

Selective Determination of Lead in Complicated Environmental Samples by Displacement Dispersive Liquid-liquid Microextraction and Graphite Furnace Atomic Absorption Spectrometry

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INTRODUCTION

Lead (Pb) is one of the most toxic elements, with an accumulative effect and environmental toxicity, and is classified as a Group B2 (probable) human carcinogen by the United States Environmental Protection Agency (USEPA) (1). Pb can affect almost all organs and systems in the human body, resulting in blood enzyme changes, hyperactivity, and neurological disorders (2, 3). However, its unique properties make it useful as an industrial material in diverse fields, but released into the environment in considerable amounts finally leads to bioaccumulation in the living organisms through diverse pathways. Consequently, the development of reliable analytical methods for the determination of Pb is of great importance for the effective monitoring of pollution levels in the environment and the critical evaluation of possible risks to human health.

The direct determination of Pb in environmental samples is often difficult due to matrix effects and the low concentration of Pb. In order to achieve accurate and reliable analytical results, an initial sample pretreatment procedure for analyte preconcentration and matrix separation is often required. Several methods have been reported for the separation and preconcentration of Pb, such as co-precipitation (4), liquid-liquid extraction (LLE) (5), solid-phase extraction

ABSTRACT

A novel method was developed for the selective determination of lead (Pb) in environmental samples by displacement dispersive liquid-liquid microextraction (D-DLLME) combined with graphite furnace atomic absorption spectrometry (GFAAS). This D-DLLME method involves two steps of dispersive liquid-liquid microextraction (DLLME). Firstly, Zn^{2+} reacted with diethylthiocarbamate (DDTC) to form the Zn-DDTC complex and was then extracted with the DLLME procedure. Then the sediment phase was dispersed into the sample solution containing Pb^{2+} with a dispersive solvent; then another DLLME procedure was carried out. Since the stability of Pb-DDTC is higher than that of Zn-DDTC, Pb^{2+} can displace Zn^{2+} from the pre-extracted Zn-DDTC complex and be preconcentrated into the sediment phase. The interference from co-existing metal ions with a lower DDTC complex stability was largely eliminated as they cannot displace Zn^{2+} from the Zn-DDTC complex. Under the optimal conditions, the limit of detection was 35 ng L^{-1} (3σ) for lead, and an enhancement factor of 91 was achieved with a sample volume of 5.0 mL. The proposed method has been successfully applied to the determination of trace lead in environmental samples with satisfactory results.

(SPE) (6, 7), cloud point extraction (CPE) (8, 9), and liquid-phase microextraction (LPME) (10, 11). However, disadvantages such as time-consuming, unsatisfactory enrichment factors, and requiring large amounts of organic solvents limit their application.

Dispersive liquid-liquid microextraction (DLLME) is a novel liquid-liquid extraction protocol based on ternary component solvent systems (12, 13). The method has the advantages of simplicity of operation, speed, low cost, high recovery, and enrichment factors, and has proven to be a suitable preconcentration procedure for various metal ions (14, 15). The DLLME preconcentration of metal ions often requires the formation of a hydrophobic metal chelate and also suffers undesirable interference from co-existing metal ions, especially in complicated matrices, owing to the competition for the complexing reagent. In fact, all metal chelate-based preconcentration systems have encountered such problems (16). To overcome this problem, a displacement-sorption preconcentration protocol based on the stability difference of the metal chelate was developed for highly selective quantification of metal ions in complicated matrices (17). The metal of interest (M1) with a higher complex stability can take the place of another metal (M2) with lower complex stability from its complex, whereas the reverse reaction cannot occur. Through the displacement reaction, interferences from co-existing metal ions were greatly eliminated

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and efficient analyte preconcentration can be achieved simultaneously. This displacement-sorption preconcentration method has been successfully applied for the determination of mercury (Hg) in environmental and biological samples (18), methylmercury in fish samples (19, 20), palladium (Pd) in road dusts (21), and silver (Ag) in water samples (22). This same principle was also employed by using a displacement cloud point extraction method for the selective determination of silver (Ag) and copper (Cu) (23, 24).

The purpose of this work is to apply a recently developed displacement dispersive liquid-liquid microextraction (D-DLLME) method (25) for the selective determination of Pb in complicated environmental samples by graphite furnace atomic absorption spectrometry (GFAAS). The extraction steps of D-DLLME are illustrated in Figure 1. In this work, diethyldithiocarbamate (DDTC) was selected as the chelating reagent, and Zn^{2+} was employed as the pre-extraction metal ion for best selectivity of the displacement reaction. The optimal conditions of the extraction solvent and the dispersive solvent for the DLLME preconcentration of Zn and Pb have been studied in previous works (26, 27) and are used directly in this work. For this D-DLLME method, the extraction efficiency

depends on the displacement reaction between Pb and Zn-DDTC. Systematic optimization of the conditions affecting the displacement reaction was therefore carried out to obtain optimal performance of the D-DLLME procedure.

EXPERIMENTAL

Instrumentation

A TAS-990 atomic absorption spectrophotometer (Beijing Purkinje General Instrument Co. Ltd., Beijing, P.R. China), equipped with a deuterium background corrector and GF990 graphite furnace atomizer system, was used. A Pb hollow cathode lamp was used as the radiation source at 283.3 nm. The optimum operating parameters

for GFAAS are given in Table I. All measurements were carried out in the integrated absorbance (peak area) mode. The pH values were measured with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, P.R. China). A Model 0412-1 centrifuge (Shanghai Surgical Instrument Factory, Shanghai, P.R. China) was used to accelerate phase separation. A model MK-III microwave digestion system (Shinco Institute of Microwave Digestion Technology, Shanghai, P.R. China) was used to dissolve the solid samples.

Standard Solution and Reagents

Stock standard solutions (1000 mg L^{-1}) of Pb and Zn were obtained from the National Institute of Stan-

TABLE I
GFAAS Operating Parameters

Parameters	
Lamp current	2.0 mA
Wavelength	283.3 nm
Slit/nm	0.4 nm
Ar flow rate	300 mL min^{-1} (stopped during atomizing)
Sample volume	$20 \text{ }\mu\text{L}$
Temperature Program	
Drying	$110 \text{ }^\circ\text{C}$ (Ramp 15 s, Hold 10 s)
Ashing	$500 \text{ }^\circ\text{C}$ (Ramp 15 s, Hold 10 s)
Atomizing	$1900 \text{ }^\circ\text{C}$ (Ramp 0 s, Hold 3 s)
Cleaning	$2200 \text{ }^\circ\text{C}$ (Ramp 1 s, Hold 3s)

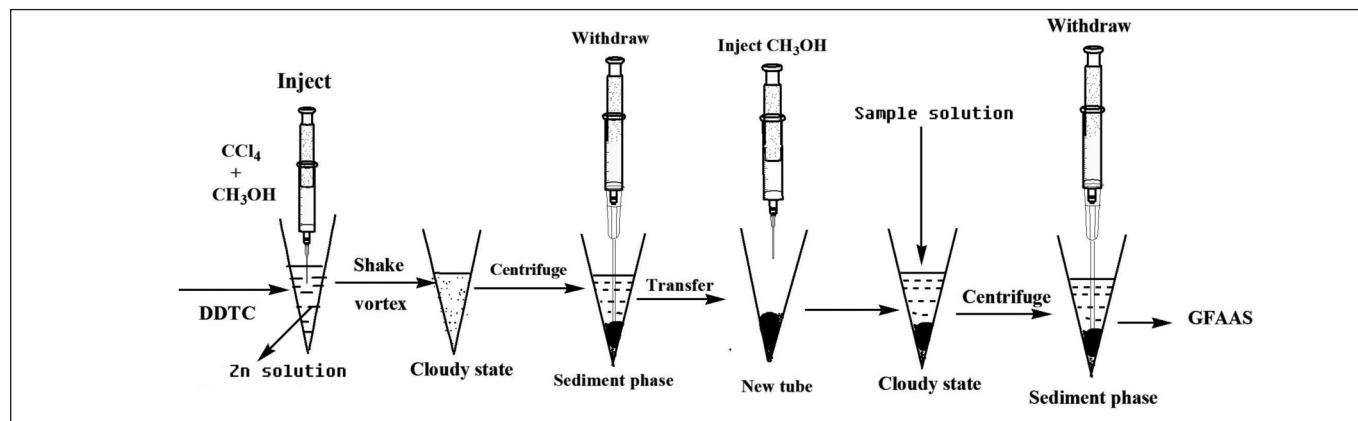


Fig. 1. Schematic of D-DLLME procedure.

dards (Beijing, P.R. China). Working standard solutions were obtained by appropriate dilution of the stock standard solution. The solution of DDTC was prepared by dissolving appropriate amounts of sodium diethyldithiocarbamate (AR, Shanghai Chemistry Reagent Company, Shanghai, P.R. China) in doubly distilled water. All other reagents used were of the highest available purity and of at least analytical reagent grade. Doubly distilled water was used throughout. Pipettes and vessels used in the experiments were kept in 10% nitric acid for at least 24 hours and subsequently washed four times with doubly distilled water.

Displacement Dispersive Liquid-liquid Microextraction Procedure

Aliquots of 5.0-mL sample solution containing $10 \mu\text{g L}^{-1} \text{Zn}^{2+}$, 0.02 g L^{-1} DDTC, and $0.02 \text{ mol L}^{-1} \text{HNO}_3$ were placed into 10-mL screw cap glass test tubes with a conical bottom. An amount of 0.5 mL of methanol (dispersive solvent) containing 60 μL of carbon tetrachloride (CCl_4 , extraction solvent) was injected rapidly into the sample solution by using a 1.00-mL microsyringe. After a cloudy solution was formed in the test tube, the Zn-DDTC complex was extracted into the fine droplets of CCl_4 . Then, the solution was centrifuged at 3500 rpm for 5 minutes, and the dispersed fine droplets of CCl_4 were deposited at the bottom of the conical test tube (about 35 μL). After removing the aqueous phase, the sediment phase was dissolved with 0.2 mL methanol and injected into a 5.0-mL sample solution containing Pb and $0.02 \text{ mol L}^{-1} \text{HNO}_3$, then another cloudy solution was formed and incubated for 5 minutes. In this step, Pb can replace Zn from the pre-extracted Zn-DDTC complex and enter into the sediment phase. After centrifuging, 20 μL of the sediment phase at the

bottom of conical test tube (about 25 μL) was removed using a 50- μL microsyringe and injected into the GFAAS for the determination of Pb.

Calibration was performed against aqueous standards submitted to the same D-DLLME procedure. A blank submitted to the same procedure described above was measured parallel to the sample and calibration solutions.

Sample Preparation

Two environmental certified reference materials (CRMs) GBW07104 Ore and GBW08401 Coal Fly Ash (obtained from the Perambulation Institute of Physical Geography and Geochemistry of the Geological and Mineral Ministry, Langfang, P.R. China) were used to check the accuracy of the developed method. All samples were dried in an oven at $60 \text{ }^\circ\text{C}$. A portion (0.1–0.2 g) of the dried samples was accurately weighed into a PTFE vessel, treated with 6 mL of HF, 5 mL of concentrated HNO_3 , and 3 mL of concentrated H_2SO_4 . Then the vessel was submitted to a power program in the microwave oven. The heating steps with a duration of 5 minutes each

and a power of 250, 400, and 650 W were applied. The program was repeated twice to obtain a clear solution. The solution was heated to near dryness and the residue dissolved in $0.1 \text{ mol L}^{-1} \text{HNO}_3$. The final volume was made up to 100 mL with doubly distilled water.

RESULTS AND DISCUSSION

Effect of Pre-extraction Solution and Sample Solution Acidity

The acidity of the pre-extraction solution (acidity of the Zn solution) influences the formation of the Zn-DDTC complex and its extraction and the subsequent extraction of Pb. The acidity of the solution was adjusted with dilute HNO_3 , its effect on the absorbance signal of Pb was investigated in the HNO_3 concentration range of 0– 0.2 mol L^{-1} , and the results are shown in Figure 2. The highest Pb signal was obtained with a HNO_3 concentration of 0.02 mol L^{-1} . Therefore, the pre-extraction process was performed in a $0.02 \text{ mol L}^{-1} \text{HNO}_3$ solution.

The sample solution acidity (acidity of the Pb solution) influences the stability of the Pb-DDTC

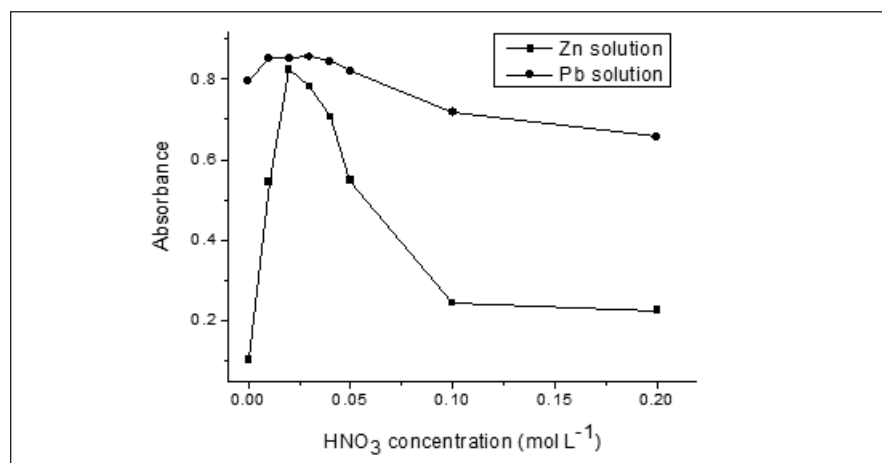


Fig. 2. Effect of acidity of the pre-extraction solution and the sample solution on the D-DLLME of Pb. Experimental conditions: Zn $10 \mu\text{g L}^{-1}$; Pb $1.0 \mu\text{g L}^{-1}$; sample volume 5.0 mL; dispersive solvent (methanol) volume, pre-extraction 0.5 mL, displacement extraction 0.2 mL; extraction solvent (CCl_4) volume 60 μL ; DDTC concentration 0.02 g L^{-1} .

complex and the displacement reaction. The effect of the sample solution acidity on the absorbance signal of Pb was investigated in the range of 0–0.2 mol L⁻¹ HNO₃, and the result is also presented in Figure 2. It can be seen that the highest signal of Pb was obtained at the HNO₃ concentration range of 0.01–0.05 mol L⁻¹. Thus, the sample solution acidity was adjusted to 0.02 mol L⁻¹ HNO₃ for the second extraction process.

Effect of DDTC Concentration

The concentration of DDTC has a direct effect on the formation of the Zn-DDTC complex and its pre-extraction as well as the displacement reaction between Pb and Zn-DDTC. The effect of DDTC concentration on the absorbance signal of Pb was investigated in the range of 0–0.1 g L⁻¹, and the result is shown in Figure 3. As can be seen, the absorbance signal of Pb increased with an increase in DDTC concentration up to 0.02 g L⁻¹, and then remained constant. Thereby, a DDTC concentration of 0.02 g L⁻¹ was selected for further studies.

Effect of Zn Concentration

The Zn²⁺ concentration influences the amount of pre-extracted Zn-DDTC and the subsequent displacement reaction. Studies on the effect of the Zn²⁺ concentration showed that the absorbance signal of Pb increased with an increase in Zn²⁺ concentration up to 10 µg L⁻¹, and then remained constant with a further increase in Zn²⁺ concentration. For further experiments, a Zn²⁺ concentration of 10 µg L⁻¹ was used.

Effect of Volume of Extraction Solvent

In the first extraction process, CCl₄ was used as the extraction solvent and is based on a previous study (26). The effect of the volume of CCl₄ on the absorbance signal of Pb was studied ranging from 40 µL to 80 µL. It was found that the absorbance signal of Pb decreased with an increase in the volume of CCl₄, and the enhancement factor also decreased from 112 to 54, because the volume of the sediment phase increased from 20 to 60 µL. In order to ensure the sediment phase enough for the second extraction process, 60 µL CCl₄

was used as the extraction solvent for this work.

Effect of Volume of Dispersive Solvent

In the second extraction process, the sediment phase of the first extraction process was dispersed into the sample solution as the extraction solvent using methanol as the dispersive solvent. The effect of the volume of methanol on the absorbance signal of Pb was studied. It was found that the absorbance signal of Pb increased with a methanol volume up to 0.20 mL, and then decreased remarkably as the volume of methanol increased. Therefore, 0.20 mL methanol was used as the dispersive solvent in the second extraction process.

Effect of Extraction Time

In the second DLLME procedure, the extraction time may affect the displacement reaction between Pb and Zn-DDTC and the extraction efficiency. The effect of extraction time was examined in the range of 30 seconds to 10 minutes using the constant experimental conditions. The obtained results showed that the absorbance signal of Pb remains constant after the extraction time exceeded 5 minutes. Thus, an extraction time of 5 minutes was employed in the second DLLME procedure.

Pyrolysis and Atomization Curves

Pyrolysis and atomization curves were established using 1.0 µg L⁻¹ of Pb solution submitted to the D-DLLME procedure, and the results are shown in Figure 4. From these curves, a pyrolysis temperature of 500 °C and an atomization temperature of 1900 °C were selected for this work.

Interference Evaluation

Due to the introduction of the displacement reaction, an improve-

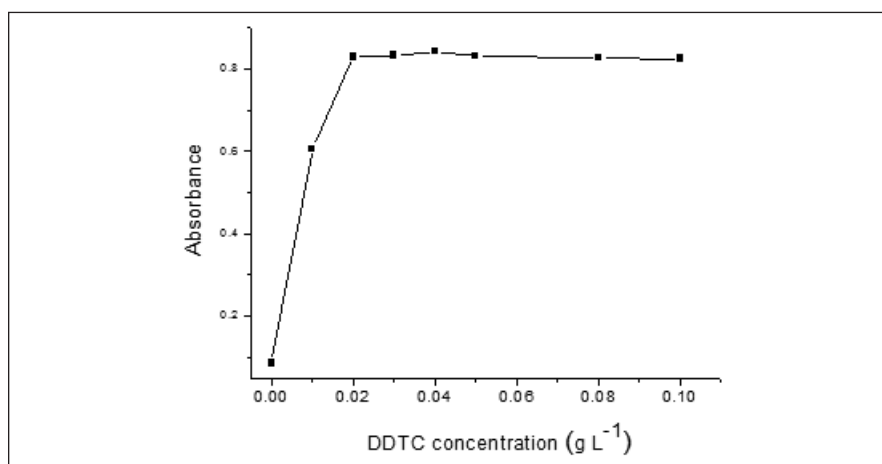


Fig. 3. Effect of DDTC concentration on the D-DLLME of Pb. Experimental conditions: Zn 10 µg L⁻¹; Pb 1.0 µg L⁻¹; sample volume 5.0 mL; HNO₃ concentration 0.02 mol L⁻¹ in the pre-extracted solution and the sample solution; dispersive solvent (methanol) volume, the pre-extraction 0.5 mL, the displacement extraction 0.2 mL; extraction solvent (CCl₄) volume 60 µL.

ment of the tolerable limits for the interference species in the D-DLLME method was expected. The effects of several potentially interfering species were carefully studied and the results are listed in Table II as well as the results obtained with the conventional DLLME method (27). The results show that the D-DLLME method has large improvements in the tolerable limit of coexisting heavy metal ions. The presence of large amounts of alkaline and alkaline earth metal ions have no interference effect on the D-DLLME extraction of Pb because they cannot complex with DDTC. These results clearly demonstrated the high selectivity of the developed D-DLLME method for the determination of trace Pb.

Characteristics of the Method

Under the optimal experimental conditions, the calibration curve was linear over the range of 0.1–10 $\mu\text{g L}^{-1}$ with a correlation coefficient (r) of 0.9993. The limit of detection

(LOD), calculated as three times the standard deviation of 11 replicate measurements of the blank solution, was 35 ng L^{-1} . The precision of this method was determined by analyzing a standard solution at 1.0 $\mu\text{g L}^{-1}$ of Pb in sequence for seven times, and the relative standard deviation (RSD) was 3.1%. The enhancement factor, calculated as the ratio of the analytical signal of Pb obtained after and before extraction, was 91 for a 5.0-mL sample solution.

Analysis of Real Samples

In order to establish the validity of the proposed method, Pb was determined in two environmental certified reference materials GBW07104 Ore and GBW08401 Coal Fly Ash. The analytical results listed in Table III show that the determined values were in good agreement with the certified values despite the complicated matrices of these samples.

The proposed method has also been applied to the determination

of Pb in river water, lake water, and tap water samples. The river water sample was collected from the Yangtze River (Wuhan, P.R. China), the lake water sample was collected from East Lake (Wuhan, P.R. China), and the tap water sample was freshly collected in our laboratory after allowing the water to flow for 5 minutes. All water samples were filtered through a 0.45- μm membrane filter and analyzed as soon as possible after sampling. In addition, the recovery experiments of different amounts of Pb were carried out. The results listed in Table IV show that the recoveries in the range of 97–104% are reasonably well for trace analysis.

CONCLUSION

Under the optimal conditions, a limit of detection of 35 ng L^{-1} and an enhancement factor of 91 were achieved for lead by the developed D-DLLME method with a sample volume of 5.0 mL. Compared with the conventional DLLME method,

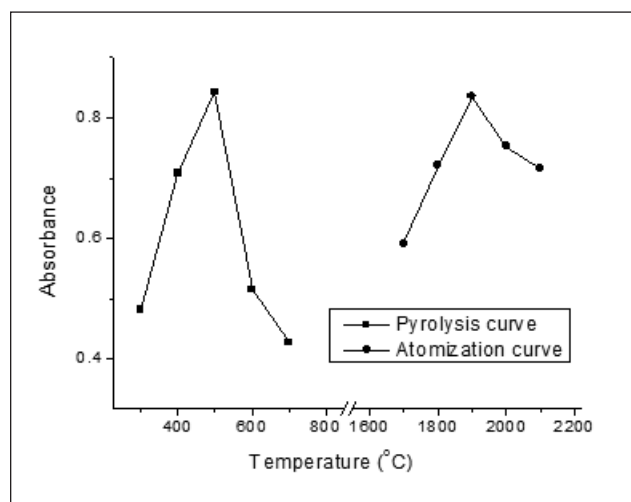


Fig. 4. Pyrolysis curve and atomization curve for Pb. Experimental conditions: Zn 10 $\mu\text{g L}^{-1}$; Pb 1.0 $\mu\text{g L}^{-1}$; sample volume 5.0 mL; HNO_3 concentration 0.02 mol L^{-1} in the pre-extracted solution and the sample solution; dispersive solvent (methanol) volume, pre-extraction 0.5 mL, displacement extraction 0.2 mL; extraction solvent (CCl_4) volume 60 μL ; DDTC concentration 0.02 g L^{-1} .

TABLE II
Tolerance Limits of Coexisting Ions

Coexisting Ions	Tolerance Limits (coexisting ion/ Pb ratio ^a)	
	Displacement DLLME	Conventional DLLME (27)
K^+ , Na^+	600,000	500,000
Ca^{2+} , Mg^{2+}	600,000	100,000
Al^{3+} , Cr^{3+}	50,000	500
Cd^{2+} , Mn^{2+} , Co^{2+}	50,000	1000
Cu^{2+} , Ni^{2+}	5,000	1000
Fe^{3+}	1,000	100
SO_4^{2-} , NO_3^- , Cl^-	1,000,000	500,000

^a Pb concentration, 1.0 $\mu\text{g L}^{-1}$.

Table III
Analytical Results for Pb in Certified Reference Materials (ng g^{-1} , mean $\pm\sigma$, n=5)

Samples	Found	Certified value
GBW07104 Ore	12.5 \pm 2.4	11.3 \pm 2.8
GBW08401 Coal Fly Ash	31.6 \pm 3.2	33.8 \pm 2.2

TABLE IV
Determination of Pb ($\mu\text{g L}^{-1}$) in Water Samples

Samples	Added	Found ^a	Recovery (%)
River Water	0	3.27±0.12	-
	5	8.12±0.54	97
	10	13.18±0.88	99
Lake Water	0	5.62±0.23	-
	5	10.83±0.68	104
	10	15.45±1.02	98
Tap Water	0	1.09±0.07	-
	0.5	1.60±0.14	102
	1.0	2.09±0.18	100

^a mean ± S.D., n=5.

the proposed D-DLLME method effectively minimizes the interference from co-existing heavy metal ions without the need of any masking reagents. These results demonstrate that the developed method is simple, rapid, selective, and sensitive, and has a promising future in routine applications for the determination of trace amounts of Pb in relatively complicated matrices.

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