

**ISTR2017 - The 9th
International Symposium on
Technetium and Rhenium:
Science and Utilization**

Report of Abstracts

Abstract ID : 0

Alkali technetium oxides and their relation to Tc loading in nuclear waste glasses

Content

Because of their radioactive nature, solid technetium-99 oxides have been rarely studied, and there is a dearth of modern spectra and diffraction patterns in the literature. This publication aims to address this by detailing a low-temperature synthesis method for pure, crystalline alkali pertechnetates, along with complete analysis by static and magic-angle-spinning nuclear magnetic resonance, Raman, neutron diffraction (ND), and X-ray absorption spectroscopy (XAS). Insight gained from these studies brings a deeper understanding of the periodic chemistry of alkali (Na,K,Rb,Cs) pertechnetates. Additionally, we report attempts to make 5- and 6-coordinate pertechnetate compounds of K, Na, and Li, i.e. TcO_5^- and TcO_6^- . It was found that higher coordinated species are very sensitive to water, and easily decompose into their respective pertechnetates. It was difficult to obtain pure compounds, but mixtures of the pertechnetate and other phases were frequently found, as evidenced by XAS, ND, and Raman spectroscopy. Additionally, we summarize other work on Tc loading in glasses, effect on glass structure, and salt formation in overloaded samples. For glasses, XAS chemometrics based on principal component analysis and linear combination fitting suggests that Tc is speciated first as isolated Tc^{4+} , as Tc content is increased, there is more Tc^{7+} which partitions first to K neighbors then to isolated sites. Preliminary work is reported assessing HTcO_4 and related compounds and their relationships to mechanisms of Tc volatility.

Country

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Status: SUBMITTED

Submitted by **Prof. MCCLOY, John** on **Thursday 08 June 2017**

Abstract ID : 1

Inclusion Extraction of Rhenium From Basic Aqueous Solutions Using Poly Dibenzo-18-Crown6 , Kinetics and Thermodynamics Study

Content

Inclusion chemistry of extraction of technetium and rhenium has been studied from basic, acidic and neutral solutions by macrocyclic compounds mainly crown ethers and cryptands [1,2]. The system has been investigated for application for removal of ^{99}Tc and ^{131}I fission products from nuclear radioactive wastes [3]. A project was initiated for the elucidation of the structure of $\text{Mn}^+\text{Ls}(\text{MO}_4^-)_n$ complexes of ReO_4^- and $^{99}\text{TcO}_4^-$ ions with the macrocycle cavity [4]. In this work data for rhenium solid-liquid extraction by the crown polymer polyDB18C6 from aqueous alkali metal hydroxides are presented. A Stock solution of (1 mg Re ml⁻¹) was prepared by weighing 0.6503 gm powder of standard Re_2O_7 of 99.9% purity dissolved in 500 ml deionized water. Rhenium concentrations were determined by uv-vis. spectrophotometry. The relation of extraction percent (E%) of ReO_4^- from aqueous solutions of alkali metal hydroxides by swelled PDB18C6 with time are constructed. The extraction selectivity of PDB18C6 toward ReO_4^- ions from aqueous solutions of alkali metal hydroxides was found to be in order $\text{K}^+ > \text{Rb}^+ > \text{Cs}^+ > \text{Na}^+ > \text{Li}^+$ which is compatible with the model of size matching M^+ /crown cavity. The extraction rate of ReO_4^- with PDB18C6 was studied as a function of shaking time and temperature . The kinetic data and Table-1 reveal that the extraction processes are pseudo- first order kinetics for each alkali metal hydroxides since variable amounts of PDB18C6 and temperature do not change the rate of extraction appreciably . On the other hand, the process was found to be markedly dependent on temperature , the parameters ΔG_{ex} , ΔH_{ex} and ΔS_{ex} are evaluated from the extraction equilibrium data. Table 1. Thermodynamical parameters of the extraction of ReO_4^- Ions by PDB18C6 , shaking time 60 minutes. cation ΔH_{ex} , KJmol⁻¹. ΔG_{ex} at 313K, KJmol⁻¹. ΔS_{ex} at 313K, Jmol⁻¹. Na^+ -19.1±0.10 -12.8 -20.1 K^+ -30.5±0.08 -14.0 -52.9 Rb^+ -24.8 ±0.05 -14.4 -33.5

1- M.G.Jalhoon , J. Radioanal. Nucl. Chem. Lett. 104(3)1986, 131-140. 2- S.K. Jewad, S.R. Al-Murab, M.G. Jalhoon, Proc. Int. Solv. Extr. Conf. Tokyo, 1990(907-911). 3- P. Paviet-Hartmann, WM, 06 Conference, Feb. 26-March 2, 2006, Tucson AZ. 4- J. Poineau, J.F. Weck, L.P. Burton-Pye, E. Kim, W. Kerlin, K.E. German, J. I. Transactions , Issue 13 (2013) .

Keyword – Inclusion Extraction , Rhenium , Polydibenzo18crown6

Country

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Track Classification : Chemistry of Technetium and the use of Rhenium as a simulant in the nuclear fuel cycle (separation, disposal, waste form)

Comments:

1- Inclusion chemistry of rhenium extraction by polymeric crown ethers displayed appreciable extraction from alkali metal hydroxides ,the system might be utilized fro the extraction of 99Tc from nuclear wastes. 2- The extraction follows the model of size matching fro the relation of Log.DRe versus cationic diametre of the hydroxide . 3- Reaction kinetics reflects pseudo order reaction and the process is more temperature dependant , thermodynamical parameters ,free energy ,enthalpy and entropic values agree in general with the model of size matching .

Status: SUBMITTED

Track Judgements:

Submitted by **Dr. AL-HUSSEINAWI JALHOOM, Moayyed Gassid** on **Tuesday 20 June 2017**

Abstract ID : 2

RECOVERY OF RHENIUM BY AMINE-CONTAINED SORBENTS

Content

Complex processing of raw material with relatively low content of rhenium includes operations of sorption using ion-exchange resins. The aim of this investigation is to determine the conditions of rhenium sorption from sulphuric acid solution by new granular ionite, Levextrel resin and impregnate contained amine or its functional group. To increase the rate of sorption two last materials with mobile phase of extractants were tested. As sorbents intended for rhenium recovery weak base ion exchangers with the functional groups of cyclohexylamine and Levextrel resin with diisododecylamine were used, produced by Joint-stock Company Leader Research Institute of Chemical Technology. The impregnate contained trioctylamine on macroporous carrier were obtained in the D. Mendeleev University of Chemical Technology of Russia. Sorption has been carried out in batch and dynamic conditions. Determination of the parameters of rhenium recovery was carried out at varying concentrations of acids and salts, temperature, ratio of sorbent to solution. Equilibrium, kinetic and dynamic characteristics of rhenium sorption were determined.

The work was partially financed by the Ministry of Education and Science of the Russian Federation within the framework of the Subsidy Agreement No. 14.580.21.0004 of 19.08.2015 (ID number of the project RFMEFI58015X0004).

Country

Russian Federation

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Track Classification : Rhenium in industry (mining, metallurgy, catalysis)

Contribution Type : Oral

Status: SUBMITTED

Track Judgements:

Submitted by **Prof. TROSHKINA, Irina** on **Friday 07 July 2017**

Abstract ID : 3

RHENIUM RECOVERY FROM SULFURIC ACID SOLUTIONS BY MODIFIED ACTIVE COALS

Content

For recovery of rhenium from solutions with low concentration impregnate containing phosphine oxide (PhOR) using carriers of natural origin - the active coal-based raw vegetable waste (rice husk and buckwheat husk) (RH BH) were obtained. Using transmission electron microscope (FEI Osiris, USA) micrographs of the surface modified active carbons were obtained and the distribution of elements (Re, P, Si) was studied. The amount of the extractant correlated with the magnitude of the surface. The equilibrium and kinetic characteristics of rhenium sorption from sulfuric acid solutions by impregnate based on active carbon R were determined in batch conditions. Cyclic studies have shown that the sorption capacity of impregnate is almost constant when performing 4 cycles. The obtained results indicate the possibility of using the impregnate- PhOR on the basis of active carbon RH in hydrometallurgical processes for processing of rhenium-containing raw materials.

The work was partially financed by the Ministry of Education and Science of the Russian Federation within the framework of the Subsidy Agreement No. 14.580.21.0004 of 19.08.2015 (ID number of the project RFMEFI58015X0004).

Country

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Track Classification : Rhenium in industry (mining, metallurgy, catalysis)

Contribution Type : Poster

Status: SUBMITTED

Track Judgements:

Submitted by **Prof. TROSHKINA, Irina** on **Friday 07 July 2017**

Abstract ID : 4

SORPTION OF RHENIUM ON THE LEVEXTREL RESIN CONTAINED DIISODODECYLAMINE

Content

To increase the rate and selectivity of rhenium sorption materials with mobile phase of extractants were used. The aim of this work is to obtain the sorption characteristics of new Levextrel resin contained diisododecylamine (DIDA), produced by Joint-stock Company Leader Research Institute of Chemical Technology (Russian Federation). Rhenium sorption was carried out under batch and dynamic conditions. It was established that the highest value of the distribution coefficient is observed at acidity of pH 2. Equilibrium, kinetic and dynamic characteristics of rhenium sorption were determined. The equilibrium constants, rate constants, diffusion coefficients and the apparent activation energy were calculated.

Country

Russian Federation

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Contribution Type : Poster

Status: SUBMITTED

Track Judgements:

Submitted by **Prof. TROSHKINA, Irina** on **Friday 07 July 2017**

Abstract ID : 5

chemical shift study in Rhenium compounds in L and M emission lines using WDXRF ttechnique

Content

Positive and negative shifts in L and M emission lines of Rhenium elements in different chemical compounds were determined first time from their recorded x-ray emission spectra in high resolution wavelength dispersive x-ray fluorescence (WDXRF) spectrometer. The effective charges (q, q/, q// and q///) were calculated from four theoretical models (Pauling method, Suchet method, Levine theory and Batsonav method) and found to be linear dependence with chemical shift. The measured chemical shifts were correlated with bond length, relative line-width (FWHM), effective charge, electro-negativity, number of ligands and Coster-Kronig (CK) transition processes.

Country

India

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Contribution Type : Oral

Comments:

I am working in WDXRF and Synchrotron field.

Status: SUBMITTED

Track Judgements:

Submitted by **Mr. KAINTH, Harpreet** on **Sunday 30 July 2017**

Abstract ID : 6

THE BEHAVIOR OF RHENIUM AND OTHER RARE METALS AT THE COMPLEX PROCESSING OF POOR COPPER-SULFIDE ORES

Content

The distribution of rare elements [U+2012] rhenium, radiogenic osmium and uranium at the hydrometallurgical processing of crude concentrate (CC) obtained by flotation of off-balance copper-sulfide ore deposits of Zhezkazgan (Republic of Kazakhstan) was studied. A method of mass spectrometry with inductively coupled plasma determine the content of rhenium, osmium and uranium in the CC [U+2012] (1,3÷2,3),(0,90÷5,61) • 10⁻³ and 1,91 g/t, respectively. After leaching C using nitric acid solutions with addition of sodium chloride rhenium absorbed by weakly basic anion exchanger with functional groups of secondary amine. Part of the radiogenic osmium is sorbed by this ion exchange resin. When rhenium is eluted by ammonia solution radiogenic osmium is desorbed also. In a second stage of rhenium sorption from the eluate of first stage using impregnate containing trialkylamine, it remains in solution. At the stage subsequent sorption of copper by macroporous ion exchanger with chelate groups osmium also accumulate in the sorbent, which after the copper sorption is a concentrate of osmium. Uranium is leached from the CC and not extracted from the productive solution at the stages of sorption of rhenium and copper, which contributes to high quality end products (Cu, Re). The specific activity of natural radionuclides in the slurry is significantly lower than the value corresponding to boundary condition of waste classification as liquid radioactive wastes.

Country

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Contribution Type : Poster

Status: SUBMITTED

Track Judgements:

Submitted by **Dr. ZAKHARIAN, Semen** on **Wednesday 16 August 2017**

Abstract ID : 7

Spectroscopic and batch studies of technetium uptake by siderite

Content

Tc-99 is of major concern for radioactive waste disposal. Redox processes, converting the highly mobile Tc(VII) into the immobile Tc(IV), are of paramount importance for the safety of radioactive waste repositories. Fe(II)-bearing minerals, ubiquitous in nature but also forming as corrosion products on steel, play a vital role in these redox reactions due to their high redox reactivity and high sorption capacity. We studied the Tc(VII) uptake by siderite (FeCO₃), a typical Fe(II) mineral in carbonate-rich environments, in the pH range 7 – 12.6 under anoxic conditions. Batch sorption experiments showed that Tc retention by siderite is fast and efficient (log Rd ~5) across the pH range and independent of ionic strength. Tc K-edge XANES data confirmed that the Tc immobilization is due to surface-mediated reduction of Tc(VII) to Tc(IV). The local structure of Tc(IV) in Tc siderite sorption samples and Tc siderite coprecipitates probed by EXAFS spectroscopy revealed three different species: Between pH 7.8 and 11.8, TcO₂-dimers form inner-sphere sorption complexes at the surface of the initial siderite phase as well as on secondary magnetite or green rust formed during the redox reaction. Between pH 11.9 and 12.6, Tc(IV) is incorporated in a mixed Fe/Tc hydroxycarbonate precipitate (chukanovite-like). The results showed that siderite contributes effectively to the retention of Tc under repository conditions through formation of strong sorption complexes and precipitation of hydroxycarbonate phases with low solubility.

Country

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Contribution Type : Oral

Status: SUBMITTED

Track Judgements:

Submitted by **Dr. SCHMEIDE, Katja** on **Monday 28 August 2017**

Abstract ID : 8

Unusual redox neighborhood in technetium compounds

Content

Technetium has a great number of oxidation states (usually we say 9 but in fact much more) and is evidently one of the elements with the most complicated chemistry. This is due its position in the center of 4d elements row with 7 electrons available for chemical bonding. One of the very special options complicating technetium chemistry is its ability to cluster formation and especially the possibility for Tc cluster to be reduced by consecutive addition of electrons one by one. So the oxidation states of Tc in hydrochloric acid could be 4+ (in K_2TcCl_6), 3+ (in $[Bu_4N]_2Tc_2Cl_8$), 2.5+ (in $K_3Tc_2Cl_8$), 2+ (in $K_2Tc_2Cl_6$), 11/6+ (in $[Me_4N]_3Tc_6Cl_{14}$ and 10/6+ (in $[Me_4N]_2Tc_6Cl_{12}$). We could imagine the number of hydroxides that could be formed starting from these compounds. Another option is the presence of Tc atoms in different oxidation states within the same compound (p.e. Tc_2Ac_4 where Tc^{3+} and Tc^{7+} coexist in the one compound. New example is the red pertechnic acid. According to new synthesis and X ray structure study it contains 4 TcO_6 octahedra with Tc^{6+} , that is usually considered extremely unstable and 16 $Tc(VII)$ tetrahedra arranged in a joint compound $[Tc^{VI} 4Tc^{VII} 1668] \cdot 16H_2O$: $a = 11.1743(6)$, $b = 12.8839(6)$, $c = 14.0661(6)$ Å, $\alpha = 71.128(2)$, $\beta = 69.015(2)$, $\gamma = 74.340(2)^\circ$, P-1, Z = 1. Of next extreme interest is new $Pu(III)(DMSO)_6[TcO_4]_3$ compound where reducing and oxidizing parts coexist.

Country

Russian Federation

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Track Classification : Fundamental chemistry of Technetium and Rhenium (synthetic, materials and coordination chemistry, inorganic and organometallic complexes, properties)

Contribution Type : Oral

Status: SUBMITTED

Track Judgements:

Submitted by **Prof. GERMAN, Konstantin** on **Wednesday 30 August 2017**

Abstract ID : 9

Luminescence-Intensity Switching of Tetracyanonitridorhenium(V) Complexes by the Solvent-Free Reactions

Content

Mechanochemical reactions giving a solid product from a solid substance and a solid reactant under solvent-free conditions are attractive because of treatment without harmful organic solvents. Reactions of solid compounds in a minimal amount of water that afford a solid compound in high yield are also useful methods. In the present study, the reversible luminescence intensity switching by solvent-free mechanochemical and vacuum elimination reactions and by an exposure of water to the solid was investigated on the basis of formation/dissociation of the coordination bond between tetracyanonitridorhenium(V) and imidazole (Him) as well as the hydrogen bond between Him molecules in the complexes. The reactions of the five-coordinate tetracyanonitridorhenium(V), $(\text{PPh}_4)_2[\text{ReN}(\text{CN})_4]$ (1) with five-membered N-heteroaromatic ligands, Him produced new complexes, $(\text{PPh}_4)_2[\text{ReN}(\text{CN})_4\text{Him}]$ (2) and $(\text{PPh}_4)_2[\text{ReN}(\text{CN})_4\text{Him}] \cdot \text{Him}$ (3). The complexes 2 showed intense luminescence in the solid state at 296 K. Luminescence of 3 was very weak in the solid state at 296 K. Luminescence intensity was drastically decreased by the mechanochemical reaction of 2 with 1 equiv. of Him to give 3 in the solid state. By placing solid of 3 in water, the solid showed intense luminescence to produce 2. The complex 3 was also obtained by the mechanochemical reaction of 1 with 2 equiv. of Him in the solid state. The complex 1 was reproduced under vacuum at 185°C from 3.

Country

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Status: SUBMITTED

Track Judgements:

Submitted by **Prof. YOSHIMURA, Takashi** on **Wednesday 30 August 2017**

Abstract ID : 10

Tc reduction by bacteria from soda lake

Content

One of the problematic types of LRW are alkaline wastes generated in some types of spent nuclear fuel reprocessing. Environmental friendly biological techniques of LRW treatment are not widespread because of its extremely high salt contents and alkalinity usually not suitable for organisms. The aim of this work was to explore the use of microorganisms from extremely alkaline habitat to process liquid alkaline radioactive waste. This involved a search of promising microbial cultures from extremely alkaline lakes of the Kulunda steppe, which composition is close to alkaline wastes. The lake sediments with medium (44-85 g/L) and extremely high (300-400 g/L) salt content were selected for investigations; the microbial associations, which capable to reduce radionuclides were received. Experiments on reduction of technetium and uranyl acetate + pertechnetate were performed. The bacteria present in the sediments and sludge of soda lakes reduced pertechnetate ions in both experiments with high salinity (2.3 M - 84% technetium reduced) and in experiment with a lower salinity (0.8 M - 86% technetium reduced) wherein uranium had no competitive effect on the recovery of technetium - in experiments with 1) technetium and 2) with technetium + uranyl acetate reduced approx. 84% of pertechnetate. When using the mixed sludge from lower salt content lake the amount of reduced technetium was lower compared to the high salinity - 55-60%. This work was supported by RFBR grant 15-05-08919

Country

Russian Federation

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Status: SUBMITTED

Track Judgements:

Submitted by **Prof. GERMAN, Konstantin** on **Wednesday 30 August 2017**

Abstract ID : 11

NEW LIGAND ADDITIVES FOR TECHNETIUM STABILIZATION IN CEMENT MATRIX FOR LONG-TERM STORAGE T COMPOUND

Content

Cementing of radioactive waste is the simplest and cheapest method of curing radioactive waste. However, some radionuclides contained in RAW may not be included in the cement matrix, since they have a high degree of leachability and are therefore easily washed by groundwater. One such radionuclide is technetium. The purpose of this paper is to search for a stabilizing ligand. The following substances were selected as stabilizing ligands: 1) PGMH-hydrochloride (polyhexamethyleneguanidine hydrochloride, 2) TFF-chloride (tetraphenylphosphonium chloride), 3) Polyethylenimine (PEI), 4) Thiourea. 5) Chitosan is a polysaccharide. This procedure would form insoluble complexes with technetium and promote strong retention of technetium in the cement compound. In the course of mechanical tests, an optimal water-cement ratio of 0.5 was chosen, which will be used later in the evaluation of leaching. The leachability assessment of the pertechnetate ion at the cement samples revealed that PGMH-HCL is the most efficient for retaintion the pertechnetate ion in the cement matrix.

Country

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Track Classification : Chemistry of Technetium and the use of Rhenium as a simulant in the nuclear fuel cycle (separation, disposal, waste form); Radioanalytical chemistry (Measurement and detection of Tc an Re in the biosphere)

Contribution Type : Poster

Status: SUBMITTED

Track Judgements:

Submitted by **Prof. GERMAN, Konstantin** on **Wednesday 30 August 2017**

Abstract ID : 12

Tc(IV) complexation with polycarboxylate and polyaminocarboxylate ligands

Content

Understanding technetium speciation in the environment is crucial for the remediation of sites contaminated with this fission product. While Tc(VII) species dominate in oxidative conditions, Tc(IV) is most prevalent under anoxic and mildly reducing conditions. As pertechnetate, Tc(VII) exhibits high aqueous mobility and solubility upwards of 11 M in neutral waters. Conversely, Tc(IV) features a high propensity for sorption onto mineral surfaces and very low solubility, on the order of 10 nM in neutral waters. Technetium is a particular problem at storage sites such as the Hanford reservation (Washington, U.S.), where an estimated 500 Ci of Tc-99 travelled to the vadose zone above groundwater reserves, due to the high mobility of Tc(VII); reduction processes to convert Tc to its lower and less soluble oxidation state, Tc(IV), has therefore been proposed as a remediation and disposal tool. However, little thermodynamic information has been available for calculations and accurate predictions for Tc mobility in the environment have been challenging. We have determined the stability constants for Tc(IV) complexation with a variety of ligands (acetate, citrate, EDTA, IDA, NTA, HEDTA, and DTPA) using liquid-liquid extraction methods. These data were used to predict Tc(IV) solubility in presence of ligands and demonstrate that complexing ligands increase Tc(IV) solubility.

Country

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Track Classification : Chemistry of Technetium and the use of Rhenium as a simulant in the nuclear fuel cycle (separation, disposal, waste form)

Contribution Type : Oral

Status: SUBMITTED

Track Judgements:

Submitted by **Prof. WALL, Nathalie** on **Wednesday 30 August 2017**

Abstract ID : 13

Comparison the Solvent Extraction Behavior of Re(VII) with Tc(VII)

Content

Heptavalent rhenium, Re(VII), is often considered an acceptable analog for Tc(VII); use of stable Re instead of radioactive Tc would simplify experimental work. This study investigates the validity of the analogy for solvent extraction systems. Dual radioisotope-labelled liquid-liquid extraction (LLE) experiments were carried out incorporating both Tc-99m(VII) (with Tc-99(VII) carrier) and Re-186,188(VII) tracers (with stable Re carrier) in order to quantify the suitability of Re(VII) to act as an analog for Tc(VII). Extraction of each metal by tetraphenylphosphonium chloride in chloroform from a 1 M ionic strength aqueous solution was quantified. The distribution coefficient, D , of each metal was determined using gamma spectrometry and as a function of the extractant concentration (0.00 to 1.00 mM) and pH (0, 2, 4, 6, 8). The extraction equilibrium constant, K_{ex} , was quantified for each metal. Results show that, while extraction of Tc(VII) was characterized by a greater K_{ex} value than for Re(VII) extraction across the pH range, the trend of K_{ex} as a function of pH was virtually identical for both metals. Additional LLE experiments using Re(VII) and Tc(VII) individually were carried out under identical conditions that were employed for the dual radioisotope-labelled samples. These results are in good agreement with the dual-metal LLE experiments.

Country

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Track Classification : Chemistry of Technetium and the use of Rhenium as a simulant in the nuclear fuel cycle (separation, disposal, waste form)

Contribution Type : Oral

Status: SUBMITTED

Track Judgements:

Submitted by **Prof. WALL, Nathalie** on **Wednesday 30 August 2017**

Abstract ID : 14

POLYMERIC IONOSELECTIVE SENSORS FOR THE DETERMINATION OF PERRENATE AND PERTEHNATATE IONS WITH HEXAETOXYCYCLO-TRIOPHOSPHANE AS A PLASTICIZER

Content

A new supramolecular system, polymer-hexaethoxycyclotriphosphazene (GETTSF), ionophore, has been proposed and investigated for the creation of new electrochemical sensors with improved electroanalytical parameters for the determination of TcO_4^- and ReO_4^- . As a sensitive element, we use a membrane based on polyvalylchloride matrix containing hexaethoxycyclotriphosphazene as a plasticizer with dissolved ionophore tetradecylammonium pertechnetate (perrhenate) at a concentration of 10^{-2} M. The main electroanalytical parameters of the proposed ion-selective electrodes (selectivity, linear response range, and potential stability) are measured. The detection limit of the electrode was 7×10^{-7} M. (TcO_4^-) and 1.5×10^{-7} M ReO_4^- . The study of the membrane composition effect on the detection limit for anions in aqueous solutions, the optimum membrane composition was determined: 60% of the GETTSTF (I-10-2M) - 40% PVC. The new plasticizer allows improve the detection limit of ions in comparison with dibutyl phthalate (8×10^{-6}). This is explained by higher distribution coefficients and the dielectric constant of the GETCTF. Series of membrane potentiometric selectivity has been shown to correlate with the Hofmeister series for anions. In this case, the differentiating effect of GETTST on membrane selectivity coefficients was noted, as compared to the selective characteristics of polymer compositions containing dibutyl phthalate plasticizer. These potentiometric sensors may apply to determination of perrhenate or pertechnetate content in aqueous solutions of complex salt composition and are not sensitive to other Tc and Re species.

Country

Russian Federation

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Track Classification : Radioanalytical chemistry (Measurement and detection of Tc an Re in the biosphere)

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Track Judgements:

Submitted by **Prof. GERMAN, Konstantin** on **Thursday 31 August 2017**

Abstract ID : 15

Determination of Magneto-Structural Relationships in Tc, Re, Os Double Perovskites

Content

Tc and Re containing perovskites have shown interesting electronic and magnetic properties, such as half metallic behaviour, magnetoresistance and high temperature ferrimagnetism in the double perovskite Sr₂FeReO₆,^[1] high temperature antiferromagnetism in SrTcO₃^[2] and low temperature glassy canted antiferromagnetism and field dependent magnetic ordering in Sr₂MnReO₆.^[3] In order to further probe these interesting behaviours, double perovskites of the type Sr₂Fe(1-x)Mn(x)MO₆, 0 ≤ x ≤ 1, step = 0.1, M = Tc, Re, Os are proposed. Compounds with M = Re have been synthesised to high purity, and across the series the following progression of crystal symmetries were observed: I4/m (x = 0, 0.1, 0.2, 0.3), I2/m (x = 0.4, 0.5), P2₁/n (x = 0.6, 0.7, 0.8, 0.9, 1). This trend was elucidated by refinements carried out against synchrotron powder X-ray diffraction data. Further analysis of the physical properties of these compounds via magnetic susceptibility, magnetisation, heat capacity and resistivity measurements are being undertaken. Neutron powder diffraction is proposed for determination of magnetic structures and determination of oxygen positions/stoichiometry to high precision. Ultimately this project seeks to understand how these properties evolve within this class of materials by systematic substitution of Mn for Fe as well as the role which Tc, Re and Os play in these crystal systems.

[1] Physical Review B 1999, 59 (17), 11159-11162.

[2] Physical Review Letters 2011, 106 (6), 067201.

[3] Journal of Physics: Condensed Matter 2004, 16 (1), 135.

Country

Australia

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Track Classification : Fundamental chemistry of Technetium and Rhenium (synthetic, materials and coordination chemistry, inorganic and organometallic complexes, properties)

Contribution Type : Oral

Status: SUBMITTED

Track Judgements:

Submitted by **Mr. INJAC, Sean** on **Thursday 31 August 2017**

Abstract ID : 16

Neutron scattering for Tc and other Nuclear Fuel Cycle materials: why and how

Content

Elastic and inelastic scattering of cold and thermal neutrons ($E < 0.1$ eV) is an experimental technique that allows to study samples in a wide range of temperature (<1 K – 2000 K), pressure, magnetic and electric field, etc. that provides unique information on structure and dynamics of a material of interest. The simplest form of neutron scattering is diffraction done on polycrystalline samples, analogous to widely used X-ray diffraction. However, in contrast to the latter, neutron diffraction can be done non-destructively on bulk centimetre-scale samples. That allows to accurately determine quantitative phase composition on large-grain and/or textured samples which are difficult to study with X-ray diffraction due to poor grain statistics. When done in situ, neutron diffraction on bulk samples also better approximates industrial processes, such as sintering, annealing, oxidation/reduction, etc. Finally, neutron diffraction is the most direct way to experimentally determine magnetic structure of a material in its magnetically ordered state. That in turn allows more accurate ab initio (DFT) modelling of structure and properties of a material of interest. I will present examples of neutron diffraction studies on Nuclear Fuel Cycle relevant Tc, U, Th containing materials done as a part of the user program at the Australian Centre for Neutron Scattering (ANSTO). These include in situ studies of phase transformations at high temperature and magnetic structure determination. Access to neutron scattering instruments, which is open to external users, logistics and safety arrangements for neutron scattering experiments will also be discussed.

Country

Australia

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Track Classification : Fundamental chemistry of Technetium and Rhenium (synthetic, materials and coordination chemistry, inorganic and organometallic complexes, properties)

Contribution Type : Poster

Status: SUBMITTED

Track Judgements:

Submitted by **Dr. AVDEEV, Max** on **Friday 01 September 2017**

Abstract ID : 17

Applying Rhenium Coordination towards the Improved Fluorine-18 Radiolabelling of Bipyridine Nuclear Medicines

Content

An initial design concept towards a nuclear-optical hybrid imaging agent was pursued, whereupon rhenium(I) was incorporated to allow for optical imaging, and fluorine-18 was implemented to allow for nuclear imaging via positron emission tomography (PET). However, in the process of radiolabelling this molecule it was discovered that rhenium(I) coordination facilitates the incorporation of the fluorine-18 radioisotope, leading to improved radiochemical yields (RCYs) over the ligand. Furthermore, the complexation of rhenium also enabled these heightened RCYs without the traditional need to azeotropically dry the radiofluorinating media, which is an often quoted issue associated with reactions involving fluorine-18. Further expansion of this work has demonstrated that rhenium coordination can in fact enable the radiolabelling of bipyridine systems formally unable to be synthesised, thus expanding the scope of PET nuclear medicines which can be made available to researchers. Future directions towards ligand dissociation methods will be discussed, alongside the implementation of microfluidic technologies which were applied to automate the fluorination and rhenium complexation syntheses.

Country

Australia

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Track Classification : Technetium and Rhenium in nuclear medicine (isotope production, labelling, coordination chemistry)

Contribution Type : Oral

Status: SUBMITTED

Track Judgements:

Submitted by **Mr. KLENNER, Mitchell Ashley** on **Sunday 10 September 2017**

Abstract ID : 18

Comparison of thermal expansion of Tc and Re salts.

Content

Tc 7+ compounds are highly mobile in the environment. Relatively little is known regarding the solid state chemistry of Tc. Recently we studied the structural properties of (NH₄)TcO₄ (Tc⁷⁺) and confirmed that this is isostructural with (NH₄)ReO₄ adopting a tetragonal scheelite type structure in space group I4₁/a. The unit cell parameters of (NH₄)TcO₄ are strongly temperature dependent with the structure showing negative thermal expansion along both the a- and c-axis, albeit at different temperatures. This behaviour is significantly different to that previously reported for the isostructural oxide (NH₄)ReO₄, although we note that the data for (NH₄)ReO₄ was collected at much lower resolution. Nevertheless it is clear in the literature that the thermal expansion behaviour of (NH₄)ReO₄ is highly anisotropic. Despite the difference in the thermal expansion between what we have observed for (NH₄)TcO₄ and that described by others for (NH₄)ReO₄ it is likely that the origin of the anomalous thermal expansion in is the same in both cases, namely it is a consequence of re-orientation of the ammonium ions in the surrounding cage of eight oxygen atoms. To verify this for (NH₄)TcO₄ requires we replace the ammonium cation with another small cation. Therefore we have compared the thermal behaviour of AReO₄ with ATcO₄ to determine if Re oxides are suitable surrogates to predict the behaviour of Tc oxides and how they may behave in the environment.

Country

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