

## A COMPARATIVE STUDY OF VARIOUS COMPLEXING REAGENTS FOR THE SOLVENT EXTRACTION BASED REMOVAL OF MERCURY FROM NATURAL WATERS

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Using the ability of mercury to form inner complexes in acidic medium with a variety of reagents, the possibility for the use of a solvent extraction based method for the removal of mercury from natural waters is explored from the view point of reagent sensitivity and selectivity. The reagents used are dithiozone (HDZ), Thio-Michler's Ketone (TMK), 1,5-diphenylcarbazine (DPC) and 4-methoxy-2-(thiazolylazo) phenol (TAM). The isothermal extraction conditions are optimized in terms of variables such as matrix pH, equilibration time and amount of the reagent. The reagent-mercury equilibria are materialized by using carbon tetrachloride, iso-amyl alcohol, ethanol and benzene as solvents. The aqueous-phase mercury is estimated through flameless atomic absorption method while parallel organic phase mercury is quantified absorptiometrically. The method is applied for the extraction of mercury from various natural waters including well, spring and lake waters. The results show that maximum extraction (about 94 %) is achieved in a single-step extraction with HDZ and DPC, while the remaining reagents can go up to a maximum 78-82 % extraction. The data are reported at  $\pm 2S$  confidence level for triplicate runs. The method warrants potential of application of HDZ for the removal of Hg from natural, polluted and waste waters to render them suitable for specific analytical use demanding mercury concentrations at fraction of nanogram level.

**Key words:** Liquid-liquid extraction; Solvent extraction, Mercury removal by complexation.

### INTRODUCTION

Mercury contamination of the aquatic environment became a major subject of scientific investigation ever since the health hazards of mercury and its compounds found in human environment were established [1,2]. This led to the rapid development and introduction of several analytical methods of high selectivity and sensitivity for the detection of mercury at trace levels in natural waters. The most common method is based on the complexation, extraction and spectrophotometric detection of mercury [3], while others include the colorimetric [4], neutron activation [5] emission spectrometry [6], and the atomic absorption method [7,8,9]. Matsubara *et al.* [10] used the thioketone extraction based technique for the estimation and removal of mercury from waste waters. They used ethanol and dimethyl formamide as the solvents. An automated system for the determination of total mercury by cold-vapour atomic absorption method was developed by Goto *et al.* [11]. Preconcentration methods [12,13] also appeared for quantification of mercury in sea water. Bis (diethylthiocarbamate) copper in carbon tetrachloride was employed by Smejkal *et al.* [14] as a complexing reagent for mercury. A similar method based on preconcentration and extraction of mercury was propo-

sed by Lobanov *et al.* [15]. However, all these methods were designed for specific application to mercury estimation and removal from either waste water or sea water, and only a limited attention was given to natural waters containing excessive mercury content. It was thus felt desirable to introduce a general method for the extraction of mercury from natural waters based on its complexation with specific reagents.

Based on the ability of mercury to form complexes with many reagents in acidic medium, and their high solubility in different solvents, a comparative study of various partition equilibria was undertaken during the present investigation in terms of variables defining the complexation systems. The separation process in each case was optimized as a function of pH of the medium, equilibration time and the amount of the reagent. The investigation encompassed ten different surface, underground and spring waters, both treated and non-treated, for mercury extraction. The aqueous phase pre-and post-extraction mercury content was estimated by the flameless atomic absorption method [16]. Colorimetric absorption method was used as a parallel check for the amount of mercury in the organic phase, or for that matter, the amount of mercury removed.

## MATERIALS AND METHODS

Stock reagent solutions with a concentration of 200  $\mu$  mole/L were prepared by taking appropriate quantities of HDZ, TMK, DPC and TAM in carbon tetrachloride, iso-amyl alcohol, ethanol and benzene, respectively. The solutions were stored in brown bottles and refrigerated until use at room temperature. Working standards were prepared from the stock solutions by dilution with the respective solvents to the desired levels. Extraction of mercury from various natural waters was conducted by taking 50.0 mL aliquot of the water sample to which enough 0.5 M  $H_2SO_4$  was added to bring the pH to the desired level. The extraction pH for HDZ, TMK, DPC and TAM was maintained at pH 4.5, 3.0, 2.8 and 5.0 at  $\pm 0.2$  pH level. No buffers were used.

2 cm cells using the above mentioned solvents as blank at the following wavelengths: HDZ (480 nm); TMK (560 nm), DPC (540 nm); TAM (520 nm). All reagents used were of Merck origin and of ultra high purity spectroscopic grade. The water samples were collected during February through April, 1988, from sites given in Table 1 as per procedure given elsewhere [16].

## DISCUSSION

Table 1 summarizes the pre-and post-extraction mercury levels in various natural waters. The relevant data for other reagents are summarized in Fig. 2. Fig. 1 displays comparative percent recovery of mercury as a function of the amount of a given reagent while Fig. 2 shows a typical pH dependence of percent extraction. The levels of estima-

Table 1. Pre-and post extraction concentrations\* of mercury at  $\pm 2S$  level in various natural waters estimated by flameless atomic absorption method.

Sample code	Sample description**/location	Estimated mercury level ( $\mu\text{g/L}$ )		% Extraction
		Pre-extraction	Post-extraction	
S-1	Well water (Municipal supply, Rawalpindi)	0.780 $\pm$ 0.020	0.050 $\pm$ 0.003	93.6
S-2	Lake water (Rawal lake)	1.193 $\pm$ 0.025	0.072 $\pm$ 0.002	93.9
S-3	Lake water (Mangla lake)	0.613 $\pm$ 0.022	0.039 $\pm$ 0.003	93.6
S-4	Lake water (Samli lake)	0.813 $\pm$ 0.034	0.029 $\pm$ 0.004	96.4
S-5	Lake water (Tarbella lake)	0.613 $\pm$ 0.030	0.039 $\pm$ 0.003	93.7
S-6	Spring water (Murree hills)	1.370 $\pm$ 0.042	0.061 $\pm$ 0.004	95.5
S-7	Spring water (Plundri, AK)	1.902 $\pm$ 0.047	0.098 $\pm$ 0.005	94.8
S-8	Well water (Sahala)	0.513 $\pm$ 0.034	0.029 $\pm$ 0.003	94.3
S-9	Stream water (Salgaran)	1.387 $\pm$ 0.027	0.079 $\pm$ 0.004	94.3
S-10	Hot spring water (Mirpur, AK)	0.497 $\pm$ 0.020	0.028 $\pm$ 0.002	94.4

\*Based on single step extractions for triplicate runs. \*\*All samples are non-treated except S-2 and S-4.

Extractions were carried out by adding 10.0 mL of the reagent solution to the sample. The aqueous phase was centrifuged at 3000 rpm for 10 minutes to separate any suspended organic phase. Mercury content of the pre-and post extraction aqueous phase was estimated by the flameless atomic absorption method using Shimadzo Atomic Absorption Spectrophotometer, model AA-670 equipped with microprocessor based automatic background error correction. Reagent/standard solutions alongwith the blanks were run through the same procedure. The organic phase in each case was employed for parallel estimation of extracted mercury colorimetrically, using Hitachi Colorimeter, model 100-50. The absorptions were recorded in

ted mercury appearing in Table 1 are quoted at  $\pm 2S$  confidence level for triplicate measurements in each case. The lower limit of detection achieved for the flameless quantification of mercury is 10 ng/L, while it ranges from 0.01-0.02  $\mu\text{g/L}$  for the colorimetric method.

The mercury dithizonate complex,  $HgDZ_2$ , is a well known inner complex formed readily in acidic medium alongwith the dithizonates of copper and bismuth. The complex is readily soluble in non-polar solvents and is capable to exist as a stable species within a pH range of 4-4.5. The separation/extraction conditions of copper and bismuth in relation to mercury are governed in an alkaline medium based on the partition of the complexes between

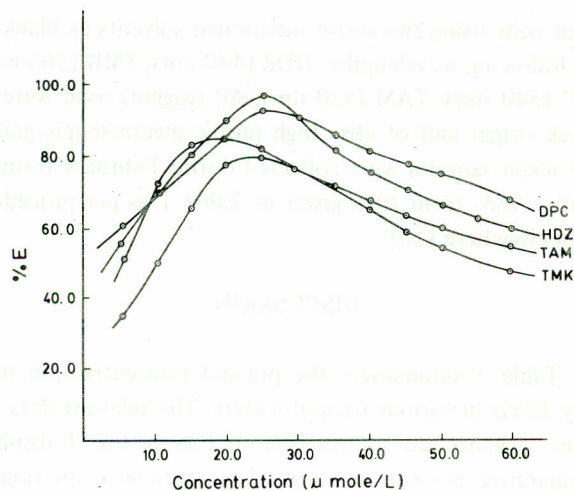


Fig. 1. Dependence of % Hg extraction on concentrations of various reagent solutions for S-6.

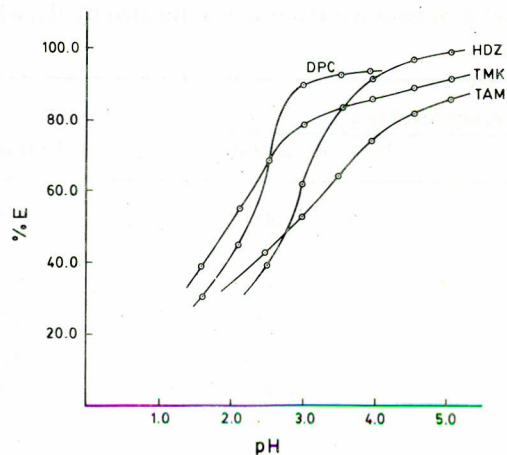


Fig. 2. Typical pH dependence of percent extraction (% E) of mercury at fixed amounts of various reagents.

the organic and inorganic phase. The TMK forms a purple mercury complex soluble in iso-amyl alcohol. The complex is formed at  $\text{pH } 3.0 \pm 0.2$ , while the palladium complex is formed at  $\text{pH } 3.5 \pm 0.2$ . As natural waters do not contain palladium above a fraction of a nanogram per litre, it was safely assumed that no palladium complex was formed at pH 3. The DPC yields a violet coloured mercury complex at  $\text{pH } 2.8 \pm 0.2$ . The complex, largely specific for mercury, is soluble in benzene. Similarly, TAM yields mercury complex at pH 5.0. The complex is readily soluble in benzene and carbon tetrachloride.

The variables of the mercury extraction system, namely the amount of the complexing reagent, pH of the medium and the equilibration time were studied quantitatively. Fig. 1 illustrates the functional dependence of percent extraction on the amount of the individual reagents.

An examination of the figure reveals that this dependence is rather critical. A full range of the amounts of the reagents from  $5.60 \mu\text{mole/L}$  was examined to this effect. It turned out that in case of HDZ,  $25 \mu\text{mole/L}$  is the optimum amount of dithiozone yielding above 94 % extraction of mercury in a single-step. In the case of TMK, although relatively less amount of the reagent is required for optimum complexation yet the single-step extraction is no better than 82 %. DPC lags a little behind HDZ in terms of its ability for complexation with the same range of reagent concentration and % extraction. The case of TAM is just comparable with TMK. This suggests that of the given reagents HDZ or DPC might be quite selectively used in preference to other reagents. However, the sensitivity certainly goes in favour of the former.

Fig. 2 shows the dependence of % extraction on pH of various extraction media. The plots illustrate a substantial dependence of the extraction process on the pH of an individual extraction medium. It may be seen that extractions are no better than 30 % upto pH 2 but then rise sharply between pH 3 and 4.5. This pH region is quite significant in that it provides maximum extraction. The present study reveals that for almost all the natural waters studied a pH value of 4.5 was found to be optimal for mercury extraction by HDZ.

The mercury complexation process is found to be kinetically slow as prolonged manual shaking and subsequent standing of the equilibrating phases yields higher percent extraction. A shaking time of 10 minutes on an automatic shaker was found to be adequate towards establishing the equilibrium.

The consistent extraction data listed in Table 1 indicate very large partition coefficient for the extraction equilibrium, warranting within a valid approximation, that of the total metal bound in the form of uncharged chelate only a negligible amount was left in the aqueous phase upon partitioning with carbon tetrachloride. The pre and post-extraction concentrations of mercury in the aqueous and organic phases might thus be expected to have linear inter-relationship to conform to an ideal linear partition system. In the case of other reagents, a non-linearity between the aqueous phase and organic phase concentration was met with. The mercury dithiozonate system thus may be taken as behaving in a thermodynamically ideal way.

The problem of interference in the HDZ extraction of mercury caused by other cations and anions was also investigated. Since natural waters contain variable amounts, not exceeding a few ppm level, of Zn, Cd, Co, Ni, Cu, Fe and Sn, and  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  at the same

levels, no interferences were caused by these entities towards complexation process. In fact even increasing their concentrations 10 times did not present any interference. The same was true about other reagents. In general,  $\text{Br}^-$ ,  $\text{CN}^-$  and  $\text{S}^{2-}$  interfere beyond 0.01M concentration since they complex mercury more strongly than the reagents.

In conclusion, the present investigation showed that HDZ is a better complexing reagent for mercury extraction as compared with the other reagents included in the study. The reagent warrants above 94 % removal of mercury from natural waters in a single-step extraction operation under defined conditions of extraction. Since the mercury content of natural waters is generally low as compared with polluted and waste waters, the method has a potential of application for the removal of mercury successfully and conveniently from these waters as well.

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