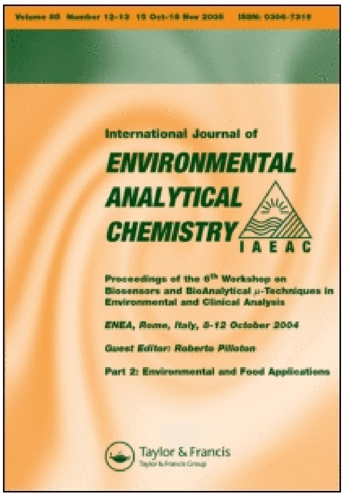

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DPP DETERMINATION OF TRACE LEVEL OF As(III) AND TOTAL INORGANIC ARSENIC IN DRINKING WATERS*

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A method for the determination and speciation of As(III), As(V) and total inorganic arsenic in drinking waters by Differential Pulse Polarography (DPP) is described. As(III) is determined directly and total inorganic arsenic is measured after reduction of electroinactive As(V). The latter is evaluated by difference.

The method involves the removal of interfering ions by anion exchange with Amberlite IRA-400 and the reduction of As(V) to As(III) with a boiling solution of $NaHSO_3$. The efficiency of both procedures is evaluated.

The operational and analytical conditions are optimized in order to allow the detection of low arsenic levels.

The detection and quantitation limits (8.16 and 9.88 ng/ml, respectively) and the precision of the decribed procedure are evaluated. They prove the usefulness of the method.

KEY WORDS: Arsenic, drinking waters, speciation, differential pulse polarography.

INTRODUCTION

Arsenic is a trace element which is toxic, suspected of being carcinogenic and yet essential for different animal species. It is widely distributed in the environment and as a consequence of increased concern about environmental pollution, there is a growing demand for knowledge about arsenic content in soils, water, air, foods and beverages.

Studies on the biochemical cycles of arsenic show that there are different oxidation states. Its toxicity, biological properties, bioavailability and geochemical activity depend on the chemical form of arsenic. Therefore, it is of interest to know not only the total arsenic content, but the speciation of the arsenic.

The aim of this work is to develop a method that is useful for determining As(III), total arsenic and As(V) in drinking waters, as a first step in a series of

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studies dealing with arsenic determination in more complex materials like waste waters, soils, foods and beverages.

Studies on arsenic content in water show that the main arsenic species are inorganic arsenite, arseniate and organic dimethylarsinic and monomethylarsonic acids and the distribution of arsenic between these forms is dynamic.[1,2] In European countries, the maximum level of arsenic allowed in water is 50 ng/mg[3]. One of the methods applied in routine analysis is spectrophotometric determination, which involves generation of H_3As and reaction of this compound with AgDDTC/Pyridine. The entire procedure is time consuming, and though it helps establish whether the arsenic level is above or below the maximum allowed, it is not sensitive enough for use in analyses of waters.

Several other methods have been proposed for arsenic determination in water and other materials. In the most common methods, arsine is first generated and then determinated by Atomic Absorption Spectroscopy (AAS) or Emission Spectroscopy (ES). However, it has been reported that it is difficult to small quantities of H_3As[4]. Furthermore, as has been stated previously, there is a need for an analytical method that is capable of differentiating between possible oxidation states of arsenic, and the ones mentioned above are unable to make such a distinction.[5]

For the selective determination of organic and inorganic arsenicals, several procedures also based on H_3As generation has been described, but they are slow and rather insensitive.[6]

It is well known that the principle behind voltammetric techniques makes them very suitable for determining different species of the same element.

In addition, they are very sensitive and the equipment required is relatively simple and generally costs far less than the spectrochemical techniques. Determination requires an analytical technique capable of detecting arsenic at concentrations of a few parts per billion. Of the voltammetric techniques, Stripping Voltammetry (SV) and Differential Pulse Polarography (DPP) are the ones most used in trace element analysis because of their high sensitivity.[7] Although SV has been applied several times to arsenic determination, it has two disadvantages when compared with DPP:

—The procedure is slow, especially when low concentrations of ng/ml are measured.

—Because of its high sensitivity, any change in the sample or in analytical conditions is reflected in the shape of the polarogram.

On the other hand, in the case of arsenic determination when a hanging drop mercury electrode is used, the application of this technique is controversial.

The DPP technique is faster than SV and offers an acceptable precision. Though its sensitivity is lower than that of stripping voltammetry techniques, it allows detection limits of ng/ml.

While arsenic determination in drinking waters by voltammetry techniques[8,9] and also by DPP has been reported previously, the present study deals with the parameters likely to affect sensitivity and accuracy.

Our purpose is to present a sensitive, easy-to-use, precise and reliable polarographic method for arsenic determination and speciation in drinking water. The application of this method to the analysis of arsenic in several drinking waters will also be shown.

The operational conditions are: instrumental parameters, supporting electrolytes, removal of interferences and the reduction of As(V) to As(III).

MATERIAL AND METHODS

Instrumentation

—pHmeter Crison Digilab 507

—Methrom 506 Polarecord with Polarography Stand.
Electrodes:—work electrode: DME
—reference electrode: Ag/AgCl KCl 3 M
—counter electrode: Pt

—Water bath Selecta mod. 207060040086

—Eppendorf pipettes (10, 20 and 50 μl) were used to add arsenic to the cell as required.

NOTE: All glassware and polyethylene containers were soaked in 10% V/V nitric acid and then rinsed with deionized water.

Reagents

All the reagents were of reagent grade and were used without further purification, though normal precautions for trace element analysis were taken.

—Distilled and deionized water was used throughout

—Double distilled mercury was used.

—Stock solution of As(III) (1000 μg/ml) was made by dissolving 1.320 g of primary standard As_2O_3 in 25 ml NaOH 1 M and water was added to about 500 ml. 132 ml of HCl 30% were then added and the solution was completed to 1 l with water.

—Stock solution of As(V) (1000 μg/ml) was made by dissolving 4.164 g of $Na_2HAsO_4 \cdot 7H_2O$ in 132 ml of HCl 30% and then the solution was completed to 1 l with water.

—Stock solution of Pb(II) (1000 μg/ml) was prepared by dissolving 1.598 g of $Pb(NO_3)_2$ and then the solution was completed to 1 l with water.

—Amberlite IRA-400 (FLUKA AG.)

—Solution of Ce(IV) 0,1 M from $Ce(SO_4)_2$ $4H_2O$. 4 g were mixed with 3 ml of H_2SO_4 conc. The paste formed from this mixture was dissolved by slowly adding water to complete to 100 ml.

—Hydrochloric acid sp. gr. 1.19

—Hydrochloric acid 1 M

—Nitric acid 60% V/V

Table 1 DPP arsenic determination-instrumental parameters

Technique: Differential pulse polarography
Sensitivity: $1.5 \cdot 10^{-10}$ A/mm
Amplitude: 50 mV
Damp: 2
Drop time: 0.8 sec.
Reference electrode: Ag/AgCl KCl 3 M

—Perchloric acid 60% V/V
—Perchloric acid 1 M
—Sodium Hydroxide 1 M and 2 M
—Sodium Hydrogen Sulphite 1 M was prepared from $Na_2S_2O_5$, 10.410 g were dissolved in 100 ml of water.
—Sulphuric acid 96% V/V

Working standard solutions were prepared from stock solutions by dilution with distilled and deionized water.

Water samples were collected in a polyethylene container containing 1 ml Nitric acid/l.

POLAROGRAPHIC DETERMINATION

1. Operational Conditions

Instrumental parameters are shown in Table 1.

2. Determination of As(III) by DPP[7]

Procedure: 10 ml of the sample at pH = 0 adjusted with hydrochloric acid was pipetted into the cell and 10 ml of supporting electrolyte HCl 1 M and then 2 g of the resin were added.

Nitrogen was bubbled through the solution to remove the oxygen from the solution. Then the polarographic determination by DPP technique was carried out under the operational conditions shown in Table 1.

The standard addition method was used for quantitative determination using Eppendorf pipettes and standard arsenic solutions (20, 50 and 100 ng/ml). Nitrogen was bubbled through the solution for 10 min, and the polarograms are recorded.

Both sample and each aliquot were measured three times; the mean value was used in calculation.

The amount of arsenic added was plotted versus peak current and the arsenic concentration was obtained from this curve.

A linear response was obtained for the range of concentrations between 20 and 170 ng/ml.

3. *Determination of Total Arsenic*

Procedure: 5 ml of $NaHSO_3$ 1 M were added to 5 ml of the sample at $pH=3$ and the value was readjusted to $pH=3$, with HCl 1 M. The solution was transferred to a round bottom flask fitted with two openings. An air-condensor was connected to one of these openings and an inert gas, nitrogen, was bubbled through the second.

The solution was boiled for 30 minutes, was then allowed to cool and an excess of HCl or $HClO_4$ was added in order to eliminate the excess of HSO_3^- as SO_2 by simultaneously heating and bubbling nitrogen. The flask content was then completed to 10 ml with deionized water and the pH was adjusted to $pH=0$.

Then the procedure described in As(III) was followed.

4. *As(V)*

The As(V) content was evaluated by difference between total arsenic and As(III).

RESULTS AND DISCUSSION

1. *Polarogram Recording*

A drop time of 0.8 sec was chosen as an intermediate value between those (1, 2, 3,..., sec) that provide smaller background current and those (1, 0.8, 0.5,..., sec) that offer higher sensitivity.

A pulse amplitude of -50 mV was used to get the maximum resolution peaks and adequate sensitivity.

2. *Supporting Electrolyte*

A variety of supporting electrolytes are suitable here. The use of HCl 1 M and $HClO_4$ 1 M as supporting electrolytes has been reported by other authors. These acids were chosen from among those mentioned by MYERS and OSTERYOUNG[5] because the polarogram obtained in these media shows high intensity peaks and, furthermore, these acids are used to dissolve the residues after the destruction of organic matter (for these reasons they are preferred to organic acid media).

ARNOLD and JOHNSON[10] published a review of the polarographic behaviour of arsenic in various media. They stated that in most supporting electrolytes, the reduction of arsenic gives rise to complicated polarograms that are not suitable for analytical work. In both HCl 1 M and $HClO_4$ 1 M, the DPP arsenic polarogram shows two peaks. The first one, at -0.40 V, is due to the reduction of As(III) to As (0), according to the reaction:

$$As^{3+} + 3e- \rightarrow As^0$$

The second peak, at −0.76 V is due to a further reduction to arsine by the reaction:

$$As^0 + 3e- + 3H^+ \rightarrow H_3As \text{ (see Figure 1)}$$

The first peak is sharper than the second. A third peak (between the first and second) is a polarographic maximum which disappears at arsenic concentrations lower than 300 ng/ml.

MEITES[11] contributed to the knowledge of polarographic characteristic of +3 and +5 arsenic in hydrochloric acid solutions.

At arsenic concentrations of 500 ng/ml, the use of HCl 1 M gives a higher peak at −0.40 V than the $HClO_4$ 1 M. Therefore, the best supporting electrolyte of those which were studied is 1 M HCl because the separation between the first peak and the maximum, the second peak, and the cathodic background is larger.

As(V) is electroinactive in this supporting electrolyte.

3. Interferences

The inorganic ions with a halfwave potential approximately equal to that of arsenic will interfere in the determination of arsenic. In drinking water these are Pb(II), Cd(II), Cu(II) and Sn(II) and (IV). Lead with a $E_{1/2}$ of −0.40 V could be considered the main interference, but Cu(II) with a $E_{1/2}$ of −0.10 V is likely to cause more problems because its concentrations in drinking water can be thirty times that of lead. (The maximum Cu(II) level allowed in drinking water is 1500 ng/ml, in comparison with the 50 ng/ml for lead).

In order to eliminate interference as far as possible, two procedures were assayed:

I) *The oxidation of As(III) to the electroinactive As(V) with Ce(IV).*[5,7]; This procedure involves the registration of two polarograms; the first one corresponds to arsenic plus interferences (see Figure 2A). The second polarogram is registered after oxidation of As(III) to As(V) with Ce(IV). It shows only the interferences and the residual current caused by capacitance and the reduction of interfering inorganic ions.

The signal is subtracted from the first polarogram to give the arsenic signal (see Figure 2B).

The procedure is rapid and has proved to be satisfactory at arsenic concentrations of 20 ng/ml and higher, but it significantly raises the position of the base line at lower concentrations of arsenic.

II) Interference removal by anion exchange with resin (Amberlite IRA-400)[9,12,13]; Pb(II), Cu(II), Sn(II) and Sn(IV) are present in the form of anionic complexes in hydrochloric acid medium and are adsorbed by a strongly basic anion resin. Under the same conditions arsenic, which is present as uncharged H_3AsO_3 is not

SENSITIVITY: $1.5 \cdot 10^{-10}$ A/mm
AMPLITUDE: -50mV
DAMP: 2
DROP TIME: 0.8 sec.
REFERENCE ELECTRODE: Ag/AgCl KCl 3 M

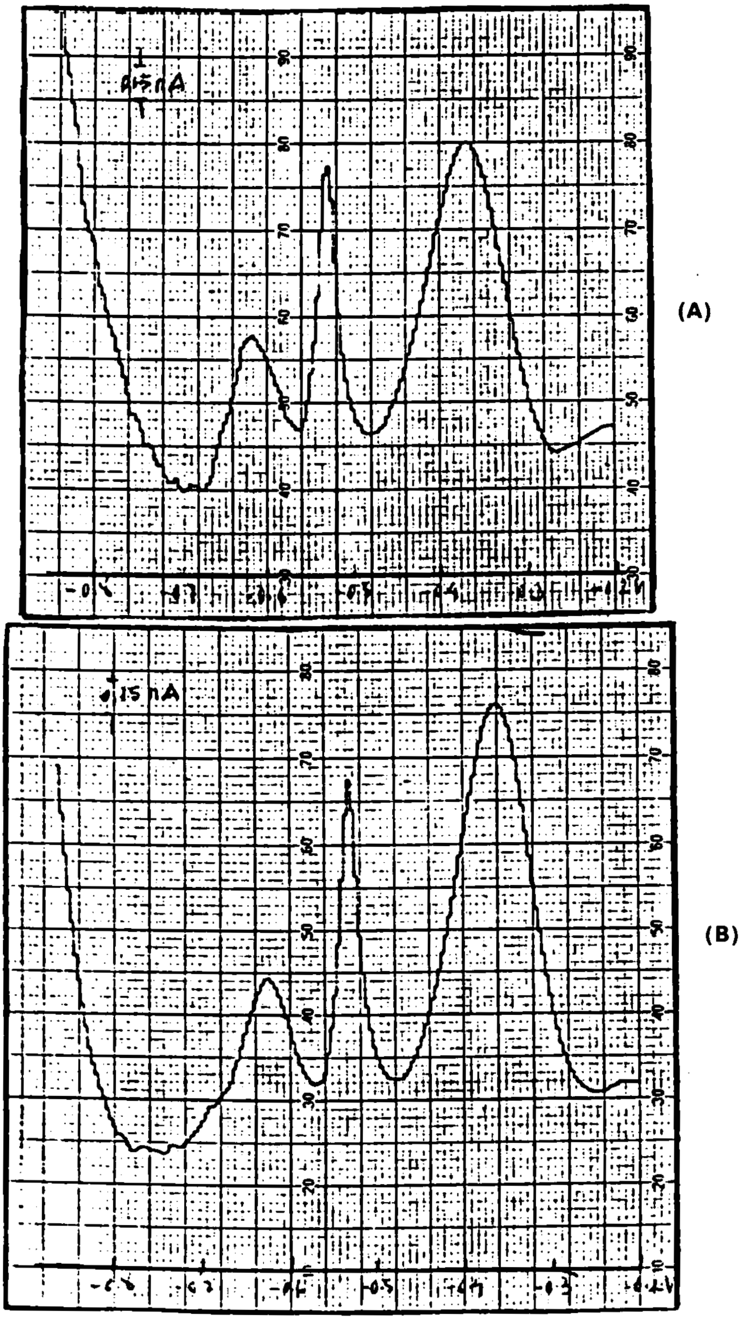

Figure 1 DPP polarogram of 500 ng/ml of As(III) in HCl 1 M (B) and in $HClO_4$ 1 M (A).

SENSITIVITY: 1.5 .10-10 A/mm

AMPLITUDE: -50 mV

DAMP: 2

DROP TIME: 0.8 sec.

REFERENCE ELECTRODE: Ag/AgCl KCl 3 M

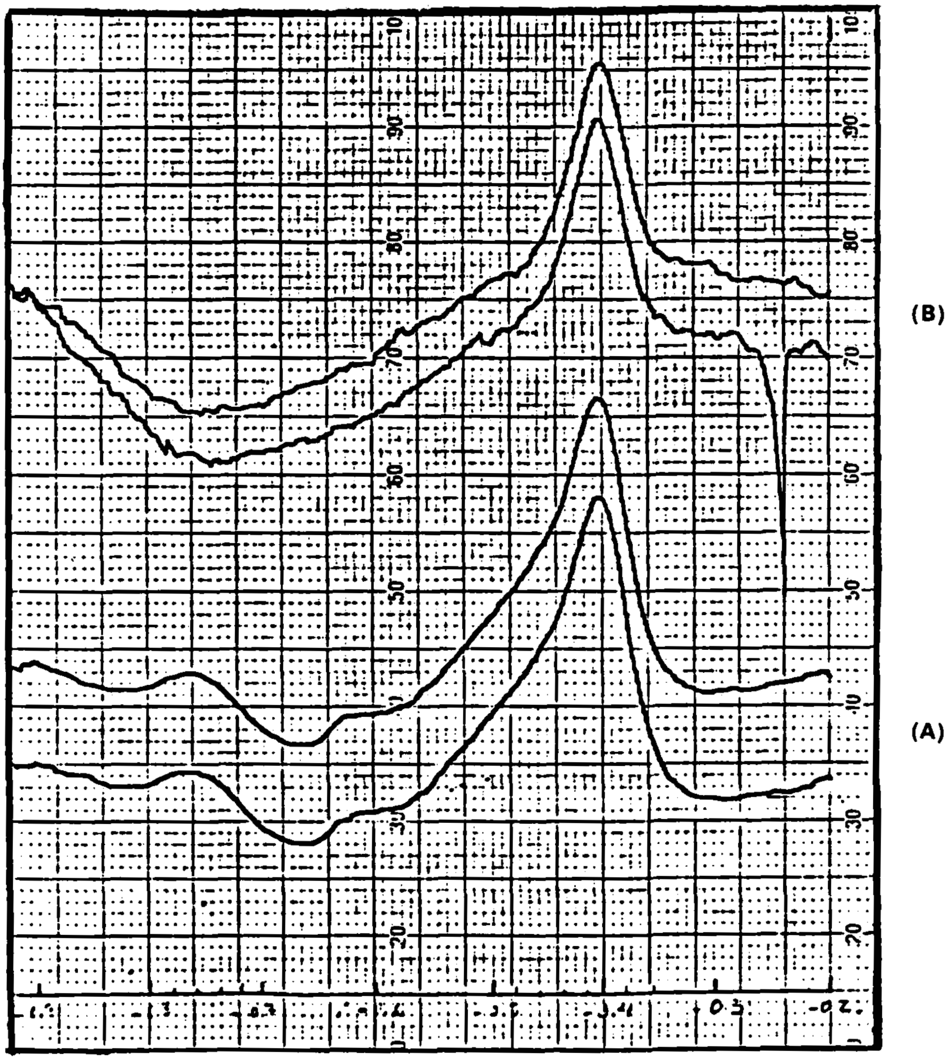

Figure 2 DPP polarogram of 500 ng/ml of As(III) and 500 ng/ml of Pb(II) in HCl 1 M (A) before and (B) after adding 0.1 ml of Ce(IV) 1 M.

adsorbed. The polarogram recorded after shaking the sample with the resin shows only the waves corresponding to the reduction of As(III) (Figure 3).

When this procedure is followed, the As(III) is measured directly, whereas the method that involves the oxidation of As(III) with Ce(IV) is an indirect one which in fact determines the interferences and estimates the As(III) by difference. In the latter, larger signals due to high concentrations of interferences lead to poor precision and accuracy because the arsenic concentration is estimated as a small difference between two large numbers.

Therefore, the method based on removing the interfering ions by ion exchange resin was used here.

4. *Reduction of As(V) to As(III)*[5]

As(V) is a polarographically inactive form when HCl 1 M is the supporting electrolyte, but it could be determined if it were reduced to As(III).

The following have been proposed as suitable reducing agents prior to polarographic determination Hydrazine salts, SO_2, acidic KI, Cu(I) in conc. HCl, followed by extraction of $AsCl_3$ into benzene and extraction into water.

The Hydrazine chloride and the $NaHSO_3$ are the reducing agents usually used in the determination of arsenic by DPP when HCl 1 M is used as a supporting electrolyte.

The use of $NaHSO_3$ offers advantages because it quantitatively reduces the As(V) to As(III), the reduction products do not interfere in the measuring and the excess of $NaHSO_3$ is easily eliminated as SO_2.

The efficiency of the reduction was estimated at different arsenic levels and the results were: 95.38% at a concentration of 10 ng/ml, 97.62% at 20 ng/ml, and 98.42% when the concentration was 30 ng/ml.

To test the linearity of the polarographic responses, 20, 50 and 100 ng/ml of As(V) were prepared and subjected to the reduction process.

Figure 4 shows the polarograms and also the regression equation and correlation coefficient obtained.

The results obtained show that reduction with $NaHSO_3$ is useful in measuring total arsenic.

5. *Analytical parameters*

Precision: The precision of the method was determined from the variation coefficient. It was calculated from the analysis of six aliquots of the same water. The variation coefficient is 9.95%.

The instrumental precision was calculated from six consecutive readings of a water aliquot. The variation coefficient is 3.35%.

Detection and quantitation limits: Detection(LOD) and quantitation(LOQ) limits are calculated according to the definitions $\bar{x}_b + 3\sigma_b$ and $\bar{x}_b + 10\sigma_b$ respectively (ACS,

A-DEIONIZED WATER(BLANK)
B-ADITION OF 100 ng/ml OF As(III)
C-ADITION OF 100 ng/ml OF Pb(II)
D-INTERFERENCE REMOVAL BY 2 g OF RESIN

SENSITIVITY= 0.5 10^{-10} A/mm
AMPLITUDE= -50 mV
DAMP= 1
DROP TIME= 0.5 sec
REFERENCE ELECTRODE: Ag/AgCl KCl 3 M

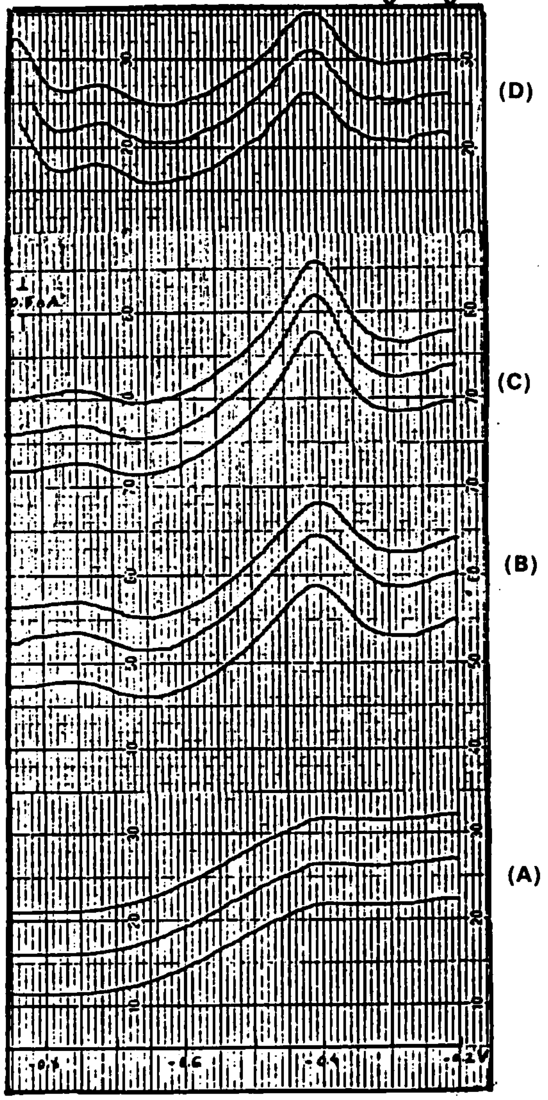

Figure 3 Interference removal by an anion exchange resin.

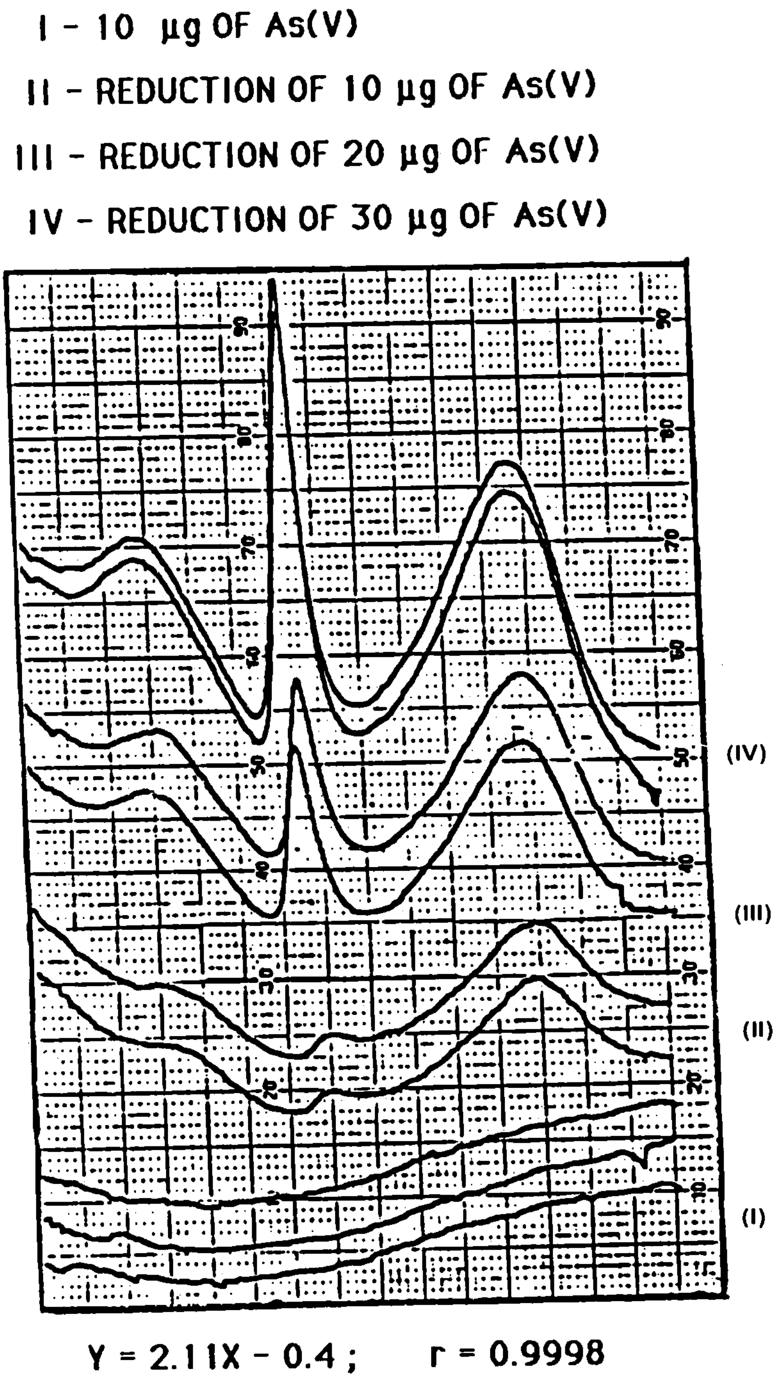

Figure 4 DPP polarogram recorded after reduction of As(V) to As(III) with a boiling $NaHSO_3$ solution.

Table 2 Levels of As(III), As(V) and total arsenic (ng/ml) in drinking water determination by DPP

AGUA problema	*As(III)*	*As(total)*	*As(V)*	*Pb(II)*
A	40 ng/ml	52.3 ng/ml	12.3 ng/ml	5 ng/ml
B	40.1 ng/ml	48.2 ng/ml	8.1 ng/ml	5 ng/ml
C	22.4 ng/ml	31.7 ng/ml	9.3 ng/ml	5 ng/ml

1980),[14] where $\bar{x}_b$ is the field blank and σ_b is the variability in the field blank for a total of six blanks. The blanks consist of: 10 ml deionized water at $pH = 0$, 10 ml HCl 1 M and 2 g of Amberlite IRA 400.

The values obtained were: LOD 8.158 ng/ml and LOQ 9.875 ng/ml.

6. *Application of DPP arsenic determination and speciation to water*

Once the usefulness of the assayed method for determining arsenic in water was demonstrated, the method was used to measure the level of this element in five samples of drinking water. The method used can be outlined as follows:

1. Removal of interferences by stirring with a resin Amberlite IRA-400.
2. Determination of As(III).
3. Determination of total arsenic after reduction of As(V) to As(III) with $NaHSO_3$.
4. Estimate of As(V) by difference, arsenic total minus As(III).

The results obtained after applying the proposed method to 3 samples of water are shown in Table 2.

The total arsenic content in the analysed waters was below the maximum level allowed by the EEC.

CONCLUSION

The values obtained in the determination of analytical parameters (sensitivity expressed as LOD and LOQ, and precision) show that the proposed method is adequate for arsenic determination in drinking waters.

Its application to samples of natural waters proved that the DPP method is easy to use, fast, sensitive and, because of the elimination of main interferences, reliable.

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