

**SYNTHESIS, CHARACTERIZATION AND
ION EXCHANGE PROPERTIES OF TIN
TUNGSTATE MATRICES**

A Thesis submitted

By

**Ashgan Fouad Mahmoud Hassan
(B.Sc., Cairo University)**

To

**Department of Chemistry
Faculty of Science
Cairo University**

In

Partial Fulfillment For

**The Requirements of The Degree of Master
In Science M.SC (Chemistry)**

2009

ACKNOWLEDGEMENT

Before all, I thank **Allah**, the **Lord** of the world, for unlimited help and blessings.

I would like to express my deep gratitude to Dr. *M. M. Naoum*, Prof. of physical chemistry, Faculty of Science, Cairo University for helpful guidance during the scope of the work.

I am greatly indebted to Prof. Dr. *S. E. Soliman*, Vice Chairman of nuclear fuel management division and Radioisotopes Production Facility manager, Atomic Energy Authority. Egypt, for suggestion the point of research, valuable comments, guidance and continuous help throughout the course of the present work and for having many fruitful discussions regarding interpretation of the data.

I would like to express my sincere appreciation to Dr. *M. Abou El-Enien*, Lecturer of Chemical Engineering, Hot Laboratories Center, Atomic Energy Authority for his interest and valuable help in all experimental part and kind help in revising these work.

The Author would like also to thank Dr. *M. Mostapha*, Lecturer of radiation chemistry, Hot Laboratories Center, Atomic Energy Authority for his cooperative interactions and support.

I finally thank, all the staff members and colleagues of Radioisotopes Production facility, (EAEA) for their fine sympathy.

Abstract

Name of Candidate : Ashgan Fouad Mahmoud Hassan

Title of Thesis : "Synthesis, Characterization, and Ion Exchange Properties of Tin Tungstate Matrices"

Degree : M.Sc. Master of Science Thesis, Faculty of Science, Cairo University, 2009.

This work has been carried out to prepare, characterize, and study the ion exchange properties of tin tungstate inorganic ion exchanger that can be used in various nuclear applications as a chromatographic column matrix. Factors which affect the preparation of the tin tungstate gel matrices were investigated. The apparent capacities for different metal cations on the different types of the tin tungstate gel matrices, were determined. Characterization studies of the tin tungstate gel matrix including density, chemical stability, thermal analysis, IR spectra, X-ray diffraction pattern, chemical composition and acid-base characteristics were conducted. Equilibrium time measurements for ^{134}Cs (I) ions at different temperatures on the tin tungstate gel were radiometrically determined. The distribution coefficient values for ^{134}Cs (I), $^{131,133}\text{Ba}$ (II), ^{60}Co (II), ^{115}Cd (II), ^{65}Zn (II), ^{113}Sn (IV), $^{113\text{m}}\text{In}$ (III), ^{95}Zr (IV), ^{181}Hf (IV), ^{95}Nb (V), ^{99}Mo (VI) and $^{99\text{m}}\text{Tc}$ (VII) radiotracers on the tin tungstate gel matrix were radiometrically determined. Due to its pronounced selectivity, tin tungstate has been used for the preparation of ^{113}Sn - $^{113\text{m}}\text{In}$ radioisotope generator. Quality control studies of the obtained eluate were also investigated.

Key words: Inorganic ion exchangers; Synthesis and characterization; Ion exchange properties; Tin tungstate.

Supervisors:

Prof. Dr. M. M. Naoum

Prof. Dr. S. E. Soliman

Signature:

Signature:

Prof.Dr. Mohammed Shokry

Chairman of Chemistry Department
Faculty of Science Cairo University

المستخلص

أسم الطالب : أشجان فؤاد محمود حسن
عنوان الرسالة : تحضير و توصيف و خواص التبادل الأيوني لمادة تنجستات القصدير
الدرجة : رسالة ماجستير فى العلوم، كلية العلوم، جامعة القاهرة، ٢٠٠٩

تم هذا العمل لتحضير و توصيف و دراسة خصائص المبادل الأيوني غير العضوى تنجستات القصدير و الذى يمكن استخدامه كمادة لعمود كروماتوجرافى فى العديد من التطبيقات النووية. تم دراسة العوامل التى تؤثر على تحضير جل تنجستات القصدير مثل النسب المولارية للمتفاعلات ، الرقم الهيدروجينى لمحلول تنجستات الصوديوم و طبيعة وسط التفاعل. تم تحديد السعة الظاهرية للأنواع المختلفة من جل تنجستات القصدير لكاتيونات العناصر المختلفة. تم توصيف مادة تنجستات القصدير من حيث الكثافة، الثبات الكيميائى و التحليل الحرارى، و طيف الأشعة تحت الحمراء و حيود أشعة اكس والتركيب الكيميائى و معايرة الحامضية و القاعدية. تم تعيين تعادل الأتزان لأيون السيزيوم-١٣٤ عند درجات الحرارة المختلفة. تم تعيين معاملات التوزيع لأيونات بعض العناصر إشعاعيا على جل تنجستات القصدير مثل:

^{134}Cs (I), $^{131,133}\text{Ba}$ (II), ^{60}Co (II), ^{65}Zn (II), ^{115}Cd (II), $^{113\text{m}}\text{In}$ (III), ^{113}Sn (IV), ^{95}Zr (IV), ^{181}Hf (IV), ^{95}Nb (V), ^{99}Mo (VI) and $^{99\text{m}}\text{Tc}$ (VII)

و كنتيجة للانتقائية الواضحة لجل تنجستات القصدير فقد تم استخدامه لتحضير مولد الأندسيوم-١١٣م. تم أيضا دراسة قياسات مراقبة الجودة لنواتج استخلاص العمود الكروماتوجرافى التى تم الحصول عليها.

الكلمات الدالة: المبادلات الأيونية غير العضوية، تحضير و توصيف، خواص التبادل الأيوني، تنجستات القصدير.

السادة المشرفون :

١- أ. د. مجدى ميخائيل نعيم التوقيع:

٢- أ. د. صلاح الدين السيد سليمان التوقيع:

رئيس مجلس قسم الكيمياء

أ. د. محمد محمد شكرى

CONTENTS	Page
LIST OF FIGURES.....	v
LIST OF TABLES	viii
AIM OF WORK.....	ix

CHAPTER I

INTRODUCTION

1.1. General considerations.....	1
1.2. Ion exchange chromatography.....	2
1.2.1. Ion exchange reaction.....	3
1.2.2. Ion exchange applications.....	3
1.2.3. Classification of inorganic ion exchange materials.....	4
1.2.3.1. Hydrous oxides.....	4
1.2.3.2. Acid salts of multivalent metals.....	6
1.2.3.3. Heteropolyacids and their salts.....	7
1.2.3.4. Insoluble ferrocyanides.....	8
1.2.3.5. Synthetic aluminosilicates.....	8
1.2.3.6. Other certain substances.....	9
1.2.4. Characteristic properties of inorganic ion exchangers.....	9
1.2.4.1. Acid base properties.....	9
1.2.4.2. Ion exchange capacity.....	9
1.2.4.3. Distribution behavior.....	10
1.2.4.4. Selectivity.....	12
1.2.5. Literature review on the synthesis of some inorganic ion exchangers.....	16
1.2.6. Ion exchange separation of some radionuclides of interest.....	19
1.3. Chemistry of tungsten and tin.....	22
1.3.1. Chemistry of tungsten.....	22
1.3.2. Chemistry of tin.....	22

1.4. Radioisotope generators.....	23
1.4.1. $^{113}\text{Sn} / ^{113\text{m}}\text{In}$ radioisotope generators.....	27

CHAPTER II

EXPERIMENTAL

2.1. Chemicals and Solutions.....	31
2.1.1. Chemicals.....	31
2.1.2. Solutions.....	32
2.2. Equipments.....	32
2.3. Radioactive tracers.....	34
2.4. Factors affecting the preparation of tin (IV)- tungstate matrices.....	34
2.4.1. Effect of W (VI): Sn (IV) molar ratio.....	36
2.4.1.1. Radiometric determination of the tungsten and tin contents.....	36
2.4.2 Effect of the acidity of the reaction medium.....	37
2.4.3. Effect of nature of the reaction medium.....	37
2.5. Apparent capacities and uptake values.....	38
2.5.1. Apparent capacities for mono and divalent metal cations.....	38
2.5.2. Apparent capacity for ^{134}Cs ions.....	38
2.6. Preparation of tin (IV)- tungstate gel matrix.....	38
2.7. Characterization of the tin (IV)- tungstate gel matrix.....	39
2.7.1. Density	39
2.7.2. Chemical stability	39
2.7.3. Thermal analysis.....	39
2.7.4. Infrared spectra.....	40
2.7.5. X- ray diffraction patterns.....	40
2.7.6. Acid –base properties of tin (IV)- tungstate gel matrix.....	40
2.8. Equilibrium time.....	40
2.9. Determination of the distribution coefficient (K_d) values.....	41
2.10. $^{113}\text{Sn} / ^{113\text{m}}\text{In}$ radioisotope generator.....	41
2.10.1. Determination of the parent radioisotope uptake.....	41
2.10.2. Elution studies of $^{113\text{m}}\text{In}$ from ^{113}Sn- tin (IV)- tungstate	

	<i>Contents</i>
chromatographic column.....	42
2.10.2.1. Preparation of the radioisotope generator.....	42
2.10.2.2. ^{113m}In elution behaviour.....	42
2.10.2.3. Elution yield.....	43
2.10.3. Quality control of ^{113m}In eluates.....	43
2.10.3.1. Radionuclidic purity of the ^{113m}In eluate.....	43
2.10.3.2. Radiochemical purity of ^{113m}In eluate.....	43
2.10.3.3. Chemical purity of the ^{113m}In eluate.....	44
2.10.3.3.1 Determination of inactive tin.....	44
2.10.3.3.2. Determination of tungsten.....	45

CHAPTER III

RESULTS AND DISCUSSION

3.1. Preparation of the tin (IV) tungstate gel matrices.....	46
3.1.1. Effect of W/Sn molar ratio at different initial pH values.....	46
3.1.2. Effect of the nature of the reaction medium.....	48
3.2. Ion exchange capacity of the different tin (IV)- tungstate.....	49
3.2.1. Apparent capacities for mono and divalent metal cations	49
3.2.2. Apparent capacity for ^{134}Cs ions.....	52
3.3. Characterization of the selected tin (IV)- tungstate gel matrix SnW-2.....	54
3.3.1. Density.....	54
3.3.2. Solubility.....	54
3.3.3. Thermal analysis.....	56
3.3.4. Infrared spectra studies.....	56
3.3.5. X-ray diffraction patterns.....	59
3.3.6. Chemical composition.....	59
3.3.7. Acid- base Titration curve.....	61
3.4 Equilibrium time.....	61
3.5. Cation exchange properties.....	64
3.5.1. Static distribution behaviour studies (K_d values).....	64
3.5.1.1. Cs (I) – Ba (II) couple.....	65
3.5.1.2. Zn (II), Cd (II) and Co (II).....	72

	<i>Contents</i>
3.5.1.2.1. From HCl acid solution.....	72
3.5.1.2.2. From nitric acid solution.....	75
3.5.1.3. Zr ⁴⁺ , Hf ⁴⁺ , and Nb ⁵⁺ trible.....	78
3.5.1.3.1. From HCl acid solution.....	78
3.5.1.3.2. From nitric acid solution.....	80
3.5.1.4. ⁹⁹ Mo (VI) - ^{99m} Tc (VII) couple.....	82
3.5.1.5. Sn (IV) – In (III) Couple.....	88
3.5.1.5.1. Determination of the uptake value of the parent radioisotope (¹¹³ Sn).....	91
3.5.1.5.1.1. Breakthrough technique.....	91
3.6. ¹¹³ Sn / ^{113m} In generator.....	93
3.6.1. Loading and elution studies.....	93
3.6.2. Elution performance of ¹¹³ Sn / ^{113m} In generator.....	95
3.6.2.1. Elution profile and yield of ^{113m} In.....	95
3.6.2.2. Radionuclidic purity.....	97
3.6.2.3. Radiochemical purity.....	100
3.6.2.4. Chemical purity.....	100
Summary and conclusion.....	102
REFERENCES.....	108

LIST OF TABLES

	Page
Table (2.1) Radioactive tracers and their characteristic nuclear properties.....	35
Table (3.1) Experimental conditions of the tin (IV)- tungstate precipitate obtained by mixing 100 ml of different concentration of tungstate solution (acidified with H ₂ SO ₄ to initial pH values of 1, 3, 5 and 8) with 100 ml 0.1 M Sn (IV) solution at 20±1°C.....	47
Table (3.2) The preparation conditions and some characteristic properties of the tin (IV)- tungstate precipitates	50
Table (3.3) Apparent capacity of different tin (IV)- tungstate gel matrices for some alkali and alkaline earth metal ions and NH ₄ ⁺ at room temperature 20±1°C.....	51
Table (3.4) Apparent capacity of different tin (IV)- tungstate gel matrices for cesium ions at room temperature 20±1°C.....	53
Table (3.5) Solubility of the tin (IV)- tungstate gel matrix SnW-2 in different aqueous solutions at 20±1°C, mg/ml.....	55
Table (3.6) Separation factors of Cs (I) and Ba (II) ($\alpha = K_{d\text{Ba(II)}}/K_{d\text{Cs(I)}}$) from different media on tin (IV)- tungstate gel matrix SnW-2 at 20±1°C.....	71
Table (3.7) The calculated separation factors of Co (II), Cd (II) and Zn (II) from HCl and HNO ₃ acid solutions on tin (IV)- tungstate gel matrix SnW-2 at 20±1°C.....	77
Table (3.8) The calculated separation factors of Zr (IV), Nb (V) and Hf (IV) from HCl and HNO ₃ acid solutions on tin (IV)- tungstate gel matrix SnW-2 at 20±1°C.....	83
Table (3.9) Separation factors of Mo (VI) and Tc (VII) ($\alpha = K_{d\text{Mo(VI)}}/K_{d\text{Tc(VII)}}$) from HCl and HNO ₃ acid solutions on tin (IV)- tungstate gel matrix SnW-2 at 20±1°C.....	87
Table (3.10) Separation factors of Sn (IV) and In (III) ($\alpha = K_{d\text{Sn(IV)}}/K_{d\text{In(III)}}$) from HCl and HNO ₃ acid solutions on tin (IV)- tungstate gel matrix SnW-2 at 20±1°C.....	94

LIST OF FIGURES

	Page
Fig.(1.1) Parent- daughter radionuclide transient equilibrium relationship.....	26
Fig.(1.2) Parent- daughter radionuclide secular equilibrium relationship	27
Fig.(3.1) Thermogravimetric (a) and differential thermal (b) analysis curves for tin (IV)- tungstate SnW-2 ion exchanger dried at 50° C.....	57
Fig.(3.2) IR Spectra for tin (IV)- tungstate gel matrix SnW-2 dried at 50° C.....	58
Fig.(3.3) X-ray diffraction patterns for tin (IV)- tungstate gel matrix SnW-2 dried at 50° C.....	60
Fig.(3.4) pH titration curve of the tin (IV)- tungstate gel matrix SnW-2 dried at 50° C. Exchanger, 0.1 g; total volume, 10 ml; ionic strength, 0.1 M (HNO ₃ + NaNO ₃) or (NaOH + NaNO ₃).....	62
Fig.(3.5) Time-variation of adsorption of 10 ⁻⁴ M Cs ⁺ ions from HCl acid solution of pH=3 on tin (IV)- tungstate gel matrix SnW-2 at different temperatures.....	63
Fig.(3.6) Distribution coefficient values of 10 ⁻⁴ M Cs ⁺ and Ba ²⁺ on tin (IV)-tungstate gel matrix SnW-2 as a function of HCl acid concentration at 20±1° C.....	66
Fig.(3.7) Distribution coefficient values of 10 ⁻⁴ M Cs ⁺ and Ba ²⁺ on tin (IV)-tungstate gel matrix SnW-2 as a function of HNO ₃ acid concentration at 20±1° C.....	67
Fig.(3.8) Distribution coefficient values of 10 ⁻⁴ M Cs ⁺ and Ba ²⁺ on tin (IV)-tungstate gel matrix SnW-2 as a function of NaCl concentration at 20 ±1° C.....	69
Fig.(3.9) Distribution coefficient values of 10 ⁻⁴ M Cs ⁺ and Ba ²⁺ on tin (IV)-tungstate gel matrix SnW-2 as a function of NH ₄ Cl concentration at 20 ±1° C.....	70

Fig.(3.10) Distribution coefficient values of 10^{-4} M Co^{2+}, Cd^{2+}, and Zn^{2+} on tin (IV)- tungstate gel matrix SnW-2 as a function of HCl acid concentration at $20\pm 1^\circ \text{C}$.....	73
Fig.(3.11) Distribution coefficient values of 10^{-4} M Co^{2+}, Cd^{2+}, and Zn^{2+} on tin (IV)- tungstate gel matrix SnW-2 as a function of HNO_3 acid concentration at $20\pm 1^\circ \text{C}$.....	74
Fig.(3.12) Distribution coefficient values of 10^{-4} M Zr^{4+}, Hf^{4+}, and Nb^{5+} on tin (IV)- tungstate gel matrix SnW-2 as a function of HCl acid concentration at $20\pm 1^\circ \text{C}$.....	79
Fig.(3.13) Distribution coefficient values of 10^{-4} M Zr^{4+}, Hf^{4+}, and Nb^{5+} on tin (IV)- tungstate gel matrix SnW-2 as a function of HNO_3 acid concentration at $20\pm 1^\circ \text{C}$.....	81
Fig.(3.14) Distribution coefficient values of 10^{-4} M Mo^{6+} and carrier free Tc^{7+} on tin (IV)- tungstate gel matrix SnW-2 as a function of HCl acid concentration at $20\pm 1^\circ \text{C}$.....	84
Fig.(3.15) Distribution coefficient values of 10^{-4} M Mo^{6+} and carrier free Tc^{7+} on tin (IV)- tungstate gel matrix SnW-2 as a function of HNO_3 acid concentration at $20\pm 1^\circ \text{C}$.....	85
Fig.(3.16) Distribution coefficient values of 10^{-4} M Sn^{4+} and carrier free In^{3+} on tin (IV)- tungstate gel matrix SnW-2 as a function of HCl acid concentration at $20\pm 1^\circ \text{C}$.....	89
Fig.(3.17) Distribution coefficient values of 10^{-4} M Sn^{4+} and carrier free In^{3+} on tin (IV)- tungstate gel matrix SnW-2 as a function of HNO_3 acid concentration at $20\pm 1^\circ \text{C}$.....	90
Fig.(3.18) Breakthrough curve of ^{113}Sn from 1 g tin (IV)- tungstate SnW-2 column (0.6 cm i.d) using 10^{-2} M Sn (IV) in 0.1 M HCl acid solution at a flow rate of 0.67 ml/min and the room temperature $\sim 20\pm 1^\circ \text{C}$.....	92
Fig.(3.19) A typical elution profile of carrier free $^{113\text{m}}\text{In}^{3+}$ from 1 g tin (IV)- tungstate SnW-2 column matrix loaded with 3.53 ml of ^{113}Sn solution (10^{-2} M Sn in 0.1 M HCl acid solution) eluted with 0.1M HCl acid solution at a flow rate 0.77 ml/min and $20\pm 1^\circ \text{C}$.....	96

Fig (3.20) Gamma-ray spectra of a) tin (IV)- tungstate-¹¹³Sn column;	
b) ^{113m} In eluate of measured immediately after elution;	
c) ^{113m} In eluate measured after 72 h decay.....	98
Fig.(3.21) Decay curve for ^{113m}In eluted from tin (IV) tungstate-¹¹³Sn	
column matrix.....	99
Fig.(3.22) Radiochromatogram of ^{113m}In eluted from tin (IV) tungstate-	
¹¹³ Sn column matrix.....	101