

Original research

Determination of Cd²⁺, Cu²⁺, Mn²⁺, Pb²⁺, and Zn²⁺ in Aqueous Solution after Their Separation and Preconcentration as Metal - Dithizone Complexes on Activated Carbon

S. M. N. Moalla¹, M. Nageeb Rashed², A. Abd El Aziz² and Marwa A. Maghazy^{2,*}

¹Chemistry Department, Faculty of Science, Port Said University, Port Said, Egypt

²Chemistry Department, Faculty of Science, Aswan University,
81528, Aswan, Egypt.

Received: 15/8/2020

Accepted: 24/11/2020

© Unit of Environmental Studies and Development, Aswan University

Abstract:

A simple and sensitive method for preconcentration and determination of Cd²⁺, Cu²⁺, Mn²⁺, Pb²⁺ and Zn²⁺ by flame atomic absorption spectrophotometer was developed. The method is based on the sorption of the studied elements as metal-dithizone complexes (M-DZ) on activated carbon (AC). The effect of various parameters (pH, shaking time, AC amount, ligand concentrations, eluent concentration, and solution volume) on quantitative sorption of metal-dithizone chelates using AC was investigated. The studied elements were eluted from AC simply with HNO₃ acid. The results revealed that the optimum pH values for the sorption were 4 for Cu²⁺, 6 for Zn²⁺, 8 for Pb²⁺ and 10 for Cd²⁺ and Mn²⁺; shaking time was 10 min for Mn²⁺ and Pb²⁺, 30 min for Cu²⁺ and Zn²⁺ and 50 min for Cd²⁺; AC amount was 0.2 g for Zn²⁺, 0.3 g for Cd²⁺, 0.5 g for Pb²⁺, 0.6 g for Mn²⁺ and 0.8 g for Cu²⁺; metal: ligand ratio was found to be (1:2 ratio), and eluent concentration used was 1 mol L⁻¹ for Cd²⁺ and Mn²⁺, 2 mol L⁻¹ for Zn²⁺ and 4 mol L⁻¹ for Cu²⁺ and Pb²⁺. The method can be applied with a preconcentration factor of 20 for Cd²⁺, and 40 for Cu²⁺, Mn²⁺, Pb²⁺, and Zn²⁺. Preconcentration from various water samples showed recovery in the range 95-108 %, confirming the effectiveness and precision of the solid-phase method developed using activated carbon for enrichment of metals examined.

Keywords: Preconcentration, Dithizone, Activated carbon, Trace metals

1- INTRODUCTION

Several heavy metals were results from human progress and their concentration increased in the environment. These metals have a lot of influences on the environment, and serious health problems (Marahel et al., 2011). To study their influences a good and accurate method was needed (Yin et al., 2005). The direct determination of trace amounts of these metals in environmental samples is beyond the scope of flame AAS which is a commonly used instrument technique because of its robustness, accuracy and cheapness (Thompson & Davidow, 2009)

Corresponding authors*: E-mail addresses: marwa_ch@aswu.edu.eg

Nevertheless, owing to some limitations, it has minimal sensitivity, which inhibits the trace level determination of metals (Tokalioglu et al., 2017). Thus, preconcentration methods capable of yielding high enrichment factors to bring the concentration levels of these metals within the scope of such instrument determination is required (Zhao et al., 2012; Zounr et al., 2018). Various methods of preconcentration techniques include solid-phase extraction (SPE), electrochemical methods (Yao et al., 2019), co-precipitation (Kagaya, 2016), membrane extraction (Bu et al., 2017), solvent extraction (Sorouraddin et al., 2020a) flame atomic absorption spectrometry (FAAS) (Er et al., 2013), graphite furnace atomic absorption spectrometry (GFAAS) (Soares & Nascentes, 2013), inductively coupled plasma-mass spectrometry (ICP-MS) (Javad et al., 2018) and inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Pilarczyk et al., 2013), have been used for settling the above problems. Among these methods solid-phase extraction is considered the best one because of the low consumption of solvents, short time consuming, high preconcentration factor, safety in use and the technique of the work was easy and simple (Zhou et al., 2014). Therefore the solid-phase extraction method was used for the preconcentration of heavy metals in real samples (Ghaedi et al., 2007).

Numerous SPE sorbents differ in affinity, selectivity and ability, which, in addition to their existence, depend on the physical and chemical properties of the analyte (Musile et al., 2018). Activated carbon (AC) has proven to be an outstanding collector for many trace metals among adsorbents used in metal pre-concentration due to its high adsorption ability, large micropore structure and a high degree of surface reactivity. (Alkherraz et al., 2020). Activated carbon not only micropores but also contains meso- and macropores which have a significant effect of transporting the adsorbed substances to the inside of the micropores (Feist & Mikula, 2014; Pradhan & Sandle, 1999). Since organic compounds are generally more effectively adsorbed on activated carbon than inorganic solutes, better results may be expected when the metal ions are chelated by organic ligands before the adsorption step (Daorattanachai et al., 2005).

Dithizone (diphenyl thiocarbazon) was an old ligand that can form complexes with heavy metals (Fan & Zhou, 2006; Ntoi et al., 2017). It considers a good ligand because of its structure contains both nitrogen and sulfur atoms which can form coordination bonds easily with heavy metals (Ntoi, 2016). The existence of the sulfur atom made the selectivity of the dithizone for heavy metals was high (Senkal et al., 2007).

The present study aims to preconcentration trace concentrations of Cd^{2+} , Cu^{2+} , Mn^{2+} , Pb^{2+} and Zn^{2+} ions using dithizone as a complexing agent and activated carbon as an adsorbent. The percent of the metal recovery was determined using atomic absorption spectrophotometer. The results obtained were applied to the preconcentration of study metals to various water samples.

2- MATERIALS AND METHODS

2.1- Instruments and Equipment's

A flame atomic absorption spectrophotometer (Model 3110 Perkin-Elmer) equipped with a digital and direct concentration readout and an air-acetylene burner was used for the element determinations. Single-element hollow cathode lamps and standard instrumental conditions were used for each element. The pH was measured with Orion Research Model SA211/Digital pH meter. For the preconcentration procedure, a wrist-action shaker (Burrell Corporation Scientific Instruments), oven furnace (Heraeus Instruments) and an electric balance (Denver instrument) were used.

2.2- Reagents and Standard solutions

All reagents used in this study were of analytical grade (A.R.). The stock standard solution of Cd^{2+} , Cu^{2+} , Mn^{2+} , Pb^{2+} and Zn^{2+} ($1000 \mu\text{g mL}^{-1}$) were prepared by dissolving each of $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ (2.26 g), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (3.9 g), $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (3.076 g), $\text{Pb}(\text{NO}_3)_2$ (1.598 g), and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (2.469 g) in 1000 mL double-distilled water. Working standard solutions were prepared daily by appropriate dilution with double-distilled water.

Buffer solutions of pH 2-10 were prepared by mixing the appropriate volumes of 0.04 N boric acid, 0.04 N acetic acid, 0.04 N phosphoric acid and 0.2 N NaOH solutions. The pH values were checked using Orion Research Model SA211/Digital pH meter. Concentrated nitric acid (65 %) and ammonia solution (33 %) were used.

A solution of $3.9 \times 10^{-3} \text{ mol L}^{-1}$ of dithizone (diphenylthiocarbazone) was prepared by dissolving 0.1g of the reagent in 100 mL of 0.1 M NH_4OH solution.

The activated carbon (Merck) was purified by treating with 3 M HCl and boiled for about 5 min to leach out trace elements that may be present as impurities. The mixture was filtered, washed with bi-distilled water and dried at 110°C .

2.3- General Preconcentration Procedure

All the sorption experiments were carried out by using the batch technique. An activated Carbon amount of 0.2- 1.0 g was equilibrated with a certain solution volume of various metals: ligand ratios in polyethylene bottles. The mixture was adjusted to values in the pH range 2-10 by the addition of a universal buffer solution. The mixture was shaken at room temperature for a predetermined time. The mixture was filtered through a double range filter paper (No. 102) which was washed with about 10 ml 4M nitric acid solution. The obtained metal solution was evaporated on a water bath to reduce the volume which finally made up to 5 mL and the metal concentration was determined using flame atomic absorption spectrometry (FAAS).

For all experiments, the percentages of metal recovery were calculated using the following equation:

$$\% \text{ Recovery} = \frac{C_f}{C_i} \times 100$$

Where C_f and C_i were the final and initial concentrations of the metals under study. The step details of the experiments are described below:

2.3.1- Effect of pH

Dithizone ligand was added in metal: ligand ratio of 1:2. The pH of the solution was adjusted to values in the pH range of 2, 4, 6, 8 and 10 using universal buffer solutions. One gram of activated carbon was added to the solution and then the mixture was shaken for 60 min. After filtration of the mixture, the adsorbed metal chelates were eluted from the activated carbon by 4M nitric acid. The obtained solution after recovery was reduced by evaporation to 5 mL and metal concentration was determined using FAAS.

2.3.2- Effect of Activated Carbon amount

The effect of variation of activated carbon amount on the adsorption efficiency of metal-dithizone complexes was investigated. The amount of activated carbon was varied from 0.2-1.0 g and equilibrated with 100 mL solution at metal: ligand ratio of 1:2. min. The pH of the solution was kept constant at pH 10 for Cd^{2+} and Mn^{2+} , 4 for Cu^{2+} & Zn^{2+} and 8 for Pb^{2+} . The mixture was

shaken for 60 min. and after filtration; the metal recovery was done by washing with 10 mL of 4 M HNO₃. The obtained solution was evaporated to 5 mL and metal concentration was determined using FAAS.

2.3.3- Effect of shaking time:

To 100 mL of metal: ligand solution, AC was kept constant at 0.3 g for Cd²⁺, 0.8 g for Cu²⁺, 0.6 g for Mn²⁺, 0.5 g for Pb²⁺ and 0.2 g for Zn²⁺. The shaking time was varied from 10 min to 60 min while the other parameters were kept constant. After filtration of the solution, the recovery was done by 10 mL of 4 M HNO₃. The obtained solution after recovery was reduced by evaporation to 5 mL and metal concentration was determined using FAAS.

2.3.4- Effect of metal: ligand ratio

The metal: ligand ratio was adjusted at the ratio of 1:1, 1:2 and 1:3 while pH, AC amount were kept constant. The mixture was shaken for 50 min for Cd²⁺; 30 min for Cu²⁺ and Zn²⁺; and 10 min for Mn²⁺ and Pb²⁺. After filtration of the solution, the recovery was done by 10 mL of 4M nitric acid solution. The obtained solution after recovery was evaporated to a volume of 5 ml and metal concentration was determined using AAS.

2.3.5- Effect of eluent concentration:

To 100 mL of metal: ligand solution of 1:2 ratio. The pH, AC amount and shaking time were kept constant. The recovery of the solution was done by 10 mL of HNO₃ acid concentration range: 1M - 6 M. The obtained solution after metal recovery was reduced by evaporation to 5 ml and metal concentration was determined using FAAS.

2.3.6- Effect of solution volume

To different volume (50 – 1000 mL) of the standard metal solution, dithizone was added in metal: ligand ratio of 1:2. The pH, AC amount, and shaking time were kept constant. The recovery of the metal was done by eluting with 10 mL of HNO₃ of concentration 1M for Cd²⁺ and Mn²⁺, 4M for Cu²⁺ and Pb²⁺, and 2M for Zn²⁺. The obtained solutions were reduced by evaporation to become 5 mL and metal concentration was determined using FAAS.

2.3.7- Effect of interference ions

Several metal ions can react with dithizone ligand but only the major cations (Ca²⁺, Mg²⁺, K⁺ and Na⁺) exist in the water sample were taken as interference. To 100 mL solution of Cd, Cu, Mn, Pb and Zn (0.1 ppm), the following concentrations of the interfering ions were added to each solution: 32 ppm Ca²⁺, 8 ppm Mg²⁺, 3 ppm K⁺ and 14 ppm Na⁺. Dithizone was added to give metal: dithizone ratio of 1:2 where pH, AC amount, shaking time and HNO₃ volume were kept constant. The obtained solution after the recovery process evaporated to a volume of 5 mL and the percentage of the metal recovery was determined using FAAS.

2.4- Analysis of real samples

The presented preconcentration procedure was applied to three types of water samples (natural Nile water and drinking tap and mineral water samples). The water samples analyzed were filtered through a double range filter paper No. 102. One hundred milliliters of water samples were analyzed by applying the procedure given above.

3. RESULT AND DISCUSSION

3.1. Effect of pH

The pH was the first parameter examined for its effect on the extraction of the studied metals. The pH value of sample solutions was varied in the range of 2-10 by maintaining the other parameter constant. From Fig (1), it was observed that the best pH for extraction was 10, 4, 10, 8, and 6 for Cd^{2+} , Cu^{2+} , Mn^{2+} , Pb^{2+} , and Zn^{2+} , respectively. This means that Cd^{2+} , Mn^{2+} , and Pb^{2+} extracted on basic medium, but Cu^{2+} and Zn^{2+} extracted on acidic medium. These results may be attributed to that in the very acidic medium there is a competition between hydrogen ions and metal ions in the solution to adsorb on the activated carbon surface and the adsorbent surface becomes a positive charge (Alkheraz et al., 2020). When the acidity effect of the solution decreased, the competition between hydrogen ions and metal ions decreased. Therefore, the metal ions could adsorb easily on the activated carbon surface (Mudasir et al., 2008; Tokalioğlu et al., 2017).

The obtained results for dithizone-metal preconcentration on activated carbon were in agreement with the findings of literatures (Ajmal et al., 2000; Di Nezio et al., 2004; Romberg and Müller, 1997; Saitoh et al., 2005; Salih et al., 1998; Shah and Devi, 1998; Tokalioğlu et al., 2017; Zaporozhets et al., 1999).

3.2. Effect of Activated Carbon Amount

Activated carbon (A.C.) has a high capability to adsorb several types of non-polar and polar compounds (Daorattanachai et al., 2005). The influence of the amount of activated carbon on the adsorption efficiency of metal-dithizone complexes was investigated and the results were represented in Table (1). Quantitative recoveries for the studied metals were obtained using 0.3, 0.8, 0.6, 0.5, 0.2 g of A.C. for Cd^{2+} , Cu^{2+} , Mn^{2+} , Pb^{2+} and Zn^{2+} , respectively. A convenient amount of A.C. was needed to increase the adsorption process, but the overabundance dosage of A.C. led to hinder the elution process (Narin et al., 2000). The adsorption of metal-dithizone complex from the solution increase as the adsorbent amount increase due to the availability of greater surface area of the adsorbent to adsorb the complex (Babel and Kurniawan, 2004; Vellaichamy, 2017), while after equilibrium occurs the recovery decrease; this may be because the energetic site on the adsorbent surface was filled with the metal-dithizone complex so there was no chance for adsorption new amounts of the complex.

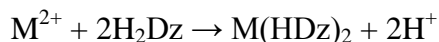
3.3. Effect of Shaking Time

Shaking time plays an important role in the study of the adsorption of metal-dithizone complexes on activated carbon. Table (2), shows that the best recovery was obtained at a shaking time of 50 min for Cd^{2+} , 30 for Cu^{2+} and 10 min for Mn^{2+} , Pb^{2+} and Zn^{2+} , respectively. It could be explicated by increase the adsorption time led to increase the chance of the metal complex to fix with the adsorbent surface by the diffusion of adsorbed metals into the surface of the adsorbent (Sasithorn et al., 2010), so the complex carried into the pores of the adsorbent until equilibrium was reached. After equilibrium is reached, excess shaking time led to low recovery of the metal because of decreasing the elution process. This conclusion is in line with that reported by (Xingguang et al., 2003).

3.4. Effect of Metal: Ligand Ratio

The concentration of the dithizone was subsequently studied for its effect on the extraction of the studied metals. The effect of metal: Dz ratio was studied on the range of 1:1, 1:2, 1:3. From Fig

(2) it was observed that 1:2 ratio was given best recovery of the percentage 83.1% for Cd²⁺, 100% for Cu²⁺, 100% for Mn²⁺, 99.755 for Pb²⁺ and 96.25% for Zn²⁺. These results agree with the findings of (Cheng et al., 2017; Kawamoto et al., 1992) whose illustrated that M²⁺ ions preconcentration with dithizone (Dz) achieved according to the equation:



An explanation for this result is that at a 1:1 ratio ligand amount in the solution is insufficient to form complexes with the studied metals. At the same time, at 1:3 ratio it was observed that the recovered value also decreased. This may be attributed to the blocking of the active sites on the adsorbent surface, available for metal complex, by a large amount of ligand.

Table (1): Effect of Activated Carbon Amount on Preconcentration of Cd, Cu, Mn, Pb and Zn ions

A.C., g.	Cd	Cu	Mn	Pb	Zn
	%	%	%	%	%
0.2	80	75	56	79.5	100
0.3	90	50	72.1	64.5	100
0.4	90	50	75.2	99.5	102.2
0.5	90	75	95.9	106	100
0.6	90	75	106.3	76	102.44
0.7	90	50	70.1	71.7	100
0.8	90	100	70.3	36	101.76
0.9	60	100	77.8	39	102.9
1	20	75	78.7	39	99.5

Table (2): effect of shaking time on preconcentration of Cd, Cu, Mn, Pb and Zn ions

Shaking time, min	Cd	Cu	Mn	Pb	Zn
	%	%	%	%	%
10	73.5	75	107	108.6	80.6
20	53.5	75	92	90	60.86
30	23.5	100	72	96	114
40	23.5	100	77	99.8	101.5
50	93.5	100	79	71.8	23.4
60	93.5	100	92	71.8	23.4

3.5. Effect of Eluent Concentration

Atomic absorption spectrometer may be blocked by the presence of a complex organic matrix that causes severe suppression of the analyte signal (Lelievre et al., 2000). It is well known that strong acids are very efficient to liberate metallic ions from their complexes (Pourreza and Hoveizavi, 2005; Zougagh et al., 2004). So, Nitric acid was chosen as an eluent owing to its effective elution of the adsorbed metal complex and its efficiency to release metallic ions from their complexes. The results of the eluent concentration were shown in Fig (3). It appears that the effective elution of Cd²⁺- and Mn²⁺- Dz complexes occurred in the nitric acid concentration of 1 mol L⁻¹ and at a concentration of 2 mol L⁻¹ for Zn²⁺ - Dz complex, and at a concentration of 4 mol L⁻¹ for Cu²⁺- and Pb²⁺- Dz- complexes

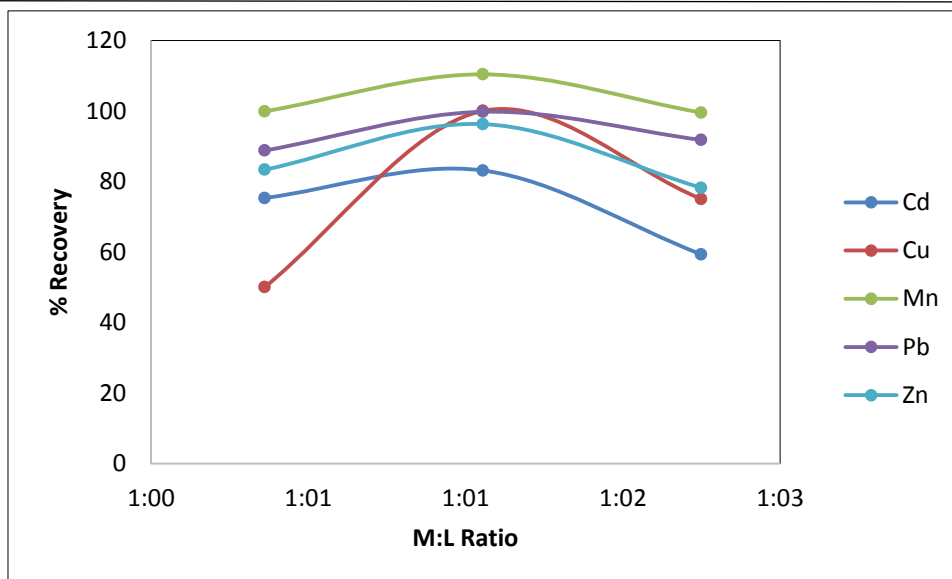


Fig 1: Effect of metal –ligand ratio on pre-concentration of Cd, Cu, Mn, Pb and Zn ions

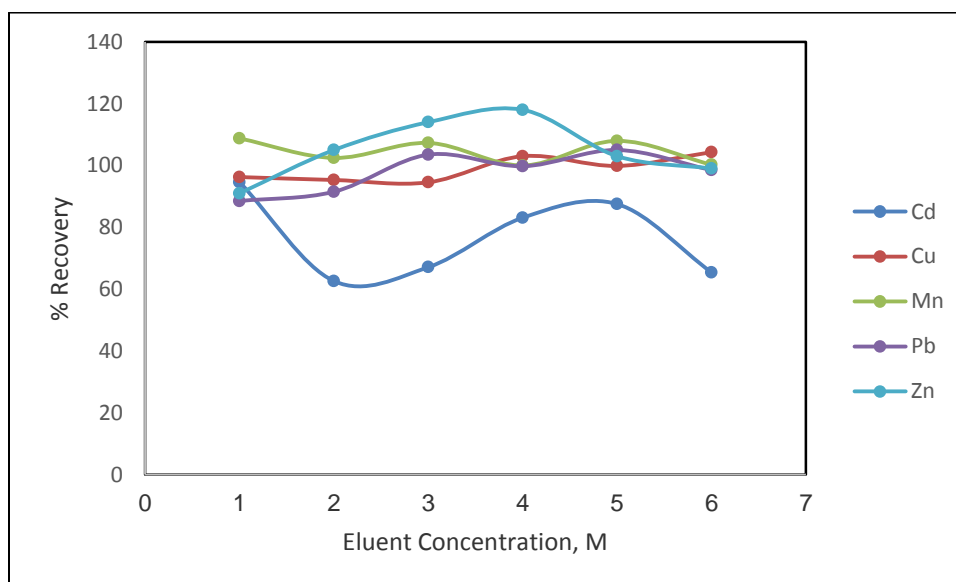


Fig 2: Effect of Eluent Concentration on Pre-concentration of Cd, Cu, Mn, Pb and Zn ions

3.6. Effect of Solution Volume

A significant parameter in SPE is the initial analyte volume since the pre-concentration factor is depending on the volumes of the analyte and amount of eluate (Er et al., 2013). The extraction of the metals was studied at a varying volume of the aqueous phase from the range 50 mL to 1000 mL. The results were shown in Fig (4). It was found that the best results were obtained from 50-100 mL for Cd^{2+} and from 50- 200 mL for Cu^{2+} , Mn^{2+} , Pb^{2+} and Zn^{2+} . 100 mL solution volume was chosen with pre-concentration factor 20 for Cd^{2+} while 200 mL solution volume was chosen for Cu^{2+} , Mn^{2+} , Pb^{2+} and Zn^{2+} with a pre-concentration factor of 40. The decrease in the recovery value in high solution volume may be due to the elution effect of high sample, as well as at higher volumes the time consumed for pre-concentration was increased. This is consistent with (Aydin and Soylak, 2007; Pourreza and Hoveizavi, 2005).

3.7. Effect of Differ Ions:

Several metal ions might react with dithizone cause interference for the preconcentration process; of these metals, the interference of the major metals ions in a water sample (Ca, Mg, K and Na) was investigated. From Table (3) it was found that the recoveries of the metals under study were almost quantitative in the presence of interfering cations except in the presence of Na^+ which interferes with Cd^{2+} and Zn^{2+} ions. From the results, it was observed that the presence of these cations at normal concentrations in water samples does not affect the preconcentration process indicating the suitability of the present preconcentration method for the determination of trace amounts of the studied metals in water samples.

3.8. Accuracy and Applications

To ensure that this method was valid, recovery of the studied metal ions (Cd^{2+} , Cu^{2+} , Mn^{2+} , Pb^{2+} and Zn^{2+}) from three water samples spiked with 0.1 ppm of each of these metal ions were found and are shown in Table (4). It was found that the Cd^{2+} , Cu^{2+} , Mn^{2+} , Pb^{2+} and Zn^{2+} ions were recovered by at least 98.8%, 75.44%, 100 %, 95.5%, and 68.9%, respectively by using the proposed method. This confirms the validity of the proposed method. A comparison between this study and other preconcentration methods using different ligands and adsorbents was presented in Table (5). It was evident that for this paper technique, high preconcentration factor was observed for Cu^{2+} , Pb^{2+} and Zn^{2+} , while for Cd^{2+} the other studies reported high preconcentration factor compared to our research. For Mn^{2+} using Triton X-114 gave high preconcentration factor 50 compared with 40 for activated carbon. Activated carbon adsorbent using dithizone as ligand yields up to 95% recovery for all studied metals except for Cu^{2+} and Zn^{2+} .

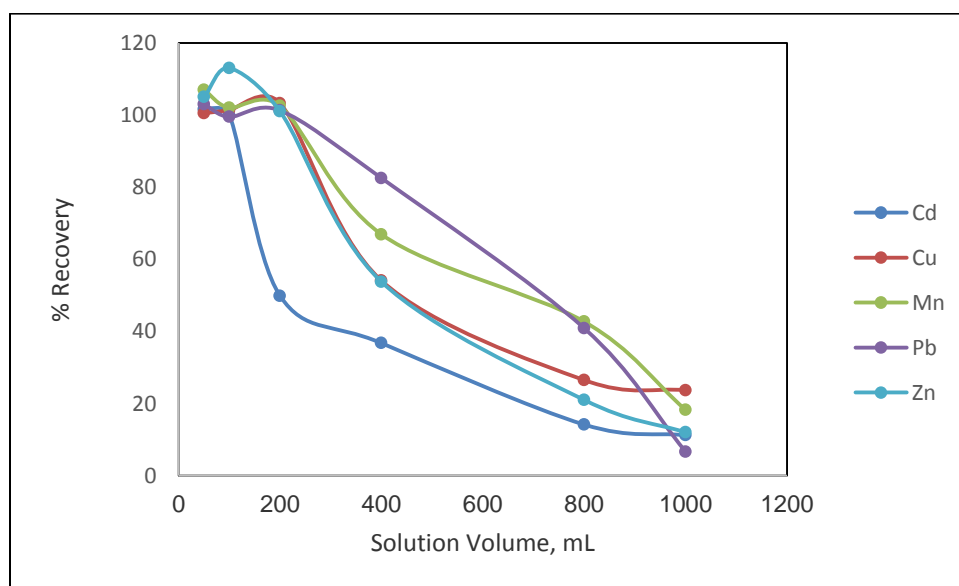


Fig 3: Effect of Solution Volume on Preconcentration of Cd^{2+} , Cu^{2+} , Mn^{2+} , Pb^{2+} and Zn^{2+}

Table (3) Effect of Differ Ions on Preconcentration of Cd²⁺, Cu²⁺, Mn²⁺, Pb²⁺ and Zn²⁺ with Dithizone and Activated Carbon.

ions	Cd ²⁺			Cu ²⁺			Mn ²⁺			Pb ²⁺			Zn ²⁺		
	Added (ppm)	Found (ppm)	recovery, %	Added (ppm)	Found (ppm)	recovery, %	Added (ppm)	Found (ppm)	Recovery, %	Added (ppm)	Found (ppm)	Recovery, %	Added (ppm)	Found (ppm)	Recovery, %
Ca ²⁺	0.1	0.097	97.5	0.1	0.101	101.1	0.1	0.100	100.6	0.1	0.103	103	0.1	0.097	97.25
Mg ²⁺	0.1	0.105	105.3	0.1	0.106	106.2	0.1	0.104	104.85	0.1	0.120	102.9	0.1	0.097	97.75
K ⁺	0.1	0.101	101.4	0.1	0.100	100.5	0.1	0.099	99.1	0.1	0.090	90.5	0.1	0.102	102
Na ⁺	0.1	0.100	55	0.1	0.108	108.1	0.1	0.109	109.5	0.1	0.100	100	0.1	0.075	75.75

Table (4) Determination of Cd²⁺, Cu²⁺, Mn²⁺, Pb²⁺ and Zn²⁺ in water samples

Sample	Concentration (ppm)														
	Cd ²⁺			Cu ²⁺			Mn ²⁺			Pb ²⁺			Zn ²⁺		
	Added (ppm)	Found (ppm)	% recovery	Added (ppm)	Found (ppm)	% recovery	Added (ppm)	Found (ppm)	% recovery	Added (ppm)	Found (ppm)	% recovery	Added (ppm)	Found (ppm)	% recovery
Nile water	0	0	-	0	0.124	-	0	4.45×10 ⁻³	-	0	0.014	-	0	9.95×10 ⁻³	-
	0.1	0.100	100	0.1	0.226	102	0.1	0.113	108	0.1	0.109	95.5	0.1	0.111	101.05
Tap water	0	-	-	0	0.045	-	0	0.010	-	0	0	-	0	0.064	-
	0.1	0.103	103	0.1	0.145	99.6	0.1	0.116	106	0.1	0.098	98	0.1	0.160	95.6
Mineral water	0	-	-	0	0.060	-	0	0.092	-	0	0	-	0	2.55×10 ⁻³	-
	0.1	0.098	98.8	0.1	0.136	75.44	0.1	0.192	100	0.1	0.105	104.5	0.1	0.072	68.9

4- Conclusion

In this study, an effective method for preconcentration and determination of trace amounts of Cd^{2+} , Cu^{2+} , Mn^{2+} , Pb^{2+} and Zn^{2+} ions by FAAS has been achieved. The presented procedure is simple, fast, inexpensive, effective and virtually solvent-free. The preconcentration occurs in the basic medium for Cd^{2+} , Mn^{2+} and Pb^{2+} (pH 10, 10 and 8, respectively), while for Cu^{2+} and Zn^{2+} the recommended pH occurs in acidic medium (pH 4 and 6, respectively). Cadmium and zinc complexes need a small amount of activated carbon (0.3 and 0.2 g, respectively) compared with other metals, whereas Mn^{2+} and Pb^{2+} consumed shorter time (10 min) for adsorption on the adsorbent surface. High preconcentration factors (PF=40) were obtained for Cu^{2+} , Mn^{2+} , Pb^{2+} and Zn^{2+} and 20 for Cd^{2+} ions. Dithizone legend shows high selectivity for the studied metals except in the presence of Na^+ ion in the case of Cd^{2+} and Zn^{2+} .

5- References

- Ajmal, M., Rao, R. A. K., Ahmad, R., & Ahmad, J. J. J. o. h. m. (2000). Adsorption studies on Citrus reticulata (fruit peel of orange): removal and recovery of Ni (II) from electroplating wastewater. *79*(1-2), 117-131.
- Alkheraz, A. M., Ali, A. K., & Elsherif, K. M. (2020). Removal of Pb(II), Zn(II), Cu(II) and Cd(II) from aqueous solutions by adsorption onto olive branches activated carbon: Equilibrium and thermodynamic studies. *Chemistry International*, *6* (1), 11-20. doi:10.5281/zenodo.2579465
- AlMasoud, N., Habila, M. A., Alothman, Z. A., Alomar, T. S., Alraqibah, N., Sheikh, M., . . . Soylak, M. (2020). Nano-clay as a solid phase microextractor of copper, cadmium and lead for ultra-trace quantification by ICP-MS. *Anal Methods*. doi:10.1039/d0ay01343a
- Arpa Sahin, C., Efecinar, M., & Satiroglu, N. (2010). Combination of cloud point extraction and flame atomic absorption spectrometry for preconcentration and determination of nickel and manganese ions in water and food samples. *J Hazard Mater*, *176*(1-3), 672-677. doi:10.1016/j.jhazmat.2009.11.084
- Aydin, F. A., & Soylak, M. J. T. (2007). A novel multi-element coprecipitation technique for separation and enrichment of metal ions in environmental samples. *73*(1), 134-141.
- Babel, S., & Kurniawan, T. A. J. C. (2004). Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *54*(7), 951-967.
- Bu, Y., He, X., Hu, Q., Wang, C., Xie, X., & Wang, S. (2017). A novel cell membrane affinity sample pretreatment technique for recognition and preconcentration of active components from traditional Chinese medicine. *J Scientific reports*, *7*(1), 1-11.
- Cheng, K. L., Ueno, K., & Imamura, T. (2017). *CRC handbook of organic analytical reagents*: Routledge.
- Daorattanachai, P., Unob, F., & Imyim, A. J. T. (2005). Multi-element preconcentration of heavy metal ions from aqueous solution by APDC impregnated activated carbon. *67*(1), 59-64.

- Di Nezio, M. a. S., Palomeque, M. E., & Band, B. S. F. J. T. (2004). A sensitive spectrophotometric method for lead determination by flow injection analysis with on-line preconcentration. *63*(2), 405-409.
- Er, C., Filiz Senkal, B., & Yaman, M. (2013). Determination of lead in milk and yoghurt samples by solid phase extraction using a novel aminothioazole-polymeric resin. *Food Chem*, *137*(1-4), 55-61. doi:10.1016/j.foodchem.2012.10.013
- Fan, Z., & Zhou, W. J. S. A. P. B. A. S. (2006). Dithizone–chloroform single drop microextraction system combined with electrothermal atomic absorption spectrometry using Ir as permanent modifier for the determination of Cd in water and biological samples. *61*(7), 870-874.
- Feist, B., & Mikula, B. (2014). Preconcentration of heavy metals on activated carbon and their determination in fruits by inductively coupled plasma optical emission spectrometry. *Food Chemistry*, *147*, 302-306. doi:<https://doi.org/10.1016/j.foodchem.2013.10.002>
- Ghaedi, M., Ahmadi, F., & Shokrollahi, A. J. J. o. h. m. (2007). Simultaneous preconcentration and determination of copper, nickel, cobalt and lead ions content by flame atomic absorption spectrometry. *142*(1-2), 272-278.
- Gouda, A. A. (2014). Cloud point extraction, preconcentration and spectrophotometric determination of trace amount of manganese(II) in water and food samples. *Spectrochim Acta A Mol Biomol Spectrosc*, *131*, 138-144. doi:10.1016/j.saa.2014.04.075
- Javad, M. T., Vahidinia, A., Samiee, F., Elaridi, J., Leili, M., Faradmal, J., . . . Biology. (2018). Analysis of aluminum, minerals and trace elements in the milk samples from lactating mothers in Hamadan, Iran. *50*, 8-15.
- Kagaya, S. (2016). Rapid coprecipitation technique for the separation and preconcentration of trace elements. *Bunseki Kagaku*, *65*(1), 13-23.
- Karimi, M., Shabani, A. M. H., & Dadfarnia, S. (2015). Deep eutectic solvent-mediated extraction for ligand-less preconcentration of lead and cadmium from environmental samples using magnetic nanoparticles. *Microchimica Acta*, *183*(2), 563-571. doi:10.1007/s00604-015-1671-9
- KAWAMOTO, H., YAMAZAKI, S., KATOH, E., TSUNODA, K.-i., & AKAIWA, H. J. A. s. (1992). Preconcentration of Heavy Metal Ions Using Synergistic Extraction with Dithizone and Tributylphosphine Oxide on the Basis of HSAB Rule. *8*(2), 265-266.
- Lelievre, C., Hennequin, D., Lequerler, J., & Barillier, D. J. A. S.-N. C.-. (2000). A rapid method for the direct determination of copper and iron in butter by GFAAS. *21*(1), 23-29.
- Marahel, F., Ghaedi, M., Montazerzohori, M., Biyareh, M. N., Kokhdan, S. N., & Soylak, M. (2011). Solid-phase extraction and determination of trace amount of some metal ions on Duolite XAD 761 modified with a new Schiff base as chelating agent in some food samples. *Food Chem Toxicol*, *49*(1), 208-214. doi:10.1016/j.fct.2010.10.018
- Mudasir, Raharjo, G., Tahir, I., & Wahyuni, E. T. (2008). Immobilization of Dithizone onto Chitin Isolated from Prawn

- Seawater Shells (*P. merguensis*) and its Preliminary Study for the Adsorption of Cd(II) Ion. *Journal of Physical Science*, 19 (1), 63–78.
- Musile, G., Cenci, L., Piletska, E., Gottardo, R., Bossi, A. M., & Bortolotti, F. (2018). Development of an in-house mixed-mode solid-phase extraction for the determination of 16 basic drugs in urine by High Performance Liquid Chromatography-Ion Trap Mass Spectrometry. *Journal of Chromatography A*, 1560, 10-18. doi:<https://doi.org/10.1016/j.chroma.2018.05.019>
- Narin, İ., Soylak, M., Elçi, L., & Doğan, M. (2000). Determination of trace metal ions by AAS in natural water samples after preconcentration of pyrocatechol violet complexes on an activated carbon column. *J Talanta*, 52(6), 1041-1046.
- Ntoi, L. L. A. (2016). Multiple Chromisms Associated with Dithizone. *Doctoral dissertation, University of the Free State*.
- Ntoi, L. L. A., Buitendach, B. E., & von Eschwege, K. G. (2017). Seven Chromisms Associated with Dithizone. *J Phys Chem A*, 121(48), 9243-9251. doi:10.1021/acs.jpca.7b09490
- Pilarczyk, R., Wójcik, J., Czerniak, P., Sablik, P., Pilarczyk, B., Tomza-Marciniak, A. J. E. m., & assessment. (2013). Concentrations of toxic heavy metals and trace elements in raw milk of Simmental and Holstein-Friesian cows from organic farm. *185(10)*, 8383-8392.
- Pourreza, N., & Hoveizavi, R. J. A. C. A. (2005). Simultaneous preconcentration of Cu, Fe and Pb as methylthymol blue complexes on naphthalene adsorbent and flame atomic absorption determination. *549(1-2)*, 124-128.
- Pradhan, B. K., & Sandle, N. (1999). Effect of different oxidizing agent treatments on the surface properties of activated carbons. *J Carbon*, 37(8), 1323-1332.
- Romberg, B., & Müller, H. J. A. c. a. (1997). Photometric screening-test for heavy metals under flow injection conditions using extractive determination with dithizone. *353(2-3)*, 165-172.
- Saitoh, T., Hattori, K., & Hiraide, M. (2005). Aerosol-OT micelles in Sephadex gels for concentrating metal-dithizone chelates from water. *J Analytica Chimica Acta*, 543(1-2), 25-30.
- Salih, B., Denizli, A., Kavaklı, C., Say, R., & Pişkin, E. (1998). Adsorption of heavy metal ions onto dithizone-anchored poly (EGDMA-HEMA) microbeads. *J Talanta*, 46(5), 1205-1213.
- Sasithorn, J., Wiwattanadate, D., & Sangsuk, S. (2010). Utilization of fly ash from power plant for adsorption of hydrocarbon contamination in water. *Journal of Metals, Materials*, 20(1).
- Senkal, B. F., Ince, M., Yavuz, E., & Yaman, M. (2007). The synthesis of new polymeric sorbent and its application in preconcentration of cadmium and lead in water samples. *J Talanta*, 72(3), 962-967.
- Shah, R., & Devi, S. (1998). Chelating resin containing s-bonded dithizone for the separation of copper (II), nickel (II) and zinc (II). *J Talanta*, 45(6), 1089-1096.

- Soares, A. R., & Nascentes, C. C. (2013). Development of a simple method for the determination of lead in lipstick using alkaline solubilization and graphite furnace atomic absorption spectrometry. *Talanta*, 105, 272-277. doi:10.1016/j.talanta.2012.09.021
- Sorouraddin, S. M., Farajzadeh, M. A., & Dastoori, H. (2020a). Development of a dispersive liquid-liquid microextraction method based on a ternary deep eutectic solvent as chelating agent and extraction solvent for preconcentration of heavy metals from milk samples. *J Talanta*, 208, 120485.
- Sorouraddin, S. M., Farajzadeh, M. A., & Dastoori, H. (2020b). Development of a dispersive liquid-liquid microextraction method based on a ternary deep eutectic solvent as chelating agent and extraction solvent for preconcentration of heavy metals from milk samples. *Talanta*, 208, 120485. doi:10.1016/j.talanta.2019.120485
- Thompson, J., & Davidow, L. (2009). A practical guide to Contemporary pharmacy practice. In: Wolters Kluwer Health/Lippincott Williams & Wilkins.
- Tokaloğlu, Ş., Papak, A., & Kartal, Ş. (2017). Separation/preconcentration of trace Pb(II) and Cd(II) with 2-mercaptobenzothiazole impregnated Amberlite XAD-1180 resin and their determination by flame atomic absorption spectrometry. *Arabian Journal of Chemistry*, 10(1), 19-23. doi:10.1016/j.arabjc.2013.04.017
- Vellaichamy, S. (2017). Adsorptive separation of copper, nickel, lead, zinc and cadmium from aqueous solution using MWCNTs impregnated with D2EHPA and prior to their determination by FAAS: Kinetic and equilibrium studies. *Separation Science and Technology*, 52(4), 644-656. doi:10.1080/01496395.2016.1263660
- Xingguang, S., Meijia, W., Yihua, Z., Jiahua, Z., Hanqi, Z., & Qinhan, J. (2003). Semi-online preconcentration of Cd, Mn and Pb on activated carbon for GFASS. *J Talanta*, 59(5), 989-997.
- Yao, Y., Wu, H., & Ping, J. (2019). Simultaneous determination of Cd(II) and Pb(II) ions in honey and milk samples using a single-walled carbon nanohorns modified screen-printed electrochemical sensor. *Food Chem*, 274, 8-15. doi:10.1016/j.foodchem.2018.08.110
- Yin, J., Jiang, Z., Chang, G., & Hu, B. (2005). Simultaneous on-line preconcentration and determination of trace metals in environmental samples by flow injection combined with inductively coupled plasma mass spectrometry using a nanometer-sized alumina packed micro-column. *J Analytica Chimica Acta*, 540(2), 333-339.
- Zaporozhets, O., Petruniok, N., & Sukhan, V. (1999). Determination of Ag (I), Hg (II) and Pb (II) by using silica gel loaded with dithizone and zinc dithizonate. *J Talanta*, 50(4), 865-873.
- Zhao, L., Zhong, S., Fang, K., Qian, Z., & Chen, J. (2012). Determination of cadmium(II), cobalt(II), nickel(II), lead(II), zinc(II), and copper(II) in water samples using dual-cloud point extraction and inductively coupled plasma emission spectrometry. *Journal of Hazardous Materials*, 239-240, 206-212. doi:<https://doi.org/10.1016/j.jhazmat.2012.08.066>
- Zhou, Q., Xing, A., & Zhao, K. (2014). Simultaneous determination of nickel, cobalt and mercury ions in water samples by solid phase extraction using multiwalled carbon

nanotubes as adsorbent after chelating with sodium diethyldithiocarbamate prior to high performance liquid chromatography. *Journal of Chromatography A*, 1360, 76-81. doi:<https://doi.org/10.1016/j.chroma.2014.07.084>

Zougagh, M., De Torres, A. G., Alonso, E. V., & Pavón, J. C. (2004). Automatic on line preconcentration and determination of lead in water by ICP-AES using a TS-microcolumn. *J Talanta*, 62(3), 503-510.

Zounr, R. A., Tuzen, M., Deligonul, N., & Khuhawar, M. Y. (2018). A highly selective and sensitive ultrasonic assisted dispersive liquid phase microextraction based on deep eutectic solvent for determination of cadmium in food and water samples prior to electrothermal atomic absorption spectrometry. *Food Chem*, 253, 277-283. doi:10.1016/j.foodchem.2018.01.167