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Summary of Scientific Achievements  
An Overview of a Monothematic Series  
of Scientific Publications

**Appendix 3**  
**attachment to the habilitation application**

**Faculty of Chemistry University of Warsaw**  
**Warsaw 2018**

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## I. Name and Surname

Maciej Chotkowski

## II. Information on diplomas and academic degree

2008	<b>Ph.D. degree in Chemical Sciences, Doctoral Thesis title:</b> <i>„Electrochemical and „in situ” spectroscopic investigations of manganese and rhenium compounds in acidic environment”</i> Doctoral dissertation supervisor: prof. Andrzej Czerwiński (Faculty of Chemistry, University of Warsaw)
2005	<b>M.Sc. degree in Psychology:</b> <i>„Modification of explicit and implicit attitudes towards alcohol by generation and providing information against drinking alcohol”</i> Supervisor: Dominika Maison, Ph.D., D.Sc. (Faculty of Psychology, University of Warsaw)
2004	<b>M.Sc. degree in Chemistry:</b> <i>„Spectroelectrochemical investigations of selected manganese compounds”</i> Supervisor: prof. Andrzej Czerwiński (Faculty of Chemistry, University of Warsaw)

## III. Information on employment

since 02.2009	adjunct, Laboratory of Electrochemical Power Sources, Faculty of Chemistry, University of Warsaw
02.2009 ÷ 01.2012	adjunct, Department of Electrochemistry and Fundamentals of Technology, Industrial Chemistry Research Institute
09.2004 ÷ 02.2009	assistant, Department of Electrochemistry and Fundamentals of Technology, Industrial Chemistry Research Institute

**IV. Indication of the achievements resulting from Article 16, paragraph 2 of the Journal of Laws of 14 March 2003 on Academic Degrees and Title in Art (Journal of Laws 2016, item 882, with later amendments)**

A) Title of scientific achievement

*Electrochemistry, spectroscopy and extraction of ionic technetium species*

B) Publications included in the scientific achievement

No.	Autor/autorzy, data wydania, tytuł, czasopismo, tom, strony	Impact Factor <sub>(year)</sub>
[H1]	<b>M.Chotkowski</b> , A.Czerwiński*, 2012, <i>Electrochemical and spectroelectrochemical investigations of pertechnetate ions electroreduction in acidic media</i> , Electrochim. Acta 76, 165-173	3.777 <sub>(2012)</sub>
[H2]	<b>M.Chotkowski*</b> , A. Czerwiński, 2014, <i>Thin layer spectroelectrochemical studies of pertechnetate reduction on the gold electrodes in acidic media</i> , Electrochim. Acta, 121, 44-48	4.504 <sub>(2014)</sub>
[H3]	<b>M.Chotkowski*</b> , A.Czerwiński, 2014, <i>Thin layer spectroelectrochemical (RVC-OTTLE) studies of pertechnetate reduction in acidic media</i> , J. Radioanal. Nucl. Chem., 300, 229-234	1.034 <sub>(2014)</sub>
[H4]	<b>M. Chotkowski*</b> , B. Wrzosek, M. Grdeń, 2018, <i>Intermediate oxidation states of technetium in concentrated sulfuric acid solutions</i> , J. Electroanal. Chem., 814, 83-90	3.235 <sub>(2017)</sub>
[H5]	<b>M. Chotkowski*</b> , 2018, <i>Redox interaction of technetium with neptunium in acidic media</i> , J. Radioanal. Nucl. Chem., 317, 527-533	1.181 <sub>(2017)</sub>
[H6]	<b>M. Chotkowski*</b> , M. Grdeń, B. Wrzosek, <i>Intermediate oxidation states of technetium in alkaline solutions</i> , J. Electroanal. Chem., 829, 148-156	3.235 <sub>(2017)</sub>
[H7]	<b>M.Chotkowski*</b> , 2016, <i>Extraction of moderate oxidation state technetium species between 30% tri-n-butyl phosphate and H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub></i> , J. Radioanal. Nucl. Chem., 307, 457-462	1.282 <sub>(2016)</sub>
[H8]	<b>M. Chotkowski*</b> , D. Połomski, 2017, <i>Extraction of pertechnetates from HNO<sub>3</sub> solutions into ionic liquids</i> , J. Radioanal. Nucl. Chem., 314, 87–92	1.181 <sub>(2017)</sub>

\* corresponding author

## C) Scientific goals of the research, obtained results and their practical importance discussed in abovementioned publications

### *Introduction*

The publications included in the scientific achievement describe physicochemical (mainly electrochemical and spectroscopic) properties of ionic forms of technetium in aqueous media and a process of their extraction in selected liquid-liquid systems.

The results of my research are of crucial importance for nuclear medicine and nuclear power industry.

About 80% of all diagnostic tests in nowadays nuclear medicine is carried out using  $^{99m}\text{Tc}$ , which is a short-lived technetium radioisotope with half-life of 6 hours [OECD, 2017; IAEA, 2015; Nowak, 1998]. The  $^{99m}\text{Tc}$  used in synthesis of radiopharmaceuticals is eluted from a  $^{99}\text{Mo}/^{99m}\text{Tc}$  generator as a pertechnetate ion,  $\text{TcO}_4^-$ . Various radiopharmaceuticals require technetium with different oxidation states [Abram, 2006] and most common used are complexes of technetium containing cores, such as  $[\text{TcO}]^{x+}$ ,  $[\text{TcN}]^{2+}$ ,  $[\text{Tc}(\text{CO})_3]^+$  or  $\text{Tc}^{3+}$ , with large organic molecules. Synthesis of such technetium species with oxidation state and chemical composition required for a specified radiomedical application creates a challenging task for modern chemists. The most common approach in radiopharmaceuticals synthesis relies on chemical reduction of eluted pertechnetates using reducing agents, such as  $\text{Sn}^{2+}$  [Nowak, 1998 Saha, 2004]. In the course of these reactions the  $\text{TcO}_4^-$  ions are reduced to lower valency Tc species, "reduced Tc", that are easily complexed by selected agents while the  $\text{Sn}^{2+}$  ions are simultaneously oxidised to  $\text{Sn}^{4+}$ . The latter, however, are hard to remove from the reaction mixture and can be present in the radiopharmaceutical administered to the patient even after several steps of purification. Therefore, there is a growing interest in alternative methods of the pertechnetates reduction that do not require presence of reducing agents. Electrochemical reduction of  $\text{TcO}_4^-$  ions on solid electrodes offers an interesting alternative to the chemical reduction approach. This is a "pure" method of generation of desirable forms of the element but its successful application requires thorough knowledge of technetium electrochemistry. Despite the fact that the electrochemical properties of technetium have been the

subject of research since the end of the 1930s, many aspects of technetium electrochemistry, particularly stability of its ionic forms in aqueous solutions, have not been discussed in detail so far. The most important aspects of technetium electrochemistry which require a thorough analysis include:

- a) influence of the electrolyte solution composition on processes of reduction of the pertechnetates, especially composition and structure of generated products;
- b) mechanism of formation of Tc(IV) polymer forms, proposed pathways include a synproportionation between Tc(III) and Tc(VII) to dimers, such as  $[\text{Tc}_2\text{O}_2]^{3+/4+}$  and a direct polymerization of electrogenerated  $\text{TcO}^{2+}$  ions,
- c) standard red-ox potential values of various red-ox couples containing “reduced” technetium, e.g. Tc (IV) and Tc (III),
- d) spectroscopic characterisation of unstable technetium forms, e.g. Tc (V) and Tc (III).

For these reasons, I decided to perform detailed spectroelectrochemical studies with the aim of extending our knowledge on technetium electrochemistry.

Apart from the medical applications the red-ox processes of technetium play a very important role in many aspects of industrial management of radioactive waste, including:

- a) reprocessing of spent nuclear fuel in extraction processes (e.g. PUREX, UREX)
- b) disposal and storage of liquid radioactive waste.

Relatively large amounts of technetium are produced during normal operation of a light-water nuclear reactor [DOE, 1996]. About 6% of  $^{235}\text{U}$  fissions leads to generation of  $^{99}\text{Tc}$ , a long-lived isotope with a half-life of  $2.11 \cdot 10^5$  years. Thus, 1 ton of spent fuel with an initial enrichment at level 3.2% and burnup 45 GWd / tHM contains approximately 1 kg of  $^{99}\text{Tc}$  [Bonnerot, 2005].

Nuclear fuel reprocessing is one of the most important methods of its disposal. Currently, PUREX (Plutonium Uranium Recovery by Extraction) is the only method of nuclear fuel reprocessing that found a practical industrial application in large-scale facilities. A simplified scheme of the PUREX is shown in Figure 1 [Lieser, 2001]. This process relies on ability of TBP (tri-n-butyl phosphate) to extract uranium (VI) and plutonium(IV) (as well as plutonium(VI)) from aqueous to organic

phase without extracting fission products and other cations containing actinides (e.g.  $\text{NpO}^{2+}$ ).

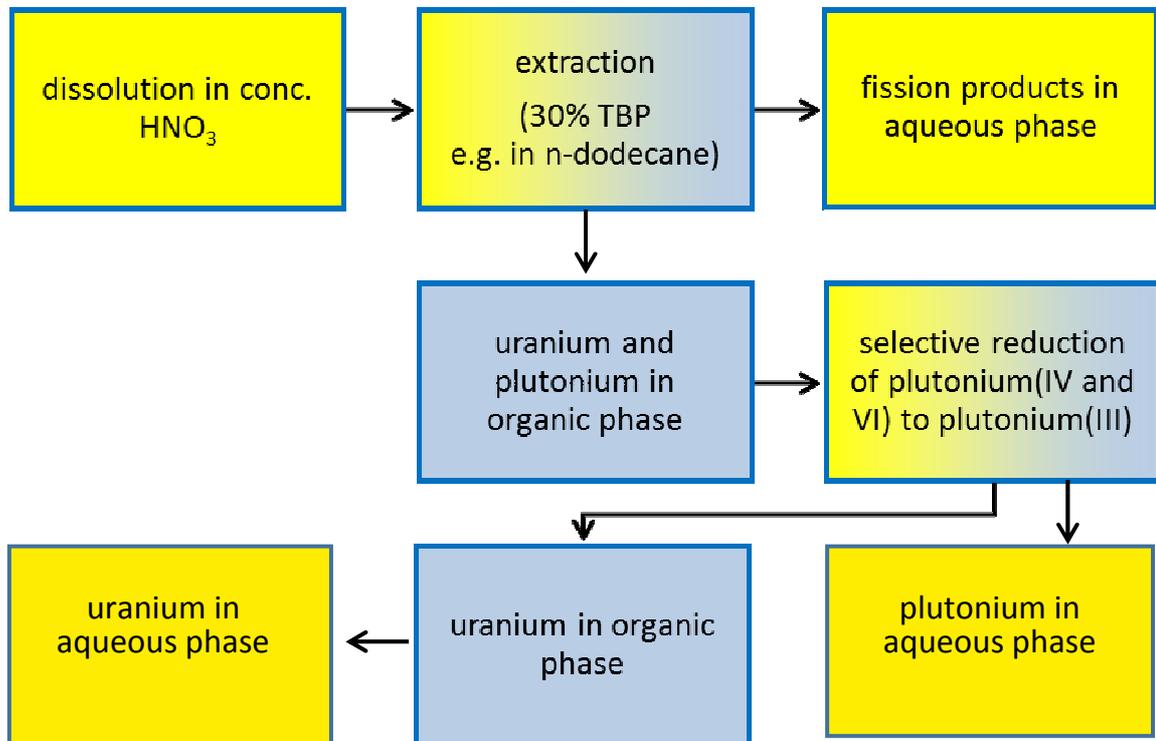


Figure 1. Simplified schematic of the main stages of the PUREX process.

The PUREX process is carried out in several stages:

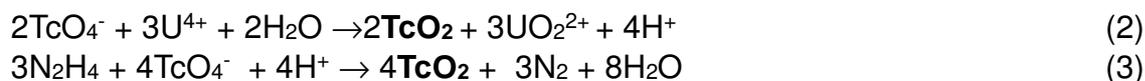
- dissolution of spent nuclear fuel in concentrated nitric acid,
- extraction of uranium and plutonium from the aqueous phase (1-3M  $\text{HNO}_3$ ) to the organic one (e.g. n-dodecane) using TBP (typically a 30% solution)
- reduction of  $\text{Pu}^{4+}$  to  $\text{Pu}^{3+}$  using selective reducers, such as  $\text{Fe}^{2+}$  or  $\text{N}_2\text{H}_4$ .
- reextraction of reduced plutonium ( $\text{Pu}^{3+}$ ) from the organic to the aqueous phase
- reextraction of uranium from the organic to the aqueous phase using diluted  $\text{HNO}_3$

In order to obtain high purity salts of U and Pu, the extraction and reextraction processes are repeated several times until satisfied results are obtained. Further purification can be carried out using ion exchange resins.

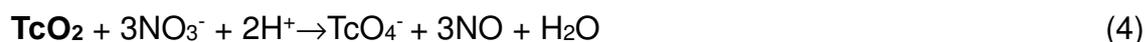
Biologically hazardous products of  $^{235}\text{U}$  fission, such as  $^{137}\text{Cs}$  or  $^{90}\text{Sr}$ , are not extracted from aqueous nitric acid solutions to the organic phase and remain in the water stream. Unfortunately, technetium as pertechnetates ( $\text{TcO}_4^-$ ) undergoes a co-extraction with uranyl ions into the organic phase (equation (1)). Despite of numerous studies on PUREX process, this co-extraction phenomenon remains a serious problem which strongly complicates uranium and plutonium purification [Jassim, 1984; Garraway, 1984; Dileep, 2008].



Although reaction 1 is not very efficient (distribution coefficient,  $D_{\text{Tc}}(\text{org./aq.}) < 1$  [e.g. Dileep 2008, Pruett 1984]), it results in a considerable contamination of the organic phase with  $^{99}\text{Tc}$ . In addition, selective reducers such as,  $\text{U}^{4+}$ ,  $\text{N}_2\text{H}_4$ , or  $\text{Fe}^{2+}$ , which are used for reduction of  $\text{Pu}^{4+}$  to  $\text{Pu}^{3+}$  also reduce the pertechnetates [Dileep, 2008] (equations (2) - (3)):



Reduced technetium species, such as  $\text{TcO}_2$  from reactions 2 and 3, can be oxidised by nitrates from dissociation of  $\text{HNO}_3$ , according to a simplified scheme (4):



Most of the literature reports technetium dioxide as the end product of reactions 2 and 3 and assumes molecular  $\text{TcO}_2$  as a species containing the lowest oxidation state of technetium stable in aqueous solutions [Dileep, 2008]. Formation of stable ionic species containing reduced technetium is usually disregarded in the literature. Similarly, only a handful of papers point out to formation of unstable  $\text{Tc(V)}$  and  $\text{Tc(IV)}$  species which are reduced to some  $\text{Tc(IV)}$  forms [Ozawa, 2003].

Finally, the technetium participates in red-ox reactions with actinides, e.g. plutonium and neptunium, and these reactions additionally complicate the extraction process. This is one of the factors that dictates application of a strict control of uranium contamination with Tc [IAEA, 2007].

In order to reduce content of the technetium contaminants in the „uranium fraction”, a series of techniques, based on selective reduction of pertechnetates, is proposed. For example, the extraction coupled with ion exchange with resins has been proposed and was a subject of patent applications [Pruett, 1984; Friedman 1985; Gong, 2008]. Extraction of technetium from an aqueous to an organic phase in the absence of actinides was also investigated by several authors [El-Kot, 1992; Schwochau, 2000; Spitsyn 1981].

Technetium studies related to the nuclear power industry focus on acidic solutions which are the main aqueous media used in the extraction processes. Considerably less articles deal with technetium chemistry in aqueous alkaline solutions [Robbins, 2013] although this topic is important for liquid radioactive waste storage sector of the nuclear industry. For instance, 28.4 thousand tons of liquid waste and 4.7 thousand tons of highly radioactive sludge are stored in Hanford Site, USA [Min. Energii USA, 1]. The total activity of  $^{99}\text{Tc}$  collected in this facility is estimated at approx. 26,000 Ci (9.62 TBq) [Min. Energii, USA, 2]. Long term storage of liquid solutions with extremely high ionic strength and pH in stainless steel tanks accelerates corrosion of the latter. The corrosion rate strongly depends on composition of the liquid phase being in contact with corroding surfaces and it is known that technetium can inhibit corrosion of the iron [Pourbaix, 1966; Cartledge, 1971; Magee, 1974].

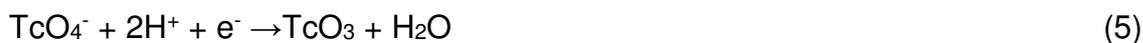
Knowledge about stability of ionic species containing technetium with various valences is very important for understanding numerous processes crucial for the nuclear medicine and for the nuclear power industry. Detailed description of the electroreduction of  $\text{TcO}_4^-$  in the aqueous environment is the subject of seven articles included in the habilitation application [H1-H7]. Additional paper [H8] focuses on extraction of pertechnetates from aqueous to ionic liquids phases.

The articles [H1-H4] focus on studies of pertechnetates electroreduction in an acidic environment. Paper [H5] deals with studies on interaction of ionic forms of Tc with Np in an acidic environment [H5]. Pertechnetate ions reduction in an alkaline environment is discussed in paper [H6]. Processes of extraction of individual ionic forms of technetium in aqueous acid solutions/organic solvent systems are covered by publications [H7] and [H8].

*Electrochemical and spectroscopic properties of ionic forms of technetium in acidic solutions*

Scientific research on electrochemical properties of inorganic technetium compounds started already at the end of 1930s. Shortly after discovery of Tc, the 43rd element in the periodic table [Perrier, 1937], its small amounts were electrochemically deposited from an acidic solution on a platinum substrate [Perrier, 1939] using a procedure developed several years earlier for rhenium electrodeposition [Hölemann, 1933]. Since then, numerous works focused on electroreduction of pertechnetates in aqueous media appeared in scientific journals.

As it was mentioned above (page 8, equation 2), most of the authors indicates  $\text{TcO}_2$  as the final product of  $\text{TcO}_4^-$  ions reduction in the acidic environment. This reaction, however, cannot be completed in a single step. Pihlar [Pihlar, 1979] proposed a multi-step mechanism which starts with electroreduction of  $\text{TcO}_4^-$  ions to Tc(VI) containing  $\text{TcO}_3$  (equation (5)):



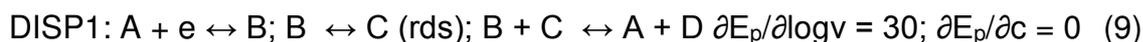
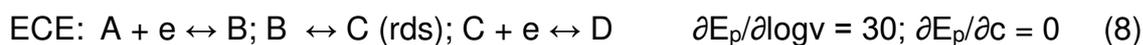
Also other authors [e.g. Horányi, 1994; Courson 1999] pointed to possible generation of unstable Tc (V) and Tc (VI) species in the initial stages of the discussed process. Both Tc (VI) and Tc (V) are very unstable and undergo disproportionation reactions (equations (6) - (7)):



Results presented in **[H1]** indicate the possibility of generation Tc(VI) and Tc (V) species in the initial steps of the electroreduction of pertechnetates. An analysis of results of rotating disc-ring electrode experiments show indicate formation of Tc(V) species in sulfuric acid solutions. Due to their instability these species cannot be detected using UV-Vis spectroscopy. Generation of Tc(VI) was deduced on the basis of calculated change of standard entropy accompanying the  $\text{TcO}_3$  formation reaction. The experimentally determined value of the reaction standard entropy is

equal to  $-53,1 \text{ J M}^{-1}\text{K}^{-1}$  and is close to the value of  $-57.25 \text{ J M}^{-1}\text{K}^{-1}$  calculated on the basis of the literature data [Rard, 1983].

Chronoamperometric measurements produced results which I have analysed in terms of most common reaction models which involve mixed electrochemical-chemical mechanisms [Compton, 2011] (equation (8) - (10)):



(rds) – rate determining step

The measurements allowed determining  $\partial E_p/\partial \log v$  and  $\partial E_p/\partial c$  values for reduction of pertechnetates in the acidic solutions. These values are equal to 14 and 0, respectively, clearly indicating **that this process is significantly more complex than simple ECE or DISP mechanisms**. Cyclic voltammetry measurements carried out in aqueous electrolytes containing pertechnetates and sulfuric acid with various concentrations (Figure 2) allowed me to analyse influence of the solution acidity on reduction of the pertechnetates. Voltammetry curves reveal currents due to red-ox of technetium at potentials lower than ca. 1.1 V, and currents due to oxidation and reduction of surface of gold substrate which are located above ca. 1 V. An analysis shows that an increase in the solution acidity enhances currents of the reduction peak (peak 1) which is attributed to generation of Tc(VI) and Tc(V) on the electrode surfaces (Figure 2). The next reduction signal, very wide peak (2), is associated with formation of Tc (III) and Tc (IV) species. Anodic section of the voltammetric curves recorded after changing direction of the potential scan reveals 3 partially overlapping current peaks located below ca. 1.1 V and related to electrochemical reactions of technetium. The first of them, peak 3, is attributed to oxidation of Tc (III) forms to Tc (IV). The smallest of the anodic signals, peak 4, is related to the oxidation of Tc(V) and Tc(VI) to Tc (VII). The last of the anodic signals, asymmetric peak 5 which currents have the highest values for 1 M H<sub>2</sub>SO<sub>4</sub>, is connected with oxidation of polymeric forms of Tc(IV) to Tc (VII). All these observations are reported and discussed in detail in publication [H1].

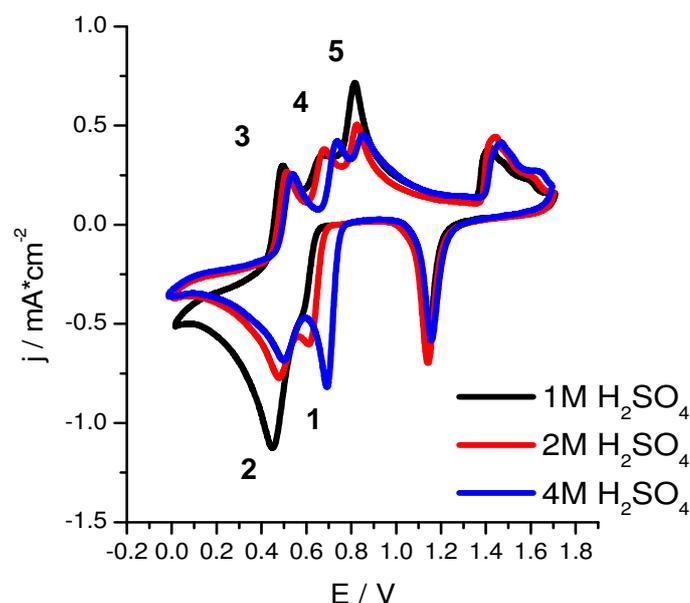


Figure 2. Typical cyclic voltammograms recorded for a gold electrode in  $\text{H}_2\text{SO}_4$  solutions with 1 mM  $\text{KTcO}_4$ , scan rate of  $100 \text{ mVs}^{-1}$ .

Further investigations of the  $\text{TcO}_4^-$  ion electroreduction in acidic solutions were carried out using thin-layer Au/RVC-OTTLE ([H2]) or RVC-OTTLE ([H3]) spectro-electrochemical cells.

The results presented in the publication [H2] indicate a **significant influence of the electrode material on the process of pertechnetates electroreduction in acidic solutions**. This effect was not reported in the literature until now and was shown for the first time in [H2]. Only gold electrodes reveal well-shaped current peaks due to red-ox reactions of Tc, they include two very strong reduction waves and three oxidation signals. The electrochemical signals recorded using a platinum electrode are very similar to those reported for electrolytes containing rhenium [Méndez, 2003; Szabó, 2004]. The latter indicate a strong adsorption of  $\text{ReO}_4^-$  ions on the electrode surface and formation of  $\text{ReO}_2$  oxides as well as  $\text{Re}_2\text{O}_5$  and  $\text{ReO}_3$  during the perrhenates electroreduction. Currents due to oxidation and reduction of Tc on glassy carbon (GC), which was the third type of the electrode material studied by me in the course of the research reported in [H2], are much weaker developed as compared to Au and Pt substrates. Results of electrochemical measurements performed on Au, Pt and GC (glassy carbon) under hydrodynamic conditions led to me to the conclusion that **well-developed limiting currents of red-ox reactions of**

**technetium are observed only for gold surface. These currents are due to reduction of Tc(VII) ions to Tc(III, IV).** Activation energy of these reactions determined by me in [H2] is in the order of dozen of  $\text{kJ mol}^{-1}$  and decreases with an increase in the acid concentration. Additional spectroelectrochemical measurements carried out using a Au/RVC-OTTLE system enabled me to determine the standard redox potential,  $E^0$ , for  $[\text{Tc}(\mu\text{-O})_2\text{Tc}]^{3+}/\text{TcO}(\text{OH})$  red-ox couple. Its value is equal to 512 mV (vs. SHE) and is very close to 516 mV reported in the literature for Tc(IV)/Tc(III) [Rard, 1983]. The latter  $E^0$  value is the only one reported so far in the literature for Tc(III, IV)<sub>polymer</sub>/Tc(III) system.

Results of spectroelectrochemical studies with RVC as a working electrode reported in [H3] were analysed using a procedure proposed by Marassi et al. [Zamponi, 1992; Zamponi 1989]. This approach enables deconvolution of overlapped spectroscopic signals into separate waves with maxima at 320 and 500 nm. Both these bands are very often observed for Tc containing aqueous acidic solutions but until now they were attributed to the same technetium species. In [H3] I have shown for the first time that the bands at 320 and 500 nm are attributed to separate forms of Tc(IV). **The ionic form of technetium(IV) connected with the wave with maximum at 320 nm is easier to oxidize than polymeric forms of Tc(IV or III,IV)** which are characterized by the wave with the maximum at 500 nm. Additionally, Tc(III) is also generated during the electroreduction of Tc(VII). This form of technetium is responsible for formation of a wave with a maximum at ca. 440 nm.

On the basis of spectroelectrochemical measurements (UV-Vis) I identified two additional ionic forms of technetium which are generated during the electrochemical reduction of pertechnetates in aqueous acidic solutions:

- a) polymeric forms of Tc(III,IV or IV) characterized by a wave with a maximum at ca. 500 nm
- b) oxotechnetium(IV),  $\text{TcO}^{2+}$  ions, characterized by a wave with a maximum at 400 nm.

In my further research, reported in [H4], I extended range of the acid concentrations up to extremely acidic solutions containing 12M  $\text{H}_2\text{SO}_4$ . In these electrolytes I recorded generation of Tc(V) forms. Analysis of spectroelectrochemical results (SERS) showed **existence of a band at  $792 \text{ cm}^{-1}$  which has not reported in previous literature. This band most likely**

**corresponds to Tc(V).** The latter species appears when the Tc(IV) deposit is oxidized on the electrode surface in 4M H<sub>2</sub>SO<sub>4</sub>. Preliminary tests carried out in a system containing pertechnetates and H<sup>+</sup> showed that irradiation of the electrode surface with **a laser beam with a power of 1 mW leads to a photo-reduction of TcO<sub>4</sub><sup>-</sup> to TcO<sub>2</sub> or Tc(IV) polymeric forms.** This conclusion has a very important practical significance and described effect must be taken into account in Raman Surface Enhance Spectroscopy studies, particularly those devoted to determination of Tc concentration in aqueous solutions [Gu, 2007].

Concentration of strongly concentrated solutions of salts or acids has a strong influence on solution's viscosity and, as a consequence, also on diffusion coefficients of ions. As an example, the kinematic viscosity of 8M H<sub>2</sub>SO<sub>4</sub> at 25<sup>o</sup>C is about 3 times higher as compared to 0.5M H<sub>2</sub>SO<sub>4</sub> [Rhodes, 1923]. The concentration influence on the diffusion coefficient must be taken into account in analysis of electrochemical equations which contain this parameters, e.g. Levich, Randles-Sevcik, Cottrell or Sand equations. In order to avoid discussion of concentration influence on diffusion coefficients I combined the Sand equation, which shows a relation between the transition time and the current density ( $\tau^{1/2} = f(j^{-1})$ ), with the Koutecky-Levich equation which describes influence of the electrode rotation rate on the current density as a function of ( $j^{-1} = f(\omega^{-1/2})$ ). Such approach allows me determining number of the electrons exchanged in the first step of the Tc(VII) electroreduction process ( $n = 2$ ) without knowledge of the value of the pertechnetates diffusion coefficient in 8M H<sub>2</sub>SO<sub>4</sub>. The Tc(V) containing TcO<sup>3+</sup> ions are stable in concentrated H<sub>2</sub>SO<sub>4</sub> solutions as it was shown by Poineau et al. [Poineau, 2013].

On the basis of an analysis of voltabsorbommograms I proposed a mechanism of **generation of polymeric technetium(III,IV and IV) forms during the electroreduction of pertechnetates in acidic solutions. There are two reaction pathways which lead to their formation: a polymerization of monomeric forms of Tc(III) and Tc(IV) and a synoproportionation of Tc(VII) and Tc(III),** which are schematically presented by equations (11) - (13):



Application of differential pulse voltammetry (DPV) allowed me to determine detection limits of the pertechnetates in concentrated sulfuric acid solutions in presence of impurities, such as  $\text{Fe}^{3+}$  or  $\text{Cl}^-$  ions. These detection limits are in the range of 1  $\mu\text{mol dm}^{-3}$  and are higher than those reported described in the literature [Torres, 1988; Ruf, 1988; El-Reefy, 1990]. It should be noted that [H4] is the first paper which reports analytical determination of trace amounts of Tc in such high concentrated acid solutions as 8 M.

In order to extent our knowledge about chemical processes of technetium in nuclear waste containing actinides I have conducted additional research on interactions of ionic forms of neptunium(III, IV and VI) with ionic forms of technetium. Results of these studies are reported in work [H5].  $\text{NpO}_2^+$  ions are assumed to be the most stable forms of neptunium present in acidic solutions [Chairman, 2001] and their disproportionation, if possible, is considered as a very slow process [Lemire, 2001].  $\text{Np}^{4+}$  ions appeared to be stable in 4 M  $\text{H}_2\text{SO}_4$ . Most of scientific research carried out with solutions containing ionic forms of Tc and Np reported so far was focused on spectroscopic measurements [Zhou, 2014; Marchenko, 2008], less often applied electrochemical techniques were used only to reduce Tc or selected actinides [Ozawa, 2003].

The electrochemical studies of processes involving ionic species containing Tc and Np which were included in my research on technetium electrochemistry were carried out in strongly acidic solutions. The results obtained in the course of these studies show that the presence of  $\text{Np}^{4+}$  ions does not affect the electroreduction of pertechnetates nor the oxidation of reduced forms of Tc.  $\text{Np}^{3+}$  ions, on the other hand, exhibit strong reducing properties towards  $\text{Tc(VII)}$  which are reduced to  $\text{Tc(IV)}$  with a polymeric rather than a simple oxide structure. The reactions which occur between the reduced forms of technetium, e.g.  $\text{TcO}^{2+}$ ,  $\text{TcO}^+$ ,  $\text{Tc(IV)}$ -polymer, and  $\text{NpO}_2^{2+}$  ions lead to formation of unstable  $\text{Tc(V)}$  and  $\text{Np(V)}$  ions. Such generated  $\text{Tc(V)}$  containing ions are characterized by a wave with a maximum at approx. 460 nm while the  $\text{Np(V)}$  ions generate a signal at ca. 980 nm. The rate of oxidation of reduced Tc species varies depending on their structure. **I have found that  $\text{Tc(III)}$  tends to be oxidized by  $\text{Np(VI)}$  most rapidly while the slowest oxidation rate was recorded for polymeric forms of  $\text{Tc(IV)}$ .**

The electrochemical reactions of the pertechnetates which take place on surfaces of solid electrodes strongly depend on chemical form of Np present in the

solution and are distinctly different for a strong oxidant, such as  $\text{NpO}_2^{2+}$  ion, and for a strong reducer, such as  $\text{Np}^{3+}$  ion.

A comparison of voltammetric curves recorded in acidic solutions of pertechnetates in presence and absence of Np species shows that a very fast oxidation of Tc(V) by Np(VI) leads to disappearance of the first wave of the pertechnetates electroreduction observed for the electrolytes free of neptunium (peak 1 in Fig. 2).  $\text{Np}^{3+}$  ions reduce  $\text{TcO}_4^-$  and this process results in formation of polymeric forms of Tc(IV). An additional consequence of presence of the Np containing ions in the electrolyte is formation of a large reduction wave seen on voltammetric curves below 0.6 V. These currents are associated with red-ox processes between technetium species at lower oxidation states.

*Electrochemical and spectroscopic properties of ionic forms of technetium present in alkaline solutions*

Red-ox processes of pertechnetates in alkaline solutions are poorly resolved with only a handful of papers focused on this topic. Publication [H6] deals with electrochemical and spectroelectrochemical studies on oxidation and reduction of inorganic forms of technetium in NaOH solutions with a wide range of concentrations from 0.3M to 10.6M NaOH.

Most of the research on pertechnetates electroreduction in alkaline solutions published so far focus mainly on stability of Tc(V) and Tc(VI) species [Rard, 1999; Kissel, 1969]. The earliest of these works shows that ionic forms of Tc(VI) are very unstable in alkaline solutions [Kissel, 1969]. The rate constant of their disproportionation calculated by Deutsch et al. [Deutsch, 1978] is equal to  $2.48 \pm 0.05 \cdot 10^{10} \text{ M}^{-1}\text{s}^{-1}$ . This disproportionation reaction, which is usually described using a net equation (14):



is a complex process and, according to Founta et al. [Founta, 1987] involves hydrolysis of Tc (VI) according to equations (15) and (16):



Therefore, a more proper net equation of this reaction should be as follows (17):



The same authors found that Tc(IV) (with undefined structure) is the most probable product of the pertechnetates reduction in alkaline solutions.

The results of my research show that **the reduction of  $\text{TcO}_4^-$  ions leads to various products depending on the NaOH concentration.** Results of spectroelectrochemical measurements enabled me to draw a conclusion that the main products of the discussed process taking place in 0.3M NaOH are hydrated  $\text{TcO}_2$  and  $\text{TcO}_4^{3-}$  ions characterized by a wave in the Vis range with a maximum at approx. 460 nm. The SERS measurements showed that these forms, Tc (V), are characterized by a band with a maximum at approx.  $700 \text{ cm}^{-1}$ .

**The predominant reduced forms of Tc present in highly concentrated NaOH solutions are Tc(IV) polymeric structures** which absorb the light in the Vis range ( $\lambda_{\text{max}} = 500 \text{ nm}$ ). Similarly to the results obtained in highly concentrated acid solutions, also strongly alkaline solutions reveal formation of a well-developed limiting current under hydrodynamic conditions. An analysis of the limiting current using Koutecky-Levich equation shows that the process of the pertechnetates electroreduction leads to generation of a mixture of Tc(IV) and Tc(V) forms.

Simulation and modeling of the processes of oxidation of the reduced Tc species taking place in alkaline solutions enable me to conclude that that this process follows two parallel pathways, one with surface processes only controlled by kinetics and another one with reactions controlled by diffusion in the electrolyte. The slowest step turned out to be the oxidation of the most likely polymeric forms Tc(IV) to Tc(V) ( $k_0 = 7.2 \cdot 10^{-4} \text{ s}^{-1}\text{cm}^{-2}$ ) and Tc(V) to Tc(VI) ( $k_0 = 1.8 \cdot 10^{-4} \text{ s}^{-1}\text{cm}^{-2}$ ) associated by diffusion of these species in the electrolyte. Processes involving deposits or adsorbates containing technetium are much faster. In this case, the oxidation of Tc(VI) to Tc(VII) ( $k_0 = 0.5 \div 2 \text{ s}^{-1}\text{cm}^{-2}$ ) is the fastest step. **These are the first rate constant values published in the literature for the oxidation of Tc(IV) to Tc(VII) in an alkaline solutions.**

*Extraction of ionic forms of technetium in selected liquid-liquid systems.*

Most of the research devoted to the process of extraction of ionic forms of technetium from aqueous to organic phase focus on pertechnetates as the most common ionic form of Tc [Schwochau, 2000; Spitsyn, 1981; Boyd, 1960; Campbell, 1963; El-Kot, 1992; Pruett, 1981]. Only few papers deal with results of studies on extraction of the reduced forms of technetium [Shkrob, 2011; Kumari, 2010]. It follows that the latter Tc forms, eg. complexed Tc(IV) species, are much less extracted from the aqueous to organic phase than the pertechnetates. The latter effect has a strong impact on the process of effective separation of technetium and uranium.

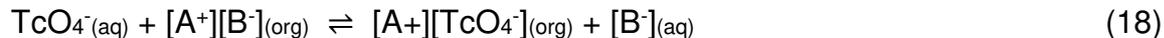
The experience gained in the course of the research reported in publications [xx] allowed me to develop methods of generation of specified reduced ionic forms of technetium with a required structure through electrochemical reduction of the pertechnetates.

The results presented in the publication [H7] describe the process of the extraction of the reduced forms of technetium in systems containing  $\text{H}_2\text{SO}_4 + \text{HNO}_3$  as an aqueous phase and kerosene containing 30% TBP as an organic medium. The reduced technetium forms were obtained by means of chronoamperometric reduction of  $\text{TcO}_4^-$  in a thin-layer cell. **The distribution coefficients of investigated Tc reduced forms between aqueous (4M  $\text{H}_2\text{SO}_4 + \text{HNO}_3$ ) and organic phase are several times smaller than those for of pertechnetates under the same conditions from.** Nitrate ions act as strong oxidants in acidic solutions and slowly oxidise Tc(III),  $\text{TcO}_2$  or Tc(IV) polymeric forms to  $\text{TcO}_4^-$  ions. These processes are reflected by the slow increase of distribution coefficient,  $D_{\text{Tc}}(\text{org})/(\text{aq})$ , as a function of time of contact of both phases. Thus, for 4M  $\text{H}_2\text{SO}_4$  (+0.14M  $\text{HNO}_3$ ) as the aqueous phase the distribution coefficient of Tc(III) is equal to only ca. 70% of the value measured for pertechnetates. For  $\text{TcO}_2$  + or Tc (IV) polymeric systems, the distribution coefficients are even smaller and constitute from 52% to 31% of the value for the pertechnates, respectively. The  $D_{\text{Tc}}$  of reduced Tc species measured in 0.5M  $\text{H}_2\text{SO}_4$  (+0.14 M  $\text{HNO}_3$ ) after 35 min. from contacting both phases are at the level of 80% of the value for pertechnetates. These results clearly show that **the extraction of reduced forms of technetium in aqueous acidic solution/TBP systems in kerosene is much weaker than for**

**perchnetates, even after a prolonged contact of aqueous and organic phases.** In publication [H7] I also show that the rate of oxidation of reduced Tc forms by nitrates in acidic solutions is relatively slow. This knowledge would be helpful in further development of extraction processes used to separate technetium from other radionuclides, especially uranium.

Apart from studies on the extraction of reduced, ionic forms of technetium, to the organic phase based on kerosene or n-dodecane my research include also analysis of the extraction of technetium (VII) ions from the aqueous phase containing nitric acid (V) to ionic liquids as the other type of the organic phase. The ionic liquids are referred to as programmable solvents due to possibility to control their properties by changing structures of cations or anions [Handy, 2011]. Their moderate stability under irradiation conditions [Mincher, 2014] makes them solvents of potential interest for application in systems used for separation of uranium from trace amounts of technetium.

The process of extraction of perchnetates from the aqueous phase to ionic liquids can be described by equation (18) [Stepinski, 2010]:



It is worth mentioning that studies on the solubility of tetra ( $\text{C}_n\text{H}_{2n+1}$ ) ammonium perchnetates salts carried out by Peretrukhin et al. [Peretrukhin, 2008] have shown that their solubility in water decreases as the aliphatic chains are extended. Considering this fact and taking into account the lack of systematic data on the extraction of technetium in  $\text{HNO}_3$  / selected ionic liquids systems, I focused my research on analysis of how the extraction of perchnatets into the ionic liquid phase is affected by the following factors:

- a) concentration of the acid in the aqueous phase (0.1-8 M  $\text{HNO}_3$ )
- b) temperature (25, 50 and 70°C)
- c) contacting time of both phases (aqueous and organic)
- d) technetium concentration in the aqueous phase
- e) type of cation and anion of the ionic liquid.

The results of these works are described in publication [H8].

Amongst the 7 analyzed ionic liquids with imidazolium, sulfonium, phosphonium, pyridine and alkylammonium cations and bis((trifluoromethyl)sulfonyl)imide and

hexafluorophosphate anions **the relatively efficient extraction of the pertechnetates is observed only for ionic liquids with alkylammonium cations with long aliphatic chains**, e.g. methyltrioctylammonium bis((trifluoromethyl)sulfonyl)imide. The highest value of the technetium distribution coefficient,  $D_{Tc}(org)/(aq)$ , is equal to 18.85 and was measured for 60  $\mu\text{mol dm}^{-3}$   $\text{TcO}_4^- + 0.1\text{M HNO}_3$  / methyltrioctylammonium bis((trifluoromethyl)sulfonyl)imide system at 25°C. The efficiency of the extraction process increases with the decrease in the acid concentration. Further on, an increase in the concentration of the pertechnetates in the aqueous phase leads to a decrease in  $D_{Tc}$  to the value of 1 for a solution containing 3  $\text{mmol dm}^{-3}$  of  $\text{TcO}_4^-$ . No significant influence of the cation identity on the Tc partition coefficient was observed for ionic liquids with sulfonium, phosphonium or pyridinium cations and for all these liquids the  $D_{Tc}$  is in the range from ca. 0.1 to ca. 1. It was also shown that the extraction of the pertechnetates from the aqueous to the ionic liquids is a relatively slow process and the dynamic equilibrium between both phases is established only after about 30 minutes of shaking.

Industrial processes of purification of substances from technetium require very fast transfer of Tc containing species from organic phases so the latter can be used multiple times in the extraction process. Removal of technetium from ionic liquids without use of appropriate reducers proved to be inefficient. In addition, ionic liquids with hexafluorophosphate anions are not suitable for carrying out extraction in systems in which the aqueous phase is strongly acidic.  $\text{PF}_6^-$  anions undergo hydrolysis in presence of  $\text{H}^+$  anions and such decomposition of the ionic liquids leads to disappearance of the boundary between both phases.

## D) Summary

The series of the scientific works included in the habilitation application discusses electrochemical and spectroscopic properties of ionic forms of technetium in strongly acidic and alkaline solutions. These works also discuss the process of the extraction of technetium in various liquid-liquid systems. The subjects of the research are very important for understanding oxidation-reduction processes of ionic forms of technetium. Many aspects of the technetium chemistry, such as stability of Tc (IV) polymer forms and mechanism of their formation, have been described for the first time in this series of publications.

The electrochemical processes involving technetium are complex and very difficult to interpret due to existence of numerous oxidation states of this element. Chemical behavior of technetium in aqueous media is additionally complicated by chemical reactions, such as hydrolysis, syn- and disproportionation, taking place simultaneously to the electrochemical processes. Finally, any research involving technetium must be carried out in radiochemical laboratories due to radioactivity of this element. As a result, only few research groups in the world (e.g. in USA, Russia and France) are involved in research on the technetium electrochemistry. As a result, publications which focus on this subject are directed to a relatively narrow scientific audience and are published mainly in highly specialized scientific journals with moderate values of the impact factor (IF, e.g. Journal of Radioanalytical and Nuclear Chemistry).

The summary of my accomplishments described in the series of publications:

1. Based on spectroelectrochemical measurements, I was able to determine the ionic forms of technetium in which this element occurs on the III, IV or V oxidation states:
  - a) Tc (III):  $\lambda_{\max} = 440 \text{ nm}$
  - b) Tc (IV):  $\lambda_{\max} = 320 \text{ nm}$  (I determined that this structure is different from the well-described in the literature polymeric form of Tc (IV))
  - c) Tc (V):  $\lambda_{\max} = 460 \text{ nm}$

2. Based on SERS spectroscopy, I observed (not described so far in literature) the reduced forms of Tc by the bands with maxima at  $792\text{ cm}^{-1}$  (acidic solutions) or  $700\text{ cm}^{-1}$  (alkaline solutions).
3. I have observed that strongly acidic solutions causes Tc(V) stabilization, which is manifested by the separation of signals from electrochemical processes associated with the reduction of Tc(VII) to Tc(V) and Tc(V) to Tc(III, IV). Potentially, it can be used in the determination of technetium in the presence of contaminants such as  $\text{Fe}^{3+}$  and  $\text{NO}_3^-$  during rapid determinations of the content of this element in strongly acidic solutions of radioactive waste.
4. I have described the strong influence of the surface on the recorded current signals related to electrochemical processes involving ionic forms of technetium. At the same time, the best-developed current signals are observed for gold. These results can be used to develop an efficient, electrochemical method of obtaining desirable, reduced forms of technetium, useful in nuclear medicine.
5. In systems containing ionic forms of technetium and neptunium, I observed the formation of transient forms of Tc(V) and Np(V). This description is the first available in the literature taking into account the deliberations concerning various, reduced forms of technetium, in particular Tc(III) and Tc(IV).
6. I determined that ionic forms of Tc, in which this element occurs as  $[\text{Tc}_2\text{O}_2]^{3/4+}$ , are definitely less extracted from the aqueous to organic phase compared to  $\text{TcO}_4^-$  ions. Their oxidation under the influence of  $\text{HNO}_3$  proceeds relatively slowly, which apart from co-extraction of pertechnetates with uranyl ions, explains the occurrence of technetium in all stages of reprocessing of spent nuclear fuel. This problem is a serious challenge for technologists trying to improve the separation technologies in the nuclear industry based on liquid-liquid extractions with reducers.

I intend to continue research on the electrochemical properties of technetium, paying particular attention to:

1. optimization of the process of obtaining cationic Tc forms from pertechnetates, especially  $TcO^{3+}$  and  $Tc^{3+}$  (including in non-aqueous solutions), which in the presence of chelating substances can be used to develop an electrochemical procedure for preparation of radiopharmaceutical free of impurities (e.g. reducing agent such as tin).
2. identification and description of the stability, undiscovered so far in aqueous solutions (but suggested in the literature) of the  $Tc^{2+}$  cation (as the  $Mn^{2+}$  analogue). This issue is important from the point of view of understanding the basic chemistry of technetium.
3. electrodeposition of metallic technetium from the solutions containing pertechnetates without losses caused by the generation of Tc(IV) polymer forms. Precision description of this process will be used for effective separation of Tc from radioactive waste containing fission products.

## E) Literature

1. Abram U., Alberto R. (2006) Technetium and rhenium - coordination chemistry and nuclear medical applications, *J. Braz. Chem. Soc.* 17(8), 1486-1500
2. Bonnerot J.M., Broudic V., Phélip M., Jégou C., Varaine F., Deschanel X., Arnoux M.F., Faugère J.L. (2005) Transmutation in Reactor and Aqueous Corrosion Resistance of Technetium Metal, *J. Nucl. Radiochem. Sci.* 6(3), 287-290
3. Boyd G.E., Larson Q.V. (1960) Solvent extraction of heptavalent technetium. *J. Phys. Chem.* 64, 988-996
4. Campbell M.H. (1963) Separation of technetium from mixed fission products by solvent extraction with tributyl phosphate. *Anal. Chem.* 35(13), 2052-2054
5. Cartledge G.H. (1971) The Electrochemical Behavior of Technetium and Iron Containing Technetium, *J. Electrochem. Soc.* 118(11), 1752-1758
6. Compton R.G., Banks C.E. (2011) *Understanding Voltammetry*, 2<sup>nd</sup> ed., Ch. 7, Imperial College Press
7. Courson O., Le Naour C., David F., Bolyos A., Maslennikov A., Papadopoulos N (1999) *Czechoslovak J. Phys.* 49/S1, 687-694
8. Deutsch E., Heinemann W.R., Hurst R. (1978) Production, Detection and characterization of transient hexavalent technetium in aqueous alkaline media by pulse radiolysis and very fast scan cyclic voltammetry, *J. Chem. Soc. Chem. Comm.* 23, 1038-1040
9. Dileep C.S., Jagasia Poonam, Dhama P.S., Achuthan P.V., Dakshinamoorthy A., Tomar B.S., Munshi S.K., Dey P.K., (2008) Distribution of technetium in PUREX process streams, *Desal.* 232, 157–165
10. DOE Report (1996) Selected Radionuclides Important to Low-Level Radioactive Waste Management (DOE/LLW-238), USA
11. El-Kot A.M. (1992) Solvent extraction of heptavalent technetium. *J. Radioanal. Nucl. Chem.* 163(2), 363–373
12. El-Reefy S.A., Ruf H., Schrob K. (1990) Cathodic stripping voltammetry in the tetraphenylarsonium chloride/chloroform extract at a hanging mercury drop electrode, *J. Radioanal. Nucl. Chem.* 141(1), 179-183

13. Escure H. (1974) Studies of Np(V) disproportionation in acid solutions, Raport CEA-R-4574
14. Founta A., Aikens D.A., Clark H.M. (1987) Mechanism and kinetics of the stepwise voltammetric reduction of pertechnetates in alkali solutions to Tc(VI), Tc(V) and Tc(IV), J. Electroanal. Chem. 219, 221-246
15. Friedman H.A (1985) Patent US4528165A, Separation of uranium from technetium in recovery of spent nuclear fuel
16. Garraway J. (1984) The behaviour of technetium in a nuclear fuel reprocessing plant, Extraction '84 Symposium on Liquid-Liquid Extraction Science, pp. 47-56
17. Gong Cynthia-May S., Poineau F., Czerwinski K.R., (2008) Patent US7854907B2, Process for the extraction of technetium from uranium
18. Gu B., Ruan C. (2007) Determination of Technetium and Its Speciation by Surface Enhanced Raman Spectroscopy, Anal. Chem. 79 (6) 2341-2345
19. Handy S. (ed.) (2011) Ionic Liquids. Classes and properties, InTech
20. Hölemann H (1933) Beiträge zur Chemie und Elektrochemie des Rheniums. II. Über elektrochemische Reduktionsprodukte in Lösungen, die Chlorion oder Fluorion enthalten, und Über die chemischen Bildungsweisen von niedrigen Wertigkeitsstufen in schwefelsauren Lösungen, Z. Anorg. Allg. Chem. 211, 195-203
21. Horányi G., Bakos I. (1994) Coupled radiometric and electrochemical study of the reduction of  $TcO_4^-$  ions at a gold electrode in acidic medium (mechanistic aspects of Tc deposition), J. Electroanal. Chem. 370, 213-218
22. IAEA (2015) Feasibility of Producing Molybdenum-99 on a Small Scale Using Fission of Low Enriched Uranium or Neutron Activation of Natural Molybdenum, Technical Reports Series No.478
23. IAEA (2007) TECDOC-1529, Management of Reprocessed Uranium. Current Status and Future Prospects, Vienna
24. Jassim T.N., Liljenzin J.O., Lundqvist R., Persson G. (1984) Coextraction of uranium and technetium in TBP-systems, Solvent Extr. Ion Exch. 2(3), 405-419

25. Kissel G., Feldberg S. W. (1969) Disproportionation of the technetate ion in aqueous alkaline media. An electrochemical study, *J. Phys. Chem.* 73 (9), 3082-3088
26. Kumari N., Pathak P.N., Prabhu D.R., Manchanda V.K. (2010) Role of acetohydroxamic acid in selective extraction of technetium and uranium employing N,N-dihexyloctamine as extractant, *Sep. Sci. Tech.*, 46, 79-86
27. Lemire R.J., Fuger J., Nitsche H., Potter P., Rand M.H., Rydberg J., Spahiu K., Sullivan J.C., Ullman W.J., Vitorge P., Wanner H. (2001) *Chemical Thermodynamics of neptunium and plutonium*, vol. 4, str. 91-104, Elsevier, Amsterdam
28. Lieser K.H., (2001) *Nuclear and Radiochemistry. Fundamentals and Application*, pp. 228-229, Wiley
29. Magee R.J., Cardwell T.J. (1974) Rhenium and technetium [w:] *Encyclopedia of electrochemistry of the elements* (Bard A.J. (ed.)), vol. II, p. 183, Marcel Dekker
30. Marchenko V.I., Zhuravleva G.I., Dvoeglazov K.N., Savilova O.A. (2008) Behaviors of Plutonium and Neptunium in Nitric Acid Solutions Containing Hydrazine and Technetium Ions, *Theoret. Found. Chem. Eng.* 42(5), 733–739
31. Méndez E., Cerdá M.F., Luna A.M.C., Zinola C.F., Kremer C. Martins E. (2003) Electrochemical behavior of aqueous acid perrhenate-containing solutions on noble metals: critical review and new experimental evidence, *J. Coll. Interfac. Sci.*, 263, 119-132
32. Mincher B.J., Wishart J.F. (2014) The radiation chemistry of ionic liquids: a review. *Solvent Extr. Ion Exch.* 32, 563-583
33. Min. Energii USA, 1: <https://www.energy.gov/em/hanford-site> (Accessed: 20.08.18)
34. Min. Energii USA, 2: Technetium Management at the Hanford Site <https://www.osti.gov/biblio/1091341> (Accessed 20.08.18)
35. Nowak S., Rudzki K., Piętka E., Czech E. (1998) *Zarys medycyny nuklearnej*, PZWL

36. OECD (2017) The Supply of Medical Radioisotopes. 2017 Medical Isotope Supply Review: <sup>99</sup>Mo/<sup>99m</sup>Tc Market Demand and Production Capacity Projection 2017-2022 Nuclear Development NEA/SEN/HLGMR (2017) 2 April 2017
37. Ozawa M., Ishida M., Sano Y. (2003) Strategic Separation of Technetium and Rare Metal Fission Products in Spent Nuclear Fuel: Solvent Extraction Behavior and Partitioning by Catalytic Electrolytic Extraction, *Radiochem.* 45(3), 225 – 232
38. Peretrukhin V.F, Moisy F., Maslennikov A.G., Simonoff M., Tsivadze A.Yu., German K.E., David F., Fourest B., Sergeant C., Lecomte M. (2008) Physicochemical behavior of uranium and technetium in some new stages of the nuclear fuel cycle. *Russ. J General Chem.* 78(5), 1031-1046
39. Perrier C, Segrè E (1937) Some chemical properties of element 43. *J Chem Phys* 5, 712-716
40. Perrier C, Segrè E (1939) Some Chemical Properties of Element 43. II, *Journal of Chemical Physics*, 7, 155-156
41. Pihlar B. (1979) Electrochemical behaviour of technetium(VII) in acidic medium, *J. Electroanal. Chem.*, 102, 351-365
42. Poineau F., Weck P. F., Burton-Pye B. P., Denden I., Kim E., Kerlin W., German K. E., Fattahi M., Francesconi L. C., Sattelberger A. P., Czerwinski K. R. (2013) Reactivity of HTcO<sub>4</sub> with methanol in sulfuric acid: Tc-sulfate complexes revealed by XAFS spectroscopy and first principles calculations, *Dalton Trans.* 42(13), 4348-4352
43. Pourbaix M (1966) Atlas of electrochemical equilibria in aqueous solutions, pp. 298-299, Pergamon Press
44. Pruett D.J. (1981) The solvent extraction behavior of technetium. *Radiochim Acta.* 28, 153-157
45. Pruett D.J. McTaggart D.R., (1984) Patent US4443413A, Separation of uranium from technetium in recovery of spent nuclear fuel
46. Pruett DJ (1984) The solvent extraction of heptavalent technetium and rhenium by tributyl phosphate, ORNL-8668
47. Rard J., Rand M.H., Anderegg G., Wanner H. (1999) Chemical thermodynamics of technetium, vol 3. Elsevier, Amsterdam

48. Rard J.A. (1983) Critical Review of the Chemistry and Thermodynamics of Technetium and Some of its Inorganic Compounds and Aqueous Species; Lawrence Livermore National Laboratory, Manuscript
49. Rhodes F.H., Barbour C.B. (1923) The viscosity of sulfuric acid and water, *Ind. Eng. Chem.*, 15(8), 850-852
50. Robbins R.A (2013) Technetium Management at the Hanford Site. United States: N., 2013. Web.
51. Ruf H. (1988) Quantitative analytical assay of small amounts of technetium by stripping chronopotentiometry at a glassy carbon electrode, *J. Electroanal. Chem.*, 241, 125-131
52. Saha G.B. (2004) *Fundamentals of Nuclear Pharmacy*, 5th ed., Springer
53. Schwochau K. (2000) Technetium. Chemistry and radiopharmaceutical applications, pp. 67-79, Wiley-VCH
54. Shkrob I.A., Marin T.W., Stepinski D.C., Vandegriff III G.F., Muntean J.V., Dietz M.L. (2011) Extraction and reductive stripping of pertechnetate from spent nuclear fuel waste streams, *Sep. Sci. Tech.* 46, 357-368
55. Spitsyn, V.I., Kuzina A.F., Pirogova G.N., Balakhovskii O.A. (1981) Investigations in the field of technetium chemistry, pp. 1-74 [w:]: *Chemistry Review (Vol'pin M.E. (ed.)) vol 3*, OPA, Amsterdam B.V.
56. Stepinski D.C., Wishart J., Vandegriff, III G.F., Shkrob I.A., Kerr K., Dietz M.L., Qadah D.T.D., Garvey S.L (2010) Extraction of Tetra-oxo Anions into a Hydrophobic, Ionic Liquid-Based Solvent Without Concomitant Ion Exchange, *Ind. Eng. Chem. Res.* 49(12), 5863-5868
57. Szabó S., Bakos I., (2004) Electrodeposition of rhenium species onto a gold surface in sulfuric acid media, *J. Solid State Electrochem.* 8, 190-194
58. Torres Lhosa J.M., Ruf H., Schrob K., Ache H.J. (1988) Stripping voltammetry assay of trace technetium with a TOPO coated glassy carbon electrode, *J. Res. Nation. Bureau Stand.* 93(3), 493-495
59. Zamponi S., Czerwiński A., Gambini G., Marassi R. (1992) Linear sweep voltabsorptometry with finite diffusion space, *J. Electroanal. Chem.* 332, 63-71

60. Zamponi S., Czerwiński A., Marassi R. (1989) Thin-layer derivative cyclic voltabsorptometry J. Electroanal. Chem. 266, 37-46
61. Zhou X., Ye G., Zhang H., Li L., Luo F., Meng Z. (2014) Chemical behavior of neptunium in the presence of technetium in nitric acid media, Radiochim Acta, 102(1–2), 111–116

## V. Other scientific publications and achievements

### A) Bibliographic summary of the scientific achievements

Total number of publications:	<b>22</b>
Total impact factor (according to the year of publication):	<b>57.308</b>
Total number of citations based on Web of Science as of December 6, 2018:	<b>140</b>
Total number of citations without self-citations as of December 6, 2018:	<b>122</b>
Hirsch index :	<b>7</b>

My scientific interest mainly focuses on various aspects of the electrochemistry of transition elements. Although the latter topic is my main field of expertise, I was also involved in studies on electrochemistry of various organic compounds and physicochemical properties of selected gases.

The main subject of my Masters Thesis research was analysis of electrooxidation of  $Mn^{2+}$  ions in acidic solutions. My PhD thesis was supervised by Professor Andrzej Czerwiński and focused on spectroelectrochemical studies on reduction of permanganates and perrhenates in aqueous media. The results of the research on the electrochemical and spectroelectrochemical properties of manganese compounds are reported in publications **B1-B6**.

After completing my PhD thesis I participated in various scientific research related both to the nuclear chemistry and non-nuclear aspects of the chemical sciences. The topics of the latter studies that are not related to the habilitation application are briefly summarised in this paragraph. Thus, I conducted research focused on the methods of preparation of platinum and platinum alloys catalysts with potential application in fuel cells systems. These catalysts were obtained by means of electrodeposition (PtRhRu alloys, **B7**) and decomposition of platinum carbonyls (**B9**). I was engaged in scientific cooperation with Professor Daniel Gryko which focused on electrochemical studies on selected organic red-ox systems. These include photosensitive, cyclic organic systems based on e.g. derivatives of

corroles or porphyrins and an analysis of the electrochemical data allowed me to determine several electrochemical parameters, including respective  $E_{1/2}$  values, of the electrochemical processes involving these compounds (**B8**, **B10**, **B12**, **B13**). Another one of the research projects in which I have been involved was devoted to detection of noble gas radioisotopes (Xe-133); the results of these studies are reported in publication **B10**.

During a short-term postdoctoral internship at the Tokyo Institute of Technology I started a new research project related to the treatment of nuclear waste, which I have continued after returning to the country. A patent pending low-temperature decomposition of transition metal hexacyanoferrates has been developed in this research project. These compounds are the “key adsorbents” which are used for removal of radioactive contaminations, such as Cs-137, which are released to the environment during nuclear accidents in nuclear power plants. While radiochemistry remains my main field of the scientific research, I have also participated in the studies aimed at NMR characterization of hydrogen isotopologues (**B14**).

B) List of the publications published in scientific journals from the Journal Citation Reports database (with the exception of the papers listed in chapter IV and included in the habilitation application). IF values according to the year of publication.

- before Ph.D. degree

[B1]. **M.Chotkowski**, Z.Rogulski, A.Czerwiński\* (2006) Badanie mechanizmów reakcji zachodzących podczas elektrochemicznego wytwarzania  $MnO_2$ ,

Przemysł Chemiczny 85(8-9) 1183-1185, IF = 0.429

[B2]. Z.Rogulski, **M.Chotkowski**, A.Czerwiński\* (2006) Electrochemical behavior of  $MnO_2/RVC$  system,

Journal of New Materials for Electrochemical Systems, 9(4), 401-408, IF=1.095

[B3]. Z.Rogulski, **M.Chotkowski**, A.Czerwiński\* (2006) New generation of the zinc-manganese dioxide cell,

Journal of New Materials for Electrochemical Systems, 9(4), 333-338, IF = 1.095

[B4]. **M.Chotkowski**, Z.Rogulski, A.Czerwiński\* (2006) Wykorzystanie spektroskopii UV-Vis w badaniach elektrochemicznych,

Przemysł Chemiczny 85(11) 1481-1487, IF = 0.429

- after Ph.D. degree

[B5]. A. Czerwiński\*, Z.Rogulski, J.Kotowski, Sz. Obrębowski, H.Siwiek I. Paleska, **M.Chotkowski**, M. Łukaszewski (2009) RVC as new carbon material in batteries,

Journal of Applied Electrochemistry 39(5), 559-567, IF = 1.697

[B6]. **M. Chotkowski**, Z. Rogulski, A. Czerwiński\* (2011) Spectroelectrochemical investigation of MnO<sub>2</sub> electro-generation and electro-reduction in acidic media,

Journal of Electroanalytical Chemistry, 651(2), 237-242, IF = 2.905

[B7]. **M. Chotkowski**, J. Dłubak, M. Uklejewska, H. Siwek, A. Czerwiński\* (2011) Characterisation of PtRhRu catalysts for metanol oxidation,

Functional Material Letters 4(2), 187-191, IF = 0.724

[B8]. R. Voloshchuk, D. T. Gryko\*, **M. Chotkowski**, A. I. Ciuciu, L. Flamigni (2012) Photoinduced Electron Transfer in an Amine-Corrole-Perylene Bisimide Assembly: Charge Separation over Terminal Components Favoured by Solvent Polarity,

Chemistry A European Journal, 18(46), 14845-14859, IF = 5.831

[B9]. **M.Chotkowski**, F. Mikłaszewicz, A. Czerwiński\* (2013) Platinum catalyst prepared from platinum carbonyls,

Journal of New Materials for Electrochemical Systems, 16(4) 263-267,  
IF = 0.659

[B10]. A. Nowak-Król, M. Grzybowski, J. Romiszewski, M. Drobizhev, G. Wicks, **M. Chotkowski**, A. Rebane, E. Górecka, D. T. Gryko\*(2013) Strong two-photon

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absorption enhancement in a unique bis-porphyrin bearing a diketopyrrolopyrrole unit,

Chemical Communications, 49(75), 8368-8370, IF = 6.718

- [B11]. **M.Chotkowski\***, A.Siporska, Z.Rogulski, J.Szydłowski, A.Czerwiński (2014) Ocena szczelności prętów paliwowych w reaktorach lekkowodnych na podstawie detekcji radioizotopów gazów szlachetnych,

Przemysł Chemiczny, 93(12) 2259-2263, IF = 0.399

- [B12]. M.Tasior, **M.Chotkowski**, D.T.Gryko\* (2015) Extension of pyrrolopyrrole pi-system: Approach to constructing hexacyclic nitrogen-containing aromatic systems,

Organic Letters, 17(24), 6106-6109, IF = 6.732

- [B13]. M. Grzybowski, I. Deperasinska, **M. Chotkowski**, M. Banasiewicz, A. Makarewicz, B. Kozankiewicz, D.T. Gryko (2016) Dipyrrolonaphthyridinediones - structurally unique cross-conjugated dyes,

Chemical Communications, 52(29), 5108-5111, IF = 6.319

- [B14]. P.Garbacz\*, **M.Chotkowski**, Z.Rogulski, M.Jaszuński (2016) Indirect Spin-Spin Coupling Constants in the Hydrogen Isotopologues,

Journal of Physical Chemistry A, 120(28) 5549-5553, IF = 2.847

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