

Extractive Spectrophotometric Determination of Trace Amounts of Gold(III) with Benzyltrimethylphenylammonium Chloride

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For spectrophotometric determination of gold, the use of the formation of $[\text{AuX}_4]^-$ anion, where $X = \text{Cl}, \text{Br}$ or I has long been known. For extraction of the complex anion, the uses of tetraphenylarsonium chloride¹, cetyltrimethylammonium bromide², $[\text{Fe}(\text{o-phenanthroline})_3]^{3+}$ (Ref. 3) etc have been reported. Here we report the use of benzyltrimethylphenylammonium (BDPA) chloride, a quarternary ammonium salt, for the determination of gold. This reagent possesses considerable potentiality to find application for the determination of a number of metal ions⁴ when present in trace amounts in solution. In the present investigation, we noted that an aqueous solution of benzyltrimethylphenylammonium chloride forms a yellow coloured ion-association complex with tetraiodoaurate(III), which is completely extractable into chloroform. This forms the basis of the present method which has proved to be very simple, sensitive and selective.

Results and Discussion

Gold(III) forms a yellow colouration due to the formation of $[\text{AuI}_4]^-$ with potassium iodide. The complex anion is not extractable into chloroform. On addition of an aqueous solution of BDPA to this solution, an ion-association complex $[\text{BDPA}][\text{AuI}_4]$ is formed which is extractable into chloroform. Some other solvents, like 1,2-dichloro ethane, benzene, 1-butanol, isobutanol, amyl alcohol, ethyl acetate and methyl isobutyl ketone, were also tested as extractants but chloroform was found to be the best.

The reagent blank itself shows negligible absorbance at 363 nm. Gold(III) complex shows constant and maximum absorbance (363 nm) when the extraction was carried out in the pH range 5.8–8.0 yielding quantitative recovery of gold in a single extraction. Beer's law is obeyed over the concentration range 1.1–14.0 ppm of gold(III) at 363 nm. Molar absorptivity and Sandell's sensitivity are $2.48 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and $0.0079 \mu\text{g cm}^{-2}$ respectively.

Effect of potassium iodide concentration on the absorbance was studied by using potassium iodide solution of varying concentrations. It was found that concentration below 0.02 M in the aqueous layer, produced low values of absorbance and beyond 0.08 M, without any effect. As regards BDPA concentration, 1 ml of 0.01 M solution of BDPA was

adequate for the complete extraction of the complex for the given range of gold concentration. The BDPA concentration below 0.001 M in the aqueous layer produced low values of absorbance while higher concentration upto 0.1 M did not bring about any significant change in the values of absorbance. The absorbance values remains constant over a period of more than 12 h.

A number of diverse ions were examined for their interferences in the determination of gold ($4.76 \mu\text{g ml}^{-1}$) by the recommended procedure. The tolerance limit was set at the amount required to cause less than 3% error in the recovery of gold, but the upper concentration limit investigated was restricted to 2000-fold (w/w) of gold. Estimation of gold(III) in presence of Cu^{II} and Pt^{IV} was done by using cyanide as masking agent, and in the presence of Sb^{III} , fluoride was used for masking. Interference due to Fe^{II} can be removed by oxidising it to Fe^{III} with concentrated HNO_3 . Pd^{II} and Hg^{II} interfere seriously and require prior removal. The following foreign ions (I) caused no interference at I : Au weight ratio : $\text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Ag}^{\text{I}}, \text{Zn}^{\text{II}}$, and $\text{Mn}^{\text{II}} \leq 160$; $\text{Cl}^{\text{III}} \leq 50$; $\text{Fe}^{\text{II}}, \text{Fe}^{\text{III}}$ and $\text{V}^{\text{V}} \leq 25$; $\text{Pd}^{\text{II}}, \text{Rh}^{\text{III}}$ and $\text{Cr}^{\text{VI}} \leq 12$; $\text{Bi}^{\text{III}}, \text{Ir}^{\text{III}}, \text{Mo}^{\text{VI}}, \text{W}^{\text{VI}}$ and $\text{As}^{\text{V}} \leq 1.2$; acetate, phosphate and fluoride ≤ 160 ; oxalate, sulphate, nitrate and cyanide ≤ 20 .

The method was applied for determination of gold in different synthetic mixtures containing different diverse ions. The compositions of mixtures and percentage recovery of gold are given in Table 1.

TABLE 1—ANALYSIS OF SYNTHETIC MIXTURES

Sl. no.	Composition with amount (μg)	Au found %
1.	$\text{Au}^{\text{III}}, 47.6$; $\text{Mn}^{\text{II}}, 300$; $\text{Cd}^{\text{II}}, 800$; $\text{Fe}^{\text{II}}, 1200$	99.03
2.	$\text{Au}^{\text{III}}, 47.6$; $\text{Fe}^{\text{III}}, 1000$; $\text{W}^{\text{VI}}, 86$; $\text{Mo}^{\text{VI}}, 816$	100.5
3.	$\text{Au}^{\text{III}}, 47.6$; $\text{Co}^{\text{II}}, 1000$; $\text{Ni}^{\text{II}}, 1000$; $\text{Cu}^{\text{II}}, 667$	99.6
4.	$\text{Au}^{\text{III}}, 47.6$; $\text{Pd}^{\text{II}}, 50$; $\text{Pb}^{\text{II}}, 640$; $\text{Zn}^{\text{II}}, 980$	97.5

A standard solution containing $4.76 \mu\text{g ml}^{-1}$ of gold was estimated (10 times) by the recommended procedure. The average absorbance was 0.60 with a standard deviation of 0.0085 absorbance unit and a coefficient of variation of 1.4%. Thus the present method is very simple, selective and sensitive. The

sensitivity of the present method ($0.0079 \mu\text{g cm}^{-2}$) is better than most of the commonly used spectrophotometric methods using different reagents, viz. trifluoroethylxanthate⁵ ($0.018 \mu\text{g cm}^{-2}$), cetyltrimethylammonium bromide³ ($0.015 \mu\text{g cm}^{-2}$), acetyl pyridine thiosemicarbazone⁶ ($0.0156 \mu\text{g cm}^{-2}$), hydrobromic acid⁷ ($0.04 \mu\text{g cm}^{-2}$), stannous chloride⁷ ($0.05 \mu\text{g cm}^{-2}$) for determination of gold in microamounts. The total operation time in each run is 15–20 min. Good recovery of gold was achieved in presence of most of the common ions and the results were accurate and precise to a high degree.

Experimental

A Hitachi U-3210 spectrophotometer was used for absorbance measurements and pH values were determined with an Elico LI-10 pH-meter.

A stock solution of gold(III) was prepared from gold chloride (Johnson and Mathey) and was standardised by known method⁸. Solutions of lower concentration were prepared by appropriate dilution of the stock solution.

The reagent benzyltrimethylphenylammonium chloride was prepared by mixing equimolar amounts of benzyl chloride and dimethyl aniline and allowing the mixture to stand until crystallisation was effected. The solid after washing with acetone was recrystallised from alcohol. A 0.01 M solution of benzyltrimethylphenylammonium chloride, 0.3 M solution of potassium iodide and buffer solutions with potassium dihydrogen phosphate and sodium hydroxide (pH 5.8–8.0) were prepared in distilled water.

All chemicals and solvents used were of analytical grade.

Procedure: To an aliquot of the test solution, containing 11–140 μg of gold(III), 0.3 M potassium iodide (1 ml) and 0.01 M BDPA (1 ml) were added and the total volume was made up to 10 ml with buffer solution and distilled water so that pH of the aqueous phase was around 7.0 ± 0.5 . To it chloroform (10 ml) was added and the resulting mixture was shaken for 30 s. The organic layer was separated and the absorbance of the extract was measured at 363 nm against the reagent blank. The amount of gold in unknown solution was calculated from the standard calibration curve.

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Identification of Vanadium by using a Schiff Base derived from 2-Furfuraldehyde and *p*-Aminophenylmercaptoacetic Acid†

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Among the few reagents proposed for the identification of vanadium¹, mention may be made of hydrogen peroxide, α -benzoinoxime, 8-hydroxyquinoline, diaminobenzidine and based on catalytic oxidation of aniline. Some of the methods are subject to many interferences, less sensitive and

require heating also. Recently, *p*-aminophenylmercaptoacetic acid has been used as a new diazotisable amine for the spectrophotometric determination of nitrite², cerium³ and chromium⁴ based on azo dye formation. In the present communication, a new Schiff base derived from 2-furfuraldehyde and

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p-aminophenylmercaptoacetic acid has been used as a reagent for the identification of vanadium.

Results and Discussion

The structure of the Schiff base is supported by elemental analysis, ir spectra and negative test for a free amino group. The elemental analyses data were found to be in agreement with those of the calculated values. The Schiff base showed ir bands at 1490 and 1510 (furan oxygen)⁶ and 1600 cm^{-1} (C=N) indicating that aldehyde has condensed with *p*-aminophenylmercaptoacetic acid⁶. The solution of the Schiff base failed to give positive test for diazotisation-coupling reactions².

Vanadium gives a bluish violet colour with the Schiff base in the pH range 1.0–3.5; pH \sim 2 was found to give maximum colour intensity. A 0.01 ml of KCl-HCl buffer solution (pH \sim 2) and 0.01 ml of 0.2% Schiff base reagent were found to be optimum. The bluish violet vanadium Schiff base complex starts appearing within 10 min. The colour was found to be stable for 1 h.

The effect of foreign ions that often accompany vanadium in diverse geological samples was examined by carrying out identification of 0.01 ml of 50 $\mu\text{g ml}^{-1}$ of vanadium on a spot plate in the presence of each of these ions. The tolerance limits (ppm) of foreign ions were found as follows: Co^{II}, Ni^{II}, Mn^{II}, Cr^{VI}, Zn^{II}, Cd^{II}, Hg^{II}, Ca^{II}, Mg^{II}, UO₂^{II}, Cu^{II}, Al^{III}, Sr^{II}, Ba^{II}, Se^{IV}, Pb^{II}, Th^{IV}, Nb^V, Ta^V and Be^{II} (100 each); Ce^{IV} (50), Mo^{VI} and Fe^{III} (20). Fluoride, chloride, sulphate, nitrate, citrate, oxalate, phosphate and tartrate did not interfere. Higher concentration of Fe^{III} gave positive interference. The positive interference due to Fe^{III} could be prevented by the addition of phosphoric acid or fluoride ion. The interference due to Ti^{IV}, Bi^{III}, Zr^{IV} and W^{VI} could be masked by using tartaric acid.

Simplicity, temperature-independence, sensitivity and selectivity are the advantages of the proposed method.

Experimental

p-Aminophenylmercaptoacetic acid (98% purity, Evans) and 2-furfuraldehyde (Merck-Schunhardt) were used as such. All other chemicals were of A.R. grade. A stock solution of vanadium (5 mg ml^{-1}) was prepared from ammonium metavanadate and standardised titrimetrically⁷ and diluted to give a standard solution containing 100 $\mu\text{g ml}^{-1}$ of

vanadium. Solution of other elements were prepared by dissolving suitable salts in water or dilute hydrochloric acid. An aqueous solution of Schiff base reagent (FAPMA; 0.2%, w/v) was prepared. Buffer solution (pH \sim 2) was prepared by adding 0.2 M KCl (12.5 ml) to 0.2 M HCl (3.25 ml) and diluting the solution to 50 ml. Ir spectra were recorded on a Carl Zeec M-80 spectrophotometer.

2-Furfuraldehyde-4-aminophenylmercaptoacetic acid Schiff base (FAPMA): 2-Furaldehyde (5.26 ml) was added gradually to a solution of *p*-aminophenylmercaptoacetic acid (1 mol, 100 ml) in 1 M HCl with vigorous stirring when the solution turned dark reddish and started precipitating within 10 min. The resulting mixture was heated and allowed to stand overnight. The resulting reddish brown solid was washed with alcohol and dried over anhydrous calcium chloride, (80%) (Found: C, 59.9; H, 4.2; N, 5.2. C₁₃H₁₁NO₃S calcd. for: C, 59.8; H, 4.2; N, 5.4%).

Procedure: A drop (0.01 ml) of the test solution was treated on a spot plate with KCl-HCl buffer (pH \sim 2; 0.01 ml) and a 0.2% aqueous solution of the Schiff base reagent (0.01 ml). A bluish violet colour appeared within 10 min, indicating the presence of vanadium. Identification limit was 0.2 μg vanadium and the limit of dilution was 1 : 50000.

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