

# Determination of Pb and Ni in natural water samples after solid phase extraction with layered double hydroxide (LDH) nano-particles

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**Abstract:** Due to the industrialization, especially in the developing countries, the emission of the heavy metals as lead, cadmium, chromium, nickel, arsenic, and mercury are highly concerned to public and aquatic health. Lead is released with the effluent from the paint, batteries, and automobiles manufacturing units. Lead is one of the toxic metals and largely affects the central, peripheral nervous system. In this study, a suitable and reliable method for the direct determination of Pb and Ni ions in environmental water is proposed. Pb and Ni ions were extracted and precocentrated with layered double hydroxides (LDHs) nano-particles. LDHs, relatively inexpensive and simply prepared material, was synthesized and used as a solid phase extraction (SPE) adsorbent to quantitatively determine the concentration of Pb and Ni ions in natural water samples. Several factors affecting the extraction efficiency, such as, eluent type, eluent volume, flow rate of sample, sample volume, and amount of adsorbent, were investigated and optimized in detail. Pb and Ni ions can be quantitatively retained by LDH nano-particles, then eluted completely by 1 mL of  $\text{CO}_3^{2-}$  ( $1.5 \text{ mol L}^{-1}$ ) and 1 mL EtOH (65% v/v), respectively. The detection limit of this method for Pb and Ni ions was  $17 \text{ ng mL}^{-1}$  with an enrichment factor of 100, and the relative standard deviation (RSD) was 1.4%.

**Keywords:** Pb, Ni, Nano-Particle, Solid Phase Extraction, Layered Double Hydroxide (LDH)

## 1. Introduction

Trace metal ions have important roles in our life functioning in a wide spectrum. Thus, the determination of trace metal ions is becoming increasingly important because of the increased interest in environmental samples including water, soil and plant, etc.

Toxic heavy metals constantly released into the environment. They are dangerous environmental pollutants due to their toxicity and strong tendency to concentrate in environment and in food chains [1-2]. The source of environmental pollution with heavy metals is mainly industry, i.e. metallurgical, electroplating, metal finishing industries, tanneries, chemical manufacturing, mine drainage and battery manufacturing [3].

Layered Double Hydroxides (LDHs), also called anionic clays, are clay-like materials that show promising properties for a large number of applications. These materials exhibit

unique physical and chemical properties such as high specific surface area, swelling property, memory effect, high anion exchange capacity, and dispersive property. Moreover, LDHs have many pharmaceutical properties such as improving solubility of poorly water-soluble drugs and also barrier properties similar to those of gastric mucosa. Anionic clays are promising materials for the immobilization of biomolecular and development of biosensor electrodes due to their anion exchange and intercalation capacity, hydrophilicity, and adsorption of biomolecular such as proteins and enzymes. Also, they are nontoxic and show good biocompatibility.

Clays can be divided into two main classes: cationic clays that have negatively charged aluminosilicate layers; and anionic clays, with positively charged hydroxide layers. The neutrality of these materials is ensured by intercalation of cations or anions in the interlayer space. Layered Double

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## 2. Methods

Layered double hydroxides (LDHs) have been known for over 150 years since the discovery of the mineral hydrotalcite. They are a broad class of inorganic lamellar compounds with high capacity for anion intercalation. LDHs are also widely known as hydrotalcite-like compounds due to their structural similarities to hydrotalcite, a mineral with the formula  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$  which was first studied by Manasse in 1915. The X-ray diffraction (XRD) studies on mineral samples were carried out by Allmann and Taylor. The hydrotalcite structure results from the stacking of brucite-like layers  $[\text{Mg}(\text{OH})_2]$  containing extra positive charge due to the partial isomorphous substitution of  $\text{Mg}^{2+}$  by  $\text{Al}^{3+}$ . This positive excess charge is balanced by carbonate anions, which exist in the interlamellar spaces [4-6]. The structure of LDHs is represented by the general formula of  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+} (\text{An})_{x/n} \cdot m\text{H}_2\text{O}$  where  $\text{M}^{2+}$  and  $\text{M}^{3+}$  can be any divalent and trivalent metal ions (whose ionic radius is not so different from that of  $\text{Mg}^{2+}$ ), which can be accommodated in the octahedral sites in the brucite-like layers and  $x$  is the metal ratio  $\text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$ . An- in the interlamellar region can be any anion (organic or inorganic) and  $m$  is the amount of water in mol, present in the same region. The amount of water in the interlayer region can be determined by factors such as the nature of the anions, the water vapor pressure and temperature [7].

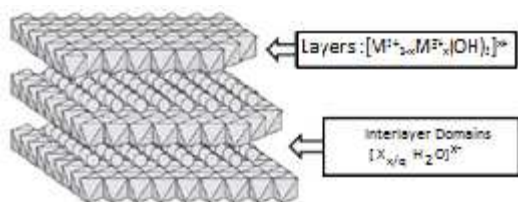


Fig 1. Structure of LDH

The accurate and precise determination of metal ions at trace levels is an important field in analytical and environmental chemistry [8–11], because of their roles in the human body and environment. Inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-optical emission spectrometry (ICP-OES), graphite furnace (GFAAS) and flame (FAAS) atomic absorption spectrometry are the main analytical instruments used currently [12–14]. Element concentrations those are low relative to the detection limits of ICP-OES and atomic absorption spectrometry. Even  $\text{ng L}^{-1}$  level of trace metal could be determined by ICP-MS, the interference effects caused by the matrix components of real samples is problematic for ICP-MS, ICPOES and GFAAS [15–18]. These difficulties can generally be avoided by using enrichment-separation techniques such as solvent

extraction, cloud point extraction, membrane filtration, coprecipitation and electrodeposition [19–22]. Solid phase extraction (SPE) is a cost-effective and important preconcentration-separation technique for separation enrichment of trace metal ions that offers important advantages, including simplicity, rapid analysis, and simple adaptation to automation [23–27]. Solid phase extraction also performs well in the preconcentration of trace metals with respect to minimizing solvent waste generation and the adsorption of analytes on the adsorbent in a more stable chemical form [28–31]. Adsorbents are preferred for the SPE of metal ions from environmental samples and these should have the following properties: the possibility for extracting a variety of metal ions over a wide pH range, high surface area, fast and quantitative adsorption and easy elution, ultra purity, repeated usability and accessibility [32–36]. Carbon nanotubes possess these properties and their use for enrichment and separation of metal ions at trace levels has been very popular in recent years.

## 3. Results and Discussion

Trace concentrations of metals were determined by FAAS using a WFX210 Model Atomic absorption spectrometer. The air-acetylene flame was adjusted according to the manufacturer's recommendations. A Hanna Instrument pH 211 microprocessor pH meter equipped with a combined glass calomel electrode was used for the pH adjustment. All solutions were delivered to pass through the glass column, having a stopcock and a porous disk was 10 cm long and 1.0 cm in diameter packed with Chromosorb 105.

The first prepared different concentrations of the sample after solid phase extraction were added to the sample layered double hydroxide (LDH) nano-particles finally were read absorption the samples with AAS. Pb and Ni ions can be quantitatively retained by LDH nano-particles, then eluted completely by 1 mL of  $\text{CO}_3^{2-}$  ( $1.5 \text{ mol L}^{-1}$ ) and 1 mL EtOH (65% v/v), respectively. Flame atomic absorption spectrometry (FAAS) with its relative low cost and good analytical performance, is the main instrument in the research laboratories for determining a variety of heavy metals. The detection limit of this method for Pb and Ni ions was  $17 \text{ ng mL}^{-1}$  with an enrichment factor of 100, and the relative standard deviation (RSD) was 1.4%.

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