

A Portable Non-Destructive Tool for Uranium Determination in Aqueous Samples

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Abstract: *The interest in nuclear safeguards is constantly growing, as more nuclear programs are being exposed all over the world. In this work, a simple, rapid and reliable method has been applied for the determination of uranium content in aqueous media based on using potentiometric sensor. The developed tool was found to be capable of verifying the operator declarations in a wide concentration range with a considerable accuracy and precision. The developed tool offers the advantage of field verification of uranyl concentration rather than taking samples for further analysis. Effect of temperature of the test solution was investigated and the isothermal temperature coefficient of the electrode was estimated. The results obtained applying this potentiometric electrode is comparable with the data obtained using UV-Visible and ICP-OE spectrometers.*

Keywords: *Nuclear safeguards; Potentiometric electrodes; Non-Destructive assay; Uranyl ions.*

I. Introduction

The nuclear safeguards system which is used to monitor compliance with the Nuclear Non-proliferation Treaty (NPT) relies to a significant degree on Nuclear Material (NM) accountancy to assure that NM is not diverted from declared activities, and that undeclared activities have not occurred. NM accountancy relies on both Non-destructive analysis (NDA) and Destructive analysis (DA) in order to independently verify state declarations. DA of NM samples plays an important role in the verification of the declared inventories of U, Pu and Th element amounts and ²³⁵U and ²³³U isotopic amounts in bulk handling facilities along all points of the nuclear fuel cycle. NDA offers rapid analysis times and percent-or-better levels of precision, all within ever smaller and portable packages. These systems are therefore used in bulk handling facilities for tracking material movement and confirming item-level declarations. Nevertheless, the precision of destructive analytical techniques is in most cases superior because the effect of the sample matrix can be eliminated or corrected for. In addition the detection limit of destructive analysis techniques is usually lower than non-destructive techniques because the measurement methods involve counting of atoms versus activity counting. On the other hand, destructive analysis techniques are labor intensive and time consuming to conduct, requiring days or weeks for sample preparation [1-2].

Using of reliable techniques is very vital for verification and control of uranium in the field of nuclear safeguards and ultra-trace environmental analysis. In the framework of the international safeguards, uranium in all stages of the nuclear fuel cycle must be quantitatively and precisely determined [3]. Selection of the most appropriate method for the determination of uranium depends on many parameters: the purpose of analysis, the nature of sample, the concentration of uranium, the presence and concentration of the other elements in the matrix, the methodology available, the accuracy required, simplicity, rapidity, easy calibration and optimization of the instrument, minimum generation of analytical waste, etc [4, 5]. There are various analytical methods available for the determination of uranium in various matrices. Different radiometric methods, such as gamma (γ)- spectrometry [6], alpha (α)-spectrometry [7] and beta (β)-counting [8], and mass spectrometric methods, such as inductively coupled plasma mass spectrometry [9], accelerator mass spectrometry [10], thermal ionization mass spectrometry [11], resonance ionization mass spectrometry [12] and secondary ion mass spectrometry [13] and their application for the determination of radionuclides are existed. The determination of uranium using colorimetric and atomic spectrometric techniques is widely practiced [14-18]. Electroanalytical techniques such as amperometry [19], voltammetry [20] and potentiometry [21] were also applied for uranium determination.

The development and application of ion-selective electrodes (ISEs) continue to be interesting and expanding areas of analytical research. ISEs are suitable for use in routine analysis and field applications owing to their portable instrumentation character, low power requirements, fast analysis time, adequate accuracy and precision and wide working concentration range. Clearly the ability to make direct or indirect measurement in complex samples without concerning about sample color or turbidity and the fact that such measurements require relatively simple and inexpensive equipment make ISE-based techniques attractive to scientists in any disciplines [22].

Uranyl ion selective electrodes (UO_2^{2+} - ISE) method is one of the sensitive and fast methods for the determination of uranium. Several developed or commercially available UO_2^{2+} - ISEs have been employed to determine uranium [23-26]. However, to our best knowledge, no information is available on the in-field determination of uranium employing UO_2^{2+} - ISE in nuclear safeguards applications. Recently, we developed a uranyl polymeric membrane electrode based the low-cost and commercially available Cyanex extractants and different parameters affecting its response such as membrane composition, response time, medium pH, and interfering ions were optimized [24]. In this study, the optimized membrane electrode based on Cyanex 301 was applied for in-field determination of uranyl ion concentration in real samples at some Egyptian nuclear facilities and other locations for safeguards verification purposes.

II. Experimental

2.1. Apparatus

All potentiometric measurements were made at ambient temperature with eight-channel electrode-computer interface (Nico2000 Ltd., UK) controlled by Nico-2000 software. A double junction Ag/AgCl reference electrode (Sentek, UK) was used for all mV measurements and combination glass electrode (Sentek, UK) was calibrated daily with pH 4.0 and 7.0 buffer solutions and was used for all pH measurements.

Philips IS-561 electrode body (Glasblaserei Möller, Zurich, Switzerland) was used as electrode body for the working electrode.

The working ion selective electrode, reference electrode, pH electrode, the eight-channel electrode-computer interface, laptop and an electrode stand were assembled and used as a portable kit in-field measurements.

The spectrophotometric analysis of uranium was performed on a UV-Visible spectrophotometer (Thermo Evolution 300- England) and inductively coupled plasma optical emission spectrometer (ICP-OES) (Thermo iCAP6500 - England).

2.2. Reagents

All chemicals used were of analytical reagent grade. All solutions were prepared with deionized water (18.2 M Ω cm) obtained from a SG, Ultra Clear purification system (UK). High molecular weight poly(vinyl chloride) (PVC) and selectphore grade tetrahydrofuran (THF) were obtained from Sigma-Aldrich (USA). Potassium tetrakis(4-chlorophenyl)borate (KTpCIPB) were obtained from Fluka (USA). Dioctyl adiapate (DOA) were obtained from Merck (Germany). Uranyl nitrate hexahydrate was obtained from Mallinckrodt Company and used as received. Cyanex 301 was supplied by Cytec Inc. (Canada) and used as received. Arsenazo III was obtained from Sigma-Aldrich (USA). Hydrochloric acid (Carlo Erba) and pure sodium hydroxide pellets (Merck) was used to adjust the sample pH.

2.3. Procedures

2.3.1. Construction of membrane electrodes

Polymer membrane electrodes were prepared according to the literature procedures [24]. Membrane cocktails were prepared by dissolving (relative to the ionophore weight) in ca. 2 mL of THF. A homogeneous mixture was obtained after complete dissolution of all membrane components. Then the mixture was poured into a 22 mm i.d. glass ring placed onto a glass plate and the ring was covered with a filter paper till complete evaporation of THF and formation of a transparent membrane (average thickness of ~ 0.2 mm). Smaller disks were cut and placed at the tip of a Philips IS-561 electrode body. The assembled electrode was then conditioned overnight in a solution composed of an equal volume of 10^{-3} mol L $^{-1}$ uranyl nitrate and sodium nitrate solutions.

2.3.2. Calibration of electrodes

The working electrode was calibrated by transferring certain aliquots of 10^{-7} to 10^{-1} mol L $^{-1}$ uranyl solutions into 100 mL beaker at 25°C followed by immersing the ISE in conjugation with Ag/AgCl reference electrode in the solution. The potential readings were recorded at a constant stirring when stabilized to ± 0.2 mV, and then the potential change was plotted against the logarithm of uranyl concentration to obtain the calibration curve which was used for determination of uranium content in real samples.

2.4. Real sample analysis

The real samples used in this study were uranyl nitrate solutions collected from one of the Egyptian nuclear facilities as a result of the uranyl solvent extraction research. Certain aliquot of each sample were transferred to a 50 mL beaker, the pH of the samples were adjusted to 3 using HNO_3 or NaOH, then it was transferred to 50 ml volumetric flask and made up to the mark with deionized water. The solution was finally transferred to a 100 mL beaker and these samples were used for UO_2^{2+} ion determination by ISE, UV and ICP-OES measurements for nuclear safeguards verification purposes.

2.4.1. UO_2^{2+} determination in real samples by direct potentiometry

Potential was measured employing the proposed ion selective electrode with respect to the Ag/AgCl reference electrode and the potential readings were recorded at a constant stirring when stabilized to ± 0.2 mV.

2.4.2. UO_2^{2+} determination in real samples by UV- Visible spectrophotometry

The standard Arsenazo III spectrophotometric method based on the formation of colored complexes was used for determination of uranium [27]. A 0.1% (w/v) arsenazo-III solution was prepared by dissolving appropriate amount of arsenazo-III in deionized water. A solution containing no more than 3.0 g of U(VI) transferred into a 25mL volumetric flask and 1.0 mL of 0.1% Arsenazo III solution was added. The concentration of hydrochloric acid was adjusted to 2.5 mol L^{-1} . The volume was made up to the mark with deionized water and the solution was mixed. After 15 min, the absorption spectra were recorded at λ_{max} of 650 nm against a reagent blank in a 3.3 mm cell [27].

2.4.3. UO_2^{2+} determination in water samples by ICP-OE spectrometry

For ICP measurements the ICP-OES adjusted at 385.4 nm [28] and was allowed to warm up for about 30 min with the continuous aspirating of deionized water and UO_2^{2+} standards [24]. The optimum operating conditions for ICP-OE are given in Table 1. The nebulizer flow was optimized for the highest intensities. Calibration standards were prepared by serial dilutions of 1000 ppm certified solution.

Experimental work using uranyl nitrate hexahydrate was carried out in the safeguards destructive analysis laboratory (KMP-I) at the Egyptian Nuclear and Radiological Regulatory Authority (ENRRA).

Table 1. Instrumental parameters used for uranium determination by ICP-OES

Parameter	Setting
RF power (W)	1150
Plasma gas flow rate (L/min)	12
Auxiliary gas flow rate (L/min)	0.5
Nebulizer gas flow rate (L/min)	0.7
Max integration times (s)	30
Number of replicate	3
Purge gas	Ar
Analytical wavelength (nm)	385.4

III. Results and discussion

Under a Comprehensive Safeguards Agreement (CSA) [29], the International Atomic Energy Authority (IAEA) in-field verification activities focus primarily on verifying the State's declarations on facility design/operation and on nuclear material flows and inventories. Nuclear material verification activities are aimed at verifying the nuclear material accounting records of inventories and inventory changes of nuclear material maintained by operators for each facility or location outside facilities (LOF) and reported through the State authorities to the Agency. This nuclear material accountancy verification may include records examination, identification measurements using non-destructive assay measurements, sampling nuclear material for DA measurements and is often complemented by containment/surveillance (C/S) measures (e.g., seals and cameras).

This paper represent electrochemical mobile tool which may be applied for the estimation of uranium concentration in the facility, rather than taking samples and analyzing these samples in the analytical laboratory. This will help the safeguards inspector to verify the completeness as well as the correctness of the operator's declaration, and also save the extra time required for DA results, together with the high cost of recruiting, training and retaining a proficient laboratory and support staff, maintaining a nuclear material laboratory.

In our previous work, we have reported that the electrodes used in the current work have a Nernstian response towards uranyl ion in a wide linear concentration range and relatively low detection. These results in addition to the sensor fast response time and high selectivity encouraged us for the continuous use of the developed sensor for in-field uranium determination. General performance characteristics of the developed sensor are given in Table 2.

Table 2. Performance characteristics of the developed sensor

Parameter	Electrode
Slope (mV decade^{-1})	29.33 ± 0.75
Concentration range (mol L^{-1})	$5.0 \times 10^{-6} - 1 \times 10^{-1}$
Correlation coefficient, r	0.9997
Lower detection limit (mol L^{-1})	3.3×10^{-6}
Upper detection limit (mol L^{-1})	1×10^{-1}

Working pH range	2.2–3.7
Intercept (mV)	358.50
Life time (weeks)	10
Standard deviation (SD)*	0.51

* Average of three determinations

3.1. Effect of temperature

Effect of test solution temperature on the electrode performance was investigated at temperatures: 20, 25, 30, 35, 40, 45, 50°C for the developed UO_2^{2+} electrode. The electrode exhibits good Nernstian behavior in the temperature range (25–50 °C). The standard cell potentials (E°_{cell}) were determined at different temperatures from the respective calibration plots as the intercepts of these plots at $\text{p UO}_2^{2+}=0$, and were used to determine the isothermal temperature coefficient (dE°/dt) of the cell with the aid of the Antropov's equation [30],

$$E^\circ_{\text{cell}} = E^\circ_{\text{cell}}(25^\circ\text{C}) + [(dE^\circ_{\text{cell}}/dt)(t-25)] \quad (1)$$

Where $E^\circ_{\text{cell}}(25)$ is the standard electrode potential at 25 °C and the slope of the straight-line obtained represents the isothermal coefficient of the electrode. Plot of E°_{cell} vs $(t-25)$ produced a straight line, as shown in Fig. 1.

The slope of this line was taken as the isothermal temperature coefficient of the cell which was found to be equal to $3.5 \times 10^{-4} \text{ V } ^\circ\text{C}^{-1}$. The value of the obtained isothermal coefficient of the developed electrode indicates that the electrode has a fairly high thermal stability within the investigated temperature range.

The values of the standard potentials of UO_2^{2+} electrode were calculated at different temperatures from the relation,

$$E^\circ_{\text{cell}} + E^\circ_{\text{ref}} = E^\circ_{\text{electrode}} \quad (2)$$

Plot of $E^\circ_{\text{electrode}}$ versus $(t - 25)$ gave a straight line; its slope was taken as the thermal temperature coefficient of the electrode which amounts to $3.5 \times 10^{-4} \text{ V } ^\circ\text{C}^{-1}$. The small values of $(dE^\circ/dt)_{\text{cell}}$ and $(dE^\circ/dt)_{\text{electrode}}$ reveal the high thermal stability of the electrode within the investigated temperature range.

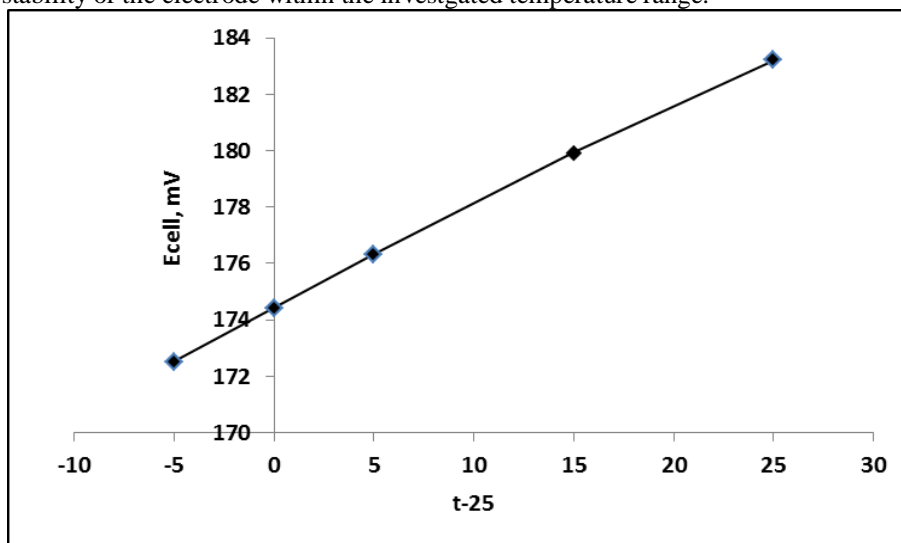


Figure. 1. Variation of standard potential of the cell with changes of test solution temperatures

3.2. Method validation

Before an analytical method can be implemented for routine analysis, it should be first be validated to demonstrate that it is suitable for its intended purpose, so different parameters was calculated for the proposed method as per the ISO guideline in order to evaluate its applicability.

3.2.1. Linearity and Range

The calibration curve for uranyl ion was obtained by plotting the measured potential (mV) versus logarithm value of concentration. A linear response was obtained based on the form of the Nernst equation [31] over linear concentration range of 5.0×10^{-6} to $1.0 \times 10^{-1} \text{ mol L}^{-1}$ with with slope of $29.3 \text{ mV decade}^{-1}$, detection limit of $3.3 \times 10^{-6} \text{ mol L}^{-1}$.

3.2.2. Limit of Detection and Limit of quantification

The limit of detection (LOD) is defined as the amount of uranyl ion corresponding to the lowest measurement signal may be interpreted as indicating that the analyte is present in the solution, but not necessarily allowing exact quantification [32]. The limit of detection of the proposed method (LOD) was

calculated to be three times the standard deviation of the average blank (n=5) and it was found to be 3×10^{-7} mol L⁻¹.

The limit of quantification (LOQ) is the lowest amount of analyte in a sample which can be quantitatively determined with suitable precision and accuracy. LOQ was calculated to be ten times the standard deviation of the average reagent blank it was found to be 1×10^{-6} mol L⁻¹.

3.2.3. Specificity

The first criterion for an analyst when evaluating an analytical method consists in its capability of delivering signals or responses that are free from interferences and give true results. The specificity of the method was investigated by observing any interference encountered from the common inorganic cations and it was found that these cations did not interfere with the results of the proposed method [24].

3.2.4. Repeatability (Precision)

Repeatability which expresses the precision under the same operating conditions over a short interval of time [32] and checks the consistency of calculated results for the analyte over a short time period. The repeatability of the developed electrode was examined by measuring the potential response of different concentrations of pure UO₂²⁺ solutions in the same day (intra-day precision) (n = 5) and over a wide time interval of 5 days (inter-day precision) and it was listed in Table 3. The repeatability of the measuring solution has been found to be within ±0.9 mV over 5 days.

Table 3. Evaluation of intra- and inter-day precision of the developed sensor

Sample	U(IV) Taken,(ppm)	Intra day				Inter day			
		Found, (ppm)	Recovery*(%)	SD ^a	RSD ^a	Found, (ppm)	Recovery*(%)	SD ^b	RSD ^b
1	15.53	14.89	95.87	0.14	0.97	14.60	94.01	0.16	0.99
2	27.55	26.93	97.74	0.17	0.8	27.0	98.00	0.19	0.79
3	35.00	35.21	100.05	0.09	1.00	34.7	99.14	0.067	1.152

a Mean values for five experiments carried out on the same day.

b Mean values for five experiments carried out on five different days.

* Average of five determinations

3.2.5. Accuracy (Trueness)

The accuracy of an analytical procedure expresses the closeness of agreement between the value which is accepted either as a conventional true value or an accepted reference value and the value found [32]. Accuracy of an analytical method is usually determined by studying relevant reference materials or by spiking studies. The accuracy of the proposed method was evaluated by measuring the potential response of water samples spiked with UO₂²⁺. The low values of the relative standard deviation (RSD%) and standard deviation (SD) indicate the high precision and the good accuracy of the proposed method (Table 4).

Table 4. UO₂²⁺ concentration in spiked water samples

Sample	U(IV) added, (ppm)	Found, (ppm)	Recovery* (%)	SD ^a	RSD ^a
1	20.00	19.73	98.65	0.231	0.678
2	30.00	29.28	97.60	0.088	0.598
3	40.00	39.31	98.27	0.173	1.031

* Average of five determinations

^a Mean values for five experiments.

3.3. Real samples measurements

In order to assess the accuracy and validity of the proposed UO₂²⁺ potentiometric electrode real samples analysis were conducted using direct potentiometry technique. For comparison purposes, UO₂²⁺ content in the same samples were determined using reference UV-Visible and ICP-OE spectrometric method.

The potentiometric calibration curve used for real sample determination is represented in Fig. 2. The linear regression equation for the calibration graph is $y = 29.304x + 151.02$ where, $x = \log [UO_2^{2+}]$. The potential of each sample was measured by the proposed sensor and the obtained results are summarized in Table 5.

A calibration curve for UV-visible spectrophotometric method was constructed with a linear regression equation for uranium concentration range of 1–4 μgmL⁻¹ is $A = 0.0002 + 0.2214C$, where C was the concentration of uranium (VI). The correlation coefficient for the calibration curve is 0.999 which is considered

as a good linearity and the curves was used for estimating the concentration of uranium in the real samples as listed in Table 5.

ICP-OE measurements for uranium concentrations were made at 385.4nm. A calibration curve was obtained with correlation coefficient of 0.998 which is considered as a good linearity and the curve was used for estimating the concentration of uranium in real samples (see Table 5). As it is observed in Table 5 that, the obtained results are comparable with those acquired through the UV-Visible and ICP-OE spectrometric analysis of the same samples, which is a good indication of the applicability of the developed electrode for real samples analysis. However the developed method offer an advantage of direct determination of the UO_2^{2+} in the sample with no need for dilution due to its wide linear range.

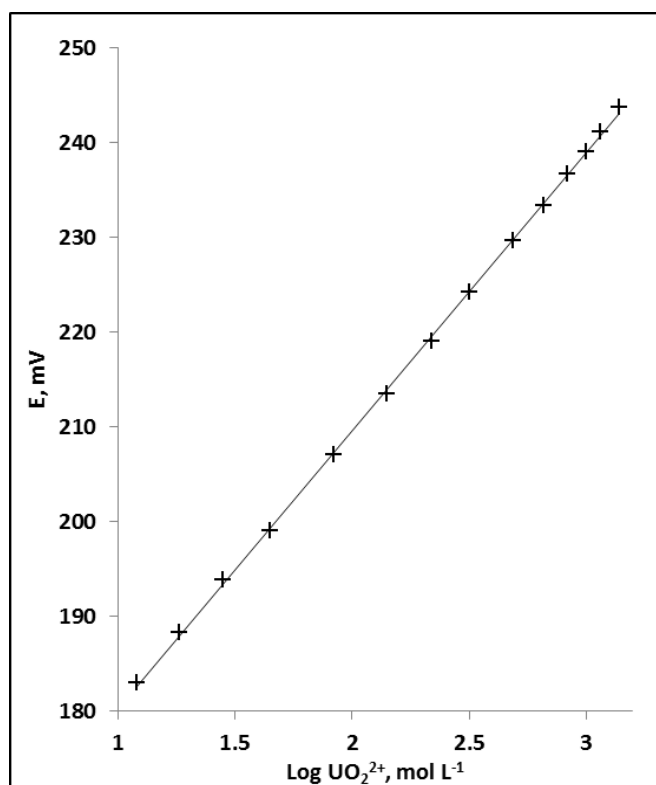


Figure. 2. The calibration curve for determining of uranyl ion by potentiometric method

IV. Conclusion

The present work describes an analytical methodology for determination of uranium content in some real samples by potentiometry with UO_2^{2+} - ion selective electrode. The method was validated and accuracy of the proposed method was determined. The results of the assay of the studied UO_2^{2+} in different real samples were compared with UV-Visible and ICP-OE spectrophotometers. In conclusion using ion selective potentiometric method for in-field measurements of uranium concentration has many advantages in reference to spectrometric method. Portable potentiometric method is cheaper than other techniques, easy to use, fast, nondestructive, and it's possible to direct measure in troubled and viscous solutions and it has a wide range of applications.

Table 5. Determination of UO_2^{2+} contents in real samples using potentiometric and spectrometric methods

Sample ID	Concentration (ppm)			SD			RSD		
	ISE	UV	ICP-OE	ISE	UV	ICP-OE	ISE	UV	ICP-OE
S1	18.50	17.54	18.98	0.24	0.78	0.252	1.54	1.79	1.062
S2	29.83	28.37	29.71	0.19	0.54	0.343	0.89	0.53	1.155
S3	39.25	37.96	36.17	0.20	0.86	0.334	1.10	1.67	1.279
S4	103.43	102.88	100.78	0.63	0.69	0.166	0.43	0.68	1.195
S5	116.79	114.31	115.65	0.62	1.83	0.247	0.62	1.83	1.157
S6	164.10	164.30	165.86	0.63	0.81	0.057	1.78	1.31	0.506
S7	235.04	240.18	237.54	0.71	0.81	0.082	0.71	0.81	1.268
S8	377.29	379.44	277.43	0.58	1.61	0.242	1.78	2.01	1.008
S9	563.21	564.30	560.61	0.56	0.69	0.129	0.66	0.79	1.483
S10	781.83	790.86	785.13	0.83	0.88	0.330	0.93	0.88	1.810

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