

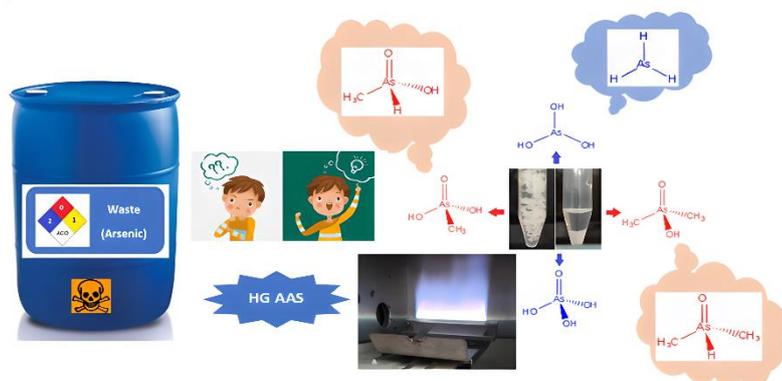
Full Paper | <http://dx.doi.org/10.17807/orbital.v16i2.19940>

Exploring the Selective Generation of Arsenic Hydrides in Quaternary Ammonium Salt Suspension: A Didactic and Systematic Qualitative Approach Applied to Wastewater Treatment

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The treatment of laboratory waste containing arsenic compounds should be part of the chemical analysis protocol in educational and research institutions. An alternative procedure for the treatment of these residues is proposed for the development of a didactic analytical route in the detection of As^{3+} , As^{5+} , MMA (monomethylarsonic acid) and DMA (dimethylarsinic acid). The treatment is based on the coprecipitation of inorganic arsenic species with a quaternary ammonium salt (tetra-*n*-butylammonium perchlorate) in suspension. Detection occurred by controlling the hydride generation reactions and Atomic Absorption Spectrometry. The methylated species MMA and DMA remain in the supernatant and can be monitored by adjusting the pH, concentration of the borohydride reducer, and the use of auxiliary reducers (hydroxylamine hydrochloride and KI). Satisfactory selective detectability was obtained for each arsenic species present in the waste sample. This work contributes to the development of experiments to be implemented in Qualitative Analytical Chemistry and Instrumental Analysis classes. The results allow to approach the chemical vapor generation, which is generally not well explored in undergraduate classes. Discussion of this procedure is supported by a teaching proposal based on the theory of nascent hydrogen for inorganic arsenic species and the nucleophilic performance of the hydride ion for methylated species. This approach allows the student to contextualize important concepts such as Lewis structure, oxidation state and kinetics of arsenic hydride generation reactions. This interdisciplinary contextualization forms a common theoretical basis, preparing and enabling the student to research speciation analysis by hydride generation and to understand the most accepted theories.

Graphical abstract



Keywords

Analytical Chemistry Learning
Arsenic speciation
Atomic Spectrometry
Reuse of waste
Vapor chemical generation

Article history

Received 29 Dec 2023
Revised 9 Mar 2024
Accepted 12 Marc 2024
Available online 26 Jun 2024

Handling Editor: Marcelo F. Oliveira

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1. Introduction

Important research centers in Universities around the world have been dedicated to exhaustive studies of chemical speciation analysis. This topic is particularly useful for monitoring the ways in which an analyte manifests itself in environmental, clinical, and food samples. Due to the problem of contamination, ease of absorption in the body and serious effects on health, arsenic compounds are highlighted in speciation studies.

Despite being a known dangerous element, the toxicological properties of arsenic vary due to its different inorganic and organic forms. These properties are strongly dependent on physicochemical parameters, such as: pH, redox potential, relative mobility, among others [1]. In detriment to what is only standardized for total arsenic content, these studies are essential to contribute to the establishment of tolerated values for different arsenic species, which are not yet formalized in all regulations.

New procedures of arsenic speciation have been increasingly required to meet this need, especially with regard to the inorganic species As^{3+} and As^{5+} . These arsenic species are about a hundred times more toxic than organic forms. The lack of information related to the distribution of these species is still a limiting factor for the quality control of different classes of samples [2].

The waste generated during the development of such procedures is also the institution's responsibility. Valuing the safety of the professionals involved is also part of the research, as well as the preservation of the environment affected by inadequate management in the treatment of these wastes. That is why it is essential that the concept of Clean Chemistry is widely disseminated in society.

The awareness of sustainability must be consolidated in chemistry professionals, from the beginning of their academic training. The success of this awareness is possible as long as pedagogical practices are combined with learning resources that generate positive reinforcement. When associated with the syllabus of the subjects involved, a more efficient contextualization by the student is promoted, in order to enable them to make safe and assertive decisions.

In accordance with this premise, a question can be proposed for discussion with students from institutions that have researches aimed at analyzing arsenic speciation: Develop a protocol for reusing the waste generated, while it could also be treated, in an experimental class. The evaluation will consist of solving the following question: How to provide an analytical detection route way for each arsenic species present in a simulated sample (waste), having only a single measurement instrument? An interesting possibility comes from the ability to combine a previous partial separation procedure, during the waste treatment step, with a sufficiently fast and selective detection technique such as Atomic Spectrometry.

Several technologies have been investigated for the treatment of residues containing arsenic, aiming for application on an industrial scale and in research. Conventional techniques are based on physicochemical processes such as coprecipitation [3,4], (electro)coagulation [5-7], (bio)adsorption [8-10], reverse osmosis [11,12], ion exchange [13,14], among others.

Arsenic co-precipitation in Fe^{3+} compounds has been widely used in waste treatment, contaminated effluents, and for arsenic removal purposes in natural waters [15,16]. The

procedure generally involves an oxidation step, as the process is more efficient for As^{5+} , followed by pH adjustment and the addition of Fe^{3+} salts (chloride, sulfate) or ferric oxides as a precipitating agent. However, this procedure requires a long period of time (usually hours), and co-precipitation has low selectivity for different arsenic species. The presence of sulfate compromises arsenic removal when using ferric chloride, and is susceptible to interference from concomitant metals. In addition, this procedure usually generates residual sludge, which requires an additional step of further treatment.

Recently, the coprecipitation of inorganic arsenic through the use of suspended quaternary ammonium salts has been investigated. The in-situ formation of solid microparticles of tetra-n-butylammonium perchlorate (TBAP) has been successfully employed in a selective extraction method to monitor inorganic arsenic in rice samples. For the determination, Atomic Absorption Spectrometry with Hydride Generation was used, in a flow injection analysis system (FI-HG AAS) [17]. The sediment is easily leached in an acidic medium allowing the analyte to be recovered for use in the detection step.

The coprecipitation of As^{3+} in TBAP suspension is a more efficient alternative to coprecipitation with Fe^{III} . The extraction takes place through different interactions with the arsenic species available in the medium: As^{3+} is selectively extracted as a complex with ammonium pyrrolidinedithiocarbamate (As^{3+} -PDC), through hydrophobic interactions with the butyl chains available in the solid phase. The pentavalent inorganic species As^{5+} , together with methylated organic arsenic species (monomethylarsenic acid: MMA and dimethylarsinic acid: DMA) are not significantly extracted, and remain in solution [17]. This procedure has the advantage of providing a specific interaction with As^{3+} . Non-specific interactions with pentavalent species occur through the formation of ionic pairs between the quaternary ammonium salt (TBA^+) with anions of As^{5+} , MMA and DMA. This mechanism can be advantageous in the development of procedures similar to phase-transfer catalysis, of which quaternary ammonium salts are commonly used as catalysts [18].

Regarding the detection step, methods involving chromatography coupled with mass spectrometry, such as HPLC-ICP-MS, represent the state of the art in speciation analysis with high sensitivity [19,20]. However, instrumentation is quite expensive and is not available in most laboratories, especially those dedicated to teaching practices. The interest in promoting non-chromatographic procedures for arsenic speciation comes to meet the lack of feasible didactic experiments to explore this theme in an undergraduate or graduate class.

The dissemination of non-chromatographic arsenic speciation methods, with an emphasis on atomic detectors, has been gaining more and more space in the literature: López-García and collaborators developed a method capable of discriminating inorganic arsenic, MMA, DMA and arsenobetaine in baby foods by Electrothermal Atomic Absorption Spectrometry in a Graphite Furnace [21]. The method was based on the use of different chemical modifiers combined in order to obtain discriminatory signals between the species of interest. However, the procedure is hampered by the need to permanently modify several graphite tubes for application to a single sample, which also increases acquisition costs.

The technique of controlled generation of arsenic hydrides in absorption (HG AAS) or fluorescence (HG AFS) modes becomes a more attractive alternative, due to its consolidated efficiency, lower cost and greater simplicity. It is also noteworthy that it is cleaner and more accessible to undergraduate students than sophisticated chromatographic techniques [22-25].

This work aims to propose an analytical approach to monitor the differentiated detection of arsenic species (As^{3+} , As^{5+} , MMA and DMA) from laboratory waste, using only the HG AAS technique. First, the sample is subjected to a partial separation by co-precipitation of As^{3+} -PDC in suspension of TBAP formed in-situ, followed by an experimental route for selective generation of hydrides from the remaining species in solution. This is the first time that TBAP is used for the purpose of pre-treatment of waste.

It is also proposed to provoke discussions in the classroom, to systematically address the pathways of hydride generation mechanisms with the evolution of nascent hydrogen, including a brief critical review of the literature. Thus, it is intended that this work be considered as support material in Instrumental Analysis classes, with regard to the teaching of Atomic Spectrometry

2. Material and Methods

The waste samples were collected from the Laboratory of the Instrumentation and Analytical Separations Group, located at the Institute of Chemistry of the Federal University of Uberlândia. The residue samples consist only of aqueous solutions of arsenic compounds that were discarded from previous experiments with no apparent turbidity and no considerable organic matter content. The samples were used without any prior treatment. Studies involving arsenic speciation analysis have been continuously developed by the group, and applied to samples of environmental interest (natural waters, sediments and fertilizers) and to foods such as rice [26-29].

Graduate students engaged in arsenic speciation studies were instructed to store the residues of their experiments in a separate bottle for further treatment. According to the proposed objective, this treatment consisted of selectively co-precipitating the As^{3+} species in a suspension of TBAP formed in-situ after complexing with APDC in an acidic medium (pH 1.0). The complete procedure of previous separation of the As^{3+} species was carried out as described in the work previously developed by the authors [17]. This same procedure now serves as a guide for the elaboration of a script for an experiment of systematic qualitative analysis of the arsenic species present in these waste samples (As^{3+} , As^{5+} , MMA and DMA).

The purpose of this guide is to be applied in practical classes taught in Analytical Chemistry disciplines, at undergraduate and graduate levels. The use of the residue as an alternative sample, saves the expense of primary arsenic standards, avoiding cross contaminations, besides being useful as a possibility of alternative treatment of residues to be implemented in the laboratory.

For this purpose, a 1.0 mL aliquot of the already acidified residue sample, with total arsenic content in the order of mg L^{-1} , was diluted to 10 mL. The resulting solution was subjected to co-precipitation treatment with addition of the chelating agent APDC 0.038% m/v for formation of the As^{3+} -PDC complex, and subsequent formation of TBAP. Solid microparticles were formed with 0.015 mol L^{-1} tetra-n-butylammonium bromide (TBAB), followed by addition of ClO_4^- 0.075 mol L^{-1} . The complex is instantly adsorbed on the TBAP microparticles suspended in the sample, being separated from the supernatant after sedimentation of the solid phase, through centrifugation at 4000 rpm for 20 min. For the detection of previously separated As^{3+} , the sediment was leached with 1.0 mL of concentrated HCl (12 mol L^{-1}) and introduced into the HG AAS equipment through an injection analysis system in flow through merging zones, as shown in Figure 1. All experiments were performed in triplicate.

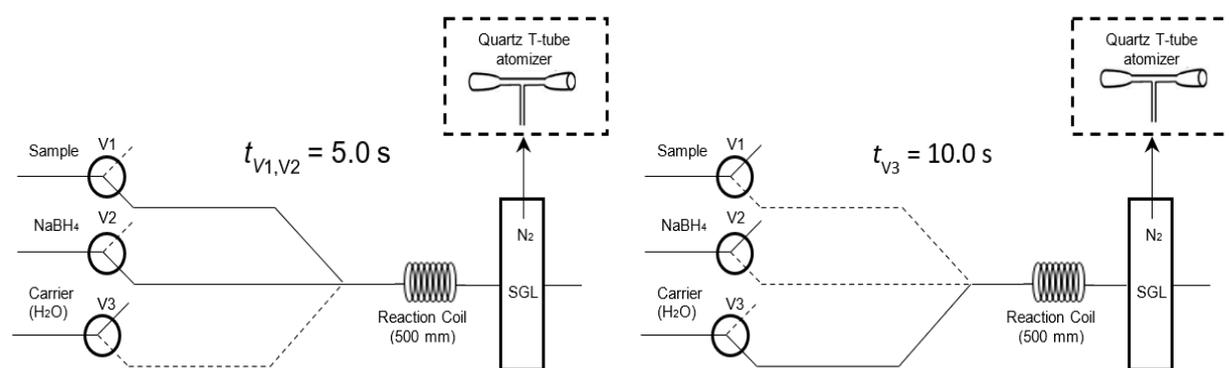


Fig. 1. Diagram representing the HG AAS system operating in the merging zones flow injection, where t is the activation time of valves V_1 , V_2 and V_3 and SGL is the gas-liquid separator. The solid line represents on-flow, the dashed line represents off-flow.

The propulsion of the reagents and sample solutions was performed with a peristaltic pump with variable flow rate. The volume injected into the reaction coil was controlled by the opening of the solenoid valves, through the activation time for the injection of the sample simultaneously with the NaBH_4 reducer, followed by the injection of the carrier solution. The volatile portion containing the generated arsenic hydride (AsH_3) was transported to the equipment by means of a gas-

liquid sweeping separator, using nitrogen as carrier gas (100 mL min^{-1}). Signals were recorded as absorbance, coming from the atomization of arsenic hydride in the quartz cell, placed on a burner of an Atomic Absorption Spectrometer (Varian® Spectra AA-220) operating with an air-acetylene flame. Hollow cathode lamp was used as a radiation source, emitting a resonance line at 193.7 nm.

To avoid turbulence, it is important to ensure that the sample solution does not contain residual solid sediment dispersed at the time of introduction into the flow system. After pre-treatment of the residue sample, it was observed that a small portion of concentrated HCl (up to 1.0 mL) was needed to dissolve the amount of sedimented solid phase. In case of persistent turbidity, the sample may be submitted for a few minutes in an ultrasound bath to enhance the leaching action and achieve complete solubilization, or with syringe filtration using a 0.45 μm cellulose acetate membrane.

As this is a destructive technique, and due to the small volume of sample introduced into the HG AAS system, practically all the arsenic content present is purged by the exhaust system, together with other volatile products from the reaction with NaBH_4 . In this way, the secondary residues will consist predominantly of dilute acidic solution, in the order of microliters for each determination. Other flow injection systems have also been explored for didactic purposes and become particularly useful also for the low consumption of sample and reagents [30].

The species remaining in the supernatant (As^{5+} , MMA and DMA) were tested under conditions of differentiated detectability against HG AAS, using pre-reduction with hydroxylamine hydrochloride, potassium iodide, and pH control with acetate buffer, as well as the concentration of the NaBH_4 reducer. Different analytical signals were obtained for each species in relation to each arsenic hydride generation condition.

Analytical curves for the arsenic species in its detection condition were constructed and evaluated using some merit figures. The limits of detection (LOD) and quantification (LOQ) were calculated, respectively, as three and ten times the standard deviation of the analytic measurement of ten blanks samples divided by the slope of the analytical curve (sensitivity). Precision was determined using the coefficient of variation (CV) from 10 measurements of As^{3+} 10 $\mu\text{g L}^{-1}$ solution.

3. Results and Discussion

3.1. Optimization of the HG AAS system for As^{3+} in the sedimented phase

The As^{3+} extracted on the TBAP microparticles was resuspended by adding 1.0 mL of concentrated HCl or diluted HCl solution (0.5–4.0 mol L^{-1}) and introduced into the HG AAS flow system. The signal obtained was optimized by varying the concentration of the reducing solution NaBH_4 (0.10–0.50 % m/v) and the carrier solution (water or 0.5–4.0 mol L^{-1} HCl) in relation to the efficiency of generating the hydride arsenic (AsH_3).

The acid solution of the flow system carrier line was the same used to leach the sedimented solid phase, in order to maintain the same composition of the medium. When the water was tested as a carrier, concentrated HCl was used as an eluent. Figure 2 shows the absorbance signals obtained for each condition tested.

The effect of the acid solution concentration in the solid phase leaching, as well as in the carrier line, presented similar profiles in relation to the variation of the NaBH_4 concentration. However, it was observed that the quality of the analytical signal decreased when dilute acid solutions were used in the carrier line. It was also observed that better signals were obtained using concentrated HCl as an eluent and water in the carrier line. Probably, during the contact of the acidic sample

solution with the reducer, followed by the water carryover, there was the formation of a more defined interface in the merging zones. The difference in viscosity caused, avoided a greater dilution of the sample during the course of the flow system.

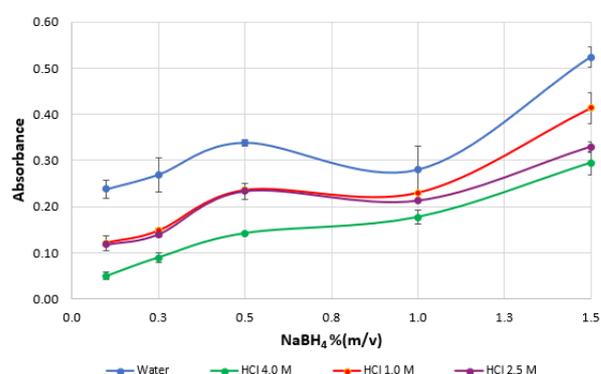


Fig. 2. Optimization of the concentration of the NaBH_4 reducer and the carrier solution in the generation of AsH_3 ($n=3$).

Regarding the variation in the concentration of the NaBH_4 reducer, an increase in signal up to 0.5% m/v was observed in all cases. When the 1.0% concentration was used, there was a decrease in the signal. At this concentration, the effect of acid hydrolysis of BH_4^- was predominant, with sufficient hydrogen gas evolution to cause AsH_3 dilution. As for the highest concentration of the reducer (1.5% m/v), it was observed the occurrence of small explosions inside the cell due to the ignition of excess H_2 generated, causing high background signals.

For the determination of As^{3+} , the concentration of 0.5% m/v of NaBH_4 was chosen for the reducer. The sample was aspirated in the HG AAS system in concentrated HCl medium, coming from the leaching of the sedimented solid phase, and using water in the carrier line. Further information about optimizing sample flow rates, reducer, drainage, injected volume and reaction coil length is detailed in the Supplementary Information.

3.2. Optimization of the HG AAS system for the remaining species in the supernatant

Since As^{3+} was previously separated and the best conditions for detection in the HG AAS system were determined, the As^{5+} , MMA and DMA species remaining in the supernatant were also able to generate their respective hydrides, from the establishment of conditions that allowed selective detection.

Most of the literature with scope in non-chromatographic speciation does not describes an analytical march that allows the individual identification of the species of interest. In monitoring arsenic by HG AAS, particularly involving pentavalent species, it is common to obtain signals from the combination of two or more species [31]. The determination of each analyte in this case is given indirectly as a function of information obtained from another species, either through the difference of the total content or through an adequate algebraic operation involving combinations of these species. However, the results obtained in this way may also express error propagations that do not reflect the true identity of the sample. The coprecipitation procedure for prior separation of As^{3+} allows each species of interest to be monitored from its

own analytical signal, under conditions that preserve detectability and avoid signal ambiguity.

Appreciable signals of As^{5+} can only be obtained under strongly acidic conditions and in sufficiently high concentration of BH_4^- to promote the quantitative pre-reduction of As^{5+} to As^{3+} , and the subsequent AsH_3 generation step. Direct detection of As^{5+} in the form of AsH_5 is not kinetically favored and is not trivial. In order to avoid drastic conditions for the system and the interference of the methylated species on the direct detection of As^{5+} , it was decided to co-precipitate it in the form of As^{3+} . For this, the supernatant was filtered and a 5.0 mL aliquot of 2.5% m/v of hydroxylamine hydrochloride was added to promote the pre-reduction of inorganic As^{5+} [17]. Once reduced to As^{3+} , the TBAP coprecipitation procedure was applied again.

To compare the efficiency of the process, Figure 3 illustrates the analytical curves obtained in the analysis of the supernatant, as well as those obtained for As^{3+} and for As^{5+} pre-reduced and separated by coprecipitation.

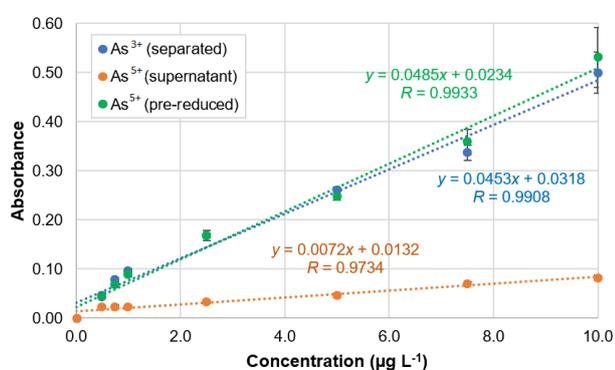


Fig. 3. Analytical curves obtained for inorganic arsenic species under the same conditions as the HG AAS system for detection of As^{3+} after coprecipitation with TBAP ($n=3$).

The determination of As^{5+} directly from the supernatant did not show satisfactory sensitivity. After pre-reduction to As^{3+} followed by the coprecipitation procedure with TBAP, the signals showed a sensitivity profile equivalent to that found for As^{3+} . This result demonstrates that the pre-reduction process with hydroxylamine hydrochloride was efficient for indirect detection of signals from As^{5+} . A classic alternative to confirm the presence of inorganic As^{5+} in the supernatant is to precipitate it in the form of sulfide generated in-situ, by adding thioacetamide under acidic hydrolysis.

Generally, L-cysteine is the most used reagent for pre-reduction of As^{5+} to As^{3+} so that it can be efficiently determined by HG AAS. However, in this case, the use of L-cysteine constitutes a potential interferent to also cause the reduction of the methylated species MMA and DMA, which are concomitantly present in the supernatant [32]. Furthermore, the thiol group (-SH) characteristic of the L-cysteine structure can complex As^{3+} under strongly acidic conditions. Excess of this reagent can compromise the sensitivity of the signal, in competition with the As^{5+} pre-reduction step. Due to these factors, the use of hydroxylamine hydrochloride is recommended for the effect of pre-reduction of As^{5+} under the conditions of the proposed procedure [33].

Works involving sequential arsenic extraction by method BCR (now the Standards, Measurements and Testing Program; SM&T), using hydroxylamine hydrochloride are reported [34,35]. The results indicate that the use of hydroxylamine hydrochloride does not affect the stability of

the methylated arsenic species. Samples consisting of reducing matrices can be solubilized with hydroxylamine hydrochloride without significant interference in the distribution of arsenic species.

After separating the inorganic arsenic species, the respective analytical curves for MMA and DMA have been represented in Figure 4, using 1.0 mol L⁻¹ HCl and 0.5% NaBH_4 m/v. This hydrochloric acid concentration was chosen as an intermediate acidity condition, which allows the generation of MMA and DMA hydrides in the form of $\text{CH}_3\text{AsO}(\text{OH})_2$ and $(\text{CH}_3)_2\text{AsO}(\text{OH})$ respectively. If the readings were carried out under the same conditions used to detect the inorganic species, no appreciable signals would be obtained for MMA and DMA since the conversion to the respective hydrides does not occur in concentrated HCl medium [32].

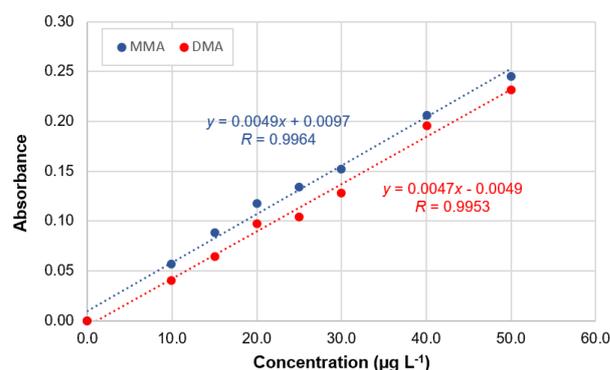


Fig. 4. Analytical curves obtained for methylated species MMA and DMA by HG AAS, after separation and detection of inorganic species As^{3+} and As^{5+} ($n=3$).

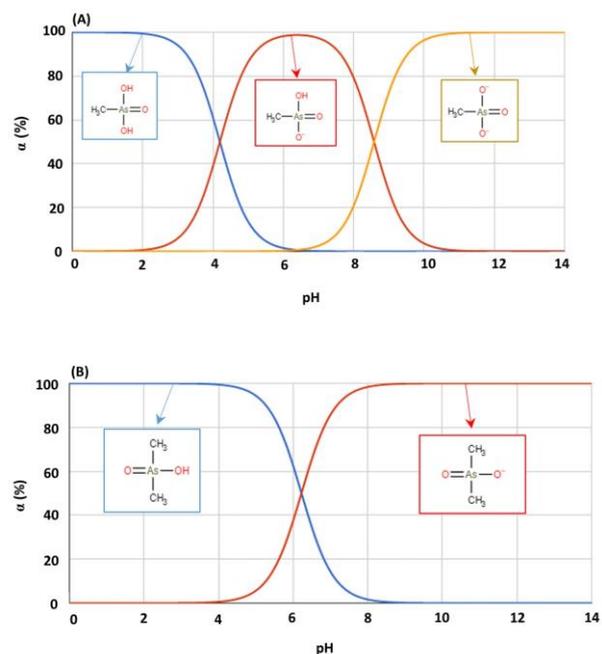


Fig. 5. Distribution graph of MMA (A) and DMA (B) species as a function of pH.

The results indicate that the use of 1.0 mol L⁻¹ HCl and NaBH_4 provides the generation of hydrides of the methylated species. However, despite the reasonable sensitivity, it is not possible to distinguish between MMA and DMA. The pH adjustment of the secondary supernatant (after separation of inorganic arsenic) becomes a fundamental step in achieving

selectivity between these species. The distribution curves relating to the degree of ionization (α) for MMA and DMA as a function of the pH of the medium are illustrated in Figures 5A and 5B respectively.

If the pH of the supernatant is adjusted so that one of the methylated species appears negatively charged, then its reaction with BH_4^- is inhibited, due to the repulsion of the negative charges. The graphs in Figure 5 indicate a promising condition for achieving selectivity in the generation of hydrides of the methylated species. It is verified that at pH 5.0, MMA manifests itself mostly, in a fraction of 86.4%, as a kind of charge -1, as a result of the first deprotonation. At this same pH, approximately 94% of DMA is found as a neutral species. To test this new condition, new analytical curves for the methylated species were constructed, replacing the 1.0 mol L^{-1} HCl solution with the 0.5 mol L^{-1} acetate buffer at pH 5.0. The results are shown in Figure 6.

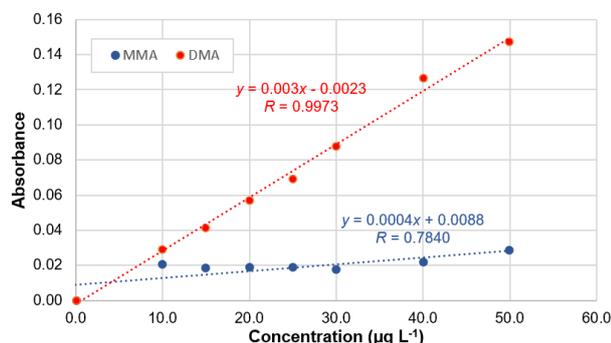


Fig. 6. Analytical curves obtained for methylated species MMA and DMA by HG AAS in acetate buffer pH 5.0 and NaBH_4 0.5% m/v ($n=3$).

The results demonstrate that the acidity of the supernatant adjusted with acetate buffer to pH 5.0 is able to promote a reasonably selective detection of DMA at concentrations close to $50.0 \mu\text{g L}^{-1}$. The calibration obtained with MMA did not show satisfactory sensitivity in this same condition. The highest registered MMA signal corresponds to only 19.2% of the highest DMA signal. In order to improve the magnitude of the DMA signal in relation to the MMA, the concentration of the reducer NaBH_4 was varied in the range of 0.1–1.5% m/v in two different aspiration flow rates of the sample solution (supernatant): 2.5 mL min^{-1} and 1.5 mL min^{-1} as show in Figure 7.

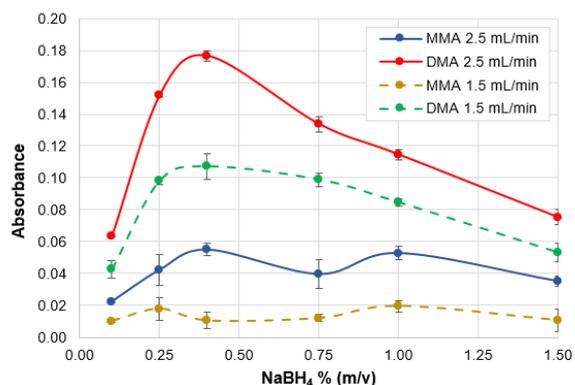


Fig. 7. Study of the variation of the concentration of the reducer NaBH_4 on the detection of MMA and DMA by HG AAS in a buffered medium at pH 5.0 ($n=3$).

By employing NaBH_4 at 0.4% m/v, analytical signal gain is obtained in the generation of the DMA hydride when the supernatant is aspirated at the same flow rate in relation to the previous experiments. However, there was also an increase in MMA interference, with approximately 31% of the DMA signal corresponding to the magnitude of this interference. Decreasing the sample flow is a possibility for significantly reducing this interference. By decreasing the sample flow rate to 1.5 mL min^{-1} , the signal contribution of the MMA becomes less than 10% in relation to the highest signal obtained for the DMA in this condition. Despite the loss in detectability of DMA, the concentration of 0.4% m/v NaBH_4 with the sample being aspirated at 1.5 mL min^{-1} is the most suitable condition. The analytical signal is registered without compromising the sensitivity, the interference from the MMA is now neglected.

In case the MMA and DMA are concomitantly present in the supernatant, the obtaining of the analytical signal coming only from the MMA, even in the presence of DMA, can be achieved starting from a condition similar to that obtained by Bundaleska and collaborators (2005) [36]. This condition allowed the detection of hydrides formed from As^{3+} , As^{5+} and MMA using 0.6% NaBH_4 and 1.0 mol L^{-1} HCl in the acid channel of the HG AAS system. For this purpose, samples of natural water acidified with 0.1 mol L^{-1} HCl were treated with 0.1 mol L^{-1} KI. This procedure was able to detect MMA separately from DMA. Signals from DMA were obtained when the acid channel in the system consisted of a 6.0 mol L^{-1} CH_3COOH solution, which is, therefore, a condition similar to what was observed in this work.

The flowchart in Figure 8 summarizes all the conditions for the selective detection of hydrides of each arsenic species tested, starting from the pre-treatment of the residue sample by coprecipitation with TBAP. Such conditions now allow conclusions about the composition of the sample in the possibilities of simultaneous occurrence of As^{3+} , As^{5+} , MMA and DMA.

For this proposed procedure some figures of merit were determined and presented in Table 1. Considering the As^{3+} and DMA species as more likely to be the target of study in speciation, the selective detection process presents analytical characteristics suitable for application in the monitoring of arsenic compounds in waste samples from experimental classes, being a useful and complementary alternative approach to conventional treatment.

Table 1. Figures of merit obtained for the selective detection procedure of As^{3+} and DMA.

	As^{3+}	DMA
LOD ($\mu\text{g L}^{-1}$)	0.15	0.46
LOQ ($\mu\text{g L}^{-1}$)	0.50	1.55
Linear range ($\mu\text{g L}^{-1}$)	LOQ – 10.0	LOQ – 50.0
R^2	0.9933	0.9973
CV (%) ($n=10$)	5.49	4.76

3.3. Review and Evaluation Proposal

The arsine (AsH_3) formation reaction starting from As^{3+} with the anion BH_4^- as a reductant is an example already consolidated in the literature. The example of this reaction is opportune to discuss the reactional behavior of arsenic species in the generation of their respective hydrides, described from the theory of nascent hydrogen. The reductant hydrolysis must necessarily occur in an acidic medium, so that

the H⁺ ions are reduced to nascent hydrogen [H], of radical character, highly reactive with the species of interest.

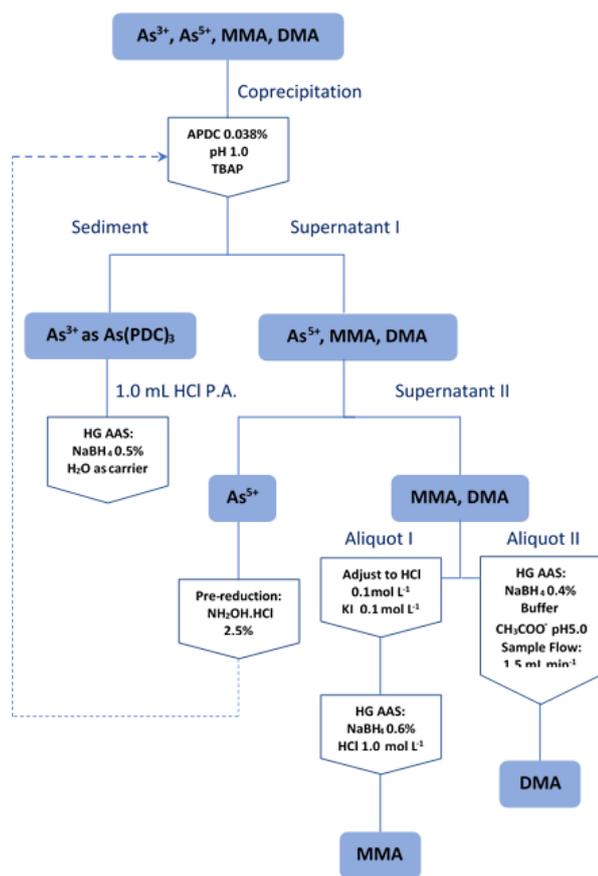
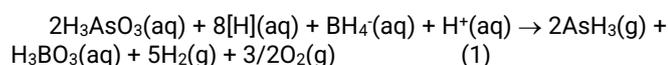


Fig. 8. Flowchart of the conditions of the HG AAS system for generation and selective detection of hydrides of arsenic species present in the waste sample.

During the explanation, the instructor should make it clear to the students that the idea of nascent hydrogen has been challenged through a series of thermodynamic studies. The most accepted proposal involves the direct transfer of the hydride through the formation of borane complexes [37-39]. However, the approach taken here is useful to enable students to develop for themselves a critical perception of the transition from a refuted theory to a more accepted current model.

At acidic pH, As³⁺ manifests as arsenious acid (H₃AsO₃), being an electrically neutral species, prone to readily react with BH₄⁻. The use of BH₄⁻ over other reducers, such as metallic zinc, is more convenient since the formation of nascent hydrogen presents a higher stoichiometric ratio (1:8). However, the excess of nascent hydrogen promotes the evolution of molecular hydrogen (H₂), which directly affects the sensitivity of the instrumental technique employed, in this case atomic absorption spectrometry. The global reaction of As³⁺ hydride (arsine) generation in aqueous medium is presented in equation (1):



With respect to As⁵⁺ species, the reaction with BH₄⁻ occurs through a preliminary step in order to reduce it to As³⁺. This pre-reduction only occurs in a medium that is sufficiently

acidic, so that the pH of the medium is lower than pK_{a1}=2.19. In this condition, the pentavalent inorganic species manifests as arsenic acid (H₃AsO₄). This electrically neutral compound is more reactive with BH₄⁻ and can be quantitatively reduced to H₃AsO₃ and thus promote hydride generation. At higher pH values, arsenic acid anions become the majority due to deprotonation equilibrium. The negative charge present in these species strongly inhibits the reaction with BH₄⁻ due to electrostatic repulsion [40].

The hydride generation reaction is not limited only to arsenic, it is also widely applied to elements such as Se, Sb, Sn, and less frequently to Pb, Te, Ge and Bi. The idea that justifies the favoring of the reaction for As³⁺, and the low efficiency of direct As⁵⁺ hydride generation, is in agreement with the fact that the hydride generation reaction kinetics of the elements Se, Sb and Te are also favored in the oxidation states lowest (Se²⁺, Sb³⁺ and Te²⁺). For the Sn and Pb elements, the reaction is more favorable when they are in their highest oxidation states (Sn⁴⁺ and Pb⁴⁺).

The Lewis structures of the respective oxyacids of these elements, under conditions where the reaction is favorable, reveals that the bonds involving the central atom are of the σ type. If this element has another oxidation state that stabilizes with π bonds, then the reaction is not kinetically favored.

According to this discussion, it is expected that students associate the presence of the As=O group, due to the higher oxidation state of arsenic, as an impediment site to the attack of the nascent hydrogen. The presence of multiple bonds indicates a higher activation energy required to reach the transition state, compared to the attack with nascent hydrogen. For elements where this trend is not observed, it is more reasonable to explain the mechanism through the direct hydride transfer model from BH₄⁻.

It is important to highlight here that these discussions contemplate a purely didactic approach, since in the absence of theoretical studies, the reaction mechanisms are not very well established in the literature, being even reported in order to promote misinterpretations by students. An example of this situation is the argument of the effect of acidity on the hydride generation kinetics of methylated species.

There are controversies to explain the compromised reaction of MMA and DMA in a strongly acidic medium: It is reported that the low efficiency of hydride generation of these species under these conditions is associated with the fact that they are protonated, and therefore not prone to volatile hydride formation [41]. Other references already clarify that this low efficiency is due to the reaction of the methylated species with concentrated acid causing an increase in the solubility of MMA and DMA hydrides (CH₃AsH₂ and (CH₃)₂AsH, respectively) in the liquid phase, compromising its volatility, and consequently the transport efficiency for the atomization system [32,42]. The degree of methylation of these species was also reported as a factor responsible for the sharper drop in the generation of DMA hydride compared to MMA hydride in strongly acidic condition [32]. These arguments reinforce the suitability of using a 1.0 mol L⁻¹ HCl solution to promote the occurrence of the generation of MMA and DMA hydrides, in detriment to the concentrated HCl used for the reaction involving the inorganic species.

It is important to emphasize that the generation of hydrides of the methylated species MMA and DMA can no longer be satisfactorily represented through direct attack with nascent hydrogen. It is not trivial to have studies dedicated to elucidating the kinetics of hydride generation reactions of organic arsenic compounds. To justify the occurrence of the

reaction for these species, the chemical vapor generation pathways are proposed as a teaching alternative based on an interdisciplinary approach, in the student's contact with Qualitative Analytical Chemistry and Instrumental Analysis disciplines.

To promote interdisciplinarity, the instructor can start the discussion by asking students to compare the electronegativity of arsenic with carbon (in relation to the knowledge that the student has about the main reaction mechanisms of organic compounds). If arsenic and carbon have similar electronegativity values, then it becomes reasonable to treat the As=O group present in MMA and DMA,

as vulnerable to nucleophilic attack by the hydride ion. It is a reduction mechanism, analogous to what is reported in textbooks for the reactions of carbonyl compounds.

After presenting the motivation, students can be evaluated through an activity in which it is proposed that the student outlines a reaction mechanism based on this theoretical foundation. Performing this activity will stimulate the ability to relate the acidity of the medium to the incidence of positively charged intermediates, as well as the mechanisms of catalysis or acid hydrolysis, which students should have already learned. Figure 9 brings a proposed mechanism, which can be used by the instructor.

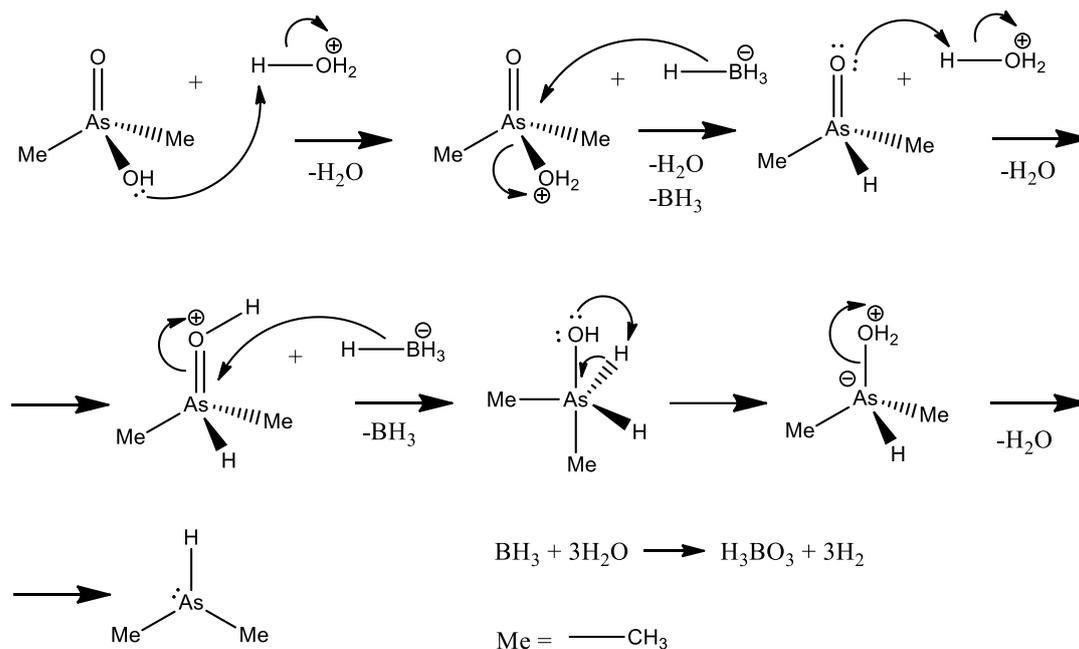


Fig. 9. Proposed mechanism for generating the DMA hydride as an evaluative activity for interdisciplinary contextualization. This proposal can be applied analogously to the MMA.

In summary, the idea of nascent hydrogen applied to the generation of hydrides from inorganic arsenic species, and the nucleophilic performance of the reducing anion BH_4^- to explain the reaction with methylated species, is more understandable in undergraduate teaching, which allows a better interdisciplinary contextualization: It is didactically useful for making associations between reaction kinetics and oxidation states based on Lewis structures of arsenic compounds.

The instructor may also be able to intuitively develop associations with reaction mechanisms that students may have already learned in other subjects. In this way, it will have created resources to consolidate the common theoretical basis and the student's training to assimilate more adequate proposals in the future

4. Conclusions

The selective coprecipitation of inorganic arsenic with TBAP proved to be an efficient alternative for the treatment of residues from research laboratories that work with arsenic speciation analysis. The procedure could also be used as a useful didactic tool for the development of an analytical that allows the differentiated identification of inorganic arsenic species (As^{3+} and As^{5+}), as well as their methylated compounds MMA and DMA. The success of the procedure is achieved through the selective generation of the respective

volatile hydrides and detection by atomic absorption spectrometry in a flow system, which can be easily implemented in undergraduate and graduate teaching laboratories.

The didactic approach of this procedure contributes to provoke the empiricism of the mechanisms of the steam generation reactions, which are not commonly explored in experimental classes. Students will be able to assimilate, in an interdisciplinary way, concepts of Lewis structures, oxidation states and reaction kinetics through a discussion based on the formation of nascent hydrogen and the nucleophilic performance of the reducing ion, during the occurrence of arsenic hydride generation reactions.

Although the mechanisms of these reactions are not well established in the literature, there is still a need for them to be discussed with an approach more focused on chemical education, and more easily understood with regard to the teaching of qualitative chemical analysis.

Supporting Information

Details of the instrumental apparatus and determination of the optimal conditions of the HG AAS flow system are presented in the Supplementary information annexed with this article.

Acknowledgments

The authors are grateful for the financial support received from the Brazilian governmental agencies Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, 241/2007), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, 305360/2018-3, 307058/2012-3) and Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG APQ-01459-13).

Author Contributions

Bruno Elias dos Santos Costa: Conceptualization, Methodology; Formal Analysis, Writing – Original Draft. Luciano Alves da Silva: Investigation, Formal Analysis; Data Curation, Software. Nívia Maria Melo Coelho: Funding Acquisition; Project Administration; Writing – Review & Editing.

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How to cite this article

Costa, B. E. S.; da Silva, L. A.; Coelho, N. M. M. *Orbital: Electron. J. Chem.* **2024**, 16, 88. DOI: <http://dx.doi.org/10.17807/orbital>