



Resonance light scattering sensor of the metal complex nanoparticles using diethyl dithiocarbamate doped graphene quantum dots for highly Pb(II)-sensitive detection in water sample

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ABSTRACT

This study was aimed to detect Pb²⁺ using diethyl dithiocarbamate-doped graphene quantum dots (DDTC-GQDs) based pyrolysis of citric acid. The excitation maximum wavelength (λ_{max} , ex = 337 nm) of the DDTC-GQDs solution was blue shift from bare GQDs (λ_{max} , ex = 365 nm), with the same emission maximum wavelength (λ_{max} , em = 459 nm) indicating differences in the desired N, S matrices decorating in the nanoparticles. Their resonance light scattering intensities were peaked at the same λ_{max} , ex/em = 551/553 nm without any background effect of both ionic strength and masking agent. Under optimal conditions, the linear range was 1.0–10.0 $\mu\text{g L}^{-1}$ ($R^2 = 0.9899$), limit of detection was 0.8 $\mu\text{g L}^{-1}$ and limit of quantification was 1.5 $\mu\text{g L}^{-1}$. The precision, expressed as the relative standard deviations, for intra-day and inter-day analyses was 0.87% and 4.47%, respectively. The recovery study of Pb²⁺ for real water samples was ranged between 80.8% and 109.5%. The proposed method was also proved with certified water sample containing 60 $\mu\text{g L}^{-1}$ Pb²⁺ giving an excellent accuracy and was then implied satisfactorily for ultra-trace determination of Pb²⁺ in drinking water and tap water samples.

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1. Introduction

Among different environment from various industrial activities including metal plating, oil refining and battery manufacturing, lead ion (Pb²⁺) can be taken into the body via inhalation, ingestion or skin adsorption. When the body is exposed to lead, it can be accumulated in the human body throughout the lifetime attributing its cumulative serious poison effects [1–5]. Water quality has become an issue of vital importance which is an essential resource that has been threatened by pollution. In drinking water, maximum allowable limit of total Pb of 50 $\mu\text{g L}^{-1}$ is considered safe by World Health Organization, whereas <15 $\mu\text{g L}^{-1}$ is adopted by the United States Environmental Protection Agency [6]. Therefore, it is important to develop a simple, fast and convenient method for lead detection, especially at ultra-trace level.

Several methods have been applied for lead determination including flame atomic absorption, inductively coupled plasma - atomic emission spectrometry, spectrophotometric methods and electrothermal atomic absorption spectrometry [7–12]. However, these methods have a greater cost, higher sample volume requirements and instrumentation complexity limiting. Therefore, this study focuses on the determination of lead in

water sample detected by resonance light scattering technique. Resonance light scattering (RLS) is a special light scattering occurring when the wavelength of the scattered light is located at or close to the molecular absorption band. The spectral characteristics and scattering intensity are strongly influenced by the molecular size, shape, conformation and interfacial properties, which further provide favorable new information for the study of the interaction of biological macromolecules and the molecular recognition [13,14]. In recent years, RLS technique has been widely applied in the quantitative analysis of drugs [15,16], surfactants [17], proteins [18,19], heavy metal ions [20–22] and nanoparticles [23] because of high sensitivity, rapidness, simplicity and convenience.

Regarding this method, Pb²⁺ forms complex with DDTC which is a chelating agent with strong tendency to form stable heavy metal complexes [24]. Furthermore, use of graphene quantum dots (GQDs) as an auxiliary ligand and substrate has attracted much attention in lead-diethyl dithiocarbamate (Pb-DDTC) interactions. GQDs possess large surface area, large diameter, fine surface grafting using the π - π conjugated network or surface groups and other special physical properties [25–27]. It has the carboxyl and hydroxyl groups at their edge enable them to display excellent water solubility and suitability for successive functionalization with various organic, inorganic, polymeric or biological species [28,29]. For these reasons, GQDs have attracted significant attention worldwide. Nowadays, it has been applied as sensor for

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