Ion-pair based liquid–liquid extraction of gold(III) from malonate media using 2-octylaminopyridine as an extractant: analysis of alloys, minerals, and drug samples

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Abstract: Liquid–liquid extraction of Au(III) from aqueous sodium malonate medium using 2-octylaminopyridine (2-OAP) as an extractant in xylene was achieved. The current work explored the influence of several experimental parameters such as pH, weak acid concentration, extractant concentration, equilibrium time, stripping agents, and aqueous:organic volume ratio on the extraction of Au(III). The experimental results showed that the Au(III) was quantitatively extracted to about 99.5% by 0.05 M 2-OAP in 0.05 M malonate at 5.0 pH. Ammonia solution was used to strip the gold-loaded organic phase and about 99.5% of Au(III) was reversibly extracted into the aqueous phase. Gold(III) was extracted into the organic phase via formation of ion-pair complex [2-OAPH$^+$.Au $(C_3H_2O_4)_2^-$]. The stoichiometry of the extracted species was 1:2:1 (metal: acid: extractant) determined by slope analysis. The method affords the binary, ternary mixture separation as well as separation of Au(III) from synthetic mixtures and alloys. The method is applicable for the determination and separation of gold from ayurvedic samples and recovery of gold from e-wastes. A reproduction of the method was checked by finding relative standard deviation for n = 5, which was 0.29%, and the limit of detection was 1.08 μg/mL.

Key words: Liquid-liquid extraction, gold(III), sodium malonate, 2-octylaminopyridine (2-OAP), e-wastes, ayurvedic samples

1. Introduction

Gold is a rare precious metal with high economic value. The gorgeousness and high luster of gold have led its use in jewelry and currency and as a standard for monetary systems throughout the world. Gold displays noteworthy applications in medicine, dentistry, industry, electronics, catalysts, cosmetics, and even in food and drinks.[1−3] Some gold salts have antiinflammatory properties depicted by their use in the treatment of arthritis and other similar conditions.[4−6] However, only salts and radioisotopes of gold are of pharmacological value, as elemental (metallic) gold is inert to all the chemicals it encounters inside the body. Due to the increasing demand for gold in the industrial sector and its scarcity, there is an immense need for its recycling. In general, gold is separated and purified from industrial wastes by hydrometallurgical processes involving chloride media.[7] Solvent extraction techniques have been widely employed for the recovery of precious metals from chloride

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solutions. From all the hydrometallurgical techniques used for the recovery of gold, solvent extraction seems to be the least used, in spite of its being a popular method. There are at least three main industrial processes for recovering gold and other precious metals by solvent extraction.[8−14]

Solvent extraction is an impressive and effective technique for recovery and separation of gold using various extractants. Some of the extractants reported for gold(III) are N-n-octylaniline,[15] Cynex 923,[16,17] tributylphosphate,[18] phospholene,[19] tri-n-octylamine,[20] tri-n-butyl phosphate,[21] Alamine,[22] LIX 79,[23] cyphos IL 101,[24,25] quarternary amine,[26] Cyanex 302,[27] Cyphos IL 109,[28] N-n-decylaminopyridine,[29] and Alamine 336[30]. Separation and enrichment of trace levels of gold in environmental samples was conducted with Amberlite XAD-2000[31] and sorbent extraction for preconcentration of gold on an activated carbon column.[32] Comparison of the previously reported solvent extraction methods with present method was given in Table 1.[15,26−28,30,33−37]

In most of the cases studied, the amine can extract the metal ion via ion-pair formation.[38−47] To date, there have been very few reports on the extraction of Au(III) in weak acid medium. So far, no work has been reported on the extraction of Au(III) using 2-OAP as an ion-pair forming reagent with malonic acid medium. Herewith, we are reporting systematic studies exploring the solvent extraction process for the recovery of Au(III) from malonate medium. This work thoroughly investigated the applications of 2-OAP for the extraction of Au(III) from various alloys. The aim of this extraction method is to separate binary and ternary mixtures of associated metal ions of Au(III). There is a large amount of gold used for the dental alloys and casting alloys; therefore, our aim was to separate gold from that waste. The effectiveness of the proposed method was also monitored by analyzing the ayurvedic samples and e-waste. Numerical treatments and graphical methods were used to determine the stoichiometry of the complexes extracted. Thermodynamic parameters were determined, providing useful insights into the solvent extraction system. In addition, stripping of Au(III) from loaded organic phase was considered, and the recycling of the organic phase was investigated in a series of extraction-stripping courses. The extraction procedure was carried out with xylene as diluent for 2-OAP; after completion of the extraction procedure the used xylene was stored and reused for further extraction after distillation. Stripping was carried out with ammonia solution, which is ecofriendly.

2. Results and discussion

2.1. Influence of pH on extraction of Au(III)

The concentration of H^+ can distinctly influence the extraction mechanism of Au(III). To investigate the effect of pH on the extraction, pH in the range 1 to 10 was examined. A set of experiments was carried out as mentioned in section 3.3. The required pH was maintained by addition of dil. HCl and NaOH. As shown in Figure 1, extraction of Au(III) ion-pair increases gradually from pH 1 to 4. Between pH 5 to 6 gold can be quantitatively extracted and beyond 6 there is a decrease in extraction. In basic pH, Au(III) was not able to form an ion-pair with extractant and therefore the extraction of Au(III) was decreased. Hence pH 5 was used for further study.

2.2. Influence of weak organic acid concentration on extraction of Au(III)

The effect of weak acid concentration on the extraction behavior of Au(III) using the 2-OAP/xylene system was investigated. The 2-OAP concentration in the organic phase was 0.05 M and the pH was adjusted to 5.0, while the malonate concentration was varied over the range $0.01−0.1$ M and extraction of Au(III) was carried out. Figure 2 shows the effect of sodium salts of weak organic acid on the extraction of Au(III). With 0.01 M

Table 1. Comparison of the previously reported solvent extraction method with the present method.

Reagent	Acidity/ pH	Solvent	Strippant	Shaking time	Determination method	Ref.
N-n-octylaniline (0.1 M)	pH = 1	Xylene	7.0 M Ammonia	1 min	Spectrophotometer	15
N-n-decylaminopyridine (1×10^{-4} M)	pH = 7–10	Xylene	1 M HNO$_3$	1 min	Spectrophotometer	26
Cyanex 302 (7.5×10^{-4} M)	0.01 M HCl	Toluene	0.1 M Na$_2$S$_2$O$_3$	3 min	Spectrophotometer	27
Cyphos IL 109 (1.01 mmol/dm^3)	0.1 M HCl	Xylene	Acidic thiourea	10 min	AAS	28
Alamine 336 (0.05 M)	pH = 1.8	Hexane	0.1 M Thiourea	20 min	ICP-OES	30
Cetylpyridinium bromide (1 M)	pH = 10.5	n-dodecane	KSCN 3 mol L^{-1}	10 min	Spectrophotometer	33
Tributylphosphate (1.83 mol/ L)	pH = 11	n-octane	–	10 min	Spectrophotometer	34
Hostarex A 327 (0.10 mmol/dm^3)	5 M HCl	n-decane	–	10 min	AAS	35
Cyanex 925 (0.01% v/v)	6 M HCl	Xylene	Water	10 min	AAS	36
Tributylphosphate (1 M)	pH = 2.5	Kerosene	–	30 min	Spectrophotometer	37
2-OAP (0.05 M)	pH = 5.0	Xylene	7.0 M Ammonia	5 min	Spectrophotometer	PM

PM: Present method

malonate, the extraction efficiency of Au(III) was 81.9%, but the extraction efficiency gradually increased to 99.5% in the range 0.02–0.04 M malonate; beyond that the extraction went on decreasing. This is due to the formation of the stable 2-OAP-malonate ion-pair, which tends to decrease the extraction. Therefore, further extraction was carried out in 0.03 M malonate. On the other hand, the extraction of Au(III) was incomplete in sodium salicylate (51.5%) sodium succinate (69.1%), sodium tartrate (52.7%), sodium oxalate (81.4%), and sodium ascorbate (9.9%).
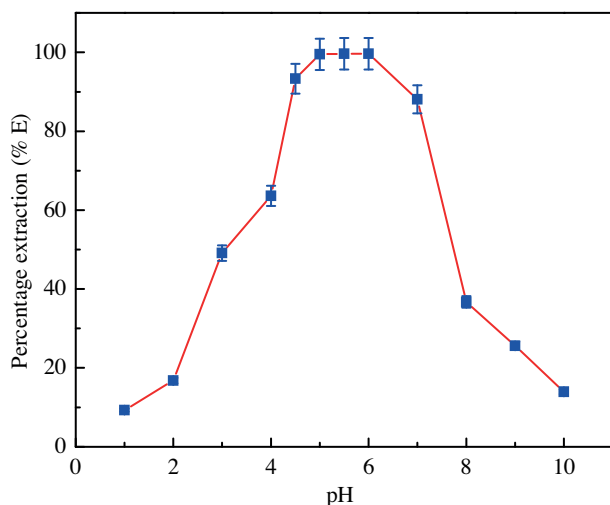

Figure 1. Influence of pH on extraction of Au(III). Condition: Au(III) = 200 μg, sodium malonate = 0.03 M, aq.: org.= 2.5:1, 2-OAP = 0.05 M in xylene, equilibrium time = 5.0 min, strippant = 7.0 M ammonia.
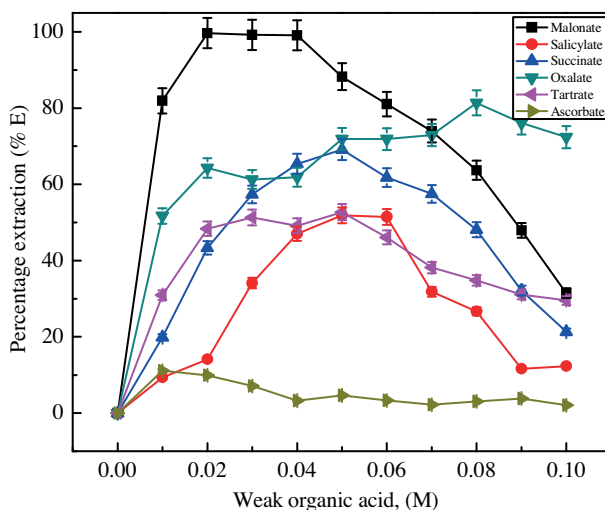

Figure 2. Influence of weak organic acid concentration on extraction of Au(III). Condition: Au(III) = 200 μg, pH = 5.0, aq.: org.= 2.5: 1, 2-OAP = 0.05 M in xylene, equilibrium time = 5.0 min, strippant = 7.0 M ammonia.

2.3. Influence of 2-OAP concentration on extraction of Au(III)

To investigate the influence of initial 2-OAP concentration on the Au(III) extraction efficiency and distribution, the 2-OAP concentration in xylene was varied between 0.001 and 0.1 M. Meanwhile, the other parameters, pH 5.0, 0.03 M malonate concentration, aq:org phase ratio 2.5:1, were kept constant and extraction of Au(III) was carried out. Figure 3 depicts that the extraction increased sharply with the increase in 2-OAP concentration from 0.001 to 0.035 M, where the yield of extraction reached 91.7%. Beyond the concentration of 0.035 M 2-OAP, the percentage extraction of Au(III) was quantitative and remained steady up to 0.1 M. Hence, to ensure the complete extraction of Au(III), an organic phase containing 0.05 M 2-OAP was chosen for further extraction study.

2.4. Influence of equilibration time on extraction of Au(III)

Influence of the equilibrium time on gold(III) extraction was studied using organic solutions of 0.05 M 2-OAP in xylene and aqueous solutions of 200 μg of gold in 0.03 M malonate media at 5.0 pH; the equilibrium time was varied from 15 s to 30 min as shown in Figure 4. The percentage extraction of Au(III) reached 99.6% within 2 min of contact time, which means rapid attainment of extraction equilibrium was achieved. To ensure the attainment of the equilibrium under all conditions, a 5 min contact time was invariably maintained in further experiments.
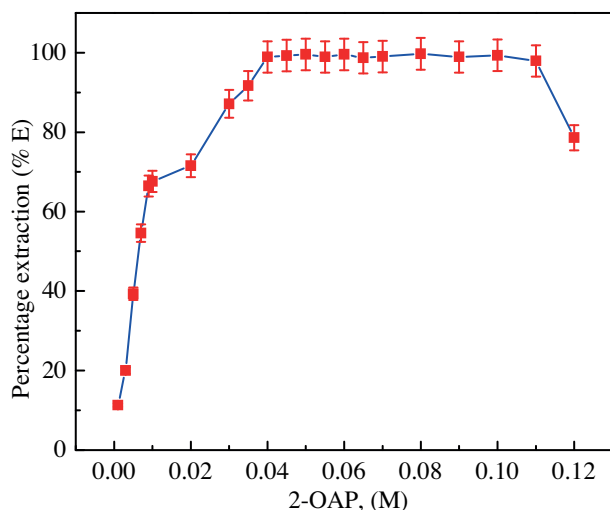
Figure 3. Influence of 2-OAP concentration on extraction of Au(III). Condition: Au(III) = 200 μg, pH = 5.0, sodium malonate = 0.03 M, aq.:org. = 2.5:1, equilibrium time = 5.0 min, strippant = 7.0 M ammonia.
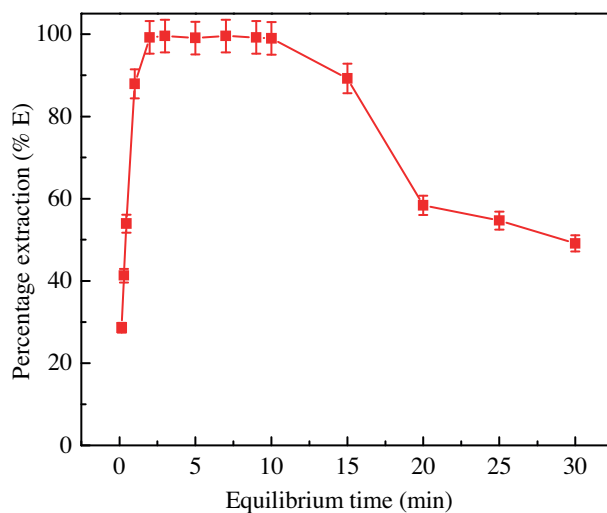
Figure 4. Influence of equilibrium time on extraction of Au(III). Condition: Au(III) = 200 μg, pH = 5.0, sodium malonate = 0.03 M, aq.:org.= 2.5:1, 2-OAP = 0.05 M in xylene, strippant = 7.0 M ammonia.

2.5. Influence of organic solvents on extraction of Au(III)

The extraction of the ion-pairs greatly depends on the nature of the organic solvent. For quantitative extraction aliphatic and aromatic hydrocarbons, higher alcohols, ketones, acetic esters, and halogen derivatives of aliphatic and aromatic hydrocarbons were investigated. To study this effect, an experiment was carried out using organic solution of 0.05 M 2-OAP in each solvent and aqueous solution of 200 μg of Au(III) in 0.03 M malonate media at 5.0 pH and equilibration time as 5 min. The results obtained are shown in Table 2, which indicate that the best extraction appeared in xylene, methyl *iso*butyl ketone, and amyl alcohol, as they have very good extractability of the ion-pairs. The percentage extraction of Au(III) ion-pair complex in toluene (82.3%), chloroform (32.9%), dichloromethane (74.5%), 1, 2, dichloroethane (68.4%), amyl acetate (63.4%), and cyclohexane (74.4%) was incomplete. There was no extraction in kerosene.

Table 2. Influence of solvents on extraction of Au(III).

Solvents	Percentage extraction, (%E)	Distribution ratio, (D)
Xylene	99.6	622.50
Toluene	82.3	11.62
Chloroform	32.9	1.23
MIBK	98.9	224.77
Dichloromethane (DCM)	74.5	7.30
1,2-Dichloroethane (DCE)	68.4	5.41
Amyl alcohol	99.2	310.0
Amyl acetate	63.4	4.33
Cyclohexane	74.4	7.27

Au(III) = 200 μg, pH = 5.0, sodium malonate = 0.03 M, org. = 0.05 M 2-OAP, aq.: org. = 2.5: 1.0, strippant = 7.0 M ammonia.

2.6. Influence of the volume ratio (V_{aq}/V_{org}) on the extraction of Au(III)

To study this parameter, the extraction of Au(III) was carried out with 10 mL of 0.05 M 2-OAP/xylene system from 0.03 M malonate at 5.0 pH. During this, the aqueous to organic phase ratio was varied from 1:1 to 20:1. Increase in the volume ratio will reduce the use of organic phase, which in turn will reduce its production cost. The influence of the volume ratio of the aqueous phase to the organic phase on the extraction percentage is shown in Table 3. The results indicate that when volume ratio ranges from 1 to 7.5 more than 99.6% of the Au(III) can be transferred into the organic phase. As volume ratio exceeds up to 20/1 from 7.5/1 the extraction of Au(III) falls to 54.6%.

Table 3. Influence of aqueous to organic volume ratio on extraction of Au(III).

Aq:org	Percentage extraction (%E)	Distribution ratio (D)
10:10	98.9	224.77
20:10	99.6	622.50
25:10	99.7	830.83
30:10	99.2	310.00
40:10	99.6	622.50
50:10	98.9	224.77
75:10	94.7	44.66
100:10	79.1	9.46
150:10	71.6	6.30
200:10	54.6	3.00

Au(III) = 200 μg, pH = 5.0, sodium malonate = 0.03 M, org. = 0.05 M 2-OAP in xylene, strippant = 7.0 M ammonia.

2.7. Influence of stripping agents

The back extraction of Au(III) from loaded organic phase was carried out and the organic phase was recycled for further extraction of Au(III). Thus, a loaded organic solution obtained from the extraction stage was used for testing acids, bases, and buffer solutions as various stripping agents. Quantitative back extraction of Au(III) was achieved from ammonia (4–10 M), ammonia buffer (pH 10), and HCl (4–10 M) solution. However, stripping of Au(III) from loaded organic phase was incomplete in water (13.6%), NaOH (31.3%), HNO$_3$ (71.7%), acetate buffer (23.4%), and H$_2$SO$_4$ (81.1%). Amongst these, the ammonia solution (7.0 M) was recommended for subsequent stripping of Au(III) from loaded organic phase because the evaporation of ammonia is an easier process compared to ammonia buffer and HCl solution. In the stripping process of Au(III) with 7.0 M ammonia, HAu(OH)$_4$ species were present in the stripped solution.[48] The back extraction capacity of various reagents is as shown in Table 4.

2.8. Loading capacity of 2-OAP

To determine how much Au(III) can be extracted by the 2-OAP/xylene system, a number of extractions were carried out with various Au(III) concentrations in the feed solution (0.03 M malonate, 5.0 pH). Extraction was carried out by keeping other parameters constant. One portion of 10 mL of organic solvent (0.05 M 2-OAP in xylene) successively extracted five portions of 25.0 mL of aqueous phase. The result showed that the Au(III)

Table 4. Influence of stripping agents.

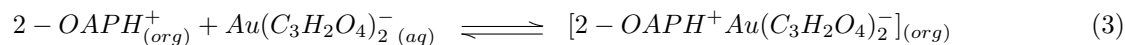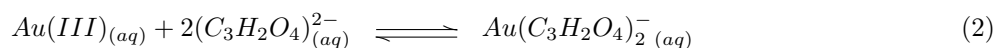| Strippant	Percentage recovery (%R)	Distribution ratio (D)
Ammonia (4 M–10 M)	99.6	622.50
HCl (4 M–10 M)	99.2	310.0
HNO_3 (4 M)	71.7	6.33
H_2SO_4 (5 M–10 M)	99.6	622.50
Ammonia buffer	99.2	310.0
Acetate buffer	23.4	0.76
Water	13.6	0.39

Au(III) = 200 μg, pH = 5.0, sodium malonate = 0.03 M, org. = 0.05 M in xylene, aq.: org. = 2.5:1.0.

in the organic phase increased to five successive contacts, and the overall quantity of Au(III) that could be transferred into the organic phase is up to 1 mg in a volume of 10 mL.
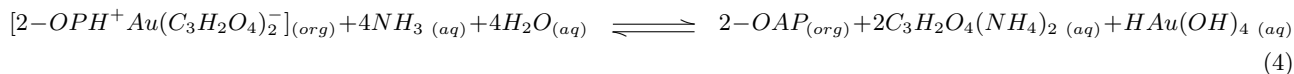
2.9. Nature of extracted species

Extraction of Au(III) ions is an ion-pair complex formation process and various factors affect it. This leads to the formation of different stoichiometry or involvement of different forms of complexes of metal ions, medium, and extractant. Thus, the probable stoichiometry of the extracted species was determined on the basis of slope analysis by plotting the graph of Log $D_{[Au(III)]}$ versus Log $C_{[2-OAP]}$ at constant malonate concentration (0.03 M). The slope values of linear plots were 1.03 and 0.97, respectively (Supporting Information Figure S1) (at pH 3.5 and 2.5). Moreover, the plots of Log $D_{[Au(III)]}$ versus Log $C_{[malonate]}$ at constant 2-OAP concentration (0.05 M) were linear, having slope values 1.94 and 1.80 as shown in Supporting Information Figure S2 (at pH 3.5 and 2.5). The slope values of both the plots indicate that there is involvement of one mole of metal, two moles of malonate, and one mole of 2-OAP; hence the probable composition of the extracted species is calculated to be 1:2:1 (metal:acid:extractant). The possible mechanism for the extracted species appeared to be protonated 2-OAP, which forms cationic species as 2-OAPH$^+$, while malonate combines with Au(III) to form anionic species as $Au(C_3H_2O_4)_2^-$ and both of them associate to form an ion-pair of type [2-OAPH$^+$. $Au(C_3H_2O_4)_2^-$]$_{org}$ and since these are neutral they are extractable species.

The probable mechanism of extraction:

$$2-OAP_{(org)} + H^+_{(aq)} \rightleftharpoons 2-OAPH^+_{(org)} \tag{1}$$

$$Au(III)_{(aq)} + 2(C_3H_2O_4)^{2-}_{(aq)} \rightleftharpoons Au(C_3H_2O_4)^-_{2\ (aq)} \tag{2}$$

$$2-OAPH^+_{(org)} + Au(C_3H_2O_4)^-_{2\ (aq)} \rightleftharpoons [2-OAPH^+Au(C_3H_2O_4)^-_2]_{(org)} \tag{3}$$

The probable mechanism of back stripping:

$$[2-OPH^+Au(C_3H_2O_4)^-_2]_{(org)} + 4NH_{3\ (aq)} + 4H_2O_{(aq)} \rightleftharpoons 2-OAP_{(org)} + 2C_3H_2O_4(NH_4)_{2\ (aq)} + HAu(OH)_{4\ (aq)} \tag{4}$$

2.10. Influence of temperature on extraction of ion-pair complex

To investigate the influence of temperature on the extraction, equilibrium constant and thermodynamic characteristics were resolute at different temperatures. Temperature was varied in the range 298–313 K using a thermostat and extraction was carried out with 10 mL of 0.05 M 2-OAP in xylene, 0.03 M malonate at 3.0 pH. The extraction reaction shown as Eq. (3) from that equilibrium constant K_{ex} (T) at different temperatures for the ion-pairs of gold is

$$K_{ex} = \frac{[2 - OAPH^+ Au (C_3H_2O_4)_2{}^-]_{org}}{[2 - OAPH^+]_{org} [Au (C_3H_2O_4)_2{}^-]_{aq}} \tag{5}$$

From Eq. (3) the distribution ratio (D) of Au(III) can be written as

$$D = \frac{[Au]_{org}}{[Au]_{aq}} = \frac{[2 - OAPH^+ Au (C_3H_2O_4)_2{}^-]_{org}}{[Au (C_3H_2O_4)_2{}^-]_{aq}} \tag{6}$$

Putting Eq. (6) in Eq. (5) we get

$$K_{ex} = \frac{D}{[2 - OAPH^+]_{org}} \tag{7}$$

Taking the logarithm of Eq. (7),

$$log\, K_{ex} = \log D - \log [2 - OAPH^+]_{org} \tag{8}$$

$$log\, D = \log K_{ex} + \log [2 - OAPH^+]_{org} \tag{9}$$

The log K_{ex} values were calculated using the experimental data and the above equations and are listed in Supporting Information Table S1. Furthermore, the change in standard Gibbs free energy ($\Delta G°$) and entropy ($\Delta S°$) was calculated from the following equation:

$$\Delta G° = -2.303\, RT\, log\, K_{ex} \tag{10}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{11}$$

Plotting the natural logarithm of K_{ex} versus the inverse temperature will yield a slope proportional to enthalpy and intercept to the entropy.

$$log\, K_{ex} = \frac{-\Delta H°}{RT} + \frac{\Delta S°}{R} \tag{12}$$

The slope of line –2.73 was obtained, as shown in Supporting Information Figure S3. Therefore, the extraction process is exothermic with $\Delta H° = –22.6227$ kJ/mol. The value of entropy suggests that the degree of order increased during the extraction process.

3. Experimental

3.1. Instrumentation

A digital UV visible spectrophotometer (Optizen-α, Mecasys Co. Ltd., Korea) with a 10-mm quartz cell was used for the absorbance measurement. The pH of the solution was measured with the help of a digital pH meter (SL-120, Elico, India) with a combined glass electrode. A digital weight balance (ML 204/AOI, Mettler Toledo, Switzerland) was used for weighing.

3.2. Chemicals and reagents

All chemicals and solvents used were of analytical reagent (AR) grade purity. Doubly distilled water was used throughout the experiment and dilutions. Stock solution (1000 μg mL^{-1}) of gold was prepared by dissolving chloroauric acid (HAuCl$_4$) (Johnson Mathey & Co., UK) in dilute hydrochloric acid (Merck, Mumbai, India) and standardized gravimetrically;[49] the working solution was prepared by appropriate dilution of stock solution with water prior to use. 2-Octylaminopyridine was synthesized by a reported method[50] and working solution of 0.05 M was prepared in xylene (Merck). Stannous chloride (SnCl$_2$) (S.D. Fine Chem. Ltd., Mumbai, India) (10% w/v) was prepared in dil. HCl and used for the determination of Au(III). All other metal ions used for the diverse ion study were prepared by dissolving their salts in dilute acid and alkali solution.

3.3. Recommended extraction procedure

To an aliquot of Au(III) (200 μg) was added sodium malonate so that the final volume had a concentration of 0.03 M in 25 mL. The pH of aqueous solution was adjusted to 5.0. To this solution was added 10 mL of 0.05 M 2-OAP in xylene followed by equilibration for 5 min in a glass stoppered separating funnel by manual shaking at room temperature using an aq:org phase ratio 2.5:1. After phase disengagement, the aqueous phase was separated and the Au(III) from the pregnant organic phase was stripped quantitatively by 7.0 M ammonia (3 × 10 mL). The stripped aqueous phase was evaporated to moist dryness and Au(III) was determined by the SnCl$_2$ method[51] spectrophotometrically. The total time required for the extraction procedure was about 25 min.

The metal distribution coefficient was calculated from the equation given below:

$$D = \frac{[M]_{org.,\ total}}{[M]_{aq.,\ total}}$$

where [M]$_{org.,total}$ and [M]$_{aq.,total}$ represent the total concentration of metal ion that has equilibrated in the organic and aqueous phases, respectively.

The extraction efficiency (%E) was calculated by using the subsequent equation:

$$\text{Extraction efficiency} (\%E) = \frac{100D}{D + V_{aq}/V_{org}}$$

where V$_{aq}$ and V$_{org}$ refer to the volume of the aqueous and organic phase, respectively.

3.4. Extraction of alloys and minerals

Extraction of alloys and minerals was carried out by the proposed method. The standard samples' alloys and minerals are not easily available in the working place for extraction studies. Therefore, samples of alloys and minerals are synthetically prepared in which a known amount of Au(III) was added and the extraction study was carried out according to the procedure given in section 3.3.

4. Applications

4.1. Influence of diverse ions

To evaluate the selectivity of the proposed method for the extraction of 200 μg mL^{-1} of trivalent gold, ions in the presence of typical potential interfering ions were studied. The tolerance limit was defined as the concentration

of the foreign ion added causing a relative error within $\pm 2\%$ of the recovery of the Au(III). Extraction of trivalent gold was carried out in the presence of various base metals as well as platinum group metals (PGMs) (Supporting Information Table S2). Some of them create interference for the Au(III) extraction, and interference due to Pd(II), Pt(IV), Ir(III), Rh(III), Os(VIII), and Ru(III) was eliminated by addition of masking agents like tartrate for Pd(II) and Ru(III), oxalate for Pt(IV) and Ir(III), citrate for Rh(III), and thiocyanate for Os(VIII) prior to the extraction. The results clearly showed that the 2-OAP/xylene is highly selective for the extraction of trivalent gold.

4.2. Separation of Au(III) from associated metal ions

To extend the utility of the 2-OAP/xylene system for the extraction of Au(III), an aqueous binary solution was prepared by adding other associated metal ions. The method allowed for separation and determination of Au(III) from a binary mixture of base metals like Fe(II), Cu(II), Ni(II), Co(II), and Zn(II) along with Se(IV), Te(IV), Ag(I), Hg(II), Bi(III), Al(III), Cd(II), and Pb(II) as well as PGMs.

The separation of Au(III) from base metals was carried out by its extraction with 0.05 M 2-OAP in xylene at 0.03 M malonate and 5.0 pH. Under this condition, all the base metals remained quantitatively in aqueous phase and were determined by the respective method. In the case of a binary mixture of PGMs the separation of Au(III) was carried out by masking the PGMs; Pd(II) and Ru(III) were masked by 15 mg of tartrate, Pt(IV) and Ir(III) were masked by 20 mg of oxalate, Rh(III) by 15 mg of citrate, and Os(VIII) by 15 mg of thiocyanate, and extraction was carried out. Under these conditions, all added metal ions remain quantitatively in the aqueous phase from which they were determined spectrophotometrically by the standard method[51−58] (Supporting Information Table S3). Gold(III) was back extracted from the organic phase by 7.0 M ammonia solution and determined by $SnCl_2$ method spectrophotometrically. The recovery of the ions was in good agreement with the amount added.

4.3. Separation of Au(III) from ternary mixture

The difference in the extraction behavior of each of the metals was fully exploited to provide complete separation of these metals from Au(III) in various mixtures. A ternary mixture of Cu(II), Ag(I); Pt(IV), Pd(II); Fe(II), Cu(II); Fe(II), Ni(II); Te(IV), Fe(II); Te(IV), Se(IV); Pb(II), Bi(III); Cd(II), Zn(II); and Zn(II), Hg(II) along with Au(III) was resolved by extracting Au(III) at a fixed concentration of 0.05 M 2-OAP, 0.03 M malonate at 5.0 pH. Gold(III) from organic phase was back stripped with 7.0 M ammonia solution and determined spectrophotometrically by the $SnCl_2$ method.

4.4. Analysis of Au(III) from a synthetic mixture corresponding to the composition of alloys

The suggested method was evaluated under the selected experimental conditions by inspecting its applicability for the separation of gold from various alloy samples. Since the standard alloy samples were not available at this working place, the synthetic mixtures of recognized composition were prepared and analyzed in which a known amount of Au(III) was added. As shown in Supporting Information Table S4 and S5, analysis of jewelry alloys, aurident porcelain alloys, and casting gold was carried out.

4.5. Validity of the method

In order to study the applicability of the proposed extraction method, the recovery of gold(III) from e-waste was carried out. The e-waste was mechanically crushed for size reduction and then leaching with nitric acid solution was done in order to remove silver and base metals. It is then dissolved in aqua regia for the metallic gold solution and diluted in a standard volumetric flask. Aliquots of the sample solution were taken and extraction of Au(III) was performed according to the procedure described in section 3.3. The results showed that more than 98% of Au(III) was extracted into the organic phase, which was in good agreement with the results obtained by the AAS method. The relative standard deviation (RSD) for the above result was 0.29%. The limit of detection and limit of quantitation were 1.08 μg/mL and 2.88 μg/mL, respectively. Hence, this study could be a promising method to recover gold from e-waste.

4.6. Determination of Au(III) in ayurvedic drug samples

The proposed method was applied for the determination of Au(III) in ayurvedic medicines such as Brahmi Vati, Vasant Kusumakar Rasa, Brihat Vat Chintamani Rasa, and Suvarna Sootshekhar Rasa No.-1.

Appropriate weight of the sample (1 or 2 tablets) was dissolved in 2 × 5 mL of aqua regia. The solution was evaporated to moist dryness. The residue was dissolved in hot dil. HCl and filtered. The filtrate was diluted up to 100 mL with water. An aliquot of this solution was taken for the extraction of Au(III) by the proposed method. The results were in good agreement with those obtained by the AAS method (Supporting Information Table S6).

5. Conclusions

The 2-octylaminipyridine/xylene system was investigated for Au(III) extraction from weak organic acid medium, i.e. malonate medium at 5.0 pH. According to the extraction mechanism, the ion-pair complex is likely to be $[2\text{-}OAPH^+\cdot Au(C_3H_2O_4)_2^-]_{org}$ confirmed by slope analysis. The stoichiometry of the extracted species was found to be 1:2:1. The noteworthy aspect of this method is the use of low reagent concentration for the extraction of Au(III). This method is utilized for the separation of gold from various synthetic mixtures and alloy samples, as well as from ayurvedic medicines. Finally, the calculated thermodynamic parameters (Δ H°, Δ S°, and Δ G°) suggest that the extraction of gold is spontaneous ($-\Delta$ G°) in nature and the process is exothermic ($-\Delta$ H°) with the formation of highly ordered complexes ($-\Delta$ S°) in the organic phase.

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Supporting Information

Table S1. Influence of temperature on extraction of Au(III). Au(III) = 200 μg, pH = 5.0, sodium malonate = 0.03 M, org. = 0.05 M 2-OAP, strippant = 7.0 M ammonia, aq:org. = 2.5:1.

Temp. K	1000/T	%E	D	Log K_{ex}	ΔG	ΔS
298	3.356	50.20	2.5120	2.6245	−14.975	−0.02580
301	3.322	54.68	3.0163	2.7039	−15.583	−0.02355
304	3.289	59.01	3.5990	2.7806	−16.185	−0.02134
307	3.257	64.39	4.5204	2.8796	−16.926	−0.01871
310	3.225	68.87	5.5308	2.9673	−17.612	−0.01632
313	3.194	73.45	6.9161	3.0643	−18.364	−0.01376

Table S2. Diverse ions.

Tolerance limit, mg	Ions
50	Bromide
25	Iodide, oxalate, U(VI), Ca(II)
20	Fluoride, citrate, Co(II), Ni(II), Cu(II), Ba(II)
15	Tartrate, acetate, EDTA, Fe(II), Zn(II), Al(III), Ga(III), Cd(III), V(V), Mn(II), Ba(II)
10	Bi(III), Te(IV), Cr(VI), In(III), Pb(II), Mo(VI), Mg(II), Fe(III)
5	Thiocyanate, Se(IV), Sr(II), Sb(III),
3	Hg(II), Tl(I),
1	Pd(II)[a], Ir(III)[b], Rh(III)[c], Os(VIII)[d], Ru(III)[a]
0.5	Pt(IV)[b]

[a]Masked by 15 mg of tartrate, [b]Masked by 20 mg of oxalate, [c]Masked by 15 mg of citrate,

[d]Masked by 5 mg of thiocyanate.

Table S3. Extraction separation and determination of Au(III) and added metal ion from binary mixture.

Amount of Au(III) ion, μg	Average recovery* (%)	Chromogenic ligand	Ref. no.
Au(III) 200 Os(VIII)^d 300	99.4	Thiourea	51
Au(III) 200 Ru(III)^a 200	99.1	Thiourea	51
Au(III) 200 Al(III) 5000	99.1	Eriochrome cyanine R	52
Au(III) 200 Bi(III) 5000	99.6	Potassium iodide	52
Au(III) 200 Co(II) 10000	99.6	Thiocyanate	52
Au(III) 200 Ir(III)^b 50	99.8	Stannous chloride	52
Au(III) 200 Fe(II) 5000	99.9	Thiocyanate	52
Au(III) 200 Ni(II) 15000	98.6	DMG	52
Au(III) 200 Pt(IV)^b 300	98.7	Stannous chloride	52
Au(III) 200 Rh(III)^c 200	99.9	Potassium iodide	52
Au(III) 200 Se(IV) 5000	99.9	4-Bromo PTPT	53
Au(III) 200 Te(IV) 5000	99.6	4-Bromo PTPT	54
Au(III) 200 Ag(I) 5000	98.7	2',4'-Dinitro APTPT	55
Au(III) 200 Cu(II) 15000	98.2	4-Chloro PTPT	56
Au(III) 200 Pd(II)^a 200	99.8	4-Chloro PTPT	57
Au(III) 200 Zn(II) 10000	99.3	PAR	58
Au(III) 200 Hg(II) 3000	99.8	PAN	58
Au(III) 200 Cd(II) 10000	99.5	PAR	58
Au(III) 200 Pb(II) 5000	99.9	PAR	58

^{a}Masked by 15 mg of tartrate, ^{b}Masked by 20 mg of oxalate, ^{c}Masked by 15 mg of citrate,

^{d}Masked by 5 mg of thiocyanate.

Table S4. Analysis of gold in jewelry alloys.

Alloy	Composition, (%)	Amount of Au(III) found*, μg	Amount of Au(III) found*, μg	%E
Red gold	Au-75, Cu-25	200	199.24	99.6
Yellow gold	Au-91.67, Ag-5, Cu-2, Zn-1.33	200	199.24	99.6
Rose gold	Au-75, Cu-22.25, Ag-2.75	200	199.00	99.5
Pink gold	Au-75, Cu-20, Ag-5	200	199.24	99.6
White gold	Au-75, Pd-10, Ni-10, Zn-5	200	200.00	100.0
Gray white gold	Au-75, Fe-17, Cu-8	200	198.28	99.1
Deep green gold	Au-75, Ag-15, Cu-6, Cd-4	200	199.24	99.6
Blue gold	Au-75, Fe-25	200	197.77	98.9
Purple gold	Au-80, Al-28	200	199.00	99.5
Green gold	Au-75, Ag-20, Cu-5	200	197.00	98.5
Jewelry alloy	Au-50, Pd-50	200	198.51	99.3
Solder alloy	Au-60, Pd-30, Pt-10	200	199.26	99.6

% E = Percentage extraction

*Average of five determinations

Table S5. Analysis of dental alloys.

Alloy	Composition (%)	Amount of Au(III) taken, μg	Amount of Au(III) found*, μg	%E
Aurident-97	Au-97.7, Pt-2.0, Pd-0.0, Ag-0.0	200	198.23	99.1
Auribond-90	Au-90, Pt-5.8, Pd-1.6, Ag-1.2	200	199.77	99.9
Elite II	Au-88.0, Pt-9.5, Pd-0.0, Ag-0.75	200	199.24	99.6
WINDSOR	Au-75.5, Pt-0.1, Pd-12.0, Ag-10.1	200	199.25	99.6
SUMMIT	Au-74.2, Pt-4.1, Pd-7.3, Ag-11.0	200	197.77	98.9
Auritex WP	Au-62.2, Pt-0.1, Pd-23.4, Ag-8.25	200	200.0	100.0
Auritex XP	Au-51.8, Pt-0.1, Pd-38.0, Ag-0.0	200	198.46	99.2

I] Aurident porcelain alloys

% E = Percentage extraction,

*Average of five determinations

Alloy	Composition (%)	Amount of Au(III) taken, μg	Amount of Au(III) found*, μg	%E
AM -II	Au-77.5, Pt-1.74, Pd-0.0, Ag-12.25	200	200.0	100.0
RM-II	Au-65.0, Pt-0.1, Pd-1.9, Ag-24.5	200	199.25	99.6
RH-II	Au-75.5, Pt-1.15, Pd-2.25, Ag-10.24	200	198.50	99.3
LH-II	Au-20.0, Pt-0.0, Pd-20.0, Ag-41.0	200	197.83	98.9
EH-II	Au-52.8, Pt-0.1, Pd-4.8, Ag-31.6	200	198.28	99.1

II] Casting gold alloys.

%E = Percentage extraction

*Average of five determinations

Table S6. Analysis of ayurvedic samples.

Samples	Certified value of Au(III), mg	Amount found by AAS, mg	Amount found by proposed method*, mg	RSD %
Brahmi Vati	0.120	0.130	0.132	0.54
Vasant Kusumakar Rasa	0.117	0.110	0.108	0.82
Brihat Shwas Chintamani Rasa,	0.151	0.140	0.137	1.50
Suvarna Sootshekhar Rasa No.-1.	0.146	0.135	0.135	0.10

*Average of five determination

RSD = Relative standard deviation

Supporting Information
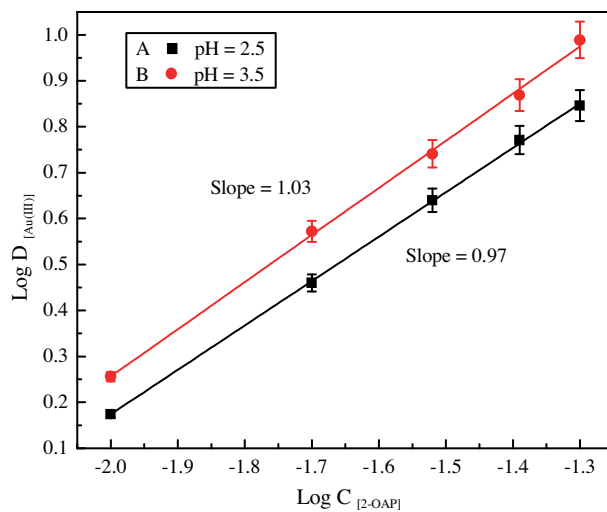
Figure S1. Log-Log plot of Log $D_{[Au(III)]}$ versus Log $C_{[2-OAP]}$. Condition: A. Au(III) = 200 μg, pH = 2.5, sodium malonate = 0.03 M, aq.:org.= 2.5:1, equilibrium time = 5.0 min, strippant = 7.0 M ammonia. B. Au(III) = 200 μg, pH = 3.5, sodium malonate = 0.03 M, aq.:org.= 2.5:1, equilibrium time = 5.0 min, strippant = 7.0 M ammonia.
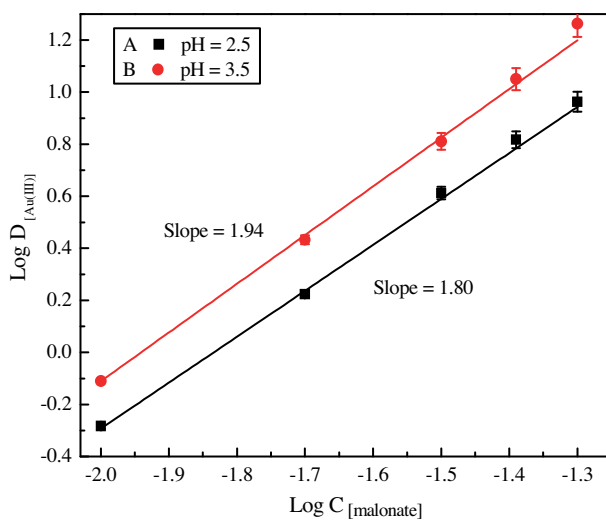
Figure S2. Log-Log plot of Log $D_{[Au(III)]}$ versus Log $C_{[malonate]}$. Condition: A. Au(III) = 200 μg, pH = 2.5, aq.:org.= 2.5:1, 2-OAP = 0.05 M in xylene, equilibrium time = 5.0 min, strippant = 7.0 M ammonia. B. Au(III) = 200 μg, pH = 3.5, aq.:org.= 2.5:1, 2-OAP = 0.05 M in xylene, equilibrium time = 5.0 min, strippant = 7.0 M ammonia.
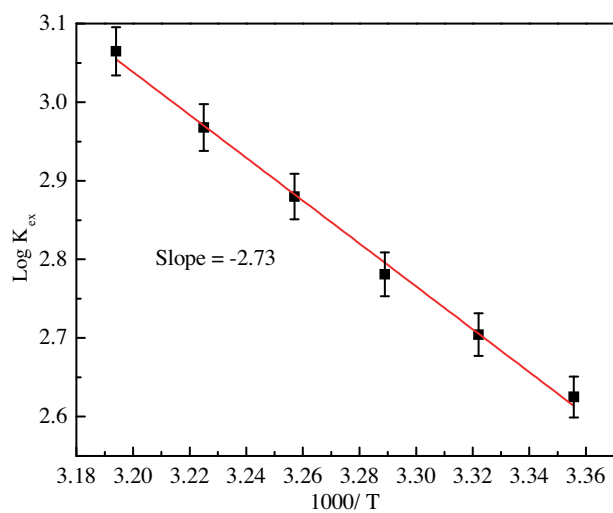
Figure S3. Influence of temperature on extraction of Au(III). Condition: Au(III) = 200 μg, pH = 3.0, sodium malonate = 0.03 M, aq.:org.= 2.5:1, 2-OAP = 0.05 M in xylene, equilibrium time = 5.0 min, strippant = 7.0 M ammonia.