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Development of novel solvent extraction method for determination of gold(III) using 4-heptylaminopyridine: Application to alloys and environmental analysis

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ABSTRACT

In this paper, the solvent extraction of gold(III) from malonate media (0.04 mol L^{-1}) has been studied by equilibrating aqueous phase having pH 2.5 with 10 mL of 0.07 mol L^{-1} 4-heptylaminopyridine (4-HAP) as a novel anion exchanger diluted in xylene for 2 min. The extracted metal from organic phase was separated by stripping with 5.0 mol L^{-1} NH_3 solution (2 × 10 mL). The effect of various parameters, such as pH, extractant concentration, weak acid concentration, equilibrium time, stripping agents, aqueous to organic volume ratio and diluents on the extraction of gold(III) was investigated. The extracted species has been evaluated from log $_D$ vs log $_C$ and species appears to be 1:2:1 (metal: acid: extractant). The selectivity of the method was checked by separating gold(III) from binary and ternary mixtures of associated metal ions as well as platinum group metals(PGMs). The separation of gold(III) from synthetic alloys and environmental samples was also carried out.

1. Introduction

Gold is one of most important nobel metals due to its wide applications in industrial and economic activities. The most common uses of gold are in the industry of jewelry and electronics [1]. On the other hand, some of the gold(I) compounds have biological activity, which are employed in medicine as anti-inflammatory drugs in the treatment of rheumatoid arthritis [2]. Nowadays, the consumption of gold has increased and therefore, the cost of gold production and its price in the market have risen rapidly. However, some wastes such as the waste of electronic equipment (e-waste) contain large amounts of precious metals compared to their own respective ores and, therefore, such wastes may be considered as a secondary source of valuable metals [3]. There is great interest in the removal and recovery of gold metals from wastewater. The two most important reasons and motivations for gold metals removal are the economical impact of losing these metals and their environmental concerns [4]. Trace amounts of these gold metals can be found in some wastewaters as a result of mining [5], electroplating industries [6], or electronic and Jewellery manufacturing. Hence, the development of low cost, and selective technologies for gold ion uptake from industrial effluents is extremely important from economic and environmental points of view, because the recovered ions can be converted into elemental gold.

Many techniques are available for the determination of gold ions from aqueous solutions, such as inductively coupled plasma mass spectrometry (ICP-MS) [7], inductively coupled plasma atomic emission spectrometry (ICP-AES) [8], electrochemical [9], neutron activation analysis [10] and atomic absorption spectrophotometry (AAS) [11]. Some factors such as the initial cost of instruments, technical know-how, consumable and costly maintenance of technique restrict the wider applicability of these techniques, particularly in laboratories with limited budgets in developing countries. Solvent extraction has been considered to be a promising technology for recovery and separation of gold with the advantages of high efficiency and simple operation [12,13]. In recent years, some papers have been published on gold(III) extraction using various extractants, such as 4-(4-methoxybenzylideneinino)-5-methyl-4H-

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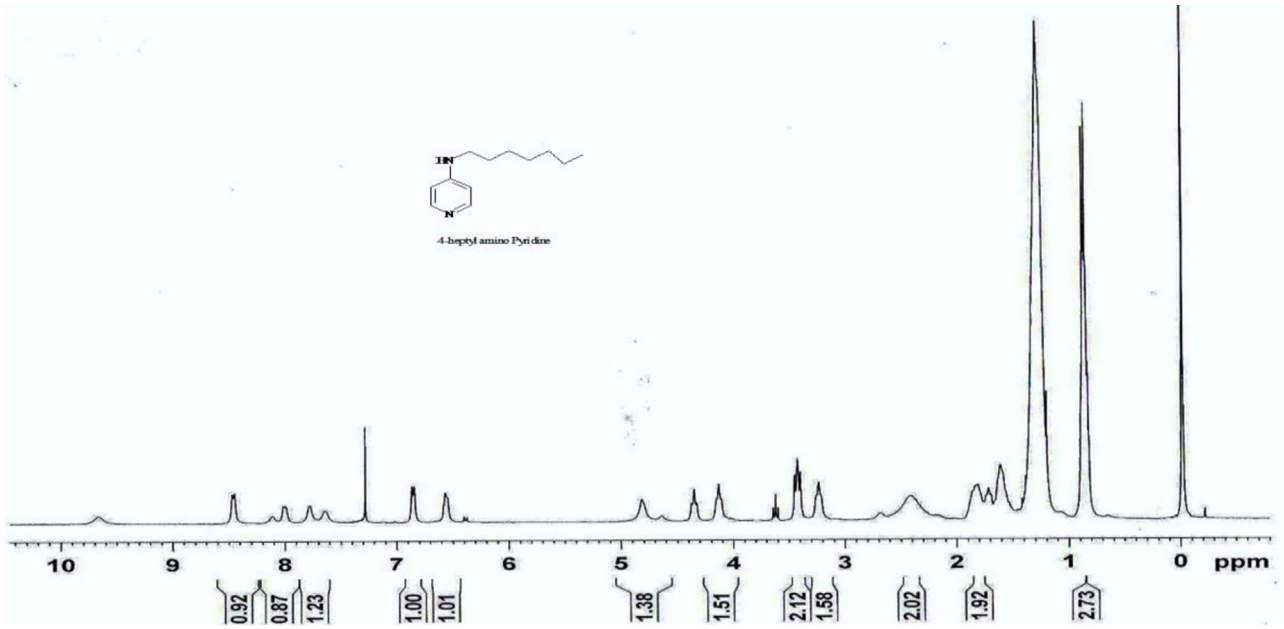
1,2,4-triazole-3-thiol [12], *N*-*n*-octylaniline [13], tri-*n*-octylamine [14], tri-*n*-butylphosphate [15], alamine [16], *N*-*n*-decylaminopyridine [17], trioctylmethylammonium chloride [18], monoamide compounds [19], 2-hydroxy-4-sec-octanoyl diphenyl-ketoxime [20], amiloride mono hydrochloride [21], cyanex 302 [22].The present method is ecofriendly as extraction is carried out from weak organic acid (malonate) media, very low extractant concentration is required and low strippant concentration is required for quantitative recovery of gold(III) from an organic phase. In addition, the cited methods are more complicated, use more reagents and need expensive and complex instruments for the determination of gold (III) than this method. The presently employed method could easily be carried out by using only a few reagents and simple apparatus (4-HAP, sodium malonate, xylene, NH_3, separation funnel and



spectrophotometer). In this work, newly synthesized ligand 4-heptylaminopyridine (4-HAP) is studied as an extraction reagent. According to our literature survey, this is the first report of this ligand. The use of this reagent is found to be advantageous as it can be synthesized at low cost, with high yield and of best purity. The present investigation describes its use in establishing the conditions for the quantitative extraction of gold(III) and the development of a rapid and selective method for the separation of gold(III) from associated elements. The method proposed here offers extraction, separation and determination of gold(III) from alloys and environmental samples. The superiority of the presently employed method is also shown in comparison with other reported methods as shown in Table 1.

2. Experimental

2.1. Apparatus

UV/VIS Spectrophotometer model-Optizen α (mecasys Co., Ltd./made in Korea) with 1 cm quartz cell has used for absorbance measurements and pH measurements are carried out with an Elico Digital pH meter Model LI-120 with a combined glass electrode.

2.2. Reagents

2.2.1. Standard gold(III) solution

A stock solution of gold(III) was prepared by dissolving 1.0 g $HAuCl_4$ (Analytical reagent grade, Johnson Matthey, and UK) in 250 mL of double distilled water and was standardized gravimetrically [23]. Working solutions were prepared by diluting the stock solution suitably. Other standard solutions of different metals used to study the effect of foreign ions were prepared by dissolving weighed quantities of their salts in double distilled water or dil. hydrochloric acid. Solutions of anions were prepared by dissolving the respective alkaline metal salts in water. Different synthetic mixtures containing gold(III) were prepared by combining with commonly associated metal ions in definite composition. All of the chemicals used were of analytical reagent grade and double distilled water was used throughout the experiments.

2.2.2. 4-heptylaminopyridine (4-HAP)

To a stirred solution of 4-aminopyridine (0.05 mol) in dry THF (40 mL), sodium amide was added at 0 °C and continued stirring for 30 min. The temperature of the reaction mixture increased to room temperature and 1-bromoheptane was added slowly. The reaction mixture was stirred at the ambient temperature for 1 h. The reaction mixture was poured to water, NH_4Cl and extracted with chloroform (150 mL). The chloroform extract was dried (Na_2SO_4) and evaporated on a rotary evaporator to yield a residue which was crystallized to afford the corresponding 4-heptylaminopyridine in 75–85% overall yield [24]. Melting point of compound is 43–45 °C and confirmed by taking its NMR spectra. It's solutions were prepared in xylene.

NMR spectra:

2.3. Extraction procedure

An aliquot of the sample containing 200 μg mL^{-1} gold(III) solution was taken with a sufficient quantity of sodium malonate