An Equilibrium Study of Mercury Dithizonate Distribution in Carbon Tetrachloride-Natural Water System

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Summary: Based on high solubility of mercury dithizonate in carbon tetrachloride, a method is developed for the removal of mercury from natural waters. Quantitative study of the factors responsible for the establishment of equilibrium for the mercury dithizonate-carbon tetrachloride-natural water system is undertaken. The variables of the system studied include pH of the medium, equilibration time and the amount of the complexing reagent. Flameless atomic absorption and colorimetric methods under optimum conditions are applied for the estimation of mercury in the aqueous phase and the organic phase. The method is found to yield above 94% extraction of mercury in a single extraction step at 20°C. The method has the potential of application to industrial effluents for mercury removal.

Introduction

Health hazards of mercury and its compounds found in human environment are well known [1,2]. With increasing urbanization and industrialization, even natural water resources are not secured today from the ill-effects of mercury pollution. Thus, there is a need to develop and introduce analytical methods to extract/remove excessive amounts of mercury in various natural waters in direct or indirect human use. Currently, attempts aiming at detection of mercury at trace levels have brought in new analytical methods of high sensitivity. The colorimetric [3], neutron activation [4] emission spectrometric [5], and the atomic absorption methods [6,7] are most commonly employed to this effect. For the elimination of organic mercury compounds [8], photo-oxidation has been used extensively. Also atomic fluorescence technique has been advantageously used for the estimation of total mercury [9]. The fractional extraction of mercury compounds through thin-layer chromatography and complexation with sodium diethyldithiocarbamate as a pre-concentration process coupled with reduction/aeration were used to this effect for sea waters [10,11]. Gas chromatography/mercury detector [12] and potentiometric [13,14] procedures for mercury determination and subsequent removal are other popular methods. All these methods are highly specific in relation to the levels of mercury present in various waters. In addition, most involve multi-step operations.

During the present investigation an attempt has been made to evolve a method of general use to remove mercury from natural waters. Based on the ability of mercury to form mercury dithizonate complex in acidic medium, and the high solubility of the complex in carbon tetrachloride-water system. The distribution process is optimized as a function of pH of the medium, equilibration time and the amount of dithizone. The proposed method is applied to different natural waters for mercury removal. The aqueous phase pre-and post-extraction mercury content was estimated by the flameless atomic absorption method [15]. Parallel colorimetric absorption method was used for the estimation of the amount of mercury extracted into the organic phase, or for that matter, the amount of mercury removed from the aqueous phase. The lower detection limit achieved in the flameless method was 10 ng/1 mercury.

Distribution Equilibrium:

Thermodynamically the distribution of mercury dithizonate in carbon tetrachloride-water system is an ideal process involving the transfer of uncharged species across the two phases. The mercury complex is practically insoluble in water and behaves as a large organic molecule having high solubility in carbon tetrachloride. The distribution of mercury between the organic (o) and aqueous (aq) phase is characterized by the distribution coefficient, K, given by the ratio of the total amount of mercury in the organic phase to that in the aqueous phase. Thus,

$$K = \frac{Wo/Vo}{Waq/Vaq} = \frac{Co}{Caq} \quad \ldots(1)$$

It can be readily shown that the fraction, F, of mercury extracted is given by

$$F = \frac{Wo}{Wo + Waq} \quad \ldots\ldots(2)$$

or

$$F = \frac{K\ Vo}{KV_o + Vaq} = \frac{KVr}{1 + KVr} \quad (3)$$

where Vr is introduced as relative phase volume ratio. Consequently, the fraction of mercury remaining, L, is given by

$$L = \frac{1}{1 + KVr} \quad \ldots\ldots(4)$$

and the fraction at nth extraction step may be shown to be

$$Fn = \frac{KVr}{(1 + KVr)^n} \quad \ldots\ldots\ (5)$$

Application of the above equations to a real practical situation is quite straightforward. However, one basic prerequisite is the attainment of the relevant equilibrium. Normally, C_o and C_{aq} are linearly related if no dissociative/associative or charge transfer phenomenon is/are taking place within the distribution phases. Under a defined pH condition, F, is constant demanding that $K = f\ (V_r)$, as given by Equation (3). This means that the phase ratio must be kept constant for obtaining a constant F. Also, both rate of complexation and the amount of complex formed are pH dependent. Thus, the variables of the distribution system need to be defined in terms of pH, equilibration time and the amount of the reagent.

Experimental

Reagent Solution:

Dissolved 0.100g dithizone in 150 ml carbon tetrachloride in a 250 ml beaker. Filtered the deep-green solution into a 500 ml separating funnel, and extracted with two 100 ml portions of 0.10 N NH_4OH solution. Rejected the organic phase. The two aqueous phases were combined. Then 200 ml carbon tetrachloride was added, acidified with 10.0 ml 1N H_2SO_4, and vigorously shaken on an automatic shaker for two minutes. Separated the organic phase and washed it with distilled water. This transfer of dithizone from carbon tetrachloride to ammonia solution and back again was repeated until extraction with ammonia solution left a practically colourless organic phase. This gave the dithizone stock solution. Making 7 ml of this solution to 500 ml with carbon tetrachloride gave a solution of 25 µmole/l concentration. All solutions were stored in brown bottles and refrigerated.

Mercury Extraction:

To 50.0 ml aliquot of the water sample added enough 1 N H_2SO_4 to bring its pH to 4.5. Extracted this in a separating funnel with two 10.0 ml portions of the reagent solution so that the second extract remained green. This required a shaking time of 3 minutes on the autoshaker and settling of the two phases for 5 minutes. Preserved the organic phases separately. Centrifuged the aqueous phase at 3000 rpm for 10 minutes to separate any suspended organic phase. Estimated the mercury content of the extracted aqueous phase by the flameless atomic absorption method. Reagent/standard blanks were run through the same procedure. The collective organic phase was employed for the estimation of removed mercury colorimetrically. The absorptions were recorded at 480 nm in 2-cm cell after treating the organic phase thrice with 10.0 ml portions of ammonia water and then once with 10 ml 15% acetic acid. Carbon tetrachloride was used as the blank.

Results and Discussion

Table 1 summarizes the % extraction data based on the present extraction process. The aqueous-phase levels

Table-1: Pre-and Post-extraction Concentrations of Mercury in Aqueous Phase of Various Natural Waters

Sample Code	Sample Description/ Location,Nature	Estimated Mercury Level (µg/l) + 2S* Pre-extraction	Post-extraction	% Extraction
(S-1)	Well Water/R.Pindi Non-treated	0.85 ± 0.021	0.047 ± 0.002	94.5
(S-2)	Lake Water/R.Pindi Non-treated	1.222 ± 0.027	0.070 ± 0.002	94.0
(S-3)	Dam Water/Mangla, Non-treated	0.783 ± 0.030	0.040 ± 0.002	94.9
(S-4)	Spring Water/Murree, Non-treated	1.272 ± 0.049	0.072 ± 0.004	94.3
(S-5)	Spring Water/Plundri, Non-treated	1.532 ± 0.043	0.090 ± 0.005	94.3
(S-6)	Deep-Well Water/Sahala, Non-treated	0.620 ± 0.031	0.037 ± 0.002	94.0

* based on single-step extractions for triplicate runs.

of mercury appearing in Table 1 are quoted at ± 2S confidence level for triplicate measurements in each case.

The mercury dithiozonate complex, $HgDZ_2$, is a well known inner complex [16], formed readily in acidic medium alongwith the dithizonates of copper and bismuth. The mercury complex is practically insoluble in water, but readily soluble in non-polar solvents such as benzene and carbon tetrachloride. The complex is capable of existing as a stable species even at low pH values and once formed is very stable. The separation/extraction conditions of mercury in relation to other metals may be evolved under defined reaction conditions based on the partition of a given metal complex between the organic phase and the inorganic phase.

The variables of the distribution system of a metal dithizonate, in general, are the amount of the complexing reagent, pH of the medium and the equilibration time required. Figure 1 illustrates the functional dependence of percent extraction of the metal on the amount of dithizone. An examination of the figure reveals that this dependence is rather critical. A full 10-fold range of the amount of dithizone from 5 μmole/l CCl_4 to 50 μmole/l CCl_4 was examined to this effect. It turned out that 25 μmole/l is the optimum amount of dithizone yielding above 94% extraction of mercury. Beyond this amount of dithizone there is a gradual fall in the amount of mercury removed. This may be accounted for by assuming that any amount of dithizone in excess to 25 μmole/l creates a situation whereby the excess reagent undergoes a new equilibrium with respect to mercury.

The quantitative dependence of % F on pH is shown in Figure 2. Which, again, illustrates a substantial dependence of the extraction process on the pH of the medium. The extractions are less than 40% below pH 3, but then rise to approximately 100%

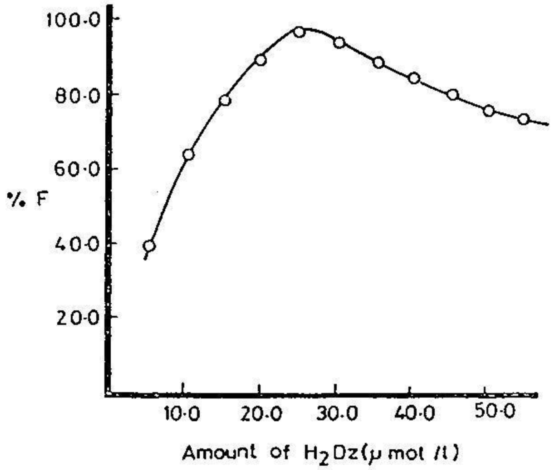

Fig.1: Dependence of % extraction on amount of dithiozone in CCl_4 solution for S-2.

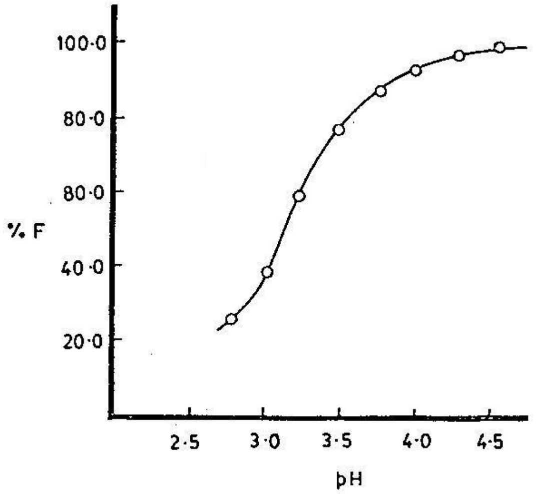

Fig.2: Typical pH dependence of percent extraction (%F) of mercury at 25 μmole/l dithizone concentration.

at pH 4.5. The present study when extended to other samples of waters reveals that for almost all natural waters a pH value of 4.0 or 4.5 is optimal for mercury extraction.

The mercury complexation process is found to be kinetically slow as prolonged manual shaking and subsequent standing of the two phases helped to yield higher per cent extraction (Figure 3). An automatic shaker was found to be a very helpful aid towards reducing the shaking plus stay time to about 8 minutes. Since the solubility of the complex is high in CCl_4, it may be inferred that the distribution coefficient for the system should have a large value demanding, within a valid approximation, that of the total metal bound in the form of uncharged chelate only a negligible amount will be left in the aqueous phase upon partitioning with carbon tetrachloride. This assumption greatly simplified the quantitative treatment of the system and is fully justified by the present work. For instance, the pre-and post-extraction data pertaining to the amount of mercury in the aqueous phase and the corresponding data for organic phase are plotted in Figure 4. The concentrations of mercury in the organic phase obtained by the colorimetric (Figure 5) and direct substraction of the pre- and post-extraction aqueous phase mercury

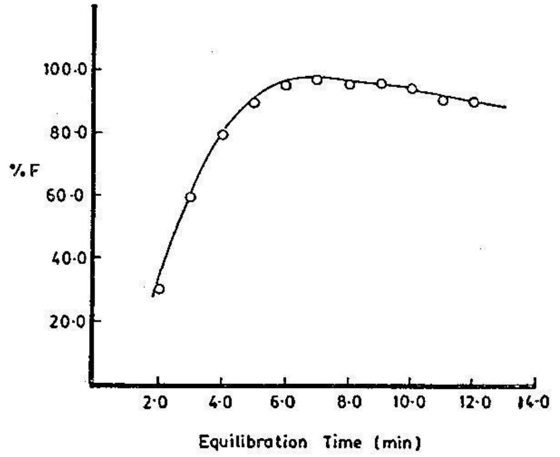

Fig.3: Equilibration time (shaking plus stay) Vs. %F.

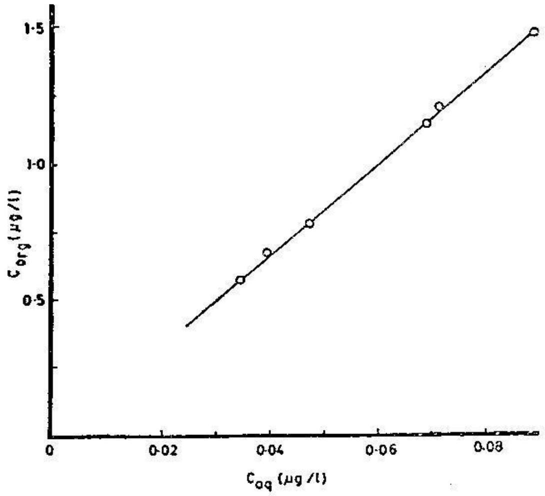

Fig.4: Mercury concentrations in aqueous and organic phases.

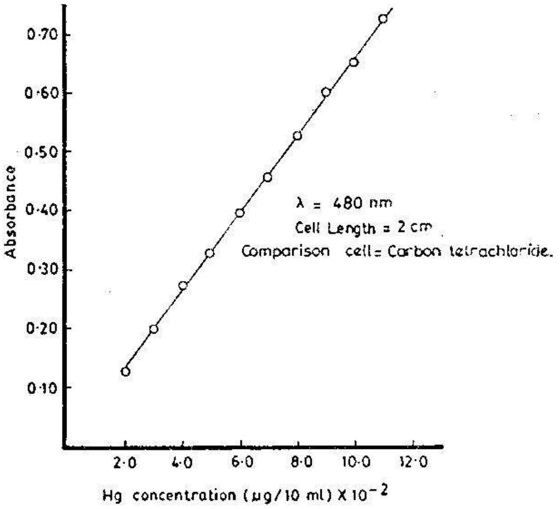

Fig.5: Standard colorimetric absorbance Vs. Hg concentration in organic phase.

contents agree within ± 5%. The linear relationship of Figure 4 demonstrates the presence of an ideal partition system having a K value of 81.5. The fraction of mercury extracted, F, is then given by: $F = KV_o/KV_o + V$, where V_o and V are the volumes of the organic and aqueous phases. Using known V_o, V and K values, F, is calculated to be 94.2% in agreement with the experimental data for a single-step extraction (Table 1). Thus, one-step extraction is found to be satisfactory for all practical purposes to effect above 94% removal of mercury form the aqueous phase. However, a second extraction step will help remove only 5.4% extra-mercury (Equation 5).

As discussed above the mercury dithizonate system is found to behave in a thermodynamically ideal way since the concentrations of mercury to be extracted from natural waters were low. In other words, the attainment of the distribution equilibrium was rather easy. Mercury extractions for other analytes would certainly demand slightly different equilibrium conditions in addition to the total amount of reagent to be used for governing not only the extent of complex formation but also the rate of complex formation.

In conclusion, the present investigation shows that the mercury dithizonate complex formation and its subsequent distribution from aqueous phase into the carbon tetrachloride phase is a promising method for the removal of mercury present at trace levels in various natural waters. As it is to be expected, the method has positive potential for application in case of those waters which have excessive mercury levels.

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References

1. J.P.Vernet and R.L.Thomas, *Eclogae Geol. Helv.*, **65**, *393 (1972).*
2. B.J.Mathis and T.F.Cummings, *J.W.P.C.F.*, **45**, *1573 (1973).*
3. E.B.Sandell: Colorimetric determination of traces of metals, 3rd ed. Interscience, N.Y. (1965).
4. H.V.Weiss and T.E.Crozier, *Anal.Chim.Acta*, **58**, *231 (1972).*
5. R.S.Braman, *Anal. Chem.*, **43**, *1462 (1971).*
6. W.Hatch and W.L.Ott, *Anal. Chem.*, **40**, *2085 (1968).*
7. G.W.Kalb, *At. Abs. New Letter*, **9**, *84 (1970).*
8. A.Seritti, A.Petrosin and R. Ferrar, *Environ. Technol. Letters*, **1**, *50 (1980).*
9. A.Seritti, A.Petrosino, *Anal.Chim.Acta*, **117**, *391 (1980).*
10. M.Fuzita, K.Iwashima, *Environ. Sci. Tech.*, **15**, *929 (1981).*
11. E.Yamagani, *Analyst*, **105**, *491 (1980).*
12. X.Zhang, X.G.Ren, *Huan Ching K'O Hsuch*, **1**, *34 (1980).*
13. S.Rubel and M.Lugowska, *Anal.Chim.Acta*, **115**, *343 (1980).*
14. S.Rubel and M.Lugowska, *ibid*, **115**, *349 (1980).*
15. M.Jaffar and M.Athar, *Pak.J.Sci.Ind.Res.*, **27(3)**, *June (1984).*
16. The Solvent Extraction of Metal Chelates, Ed. by H.Irving, Pergamon Press, (1974).