

Separation and Preconcentration of Gold, Silver and Palladium from Some Aluminium and Manganese Salts on Activated Carbon Column

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A simple method for preconcentration and separation of trace amounts of gold, silver, palladium in some aluminium and manganese salts was established by using mini column filled activated carbon prior to their atomic absorption spectrometric determinations. The dithiophosphoric acid O,O-diethyl ester complexes of the analyte ions were adsorbed on the activated carbon column and desorbed with 2M NH₃ in acetone. The effects of aluminium and manganese ions as interferent were discussed. The method was successfully applied for the determination of Au, Ag and Pd contents of some aluminium and manganese salts (recoveries > 95%, relative standard deviations < 10%).

INTRODUCTION

Simple and sensitive methods are required for the quality control of the analytical reagent and technical grade salt samples. Because of low levels of trace heavy metal ions and matrix effects, modern analytical instrumental methods are not generally suitable for that purpose. The preconcentration/separation methods including coprecipitation, ion-exchange, liquid-liquid extraction, solid phase extraction can be used for the determination of trace impurities in the analytical and technical grade salt samples¹⁻⁴. The determination of trace heavy metal impurities in the aluminium and manganese salts is also important. Various studies have been performed for the determination of gold, silver and palladium in the manganese and aluminium samples by flame atomic absorption spectrometry after preconcentration and separation procedure⁵⁻⁷.

The preconcentration and separation methods based on the sorption are considered to be superior to the liquid-liquid extraction as regards simplicity, rapidity and ability to attain a high concentration factor. Preconcentration methods based on adsorption of complexed metals on columns filled with activated carbon, have found widespread application for this purpose⁸⁻¹⁰.

The sodium salt of dithiophosphoric acid O,O-diethyl ester (NaDDTP) is a well-characterized reagent that reacts with various metal ions to form very stable complexes. One of the advantages of NaDDTP as complexing agent with some

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metal ions such as aluminium, barium, calcium, iron, magnesium, manganese, sodium, lithium, strontium, etc., are not complexed. Another advantage of NaDDTP, the DDTP complexes are stable in strong mineral acid solution¹¹⁻¹³.

In this work, a simple method for preconcentration and separation of trace amounts of gold, silver, palladium in some aluminum and manganese salts was established by using mini column filled activated carbon prior to their atomic absorption spectrometric determinations. The effects of aluminium and manganese ions as interferent were discussed. The method was successfully applied for the determination of Au, Ag and Pd contents of some aluminium and manganese salts.

EXPERIMENTAL

Analytical reagent-grade chemicals were employed for the preparation of all solutions. All aqueous solutions were prepared from doubled-quartz-distilled water. Gold, palladium and silver stock solutions were obtained from E. Merck, Darmstadt (Germany). The calibration standards were not subjected to the preconcentration procedure.

The sodium salt of dithiophosphoric acid O,O-diethyl ester (NaDDTP) solution (0.5×10^{-2} mol/L) used in this study were prepared by dissolving the requisite amounts of NaDDTP (Merck, Darmstadt) in water/ethanol mixture immediately before use.

Activated carbon powder used as adsorbent in the preconcentration of metal ions (Merck No. 2186) was treated with concentrated HCl, washed with distilled water and dried at 110°C, in order to eliminate trace metal ions and other inorganic and organic contaminants in activated carbon¹⁴.

Gold, silver and palladium determinations were performed using Perkin-Elmer Model 3110 atomic absorption spectrometer. All measurements were carried out in air/acetylene flame. The operating parameters for gold, palladium and silver were set of recommended by the manufacturer.

Preconcentration procedure

50–60 mL of solution containing 10 µg of each metal ion was added. The acidity of the solution was adjusted to 0.1 M as acid concentration with concentrated hydrochloric acid. Then ligand solution was added. After about 5 min, the metal/ligand solution was passed through the column at a flow rate of 5 mL/min by the aid of a vacuum aspirator. After the passage of this solution, the column was rinsed twice with 10 mL of water. The adsorbed metal chelates on the column were eluted with 8–10 mL of 2 M ammonia in acetone. The effluent was evaporated to near dryness, then cooled. It was transferred into a calibrated volumetric flask and made up to 5–10 mL with water. The concentrations of metal ions were determined in the final solutions by flame atomic absorption spectrometry (FAAS). Blanks were also determined by applying the same procedure.

Analysis of Aluminum and Manganese Compounds

0.5–1.0 g of aluminum and manganese compounds were dissolved in 50 mL of distilled water. Then the analyte ions were preconcentrated as described and

determined by flame atomic absorption spectrometry. The same procedure was applied to the blanks.

RESULTS AND DISCUSSION

Optimum Conditions for Quantitative Preconcentration: The effects of various analytical parameters such as the sodium salt of dithiophosphoric acid O,O-diethyl ester (NaDDTP) concentrations, eluent type, amounts of activated carbon, preconcentration factor, etc., on the recovery of gold, silver and palladium from manganese and aluminum salts were examined. The optimum conditions determined for preconcentration procedure were as follows. The quantitative recoveries of gold, silver and palladium were obtained at the range of 0.05–1.25 M of hydrochloric acid concentration. In further experiments, the hydrochloric acid concentration was selected as 0.1 M.

The optimum amounts of NaDDTP for quantitative retentions of the analyte ions was 0.5×10^{-3} mol/L. The amount of activated carbon in the column was 500 mg; the desorption of the retained metals from the activated carbon column was tested for various eluting agents. The results are given in Fig. 1. The quantitative recoveries were obtained for all working elements with 2 M NH_3 in acetone. All subsequent studies were carried out with 5–10 mL of 2 M NH_3 in acetone. The sample volume does not affect quantitative recoveries with 0.5 g activated carbon until 100 mL. These values are comparable to those described by Soyak *et al.*¹⁴

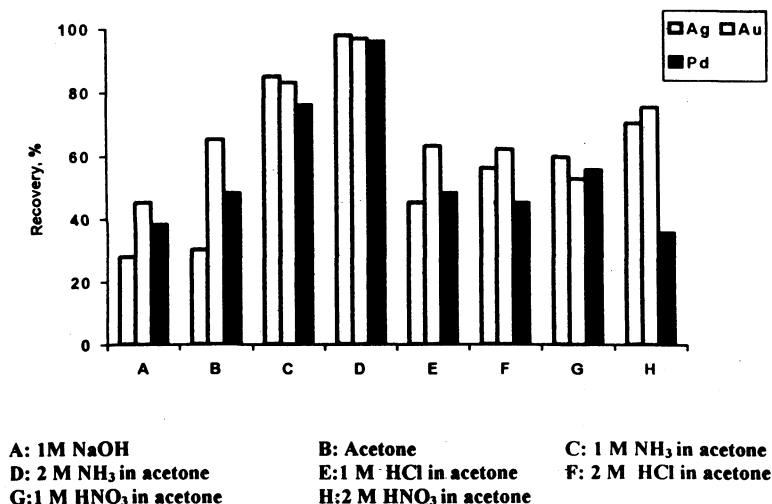


Fig. 1. Effect of eluent type on the recovery of Ag, Au, Pd on the recoveries.

Matrix Effects: The effects of manganese and aluminium on the recoveries of Au, Ag and Pd were also studied with analytical reagent grade of their nitrate salts. For this purpose, solutions of these compounds were prepared and 10 μg

of each metal ion added to the solutions; then preconcentration procedure given above was applied. The results are given in Table-1. The recoveries of Au, Ag and Pd from the column were not influenced by these compounds, because aluminium and manganese are not complexed with NaDDTP.

TABLE-1
INFLUENCES OF ALUMINIUM AND MANGANESE IONS ON THE RECOVERY
OF Au, Ag AND Pd (N = 4)

Ion	Concentration (g/50 mL)	Recovery (%)		
		Ag	Au	Pd
Mn ²⁺	0.5	97 ± 3	98 ± 4	95 ± 3
	1.0	93 ± 2	97 ± 3	98 ± 1
Al ³⁺	0.5	93 ± 3	97 ± 3	95 ± 3
	1.0	95 ± 4	96 ± 4	100 ± 2

Accuracy of the method: To estimate the accuracy of the procedure, different amounts of investigated ions were added to 1.0 g/50 mL of aluminium sulfate and manganese sulfate solution and the resulting solutions were submitted to the preconcentration procedure. The results for aluminium sulfate and manganese sulfate are shown in Tables 2 and 3, respectively. Good agreement was obtained between the added and analyte recovered content using the experimental procedure. The recovery values calculated for the standard additions were always higher than 95%, thus confirming the accuracy of the procedure and the absence of matrix effects.

TABLE-2
RECOVERY OF Au, Ag AND Pd IN ANALYTICAL REAGENT GRADE
ALUMINIUM SULFATE (N = 4)

Ion	Added (µg)	Found (µg)	Recovery, %
Au	10	10.0	100
Ag	10	9.7	97
Pd	10	10.4	104

TABLE-3
RECOVERY OF Au, Ag AND Pd IN ANALYTICAL REAGENT GRADE
MANGANESE SULFATE (N = 4)

Ion	Added (µg)	Found (µg)	Recovery, %
Au	10	9.8	98
Ag	10	10.2	102
Pd	10	10.0	100

Application to samples: The procedure described as under experimental section was applied to determine Au, Ag and Pd in technical reagent grade aluminum sulfate and manganese sulfate produced in Turkey. The results given

in Table-4 have been calculated based on the assumption of 100% recovery of working elements.

TABLE-4
Au, Ag AND Pd CONTENT OF TECHNICAL REAGENT GRADE ALUMINIUM AND MANGANESE SULFATE (N = 4, ELUENT VOLUME: 5 mL)

Sample	Concentration, $\mu\text{g/g}$		
	Au	Ag	Pd
Aluminum Sulfate	3.40 ± 0.30	6.62 ± 0.27	< 1
Manganese Sulfate	2.04 ± 0.20	3.38 ± 0.30	< 1

* $\bar{x} \pm \text{SD}$

Conclusion

The procedure proposed for the determination of gold, silver and palladium contents of some aluminium and manganese salt samples is simple, rapid and economic. The DDTP-activated carbon method can be easily applied for the preconcentration and separation of Au, Ag and Pd in the other matrices such as geological samples.

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(Received: 25 November 2000; Accepted: 2 February 2001)

AJC-2244