STUDY OF EXTRACTION-CHROMATOGRAPHIC PROPERTIES OF PERTECHNETATE WITH CYPHOS 101 IMPREGNATED ON AMBERCHROM CG-300s

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Abstract

Ionic liquids are organic salts composed by ions with melting temperature lower than 100 °C. According to their unique properties such as immeasurable vapour pressure, non-flammability, ability to solvate organic, inorganic or polymeric materials are proposed to be used in various industry applications such as catalysts or environmental friendly solvents. One of the main objectives of ionic liquids research is their ability to replace conventional organic solvents, which have high impact on environment in industrial processes. Radionuclide extraction properties of ionic liquids are studied due to their high selectivity and kinetic properties of these compounds. The possibility of solid matrix impregnation with ionic liquids shows high potential for development of new solid phase extractants for radionuclide removal or concentration. Phosphonium ionic liquid Cyphos 101 impregnated on Amberchrom CG-300s solid matrix is suitable for $TcO4^-$ extraction from aqueous phase.

Key words: *ionic liquid; technetium; extraction*

Introduction

Ionic liquids consist of organic cation associated with organic or inorganic anion. Low energy of their crystalline lattice causes that they are fluid at laboratory temperature. Their physical and chemical properties comes from a structure of a cation and anion in their structure and can be changed for example by changing an alkyl chain lenght or change of an anion. According to organic solvents, gases, microcomponents and radionuclides, extraction properties of ionic liquids are examined due to high selectivity and extraction kinetics provided by this compounds. The possibility of solid matrix impregnation with ionic liquids shows high potential for development of new solid phase extractants mainly for radionuclide, specific or low concentrated heavy metals removal or concentration in flow or column arrangement. Impregnation of solid matrixes with extracting agents or ionic liquids is simple and lowers the amount of agents needed for effective separation of metal ions. According to combination of extraction methods selectivity, advantages of sorption methods and simple elution these sorbents are suitable for use in flow systems.

Methods

First, there was a liquid-liquid extraction used to find out which ionic liquid is the most effective in pertechnetate extraction from a water phase at various condition. There were six ionic liquids used solubilized in four different organic solvents with different polarity–cyclohexane, chloroform, toluene and n-butanole with rising polarity from cyclohexane to n-butanole. Water phase to organic phase ratio of 1:1 was used for all of the liquid-liquid extraction experiments.

Effect of pH value and influence of various cations and anions was studied. Britton-Robinson buffer was used for pH dependence experiments with an increment of 10-100×10^{-6} dm^3 of pertechnetate solution (according to its activity) from Drytec pertechnetate generator. In a case of influence of various cations and anions, 1×10^{-3} $mol\cdot dm^{-3}$ water solution of chloride salts, in a case of cations, and sodium salts, in a case of anions, was used as a water phase with an increment of 10 – 100×10^{-6} dm^3 of pertechnetate solution (according to its activity) and adjusted to pH = 2 with HCl. 15 minutes was a contact time of both phases. After this, water phase was taken away quantitatively and activity was measured for 100 seconds on Perkin Elmer 1470 Wizard gamma counter. Amberchrom CG-300s was used as a solid matrix for Ionic liquid impregnation. 2 grams of Amberchrom CG-300s was placed into erlenmayer flask, mixed with 2 grams of Cyphos 101 solubilized in 20 ml of methanol. This mixture was heated and stirred under reflux. After 30 minutes the suspension was filtered and dryed for 2 hours at 100 °C. The resulting weight was 2.5 grams, which means 25 % w/w of Cyphos 101 impregnated on Amberchrom CG-300s. Teflon was impregnated by the same procedure as Amberchrom CG-300s with 10 % w/w of Cyphos 101 impregnated to its stucture. Column experiments were performed with 200 mg of this sorbent in column with a water phase flow of 1 cm^3/min. Before first usage, column was saturated with 40 cm^3 first, then with 40 cm^3 of 8 $mol\cdot dm^{-3}$ HNO_3. Sorption experiments from water phase were performed from 20 cm^3 of water with an increment 10 – 100 µl of pertechnetate generator solution and adjusted to pH = 2 with HCl. After sorption, 1 cm^3 of water phase was taken for an activity measurement. For desorption of pertechnetate from a column 8 $mol\cdot dm^{-3}$ HNO_3 and 2 $mol\cdot dm^{-3}$ $NaClO_4$ was used. After desorption there was 1 cm^3 of desorption solution taken for activity measurement.

Results

Tab. 1 TcO_4^- distribution in sorption/desorption experiment with 2 $mol\cdot dm^3$ $HClO_4$

sample	**counts**	**CPM**	**V [ml]**	**CPM_0**	**R_{sol} [%]**	**R_{column} [%]**
blank	336207	205099	20	4101980		
sorption pH = 2	4898	2857	20	57140	1,392986	98,60701
desorption 2 $mol\cdot dm^3$ $HClO_4$	297824	184479	20	3689580	89,94632	10,05368

Tab. 2 TcO_4^- distribution in sorption/desorption experiment with 2 $mol\cdot dm^3$ $NaClO_4$

sample	**counts**	**CPM**	**V [ml]**	**CPM_0**	**R_{sol} [%]**	**R_{column} [%]**
blank	271026	164552	20	3291040		
sorption pH = 2	141	4	20	80	0.002431	99.99757
desorption 2 $mol\cdot dm^3$ $NaClO_4$	253962	156806	20	3136120	95.29267	4.707327

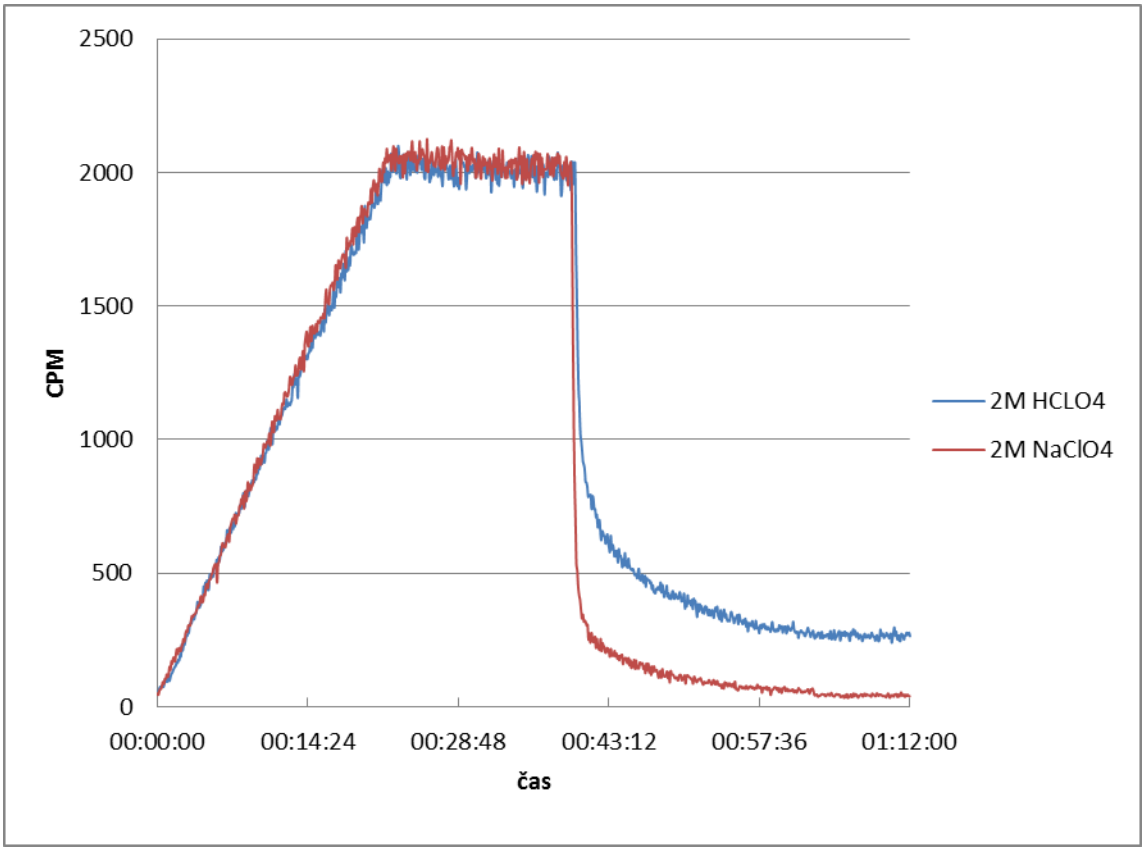

Fig. 1 TcO_4^- sorption/desorption with $NaClO_4$, $HClO_4$, Amberchrom + Cyphos IL101

Fig.1 shows sorption/desorption column experiments with Cyphos 101 impregnated on Amberchrom CG-300s. 2 $mol \cdot dm^3$ $HClO_4$ a 2 $mol \cdot dm^3$ $NaClO_4$ was used as a solution for desorption. In Tab. 1 and Tab. 2 distribution between column and water phase is shown. It is visible that sorption was almost quantitative (at least 98,6 %). When 2 $mol \cdot dm^3$ $NaClO_4$ was used for desorption 4.7 % of sorbed pertechnetate remained on a column, in a case of 2 $mol \cdot dm^3$ $HClO_4$ 10 % of sorbed pertechnetate was trapped on a column after desorption.

Conclusion

Cyphos 101 was chosen as the most suitable ionic liquid for solid matrix impregnation for pertechnetate concentration. Pertechnetate was sorbed quantitatively at 1 cm^3/ min water phase flow. Desorption curve is highly dependent on a solution used and an amount of a pertechnetate remaining sorbed on a column. 2 $mol \cdot dm^3$ $NaClO_4$ gives almost quantitative results as a solution for desorption. There were at least 5 sorption-desorption cycles performed on each column with no properties change noticed. All of the results were highly reproducible.

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Abstrakt

Iónové kvapaliny sú organické soli zložené z iónov s teplotou topenia nižšou ako 100 °C. Vzhľadom k ich unikátnym vlastnostiam ako nemerateľný tlak nasýtených pár, nehorľavosť, schopnosť solvatovať organické, anorganické a polymérne materiály sú predurčené pre použitie v priemysle ako katalyzátory a rozpúšťadlá šetrné k životnému prostrediu. Výskum sa zameriava hlavne na nahradenie konvenčných organických rozpúšťadiel iónovými kvapalinami, kvôli ich vyššej šetrnosti k životnému prostrediu. Extrakčné vlastnosti iónových kvapalín vo vzťahu k rádionuklidom sú skúmané kvôli ich vysokej selektivite a reakčnej kinetike. Možnosť impregnácie tuhých matríc iónovými kvapalinami vykazuje vysoký potenciál pre vývoj nových extraktantov na tuhej fáze pre separáciu alebo zakoncentrovanie rádionuklidov. Cyphos 101 impregnovaná na Amberchrom CG-300s je vhodná pre extrakciu technecistanu z vodnej fázy.