



MERCURY DETERMINATION AND SPECIATION IN WINE BY NEW ION-IMPRINTED SORBENTS

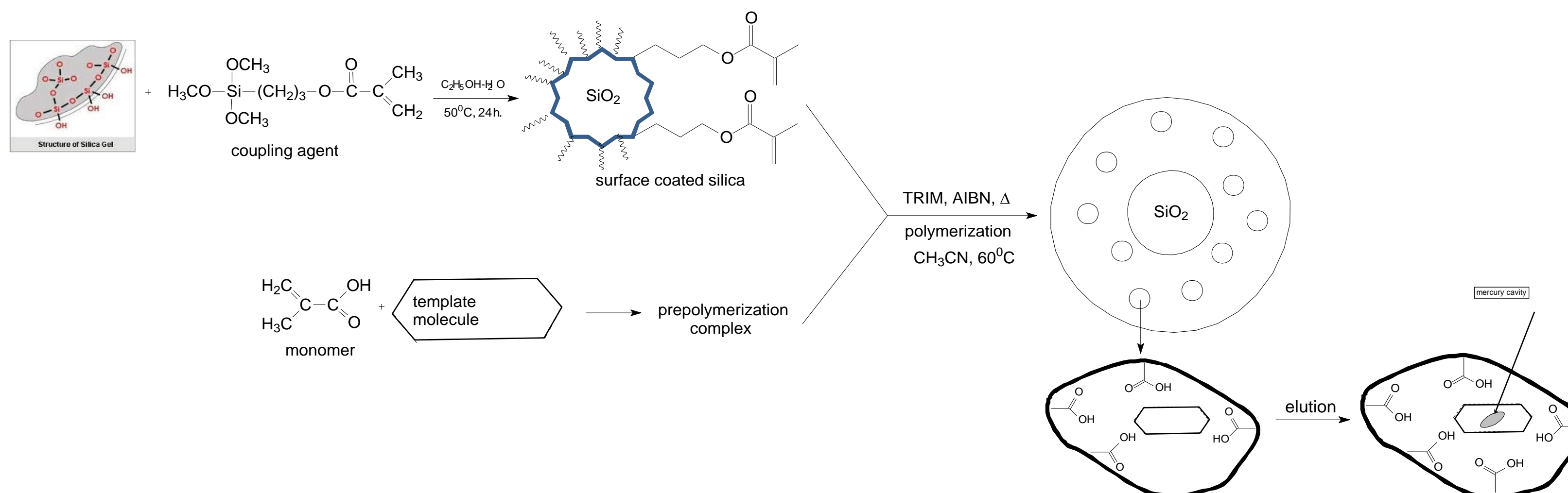


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INTRODUCTION

Wine is widely consumed beverage and strict control for toxic element content is required according to national and international legislation. The presence of toxic elements in wine results from deposition of airborne particulate matter on grapes and the intake of microelements by the grapevine from groundwater and soil. According to the Office International de la Vigne et du Vin (OIV) requirements, the content of mercury should not exceed 5 µg/L in bottled wines. Typical Hg concentrations in wine are at sub-µg/L levels and their reliable and accurate determination calls for preliminary preconcentration and separation of mercury species. This step most frequently permits also selective determination of inorganic and organic Hg species in connection with high differences of their toxicity and mobility. The solid-phase extraction using ion-imprinted sorbents is most popular analytical procedure for this purpose.

Schemes of the Hg(II) ion-imprinted copolymer layer-coated silica gel preparation



Prepared sorbents.

Abbreviation	Template
SiG(PDC-Hg)	DPC-Hg complex
SiG(PDC)	DPC
SiG(TAN-Hg)	TAN-Hg complex
SiG(TAN)	TAN
SiG(DTZ-Hg)	DTZ-Hg complex
SiG(DTZ)	DTZ
SiG(Blank)	-

Molecular and ion imprinted polymers (MIPs and IIPs) are synthetic materials with artificially generated recognition sites able to specifically rebind a target molecule or ion in preference to other closely related compounds. These materials are obtained by polymerising functional and crosslinking monomers around a template molecule, leading to a highly cross-linked three-dimensional network copolymer. Subsequent removal of the imprint molecule or ion leaves cavities with a size, shape and chemical functionality complementary to those of the template.

In this study new sorbents for mercury speciation and preconcentration are presented. The ion-imprinted copolymer is chemically bound on the silica gel surface.

Reagents

methacrylic acid (MAA)
 2,2'-azobisisobutyronitrile (AIBN)
 trimethylolpropane trimethacrylate (TRIM)

Ammonium pyrrolidine dithiocarbamate (DTC)
 1-(2-thiazolylo)-2-naphthol (TAN)
 Dithizone (DTZ)

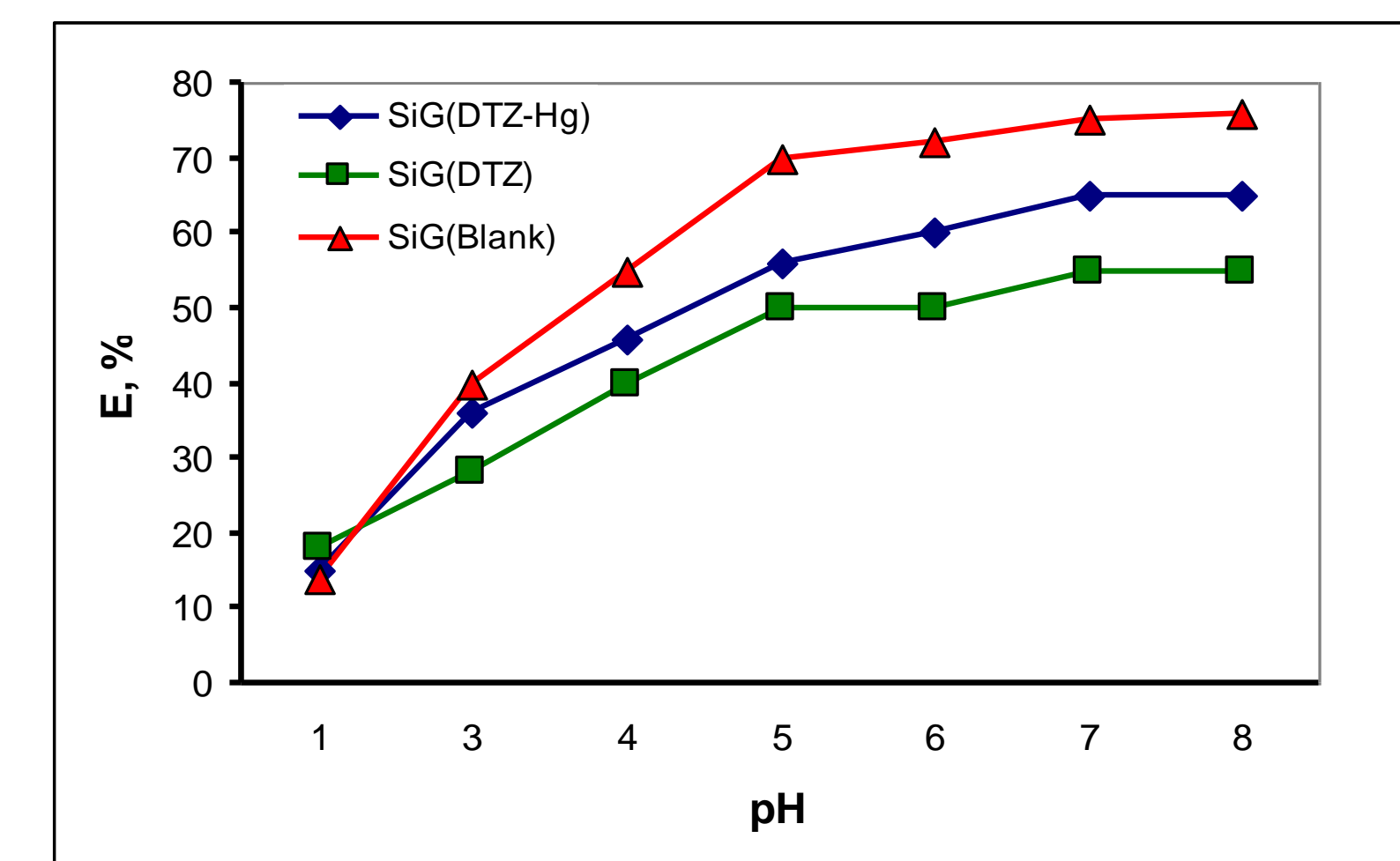
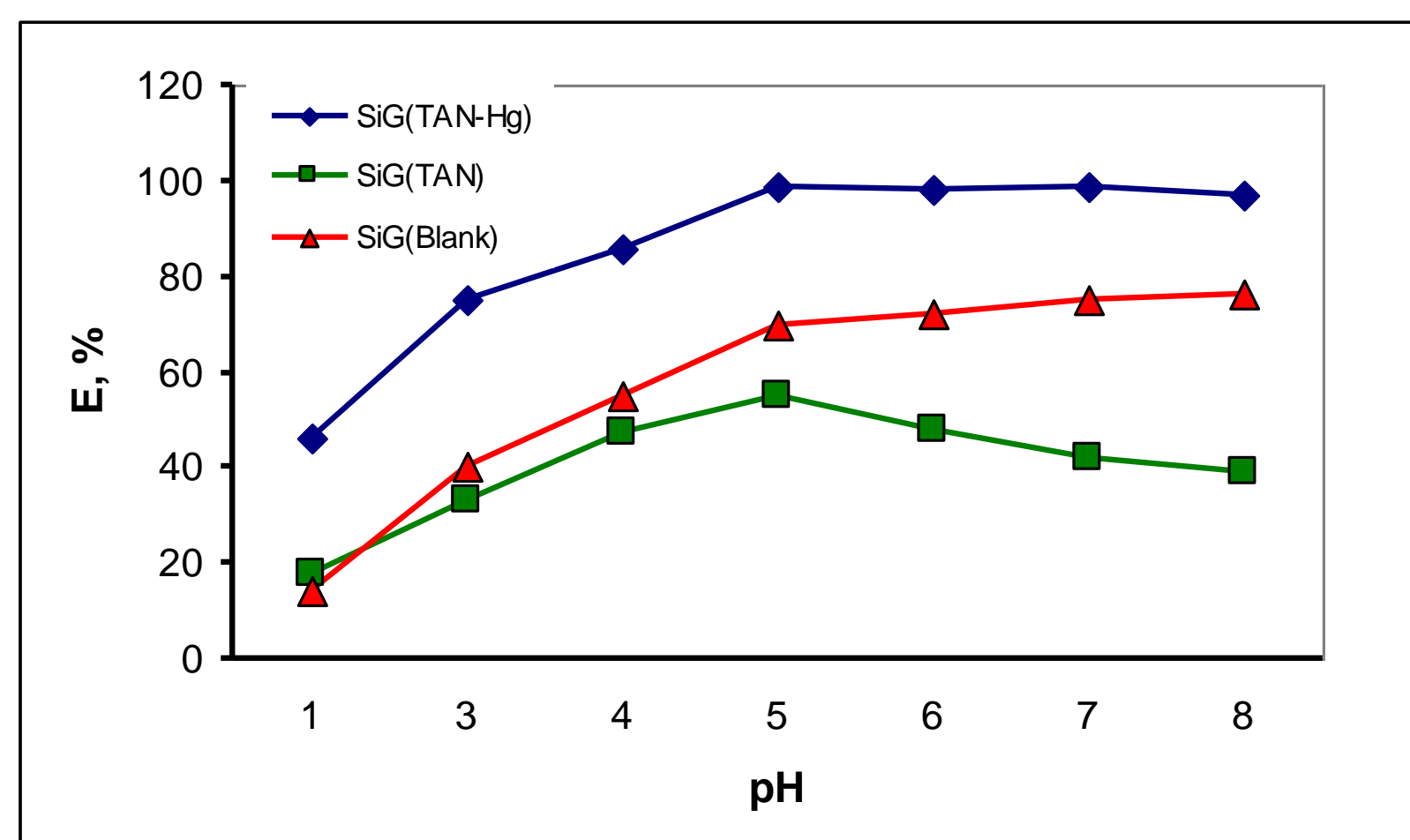
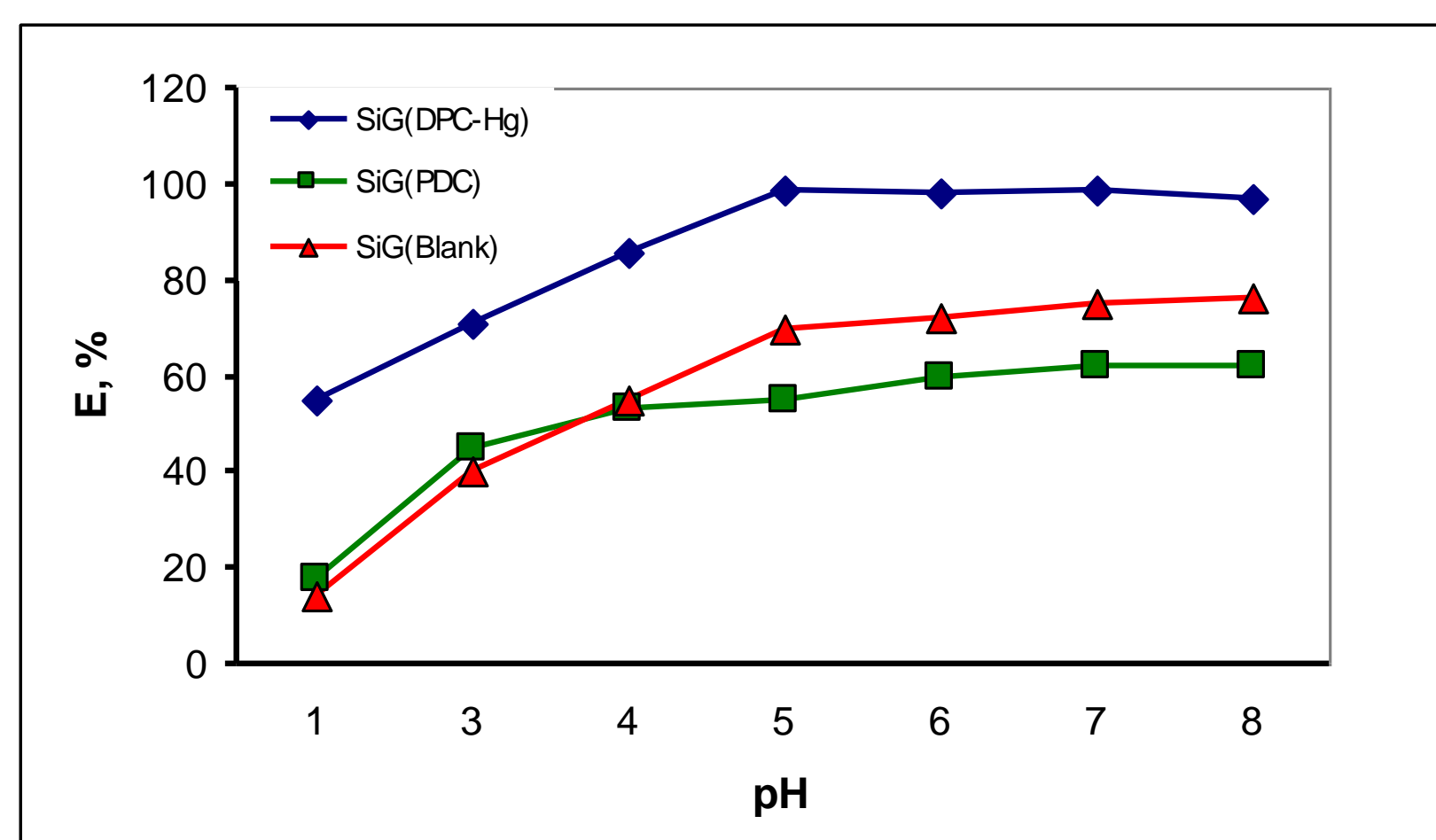
Extraction efficiency and selectivity characteristics

Extraction efficiency (E) - $E\% = [(A_i - A_{eff}) / A_i] \cdot 100$
 Distribution ratio (D) - $D = (A_i - A_{eff}) / A_{eff}$
 Selectivity coefficient $S_{Hg/Me}$ - $S_{Hg/Me} = D_{Hg} / D_{Me}$

where A_{eff} (µg) is the cation amount in the effluente solution after extraction by sorbents from a solution with a total cation amount A_i (µg).

D_{Hg} and D_{Me} are the distribution ratios for Hg(II) and $CH_3Hg(II)$, Cu(II), Cd(II), Ni(II), Pb(II) and Fe(III), respectively

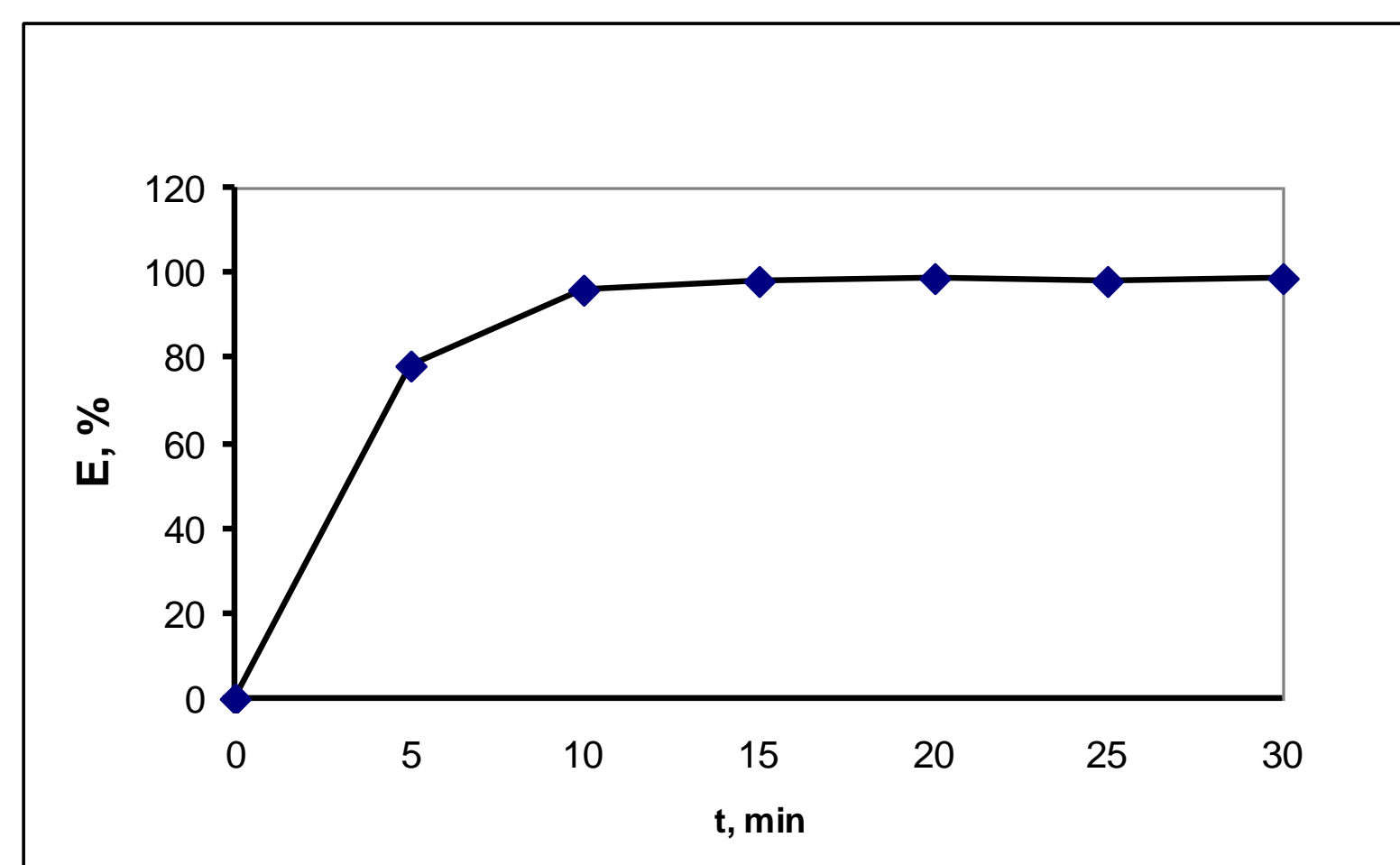
RESULTS



pH-dependence of the extraction efficiencies of Hg(II) ions with obtained IIPs and non-IIPs

Degree of Elution (%) for Hg(II) from imprinted and non-imprinted sorbents using different eluents.

Eluent	Degree of Elution (%)
2 M HCl	68±5
4 M HCl	80±4
2 M HCl + 0.1 M thiourea	> 99
0.5 M HCl + 0.1 M thiourea	> 99
0.1 M HCl + 0.1 M thiourea	> 99
2 M HNO ₃	72±4
4 M HNO ₃	> 99



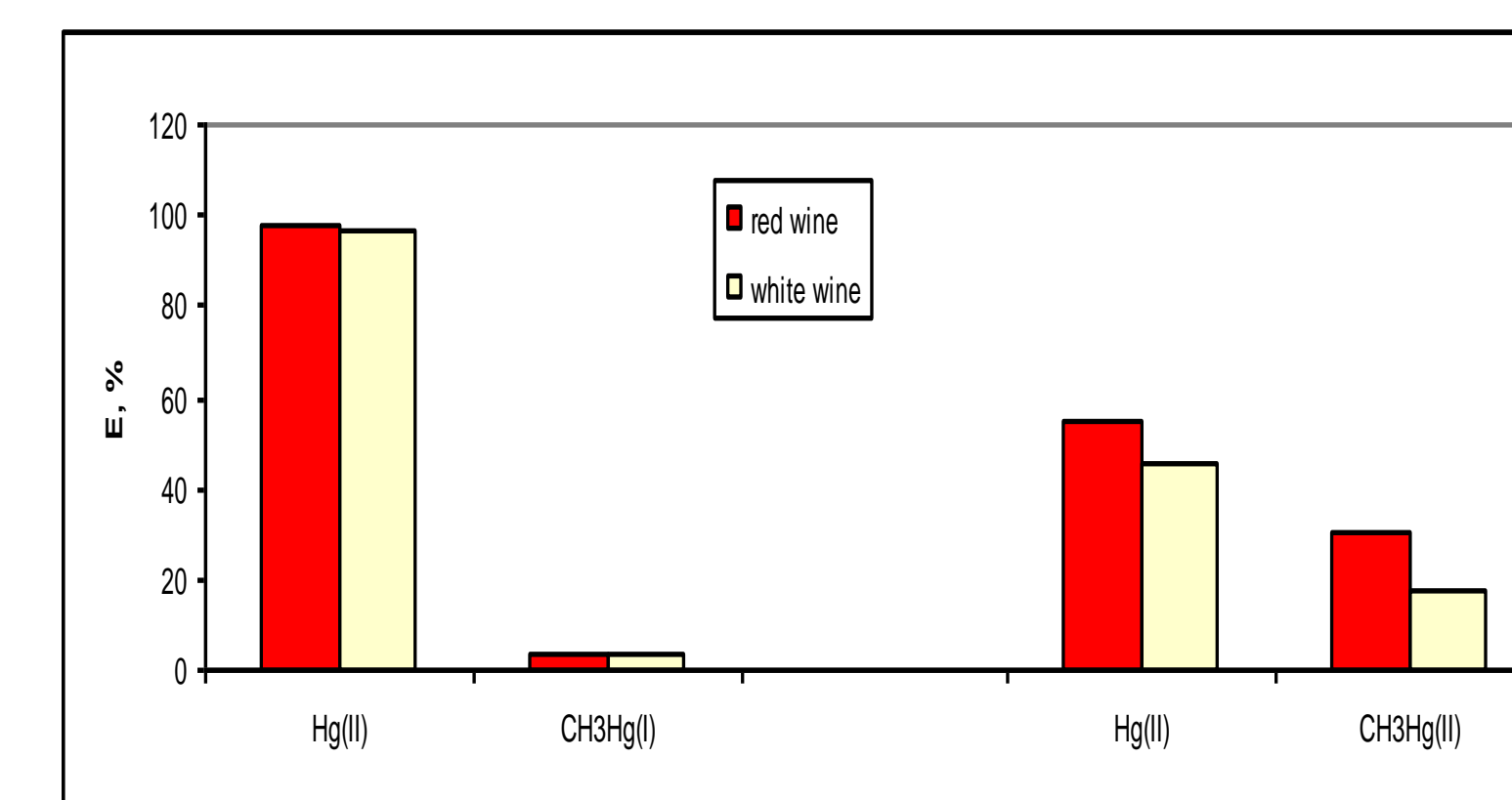
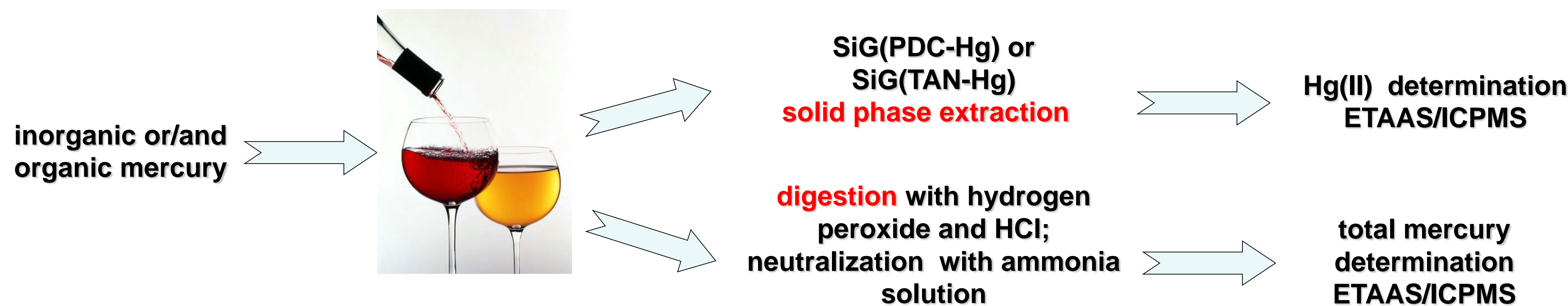
Kinetic of Hg(II) sorption

Distribution (D) and selectivity coefficients $S_{Hg/Me}$ of SiG(PDC-Hg), SiG(TAN-Hg), SiG(Blank) and P(TAN-Hg) for Hg(II) and competitive ions.

Me ion	SiG(PDC-Hg)		SiG(TAN-Hg)		SiG(Blank)		P(TAN-Hg)*	
	D	$S_{Hg/Me}$	D	$S_{Hg/Me}$	D	$S_{Hg/Me}$	D	$S_{Hg/Me}$
Hg(II)	99	-	49	-	3.0	-	49	-
$CH_3Hg(II)$	0.5	201.0	0.4	278.9	0.4	192.9	0.03	1633
Cu(II)	1.7	60.7	1.2	40.1	1.0	2.9	0.4	113.9
Ni(II)	5.7	17.5	3.0	16.3	3.7	0.8	0.2	233.3
Pb(II)	1.6	63.5	1.3	41.7	1.1	2.7	0.7	73.1
Cd(II)	4.0	24.8	3.0	16.3	3.2	0.9	0.4	132.4
Fe(III)	9.0	11.0	6.7	7.3	5.7	0.5	0.9	54.5

*I. Dakova, V. Georgieva, I. Karadjova, G. Georgiev, Talanta 78 (2009) 528

APPLICATION



SiG(PDC-Hg)

SiG(TAN-Hg)

Analytical procedure for Hg(II) determination in wine:

- > 25 mg SiG(PDC-Hg) sorbent
- > conditioning with buffer solution, pH 6
- > 10 mL wine sample, pH 6
- > washing with acetonitrile
- > analyte elution with 1 mL 0.1 M HCl + 0.1 M thiourea
- > ICPMS measurement of Hg in the eluate

Analysis results (µg/L) for Hg (mean ± standard deviation) in wine samples, 5 parallel determinations.

Sample	SPE-ISPMS	CVAFS
Cabernet Sauvignon	0.22±0.04	0.21±0.01
Merlot	0.18±0.02	0.19±0.01
Menada	0.28±0.03	0.26±0.02
Sauvignon blanc	0.15±0.02	0.12±0.02
Chardounay	0.11±0.02	0.13±0.01
Pinot-Noir	0.29±0.03	0.31±0.02

- The preparation of Hg(II) ion-imprinted polymer layer-coated silica gel particles (Hg(II)-IIP) and its application as adsorbent for the selective separation and preconcentration of Hg(II) in wine is developed.
- Newly synthesized SiG(PDC-Hg) and SiG(TAN-Hg) sorbents permit quantitative sorption at pH 5-7.
- The good selectivity of SiG(PDC-Hg) and SiG(TAN-Hg) sorbents towards Hg(II) over Cd(II), Cu(II), Fe(III), Ni(II), Pb(II), and $CH_3Hg(II)$ was established.
- The determination of Hg(II) ions in wine shows that the interfering matrix does not influence the preconcentration and selectivity values of the SiG(PDC-Hg).
- The detection limit for inorganic mercury is 0.05 µg/L (3 σ), determined by ICPMS.

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