface water and groundwater of up to 100-5000 µg/L can be found in areas of
sulfide mineralization. Indeed, in nature arsenic containing minerals undergo oxidation and release arsenic to water. This could be one explanation for the occurrence of arsenic in the groundwater of West Bengal and Bangladesh, where the groundwater usage is very high. Marine organisms accumulate considerable quantities of organic arsenic compounds. In marine animals the larger part of this arsenic is present as arsenobetaine (AsB), whereas marine algae contain most of the arsenic in the form of dimethylarsinoylribosides. Humans are therefore exposed to these arsenic compounds through all diets that include seafood.

3. Human Exposure

Although arsenic is not an essential element of human metabolism, because of its wide distribution in nature, it constantly is taken up into the human body in very small quantities through the ingestion of food and water. Food is generally the principal contributor to the daily intake of total arsenic. In some areas drinking water significantly contributes to the exposure to inorganic arsenic. Contaminated soils such as mine tailings also may contribute to arsenic exposure. The daily intake of total arsenic from food and beverages generally is between 20 and 300 µg/day. A number of data indicate that approximately 25% of the arsenic present in food is in the inorganic form, but this highly depends on the type of food. The concentration levels of inorganic arsenic compounds in fish and shellfish are low (< 1%). In foodstuffs such as meat, poultry, dairy products and cereals the levels of inorganic arsenic may be higher. As well as by ingestion, arsenic is also taken up by the human body by inhalation and through skin contact. About 4/5 of the amount of the arsenic ingested is stored and widely distributed in the tissues, including the liver, bone, skin and particularly the hair.
and nails. There it may be detected many months after it has disappeared from urine and feces. In workplaces with up-to-date occupational hygiene practices, the exposure with arsenic generally does not exceed 10 µg/m³ (8-h time-weighted average [TWA]). However, in some places workroom atmospheric arsenic concentrations as high as several milligrams per cubic meter have been reported. (www.inchem.org, 2002)

4. Effects on Human Health

Inorganic arsenic compounds generally are toxic and the ingestion of high doses may lead to gastrointestinal symptoms, disturbances of cardiovascular and nervous system functions, and eventually to death. Long-term exposure to arsenic in drinking water casually is related to increased risks for skin, lung, bladder and kidney cancer as well as for other skin changes such as hyperkeratosis and changes in pigmentation. These effects have been demonstrated in many studies, where exposure–response relationships have been observed. Occupational exposure to arsenic, primarily by inhalation, casually is associated with lung cancer (Wrobel et al, 2002)

Due to the chronic toxic effects of arsenic, the maximally permitted concentration limits in drinking water have been reduced. The earlier tolerated level of 50 µg/L arsenic in drinking water was set by EPA (Environmental Protection Agency) in 1975 and based on a Public Health Service value originally released in 1942. The WHO (World Health Organization) guideline value for arsenic in drinking water was provisionally reduced in 1993 from 50 µg/L to 10 µg/L. In March 1999, the National Academy of Sciences (NAS) completed a review of scientific data with respect to arsenic and recommended EPA to decrease the maximally permitted value for arsenic as soon as possible. The US-
EPA value was reduced from 50 µg/L to 10 µg/L in January 2001 following a long debate.

Method for Arsenic Analyze

Construction and Optimization of the Microwave Plasma Torch for Atomic Emission Spectrometer (MPT-AES) as a more recently developed microwave plasma source for atomic emission spectrometry will be used within the frame of this focus of this doctoral thesis. It was initially developed at Jilin University by Jin et al. and introduced in 1985 at the Pittsburgh Conference in New Orleans. It later was improved at Indiana University and has received substantial attention, mainly as a source for atomic emission spectrometry. More recently, Bilgic et al. introduced a modified microwave plasma torch with a mechanically simple and stable design. The MPT consists of three concentric metal tubes similar in arrangement...
to the quartz tubes of a conventional ICP torch. Through the central tube the sample (aerosol or vapor) is entered into the plasma, whereas through the intermediate tube a plasma support gas flows. The other tube usually carries no working gas flow but often is employed for creating a gas sheath to reduce air entrance into the MPT plasma. The presence of the central tube makes the MPT usually more tolerant to the introduction of molecular species, including water vapor and droplets as compared to the microwave induced plasmas sustained in a TM$_{010}$ cavity, or in the surfatron. The flame like plasma is located between, however, not anchored to the central tube and the intermediate tube. The microwave structure is designed as a simple wave guide and the intermediate as well as the outer tubes of the MPT are necessarily made of a conductive material (copper and brass). However, the central tube can be either made of a metal or of a non-conducting material (quartz), by which its performance can be improved (Pack and Hieftje, 1997) The contamination from samples can namely be substantially reduced by using a quartz tube.

A very important characteristic of the MPT when used in atomic spectrometry for elemental analysis lies in the hollow structure of the plasma. The plasma density has a minimum along the central axis of rotational symmetry by which an analyte introduced along this channel causes only very few perturbation to the plasma. The MPT is generally operated at a frequency of 2.45 GHz and at powers between 50 and 200 W. It can be operated with both argon and helium discharges of a flow rate of 50 to 5000 mL/min. The produced plasma has a length of ca 3-5 cm. MPTs are more tolerant against water-loaded aerosols and other molecular species. The most important advantages of the MPT are its robustness and the high excitation efficiency.
The high robustness and the high excitation efficiency of the MPTs can be explained through the results of diagnostic studies performed by Prokisch et al., as well as by Engel et al. Prokisch et al determined the electron number densities and the electron temperatures by Thomson scattering. Under normal operating conditions (an internal gas flow of 500 mL/min, an outer gas flow of 200 mL/min and a power level of 100 W), they range from $0.5 \times 10^{20}$ to $10^{21}$ m$^{-3}$ and from 16000 to 18000 K, respectively. The rotational temperatures in the argon MPT were determined with spatial resolution by Engel et al. They found a rotational temperature for MPT of about 300 K and this is between the rotational temperature of the MIP in a TM$_{010}$ resonator (2000 K) and the one in a CMP (3400-4200 K), which explains the high stability of the MPT, when entering variable amounts of molecular species. MPTs have found many applications in a large number of analytical tasks. The plasma in the MPT has been examined in detail by several researchers. The analytical performance of the MPT for the determination of the rare-earth elements, noble metals or mercury with atomic emission spectrometry has been described. The MPT also was successfully used for the determination of tetraethyllead and for the determination of silicon in aluminum and steel samples. The analytical performance of MPT-AES is strongly influenced by the sample introduction system. In many cases pneumatic nebulization was used. It has the advantages to be simple, to allow high sample throughput, to have a good stability and to be of low costs. However, the nebulization efficiency is poor. For sample introduction in MPT-AES also ultrasonic nebulization can be used, though it suffers from disadvantages like high costs and complexity in design. A thermospray nebulizer has been shown to be a promising sample introduction technique for MPT-AES. In addition, the
MPT has been coupled with electrothermal vaporization (ETV) for sample introduction or used for element specific detection in connection with GC, SFC or LC. In the work of Prokisch and Broekaert, it has been shown that an argon MPT can be used as a source for atomic spectrochemical analysis, when solvent loaded aerosols generated by pneumatic nebulization of both aqueous and acetonitrile containing solutions are introduced into the plasma. As an alternative to argon, also helium can be used as working gas. Apart from these sample introduction techniques, it is also possible to use the MPT in combination with hydride generation techniques. Pereiro et al. described the use of continuous hydride generation coupled directly to the He-MPT for the determination of arsenic, antimony and tin. When a plasma power of 200 W was used detection limits (3σ) of 3.2, 5.9 and 2.5 ng/mL were obtained for arsenic, antimony and tin, respectively. The MPT showed to be more tolerant against water-loaded aerosols and other molecular species. However, as with larger amounts of water vapor, excitation and ionization efficiencies in the source decrease, it remains advisable to apply desolvation unit when analyzing aqueous samples by MPT-AES. A PTFE membrane cell separator could be used successfully when

**RESULTS AND DISCUSSION**

The determination of arsenic simple and economic methods have been developed on the base of helium and argon MPTs in conjunction with different sample introduction techniques. Although the concentration of arsenic in spring water and sediment samples can be determined with plenty of instrumental methods, namely FAAS, HGAAS, GFAAS, ICP-AES, ICP-MS and XRF, in this study MPT-AES has been selected. One of the reasons for this decision is that MPT-AES can easily be applied in routine analysis. A few purely instrumental
methods those use such as neutron activation analysis, X-ray fluorescence, differential pulse polarography, etc. might indeed be much more difficult for routine purposes. In addition, the MPT offers a number of advantages are Compact design of the source, use of low power (50-200 W) as compared to other plasma sources, use of low gas flow rates (< 2 L/min), ability to sustain the plasma with a variety of gases at atmospheric pressure, a still fair tolerance to aerosols loaded with water or with other molecular species, high electron and gas temperatures, high robustness and high excitation efficiency and easy tuning to a low reflected power.

These attributes make the MPT more affordable than other excitation and ionization sources both to purchase and to operate. Also, the low gas flow rates are as often employed in gas chromatography where helium is a common carrier gas. Accordingly, the MPT is quite compatible and easy to couple with gas chromatography.

The better tolerance of the MPT to sample introduction as compared to other microwave induced plasmas is related its central channel, which keeps the interaction between sample and plasma low. Further, the separate introduction of carrier and working gas into the plasma also increases the plasma stability.

Compared to the ICP, the MPT has several considerable advantages including the low gas flows and the low power required. The lower power required sustaining the microwave plasma (< 200 W for the MPT comparing to > 1000 W in the case of the ICP) makes it very attractive. Since the power of the MPT is low, its cooling need is also low. Further, the gas consumption in the MPT (less than 2 L/min) is significantly lower than that in ICP (at least 15 L/min). In addition it becomes feasible to use other gases which are typically too
costly to use with an ICP, such as helium. Another advantage of the MPT as compared to the ICP is the ability to sustain the plasma with a variety of working gases such as helium, argon, neon, nitrogen and even with air.

The sample introduction system also makes an important contribution. The results show that the MPT is a promising radiation source for atomic emission spectrometry. The high tolerance to sample material and the excellent plasma working stability make the MPT especially attractive for real sample analysis in routine. This work was carried out only for arsenic, which is highly toxic and often needs to be determined at low concentration levels in environmental samples of the MPT as stated above, a few drawbacks exist. The power of detection obtainable with the MPT is typically lower than the one for the ICP. It is probably due to the smaller and less robust plasma as compared to the ICP. Accordingly, the interelement interferences are also more severe than those in the case of the ICP. However, the use of helium gas in MPTs has a benefit as the excitation efficiencies especially in the case of elements with high excitation potentials can be increased due to the high ionization energy of helium. The MPT is a relatively new analytical source and up to now it has not been so commonly used. This could be shown by searching references on MPT and ICP in the online version of the Science Citation Index (SciSearch). It provides access to bibliographic information, authors, abstracts and cited references found in 3700 of the world's leading science and technology journals. According to SciSearch, the trends for publications on the MPT are shown in. The total number of publications related with the MPT between 1969 and 2002 was found to amount to 143.
CONCLUSIONS

This work shows that the use of miniaturized EcHG-He-MPT-AES coupled to a graphite furnace after a selection of the appropriate experimental conditions resulted in simple, rapid, reproducible, cost-effective and environmentally friendly procedures for the determination of arsenic in environmental water and sediment samples. It can be concluded that a lot of factors have an influence on the detection limit attainable with microwave plasma systems, such as the applied microwave power, the axial position of the antenna (L₁), the depth of the cavity (L₂), the observation height in the plasma, the working and carrier gas type and flows. This work can be extended to other volatile hydride forming elements such as selenium, bismuth, tin, antimony, etc. which also certainly is challenging and interesting. Obviously, the working conditions should be optimized for the analyte of interest. Finally, it will be very interesting to couple the developed miniaturized EcHG cells to miniaturized radiation sources such as the microstrip plasma (MSP), so it can be used for the determination of volatile hydride forming elements.

LITERATURE


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