Sixth International Conference
South-West University
Faculty of Mathematics & Natural Sciences
Blagoevgrad, Bulgaria 10 - 14 June, 2015

SOLID PHASE EXTRACTION OF Au(III) USING SILICA GEL MODIFIED WITH 4-AMINOANTIPYRINE SCHIFF BASES

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Abstract. The degree of extraction of Au (III) from hydrochloric acid solutions on 4-aminoantipyrine Schiff bases modified silica gel was studied. Quantitative sorption of Au (III) on the surface of the sorbent containing azomethine group was achieved in the presence of 0.1-1 mol/L HCl. Metal retained on the sorbent surface can be recovered with 0.7 M thiourea in 2 M HCl as eluent, with desorption efficiency exceeding 99 %. FAAS was used to quantify Au (III) in eluates and effluates. The presence of competitor ions as Al (III), Cu (II), Fe (III), Mn (II), Ni (II), Zn (II) has unsignificant influence on binding properties of sorbent.

Keywords: solid phase extraction; noble metals; 4-aminoantipyrine schiff base

Introduction

The determination of gold and noble metals in complex matrices still remains a difficult task, despite the application of highly sensitive analytical methods. The direct determination of these elements in real samples is complicated because of their low concentrations in analyzed materials and the interfering effect of matrix components. To decrease the detection limits and to increase the reliability of the determination, the matrix components must be separated, which is attained by the separation/preconcentration procedures. In recent years solid phase extraction (SPE) has been successfully used for the separation and sensitive determination of metal ions (Camel, 2003).

Sorption on sorbent modified with complexing agents, which possess selective properties toward gold (III) and platinum-group metals in acidic solutions, is widely used for their preconcentration from solutions with complex composition (Tong at al., 1990; Ye et al., 2014; Fedyunina et al., 2013; Mladenova et al., 2012; Pyrsynska, 2012).

It is well known, that gold (III) in strongly acidic solutions forms complexes with nitrogen- and sulfur-containing ligands, which are more stable in comparison with complex with other base metals (Mladenova et al., 2012). This provides good possibility for selective preconcentration of Au (III) on sorbents containing nitrogen- and sulfur-containing groups.

The aim of present study is to investigate sorbent proterties of Schiff bases immobilized silica gel (SIG-Schiff bases) for selective preconcentration of Au (III), from synthetic solutions Optimal conditions (pH, sample volume, sorption time, type and concentration of eluent) for quantitative sorption/desorption of Au(III) will be defined. The influence of base metals, existing at high concentration levels in the sample solution on the degree of sorpion of Au(III) will be studied.

Experimental

Reagents

All chemicals were analytical reagent grade and are used without further purification. Stock solutions for Al(III), Cu(II), Fe(III), Mn (II), Ni(II) and Zn(II) (1000 μg mL^{-1}) were Titrisol, Merck (Darmstadt, Germany, www.merck.de) in 2% HNO_3. The stock standard solution for Au(III) were Sigma–Aldrich (Germany) in 5% HCl. Working standard solutions were obtained by appropriate dilution of the stock standard solutions. Silica gel for column chromatography (≤0.063 mm (≥230 mesh ASTM)), 4-aminoantipyrine and substituted benzaldehydes were purchased from Sigma-Aldrich Ltd. The pH was adjusted by various concentrations of HCl (Merck, 37%).

Apparatus - AAS

FAAS measurements were carried out on a Perkin- Elmer Analyst 400 spectrometer, air/acetylene flame under optimal instrumental parameters ensuring maximal signal to noise ratio. The light sources were hollow cathode lamps for Au. The spectral bandpass and wavelengths used were as recommended by the manufacturer. The wavelength used is Au 242.8 nm.

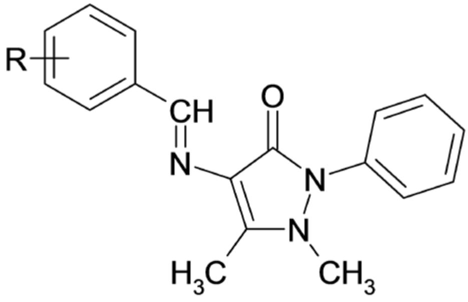
The centrifuge K-1000 (KUBOTA Corporation, Osaka, Japan) was used for centrifugation of modified silica sorbent in batch experiments.

The pH measurements were carried out with pH-meter (Hanna Instruments).

Synthesis of Schiff bases

A series of Schiff bases derived from 4-aminoantipyrine (4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one) and different substituted benzene carbaldehydes have been sonochemically synthesized (Fig. 1). The chemical structures of the products have been confirmed by ^{1}H- and 13C-NMR, IR and mass spectral data.

Synthesis of the Schiff base derivatives was carried out by using A_N reaction for the condensation of commercially available 4-aminoantipyrine and different substituted benzaldehydes in abs. ethanol. The yields of desired products varied from moderate to excellent (60–92%). The general structure of the desired Schiff base analogues is presented in Fig. 1.



R = -OH, $-OCH_3$, $-NH_2$, $-NO_2$

Fig. 1. General structure of the Schiff base analogues

Preparation of Schiff bases immobilized silica gel (SIG-Schiff bases)

For the silica gel physical immobilization with the Schiff bases the procedure, described by Bartyzel & Gurkowska (2011), is used.

The commercially available silica gel was activated by refluxing with concentrated hydrochloric acid for 4 h to remove any adsorbed metal ions. Thereafter it was filtered, washed with deionized water until the filtrate was neutral and dried in an oven at 150°C for 12 h to remove surface adsorbed water. The activated silica gel was refluxed with Schiff bases (9:1 w/w) in acetone for 8 h. After that mixture was vigorously stirred at room temperature to complete the solvent evaporation and then dried at 40 °C for 1 h.

Sorption studies: batch procedure

The static sorption mode is widely used for optimization studies of sorbent extraction efficiency.

The parameters which variation was studied are: the ratio of the volume of the solution to the mass of the sorbent, contact time, and temperature. The sample to sorbent ratio required for the complete recovery of elements depends on the properties of the sorbent: sorption capacity, swellability, structure, particle size, etc. The optimal contact time and temperature for quantitative sorption depend on the kinetic properties of the sorbent and the activity of ionic forms of metals (Zolotov et al., 2003). It is known that gold (III) and noble metals can form complex compounds exhibiting different kinetic activity depending on the degree of oxidation of the central atom, the nature and concentration of the acid and the ligand, the time of storage of the solution, etc. (Al-Bazi & Chow, 1984). The sorption of kinetically inert complexes requires special treatment, therefore different techniques of the labilization of inert complexes in solutions are used.

Aqueous standard solution 10 ml, containing Au (10 µg ml^{-1}) was mixed with 500 mg SiG- Schift bases and appropriate concentration of HCl. The mixture was stirred with an electric shaker for 30 min and then centrifuged at 3000 rpm for 5 min. In order to investigate the degree of sorption supernatant solution was removed and analyzed by FAAS as effluate. The SiG- Shift bases was washed with doubly distilled water and trace analytes were eluted for 15 min from the sorbent particles with 10 ml thiourea in HCl (the concentrations of thiourea and HCl were varied in the range 0.2–0.7 mol l^{-1} and 0.1–2 mol l^{-1} respectively). In order to investigate the degree of elution, metal ions content in eluate was determined by FAAS after centrifugation.

Results and discussion

Influence of pH on Au (III) sorption

The influence of acid concentration is a key parameter in the design of the sorption system. Au(III) and noble metals were reported to be negatively charged anions in presence of hydrochloric acid solutions (Al-Bazi & Chow, 1984).

In strongly acidic solutions Au (III) forms complexes with nitrogen-containing and sulfur-containing ligands (Mladenova et al., 2012). On the other hand increasing concentration of HCl results in the presence of increasing concentrations of Cl^-, which may compete with chloro-anionic species of Au (III) in reaction with the sorbent (Parodi et al., 2008).

The influence of pH on the degree of sorption of Au (III) was evaluated through the described batch procedure. The pH was varied in the range from 0.1 M HCl to 1 M HCl. The experiments showed that the sorption of Au (III) is quantitative in whole studied pH interval and acidity range (Table 1).

Table 1. Sorption and recovery of Au (III) under selected experimental conditions, n=3

Metal ion	Sorption, %		Recovery, %			
	0.1 M HCl	1 M HCl	0.5 M TU pH 10	0.2 M TU/ 0.1 M HCl	0.5 M TU/ 0.1 M HCl	0.7 M TU/ 2 M HCl
Au (III)	>99	>99	<1	61±4*	75±3	>99

* mean ± standard deviation

Selection of appropriate eluent for Au (III) desorption

It is necessary to achieve not only quantitative sorption but also quantitative desorption while selecting conditions of pre-concentration of Au (III) and its subsequent determination. When complexing sorbents are used for preconcentration, desorption is complicated because of the strong binding of the metal ions with functional groups of sorbents. That is why the next step of our work was to find suitable eluent for quantitative desorption of retained on the sorbent Au(III). For desorption of noble metals after preconcentration with complexing sorbents most frequently hydrochloric acid solutions of thiourea were used as eluent. Thiourea is a ligand that is well known for its affinity toward gold and precious metals due to the presence of both amine and sulfur groups, that contribute to bind metal by chelation (Fujiwara et al., 2007; Sanchez et al., 2001). In our study, various concentrations of thiourea in HCl were tested as eluents for Au (III) retained on SIG-Schiff bases (Table 1). Among them only the mixture of 0.7 M thiourea in 2M HCl provides quantitative elution of Au (III) as confirming by Ramech et al. (2008).

Effect of interfering ions

Au (III) and other noble metals are most frequently found in the presence of high concenrations of base metals (Kononova et al. 1998) In order to confirm the selectivity of SIG-Schiff bases, the degree of sorption of Au(III) was studied in the presence of such competitor ions.

In order to examine the effect of different matrix ions on the process of sorption, 10 ml solution containing Au (III) and various base metals (Al, Cu, Fe, Mn, Ni, and Zn) were mixed according to the optimized procedures. No significant interferences were observed from most of the studied ions. The results were summarized in Table 2. It was observed that the accompanying metals did not affect the retention of gold ions on the sorbent. Under the conditions examined, Au (III) was retained on the sorbent with the efficiency being 98 %

Table 2. Influence of interfering ions on the Au (III) sorption and recovery, n=3

Ions	Initial concentration (mg L^{-1})	Sorption (%)	Recovery, %
Al (III)	10	20±5*	<1
Zn (II)	10	30±6	<1
Ni (II)	10	<1	<1
Mn (II)	10	<1	<1
Cu (II)	20	<1	<1
Fe (III)	10	<1	<1
Au (III)	10	98±2	95±3

* mean ± standard deviation

Furthermore, it was established that the interfering metal ions, i.e. Cu(II), Fe(III), Mn(II) and Ni(II) were not bound on the sorbent under the mentioned experimental conditions. The degree of sorption for Zn(II) and Al(III) as a rule was low at high acidity.

Results obtained demonstrated high selectivity of the new sorbent SiG-Schiff bases toward Au (III) in acidic solutions and its possible application for gold determination in complicated matrixes.

Conclusion

In the present study a new sorbent based on schiff bases modified silica gel (SiG- Schiff bases) is proposed for preconcentration of Au (III). The main characteristics of the sorbent are high selectivity toward Au (III) in presence of base metals, fast complex formation and quantitative sorption which make Sig-Schiff bases suitable for determination of trace amounts of Au (III) in samples with variable matrix composition.

Acknowledgements. We gratefully acknowledge financial support from the South-West University "N. Rilski", Blagoevgrad, Bulgaria (Project SRP A19/15).

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