RESEARCH ARTICLE

DIRECT SPECTROPHOTOMETRIC DETERMINATION OF URANIUM IN GRANITE AFTER ITS SELECTIVE LEACHING USING LIXIVIANT REAGENTS WITHOUT ITS PRIOR SEPARATION.

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Manuscript Info	*Abstract*

A spectrophotometric determination of uranium in microgranite rock sample, Sela area, South Eastern Desert, Egypt, from its leach liquor using effective and efficient lixiviants for its selective leaching followed by its direct spectrophotometric determination using arsenazo (III) dye without prior separation, as solvent extraction or ion exchange, was proposed in the present work. Several lixiviants were studied for the selective leaching of uranium namely; citric acid, urea, ammonium acetate, ammonium carbonate, ammonium bicarbonate and ammonium nitrate. The selected ammonium bicarbonate and ammonium nitrate lixiviants gave high leaching efficiency of uranium beside the minimal dissolution concentrations of the concomitants hence lowering the matrix interfering effect of those elements during its determination. Several factors were studied for this purpose namely; the choice of proper lixiviant(s), solid to liquid ratio (S/L), leaching time, temperature, interfering matrix effect where their spectral interference on uranium was also studied. It was found that maximum leaching of uranium with the least concomitants was reached using 1M ammonium bicarbonate and 1M ammonium nitrate with percentage leaching efficiencies of 99.5% for both lixiviants. The optimized method was applied on three microgranite and two international certified samples BL-4a and DL-1a, where statistical evaluation showed that their average relative standard deviation was 0.61.

Introduction:-

Uranium was recognized to be a critical commodity in the context of satisfying the global energy demands for the twenty-first century and beyond where it was known as a material storing huge energy and its only commercial application was as nuclear fuel. But apart from its uses in nuclear power plants, the possibility of its use in nuclear weapons makes the material of strategic importance and thereby, restricting its free global trade. The growth of uranium mining normally follows the pattern of growth nuclear power generation capacity. **[1]**

Because of its dynamic oxidation state, uranium has a unique nature as compared to many other metals where it has the capability to be a part of positive, neutral and negatively charged complexes, nearly at neutral pH. Due to the strong association of uranium with other elements, its determination needs selectivity.**[2]**

A pretreatment separation step of uranium was therefore, usually, recommended before its spectrophotometric measurements in rocks. In view of the extensive usage of uranium for various industrial purposes, its precise determination is a challenging task **[3]**. Uranium, in the presence of relatively high concentration of diverse elements makes it difficult to determine directly, so, separation and preconcentration procedures were mandatory prior to its determination.**[4]**

Great attention was paid to the analytical monitoring of uranium in different samples where accurate and repeatable measurements of uranium from dilute samples or complex matrices has obliged researchers to use many techniques for determination of uranium based on preconcentration, namely; solid phase extraction **[5]**, cloud point extraction

[6], liquid–liquid extraction **[7]**coprecipitation**[8]** for the enrichment of uranium (VI) from solutions prior to determination by a variety of analytical techniques.

The extraction of uranium (VI) from 6 M nitric acid solutions using TBP was used for separation of uranium **[9]** but there were some disadvantages, where nitric acid itself was extracted, thus competing uranyl ion to transfer in the organic phase where great excess of nitrate concentration promotes the formation of unextractable anions such as $[UO_2(NO_3)_3]^-$ **[10]**. The extraction of uranium by TBP from 5 M HNO_3lead to increase the probability of extraction of a number of accompanying elements. **[11]**.

Liquid - liquid extraction of hexavalent uranium from 0.75 M nitric acid media by tributyl phosphate (TBP)/kerosene was briefly studied, where interference effects caused by Fe, Zr, Ln, Th and other elements during the determination of uranium was eliminated. The procedure was applied for the extraction and determination of uranium in rocks using arsenazo III. **[12]**

Solvent extraction of U(VI), Th(IV) and Cd(II) from chloride solutions with trioctylmethyl-ammonium chloride (TOMACl), bis (2-ethylhexyl) phosphate (D2EHPA) and dimethylformamide in cyclohexane was investigated. Uranium, cadmium and traces of thorium were extracted, and then uranium was stripped with H_2O. Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) was used for the analysis.**[13]**

The uranyl-ion-imprinted and non-imprinted cross-linked chitosan resins possessing quinoline- 8-ol moiety was prepared. The resulting ion-imprinted resin was used for solid phase extractive preconcentration of uranium (VI) prior to its determination by spectrophotometry. The proposed method was successfully applied for the determination of uranium in contaminated soil and sediment samples. **[14]**

The anion-exchange in magnesium nitrate medium was described to concentrate uranium and thorium simultaneously from mineral acid solution of phosphate rock. Consecutive chromatographic elution of the two elements yielded thorium and uranium fractions, those were sufficiently pure for their direct spectrophotometric determination with arsenazo III. **[15]**

Pyridine-2-carboxaldehyde 2-hydroxybenzoylhydrazone (PCHB) was used as an extractant for the separation and spectrophotometric determination of uranium(VI). The proposed method permits selective separation of uranium (VI) from its binary mixtures and was also applied for the estimation of uranium in multi component mixtures and monazite sand. **[16]**

Leaching is a process by which a soluble substance is removed / extracted from gangue (undesirable matter) by the action of a percolating liquid, called lixiviant**[17]**. Several elements were selectively leached using different lixiviants; the valuable elements chromium and vanadium selectively leached for their analysis in ilmenite and synthetic rutile ores **[18]**, the selectively leached thorium using 10M nitric acid from different Rosetta monazite concentrates using thorin dye where leached thorium was determined directly without prior separation using either solvent extraction or ion exchange techniques.**[19]**

Sulfuric acid was used exclusively in conventional uranium milling because of its low cost and compatibility with ion exchange recovery. In the uranium leach processes employing sulfuric acid as lixiviant, only a relatively small quantity of acid was gainfully employed in extracting uranium from the host ore. The remainder of the acid was consumed by the gangue constituent elements. Many gangue elements solubilized by the acid lixiviants were found in the leachate where their impact, in some cases, was deleterious to the extraction and determination of uranium.

In alkaline leach processes, the solubility of many of the impurity elements in uranium ores (such as Fe, Mg, and Al) was quite low. However, the alkaline operations do encounter some challenges with gangue element solubility.

Languimir**[20]** illustrated the influence of the carbonate anion, where it complexes and solubilize the uranium present in the (relatively insoluble) uranium-hydroxyl layer found on uranium minerals in a high pH aqueous leach solution. This was an important concept for the application of carbonate leaching, as the sodium carbonate and sodium bicarbonate disassociate in solution to form sodium cations, carbonate anions, and bicarbonate anions.
Because of simplicity and selectivity, different chromogenic agents and organic dyes were widely investigated and reported for the spectrophotometric determination of U(VI) **[21–27].** Among a variety of these organic reagents

which are largely based on azo-dyes for U(VI) determination, sodium salt of Az-III is reported as a responsive chromogenic reagent. Because of U(VI)-(Ar-III) high stability, its quantitative determination even in very low pH became possible, where neither hydrolysis, nor the formation of polynuclear species can take place.

Granites were considered as one of the most favorable host rocks for U mineralization in many parts of the world. The applied sample in the present study was from El Sela area, Southern Eastern Desert, Egypt having visible U mineralization.

The aim of the present work was to find out proper lixiviant(s) for the complete (maximum) selective leaching of uranium from igneous microgranite rock samples with the minimal associated interfering elements for its direct spectrophotometric determination using arsenazo (III) chromogenic dye with good accuracy and precision. Application on two international certified ones (BL-4a and DL-1a) using the optimum conditions were proposed to calculate some statistical parameters for the studied process.

Experimental:-
Apparatus:-
A Shimadzu UV-VIS 160A spectrophotometer was used for the absorbance measurements. Atomic Absorption Spectrometer (AAS) model GBC-932 was used for the determination of some trace elementsin the leach liquor. X-Ray Fluorescence (XRF) model Philips X'Unique II was used for the quantitative determination of some trace element analysisin the head samples.

Chemicals and reagents:-
All the chemicals used were highly pure Analytical Reagent grade for chemical analysis. The stock solution of uranium (VI) was prepared by dissolving 0.527 g of uranyl nitrate (BDH) in 250 ml of double distilled water containing 1 ml of concentrated nitric acid. The solution was standardized gravimetrically with oxine[28] and working solutions of uranium (VI) were prepared by further dilution of this stock solution.

Optimization of various studied factors for maximum leaching of uranium with minimal accompanying deleterious interfering elements was studied on microgranite rock sample from Sela area, Southern Eastern Desert, Egypt. The microgranite rock sample was ground to -200 mesh particle size. Complete chemical analysis of different elements by various techniques was performed[29], as shown in Table (1). The leaching experiments were carried out in 50 ml Erlenmeyer flasks containing separately 25 ml of different lixiviantsolutions (0.5 M, 1 M, 2 M and 3M). Each flask was supplemented with 1g finely ground solid sample.

Several stock solutions of various cations were prepared for studying their interference effect on the spectrophotometric determination of uranium. Arsenazo (III) dye (0.25%) was prepared by dissolving 0.25 g dye with 0.5g sodium acetate in 100ml distilled water.

Table (1): Chemical analysis of some major oxides accompanying uranium in the host microgranite studied sample before leaching**.**

Oxides	Concentration (%)
SiO_2	73.0
TiO_2	0.04
Al_2O_3	13.20
Fe_2O_3	3.50
MnO	0.02
MgO	0.24
CaO	1.07
Na_2O	3.80
K_2O	4.06
P_2O_5	0.03
L.O.I	0.4
Elements	**Concentration (ppm)**
Cr	458
Ni	145
Cu	27
Zn	82
Rb	254
Ba	1300
Pb	29
V	45
U	200

Results and Discussions:-

Spectrophotometric broad band of U-arsenazo (III), Figure (1), permits considerable interference effects caused by Fe, Zr, Ln and other elements [30]hence this work was proposed to overcome this interference which was performed using selective leaching of uranium from microgranite sample from Sela area, Southern Eastern Desert, Egypt to optimize the leaching factors for uranium with the least concomitants for direct determination of uranium without interference from other concomitants.
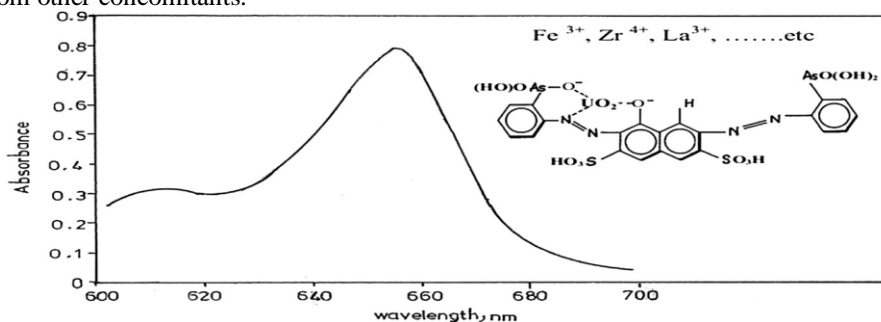

Fig. 1: Spectrum for uranium-arsenazo III complex measured against 0.25% arsenazo III as blank

The effect of different concomitants on uranium determination was studied. Different concentrations of individual elements together with uranium as a simulated solution to the studied rock type were prepared. From Figures 2-10 it can be clearly observed that there was interference effect from some accompanying elements. To avoid the interference caused by those elements for the direct determination of uranium different parameters for its selective leaching were studied.
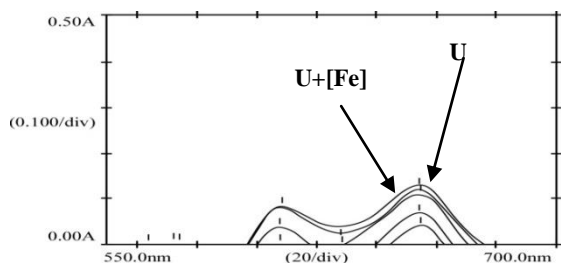
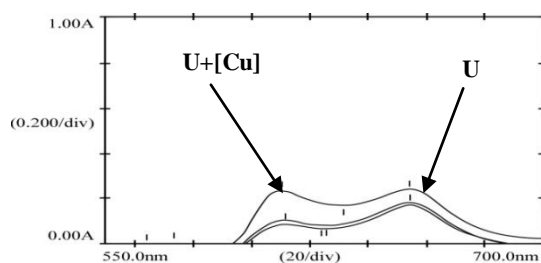**Fig. (2):** Effect of different iron concentrations
uranium determination

Fig. (3): Effect of different Copper concentration on
on uranium determination

Fig. (4): Effect of different Zinc concentrations
on uranium determination

Fig. (5): Effect of different Barium concentrations
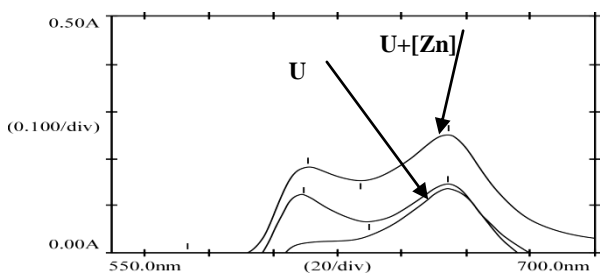on uranium determination

Fig.(6): Effect of different Nickel concentrations
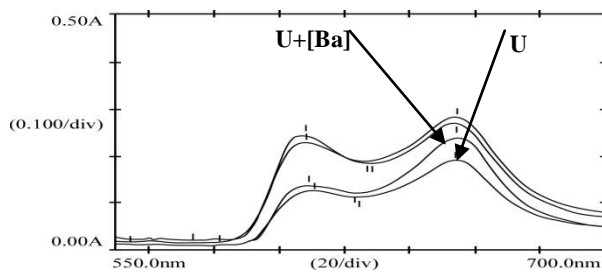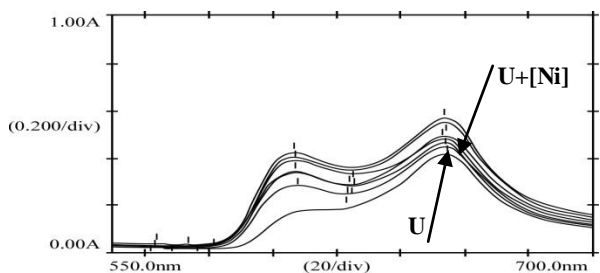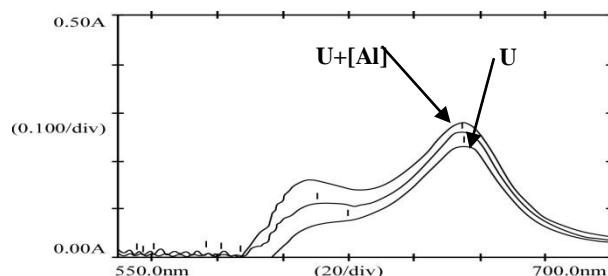on uranium determination

Fig. (7): Effect of different Aluminum concen-
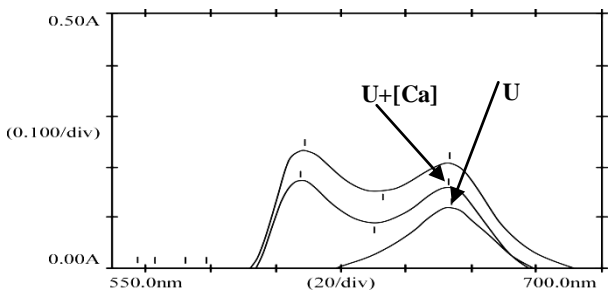trations on uranium determination

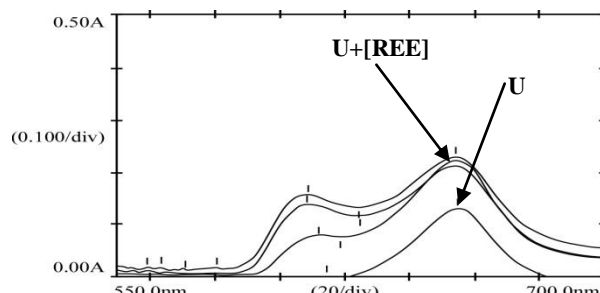**Fig. (8):** Effect of different Calcium concentrations
onuranium determination

Fig. (9): Effect of different Rare Earth Elements
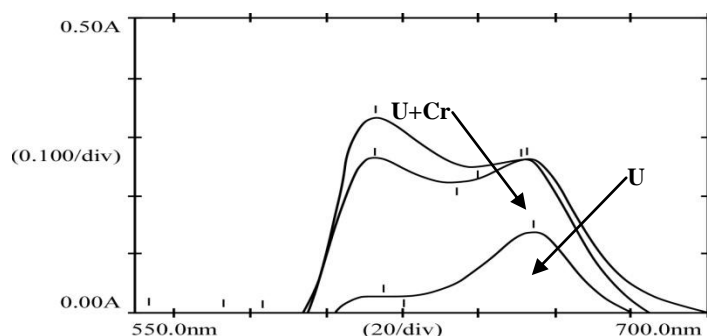concentrations on U determination

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Fig. (10): Effect of different Chromium concentrations on U determination

Several parameters were studied and optimized to reach the maximum selective leaching of uranium with the least concomitant concentrations in the applied granite sample for the direct determination of uranium using arsenazo (III) dye. Batch tests were achieved to characterize the leach properties. The concentration of uranium in the studied applied sample was found to be 200 ppm.The factors studied were; type of lixiviant, effect of lixiviant concentration, effect of leaching time, effect of leaching temperature and effect of solid to liquid ratio.

Effect of different lixiviants:-
Several lixiviants were selected for the maximum leaching of uranium from microgranite sample, namely; citric acid, urea, ammonium acetate, ammonium bicarbonate and ammonium nitrate. The conditions for leaching will be fixed until otherwise mentioned. A lixiviant concentration of 1M, solid to liquid ratio of 1:25, at $90^{o}C$ and two hours agitation time were proposed as primitive conditions till optimized. Table (2) gathered the percentage leaching efficiency of uranium using the mentioned lixiviants.

Table (2): Effect of different lixiviants on the leaching efficiency of uranium

Lixiviant	Leaching Efficiency (%)
Citric acid	77.0
Urea	80.0
Ammonium acetate	80.0
Ammonium bicarbonate	99.5
Ammonium nitrate	99.0

From the data obtained in Table (2), it can recognized that the best leaching efficiency for uranium was performed by ammonium nitrate and ammonium bicarbonate with a percentage leaching efficiencies of 99.0 and 99.5 respectively.

Effect of lixiviant concentration:-
Different concentrations of the selected lixiviants ammonium bicarbonate and ammonium nitrate (0.5M, 1.0M, 2M and 3M) were used for studying the leaching efficiency of uranium from microgranite sample. The leaching conditions used were solid to liquid ratio 1:25, $90^{o}C$, two hours agitation time and different concentrations of each lixiviant.

Table (3): Effect of ammonium bicarbonate concentration on the leaching efficiency of uranium

Ammonium bicarbonate concentration (M)	Leaching Efficiency (%)							
	U	Cu	Zn	Fe	Ni	Cr	Ca	Mg
0.5	64.0	1.0	UDL	UDL	UDL	UDL	1.87	0.33
1.0	99	3.5	UDL	$8x10^{-5}$	UDL	UDL	2.5	1.6
2.0	99.9	5.2	1.6	$4x10^{-4}$	0.7	0.3	3.7	3.85
3.0	99.9	7.2	2.3	$8x10^{-4}$	1.2	1.0	6.25	6.25

Table (4): Effect of ammonium nitrate concentration on the leaching efficiency of uranium

Ammonium nitrate concentration (M)	Leaching Efficiency (%)							
	U	Cu	Zn	Fe	Ni	Cr	Ca	Mg
0.5	60.0	3.2	UDL	UDL	UDL	UDL	3.76	3.33
1.0	99.5	6.4	3.2	$1.4x10^{-4}$	UDL	UDL	6.25	5.66
2.0	99.5	8.5	7.0	$5.0x10^{-4}$	0.9	0.5	9.35	11.33
3.0	99.9	11.2	10	$1.0x10^{-4}$	1.8	1.2	15	21.33

UDL …… Under Detection Limit
From Tables (3) and (4), it was obviously clear that the percentage leaching efficiency of both lixiviants were efficient for uranium leaching using 1M ammonium bicarbonate and 1 M ammonium nitrate, rather, the accompanying elements concentration using ammonium nitrate was relatively higher than when using ammonium nitrate for leaching.

Effect of agitation time:-
The effect of agitation time on the leaching efficiency of the granite sample was studied using the previously optimized conditions; 1M concentration of both ammonium bicarbonate and ammonium nitrate as lixiviants, solid to liquid ratio 1:25, at $90^{o}C$ and different agitation time (0.5 hr, 1.0 hr, 2 hrs, 3 hrs).

Table (5): Effect of different agitation time on the leaching efficiency of uranium using ammonium bicarbonate

Agitation Time (hours)	Leaching Efficiency (%)							
	U	Cu	Zn	Fe	Ni	Cr	Ca	Mg
0.5	60.0	UDL	UDL	UDL	UDL	UDL	1.12	0.66
1.0	83.0	1.2	UDL	UDL	UDL	UDL	1.56	1.06
2.0	99.5	3.5	UDL	8×10^{-5}	UDL	UDL	2.5	1.6
3.0	99.9	5.0	0.6	2×10^{-4}	0.6	0.4	3.75	4.0

Table (6): Effect of different agitation time on the leaching efficiency of uranium using ammonium nitrate

Agitation Time (hours)	Leaching Efficiency (%)							
	U	Cu	Zn	Fe	Ni	Cr	Ca	Mg
0.5	58.0	3.3	1.7	UDL	UDL	UDL	3.12	3.33
1.0	80.0	4.6	2.3	4×10^{-5}	UDL	UDL	4.37	4.0
2.0	99.0	6.4	3.2	1.4×10^{-4}	UDL	UDL	6.25	5.66
3.0	99.5	12	6.0	3×10^{-4}	0.5	0.4	8.75	8.13

From the gathered data in Tables (5) and (6), it was clear that the percentage leaching efficiency was affected by the time of agitation, in spite the three hours gave higher leaching efficiency than the two hours agitation time rather the concomitant concentrations in case of two hours were less than three hours which might affect in direct uranium determination.

Effect of temperature:-
The effect of different temperatures ($25^{o}C$, $50^{o}C$, $70^{o}C$ and $90^{o}C$) on the maximum leaching of uranium from the studied granite sample was studied using the previously optimized conditions; 1M concentration of ammonium bicarbonate and 1M ammonium nitrate as lixiviants, solid to liquid ratio 1:25, and 2 hrs agitation time.

Table (7): Effect of different temperatures on the leaching efficiency of uranium using ammonium bicarbonate

Temperature (^{o} C)	Leaching Efficiency (%)							
	U	Cu	Zn	Fe	Ni	Cr	Ca	Mg
25	70.0	0.6	UDL	UDL	UDL	UDL	1.25	0.60
50	78.5	1.7	UDL	4×10^{-5}	UDL	UDL	1.50	1.20
70	87.5	2.3	UDL	6×10^{-5}	UDL	UDL	1.87	1.33
90	99.5	3.5	UDL	8×10^{-5}	UDL	UDL	2.50	1.60

Table (8): Effect of different temperatures on the leaching efficiency of uranium using ammonium nitrate

Temperature (^{o} C)	Leaching Efficiency (%)							
	U	Cu	Zn	Fe	Ni	Cr	Ca	Mg
25	67.0	1.60	0.50	1×10^{-5}	UDL	UDL	3.12	2.20
50	76.0	3.70	1.60	5×10^{-5}	UDL	UDL	3.75	4.20
70	85.3	5.10	2.10	1×10^{-4}	UDL	UDL	4.68	4.66
90	99.0	6.40	3.20	1.4×10^{-4}	UDL	UDL	6.25	5.66

It was found from Tables (7) and (8) that $90^{o}C$ was the optimum temperature for maximum uranium leaching of uranium for both lixiviants.

Effect of solid to liquid ratio (S/L):-
A series of different solid to liquid ratios (1/10, 1/25, 1/50 and 1/100) were studied for the highest leaching efficiency of uranium from the studied microgranite sample. The optimum ratio was studied at the previously optimum parameters reached; 1M ammonium bicarbonate and 1M ammonium nitrate as lixiviants, at 90°C and 2 hours agitation time.

Table (9): Effect of different solid to liquid ratios on the leaching efficiency of uranium using ammonium bicarbonate

Solid /Liquid (S/L)	Leaching Efficiency (%)							
	U	Cu	Zn	Fe	Ni	Cr	Ca	Mg
1/10	82	2.80	UDL	5×10^{-5}	UDL	UDL	1.25	0.60
1/25	99.5	3.50	UDL	8×10^{-5}	UDL	UDL	2.20	1.60
1/50	99.9	5.80	1.20	2×10^{-4}	0.60	0.30	5.0	2.66
1/100	99.9	8.0	3.0	5×10^{-4}	0.90	0.70	15.0	9.70

Table (10): Effect of different solid to liquid ratios on the leaching efficiency of uranium using ammonium nitrate

Solid /Liquid (S/L)	Leaching Efficiency (%)							
	U	Cu	Zn	Fe	Ni	Cr	Ca	Mg
1/10	80.0	4.0	1.80	4.0×10^{-5}	UDL	UDL	3.75	3.0
1/25	99.0	6.4	3.20	1.4×10^{-4}	UDL	UDL	6.25	5.66
1/50	99.9	10.7	5.80	5.0×10^{-4}	0.80	0.50	15.0	21.33
1/100	99.9	13.0	8.20	1.0×10^{-3}	1.40	0.90	40.0	26.66

From the data obtained in Tables (9) and (10), it was clear that a solid to liquid ratio of 1:25 for both ammonium bicarbonate and ammonium nitrate gave the highest leaching efficiency unless there was interference from accompanying elements during uranium determination.
After optimizing several parameters for maximum leaching of uranium, Table (11) summed up all the optimum leaching parameters reached.

Table (11): Summing up of all optimum results for maximum uranium leaching efficiency using studied factors

Factor	Ammonium bicarbonate	Ammonium nitrate
Concentration (M)	1M	1M
Agitation time	2 hours	2hours
Temperature (^{o}C)	90°C	90°C
Solid / liquid ratio (S/L)	1:25	1:25

Table (12): Associated elements compared between studied lixiviants and acid leaching of uranium from microgranite

Element	Complete dissolution of rock (ppm)	Acid leaching (ppm)	Ammonium bicarbonate leaching (ppm)	Ammonium nitrate leaching (ppm)
U	200	200	199	198
Cu	27	20	1.70	0.95
Zn	82	70	2.60	UDL
Fe	25000	5000	3.50	2.0
Ni	145	130	UDL	UDL
Cr	458	375	UDL	UDL
Ba	61	50	UDL	UDL
Ca	16000	8000	400	1000
Mg	15000	7000	240	850

From the data observed in Table (12), it was clearly identified that total leaching of uranium was observed using all lixiviants used. On the other hand, the concomitant concentrations after leaching of uranium, using several lixiviants were the least when using both ammonium bicarbonate and ammonium nitrate lixiviants compared to acid leaching.

Treatment of interfering accompanying elements leached with uranium:-
The tolerance of the accompanying major and trace elements that may interfere during the spectrophotometric determination of uranium using arsenazo (III) dye in both leach liquors were studied. Table (1), showed the concentrations of those elements with uranium. The latter analyses highlighted the accompanying elements which may interfere during the spectrophotometric analysis of uranium in the leach liquors.

It was necessary to overcome this interference due to some concomitants with uranium. Several treatments were found such as the use of masking agents, where the best known was EDTA-2Na, which forms stable complexes with many elements and at the same time unstable with uranium. The quantity of EDTA required was studied for masking interfering elements during uranium determination. To a mixture of uranium and 5 ppm mixture of these interfering elements in solution, EDTA-2Na (0.2M) was added in different volumes and uranium was determined in each aqueous solution. The results obtained in Table (13) showed that 0.3 ml was sufficient for masking the interfering elements in 10 ml measuring solution.

Table 13: Effect of EDTA on masking of interfering elements during uranium extraction.

Volume of EDTA added (ml)	Masking efficiency [%]
0.1	88
0.2	92
0.3	100
0.4	100
0.5	100

By applying this study on the determination of uranium in presence of a mixture of its accompanying elements, interference was obviously clear, Figure (11). By treating the mixture with 0.3ml EDTA-2Na it was found that uranium was determined without interference from the concomitants as shown in Figure (12).
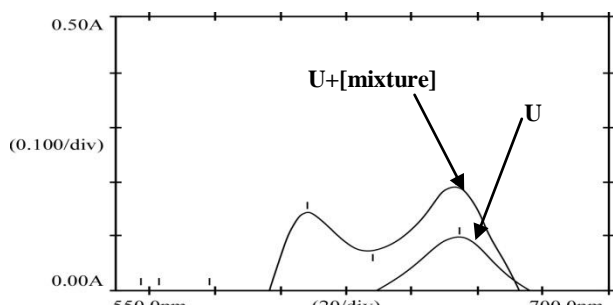

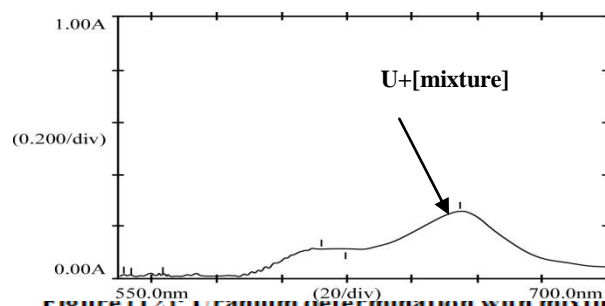Figure (11): Interference effect of mixture of concomitants on uranium determination

Figure (12): Uranium determination with mixture of concomitants after treatment of interference

Application of the proposed procedure on the determination of uranium in standard Rocks
The determination of uranium under optimum studied leaching conditions was applied on three other microgranite and two certified reference rock samples as shown in Table (14).

Table 14: Comparison between uranium concentration in reference rock samples and other three microgranite rock samples using the present method and other technique

Standard sample	Expected U concentration, (ppm)	Concentration of U found after leaching, (ppm)	Relative standard deviation (RSD)
DL-1a	116	114	0.16
		113	
		113.5	
BL-4a	1248	1245	0.40
		1242	
		1246	
1	100	95	0.79
		96	
		96.5	
2	200	196	0.81
		197	
		198	
3	150	147	0.89
		147	
		145	

Conclusion:-

A prerequisite for the direct spectrophotometric determination of uranium in microgranite rock samples using arsenazo (III) was its separation/leaching with the least concomitants using selective leaching technique. Several lixiviants were tested and it was found that 1M ammonium bicarbonate and 1M ammonium nitrate with two hours agitation at 90°C and solid to liquid ratio (S/L) ratio of 1:25 gave the maximum percentage leaching efficiency of uranium with the least concomitants, which furnished for its direct determination with good accuracy.

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