



# Dispersive solid phase extraction using graphitic carbon nitride microparticles for the determination of trace amounts of lead in water samples

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## ABSTRACT

In this work, ultrasound-assisted dispersive micro-solid phase extraction (USA-D- $\mu$ SPE) technique using graphitized carbon nitride ( $g-C_3N_4$ ) is proposed for the preconcentration of low level of lead in aqueous samples. In this method, microparticles of graphitized carbon nitride sorbent were dispersed in the samples using ultrasonic bath and Pb(II) ions were directly adsorbed on the surface of  $g-C_3N_4$  particles. After adsorption and desorption of lead ions from  $g-C_3N_4$  particles, the Pb concentration was determined by the inductively coupled plasma- optical emission spectroscopy (ICP-OES). The main advantages of this method are high speed, simplicity and cheapness. The effects of pH, sorbent amount, eluent type and time on the recovery of the analyte were investigated. Under the optimized conditions and preconcentration of 10 mL of sample, the detection limit of  $1.24 \mu\text{g L}^{-1}$  was obtained. The results were validated by standard reference materials (NIST, SRM) and spiking of real samples by USA-D- $\mu$ SPE procedure.

## 1. Introduction

With the development of various industries over the past decades and increasing the amount of pollutants entering the environment, the amount of heavy metals in soil and water increased [1]. Most of these heavy metals are not only environmentally destructive but also healthily hazardous even at trace levels. Lead is one of the most hazardous elements to human health. Metabolic poisoning, enzyme inhibition and nervous connection damages are the most important toxic effects of lead on human [2]. The first step in reducing or eliminating this metal is its accurate measurement. For this purpose,

various analytical techniques have been developed [3-5]. In all of the reported analytical techniques, sample preparation (separation and preconcentration) step is needed prior to instrumental analysis. Among different sample preparation methods, solid phase extraction is the most common one due to its unique features such as simplicity, low cost, high recoveries and low consumption of organic solvents [6,7]. Dispersive micro solid phase extraction (D- $\mu$ -SPE) is a new version of solid phase extraction (SPE) which simultaneously possesses the advantages of both dispersive liquid-liquid micro-extraction and solid phase extraction [8]. In this method a mixture of sorbent particles and carrier is injected to the aqueous sample. After formation of cloudy solution, extraction can be achieved within a few seconds because of the large surface area

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between extraction sorbent and aqueous phase [9]. Recently, D- $\mu$ -SPE has received much attention in analytical chemistry because it is a simple, fast and inexpensive method [11,12]. One of the most important parameters that affect the performance of this method is the type of sorbent [12]. The advantages of using nanoparticles as sorbent in D- $\mu$ -SPE have been demonstrated in recent reports [13-15]. Unique size and desirable physicochemical properties of nanoparticles have made them suitable options for improving DSPE method. Among different nanosorbents, cheaper and more stable ones such as graphene and carbon nanotubes have been used more frequently [16-18]. Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) is a non-toxic analogue of graphene which is very stable and inexpensive and has suitable band structure, easy synthesis method and unique physicochemical properties [19,20]. It has a 2D layered structure (2D sheets of tri-s-triazine connected via tertiary amines) and is synthesized from various simple and green nitrogen rich precursors such as melamine, thiourea, urea, cyanamide [21]. Due to the hydrophobicity, large  $\pi$ -conjugated structure and polar functional groups, g-C<sub>3</sub>N<sub>4</sub> can be a suitable and ecofriendly candidate for conventional sorbents in extraction methods [22].

In the current study, we propose a simple, fast and ligandless preconcentration technique based on ultrasound-assisted dispersive micro-solid phase extraction (USA-D- $\mu$ SPE) using graphitic carbon nitride for the determination of lead by inductively coupled plasma-optical emission spectrometry.

## 2. Experimental

### 2.1. Reagents and materials

All chemicals used in this work were of analytical grade. All aqueous solutions were prepared in double-distilled deionized water (Milli-Q system, Millipore, USA). Pb(II) stock solution was supplied by Merck (Darmstadt, Germany). The standard solution of lead (Pb<sup>2+</sup>) was purchased with a concentration of 1000 mg L<sup>-1</sup> in 1 % HNO<sub>3</sub>. Another concentration of lead was daily prepared by dilution of the standard lead solution with DW. Ultrapure water was purchased from Millipore Company.

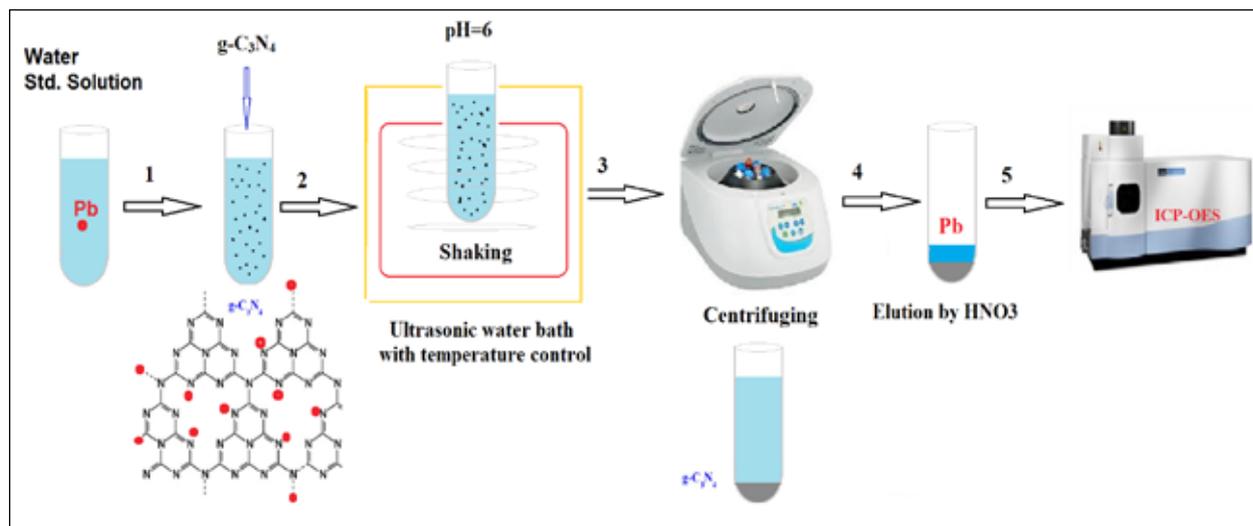
The g-C<sub>3</sub>N<sub>4</sub> was synthesized according to the previously reported method. The syntheses of graphitic carbon nitrides (g-C<sub>3</sub>N<sub>4</sub>) by heating at 300-600 °C of a mixture of melamine with the formula C<sub>3</sub>H<sub>6</sub>N<sub>6</sub> and uric acid (C<sub>5</sub>H<sub>4</sub>N<sub>4</sub>O<sub>3</sub>) in the presence of crystalline form of alumina (Al<sub>2</sub>O<sub>3</sub>) has been reported. Alumina favored the deposition of the graphitic carbon nitrides layers on the exposed surface [19].

### 2.2. Instrumentation

A Perkin Elmer inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 7300 DV) equipped with a charge-coupled device detector (CCD) and a cyclonic spray chamber with a concentric nebulizer was used for the determination of the target element. The detection wavelength for lead was 220.353 nm. A Metrohm model 744 digital pH meter, equipped with a combined glass-calomel electrode, was employed for the pH measurements. An ultrasonic water bath with temperature control (Tecno-Gaz SpA, Italy) was applied to disperse of adsorbent particles in aqueous solution. The centrifuge accessory based on the rotor with high speed (speed 2000-30.000 rpm x g, Sigma 3K30 centrifuge, UK) was used for separation nanoparticles from water samples. For sampling, all glass tubes were cleaned with a 1.0 mol L<sup>-1</sup> HNO<sub>3</sub> solution for 24 h and washed 10 times with DW. The water prepared and stored by standard method for sampling from water by adding nitric acid to waters.

### 2.3. On-line extraction procedure

Due to **Figure 1**, 6.0 mg of g-C<sub>3</sub>N<sub>4</sub> was added to 10 mL of water sample or standard solution and sonicated by an ultrasonic bath for 5 min. The chemical and physical adsorption of lead ions carried out by g-C<sub>3</sub>N<sub>4</sub> at optimized pH. The covalence bonding between nitrate and Pb cause to increase extraction efficiency in water samples. After extraction of lead ions with g-C<sub>3</sub>N<sub>4</sub>, the solution was then centrifuged for 5 min at 5,000 rpm, and the aqueous phase was removed. The preconcentrated target analyte was eluted using 1.0 mL of a 1 mol L<sup>-1</sup> solution of HNO<sub>3</sub>. Finally, the concentration of Pb(II) in acidic aqueous phase was determined by ICP-



**Fig.1.** On-line extraction procedure for lead extraction by  $g\text{-C}_3\text{N}_4$  particles

OES. The proposed procedure developed based on  $g\text{-C}_3\text{N}_4$  nanostructure with lower and upper limit quantification ( $5.0\text{--}600\ \mu\text{g L}^{-1}$ ) for lead analysis in water and standard samples by ultrasound-assisted dispersive micro-solid phase extraction (USA-D- $\mu\text{SPE}$ ).

### 3. Results and discussion

The USA-D- $\mu\text{SPE}$  procedure based on  $g\text{-C}_3\text{N}_4$  as adsorbent was used for the extraction and separation of lead ions in water samples. In order to obtain the favorite lead speciation with high extraction, the analytical parameters such; pH, the amount of adsorbent, the sonication time, the eluent type and interference ions must be optimized.

#### 3.1. Effect of pH

The pH of the sample solution is one of the most important factors in metal-adsorbent interaction in the SPE procedure. The effect of pH on the extraction of Pb(II) by  $g\text{-C}_3\text{N}_4$  was studied in the range of 3.0–8.0 using nitric acid or sodium hydroxide. The results in **Figure 2** show that the adsorption of Pb(II) is maximum in the pH range of 6.0 to 7.5. So, pH 6.0 was chosen as the optimum value. The mechanism of extraction of lead achieved based on the coordination of covalent bond of N in  $g\text{-C}_3\text{N}_4$  with the positively charged inorganic lead ( $\text{Pb}^{2+}$ ), which is highly dependent on pH ( $\text{Pb} \rightarrow \text{:N-C}$ ).

#### 3.2. Effect of $g\text{-C}_3\text{N}_4$ amount

The effect of amount of  $g\text{-C}_3\text{N}_4$  on the quantitative extraction of Pb(II) was examined in the range of 1–10 mg by ultrasound-assisted dispersive micro-solid phase extraction (USA-D- $\mu\text{SPE}$ ). The results are shown in **Figure 3**. The obtained results revealed that by increasing the sorbent amounts from 1 up to 6 mg, due to increasing accessible sites, the extraction efficiency increased and after that remained constant. Hence, the subsequent extraction experiments were carried out with 6 mg of  $g\text{-C}_3\text{N}_4$ .

#### 3.3. Effect of sonication time

By USA-D- $\mu\text{SPE}$  procedure, the sonication time is one of the main factors influencing the target analytes extraction. By favorite time for solid dispersion in liquid phase, the mass-transference was increased and so, the efficient extraction of lead based on the  $g\text{-C}_3\text{N}_4$  was obtained in water samples. The effect of the sonication time on the extraction and recovery of Pb(II) was studied in the range of 1–20 min. The obtained results indicated that there was no significant effect on the extraction efficiency when the ultrasonication time increased from 5 to 20 min. So, an ultrasonication time of 5 min was selected for the entire procedure.

#### 3.4. Effect of eluent type

The kind and value of elution for back extraction lead ions from  $g\text{-C}_3\text{N}_4$  were optimized at pH=6.

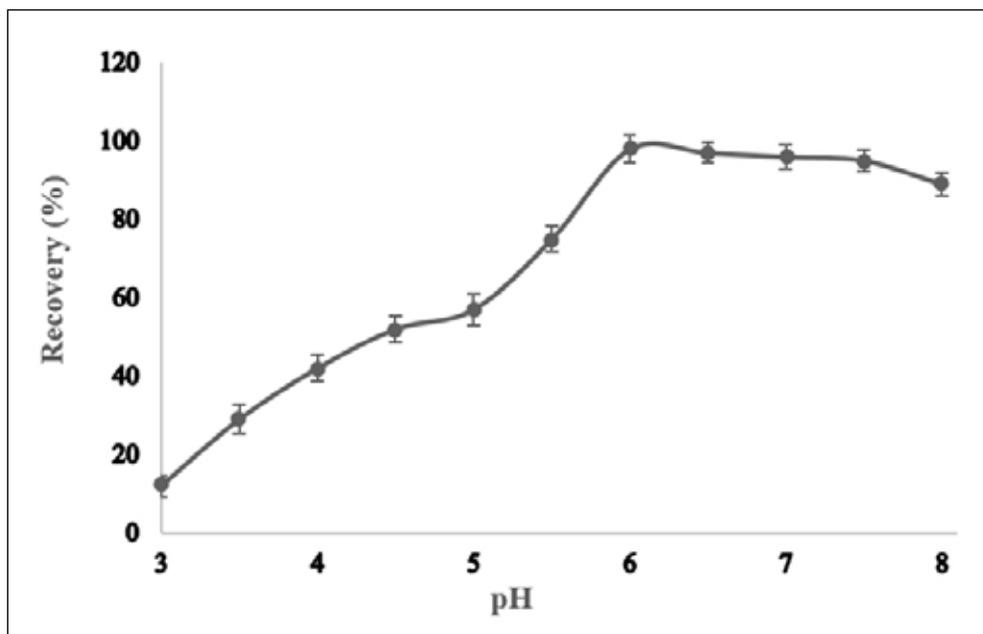


Fig. 2. Effect of pH on the recovery of Pb(II). Conditions: g-C<sub>3</sub>N<sub>4</sub> amount, 10 mg; concentration of analyte, 50  $\mu\text{g L}^{-1}$ .

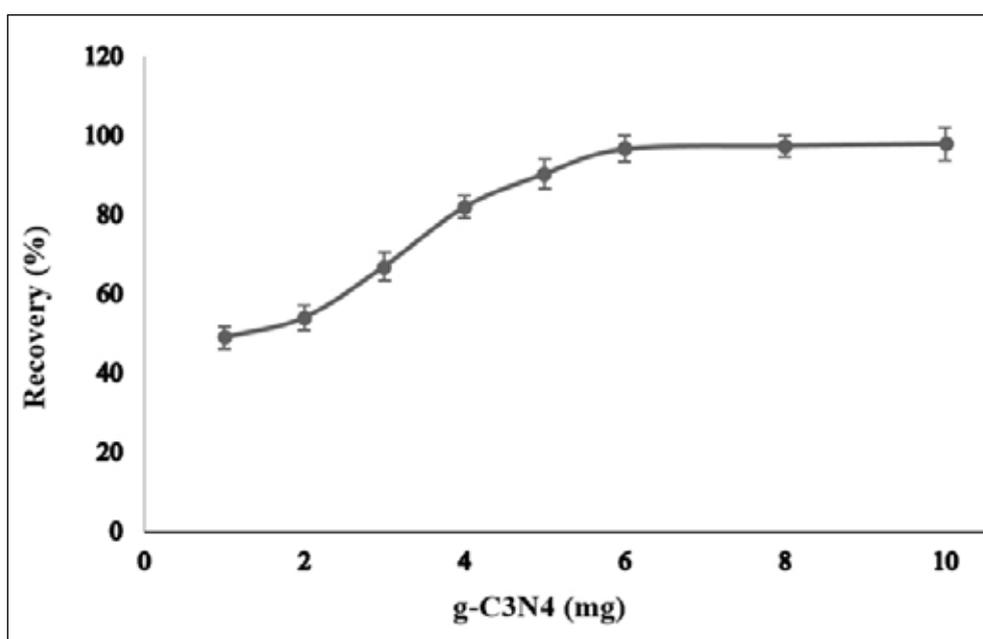


Fig. 3. Effect of the g-C<sub>3</sub>N<sub>4</sub> amount on the recovery of Pb(II). Conditions: pH, 6.0; concentration of analyte, 50  $\mu\text{g L}^{-1}$ .

Low pH caused to dissociate N-lead bonding and release the Pb (II) into the liquid phase. So, a different acid solution such as HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and CH<sub>3</sub>COOH with different concentration was used for back extraction Pb(II) in blood samples (0.5-3 mol L<sup>-1</sup>) by USA-D- $\mu$ SPE procedure. In order to

find the best eluent, different mineral acids were examined as stripping agents. The results revealed that among the tested eluents, nitric acid was the superior stripping agent for the quantitative elution of Pb(II). Therefore, HNO<sub>3</sub> solution was selected for Pb(II) desorption. The effect of nitric acid con-

centration on the recovery of the adsorbed analyte was studied in the range of 0.1 to 3 mol L<sup>-1</sup>. Based on the obtained results, 1.0 mol L<sup>-1</sup> HNO<sub>3</sub> was sufficient for complete desorption of the target analyte from the sorbent surface (Fig.4).

### 3.5. Effect of diverse ions on the recovery

In order to evaluate the analytical applicability of the developed method, the effect of commonly occurring ions in natural water samples on the extraction and determination of lead was studied. In these experiments, 10 mL of sample solutions containing 50.0 µg L<sup>-1</sup> of Pb(II) and various amounts of interfering ions were treated according to the recommended procedure. Tolerable limit was set as the highest amount of foreign ions which cause an approximately ± 5 % relative error in the determination of the analyte. The results showed that

40,000-fold Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>; 20,000-fold Ca<sup>2+</sup>, Mg<sup>2+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup>, 400-fold Ag<sup>+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, 200-fold Fe<sup>3+</sup>, Ni<sup>2+</sup>, Cr<sup>3+</sup>, Ce<sup>3+</sup>, and 100-fold Al<sup>3+</sup>, Cu<sup>2+</sup>, Hg<sup>2+</sup> ions had no significant influence on the extraction and determination of Pb(II).

### 3.6. Analytical figures of merit

The analytical parameters of the proposed are summarised in Table 1. Linear working range of the method for determination of Pb(II) was found to be 5.0–600 µg L<sup>-1</sup>. The limit of detection (LOD) of the proposed method was calculated as three times the standard deviation of 10 measurements of the blank solution over the slope of the calibration curve. The LOD for the determination of Pb(II) was found to be 1.24 µg L<sup>-1</sup>. The relative standard deviation (R.S.D) of the proposed method for determination of 50.0 µg L<sup>-1</sup> Pb(II) (n= 10) was 2.3 %.

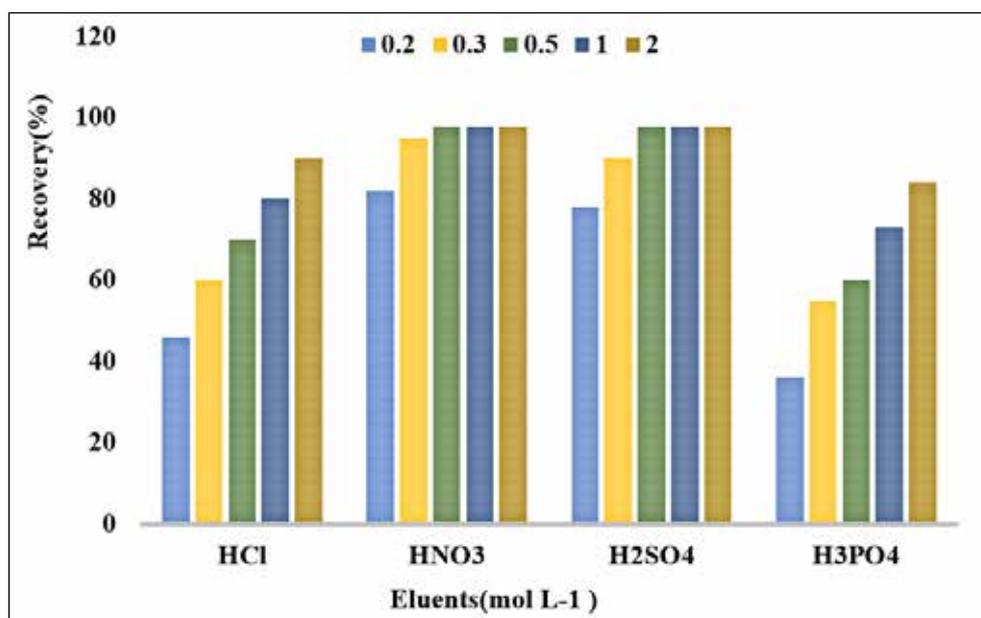


Fig.4. The effect of eluents on lead extraction based on g-C<sub>3</sub>N<sub>4</sub> particles by USA-D-µSPE procedure

Table 1. Analytical parameters of the proposed method

Parameter	Analytical feature
Linear range (µg L <sup>-1</sup> )	5.0–600
r <sup>2</sup>	0.998
LOD (ng L <sup>-1</sup> )	1.24
R.S.D. % (n = 10)	2.3
Enrichment factor	10

### 3.7. Application

The developed method was applied to find the amount of Pb(II) in tap water, well water and river water samples by USA-D- $\mu$ SPE procedure. The analytical results, along with the recovery for the spiked samples, are given in **Table 2**. The recovery values calculated for the spiked samples were in the range of 94–105 %. The results demonstrated that the UA-D- $\mu$ SPE can be used as a reliable sample treatment technique for extraction and determination of Pb(II) in real samples. Moreover, the standard reference materials (NIST; SRM) were used for validating of proposed procedure by g-C<sub>3</sub>N<sub>4</sub> nanostructure in water and urine samples (**Table 3**).

### 4. Conclusions

Apreconcentration technique based on ultrasound-assisted micro-solid phase extraction using graphitic carbon nitride microparticles was developed for the extraction and preconcentration of Pb(II) from aqueous samples, prior to ICP-OES determination. In the proposed method there is no need to use any chelating agent. The obtained results indicate that the proposed method gives a high enhancement factor and low LOD and can be used for the preconcentration and determination of lead in real water samples.

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**Table 2.** Recovery of lead from water samples based on g-C<sub>3</sub>N<sub>4</sub> particles by USA-D- $\mu$ SPE procedure

Sample	Added ( $\mu\text{g L}^{-1}$ )	Found ( $\mu\text{g L}^{-1}$ )	Recovery (%)
Tap water	0.0	<LOD	–
	10.0	10.2 (2.5) <sup>a</sup>	102
Well water	0.0	5.1 (3.2)	–
	10.0	14.5 (3.0)	94
River water	0.0	4.3 (2.9)	–
	10.0	14.8 (2.6)	105

<sup>a</sup> Values in parentheses are R.S.D.s based on three replicate analyses

**Table 3.** Validation of USA-D-SPE procedure in water by standard reference materials (SRM, NIST)

Sample	SRM ( $\mu\text{g L}^{-1}$ )	Added ( $\mu\text{g L}^{-1}$ )	Found* ( $\mu\text{g L}^{-1}$ )	Recovery (%)
<sup>a</sup> SRM1643d	18.2 $\pm$ 0.6	-----	17.4 $\pm$ 0.9	-----
		15.0	31.9 $\pm$ 1.4	96.6
<sup>b</sup> SRM 2668	137.9 $\pm$ 3.6	-----	138.6 $\pm$ 6.5	-----
		150.0	287.7 $\pm$ 11.4	99.4

\*Mean of three determinations of samples  $\pm$  SD (P = 0.95, n = 10)

<sup>a</sup>SRM1643d, trace element in water

<sup>b</sup>SRM 2668, Human Freeze-Dried Urine, level (II),  $\mu\text{g L}^{-1}$

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