European Journal of Clinical Pharmacy
Print ISSN: 2385-409X **Online ISSN**: Applied Website:
https://farmclin.com/

Indirect Potentiometric Titration Determination of Arsenic (III) in Aqueous Solutions

Huda Jaber Hussain[1]* and Yahea Kamal Al-Bayati[2]

[1]Market Research and Consumer Protection Center, University of Baghdad, Baghdad, Iraq
[2]Department of Chemistry, College for Science, University of Baghdad, Baghdad, Iraq
* Corresponding author: hudajaber@mracpc.uobaghdad.edu.iq

ABSTRACT

The accurate determination of arsenic in real samples is vital for safeguarding public health, ensuring environmental sustainability, and maintaining food safety. This paper introduces a simple and cost-effective approach for the determination of arsenic (III) concentrations using indirect potentiometric titration approach. The method utilizes the titration of a complex formed between arsenic (III) and chemically generated chloride in aqueous solutions. It was shown that the ion selective electrode exhibits a rapid response to arsenic ions under the optimized conditions, including medium pH, electrolyte type, and electrolyte concentration. The developed method enables the quantification of arsenic ion with a detection limit of 5×10-4 mol/L. Statistical analysis is employed to establish confidence limits, ensuring the accuracy and precision of this approach for the determination of arsenic ion in aqueous media. Furthermore, the efficacy of the method is validated by applying it for analysis of arsenic ion in different real samples, such as medicine, water, and solid samples, yielding satisfactory results.

KEYWORDS: Arsenic, indirect potentiometry, ion selective electrode, real sample analysis.

How to Cite: Huda Jaber Hussain and Yahea Kamal Al-Bayati., (2026) Indirect Potentiometric Titration Determination of Arsenic (III) in Aqueous Solutions, European Journal of Clinical Pharmacy, Vol.8, No.1, pp. 2529-2536

INTRODUCTION

Arsenic, a semi-metal belonging to the Nitrogen family, is odorless and tasteless. It can form both organic and inorganic compounds, with the latter being the most toxic and commonly found in water [1-3]. Arsenic occurs naturally in rocks, soil, water, air, plants, and animals. It is released into the environment through volcanic activity, rock erosion, forest fires, and industrial processes, with approximately 90 percent originating from industrial sources. Arsenic is used as a preservative in wood, paints, dyes, medicines, soaps, and semiconductors. Certain fertilizers, animal feeding processes, and practices such as copper smelting, mining, and coal combustion also contribute to environmental arsenic levels [4-7]. Exposure to arsenic can occur through inhalation or direct contact with the skin [8]. The health effects of arsenic can vary depending on its form, with the organic form being less toxic than the non-organic form [9]. The extent of exposure, duration, and an individual's ability to metabolize arsenic also influence its potential health effects [10,11]. Long-term exposure to elevated arsenic levels can lead to various health problems, including certain types of cancer (bladder, lung, skin, kidneys, prostate, and liver), fibrosis and cirrhosis of the liver, peripheral nerve damage, changes in skin color and thickness [12]. Several laboratory methods are available to detect and identify arsenic. The most common analytical procedure is Atomic Absorption Spectroscopy (AAS), while techniques such as Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) are increasingly used for arsenic analysis [13-15]. Other methods include Neutron Activated Analysis (NAA) for biological fluids and tissues, and X-ray analysis for biological materials and environmental samples [16,17]. Electrochemical methods like amperometry, kilometric voltage, and selective electrode ions [18,19] are also employed. Selective electrode ions offer several advantages, making them the subject of continuous research. They are inexpensive, easy to use, and applicable across a wide range of concentrations. Made of solid components within a plastic body, they are durable, compact, and lightweight, making them ideal for laboratory and continuous monitoring applications such as potentiometric titration and monitoring food and drug metabolism. They can also be used in aquatic solutions across a wide thermal range. Selective electrode ions have demonstrated reliability and accuracy, making them preferable to more sophisticated and costly analytical technologies [18,19]. In aqueous systems, the speciation of arsenic, particularly As(III), is governed by pH, redox potential, and the nature of dissolved species. The redox behavior of arsenous acid (H_3AsO_3) in water is central to its detection, especially due to its equilibrium with arsenite ions and sensitivity to oxidants such as chlorine. Recent studies (e.g., Smith et al., 2022; Zhang & Liu, 2023) emphasize the pH-dependent solubility and transformation of arsenic species in aqueous matrices, underlining the importance of solvent conditions in analytical methods(20,21).

This research introduces a novel approach to determine arsenic concentration in aquatic media by calibrating it with chemically generated chloride in a reaction medium using the ion selective electrode. The method is applied to environmental samples to assess the pollution effect of arsenic. The research utilizes the modern and innovative technique of indirect potentiometric titration by generating the reagent in a reaction medium.

MATERIAL AND METHODS

Chemicals

Double distilled water was utilized along with a group of high-purity materials including As_2O_3, potassium chloride, potassium permanganate, sodium hydroxide, sulfuric acid, and an ionic strength control solution for chloride ions.

Calibration of ion selective electrode

Standard stock solutions were prepared by diluting a basic chloride solution with varying concentrations ranging from 0.1 mol/L to 1 x 10^{-5} mol/L. To ensure consistent ionic strength, an ionic strength control solution was added to each standard solution. The electrode was then calibrated using the calibration method specific to the device.

RESULTS AND DISCUSSION

The calibration of arsenic with chlorine was conducted indirectly using the selective chloride electrode in aquatic media. The calibration process involved determining a specific solution volume, which was calculated based on a specific volume of chlorine generated in the reaction medium. The reactions involved in this process are represented as:

$$As_2O_3 + 6NaOH \rightarrow 2Na_3AsO_3 + 3H_2O$$

$$Na_3AsO_3 + 3H_2SO_4 \rightarrow 2H_3AsO_3 + 3Na_2SO_4$$

$$H_3AsO_3 + H_2O + Cl_2 \rightarrow H_3AsO_4 + 2HCl$$

The chloride oxidation reaction with generated chlorine involved the following steps: briefly, 10 ml of potassium chloride solution (KCl) was added to a cell to generate chloride ions. Then, 10 ml of concentrated potassium permanganate solution ($KMnO_4$) was introduced into the cell within a highly acidic medium using concentrated sulfuric acid (H_2SO_4). The solution was heated under the gas withdrawal window, causing the color of the potassium permanganate solution to partially or completely disappear. This color change indicated the release of chlorine gas. To detect the presence of chlorine gas, we used a starch-moistened sheet that was exposed to an iodine solution. The reaction can be represented as:

$$10Cl^- + 2MnO_4^- + 16H^+ \rightarrow Mn^{2+} + 5Cl_2 + 8H_2O$$

In the presence of chlorine, a blue color appears due to the formation of elemental iodine:

$$2KI + Cl_2 \rightarrow KCl + I_2$$

All oxidation reactions of chloride ions (Cl^-) occur in a strongly acidic medium, and chloride is not oxidized in a neutral medium. Potassium permanganate is preferred as the oxidizing agent because it undergoes a noticeable color change (disappears) in the presence of chloride ions (Cl^-), making the reaction more distinct. Heating serves to activate and enhance the oxidation reaction.

The effect of pH

The effect of pH on the measurement process is assessed. A series of experiments were carried out at different pH values ranging from 2 to 10. Figure 1 depict the integrated and differential curves, showcasing the changes in potentiometric values 0.05 mol/L arsenic solution. These changes were observed by varying the reagent added during the chlorine-arsenic titration at different pH values.

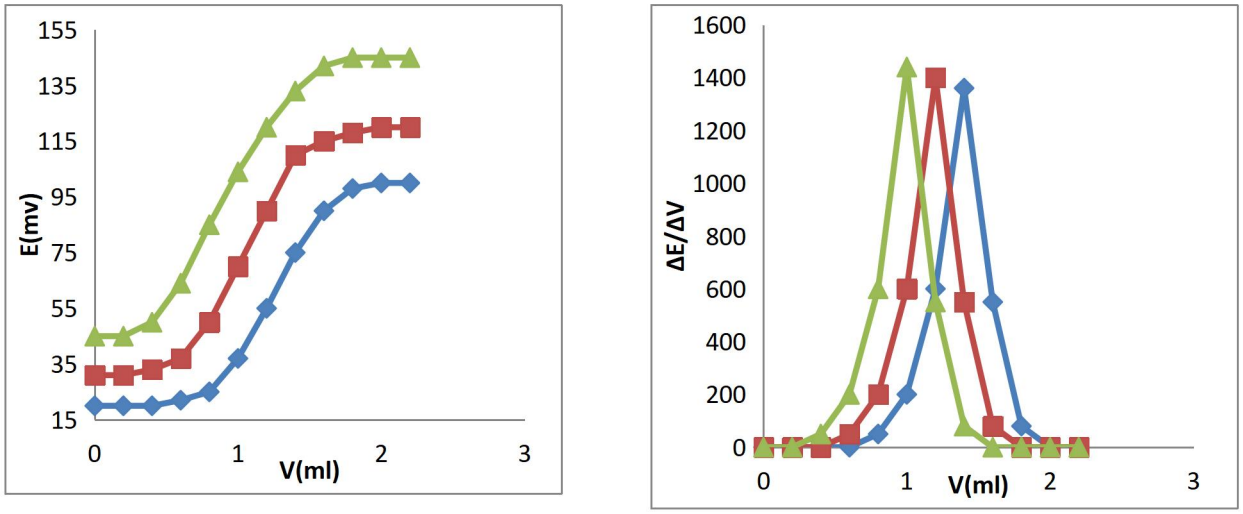


Figure 1a: The integral curves depicting the variation in the reagent volume at different pHs
1b: The differential curves illustrating the reagent volume at different pHs. (blue show pH 6, red show pH 7 and green shows pH 8).

The results of this study show that at pH values ranging from 2 to 5, the potentiogram does not provide any indication of the occurrence of the reaction. This is because chloride ion is automatically oxidized. However, at pH values between 6 and 8, a distinct curvature is observed in the potentiogram, indicating the presence of a usable calibration endpoint. The real value of the Arsenic concentration is found at pH 7. It is important to note that titration cannot be carried out in a strongly alkaline medium. In such conditions, chlorine is readily involved in the oxidation reaction and undergoes auto-return. This causes the formation of a mixture of chloride and hypochlorite ions. The results of this study indicate that the appropriate pH for titration potentiometric of Arsenic with iodine is 7.At pH 7, As(III) remains predominantly as H_3AsO_3, minimizing hydrolysis and ensuring consistent reactivity with Cl_2. Moreover, chlorine gas exhibits moderate solubility at neutral pH, enabling sufficient oxidative potential without rapid disproportionation. Thermodynamic data indicate a pKa_1 of H_3AsO_3 around 9.2, favoring the undissociated form under neutral conditions, which is essential for controlled redox interactions(22).
The effect of electrolyte

To assess the effect of electrolytes on the reaction, a series of electrolytes, including sodium hydroxide (NaOH), sodium bicarbonate ($NaHCO_3$), and sodium carbonate (Na_2CO_3), was examined.

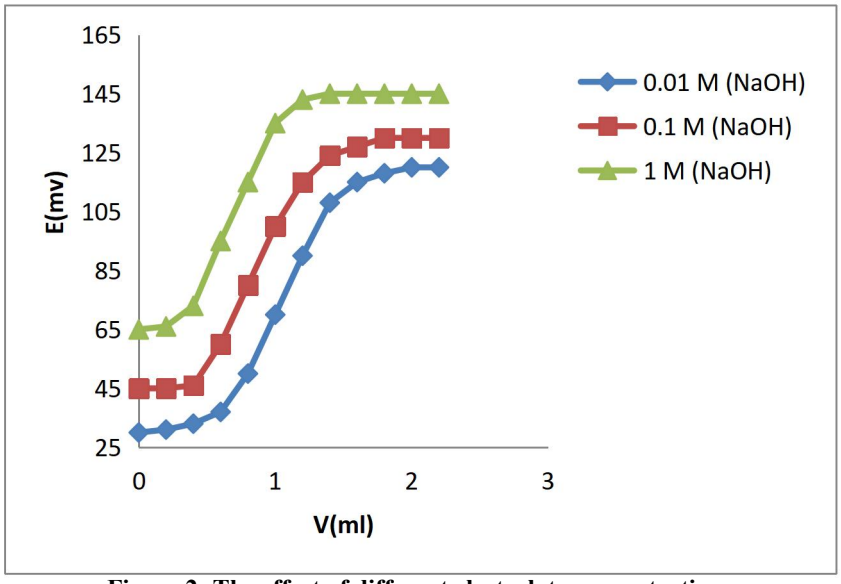


Figure 2: The effect of different electrolyte concentrations

As shown in Figure 2, the maximum signal was appeared when NaOH at concentration of 0.01 M there was a shift from the Arsenic concentration. For other electrolytes ((Na_2CO_3, $NaHCO_3$) with their different concentrations, they did not give a clear wave neither an indication of occurrence reaction thus not valid for use as electrolytes to determine Arsenic. Figure 2 illustrates the optimal analytical conditions for titration of a 0.5mol /L of Arsenic solution with chlorine in potentiometric method using the selective chloride electrode. NaOH was selected over Na_2CO_3/$NaHCO_3$ because it maintains stronger pH control around neutral levels and avoids carbonate–chlorine side reactions. Higher ionic strength from NaOH improves Cl^- activity corrections using Debye–Hückel theory(23).

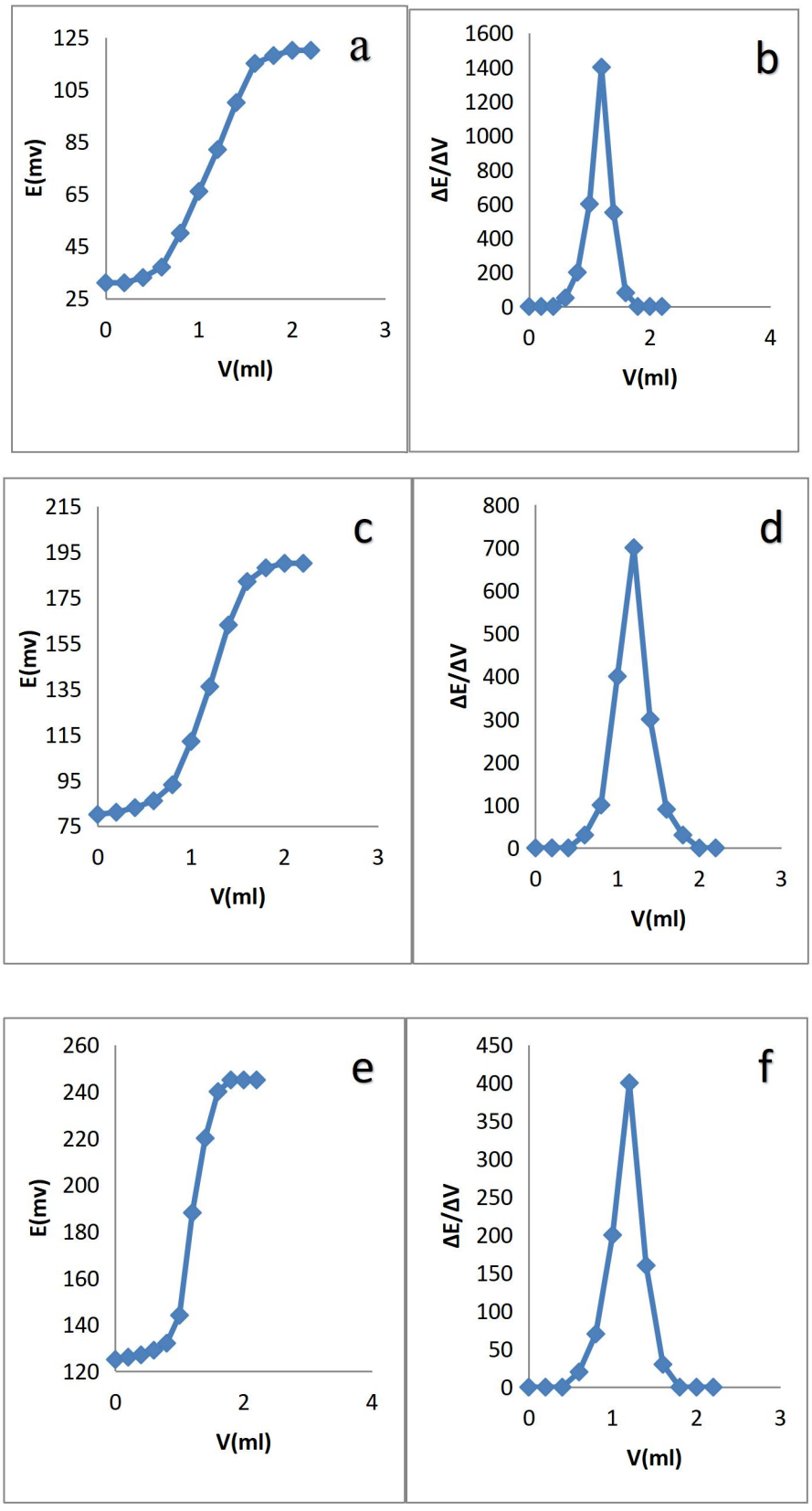
Table 1. Comparison of NaOH and carbonate-based systems in the titration of As(III) with Cl_2 (24,25)

Parameter	NaOH system	Na_2CO_3 / $NaHCO_3$ system
Conductivity (S/m)	High (strong electrolyte) → stable potential response	Moderate (weaker electrolyte) → slower electrode response
Buffer capacity (pH ~7)	Strong → maintains pH effectively	Moderate → may shift pH during titration
Cl_2 yield stability	High → minimal side reactions	Lower → carbonate may react with Cl_2 forming hypochlorite
Ionic strength effect	Predictable → Debye–Hückel corrections applicable	Variable due to carbonate equilibria
Interference risk	Low (no secondary equilibria)	Moderate (CO_3^{2-} can compete for proton equilibria)
Practicality	Preferred for precise potentiometric titration	Less accurate for potentiometric detection

Detection Limit

In order to obtain the detection limit, we prepared several Arsenic solutions with concentrations ranging from 0.5 mol/L to 5 x 10^{-4} mol/L at a pH of 7. Sodium hydroxide was used as a buffer solution at a concentration of 0.01 M. Figures 3, display the integrated and differential curves illustrating the changes in potentiometric values as the reagent volume is adjusted during the Arsenic indirect potentiometric titration using chlorine, In matrices such as sewage or soil extracts, metal cations (e.g. Fe^{3+},

Cu^{2+}) may consume Cl_2 and interfere with endpoint detection. Addition of EDTA (~1 mM) effectively masks these ions, thereby preserving accurate potentiometric detection of As(III)(26).



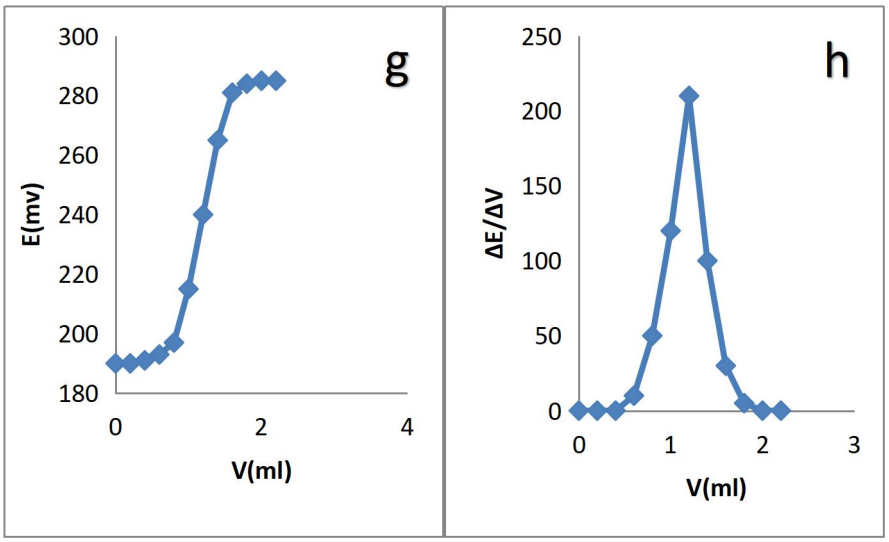


Figure 3: The potential change at a,b: 5×10^{-1}mol / L; c,d: 5×10^{-2} mol / L; e,f: 5×10^{-3}mol / L; g,h: 5×10^{-4} mol / L of Arsenic

In continue, the temporal differential curves of potentiometric changes by varying the reagent volume during the Arsenic potentiometric calibration in different concentrations was investigated. This analysis used to validate the method by comparing the values of differential timescales with the regular curves. Figures 4, present the temporal differential curves illustrating the potentiometric changes as the reagent volume is adjusted. These figures provide further insights into the kinetics of the reaction and the dynamic behavior of the system during the Arsenic potentiometric calibration process.

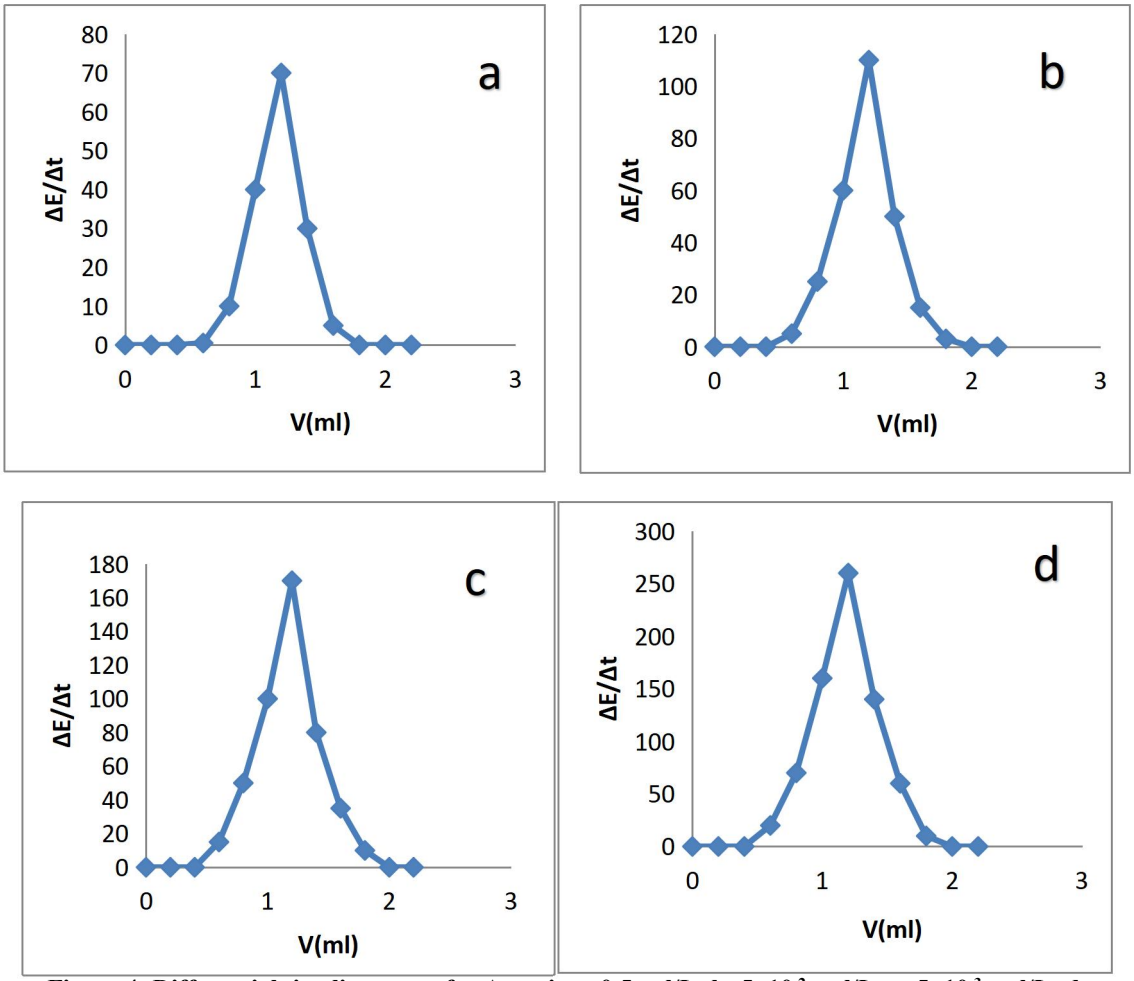


Figure 4: Differential timeline curve for Arsenic a: 0.5mol/L; b: 5×10^{-2} mol/L; c: 5×10^{-3} mol/L; d: 5×10^{-4} mol/L.

The results of this study show that the minimal concentration of Arsenic solution (5 x 10^{-4} mol/L) was successfully analyzed using indirect potentiometric titration with a ion selective electrode. Figure 5 illustrates the relationship between the concentration of the Arsenic solution and the corresponding volume. The results of this study demonstrate a linear relationship

between the concentration and volume, indicating the ability to analyze a range of concentrations within this range.

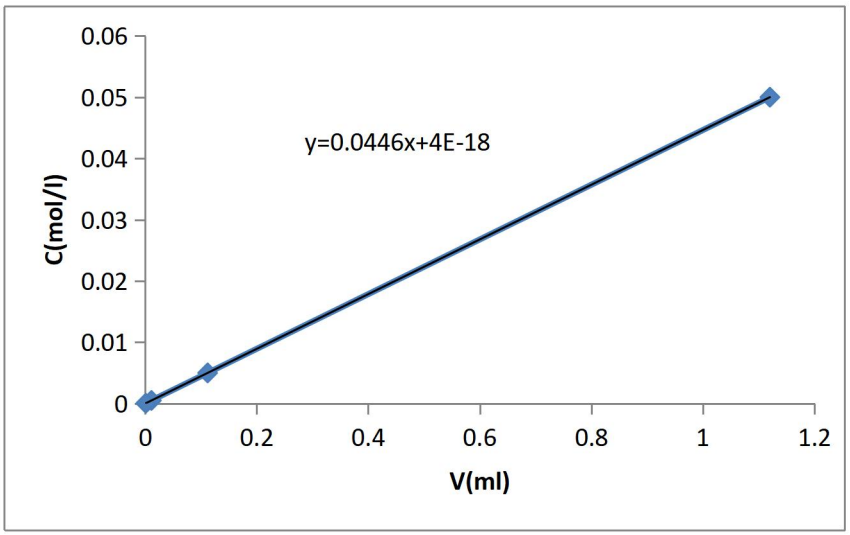


Figure 5: The relationship between Arsenic concentration with volume

Statistical Analysis

Statistical analysis was performed by calculating the standard deviation, relative standard deviation, confidence interval, and a retrospective analysis.

Retrospective Analysis

For this test, we prepared Arsenic solutions with known concentrations and analyzed them using an automatic potentiometric titration electrode based on the proposed method. The results obtained were compared to the prepared concentrations, and the difference between the calculated concentration (actual) and the prepared concentration was determined using the relationship:

$$\text{Recovery } \% = C_A/C_{th} \times 100$$

Where C_A is material concentration calculation according to proposed method (actual concentration) and C_{th} is prepared substance concentration (theoretical concentration). This retrospective analysis allowed us to evaluate the accuracy of the proposed method by assessing the agreement between the calculated concentrations and the prepared concentrations. Table 1 shows the results of calculating errors and retrospective for analyzed repeaters (n = 3).

Table 1: The Statistical results (n=3) of Arsenic solutions with different concentrations (5×10^{-1} M - 5×10^{-5} M).

Added (M)	Found (M)	Standard Deviation (SD)	Percentage Standard Deviation (RSD)	Retrospective % (R)	Confidence limit (X±ΔX)
5×10^{-1}	4.98×10^{-1}	1.2×10^{-2}	2.4	99.6	$4.98\times10^{-1}\pm 3.1\times10^{-2}$
5×10^{-2}	4.98×10^{-2}	1.3×10^{-3}	2.6	99.6	$4.98\times10^{-2}\pm 2.9\times10^{-3}$
5×10^{-3}	4.97×10^{-3}	1.5×10^{-4}	3.0	99.4	$4.97\times10^{-3}\pm 3.4\times10^{-4}$
5×10^{-4}	4.96×10^{-4}	1.7×10^{-5}	3.4	99.2	$4.96\times10^{-4}\pm 3.1\times10^{-5}$

The results of this study (table 1) show that there is an agreement between the prepared and calculated concentrations using the proposed method. This convergence indicates the effectiveness of the method in the determination of Arsenic. Additionally, we observed a significant improvement in the accuracy of the method, as evidenced by the decrease in both the RSD% and SD values. This indicates that the method consistently provides precise and reliable measurements, enhancing its overall accuracy.

Real sample analysis

This method was successfully applied to analyze a variety of real samples. The samples analyzed included a drug sample used in dental clinics, which is known to contain a high concentration of Arsenic (0.0001g of Arsenic per 1g of the drug). Additionally, sewage water samples were collected from three different areas in Baghdad city, as well as irrigated and non-irrigated soil samples with sewage water collected from two areas in Baghdad city. Table 2 presents the results of Arsenic concentration in the real samples, along with the calculation errors for the analyzed replicates (n=3).

Table 2: Real sample analysis

Sample	Found	SD	RSD (%)	Confidence limit (X±ΔX)
Medicine	0.99 g/k	1×10^{-2}	1	$0{,}99\pm 1.5\times10^{-1}$
Sewage water (Huriya)	1.3×10^{-4}g/l	1.4×10^{-6}	1.1	$1.3\times10^{-4}\pm 1.9\times10^{-6}$
Sewage water (Shaab)	1.7×10^{-4}g/l	1.9×10^{-6}	1.2	$1.7\times10^{-4}\pm 2.5\times10^{-6}$
Sewage water (Husaynia)	2.3×10^{-5}g/l	3.2×10^{-7}	1.4	$2.3\times10^{-5}\pm 2.2\times10^{-7}$
non-irrigated soil (Huriya)	2.5×10^{-5} g/kg	3.6×10^{-7}	1.5	$2.5\times10^{-5}\pm2.7\times10^{-7}$
non-irrigated soil (Shaab)	2.9×10^{-5}g/kg	3.3×10^{-7}	1.1	$3.2\times10^{-5}\pm 2.4\times10^{-7}$
irrigated soil (Husaynia)	1.4×10^{-3}g/kg	2.5×10^{-5}	1.8	$1.9\times10^{-3}\pm3.1\times10^{-5}$
irrigated soil (Huriya)	1.7×10^{-4}g/kg	1.9×10^{-6}	1.1	$1.7\times10^{-4}\pm3.4\times10^{-6}$

From the results obtained, it was found that the Arsenic concentration in the drug sample was determined to be 1 mg/g, which aligns with the known composition of the drug used in this study. This confirms the accuracy and reliability of the method used for Arsenic analysis. In the sewage samples, we noticed a higher presence of Arsenic concentrations in the Huriyaand Shaab compared to the Husaynia region. Studies have indicated that Arsenic concentrations in wastewater typically ranged between 0.1 mg/L and 2 mg/L. Upon analyzing the results, we find that the calculated Arsenic values fall within this natural limit. Regarding the soil samples, we observed that the soil irrigated with wastewater exhibited higher Arsenic concentrations compared to the soil that was not irrigated with wastewater. The presence of Arsenic in soil and sediments is influenced by geological conditions and human activities such as pesticide use, mining, and industrial processes. Studies have shown that Arsenic concentrations in unpolluted soils are usually below 15 mg As/kg, while contaminated soils can exceed 100 mg As/kg. In cases of soil contamination with industrial and electronic waste, concentrations can reach up to 27,000 mg As/kg. However, based on the results obtained, we observed relatively low Arsenic values in the irrigated wastewater samples. Overall, these findings highlight the capability of the method to accurately detect and quantify Arsenic concentrations in various samples.

CONCLUSION

In conclusion, a new, easy, and cost-effective analytical method for the determination of Arsenic in real samples was developed. The developed indirect potentiometric titration method seems to be suitable for determining the Arsenic at pH of 7, using NaOH as the electrolyte. The indirect potentiometric titration method with the ion selective electrode demonstrated its effectiveness and accuracy in determining Arsenic, as evidenced by the good retrospective values with low RSD% values.

Conflict of interest statement

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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