SUPPLEMENTARY MATERIAL

Plutonium (IV) Quantification in Technologically Relevant Media Using Potentiometric Sensor Array

Julia Savosina [1,2], Marina Agafonova-Moroz [1,2], Irina Yaroshenko [1,3], Julia Ashina [3], Vasily Babain [1], Alexander Lumpov [1,2], Andrey Legin [1,3] and Dmitry Kirsanov [1,3,*]

[1] Institute of Chemistry, St. Petersburg State University, Peterhof, Universitetsky prospect, 26, 198504 Saint-Petersburg, Russia; july-s@khlopin.ru (J.S.); ma-m@khlopin.ru (M.A.-M.); irina.s.yaroshenko@gmail.com (I.Y.); babainv@mail.ru (V.B.) ; lumpov@khlopin.ru (A.Lumpov); andrey.legin@gmail.com (A.Legin)

[2] Khlopin Radium Institute, 2 Murinsky prospect, 28, 194021 Saint-Petersburg, Russia

[3] Laboratory of Artificial Sensory Systems, ITMO University, Kronverksky prospect, 49, 197101 Saint-Petersburg, Russia; ashina.julia91@gmail.com

* Correspondence: d.kirsanov@gmail.com; Tel.: + 7-921-333-1246

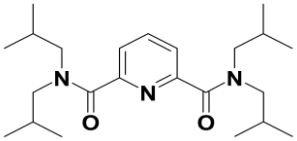
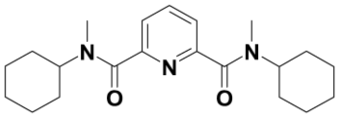
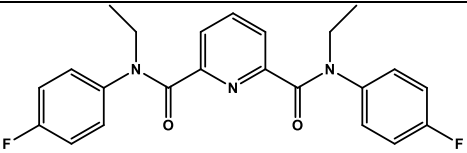
Received: 5 February 2020; Accepted: 10 March 2020; Published: date

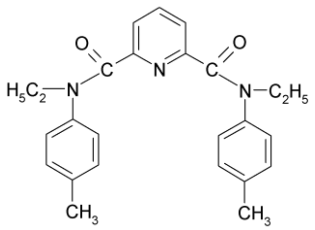
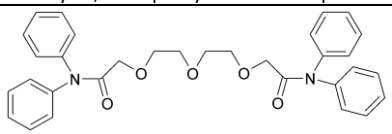
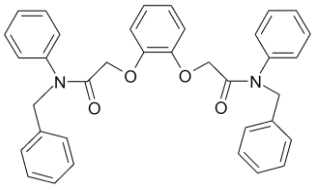
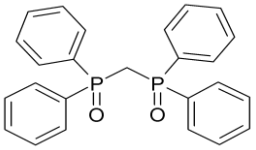
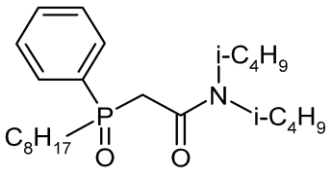
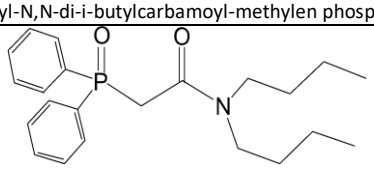
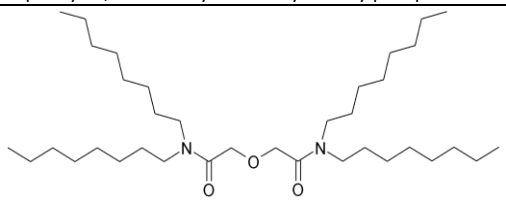
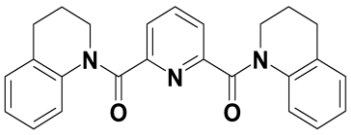
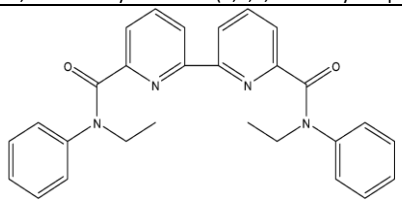
Sensor membrane preparation

The sensor membranes were prepared using a standard protocol. 17 ligands were selected for membrane preparation, based on liquid extraction literature data. The list of the ligands along with corresponding literature references describing their synthesis and extraction behavior is given in the Table S1. All ligands were kindly provided by Khlopin Radium Institute (St. Petersburg, Russia). The polymeric membrane matrix of electrodes was composed of poly(vinyl chloride) (PVC) (33 wt.%) and 2 - nitrophenyloctyl ether (NPOE) as a plasticizer (64–65 wt.%). Potassium tetrakis[3,5-bis(trifluorometyl)phenyl]borate (KTFPB) or the acidic form of chlorinated cobalt dicarbollide (CCD) were used as cation-exchangers (10 mmol/kg). PVC, NPOE and KTFPB were obtained from Merck (Darmstadt, Germany). CCD was kindly provided by Katchem (Prague, Czech Republic). All sensor membranes contained 50 mmol/kg of one of the ligands listed in the Table S1.

In order to prepare the membranes the weighted amounts of membrane components were dissolved in freshly distilled tetrahydrofuran and poured into flat bottomed Teflon beakers. The cocktails were left overnight for solvent evaporation. Three sensor membranes 4 mm in diameter were cut from the parent membrane of each composition and glued upon the end of PVC sensor bodies (6 mm in diameter) with PVC-cyclohexanone mixture. The sensor bodies were equipped with Ag/AgCl inner reference electrodes prepared from 5 mm long pieces of silver wire (0.5 mm in diameter) covered with AgCl layer in the electrochemical process.

Table S1. The components of the sensor membranes.

Nature of the ligand	Chemical structure	Cation exchanger	Sensor number	Ref.
Diamides of dipicolinic acid	 N,N',N,N'- Tetraisobutyl diamide of dipicolinic acid	KTFPB	S1	[s1]
	 N,N'-Dimethyl-N,N'-dicyclo-hexyldiamide of dipicolinic acid	KTFPB	S5	[s2]
	 N,N'-Diethyl-N,N'-di(p-fluoro)phenyl diamide of dipicolinic acid	KTFPB	S11	[s2]

	 N, N’-Diethyl-N, N’-di-p-tolyldiamide of dipicolinic acid	KTFPB	S13	[s3]
Nitrogen containing oxa-nonanes	 1,9-Bis-(diphenylcarbamoyl)-2,5,8-trioxanonane	CCD	S2	[s4]
	 1,6-Bis-(benzylphenylcarbamoyl)-3-benzo-2,5-oxahexane	KTFPB	S12	[s4]
Phosphine oxides	 Tetraphenylmethylene diphosphine dioxide	KTFPB	S3	[s5]
	 Phenyloctyl-N,N-di-i-butylcarbamoyl-methylen phosphineoxide	CCD	S8	[s6]
	 Diphenyl-N,N-di-n-butylcarbamoyl-methylphosphinoxide	CCD	S14	[s7]
Amides of organic acids	 N,N,N’,N’-Tetraoctyldiamide of diglycolic acid	CCD	S4	[s8]
	 Pyridine-2,6-dicarboxylic acid bis(1,2,3,4-tetrahydroquinolide)	KTFPB	S9	[s1]
	 N,N’-diethyl-N,N’-diphenyldiamide of 2,2’-dipyridyl-6,6’-dicarboxylic acid	KTFPB	S10	[s9]

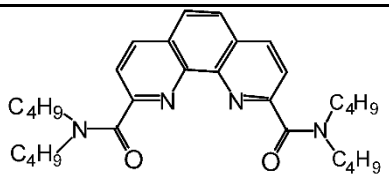
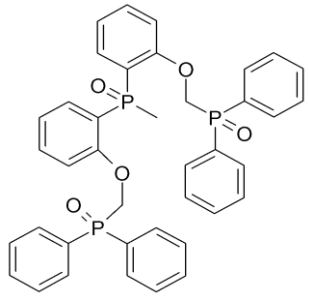
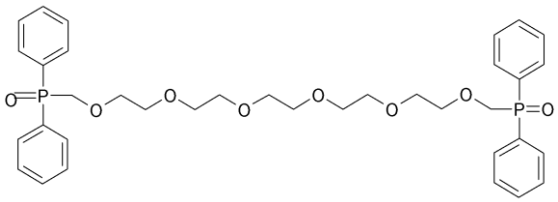
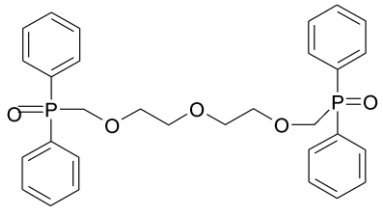
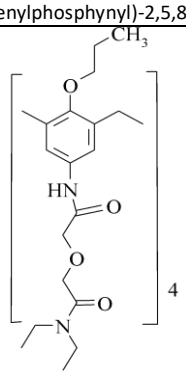
	N^2,N^2,N^9,N^9-phenanthroline-  dicarboxamide	Tetrabutyl -1,10-2,9-	KTFPB	S17	[s7]
Phosphoryl containing oxa-nonanes	 1,9-Bis-(diphenylphosphynyl) 3,6-dibenzo-2,8-dioxa-5-methyl-phosphineoxanonane		KTFPB	S6	[s10]
	 1,18-Bis-(diphenylphosphynyl)-2,5,8,11,14,17-hexaoxaoctadecane		CCD	S15	[s10]
	 1,9-Bis-(diphenylphosphynyl)-2,5,8-trioxanonane		CCD	S16	[s10]
Calixarene	 5,11,17,23-Tetra(diethylcarbamoyl-ethoxymethylcarboxamido)-25,26,27,28-tetrapropoxycalix[4]aren		CCD	S7	[s11]

Table S2. lg $K(Pu^{4+}/Me^{n+})$ selectivity values of the sensors for selected actinides and lanthanides.

	S1	S3	S4	S5	S6	S7	S8	S9	S11	S13	S14	S15	S16
La	-0.4	-0.1	0.7	-0.1	0.7	0.4	0.9	-2.4	-0.2	-0.6	-0.7	-1.2	-1.7
Ce	-0.4	-0.3	-0.6	0.0	0.4	0.0	0.4	-1.4	-0.1	-0.8	-0.5	-0.8	-1.4
Pr	0.2	0.0	0.3	0.4	0.4	0.1	0.6	-0.9	0.5	-0.4	-0.3	-0.3	-1.6
Nd	0.4	0.0	0.4	0.4	2.6	-2.0	1.1	-2.6	0.5	-0.5	-1.6	-1.4	-1.9
Sm	0.2	-0.1	0.4	0.3	1.8	-0.7	0.8	-2.6	-0.1	-0.8	-1.5	-1.4	-2.0
Eu	0.2	-0.5	0.0	-0.1	1.4	-0.5	0.6	-3.3	0.2	-0.8	-2.4	-2.0	-3.1
Gd	0.1	-0.5	-0.1	0.1	1.2	-0.8	0.6	-2.5	0.0	-0.8	-1.8	-1.5	-2.5
Yb	0.4	-0.3	0.1	0.0	1.3	-2.3	0.6	-3.7	0.3	-0.8	-3.0	-2.6	-3.2
Th	-0.9	-0.6	-0.9	-0.7	1.3	-1.3	0.1	-2.8	-2.1	-1.6	-2.0	-1.8	-2.3
U	3.1	3.3	3.5	2.2	2.4	3.7	2.5	3.7	2.3	2.8	5.9	6.2	4.1

Figure S1. Visual appearance of the developed sensor array.

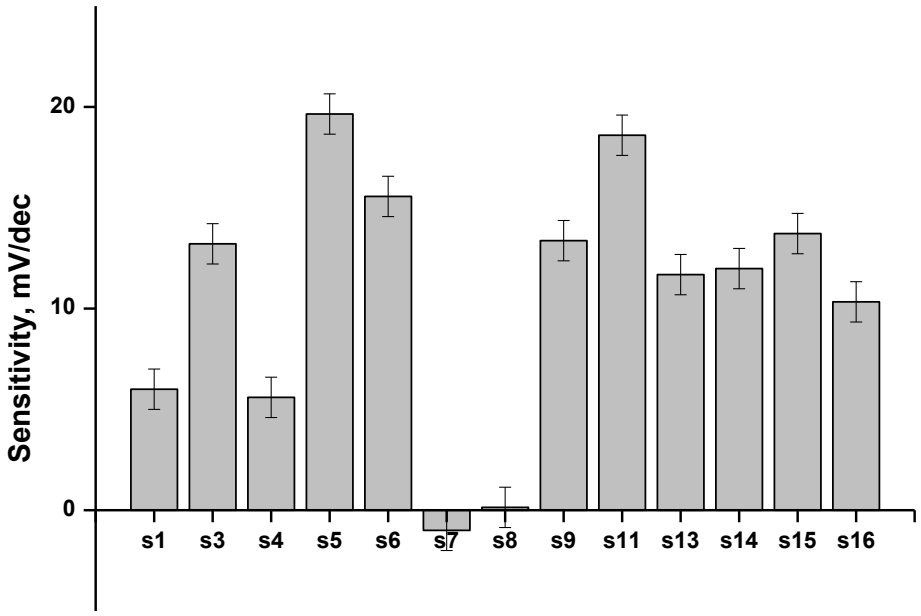


Figure S2. Sensitivity to Pu^{4+} in the presence of 500 mg/L uranium.

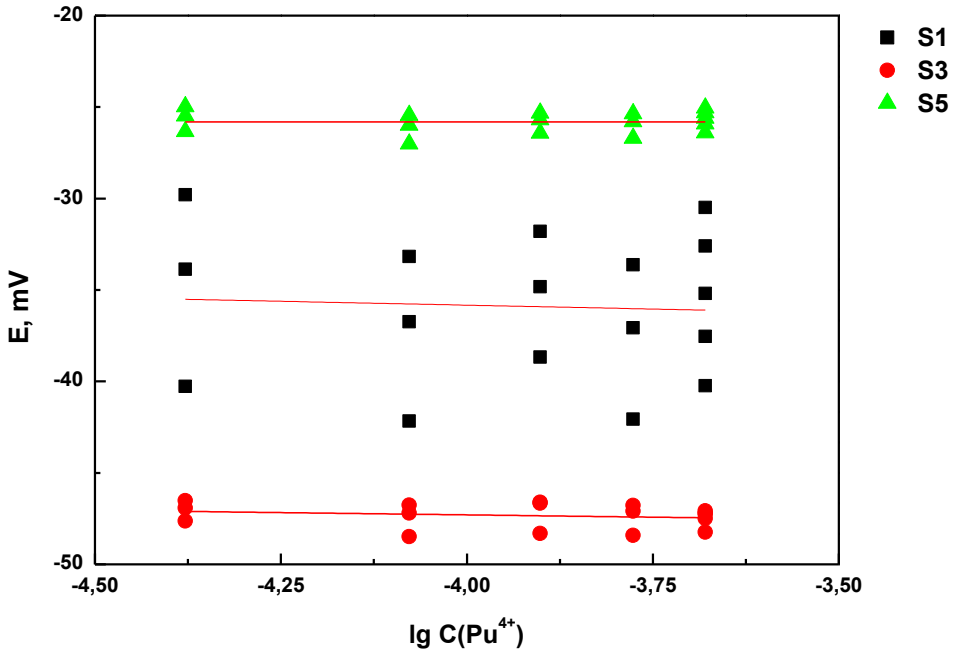


Figure S3. Sensor responses in the simulated PUREX solutions.

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