Funded by the European Union
NextGenerationEU

SUMMIT
SOFIA UNIVERSITY
MARKING MOMENTUM
FOR INNOVATION AND
TECHNOLOGICAL TRANSFER

SOFIA UNIVERSITY -
MARKING MOMENTUM
FOR INNOVATION AND TECHNOLOGICAL TRANSFER

National Recovery and Resilience Plan
OF THE REPUBLIC OF BULGARIA

Synthesis and characterization of ion-imprinted polymeric materials for solid-phase extraction of Sn(II) species

Author: Tanya Yordanova, Grant № 70-123-469, Head of the research project: Assoc. Prof. Ivanka Dakova

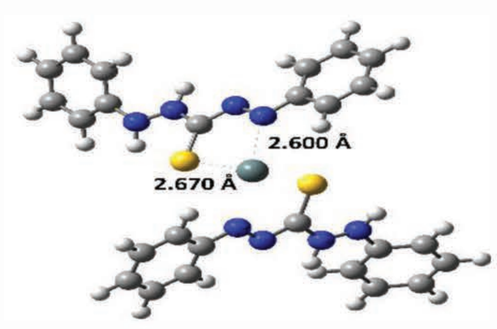
INTRODUCTION

Ion-imprinted polymers (IIPs) are synthetic materials engineered to selectively recognize and bind specific metal ions. These materials are obtained by polymerising functional and crosslinking monomers around a template molecule, leading to a highly cross-linked three-dimensional polymeric network. After polymerization, the template ion is removed, leaving behind cavities that are complementary in size, shape, and coordination environment to the target ion. This process enables IIPs to exhibit high selectivity toward their target ions, even in the presence of competing species.
In this work, two Sn(II)-IIPs were synthesized and successfully applied as sorbents for non-chromatographic speciation analysis of inorganic tin in water samples.

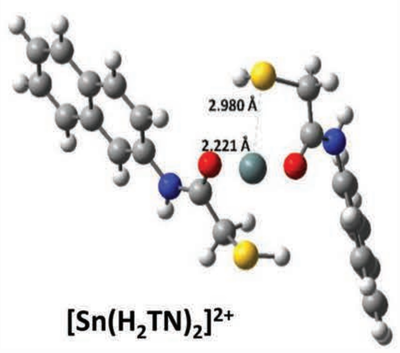
SYNTHESIS

Ion-imprinted polymers were synthesized by radical polymerization of methacrylic acid (0.15 mmol) and cross-linking agent (trimethylolpropane trimethacrylate, 1 mmol) in the presence of different chelating ligands (dithizone (DTZ) and thionalide (TN), 0.30 mmol) and Sn(II) as a template ion (0.15 mmol). Selective retention of Sn(II) was achieved due to the binding sites possessing specific structure and functionality.

OPTIMIZED STRUCTURES

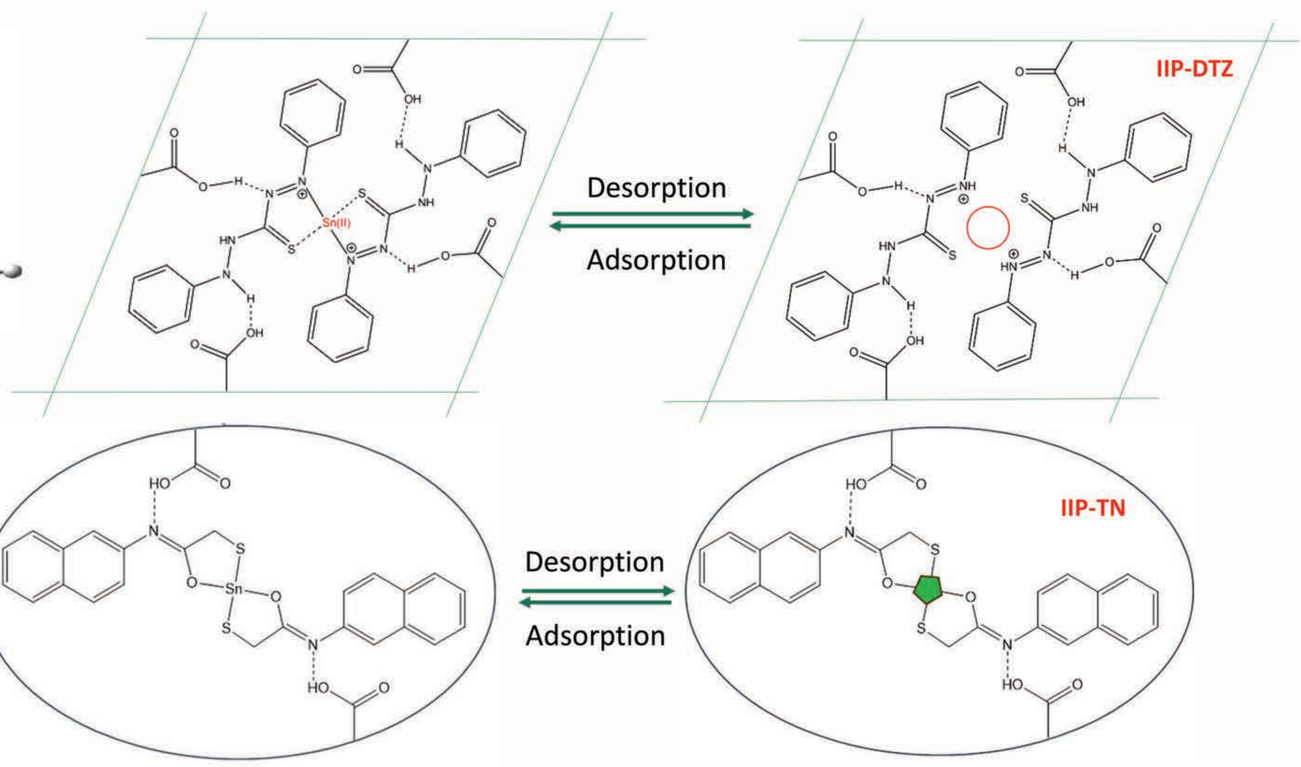


$[Sn(H_2DTZ)_2]^{2+}$



$[Sn(H_2TN)_2]^{2+}$

STRUCTURE AND FUNCTIONALITY OF THE BINDING SITES



ELEMENTAL ANALYSIS

Polymer	C, %	N, %	H, %	S, %
IIP-DTZ	43,14 ± 1,33	6,58 ± 0,31	6,49 ± 0,26	1,79 ± 0,12
IIP-TN	39,30 ± 1,25	4,38 ± 0,22	5,72 ± 0,25	1,51 ± 0,12
NIP	55,16 ± 2,29	3,60 ± 0,17	7,39 ± 0,29	-

Incorporation of chelating ligands in the polymer matrix (calculated from elemental analysis data per gram dry sorbent):
- **Dithizone – 65.1 %**
- **Thionalide – 58.5 %**

Extraction characteristics and analytical application

Extraction efficiency of IIP-DTZ, IIP-TN and non-imprinted polymer (NIP)

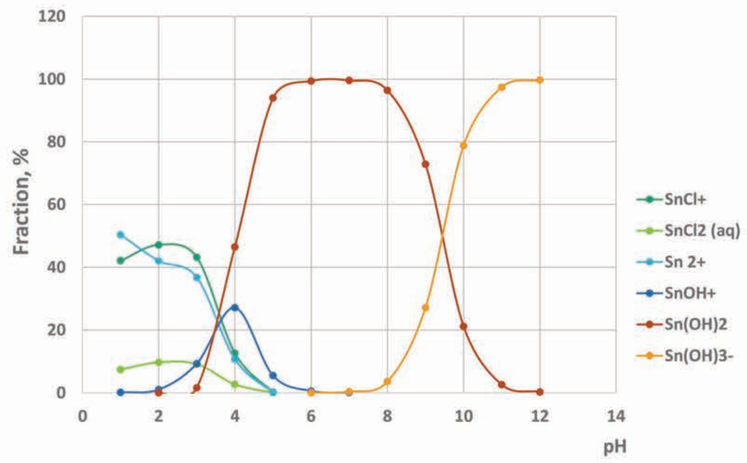
pH	Degree of sorption D_s, %		
	IIP-DTZ	IIP-TN	NIP
3	31,1	55,7	5,5
4	68,9	73,4	5,8
5	84,6	79,9	6,0
6	99,7	99,7	6,2
7	99,8	99,8	6,1
8	99,8	99,7	8,3
9	99,7	99,8	8,2
10	91,1	84,3	6,3
11	85,5	82,2	5,9

Quantitative adsorption of Sn(II) was achieved at pH 6 – 9 by both imprinted polymeric sorbents. It is considered an advantage because preliminary pH adjustment is not demanded when analyzing real water samples.

Degree of sorption: $D_S(\%) = \frac{A_i - A_{eff}}{A_i} \times 100$

Degree of elution: $D_E(\%) = \frac{A_{el}}{A_i - A_{eff}} \times 100$

A_i - total cation amount (μg)
A_{eff} - cation amount in the effluate solution after extraction
A_{el} - cation amount in the eluate solution after elution



Distribution diagram of Sn(II) species at different pH values and concentration of chlorides 1 mol/L (calculated by Visual MinteQ 3.1).

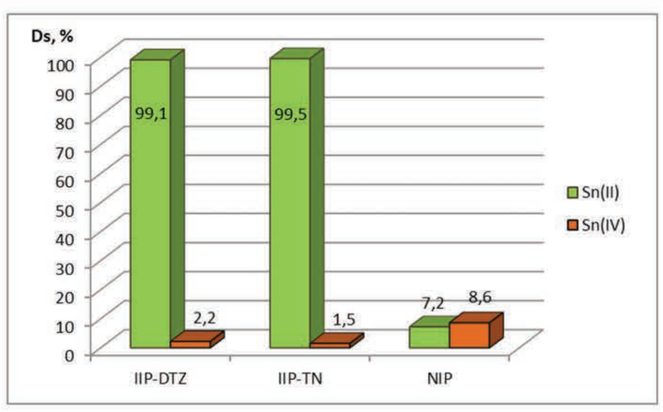
Despite the target analyte existing mainly as a neutral hydroxide at pH 5–8, quantitative retention of Sn(II) was accomplished by both IIPs. It is due to the formation of stable complexes with the chelating ligands incorporated in the active centers of the polymeric sorbents.

Elution study

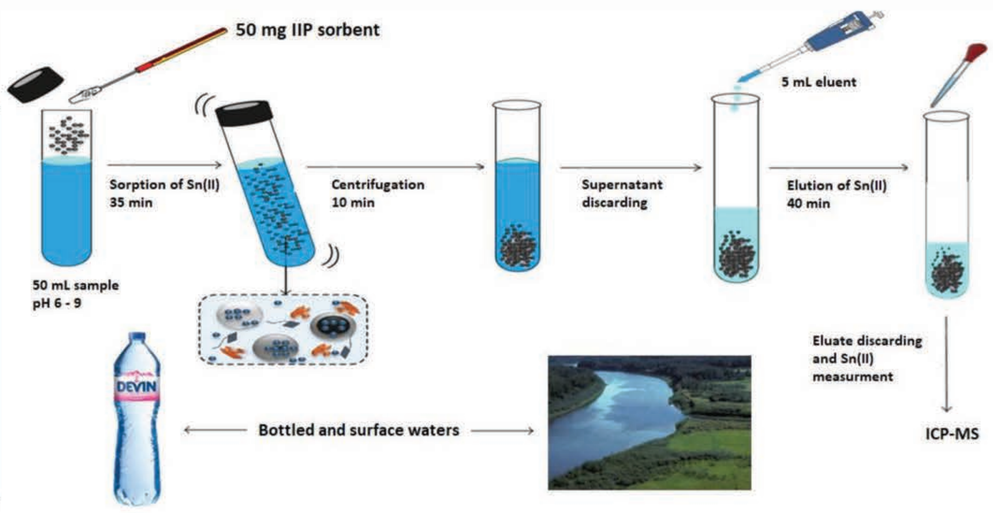
Eluent solution	Concentration	Degree of elution, %	
		IIP-DTZ	IIP-TN
HCl	1 M	18,8	12,6
	3 M	21,3	12,9
	6 M	30,4	14,8
HNO_3	2 M	16,4	10,4
	4 M	17,1	10,3
	6 M	22,5	15,9
$Fe(NO_3)_3$	100 mg/L	19,1	12,0
EDTA	10 mM	98,5	68,5
L-Cysteine	0.25 M	98,3	96,8
Thiocarbamide	0.50 M	93,9	92,5
	1.0 M	94,6	92,9

Elution study was conducted after loading IIP-DTZ and IIP-TN (50 mg portions) with 100 μg Sn(II) under optimal conditions for quantitative adsorption followed by treatment with 10 mL of tested eluent solutions for 60 min. The highest elution rates were achieved with 10 mM EDTA for IIP-DTZ and with 0.25 M L-cysteine for IIP-TN.

Selectivity of IIPs



Analytical procedure and application to real water samples



	Bottled water (Devin, TM 82 mg/L)		Surface water	
	IIP-DTZ	IIP-TN	IIP-DTZ	IIP-TN
Added, μg/L	100.0	100.0	100.0	100.0
Found, μg/L	103.5 ± 5.4	98.3 ± 4.1	105.0 ± 6.1	101.3 ± 3.5
R, %	103 ± 3	98 ± 5	104 ± 3	100 ± 2
RSD, %	5.2	4.2	5.8	3.4

Contract BG-RRP-2.004-0008 for the financing of project "Sofia University - Marking Momentum for Innovation and Technological Transfer" under pillar 2 "Establishing a network of research higher education institutions in Bulgaria", component "Innovative Bulgaria" from National Recovery and Resilience Plan part of the program to accelerate economic recovery and transformation through science and innovation