Sudarshan Publication

DETERMINATION OF ARSENIC (AS) IN SOME ENVIRONMENTAL SAMPLES UTILIZING POTENTIOMETRIC TITRATION: UNDER MODIFIED ANALYTICAL AND TECHNICAL CONDITIONS

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ARTICLE INFO

ABSTRACT

In the present research, a potentiometric technique has been developed providing modified technical and analytical conditions in order to determine Arsenic level by direct titration with iodide on Platinum electrode in aqueous media and then to apply the findings to environmental samples. It's been found appropriate value of pH for Arsenic titration using Iodide ranged from 8-9. The manual response of Arsenic on platinum electrode was quick when Na_2SO_4 was used as a buffer solution at concentration of 0.1M. The suggested method was successfully utilized for the quantitative determination of arsenic at a detection limit of $1/5 \times 10^{-7}$mol. Many values were calculated such as standard deviation, Standard deviation percentage, Threshold limiting value as well as reduction which is considered a good criterion of the quality of the followed method for precise determination of arsenic level. The validity of the applied method was studied at modified conditions for many environmental samples (water, solid, plant) samples containing arsenic that was determined precisely in the same manner.

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INTRODUCTION

Arsenic is naturally distributed in rocks, soil, water, air, plants and animals [1].Due to natural and human activities, it can be

released to environment in different ways[2]e.g. volcanoes, rock erosion, forest fires, fuel combustion, sites of waste dumping[3-6]. Besides, Arsenic is utilized in different industries such as that of cement, mineralization, insecticides,
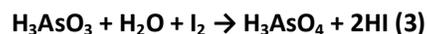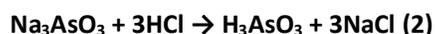
Preserving wood, dyes, drugs, glass, fertilizers, transportations [6-10].Everyone who is engaged in manufacturing of these products and using them is exposed to arsenic. The transferring of arsenic occurs through inhalation, it also moves to skin. The potential health impacts of arsenic are different due to its species, that is, organic species of arsenic is less toxic than inorganic ones[12]. Long term exposure to high levels of arsenic causes many health problems such as several types of cancer of bladder, lung, skin, kidneys, prostate, and liver[14] The liver is affected in form of fibrosis, cirrhosis. Further, the damage of peripheral nerves can be noticed, and it begin in the feet with a tingling as well as the color and thickness of skin may change. [15]. There are different lab methods to detect and to determine arsenic level some of these techniques are capable to distinguish or to differentiate chemical species of arsenic of different valents. AAS is the most common analytical procedure for the determination of arsenic in biomaterials and environmental samples. Recently ICP_AES and ICP-MS were increasingly used to determine arsenic level [17,18]. These techniques provide low limits of certain type of detection. Arsenic of biological fluids and tissues can be also determined using NAA. Moreover X-ray technique can be utilized for measuring arsenic that may be found in biological and environmental samples [19]. Electrochemical methods such as amperometry and voltammetry techniques are also involved[20]. The objective of this research is to develop an application for the determination of arsenic in many of environmental samples provided typical conditions in order to evaluate the contamination impact. It's considered a unique research due to the new involved technique in of electro-analysis like

potentiometry; previously utilized techniques for arsenic evaluation were mostly spectrophotometric and based on ICP-MS or AAS which both of them are very expensive and complicated[1-20]. Potentiometry has many features.

- Feasibility
- Instant analytical procedure
- Sensitivity
- Ultimate accuracy
- Repetition
- Validity of findings
- Low costs
- Field analysis
- Applicable to all environmental samples

MATERIALS & METHODS

Arsenic was directly titrated with iodide in water i.e. it involved certain volume of the studied solution containing arsenic versus certain volume of a standard solution of iodide using potentiometric titration apparatus operates under strictly defined conditions for arsenic evaluation in aqueous media. The occurred reactions are obvious in the following equations.

$$As_2O_3 + 6NaOH \rightarrow 2Na_3AsO_3 + 3H_2O \text{ (1)}$$

$$Na_3AsO_3 + 3HCl \rightarrow H_3AsO_3 + 3NaCl \text{ (2)}$$

$$H_3AsO_3 + H_2O + I_2 \rightarrow H_3AsO_4 + 2HI \text{ (3)}$$

APPARATUS

1-automated potentiometric titrator (Radiometer Co. France)

2-Digital pH meter.

3-Mechanical analytical balance and precise calibration balances

4- Electromagnetic stirrer and heater.

CHEMICALS AND REAGENTS

Double distilled water, arsenic oxide, iodide potassium, solid iodine, sodium hydroxide, sodium sulfate, sodium carbonate, sodium

acid carbonate NaHCO₃, sulfuric acid was utilized and they were ultrapure.

RESULTS AND DISCUSSIONS

OPTIMIZING TECHNICAL CONDITIONS FOR ARSENIC TITRATION

In addition to sample properties like weight, volume, numerical data that are necessary to obtain the findings in terms of measurement unit, standard solution concentration, there were a set of conditions that should be created to determine the actual value and end point of titration and processing of data related to standard solution titration in terms of initial speed and slowing down near the end point of titration.

Table 1 explains the optimized technical conditions for potentiometric titration of a 1×10^{-5} mol /l solution of arsenic with iodide using potentiometer.

Select method	AS
Electrode	XM120
Reference Electrode	REF361
Temperature	$25^{\circ}C$
Unit	M
Titrant	I2 ($1*10^{-4}M$)
Mode	End Point
Measurement	mV
Number of tests	3
Direction	Increasing mV
Min. speed	0.01 ml/min
Max. speed	2.00 ml/min
End point	460 mV
EP delay	0-10 s
Proportional band	350 mV
Start timer	0-10 s
Speed of Internal stirring	500 rpm

OPTIMIZING ANALYTICAL CONDITIONS FOR TITRATION

THE EFFECT OF PH ON TITRATION

It's obvious that there is a complicated relation between pH gradient and titration .i.e. arsenic does not react to iodide in acidic solutions. To insure this relation pH should be kept high taking into consideration solutions of pH higher than 10 at which iodide reacts again and gives per-iodate acid leading to titer volume.

This study aimed to choose the appropriate value of pH . As a series of trials were done at different values of pH ranged from 0-9 . Figure 1 reveals the integral curves of potential changes due to changes in reagent volume that was added for potentiometric titration of arsenic with iodide at different values of pH .
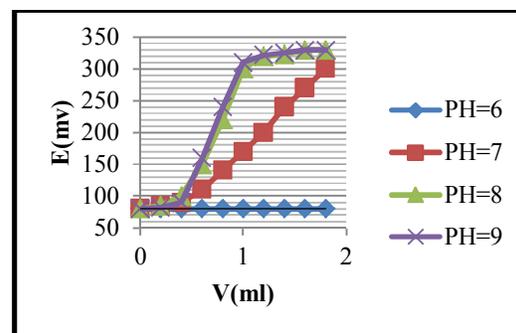

Figure 1 variations in potential versus changes in the volume of the added reagent at different degrees of pH

Figure 1 reveals the desired value of pH for arsenic titration with iodide, which ranges from 8-9.

THE EFFECT OF BUFFER SOLUTION

The structure and the concentration of the buffer solution were studied, since buffer solution effects on the response of arsenite Ion As^{+3} and its detection limit. We studied a set of buffer solutions such as Na₂SO₄ ,NaHCO₃, and Na₂CO₃. They were utilized at different concentrations that ranged from 0.1-0.001M

Fig 2 reveals the integral curves of potential value change in correspondence to the volume of the added reagent for idiometric titration of arsenic with different buffer solutions.
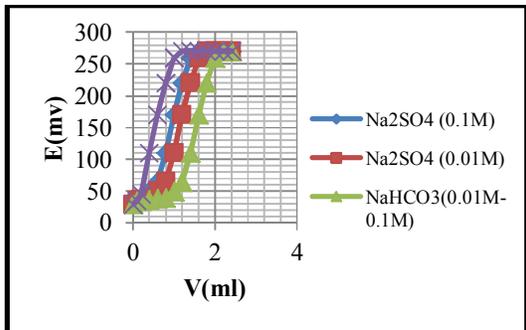

Figure 2 variations in potential versus changes in the volume of the added reagent to different buffer solutions

Figure 2 shows that the actual response of arsenic on platinum electrode was quick when Na_2SO_4 was used as buffer solution at concentration of 0.1M at which arsenic was successfully determined quantitatively. While the real concentration of arsenic in a solution with a buffer 0.1M was obtained, using Na_2SO_4 0.1M the reaction was very slow and there was a deviation from the real value of arsenic concentration.

MONITORING OF DETECTION LIMIT

The detection limit of arsenic was potentiometrically determined at pH of 8 using Na_2SO_4 0.1M as a buffer solution

Fig 3 shows the integral curves of potential changes along with the changes of reagent volume that was added for idiometric titration of arsenic of different solutions and at different concentrations
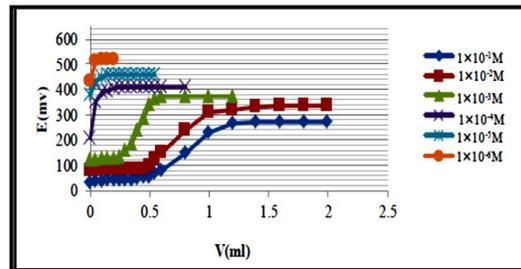

Figure 3 Integral curves of variation in potential versus change in the volume of the added reagent to solutions of different arsenic levels

It was concluded that the minimum concentration of arsenic solution which was successfully analyzed using automatic potentiometric was 1×10^6 mol / l and it was considered the experimental value of detection limit. This value is good in comparison with other techniques utilized for arsenic determination. Theoretically, the value of arsenic detection limit can be calculated by the following equation:

L=2SD

Hence, the theoretical value of detection limit equals to

L=2×(2.5×10^{-6}) =5×10^{-7} mol/l

Table 2 statistical findings of arsenic contained-solutions of different concentrations (1×10⁻¹M – 1×10⁻⁶ M)

Theoretical concentration(M)	Actual concentration(M)	Standard deviation SD	Relative standard deviationRSD %	Recovery R%	Confidencelimit
1×10^{-1}	0.99×10^{-1}	1×10^{-3}	1	99.5	$0.99\times10^{-1} \pm 2.4\times10^{-3}$
1×10^{-2}	0.97×10^{-2}	1.4×10^{-4}	1.4	98.5	$0.97\times10^{-2} \pm 3.4\times10^{-4}$
1×10^{-3}	0.98×10^{-3}	1.2×10^{-4}	1.2	99	$0.98\times10^{-3} \pm 2.9\times10^{-4}$
1×10^{-4}	0.96×10^{-4}	2.1×10^{-5}	2.1	98	$0.96\times10^{-3} \pm 5.2\times10^{-5}$
1×10^{-5}	0.97×10^{-5}	1.6×10^{-6}	1.6	98.5	$0.97\times10^{-5} \pm 3.9\times10^{-6}$
1×10^{-6}	0.94×10^{-6}	2.5×10^{-7}	2.5	97	$0.94\times10^{-6} \pm6.9\times10^{-7}$

Table 2 reveals the findings for errors calculation and regression of the analysis frequencies (n=3)

It was noticed from the findings the degree of closeness between the estimate and calculated concentrations according to the suggested method. This affirmed the effect of potentiometric titration which was reliable and precise due to the decrease in values of SD and RSD

APPLICATIONS OF POTENTIOMETRIC TITRATION TO ENVIRONMENTAL SAMPLES

Optimizing the conditions, potentiometry was applies to some model samples that were taken from environmental sources which are supposed to contain (a sample of drug used by dentist for killing tooth nerve; it contains high level of arsenic i.e. each 1 g of drug sample contains 0.0001 g of arsenic),waste water was collected from three regions on Latakia countryside, samples of waste water irrigated and unirrigated soil were collected from two sites in Latakia country side, and samples of cabbage of red and white types grown on waste water irrigated soil. The samples were then prepared for analysis as follows:

-DRUG SAMPLE:

1g of drug sample was taken and digested in 10ml of concentrated nitric acid, the solution was then filtered after cooling and diluted with 100ml of distilled water. The resulted solution was analyzed according to the suggested method [17]

 -WASTE WATER SAMPLE:

100 ml of filtered waste water and heated to obtain 10ml volume, the solution was then analyzed according to the suggested method [17]

-SOIL SAMPLE:

1g of soil sample was weighed and placed in a 100 ml beaker. The sample was four times digested using concentrated hydrochloric acid. Hence the resulted solution was boiled for half an hour and then it was left to cool at room temperature. Finally, the solution was analyzed according to the suggested method [17]

-WHITE AND RED VARIETIES OF CABBAGE

10g of cabbage was taken and digested in 50 ml of concentrated nitric acid. The solution was diluted with distilled water to obtain 100 ml volume. The resulted solution was thus analyzed according to the suggested method [17]

The following figures show the integral and differential curves of potential change along with changes in reagent volume that was added for idiometric titration of arsenic that was found in various environmental samples. Figs 4-13
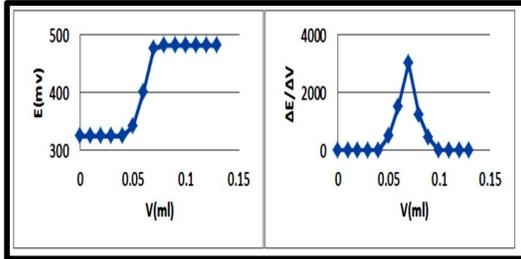

Figure 4 Differential and integral curves of variation in potential versus change in the volume of the added reagent to a drug sample
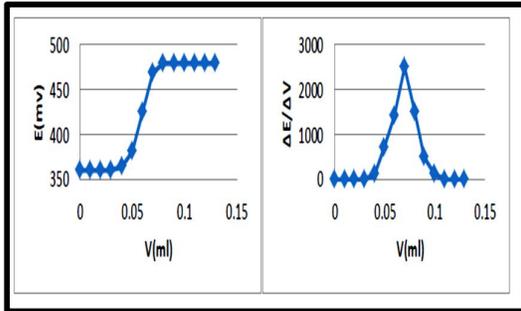

Figure 5 Differential and integral curves of variation in potential versus change in the volume of the added reagent to wastewater sample from Al-Hara region
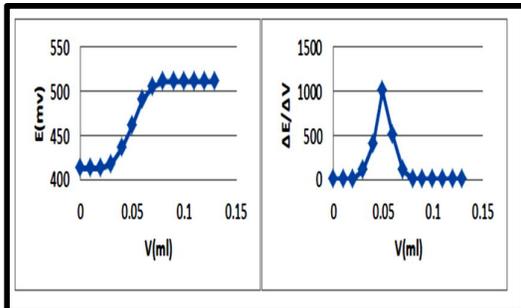

Figure 6 Differential and integral curves of variation in potential versus change in the volume of the added reagent to wastewater sample from Habeit region
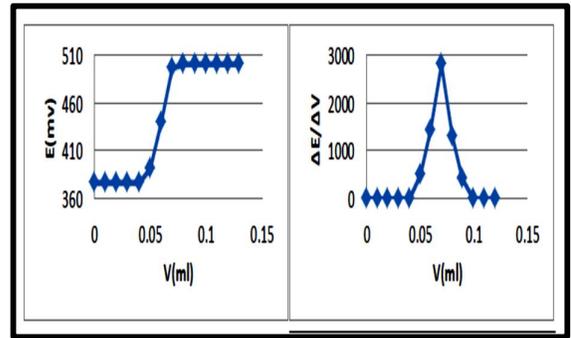

Figure 7 Differential and integral curves of variation in potential versus change in the volume of the added reagent to waste water sample from Marj -Meirban region
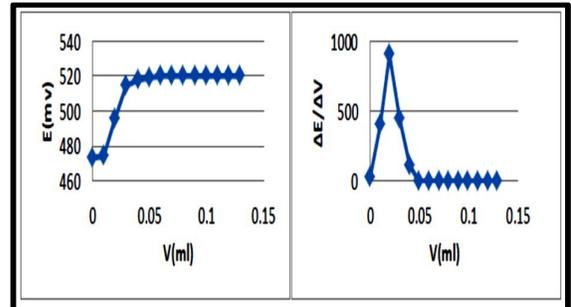

Figure 8Differential and integral curves of variation in potential versus change in the volume of the added reagent to wastewater unirrigated soil sample fromAl-Hara region
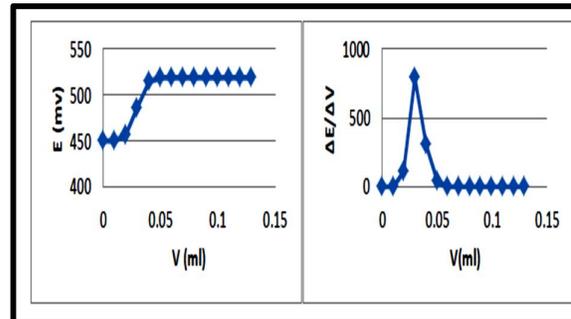

Figure 9 Differential and integral curves of variation in potential versus change in the volume of the added reagent to wastewater unirrigated soil sample from Habeit region

Figure 10 Differential and integral curves of variation in potential versus change in the volume of the added reagent to wastewater irrigated soil sample from Al-Hara region
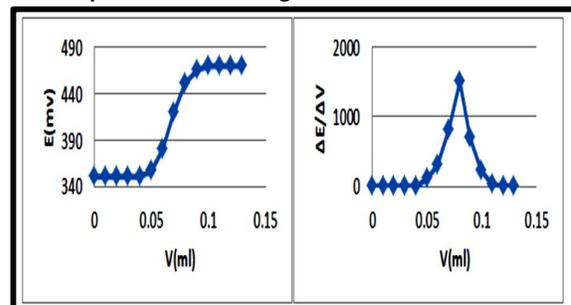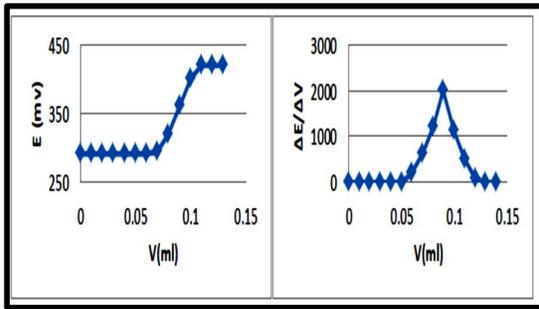
The Pharma Research (2014)10(2) 1-14

Figure 11 Differential and integral curves of variation in potential versus change in the volume of the added reagent to wastewater irrigated soil sample from Habeit region
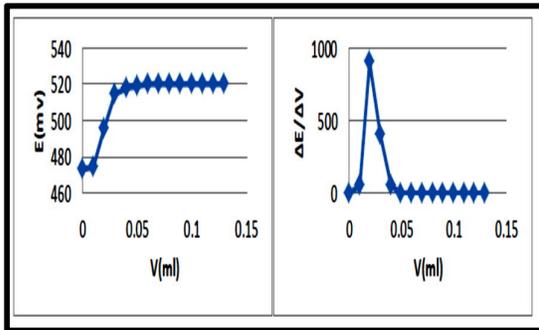

Figure 12 Differential and integral curves of variation in potential versus change in the volume of the added reagent to white cabbage sample
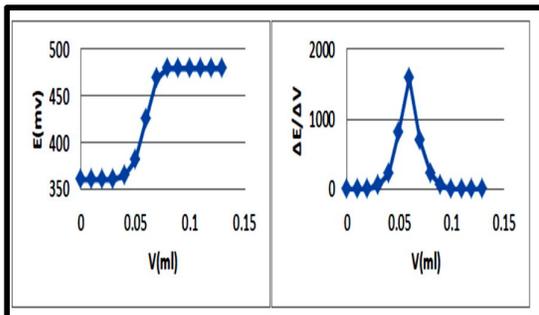

Figure 13 Differential and integral curves of variation in potential versus change in the volume of the added reagent to red cabbage sample

Table 3 arsenic levels in the studied samples considering error calculation of analysis frequencies(n=3)

SAMPLE	CONCENTRATION	STANDARD DEVIATION SD	RELATIVE STANDARD DEVIATION RSD%	CONFIDENCE LIMIT X±ΔX
Drug	1.0g/kg	0.8×10^{-1}	0.8	$1 \pm 1.4\times10^{-1}$
Waste water Al-Hara region	1.1×10^{-4}g/l	1.1×10^{-5}	1.1	$1.1\times10\text{-}4 \pm 2.2\times10^{-5}$
Waste water Habeit region	1.8×10^{-4}g/l	1.6×10^{-5}	1.6	$1.8\times10\text{-}4 \pm 2.7\times10^{-5}$
waste water Marj-Meirban region	2.2×10^{-5}g/kg	1.4×10^{-6}	1.2	$2.2\times10\text{-}5 \pm 1.9\times10^{-6}$
Waste water Unirrigated soil -Al-Hara region	2.3×10^{-5}g/kg	2.1×10^{-6}	2.1	$2.3\times10\text{-}5 \pm3.2\times10^{-6}$
Waste water unirrigated soil Habeit region	3.4×10^{-5}g/kg	1.4×10^{-6}	1.4	$3.4\times10\text{-}5 \pm 3.9\times10^{-6}$
Waste water irrigated soil Habeit region	1.7×10^{-3}g/kg	2.5×10^{-5}	2.5	$1.7\times10\text{-}3 \pm4.6\times10^{-5}$
Waste water irrigated soil-Al-Hara region	1.8×10^{-4}g/kg	1.2×10^{-5}	1.3	$1.8\times10\text{-}4 \pm3.4\times10^{-5}$
White cabbage	7.4×10^{-7}g/kg	3.1×10^{-8}	3.1	$7.4\times10\text{-}7 \pm5.3\times10^{-8}$
Red cabbage	1.2×10^{-7}g/kg	2.1×10^{-8}	2.1	$1.2\times10\text{-}7 \pm3.8\times10^{-8}$

Table 3 reveals the findings of arsenic levels in the studied samples and error calculation of analysis frequencies n=3.

It was noticed from the findings that arsenic level in drug samples and errors equals to 1mg/g, which is considered accurate according to the ingredients of the studied drug sample. Hence the applied method is effective and reliable for arsenic determination. It was also noticed that arsenic levels were high in waste water samples in **Al-Hara and Habeit** sites in comparison with that of Marj –Meirban. Previous studies showed that arsenic level in rainfall ranged from 0-5µg/l, 0.5-2µg/l in sea water 1-2µg/l in mineral water, and 48mg/l near mineralization sites. But, arsenic level ranged from 0.1-2mg /l in waste waters and all detected results were within natural limits even though. According to soil samples, it was noticed that arsenic level was low in wastewater unirrigated soil in comparison with waste water irrigated soil. Arsenic levels in soil and sediments depend on geological conditions, human activities like using insecticides, mineralization and industry. Previous studies showed that arsenic level in unpolluted soil was less than 15mg As/kg and more than 100mg As/kg in polluted soil. Besides, it could reach 27000 mg As/kg in electronic and industrial waste polluted soil. From the findings the detected value of arsenic in wastewater-irrigated soil was relatively low [20]

According to cabbage samples ,very low amount of arsenic was noticed since plants contain residues of organic arsenic which originate from inorganic species of arsenic –it accumulate in plants through root absorption or through airborne arsenic precipitation on leaves. Therefore arsenic levels are higher in living organisms that live next to pollution sources due to human activities.[21]

CONCLUSIONS

In the present research a new technique for electrochemical analysis to determine arsenic traces in water samples, potentiometric titration was involved thus the ultimate conclusions were as follows.

*utilization of new and feasible analytical method for arsenic determination

*successful utilization of potentiometric titration of arsenic as shown from accurate redox values that obtained with low RSD.

*The ability to utilize potentiometric titration of arsenic traces in a number of environmental samples at pH=8 using Na_2SO_4 as a buffer solution at a concentration of 0.1M and a potentiometer.

*The efficiency of potentiometric titration of arsenic traces in a number of environmental sample

*The sensitivity of this method was elevated with detection limit in the ppm range

ACKNOWLEDGMENTS

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