SPECTROPHOTOMETRIC STUDIES AND THE EFFECT OF SOLVENT EXTRACTION PRODUCTS AND SOME OTHER ELEMENTS ON URANIUM AND THORUIM ESTIMATION IN EGYPTIAN MINERALIZED ROCKS.

BY

MAYSA SADEK EL SAYED
NUCLEAR MATERIALS
AUTHORITY

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Thesis Advisors:

*Prof. Dr. Ahmed A. Taha, prof. of Physical chemistry and Dean of the college of Women.

Prof. Dr. Monir M. Aly, Prof. of Analytical hemistry Nuclear Material

r. Wafa S. Higazy, Associate Prof. of hysical chemistry College of Women.

Approved

"Ahmed A. Taha"

"Monir M. Aly"

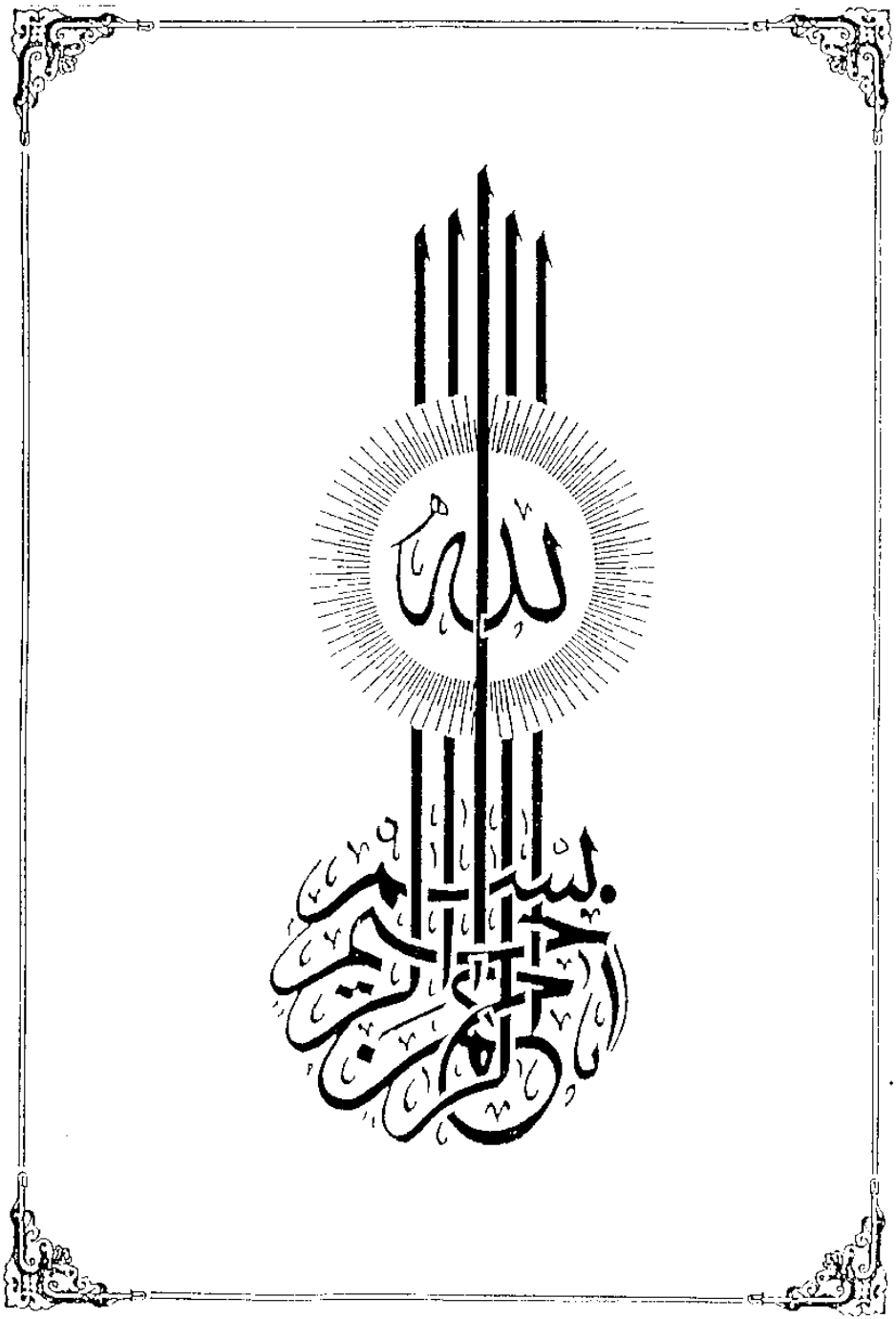
"

Appfoved

"I.M. Hilo"

Head of Ch. Department

Essam Ezzo



The present thesis is submitted to the college of Women, Ain Shams University in partial fulfillment of the requirement for the degree of Master of Science in Chemistry.

Beside the research materialized in thesis, the candidate has attended and successfully passed examination in the following courses:

1. Corrosion.
2. Photochemistry.
3. Surface chemistry.
4. Quantum chemistry.
5. Thermodynamics.
6. Kinetics.
7. Microanalysis.
8. Language (German).

Acting Head of Chemist. Dept.
Ain Shams College of Women.
Prof. Dr.

E. M. Ezzo

ESSAM EZZO

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TABLE OF CONTENTS

CHAPTER 1

INTRODUCTION

CHAPTER I

INTRODUCTION

Uranium is the primary fertile element used in commercial nuclear reactors all over the world. Thorium differs from uranium in being not fissionable by itself, however, its irradiation by slow neutrons results in a series of transformations leading to the formation of the long half life fissionable isotope ^{235}U. Thorium is therefore a fertile element and is considered as a source of secondary nuclear fuel.

Nuclear fuels are actually subjected to severe restrictions in their processing so as to ensure their extreme purity. In either ore materials or spent fuels, uranium and thorium are generally contaminated by various elements including rare earths, iron, manganese and yttrium.

To effect their separation, uranium - in particular - and thorium solutions are normally treated by various organic solvents that have, more or less, a certian selectivity for such elements. In addition, it would be possible to increase the degree of selectivity of these solvents towards uranium and thorium by mixing their aqueous solutions with some water-soluble alcohols and acetone. This is due to the fact that the latter could indeed change the extraction

behaviour of many elements in a manner to attain successful separation.

Indeed, most of the work published has utilized radioactive tracers. However, uranium does not have a suitable radioactive tracer that can be measured by the available gamma scintillation and beta counters. Therefore, spectrophotometric behaviour of both elements was chosen for the present investigation.

This work has actually started by setting up rapid methods for the spectrophotometric determination of both uranium and thorium.

The work has then studied the effects of the presence of a number of water miscible alcohols and acetone on the analysis of both uranium and thorium.

Also, this work has studied the effects of the selected water-miscible alcohols and acetone on the extraction behaviour of uranium. The selected water-miscible alcohols include methyl, ethyl and isopropyl alcohols. Moreover, this study, has investigated the effect of some trace elements that normally accompany thorium in its ore materials on its quantitative determination by the chosen method. These elements include Y, Yb, Fe, Mn and rare earth elements. Finally, the obtained results have been utilized for the

estimation of both uranium and thorium on some ore materials to investigate their applicability.

In the following, a summary of the various methods of analysis for uranium and thorium is briefly exposed. This is followed by discussing the principles of spectrophotometric analysis.

GENERAL METHODS OF ANALYSIS FOR URANIUM AND THORIUM

METHODS OF URANIUM ANALYSIS

The chemical methods for the quantitative determination of uranium from the gravimetric through the volumetric, the electrometric, the absorptiometric, the spectrometric and the fluorimetric , procedures are distinguished by their great variety and versatility. This is based on the fact that uranium may appear as both quadri and hexavalent states in many media. Uranium, furthermore, forms compounds and complexes with many reagents due to its electronic structure.

In practice, however, only a limited number of analytical techniques are preferred depending on the uranium content of the sample. For samples with high uranium content, the gravimetric method is used, with U_3O_8 as the end product of the analysis. Beside that, redox titration in phosphoric acid medium with electrometric end point indication can be carried out either volumetrically or coulometrically.

For the trace analysis of uranium, absorptiometric and radiometric analytical methods are most commonly used. The absorption spectrophotometric method employing arsenazo III, or a few other complex-forming reagents, is preferred.

For the microdetermination of uranium, the fluorimetric method is still widely used. Polarographic methods play nowadays a minor role only.

It has to be mentioned that devolopments in analytical chemistry lead more and more to methods of analysis that make separations largely superfluous. Such methods are primarily spectroscopic ones, for example, γ or X-ray fluorescence spectroscopy and emission spectroscopy, which provide element specific spectra. Furthermore, the separation processes have changed in the course of time, and the precipitation reactions that had initially played an important role have later been largely displaced by extraction and chromatographic methods. The advantage of the separation by means of solvent extraction is that it can be applied over a wide range of concentrations. The separation usually proceeds quite rapidly and leads to very pure concentrates. Interference by adsorption, characterizing many precipitation reactions, is absent.

The specially important extraction of uranyl nitrate with TBP* from nitric acid solutions proceeds quantitatively, provided that the HNO_3 concentration is 5 or 6 M or when the aqueous phase contains a high concentration of a salting agent (e.g. alkali metal nitrate, $Ca(NO_3)_2$ or $Al(NO_3)_3$).

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* Tributyl Phosphate.

Using a longer alkyl branched chain, however, raises the distribution ratio of uranium appreciably, for instance triisopropyl phosphate is a better extractant than TBP (Normura and Hara, 1961). An even larger enhancement extraction of uranium is attained when the alkoxy groups in TBP are replaced by alkyl groups yielding phosphonates, phosphinates or phosphine oxides by the replacement of 1,2 or 3 groups, respectively. Of these tri-n-octyl phosphine oxide (TOPO) is the best known extractant (Shults and Dunlop, 1963).

On the other hand, chromatographic methods of separation include ion exchange chromatography and partition chromatography. The former is the more important for uranium analysis, since it permits in many cases the isolation of the uranium from practically all the accompanying elements in a single operation.

GRAVIMETRIC METHODS :

In order to conduct a gravimetric determination, it is necessary to convert the uranium into a pure compound of stoichiometric composition. Gravimetry is a very accurate method compared with other techniques, and has gained renewed significance in connection with the specification and control of uranium as nuclear fuel. This is the method favoured for the determination of the uranium content in pure uranium compounds or mixtures of compounds.It requires,

however, substantial quantities of material (1 to 10 g) for a precision analysis (relative standard deviation <0.1%). The most commonly used form for weighing is U_3O_8 (Kato et al, 1939 and Schaefer et al, 1967). If uranium is to be determined gravimetrically in a multi component mixture, separation steps must be included. For binary systems, e.g. alloys or concentrates, precipitation reactions may be used, and in this connection they have retained their significance. A disadvantage of all gravimetric methods is the fact that they are very time consuming and therefore many well worked-out gravimetric techniques find only a limited use.

VOLUMETRIC METHODS:

When small samples are to be dealt with, titrimetric methods have the advantage of rapidity and precision over gravimetric methods. Generally, the titrimetric method is the standard procedure for the determination of macro-amounts of uranium and can even be used for the determination of as little as few tenths of a milligram of uranium. Processes that are based on the redox properties of the uranium ions are preferred for the titrimetric determination. Both the classical redox titrations, using colour indicators, and the recently favoured methods using electrometric procedures for the indication of the end point are being