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Dependence of precipitation of trace elements on pH in standard water

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ABSTRACT

The present work aimed to study the dependence of precipitation of trace elements on the pH of solution. A standard solution was prepared by using ultrapure deionized water (18.2 MΩ/cm) as the solvent and 11 water-soluble salts having different elements as solutes. Five samples of different pH values (2 acidic, 2 basic, and 1 neutral) were prepared from this standard solution. Sodium-diethyldithiocarbamate was used as the chelating agent to precipitate the metal ions present in these samples of different pH values. The targets were prepared by collecting these precipitates on mixed cellulose esters filter of 0.4 µm pore size by vacuum filtration. Elemental analysis of these targets was performed by particle-induced X-ray emission (PIXE) using 2.7 MeV protons from the single Dee variable energy cyclotron at Panjab University, Chandigarh, India. PIXE data were analyzed using GUPIXWIN software. For most of the elements, except Hg with oxidation state +2, such as Co, Ni, Zn, Ba, and Cd, a general trend of enhancement in precipitation was observed with the increase in pH. However, for other elements such as V, As, Mo, Ag, and Bi, which have oxidation state other than +2, no definite pattern was observed. Precipitation of Ba and As using this method was negligible at all five pH values. From these results, it can be concluded that the precipitation and recovery of elements depend strongly on the pH of the water sample.

1. Introduction

The contamination of water with any foreign substance that causes toxic or deleterious effects on human health leads to water pollution. In general, microorganisms, organic compounds, and toxic heavy metals are the sources of contaminations of water. Majority of these heavy metals such as Cd, Ni, As, Hg, and Zn have adverse effects on human health. It has been reported that exposure to cadmium causes kidney and bone damages. The presence of arsenic in drinking water causes skin lesions and cancer of the lungs, bladder, and kidney. Several studies have reported [1,2] acute and chronic respiratory problems due to over exposure to vanadium pentaoxide. Cobalt also causes cardiac disorders. High exposure to barium through drinking water leads to hypertension, liver congestion, kidney disorders, and adverse immunological effects. Mercury poisoning deteriorates the nervous system and can impair hearing, speech, vision, and gait. Considering the toxicity of heavy metals, the accurate determination of their concentration in water and food is highly desirable.

Various sample preparation methods, such as the evaporation method, direct method, and preconcentration method, are widely used to analyze the trace elements in water. In the direct method, no sample preparation is required, i.e., only few milliliters of water sample is used for the analysis. In the evaporation method, a large volume of water sample is evaporated, and the residue collected from the container is used to prepare pellets. However, there is always a possibility of incomplete collection of residue from the container. In the preconcentration method, trace elements are precipitated using chelating reagents such as sodium diethyldithiocarbamate (NaDDTC) and ethylenediaminetetraacetic acid (EDTA). Carbamide salts such as diethyldithiocarbamate (DDTC) are metal carriers that are used as metal conjugated systems. For heavy metal analysis, the water sample is treated with a known metal-DDTC conjugate. The heavy metal in the solution replaces the known metal in the conjugate and thus gets chelated by the carbamide salt. NaDDTC ($C_5H_{10}NaS_2H_2O$) is extensively used as one such chelating agent to precipitate metals from drinking water [3]. The precipitation of different elements in water using NaDDTC as the chelating agent may be dependent on the pH of the solution.

The trace elemental analysis depends on the sample type, elements of interest, sensitivity, and accuracy. There are many multi-elemental techniques such as the neutron activation analysis, X-ray fluorescence (XRF), particle-induced gamma ray emission, and particle-induced X-ray emission (PIXE) that are commonly used [4–8]. Some of these methods can be used in complement to the inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS), which are well suited to analyze liquid samples; however, these

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can detect only one element at a time. XRF is the strongest competitor of PIXE, but its detection limit is one order lower than that of PIXE. The main advantages of PIXE are its high sensitivity, non-destructive nature, and multi-elemental analysis capability of minor and trace elements in various samples [9–15]. Moreover, it can detect trace elements with accuracy better than 5% and has a minimum detection of ~0.1 μg/g.

The precipitation and complex-forming nature of any metal ion with different ligands depend upon various factors such as the oxidation state of metal ions, pH of the medium, temperature, pressure, and the solvent used to prepare the desired solution. Coordination behavior of the ligand also plays a considerable role in addition to the above factors. The first and second group metal ions, being electropositive, are highly soluble in polar solvents like water. The difference in solubility of transition metal ions and other heavy metal ions might be ascribed to the different sizes of transition metal ions. The size of transition metal ions increases from the first transition metal series to the second and then to the third. This large variation in size and the presence of d and f sub shells also contributed to their varied characteristics. In the presence of a strong coordinating ligand, the metal ions can be easily recovered from the aqueous solution depending upon the chelating power of the ligand. The complex-forming behavior of different metal ions is different. The amount of precipitation of different metal ions in water using complexation agents varies for different physicochemical conditions. At different pH values, the complex-forming agent or ligating agent shows different coordination behavior toward different metal ions. Hence, the amount of precipitation of different metal ions is different at different pH values.

Bag et al. [16] studied the recovery of Cr (III) and Cr (VI) from river water. Targets were prepared using the chelation technique, and variations in the recovery of Cr at different pH values (2–10) were observed. The highest recovery of Cr (III) and Cr (VI) was obtained at pH 2 and 8, respectively. At pH 6, the recovery of Cr was rather low (< 5%). Kennedy et al. [17] studied the distribution of trace elements in river water using the PIXE technique. Water targets were prepared at pH 9 by the preconcentration method using NaDDTC as the chelating agent. The detected concentration of Hg, Zn, and Pb was higher than the World Health Organization (WHO) prescribed limit. Kazi et al. [18] studied the water quality of polluted lake by AAS. Water samples from five different sites were analyzed for 16 elements (Na, Mg, Al, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Cd, and Pb). All the samples were analyzed at their original pH (i.e., 7.4–8.9). Except Cr, Mn, Co, and Cu, the concentrations of rest of the elements were observed to be higher than their safe limit. Narin et al. [19] also determined trace elemental concentrations at various pH values (2–10) by AAS. In their experiment, metal ions from water were extracted by the preconcentration method. The collected precipitates were dissolved in 5 ml 1 M HNO_3 and analyzed. It was observed that the optimum pH range for the efficient recovery of Co, Ni, and Pb was 4–8. By decreasing the pH, the precipitation of these elements decreased.

The present study was carried out to determine the role of pH in the precipitation of elements present in water. Standard solutions of 11 water-soluble metal salts were prepared using ultrapure deionized water at different pH values. NaDDTC was used as the chelating agent to precipitate the metals. Multi-elemental analysis of the prepared water samples was carried out by the PIXE technique.

2. Materials and method

2.1. Sample preparation

Analytical grade NaDDTC salt (Sigma Chemical Co., St. Louis (USA)) was used for the precipitation of metal ions. Mixed cellulose™ esters filters were obtained from Merck Millipore Darmstadt, Germany. V_2O_5, $CoCl_2{\cdot}6H_20$, $BaCl_2$, and $Bi(NO_3)_3{\cdot}5H_2O$ salts were procured from Fisher Scientific, Hampton (USA). $Ni(CH_3COO)_2{\cdot}4H_2O$, $ZnSO_4$, $AsNa_3O_4$, MoO_2, $AgNO_3$, $Cd(CH3CO_2)_2$, and $(Hg(SCN)_2)$ salts were procured from Alfa Aesar, Massachusetts (USA). To prepare the standard samples, we adopted a similar technique used by Aprilesi et al. [20]. Polypropylene (PP) bottles were first washed thoroughly with 1 N nitric acid (HNO_3) and then cleaned using ultrapure deionized water. These bottles were then used for storing the water samples. Antimony is used as a catalyst for manufacturing polyethylene-tri-phthalate (PET) bottles. Hence, leaching of Sb with time was observed when the water was stored in PET bottles [13]. Therefore, PP bottles were preferred over PET bottles. Water-soluble salts of 11 elements (V_2O_5, $CoCl_2{\cdot}6H_20$, Ni $(CH_3COO)_2{\cdot}4H_2O$, $ZnSO_4$, $AsNa_3O_4$, MoO_2, $AgNO_3$, $Cd(CH3CO_2)_2$, $BaCl_2$, $(Hg(SCN)_2)$, and $Bi(NO_3)_3{\cdot}5H_2O$) were used in the present study because of the serious health hazards associated with their contamination. Known amounts of these salts were added to 2 L of ultrapure deionized water (18.2 MΩ/cm) to prepare a standard solution. The salt quantities added were such that the elemental concentration of each element is 10 times its normal permissible limits set by the World Health Organization (WHO) [21]. The recommended limit set by the WHO for these elements are presented in Table 1. Higher amount of salts were added to ensure the unambiguous detection of elements, which might precipitate even in very low fractions.

Table 1
Recommendation limit set by the WHO.

Element	WHO Recommended Limit (μg/L)	Element	WHO Recommended Limit (μg/L)
Vanadium	200	Silver	100
Cobalt	5	Cadmium	3
Nickel	70	Barium	700
Zinc	50	Mercury	6
Arsenic	10	Bismuth	10
Molybdenum	70		

Two hundred milliliters of the solution thus prepared was taken in a beaker, and 1 N freshly prepared solution of HNO_3 or NaOH was added in a stepwise manner to set the desired pH of the solution. After setting the desired pH, 10 ml of freshly prepared saturated solution of NaDDTC was added to precipitate the metal contents as their respective carbamates. The sample was stirred using a magnetic stirrer for ~5 min. The precipitates, thus formed, were collected on a 0.15 mm thick mixed cellulose esters filter of 25 mm diameter having 0.4 μm pore size. The advantage of using a mixed cellulose esters filter for the PIXE analysis is that it has a low continuum X-ray background [22]. A Millipore vacuum filtration unit was used to filter precipitates on the filter. The glass vacuum filter holder was equipped with a fritted glass support and silicon stopper for attachment to a vacuum filtration flask. Precipitated water solution was poured slowly through the 30 ml borosilicate glass funnel placed into the vacuum filtration flask. The vacuum in the filtration flask was maintained by a vacuum pump. The flow rate of vacuum pump was maintained at 56 L/min. The entire process including the preparation of the sample at different pH values, precipitation, and filtration was completed within 10 min. A thin uniform layer of the precipitate of diameter 16 mm was formed on the filter and it was dried in an oven at 40 °C for 15 min. The dried filter was fixed on an aluminum ring (OD 24 mm, ID 20 mm, and thickness 2 mm) using epoxy adhesive as shown in Fig. 1. This assembly was used as the target for the experiments and stored individually in sterilized air-tight PP containers until analysis using the PIXE.

2.2. Experimental details

Elemental analysis was carried out using the PIXE facility at Panjab University Cyclotron, Chandigarh, India [23]. A multipurpose scattering chamber, as shown in Fig. 2, of 300 mm diameter was used. The chamber was kept at a vacuum of 2×10^{-6} torr using a turbo molecular vacuum pump. The prepared targets were fixed on a stainless steel target holder wheel, which has 12 holes of 24 mm diameter each, and