



## SYNERGISTIC EXTRACTION OF SILVER FROM NITRIC ACID MEDIUM WITH DITHIZONE IN THE PRESENCE OF A SECONDARY AMINE- AMBERLITE LA-2 USING $^{110m}\text{Ag}$ -RADIOISOTOPE

Madhusudan Mandal Ph.D.

Mahadevananda Mahavidyalaya Kolkata, West Bengal, India, m\_mandal01@yahoo.com

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## SYNERGISTIC EXTRACTION OF SILVER FROM NITRIC ACID MEDIUM WITH DITHIZONE IN THE PRESENCE OF A SECONDARY AMINE- AMBERLITE LA-2 USING $^{110}\text{mAg}$ -RADIOISOTOPE

### Abstract

Synergistic extraction of silver has been investigated in the presence of two different kinds of extractants, one of which is a chelating ligand, dithizone and the other is a long-chain secondary amine amberlite LA-2 at pH 3.0 using a radiotracer technique. The apparent formation constant, overall equilibrium constant and adduct formation constants were calculated from distribution coefficients. Interestingly, it was observed that the adduct formation constant is too high when the ligand concentration is increased by keeping the amine concentration fixed at 0.044 M compared to that obtained when the ligand concentration is kept fixed at  $8.74 \times 10^{-4}$  M.

### Keywords

Dithizone-Amberlite LA-2, Radiotracer technique, Silver, Synergistic extraction

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## 1. Introduction

The properties of metal silver have made it a valuable one and it has been in demand for as long as humans have known about it [1]. A diluted solution of silver nitrate and other compounds of silver have the properties to be used as disinfectants and micro-biocides. Antibacterial activity and the mechanism of action of the silver ion in *Staphylococcus aureus* and *Escherichia coli* have also been reported [2,3]. Recently, the antitumor activity of Ag-nanoparticles against various cancerous cell lines has emerged as a prospective application in therapeutics [4]. Silver is present in nature not only as different ores but also as impurities in micro quantities in different ores, and in photoglyphical slag. Consequently, the development of sensitive and selective method for determination and separation of silver forms an important research area. Various methods have been used for the determination of silver including AAS [5], high-resolution continuum source flame atomic absorption spectrometry (HR-CS-FAAS) (e.g., trace amount of silver in *Rhodococcus ruber* bacterial biomass has been determined by this method [6]), a spectrophotometric method [7,8], surface-enhanced Raman spectroscopy (for determination of silver nanoparticles [9]), ICPMS [10], electroanalysis [11,12], solvent extraction using bis-triazine-bipyridine, LIX 7950 etc. [13,14], isotope dilution analysis [15–18], potentiometric methods by using well-tailored ion-selective electrodes [19] etc. Silver (I) has also been determined by stripping voltammetry [20,21], and electrochemical methods [22]. Ultra-trace analysis of silver and platinum has been done by ICP-SFMS [23]. Silver has been separated from bismuth melt in a centrifugal separator with zinc as an additive [24]. A sono-cyanidation process has been used to extract silver from refractory silver ore [25]. The reagent N, N, N', N'-tetraoctyl-thio-diglycolamide has been used to extract silver [26]. However, the body of literature reports available for synergistic extraction of silver is only sparse. For example, synergistic extraction of silver (I) by using 2-hydroxy-1-naphthaldehyde thiosemicarbazone and Neutral Oxygen Donor compounds has been reported by Fleitlikh et al. [27], and by spectrophotometric method using 1-(2',4'-dinitro aminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol has been reported by Kamble et al. [28]. Chromatographic separation of silver in micro quantities using TODGA

(N,N,N',N'-tetraoctyl diglycolamide) -impregnated silica gel has been reported earlier from our laboratory [29]. A synergistic study on the extraction of silver in a green approach has also been reported by Nag et al. [30].

However, most of the methods have the drawbacks of tedious sample manipulation and the level of accuracy in the measurement technique due to the presence of foreign species in the rock samples or other complex matrices of silver. Thus, a rapid and sensitive method, which will face minimum sample manipulation and least interferences in the analysis, is required for the quantitative extraction and determination of the trace amount of silver present in rock samples. The present radiochemical method of synergistic extraction will provide us with a more accurate result. Besides, the results may enable one to explore the coordination chemistry of silver in terms of metal ligand bonding.

The phenomenon whereby two extractants in combination extract a species, mostly metal ions, with greater efficiency than that corresponding to their individual additive action, is described as synergism. The large enhancement of metal extraction has been widely investigated from a theoretical, analytical as well as from an applied point of view. In our present investigation we used a chelating ligand, dithizone accompanied by a long-chain secondary amine-amberlite LA-2 for the synergistic extraction of silver. Such type of combination is somewhat less frequently explored in this widely studied field of solvent extraction chemistry. However, the chelating ligand, dithizone has been used to extract silver by many authors [31,32]. The method is of particular interest for the extraction of precious metal ions like silver (I) on a tracer scale and can be applied to extract silver (I) from complex matrices with enhanced efficiency.

## 2. Experimental

### 2.1. Reagents and solutions

The extracting agents, dithizone (Fig. 1) and secondary amine, amberlite LA-2 (Fig. 2) were purchased from Aldrich (USA) and used as received. Different organic solvents, silver nitrate and other reagents used in this work were of AR grade. A stock solution (0.02M) of silver was prepared by dissolving ~0.170 g AgNO<sub>3</sub> (AR Grade) in 50 mL deionized water containing very little HNO<sub>3</sub>. 10 mL of this solution was

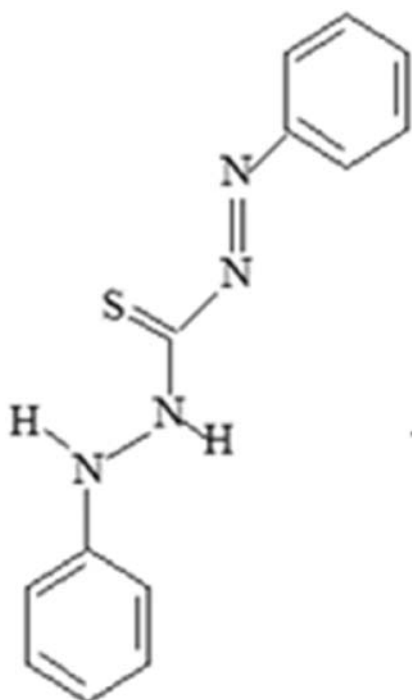


Fig. 1. Dithizone [1,5-Diphenylthiocarbazono].

diluted to 100 mL after prior addition of carrier free  $^{110m}\text{AgNO}_3$  solution to prepare a working stock solution of silver (I). The concentration of the final spiked working solution became 2 mM. The radioisotope,  $^{110m}\text{Ag}$  having  $\gamma$ -photo peak of energy, 667 keV procured from BRIT, India in the form of  $\text{AgNO}_3$ . 1 mL of this spiked solution contains 215.9  $\mu\text{g}$  of Ag (I).

## 2.2. Instruments

A digital pH-meter (Systronics, Model 335, Made in India) equipped with a single electrode was used for the measurements of pH of the solution and a single channel  $\gamma$ -ray spectrometer coupled with a well-type NaI(Tl) detector of Nucleonix, India was used for the measurement of radioactivity.

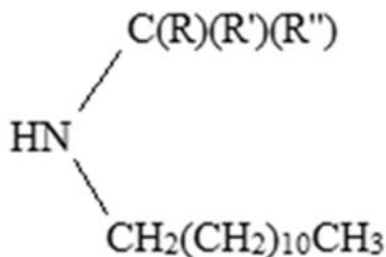


Fig. 2. Amberlite LA-2 [N-lauryl-N-trialkyl-methylamine].

## 2.3. Work safety

An integrated and consistent set of safety measures have been adopted to ensure the personal protection and the protection of the environment. Proper training was carried out prior to handling radioactive materials and before working in the dedicated nuclear chemistry laboratory. Safety measures have been followed strictly, including the wearing of appropriate lab-attire and the appropriate disposal of the radioactive waste.

## 2.4. Extraction procedures

The time of equilibration was prefixed to 10 min by preliminary experiment. An increase in pH was found to result in an increased effect on extraction, but at higher pH the extraction was sharply decreased, and the optimum pH was found to be 3.0. The decrease of extraction of silver at higher pH may be due to the hydrolysis of silver. So, to suppress the possible hydrolysis of silver at higher pH, subsequent extractions were carried out at pH 3. Extraction of silver was carried out with different solvents like chloroform, carbon tetra chloride, ethyl acetate, n-butanol, isoamyl acetate, MIBK and amyl alcohol and measured the corresponding distribution coefficient ( $K_D$ ) values. The order of the  $K_D$  values were found to be-  $\text{CCl}_4$  (11.06)  $\sim$   $\text{CHCl}_3$  (11.20)  $>$  amyl alcohol (7.33)  $>$  MIBK (6.56)  $>$  n-butanol (1.98)  $>$  ethyl acetate (1.82)  $>$  isoamyl acetate (1.04). Thus,  $\text{CCl}_4$  and  $\text{CHCl}_3$  were found to be the good diluents for this particular extraction. However, in this work,  $\text{CCl}_4$  has been preferably used for subsequent extractions as  $\text{CHCl}_3$  is more volatile than  $\text{CCl}_4$ . In the general synergistic extraction procedure, 5 mL solution of  $\text{AgNO}_3$  (1 mL 2 mM spiked  $\text{AgNO}_3$  solution diluted to 5 mL maintaining pH 3 of the aqueous phase) was extracted with a 5 mL organic solution of  $\text{CCl}_4$  with dithizone and amberlite LA-2 (1 mL  $8.74 \times 10^{-4}$  M dithizone + 1 mL 0.044 M amberlite LA2 + 3 mL  $\text{CCl}_4$ ). After equilibration, activities of both the organic and aqueous phases were measured for computation of distribution coefficient.

## 2.5. Calibration curve

To determine silver in unknown sample a calibration curve was required. For this purpose, different amounts of inactive silver (0–129.54  $\mu\text{g}$ ) were mixed with  $\sim 216$   $\mu\text{g}$  silver, spiked with  $^{110m}\text{Ag}$  in 5 mL aqueous phase at pH 3 and then extracted with 5 mL organic phase containing 1 mL  $8.74 \times 10^{-4}$  M

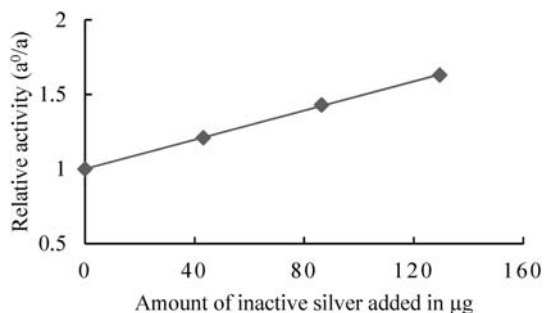


Fig. 3. Calibration curve for the extraction of silver.

dithizone and 1 mL 0.044M amberlite LA-2. The activity of 1 mL organic phase of each extraction was measured in absence of any inactive silver which is represented as  $a^0$  and in presence of different amount of inactive silver, the activity of which is represented by 'a'. The relative activity ( $a^0/a$ ) was plotted against the amount of inactive silver (Fig. 3). The linearity of the calibration curve was found to be deviated beyond addition of 129.54 µg inactive silver. Thus, the detection limit in the present investigation for the extraction silver from any matrix was found to be 129.54 µg silver (I).

### 2.6. Application of this method in the analysis of silver in rock samples

The proposed method of synergistic extraction of silver by the mixture of reagents has been employed for the determination of silver in rock samples of Rajapura and Machiamagra locality, India, obtainable from the Geological Survey of India. The rock samples

consisted of Ni-phosphate (major) and traces of silver with a few rare metals. The method of analysis of the rock samples was carried out as described by Mandal et al. [18] and Das et al. [33]. The samples were first weighed and then subjected to digestion with 60%  $\text{HNO}_3$ . The clear solutions were evaporated nearly to dryness. The residue was dissolved in deionised water containing  $\text{HNO}_3$  and the pH was adjusted to 3.1 mL solution of each of rock samples were mixed with 215.9 µg of silver, spiked with  $^{110\text{m}}\text{Ag}$  and 1 mL 0.01 M EDTA to suppress any possible interferences by the foreign metals present in the rock samples finally diluted to 5 mL adjusting the pH to 3, then extracted with 5 mL organic phase containing 1 mL  $8.74 \times 10^{-4}$  M dithizone and 1 mL 0.044 M amberlite LA-2 in  $\text{CCl}_4$ . After equilibration, the activity of 1 mL organic phase of each extraction was measured, say 'a'. The same procedure was followed to extract active silver in the absence of unknown rock sample solution, and the activity of the organic phase was denoted by ' $a^0$ '. From the value of  $a^0/a$  in the calibration plot, the amount of unknown silver present in the rock samples was measured.

## 3. Results and discussions

### 3.1. Effect of equilibration time

The time of equilibration was prefixed by measuring the activity of organic phases of a series of extractions of a fixed amount of aqueous Ag (I) solution by the same amount of chelating ligand, dithizone and amberlite LA-2 in  $\text{CCl}_4$  at different time intervals from 1 min to 20 min (Table 1). The activity was found to

Table 1

Effect of equilibration time in the extraction of Ag(I): Aqueous phase: ~216 µg of spiked silver in 5 mL pH 3 solution. Organic phase: 5 mL (1 mL  $8.74 \times 10^{-4}$  M dithizone + 1 mL 0.044M amberlite LA-2 + 3mL $\text{CCl}_4$ ).

Time of extraction (minute)	Activity of organic phase (Counts/60 s)	% Extraction
1	1037	11.8
4	4955	56.4
7	6278	71.5
10	6610	75.3
13	6592	75.1
15	6618	75.4
20	6575	74.9

Table 2

Extraction of silver(I) by dithizone [2(a)] and Amberlite LA-2[2(b)].

2(a)	Conc. of dithizone [M]	$4.37 \times 10^{-4}$	$8.74 \times 10^{-4}$	$13.11 \times 10^{-4}$	$17.48 \times 10^{-4}$
	$D_A$	0.28700	0.86200	1.91600	4.96300
2(b)	Conc. of Amine [M]	0.02200	0.04400	0.06600	0.08800
	$D_B$	0.00808	0.01120	0.02200	0.01700

Table 3

Synergistic extraction of silver by mixture of dithizone and amberlite LA-2 at a fixed concentration of dithizone: pH = 3, Conc. of dithizone =  $8.74 \times 10^{-4}$  M,  $D_A = 0.862$  ( $D_A$  = distribution coefficient in presence of pure dithizone).

Conc. of amine (B) [M]	log[B]	$D_B$	$D_{mix}$	log $D_{mix}$	$\Sigma D$	$\Delta D$	log $\Delta D$	S.C	$\beta$
0.022	-1.6576	0.0081	1.1876	0.0746	0.8702	0.3256	-0.4873	0.135	17.17
0.044	-1.3565	0.0112	3.062	.04860	0.8737	2.200	0.3424	0.545	58.00
0.066	-1.1805	0.0220	4.570	0.6599	0.8841	3.705	0.5688	0.713	65.17
0.088	-1.0555	0.0170	8.320	0.9201	0.8791	7.450	0.8722	0.976	98.32

Where,  $\Sigma D = D_A + D_B$ ,  $\Delta D = D_{mix} - D_A$ , S.C =  $\log D_{mix}/(D_A + D_B)$  and  $\beta = \Delta D/D_A[\text{amine}]$ .

Table 4

Synergistic extraction of silver by mixture of dithizone and amberlite LA-2 at a fixed concentration of amine: Conc. of amine = 0.044 M,  $D_B = 0.01124$  ( $D_B$  = distribution co-efficient in presence of pure amine), pH = 3.

Conc. of dithizone [M]	log [HDz]	$D_A$	$D_{mix}$	log $D_{mix}$	$\Sigma D$	$\Delta D$	Log $\Delta D$	S.C	$\beta$
$4.37 \times 10^{-4}$	-3.3595	0.287	1.667	0.2219	0.2982	1.656	0.219	0.747	$3.37 \times 10^5$
$8.74 \times 10^{-4}$	-3.0585	0.862	3.062	0.4860	0.8732	3.051	0.484	0.545	$3.11 \times 10^5$
$13.11 \times 10^{-4}$	-2.8824	1.916	5.328	0.7266	1.9272	5.317	0.726	0.442	$3.61 \times 10^5$
$17.48 \times 10^{-4}$	-2.7575	4.964	11.061	1.0438	4.9752	11.05	1.043	0.347	$5.62 \times 10^5$

Where,  $\Sigma D = D_A + D_B$ ,  $\Delta D = D_{mix} - D_B$ , S.C =  $\log D_{mix}/(D_A + D_B)$  and  $\beta = \Delta D/D_B[\text{dithizone}]$ .

remain same for all organic phases after 10 min. So, the equilibration time was fixed at 10 min for all the extractions.

### 3.2. Variation of ligand and donor concentrations

Silver was extracted under different concentrations of dithizone in  $\text{CCl}_4$  ( $4.37$ – $17.48 \times 10^{-4}$  M) from an aqueous solution of pH 3.0 and distribution coefficients were found to increase with the increase in concentration of dithizone (Table 2a). The same trend was observed for donor amine except one data point as shown in Table 2b.

### 3.3. Extraction of silver (I) by the mixture of dithizone and amberlite LA-2

Dithizone is a versatile bidentate chelating ligand capable of forming well defined metal complexes [34] soluble in organic solvents. On the other hand, Amberlite LA-2 is a high molecular weight secondary amine [35] and is known to extract anionic metal complexes [36] in a strongly acid solution. However, dithizone, because of its dissociation as  $\text{HDz} \rightleftharpoons \text{H}^+ + \text{Dz}^-$ , acts as a better reagent at higher pH (low acid concentration). Under such conditions, the lone pair of nitrogen of secondary amine group may be used

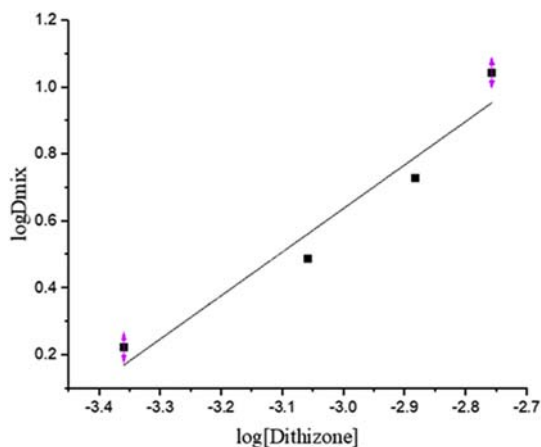


Fig. 4. Plot of  $\log D_{mix}$  of Ag(I) against  $\log[\text{dithizone}]M$ .

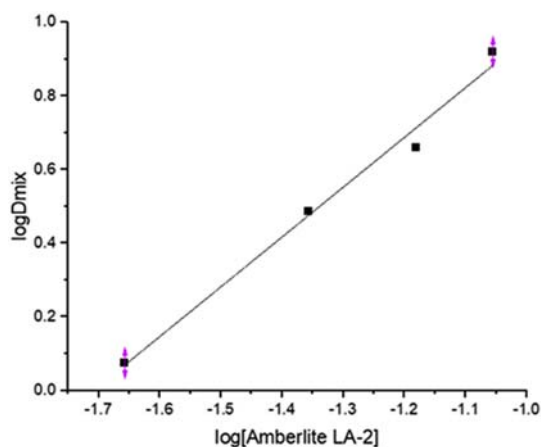


Fig. 5. Plot of  $\log D_{mix}$  of Ag(I) against  $\log[\text{Amberlite LA-2}]M$ .

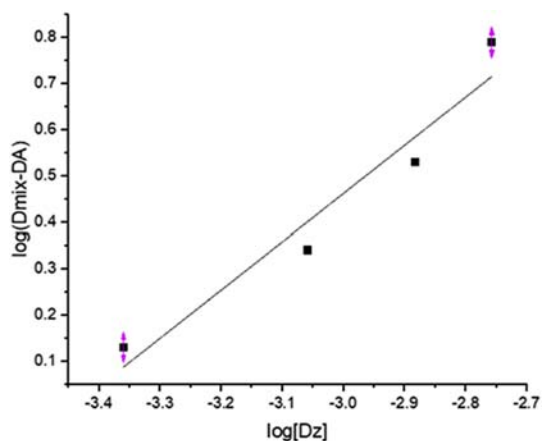


Fig. 6. Plot of  $\log(D_{\text{mix}} - D_A)$  against  $\log[\text{HDz}]$ .

to donate, rendering itself as a basic donor which is responsible for the synergism in silver extraction. The interference study had also been carried out in presence of various metal ions. Under the given condition, Zn (II) and Hg (II) strongly interfere the extraction of silver (I) but in presence of EDTA (ethylene diamine tetra acetic acid) no interference was observed in the extraction of silver (I) in presence of Zn (II). So, before extraction of silver from any complex matrix, it is to be confirmed that the sample does not contain any mercury.

### 3.4. Synergistic extraction

Extraction of Ag (I) from acidic aqueous solution (pH 3.0) was performed separately with the ligand only, the donor only, and also in the presence of both the ligand and the donor. In each extraction the

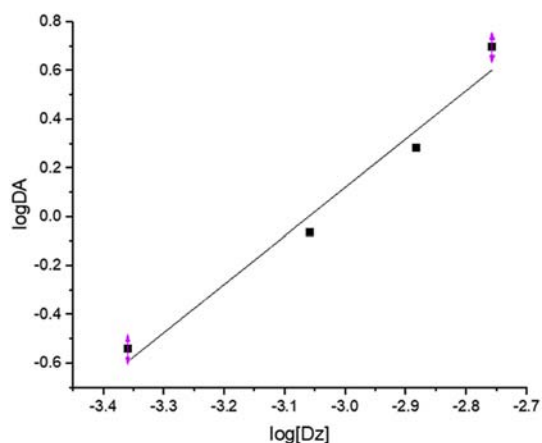
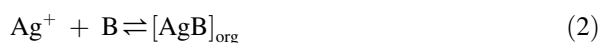


Fig. 7. Plot of  $\log D_A$  against  $\log[\text{HDz}]$ .

distribution coefficient values were measured. The effect of variation of donor concentration at a fixed ligand concentration ( $8.74 \times 10^{-4}$  M) was studied to have the  $D_{\text{mix}}$  value (Table 3) and at the same time variation of ligand concentration was also studied at a fixed donor concentration (0.044 M) (Table 4). Though higher distribution coefficient values were obtained with higher concentration of ligands and donor as well, the extraction was carried out with substoichiometric amount of ligand and donor to avoid possible interferences out of foreign metals. The values of  $\Delta D = (D_{\text{mix}} - \Sigma D)$ , Synergistic coefficient (S.C.) and apparent stability constants ( $\beta$ ) are reported in Tables 3 and 4, which show a clear identification of synergism. There is systematic variation of S.C. against amine concentration as shown in Table 3. The nature of mixed adduct was studied from log–log plot of distribution coefficient ( $D_{\text{mix}}$ ) against ligand concentration (Fig. 4) and against amberlite concentration (Fig. 5). For Fig. 4, the slope, intercept and  $R^2$  were found to be 1.30215, 4.54489 and 0.94359 respectively. The above values for Fig. 5 were found to be 1.35205, 2.30974 and 0.98828 respectively. The slopes being close to unity in both the cases. Hence it may be concluded that a 1:1 complex is responsible for the extraction of silver.

### 3.5. Calculation of equilibrium constant

The extraction of Ag(I) into  $\text{CCl}_4$  in the presence of only dithizone (HDz) and in the presence of amberlite LA-2 (Secondary amine, B) takes place as



Coefficients of HDz and B have already been determined by the slope ratio analysis, so that,

$$K_1 = \frac{[\text{Ag}(\text{Dz})]_{\text{org}}[\text{H}^+]}{[\text{Ag}^+]_{\text{aq}}[\text{HDz}]} = D_A \cdot [\text{H}^+] / [\text{HDz}] \quad (3)$$

Overall synergistic extraction does not involve any dissociation of dithizone, as the metal can accommodate only two ligands in its co-ordination sphere. i.e.,  $\text{Ag}^+ + \text{HDz} + \text{B} \rightleftharpoons [\text{Ag}(\text{Dz})(\text{B})]_{\text{org}} + \text{H}^+$

Table 5

Equilibrium constant and adduct formation constant for silver complex.

Overall constant(K)	Adduct formation constant
59.88	$2.09 \times 10^4$



Table 6  
Analysis of silver in rock samples obtained from Geological Survey of India.

Rock samples	Amount of samples in mg	Amount of silver present ( $\mu\text{g}$ ) (By AAS method)	Amount of silver obtained by isotope dilution technique	Amount of silver found (in $\mu\text{g}$ ) <sup>a</sup> (Present method)
Rock-I	500	108.5	106 $\pm$ 1.73	107.2 $\pm$ 0.71
Rock-II	500	112.5	109 $\pm$ 1.40	111.6 $\pm$ 1.20

<sup>a</sup> Results of triplicate analysis.

$$K = \frac{[\text{Ag}(\text{Dz})(\text{B})]_{\text{org}}[\text{H}^+]}{[\text{Ag}^+][\text{HDz}][\text{B}]} \quad (4)$$

$$D_m = \frac{[\text{Ag}(\text{Dz})(\text{B})]_{\text{org}} + [\text{Ag}(\text{Dz})]_{\text{org}}}{[\text{Ag}^+]_{\text{aq}}} \quad (5)$$

$$D_m - D_A = K[\text{Dz}][\text{B}]/[\text{H}^+]$$

$$\text{Or, } \log(D_m - D_A) = \log[\text{Dz}] + \log K + \log[\text{B}] - \log[\text{H}^+] \quad (6)$$

Thus, a plot of  $\log(D_m - D_A)$  vs.  $\log[\text{HDz}]$  at a fixed amberlite concentration will result in a straight line having intercept =  $\log K + \log[\text{B}] + \text{pH}$  (Fig. 6, from the plot the slope, intercept and  $R^2$  was found to be  $1.04269 \pm 0.18626$ ,  $3.59065 \pm 0.56305$  and  $0.94001$  respectively) from which the overall equilibrium constant of the reaction ( $K$ ) can be evaluated. Also,  $K$  can be obtained from the plot of  $\log D_A$  Vs.  $\log[\text{HDz}]$  (Fig. 7). From Fig. 7, the slope, intercept and  $R^2$  were found to be  $1.98533$ ,  $6.07772$  and  $0.97423$  respectively. The adduct formation constant  $K_{\text{add}}$  can be evaluated as  $K_{\text{add}} = K/K_1$  and the apparent adduct formation constant ( $\beta$ ) can be calculated by the relation,  $\beta = \Delta D/D_A[\text{donor}]$ . The results have been summarized in Table 5.

#### 4. Conclusion

The results of the present study show that the extraction of silver is greatly enhanced by the combination of dithizone with amberlite LA-2 at pH 3.0 and the method can thus be applied for effective extraction of silver from real samples under suitable conditions. Moreover, the present technique is superior to other techniques because the radiochemical method is highly sensitive, fast and the simplest measurement technique capable of measuring trace and ultra-trace amount of analyte. This technique suffers the least interference in measurement as it measures only the radioactivity.

Therefore, the requires least sample manipulation during analysis of a complex matrix containing Ag (I). The method was applied to analyze real samples and the results (Table 6) obtained in the present technique were found to be very close to the results reported by Das et al. [33] by the AAS method and also by Mandal et al. [18] by the substoichiometric isotope dilution technique which established the validity of the present method.

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