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A Study for the Evaluation of Quantitative Reaction Conditions Between As(V) and Ti(III) for the DP Polarographic Determination of Electroinactive As(V) and Application

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ABSTRACT
In this investigation a differential pulse polarographic method (DPP) is established to determine the electroinactive arsenic (V), which is formed after the wet digestion of the natural samples. For this purpose, As(V) formed is reduced into As(III) using Ti(III). According to the literature survey this redox reaction between As(V) and Ti(III) has been used first time in this work. In order to have the reaction quantitative the optimum reaction conditions such as Ti(III)/ As(V) concentration ratio, reaction pH, waiting time for reaction and temperature had to be investigated. It was found that Ti(III)/ As(V) concentration ratio had to be larger than 3-5 times, HCl concentration 0.4 to 1.0 M, reaction temperature 60 - 90 ˚C and waiting interval 3-5 minutes. Under the experimentally decided conditions the reduction was very fast and quantitative. No interference was observed from most common ions. The LOD was found as 1.5×10^{-7} M. The newly developed method is applied for the determination of arsenic in beer. The reduction procedure takes place directly in polarographic cell. This newly developed method can safely be used for the speciation of As(III) and As(V) and for total arsenic quantity determination in natural samples.
Keywords: speciation, beer, arsenic (III and V), Ti(III) reductant, DP polarography

INTRODUCTION

The danger of environmental pollution increases with the increase of toxic elements in air, soil and water. Arsenic is known as a very toxic element, its toxicity depends on its chemical form, its oxidation state and its solubility in biological media. In water arsenic is usually in the form of the arsenate and arsenite. As (III) is systematically more poisonous than

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the As(V) form [1]. This element is classified as a "class 1" human carcinogen by the World Health Organization and it has been associated with skin, lung, bladder, kidney, and liver cancers. Since arsenic is in nature at usually very low concentrations, highly sensitive methods are required for its determination. For this purpose, spectroscopic, chromatographic, voltammetric, and hyphenated methods are being used. Among these, atomic absorption spectrometry [2], graphite furnace atomic absorption spectrophotometry [3, 4], hydride generation atomic absorption spectrometry [5-9], high-performance liquid chromatography [10,11], and high-performance liquid chromatography − inductively coupled plasma mass spectrometry [12-14] can be mentioned. When arsine generation and gas-phase molecular absorption spectrometry was used, the limit of detection for As(III) and As(V) was found to be 0.5 and 3 μg mL^{-1} respectively [15]. With the use of inductively coupled plasma − atomic emission spectrometry the limit of detection was found to be 0.1 μg L^{-1} for As(III) and As(V) [16].

The above mentioned spectroscopic methods can be used safely in case of determination of metals in complex matrices; however, they are very expensive when compared with electrochemical techniques. They also need pre -concentration and extraction which are time consuming procedures, with danger of losses and contamination. Due to this, the electrochemical techniques emerge with the purpose of eliminating the disadvantages of these high-cost techniques. As main advantages we can mention, high sensitivity, high reproducibility, high selectivity, simple sample preparation, trace metal determination and direct determination of speciation.

Arsenic (III) was determined using a catalytic hydrogen wave that was obtained with a bismuth film electrode [17]. In another work, As(III) and total arsenic in a natural water source and mineral water could be determined with cathodic stripping voltammetry, with 40 s of deposition, using a hanging mercury electrode [18]. The As(III) and As(V) contents in soil were determined with cathodic stripping voltammetry. For the reduction of As(V) to As(III), ascorbic acid [19] and three different extractants were tested. Arsenic, selenium, copper, lead, cadmium, zinc, and manganese in marine environmental matrices were determined using anodic and cathodic stripping voltammetry [20]. Matrix exchange differential pulse stripping voltammetry was used for the determination of total arsenic in gold samples [21]. Cathodic stripping voltammetry with a hanging mercury drop electrode was used for the determination of As(III) and As(V) in seawater samples [22]. Using a gold electrode with differential pulse anodic stripping voltammetry, trace As(III) in natural waters and in biological samples was determined [23]. In one of our work [24], the hydrogen catalytic wave formed in the presence of Mo(VI) and As(III), could be used for the determination of 10^{-6} – 10^{-8} mol L^{-1} As(III) using differential pulse polarography (DPP) with a detection limit of 2×10^{-9} mol L^{-1} [24]. Arsenic speciation was also possible using DPP and total arsenic in Ankara City tap water was determined [25].

For the trace arsenic determination, the intermetallic compound formation between Se(IV) and As(III) by DPP has been used. With this method arsenic in beer was determined after reduction of As(V) into As(III) using KI. [26].

The aim of this work was to determine total arsenic present in biological samples using differential pulse polarography. Since As(V) is formed during wet digestion from As(III) present, and since it is electroinactive, it had to be reduced into As(III) which is electroactive. Although KI was used in previous studies for this reduction, the potential difference between As(V) and KI was only $\Delta E^\circ = +0.03V$ which is quite small for a quantitative reaction. The time needed for this reduction with KI was about 30 minutes at 90 °C. Because of this, investigations have been made in order to find a new and better reducing agent. According to the reduction potentials, between As(V) and Ti(III) with $\Delta E^\circ = +0.46$ V, Ti(III) was found to be the most suitable. This reduction reaction is used for the first time in this work. No work has been found in the literature where this redox reaction was used. In order to have the reaction quantitative, the optimum reaction conditions such as Ti(III) concentration, acidity, temperature and time have been investigated.

EXPERIMENTAL

Apparatus

A polarographic analyzer "Entek Electronics Model 2016" equipped with a mercury drop timer was used. The drop time of the electrode was in the range 2-3 s (2.4 mg s^{-1}). A Kalousek electrolytic cell with a saturated calomel electrode (SCE), separated by a liquid junction, was used in the three-electrode configuration. The counter electrode was platinum wire. The polarograms were recorded with a Linseis (LY 1600) X - Y recorder under the conditions of a drop life of 1 s, a scan rate of 2-5 mV s^{-1}, and pulse amplitude of 50 mV.

Reagents

All chemicals used were of analytical-reagent grade (proanalysis). Triply distilled water was used in the preparation of all solutions. Solutions of 1×10^{-3} M and more dilute ones were prepared before every use in order to avoid the aging process of solution. In order to expel the oxygen present in polarographic cell 99.999 % pure nitrogen was passed through the solution.

The mercury (proanalysis) used in the dropping mercury electrode was obtained from Merck (Darmstadt, Germany). Contaminated mercury was cleaned by passing it successively through dilute HNO_3 (3.0 M) and water columns in the form of fine droplets by using a platinum sieve. This mercury is then washed in the same way until no acidic reaction was observed. The collected mercury was stored in a closed vessel covered with water. It was dried between sheets of filter paper when it was needed. The mercury used is not lost since it was collected quantitatively, without causing any pollution. Thus, no mercury loss is possible and it can be used continuously. Before use, a DPP polarogram of this mercury was recorded each time in order to confirm the absence of impurities.

Preparation of Reagents

As(III) and As(V) solutions were prepared from $NaAsO_2$ and $Na_2\ HAsO_4 .7\ H_2O$ salts respectively. Ti(III) and Ti(IV) solutions were prepared from $TiCl_3$ (15% v/v and d =1.20 g mL^{-1}) and $TiCl_4$ (15% v/v and 1.12 g mL^{-1}) respectively. Ti(III) had to be kept in zinc–mercury amalgam to protect from air oxidation. In this medium it can be stored for months.

0.1 M HAc/Ac^- buffer was prepared by adding 6 g of solid NaOH, into 57 mL of 1.0 mol L^{-1}HAc, after it was washed with distilled water in order to remove the carbonate formed, and diluting into1L. The pH was adjusted to the desired value using a pH-meter.

RESULTS AND DISCUSSION

During wet digestion of a natural sample, arsenic present will be oxidized into As(V) which is not electroactive and it cannot be determined using polarography. Thus, for its determination it has to be reduced first, with a reducing agent into As(III) which is electroactive. According to the reduction potentials as given below, Ti(III) is chosen as the most suitable reducing agent for As(V).

$$TiO^{2+} + 2H^+ + e^- \leftrightarrow Ti^{3+} + H_2O \qquad E^\circ = +\,0.10\ V$$

$$AsO_4^{3-} + 2H^+ + 2e^- \leftrightarrow AsO_3^{3-} + H_2O \qquad E^\circ = +\,0.56\ V$$

Total reaction:

$$AsO_4^{3-} + 2Ti^{3+} + H_2O \leftrightarrow AsO_3^{3-} + 2\,TiO^{2+} + 2H^+ \qquad \Delta E^\circ = +\,0.46V$$

In order to find the optimum conditions for the quantitative reaction between As(V) and Ti(III) some variables such as pH, Ti(III) concentration, temperature and time were examined. To follow the effect of variables onto the reaction yield, either the change of As(III) or the change of Ti(IV) polarographic peaks have to be followed. For this purpose, the polarographic behavior of As(III) and Ti(IV) have been studied under various conditions.

Polarographic Behavior of As(III) and Ti(IV)

The polarographic behavior of As(III) was studied in various electrolyte and pH conditions. A polarogram taken in 0.1 M HCl is shown in **Figure 1**. As can be seen there are three peaks at -0.61 V, - 0.68 V and at - 0.82 V. The first one corresponds to the reduction of As(III) into elemental arsenic, the third one to the reduction of elemental arsenic into arsenide (As^{3-}) and the second one is an adsorption peak according to our former work [25].

It was found that in HAc electrolyte (pH =2), As(III) had two sharp and high peaks at about -0.65 V and -0.87 V and they responded well to standard additions. At larger concentrations a third peak at about -0.75 V appeared (adsorption peak) which did not show proportional increments by standard additions. Thus, the best medium was found HAc electrolyte (pH=2) medium for the As(III) determination because of the good response of the

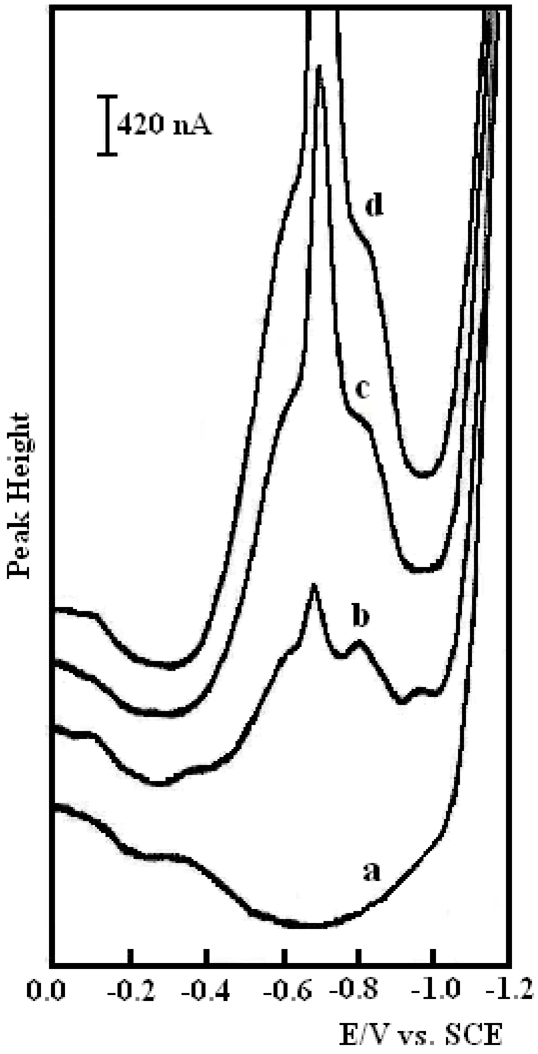

Figure 1. DP Polarographic behavior of As(III) in 0.1M HCl. **(a)** 10 mL 0.1 M HCl, **(b)** a + 0.1 mL 1.0×10^{-3} M As(III), **(c)** b + 0.1 mL 1.0×10^{-3} M As(III), **(d)** c + 0.1 mL 1.0×10^{-3} M As(III)

peaks for concentration changes. Using the peak at -0.87 V for As(III), the quantification limit was 5×10^{-7} M and the limit of detection, LOD, (S/N =3) (signal to noise ratio), was 1.5×10^{-7} M.

When the peaks of Ti(III) and Ti(IV) were examined in HAc/Ac^{-} buffer (pH=4) medium, it was observed that while Ti(III) was not electroactive, Ti(IV) had one broad and small peak at about -0.80 V. On the other hand, in HAc electrolyte (pH= 2) medium Ti(IV) had a very small and broad peak at about -0.65 V. Thus, it was decided to use HAc electrolyte at pH =2 for the determination of unknown arsenic. In this medium As(III) peak is at -0.87 V and Ti(IV) is at about -0.65 V thus, there will be no peak overlap. It is also found that the peak of As(III) is 4-5 times larger than Ti(IV) peak when they are in the same concentration, which is an important advantage.

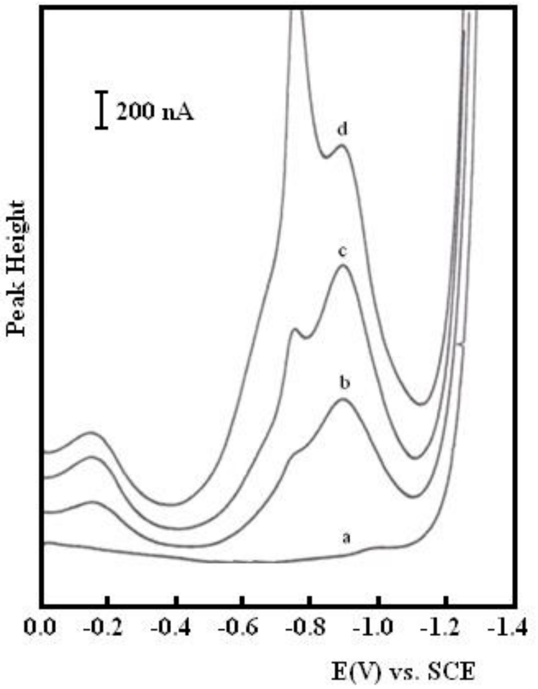

Figure 2. Determination of 1×10^{-5} M As(V) in the presence of 5×10^{-5} M Ti(III), **(a)** 10 mL 1M HAc/Ac (pH=2), **(b)** a + 0.1 mL sample, **(c)** b + 0.1 mL sample, **(d)** c + 0.1 mL 1×10^{-3} M As(III). (Sample: 1×10^{-3} M As(V), 5×10^{-3} M Ti(III), 1 M HCl)

Optimization of the reduction reaction conditions

The below given synthetic solutions were prepared in order to find the best optimum conditions for a quantitative redox reaction between As(V) and Ti(III);

a) 0.1mL 0.1M Ti(III) was added into a solution containing 5 mL 1×10^{-3} M As(V) and 0.42 mL HCl. Thus, a solution containing As(V) in the presence of 2 times higher concentration of Ti(III) was obtained.
b) For 5 times higher concentration of Ti(III), 0.25 mL 0.1M Ti(III) was added into a solution containing 5 mL 1×10^{-3} M As(V) and 0.42 mL HCl.

These solutions were kept at various temperatures and various times intervals in a reaction vessel. After cooled down, known volumes were taken and added into the polarographic cell containing certain electrolytes.

In order to decide the optimum reaction conditions, a reaction medium was prepared in a reaction vessel. The temperature and time intervals were changed and under each reaction condition the As(III) formed was determined. For this purpose, first a small sample from the synthetic solution is added to the polarograhic cell and the polarogram of reaction medium is taken. The As(III) content which was formed from the reduction of As(V) with Ti(III) was calculated by the addition of standard As(III) solution to the cell.

Table 1. Effect of acidity on the reaction between As(V) and Ti(III)*

Time (min)	Temperature (°C)	HCl (mol L^{-1})	Yield, %
5	80	1.0	73
5	80	2.0	67
10	90	0.5	56
5	90	2	77

*Ti(III) concentration is 2 times of arsenic(V)

Table 2. Effect of time duration on the reaction between As(V) and Ti(III)*

Time (min)	Temperature(°C)	*HCl (mol L^{-1})*	Yield, %
2	80	1.0	78
3	80	1.0	61
5	80	1.0	67
10	80	1.0	73

*Ti(III) concentration is 2 times of arsenic(V)

Using these results the yield of the reaction could be calculated under each reaction condition. As an example for the determination of 1×10^{-5} M As(V) in the presence of 5×10^{-5} M Ti(III) is given in **Figure 2.** For this purpose the reaction mixture is prepared. After the time needed has ended, small samples from the reaction mixture were added into the polarographic cell and the polarograms were taken. As can be seen from **Figure 2**, (curve b and c), only As(III) peak which was formed after the reduction of As(V) was present. Its quantity was determined by the addition of standard As(III) solution (curve d) which is of course equal to the reduced As(V) content. The yield is then calculated accordingly.

The results obtained are summarized below in **Tables 1** and **2** for each reaction condition.

a) *Effect of acidity*

The reaction medium was10^{-3} M As(V), 2×10^{-3} M Ti(III) and various molarities of HCl. As can be seen from **Table 1**, when the molarity of HCl was 1M and 2 M the percentage of the yield was about 70 % although Ti(III) concentration was low. As expected when HCl concentration was 0.5 M the yield was about 56 %, even at 90° C and for10 minutes of time interval. In all steps Ti(III) present was constant, it was 2 times larger than As(V) concentration. The reason that the yield was not high and it was only 70 % is because of the low concentration of Ti(III) present. Since the temperature was quite high the possibility of low temperature will not be the reason in this set of the reactions.

b) *Required time interval*

The reaction medium was 1×10^{-3} M As(V), 2×10^{-3} M Ti(III) and in 1 M HCl. In the presence of 2 times higher concentration of Ti(III), the effect of time duration (2-10 minutes), in 1.0 M HCl and 80°C have been studied. As shown in **Table 2** the yield was not high enough,

Table 3. Effect of temperature on the reaction between As(V) and Ti(III)

Time duration (min)	Temperature (°C)	HCl (mol L^{-1})	*Ti(III)/As(V)*	Yield, %
5	80	2.0	2	79
5	90	2.0	2	77
3	22	0.42	5	20
3	60	0.42	5	98
3	90	0.42	5	97

Table 4. Effect of Ti (III)/As(V) concentration ratios on the reaction between As(V) and Ti(III)

Time (min)	Temperature (°C)	HCl (mol L^{-1})	*Ti (III)/ As(V)*	Yield, %
5	90	1.0	3	100
5	90	1.0	5	100
5	90	0.42	5	100

it was between 60-75 %. The reason is of course, the low ratio of Ti(III), instead of 3 -5 it was only 2 times larger.

c) Effect of temperature

In various temperatures changing from 22 °C to 90 °C, at two different concentrations of Ti(III) and 3 and 5 minute time intervals have been studied. As can be seen from **Table 3** at low temperature (room temperature) the yield was very low (20 %), although Ti(III) concentration was 5 times larger than As(V). At higher temperatures (60 – 90 °C), when Ti(III) concentration was high, the reaction was quantitative and fast. As can be seen from **Table 3**, even at 60 °C with a 3 min reaction time the reaction was nearly complete.

d) Effect of Ti(III) / As(V) concentration ratio

In the presence of 3 or 5 times larger concentrations of Ti(III) the reaction is quantitative in HCl concentration changing 0.4 - 1 M. As can be seen from **Table 4** the yield is about 100 % at about 90 °C and when Ti(III) is more than 2 times of As(V) concentration. In the light of the foregoing findings, in order to have the reaction quantitative, the optimum reaction conditions could be designated as;

1. A ratio of Ti(III) / As(V) concentrations of 3 - 5 or larger, (the yield is low if the ratio is lower than 3).
2. An HCl acid concentration of 0.4 to 1.0 M.
3. A reaction temperature between 60 °C and 90 °C.
4. A waiting interval of 3-5 minutes, until the reaction has ended.

General Reduction Procedure for an Unknown Sample

In the light of our work, the reduction procedure for an unknown can be applied as given below;

First the sample is digested with acids such as HNO_3 and $HClO_4$, As(V) formed is reduced in 1 M HCl in the presence of Ti(III). Here it has to be mentioned that since the content of As(V) in the sample is not known, the Ti(III) concentration has to be experimentally decided. For this purpose, first a known concentration of Ti(III) has to be added to the sample and the As(III) content will be determined by measuring its polarographic peak. This procedure is repeated several times until the As(III) peak will be constant**.** In order to be on the safer side Ti(III) concentration can be taken larger than this value. For the reduction, the temperature maybe between 60- 80°C and about 3–5 minute will be sufficient.

This reduction can be followed also in 0.4–1.0 M HCl but at about 90 °C in the presence of 3-5 times or higher concentration of Ti(III). After reduction procedure a small sample portion is taken and added into the polarographic cell containing HAc electrolyte (pH=2) and the polarogram is taken. The peak of arsenic (III) formed after reduction is measured and its concentration is determined after standard addition of As(III).

Application of the newly developed method to Beer Sample

For this purpose100 ml of beer was evaporated until its volume became about 2 mL. Then a mixture of 10 mL 1:1 HNO_3:$HClO_4$ was added and was left wait overnight. It was once more evaporated until the red fumes of HNO_3 ceased and digestion was completed with the appearance of white fumes of perchloric acid when approximately 1.0 mL solution remained. The digested sample was cooled to room temperature rinsed the funnel into flask with water and the contents were transferred into a 10.0 mL calibrated flask, making up to mark with triply distilled water. This sample was kept in Teflon bottle in refrigerator. No As(III) peak was observed when the polarogram was taken, indicating that all arsenic present was oxidized during wet digestion.

Reduction of As(V) in digested beer;

According to our former studies the As(V) concentration in 10 mL sample solution after digestion will be about 4×10^{-6} M. In order to have 10 times larger concentration of Ti(III), addition of 0.4 mL portion of 10^{-3} M Ti(III) will be sufficient. This reduction is performed in the presence of about 10 times larger concentration of Ti(III), in 1.0 M HCl at about 90 °C. The reduction was quantitative in 3-5 minutes. The arsenic present in beer is determined using our developed polarographic method [24] in which catalytic hydrogen wave was used. For this purpose, Mo(VI) was added in order to form "heteropolyanion". The polarograms were taken in 10mL pH=3.0 Hac/Ac^- buffer, **Figure 3**. Arsenic content was determined by standard As(III) additions. The result found was 20.2 ± 2.6 µg L^{-1} (95 % CI, N=4). The highest allowable value for arsenic in beer is 100 µg / L in Spain, 500 µg L^{-1} in England and Ireland and 200 µg L^{-1} in Czech Republic, Bulgaria, Slovenia and Hungary.

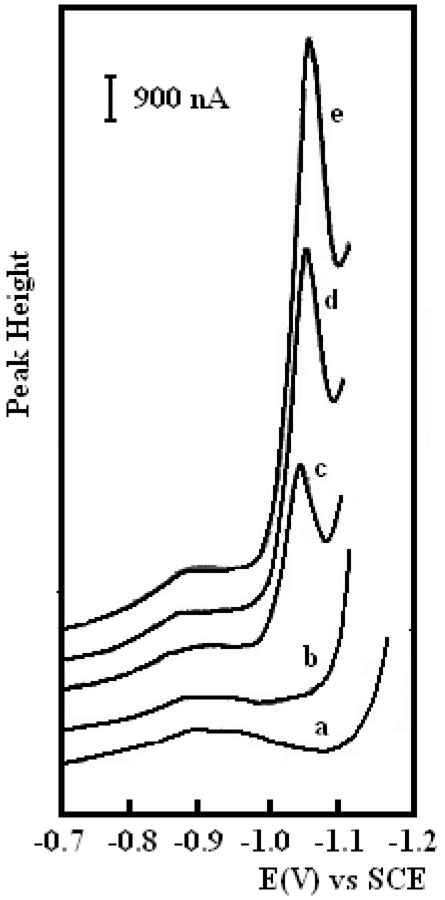

Figure 3. Determination of As(III) in beer sample using the catalytic hydrogen peak, **(a)** 10 mL 0.2 M HAc electrolyte (pH=3.2), **(b)** a + 0.05 mL 2×10^{-3} M Mo(VI), **(c)** b + 0.2 mL digested and reduced beer sample, **(d)** c + 0.1 mL 1×10^{-5} M As(III), **(e)** d + 0.1 mL 1×10^{-5} M As(III)

CONCLUSIONS

For the determination of trace elements in biological samples, first the sample has to be digested. For this purpose wet digestion using HNO_3 and $HClO_4$ is mostly preferred. However, during this digestion As(III) is oxidized into As(V), Se(IV) into Se(VI), Sn(II) into Sn(IV) and Sb(III) into Sb(V) which are not electroactive and thus cannot be determined with many methods including polarography. Thus, they have to be reduced before their determinations. In this work for the determination of arsenic using DP polarography, a reduction method has been developed.

For this purpose, Ti(III) has been used as a reducing agent for the first time in our method and the optimum conditions for the quantitative reaction have been investigated. As a result optimum reaction conditions could be designated as: A ratio of Ti(III) / As(V) concentrations of 3-5 or larger (the yield is low if the ratio is lower than 3), an HCl acid concentration of 0.4 to 1.0 M, a reaction temperature between 60 ℃ and 90 ℃, a waiting interval between 3 to 5 minutes. As given in the literature when KI was used as the reducing agent for As(V) the time needed was about 30 minutes at 90 ℃ which is quite long [26]. The newly developed method is applied for the determination of arsenic in beer.

Here it is important to mention that with this method it is also possible to speciate arsenic present in a natural sample. For this purpose, first, the As(III) present is determined before the sample is digested polarographicaly using the As(III) peak**.** Then, after digestion with acids, the developed reduction conditions are applied and total As(III) is determined.

As can be seen this redox reaction can be used for different analysis methods also, in case As(III) has to be determined after digestion of biological materials.

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