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ORIGINAL PAPER

Comparison of the performance of pyridine-functionalized nanoporous silica particles for the extraction of gold(III) from natural samples

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Abstract We have developed a technique for the solid-phase extraction of gold using various kinds of pyridine-functionalized nanoporous silica prior to its determination in various samples using FAAS. The effects of solution pH, sample and eluent flow rate, sample volume and of potentially interfering ions are compared. The limits of detections vary from 28 to 53 pg mL^{-1}. The accuracy and precision are between 99.8% and 98.3 % and 0.7 to 1.6 % (RSD), respectively. The method was successfully applied to several standard reference materials.

Keywords Pyridine-functionalized nanoporous silica · Solid-phase extraction · Gold · Flame atomic absorption

Introduction

Gold, as a global currency, an investment and simply an object of beauty, is one of the precious metals and held an allure for thousands of years. Gold possesses a unique combination of properties that have resulted in its use in a wide range of industrial applications [1]. Many techniques have been implemented for qualitative and quantitative determination and separation of gold in real samples, such as flame atomic adsorption [2-5], electrothermal atomic adsorption [6], inductive coupled plasma [7, 8] and HPLC [9]. Although, determination of gold by flame atomic absorption spectrometry is very simple and easy to operate, it has some difficulties such as lower levels of gold in samples than the limit of detection of flame atomic absorption spectrometry and effects of the matrix components of the working media [10-12]. To overcome these limitations on the determination of gold by flame atomic absorption spectrometry, separation-enrichment techniques including solid-phase extraction (SPE) [13-16], cloud point extraction [17], liquid–liquid extraction [18] and coprecipitation [19] have been used by scientists around the globe. Solid-phase extraction (SPE) has widely been employed for the preconcentration and separation of metals. The advantages of the solid-phase extraction approach include a good flexibility, ease of automation, minimal cost due to low reagents consumption and higher enrichment factors [20-22]. A number of materials in solid-phase extraction such as MCM (Mobil Crystalline Material) with a variety of functional groups have proven to be suitable adsorbents in prior studies due to their high thermal stability and large surface area [23]. The adsorption behavior of these materials is significantly affected by their functional groups. The goal of this work is to investigate the effect of type of functional group on the various parameters, including pH, analyte flow rate, eluent flow rate, etc. in extraction of gold. In this study, four structural isomers of pyridine ligand were synthesized and used for the solid-phase extraction of gold. To the best of

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our knowledge, this is the first time which the effect of the grafted group of nanoporous silica sorbents on its analytical performance is investigated.

Experimental

Reagents and materials

All the reagents used were of the analytical grade and were purchased from Merck (http://merck.de) (Darmstadt, Germany). The working solutions of Au(III) were obtained by diluting the standard solution with buffer, and pH adjustments were performed with the appropriate buffer solutions. All of the required solutions were prepared using deionized water provided by a Milli-Q (Millipore, Bedford, MA, USA) purification system. Certified reference materials were obtained from the China National Analysis Center for Iron and Steel (http://www.nacis-cn.com).

Preparation of MCM-48 mesoporous silica

MCM-48 nanoporous silica was synthesized according to the earlier report [24] and its formation was confirmed by X-ray powder diffraction.

Preparation of pyridine functionalizing agents

N-(3-(triethoxysilyl)propyl)isonicotinamide (TPI) was synthesized according to the previously reported procedure [25] and characterized by ^{1}H NMR. A similar procedure to the preparation of TPI was used to synthesis N-(3-(triethoxysilyl)propyl) picolonicamide (TPP) and N-(3-(triethoxysilyl)propyl) nicotinamide (TPN) (See Electronic Supplementary Material, ESM 1)

Preparation of pyridine functionalized mesoporous silica

Pyridine functionalized MCM-48 was synthesized by reaction of triethoxy silane agents with mesoporous silica [26, 27]. A schematic diagram for synthesis of different pyridine-functionalized mesoporous silica is illustrated in Fig. 1 (for further detail see Electronic Supplementary Material, ESM 2).

Instruments

Concentration of gold ions was determined by an AA-680 Shimadzu (Kyoto, Japan) flame atomic absorption spectrometer (FAAS) in an air-acetylene flame, according to the user's manual provided by the manufacturer. A gold hollow cathode lamp was used as the radiation source with wavelength set at 242.8 nm. All pH measurements were carried out at 25±1 °C with a digital WTW Metrohm 827 Ion analyzer (Herisau, Switzerland) equipped with a combined glass-calomel electrode. Analysis regarding flow rate were performed using a peristaltic pump obtained from Leybold (Germany). To facilitate regulation of flow rate during extraction an adjustable vacuumed gauge along with a controller was obtained from Analytichem International (Harber City, CA).

Procedures

Column preparation

A glass column (120 mm in length and 20 mm in diameter) with a porous disk was packed with 200 mg of solid-phase pyridine-functionalized MCM-48 and was blocked with two polypropylene filters at the ends to prevent loss of material during sample loading. In order to remove organic and inorganic contaminants, prior to extraction, each glass column was washed with 5 mL of 1 M hydrochloric acid, 5 mL of absolute ethanol, 5 mL of toluene and 20 mL of distilled water, in the order given here.

Preconcentration procedure

50 mL of sample solutions containing 1 μg mL^{-1} gold ions with optimized pH (pH=2) were prepared. The column was preconditioned by passing buffer solution with optimized pH. With flow rate being the single point of difference between the procedures for the four adsorbents, the resulting solutions of gold were passed through the columns at flow rates of 10 mL min^{-1}. The retained gold ions were eluted with 13 mL of 1 mol L^{-1} thiourea in 3 mol L^{-1} H_2SO_4 solution at the flow rate of 2 mL min^{-1}. Gold content was determined by FAAS. Three measurements were made for each sample and the results were subsequently averaged.

Sample preparation

Three standard materials (SRM 2711, SRM 2781 and NCS-DC-73323) with a certified amount of gold have been used. These samples were digested in an 8 mL mixture of 5 % aqua regia with the assistance of a microwave digestion system. Digestion was carried out for 2 min at 250 W, 2 min at 0 W, 6 min at 250 W, 5 min at 400 W and 8 min at 550 W, and the mixture was then vented for 8 min. The residue from this digestion, as well as a control digestion was then diluted with deionized water [28].

Results and discussion

Effect of pH

To investigate the effect of pH of the matrix on recovery of gold ions, the pH of 50 mL single sample solutions

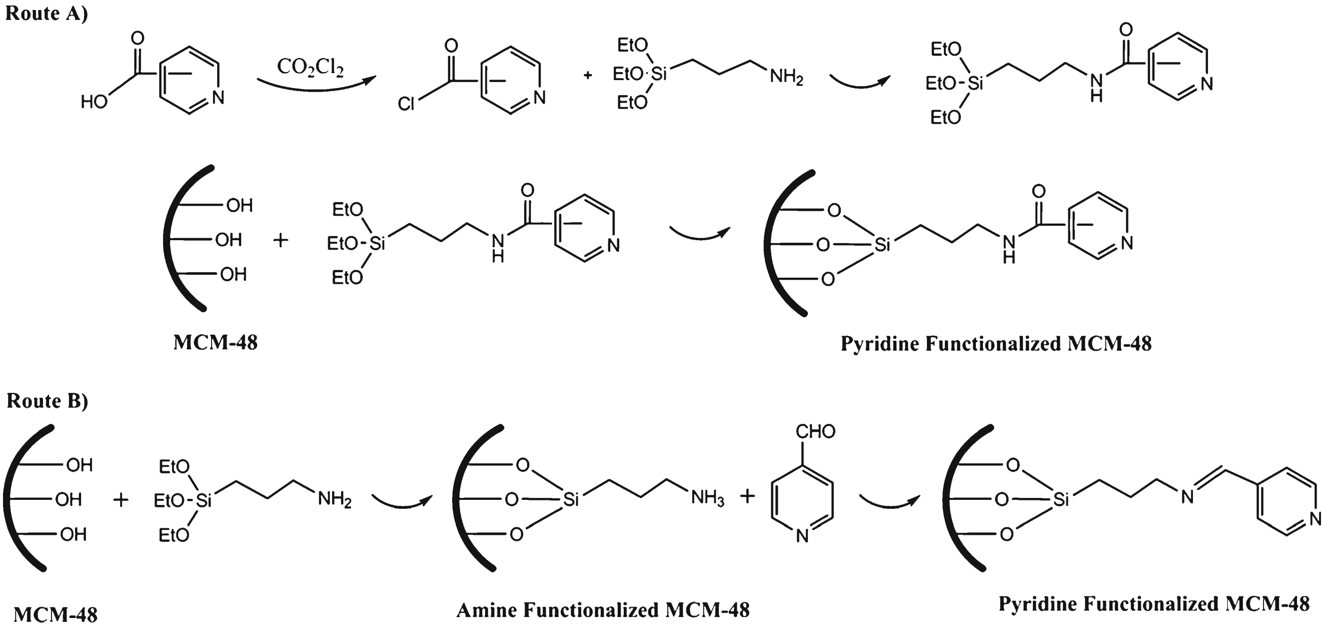

Fig. 1 A schematic route for pyridine derivates functionalization of MCM-48 mesoporous silica

containing 1 μg mL^{-1} of gold ions were adjusted in the range of 1–9 and after applying the presented method, the recoveries are represented in Fig. 2. It was figured out that the common pH for adsorption of gold ions is 2. According to our results at higher pH a lower gold ions adsorption will take place. This can be attributed to the decrease of interaction between $AuCl_4^-$ and the functional groups which have been grafted on MCM-48 mesoporous silica surface. Notably, decrease in gold ion adsorption for the 2-pyridine functionalized MCM-48 is less than 3-pyridine and 4-pyridine functionalized ones proportionally. This probably associated with the presence of the amine group in proximity of the pyridine which facilitates adsorption of gold ions in wider pHs range. A proposed mechanism for adsorption is shown in Fig. 3.

Analyte and eluent flow rate and eluent volume

Analyte and eluent flow rate and eluent volume have been optimized by same method and the results are represented in Electronic Supplementary Material (ESM 3). The possessed in common values were obtained to be 10 mL min^{-1} for sample flow rate, 2 mL.min^{-1} for eluent flow rate and 13 mL for eluent volume. According to the results (Figure 1S and 2S), adsorption and recovery for the 2-Py-MCM-48 decrease with increasing analyte and eluent flow rate, and this decrease is lower for 3-Py-MCM-48 and 4-Py-MCM-48 proportionally. As it mentioned earlier, the type of coordination of pyridine grafted on MCM with gold ion can be the cause of this event. As the gold ions adsorb on the 2-Py-MCM-48 surface by the mean of pyridine and amide groups, adsorption on the 2-Py-MCM-48 surface takes in a shorter time in comparison with 3-Py-MCM-48 and 4-Py-MCM-48, therefore, they can be used in higher flow rates and the results for desorption is vise versa. The higher flow rates for 3-Py-MCM-48 and 4-$PyCH{=}NCH_2CH_2CH_2$-MCM-48 in comparison with 4-Py-MCM could be attributed to the effect of electron withdrawing nature of the C=O groups in structures these materials. Indeed, in MCM-48 nanoporous silica that functionalized with 4-$PyCH{=}NCH_2CH_2CH_2$- group, there is no C=O group; consequently, the electron density on the pyridine group is higher and become a better coordinator for gold ions.

Influence of interference ions

The impact of a variety of cations found in natural samples on the determination of gold was studied. As their chloride salts,

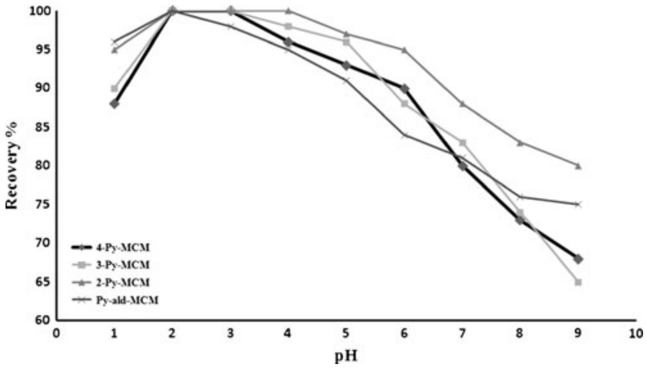

Fig. 2 The effect of sample solution pH on the recovery of gold(III) from nanoporous silicas

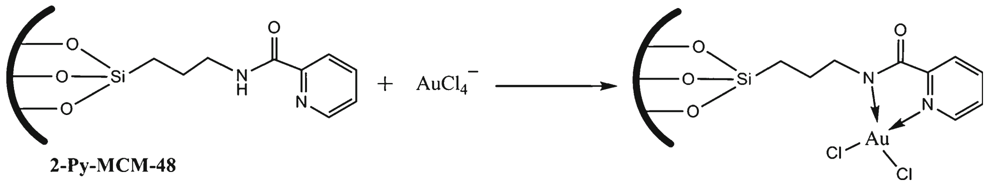

Fig. 3 Proposed mechanism for gold ions adsorption on 2-Py-MCM-48

various concentrations of Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Cd^{2+}, Fe^{2+}, Mn^{2+}, Pb^{2+}, Hg^{2+}, Pd^+, Ag^+, Pt^{2+} and Cr^{3+} was added to individual gold-containing solutions listed in Table 1. A similar procedure for gold extraction from 4-Py-MCM-48, 3-Py-MCM-48, 2-Py-MCM-48 and 4-PyCH=$NCH_2CH_2CH_2$-MCM-48 was then followed. As shown in Table 1, the vast majority of transition metals do not interfere at concentrations encountered in nature, and the method is selective toward gold extraction at pH of 2. Furthermore, extraction is not affected by high concentrations of alkaline and alkaline earth metals. Furthermore, by comparing the results, one can conclude that although 2-Py-MCM shows better performance than other derivates, the lower selectivity is its failure.

Adsorption capacity

The capacity of 4-Py-MCM-48, 3-Py-MCM-48, 2-Py-MCM-48 and 4-PyCH=$NCH_2CH_2CH_2$-MCM-48 with respect to gold ion was studied by passing 1,000 mL aliquots of aqueous solutions containing 100 mg of gold through the column, followed by determination of gold in the effluent and elution using FAAS. The capacities of 4-Py-MCM-48, 3-Py-MCM-48, 2-Py-MCM-48 and 4-PyCH=$NCH_2CH_2CH_2$-MCM-48 were found to be 290, 273, 224 and 308 mg g^{-1} for gold ions.

Table 1 The tolerance limit of various ions on the determination of gold

Interfering ions	Tolerable Concentration Ratio X/Au	Recovery %			
		4-Py	3-Py	2-Py	Py-Ald
Na^+	10000	99.1	98.7	99.2	98.1
K^+	2500	97.6	97.4	99.6	98.7
Cs^+	1500	95.2	91.7	98.7	94.8
Ca^{2+}	750	92.8	89.4	99.7	93.7
Mg^{2+}	750	97.6	91.4	97.1	93.4
Fe^{2+}	1000	91.7	85.9	93.4	89.6
Cd^{2+}	1500	97.2	93.8	98.4	95.6
Mn^{2+}	1000	94.1	88.7	96.7	89.8
Pb^{2+}	1500	90.3	87.6	94.9	91.5
Cr^{3+}	500	98.2	97.4	98.6	95.7
Pd^{2+}	10	92.2	92.5	91.7	91.9
Pt^{2+}	10	93.7	93.8	93.7	94.1
Hg^{2+}	250	97.2	97.9	97.6	97.5
Ag^+	250	95.1	95.6	95.8	96.2

Dilution and kinetic effect

The breakthrough volume of sample solutions was investigated by dissolving 1.0 mg of gold in 100, 200, 500, 1,000, 1,500, 2,000, 2,500 and 3,000 mL of distilled water and the SPE protocol was followed. Gold was quantitatively retained from 2,000 mL of sample solution. Thus, the breakthrough volume for the presented SPE method using 4-Py-MCM-48, 3-Py-MCM-48, 2-Py-MCM-48 and 4-PyCH=$NCH_2CH_2CH_2$-MCM-48 should be greater than 2,000 mL.

The enrichment factor was determined by performing the recommended column procedure using increasing volumes of a 1 μg mL^{-1} gold solution. The maximum sample volumes for SPE using 4-Py-MCM-48, 3-Py-MCM-48, 2-Py-MCM-48 and 4-PyCH=$NCH_2CH_2CH_2$-MCM-48 were found to be 2,600, 2,250, 2,000 and 2,500 mL, respectively. Gold recoveries from 4-Py-MCM-48, 3-Py-MCM-48, 2-Py-MCM-48 and PyCH=$NCH_2CH_2CH_2$-MCM-48 were 99.5, 98.3, 99.8 and 98.8 %. The loaded gold was easily desorbed from the solid phases with their respective eluent volume. As a result, the enrichment factors were found to be 258, 315, 153 and 274 using 4-Py-MCM-48, 3-Py-MCM-48, 2-Py-MCM-48 and PyCH=$NCH_2CH_2CH_2$-MCM-48, respectively.

Figures of merit

In order to determine the limit of detection (LOD) of the presented method, a 500 mL blank solution (n=10) was passed through the column under optimal experimental conditions. The values of LOD for gold using 4-Py-MCM-48, 3-Py-MCM-48, 2-Py-MCM-48 and PyCH=$NCH_2CH_2CH_2$-MCM-48 are 0.036, 0.053, 0.028 and 0.041 ng mL^{-1}, respectively. The results were obtained from the relationship expressing $C_{LOD}=3S_b/m$ [30].

The precision of the method under the optimal conditions (volume=100 mL, concentration: 1 mg L^{-1}) was determined by performing ten replicates. The gold recoveries were found to be 99.5, 98.3, 99.8 and 98.8 with RSD 0.7, 1.6, 0.4 and 0.9 from 4-Py-MCM-48, 3-Py-MCM-48, 2-Py -MCM-48 and PyCH=$NCH_2CH_2CH_2$-MCM-48, respectively.

Method validation

In order to investigate the accuracy, applicability and effect of this method on different matrices a number of several

Table 2 Determination of gold in different standard reference materials for accuracy test of the method

	Real sample/μg mL^{-1}	Found/μg mL^{-1}				Recovery, %			
		4-Py	3-Py	2-Py	Py-Ald	4-Py	3-Py	2-Py	Py-Ald
SRM 2711	0.130	0.125	0.119	0.128	0.123	96.1	91.5	98.4	94.6
SRM 2781	0.070	0.067	0.062	0.069	0.063	95.7	88.6	98.6	90.0
NCS DC 73323	0.260	0.253	0.248	0.263	0.252	97.3	95.3	101.1	96.9

reference materials containing a certified gold content and tested by the method, and in all cases, quantitative gold recovery was obtained (Table 2).

Reusability of column

As reusability of sorbents is one of the most important features of a sorbent, the reusability of sorbents was investigated by consequence sorption/desorption cycle. It was determined that the column is stable up to 10, 8, 11 and 10 adsorption-elution cycles without any noticeable decreasing for 4-Py-MCM-48, 3-Py-MCM-48, 2-Py-MCM-48 and PyCH=NCH$_2$CH$_2$CH$_2$-MCM-48 in the recovery of gold ions.

Conclusion

Different pyridine derivates include *ortho*, *metha*, *para* amide and also without an amide group have been synthesized and used for the preconcentration of gold in aqueous solutions in order to investigate the effect of ligand on recovery and analytical performance of mesoporous silica and the results were compared in (Table 3). The analytical performance and data, including relative standard deviation, LOD and gold recovery, for 2-pyridine functionalized MCM-48 mesoporous silicas are either better than or comparable to other derivates, but has lower selectivity; preconcentration factor and maximum capacity are their weak points (Table 1S). The high preconcentration factor and precision obtained from the performance of all sorbents, as well as its satisfactory reproducibility, makes it applicable to aqueous solutions in which the gold content is below the detection limit of FAAS.

Table 3 Preconcentration factor and LOD of gold for various adsorbents using FAAS

Solid phase	RSD[a] (%)	LOD[b] (ng mL^{-1})	Reference
Py-MCM-41	0.6	0.039	[29]
Py-MCM-48	0.7	0.036	[29]
Py-SBA-15	1.5	0.045	[29]
NH$_2$-MCM-41	0.7	0.056	[2]
NH$_2$-MCM-48	0.5	0.045	[2]
4-Py-MCM-48	0.7	0.036	This work
3-Py-MCM-48	1.6	0.053	This work
2-Py-MCM-48	0.4	0.028	This work
Py-Ald-MCM-48	0.9	0.041	This work

a) Relative standard deviation, b) Limit of detection

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