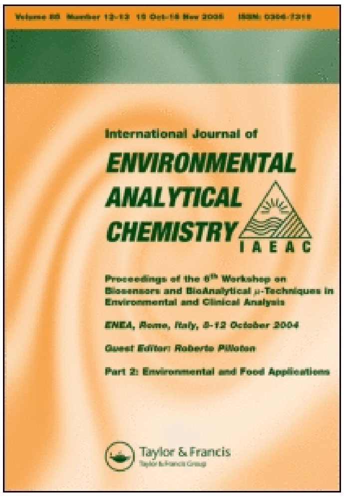

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Low-Molecular-Weight-Organic-Acids as Extractant to Predict Plant Bioavailability of Rare Earth Elements

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LOW-MOLECULAR-WEIGHT-ORGANIC-ACIDS AS EXTRACTANT TO PREDICT PLANT BIOAVAILABILITY OF RARE EARTH ELEMENTS

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A mixture of malic acid and citric acid as extractant for the evaluation of plant bioavailability of rare earth elements (REEs) in soils is presented. Extractable REEs by malic-citric acid, acetic acid (CH_3COOH), DTPA, EDTA, Mehlich 3 and total REEs in soils were compared with the REEs in winter wheat (Triticum aestivum L.) grown in the soils in greenhouse. Malic-citric acid extractable REEs gave the best prediction of plant-available REEs. The correlation coefficients between malic-citric acid extractable REEs and REEs in wheat were from 0.7153 to 0.9635. Mehlich-3 and EDTA resulted in acceptable predictions for REEs, while the total contents and CH_3COOH, DTPA extractable REEs in soil were not correlated with that in plant for most of the REEs. It was possible to infer that REEs extracted by 0.1 M malic-citric acid could be used as a predictor of available REEs in soils.

Keywords: Bioavailability; extraction; low-molecular-weight-organic-acids; rare earth elements; soil

INTRODUCTION

In recent years, millions of tons of fertilizers containing REEs are used worldwide for increasing agricultural productivity [1, 2]. It was predicted that only in China REE fertilizers intended for agriculture production was covering over 16–20×10^6 ha of agricultural land in 1995 [3, 4]. Widespread use of REEs for agricultural purpose may result in a potential increase in REE concentrations in soil and cause environmental pollution. Also it should be noted that many mineral phosphoric fertilizers, if derived from apatite, contain appreciable amounts of REEs,

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which may influence the concentration of REEs in soils and plants grown in cultivated soils [5]. Therefore, it is important to obtain more knowledge of environmental effects of REEs in order to predict any possible deleterious effect occasioned by their use.

Up to now there has been no adequate extraction method available for the evaluation of bioavailability of REEs in soil. Due to the need for establishing a common scheme for extraction, a three-stage sequential extraction procedure was proposed by European Commission's Community Bureau of Reference (BCR)[6]. BCR is now called the Standard Measurements and Testing Program of the European Community (SMT). The detailed extraction protocols was described by Ph. Quevauviller et al. [6]. This method has been widely applied in the determination of extractable trace metals in soils and sediments. Recently BCR procedure was employed to extract REEs in soil [7]. For some of the REEs, including La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb and Y, significant positive correlation existed between the REEs in soils extracted with CH_3COOH and total REEs in leaves of corn. The correlation coefficients ranged from 0.5662 to 0.8262. However, the positive correlation coefficients were existed only for leaves. As far as other parts of the corn are concerned, no significant correlation was observed. Another research [8] showed that the distribution of the individual REEs in plants had little or no agreement with that in the soil or the soil extracts. It may be contributed to the reason that question of the fractionation of the REEs has not been settled or no adequate extraction method has been established.

Li et al. [9] have shown that Low Molecular Weight Organic Acids (LMWOAs) play the very important roles during root physiological activities. As metabolic products of plant root, the LMWOAs secreted by plant roots would lower the pH of the rhizosphere and therefore solute more metals easily available for plant uptake. Also they are capable of forming complexes with metal ions and modify the mobility of the metals in soil rhizosphere [10]. It could be hypothesized that LMWOAs used as extractant might be considerably similar to the rhizosphere. So the metal species extracted by LMWOAs might represent the bioavailable fraction to plant. On the other hand LMWOAs offer favorable combination of stability constants for the simultaneous complexing of all REEs. The objective of this paper was to establish a single extraction by using LMWOAs as extractant to assess the bioavailability of REEs to plant.

EXPERIMENTAL

Soils

Soil samples (0–20cm) were collected from 10 different rural regions from northern to southern China, which were all from cultivated soils and varied widely in physico-chemical properties. The soil samples were air dried and ground to pass through a 2-mm sieve, homogenized and stored until analysis. The standard methods [11] were used for the determination of pH, cation exchange capacity and organic matter for soil characterization. Selected properties of the soils are presented in Table I.

TABLE I Selected properties of studied soils

Sample	*Geographical origin*	*Order*	*CEC (me/100 g)*	*pH*	*Organic mater (%)*
1	guizhou	Entisol	2.13	7.52	2.13
2	Yunnan	Alfisol	12.22	6.10	4.34
3	Jiangxi	Ultisol	3.33	6.35	2.12
4	Beijing	Mollisol	6.47	7.50	1.77
5	Liqiao	Mollisol	14.0	7.71	1.17
6	Shougang	Mollisol	13.6	7.82	1.76
7	Baoding	Mollisol	1.61	8.81	1.04
8	Longkou	Mollisol	13.11	8.28	1.24
9	Qinan	Mollisol	28.48	6.28	5.19
10	Jiamusi	Mollisol	19.70	6.03	3.97

Pot-culture experiment and extraction procedure

For the pot experiments, 1-kg soil was placed in a plastic pot. All pots were fertilized with NH_4NO_3, $KH_2PO_4$and K_2SO_4 in certain amounts corresponding to 800 mg N, 800 mg K, 300 mg P and 170 mg S per pot. Winter wheat (triticum aestivum L.) were sown at 20 seeds per pot and subsequently thinned to 10 plants per pot after germination. Water losses were made up by daily watering with deionized water to maintain certain moisture content. The plants were harvested 8 weeks after germination. The samples were washed thoroughly with deionized water, placed in paper bags, and dried to constant weight at 60 °C for 24h, the dried tissues were finely ground and ready for analysis.

Extraction was performed with 2.00 g of dried soil sample and 20 ml extractant in 50-ml polyethylene centrifuge tube with mechanical shaking. The extractant was the mixture of malic acid and citric acid in the ratio of one to two. The extractant concentration, shaking time and soil-extractant ratio were varied in order to optimize the extraction procedure. All extractions were made with triplicate samples from the same site. The triplicate analyses varied from their means by no more than 10%, so the average results were used for further analysis.

Elemental analysis

The total content of REEs in soil and plant were determined by inductively coupled plasma mass spectrometry (ICP-MS, PQ 3, Fisons Instruments, UK) after decomposition of 0.100g of dried soil with 3 ml of $HNO_3/HClO_4/HF$ (1+1+1) mixture [12]. The extractable REEs were analyzed after diluting the extractant 5 times with 2% of HNO_3. The ICP-MS was optimized with a solution of ^{115}In at 10 ng ml^{-1} in 2% HNO_3, which was also used as the internal standard to compensate for matrix suppression and signal drifts during analysis. The operating conditions are shown in Table II.

TABLE II ICP-MS Operating Conditions

ICP system	
Forward Power	1350 W
Reflected Power	<5 W
Coolant argon flow rate	14 L min^{-1}
Auxiliary gas flow rate	0.9 L min^{-1}
Nebulizer gas flow rate	0.8 L min^{-1}
Sample uptake rate	1.0 mL min^{-1}
Sampling depth	15 mm
Mass spectrometer	
Sampler (nickel) orifice	1.0 mm
Skimmer (nickel) orifice	0.7 mm
Vacuum	5×10^{-7} mbar
Data acquisition	Range-scanning mode
Mass range	85–175 amu
Total acquisition time	60 s

For quality control seven replicate samples of three certified reference materials (GSS-1, GSS-8 of soils and GBW 07605 of tea, from the National Research Center for Certified Reference Materials, Beijing, China) were decomposed and analyzed.

The results are summarized in Table III. A good agreement of the data with the certified values was achieved overall and the precision of the determinations was good.

TABLE III Determination of rare earth elements (REEs) in the Certified Reference Materials by ICP-MS

Element	*GSS-1 (ug/g)*		*GSS-8 (ug/g)*		*GBW07605 (ug/g)*	
	This method	*Certified*	*This method*	*Certified*	*This method*	*Certified*
Y	24.41±0.53	25±4	13.33±0.69	15±2	0.40±0.01	0.36±0.03
La	34.99+2.71	34±4	21.07±0.82	21±2	0.62±0.07	0.60±0.06
Ce	68.47±1.95	70±5	38.37±1.11	39±6	1.05±0.08	1.0±0.1
Pr	7.41±0.22	7.5±0.5	4.52±0.20	4.8±0.4	0.10±0.02	(0.12)
Nd	25.36±0.75	28±3	17.55±0.52	18.4+2.4	0.50±0.06	(0.44)
Sm	5.16±0.29	5.2±0.4	3.10±0.09	3.3±0.3	0.09±0.01	0.085±0.017
Eu	1.00±0.10	1.0±0.1	0.73±0.04	0.72±0.06	0.02±0.001	0.018±0.002
Gd	4.76±0.24	4.6±0.3	3.12±0.12	2.9±0.4	0.10±0.003	(0.093)
Tb	0.71±0.05	0.75±0.09	0.45±0.02	0.49±0.09	0.012±0.003	(0.011)
Dy	4.29±0.13	4.6±0.3	2.37±0.19	2.6±0.2	0.076±0.002	(0.074)
Ho	0.83±0.06	0.87±0.09	0.50±0.01	0.53±0.07	0.021±0.003	(0.019)
Er	2.57±0.28	2.6±0.2	1.40±0.07	1.5±0.3	0.056±0.001	–
Tm	0.42±0.04	0.42±0.07	0.27±0.01	0.28±0.06	0.018±0.002	–
Yb	2.57±0.28	2.66±0.33	1.53±0.05	1.68±0.22	0.048±0.002	(0.044)
Lu	0.36±0.02	0.41±0.06	0.23±0.02	0.29±0.33	–	–

All reagents used in the experiment were of analytical reagent grade or better.

RESULTS AND DISCUSSION

Selection of extraction solution and optimization of the procedure

Analysis [9] showed that there were many kinds of LMWOAs secreted by plant root, such as malic acid, citric acid, succinic acid, acetic acid and oxalic acid, with malic acid and citric acid being predominant and over 80% of the total. For simplifying, the mixture of malic acid and citric acid as their original ratio of 2:1 in excretion of roots was chosen as the extractant. Hereafter referred to simply the extractant as malic-citrate acid, such as 0.1 M malic-citric acid means 0.1 M malic acid and 0.05 M citric acid.

In order to determine the conditions for this extraction, the kinetics of the extraction at room temperature using varying concentrations and different soil-solution ratios were investigated. Results obtained showed that different REEs in different soils had almost the same behaviors, here take La as the example for explanation. An extraction time of 8 hours was chosen, as Figure 1 shows that most of the extraction occurred in the first 8 hours reached the equilibrium and slight variations of time would be not critical. Also the higher the concentration of the extractant solution the larger the amount of REEs are extracted. However as it is shown in Figure 2 for all the soils the amounts of La extracted by 0.05 M malic-citric acid are very close to those extracted by 0.1 M malic-citric acid. We can expect that the concentration of 0.1 M malic- citric acid is high enough for the extraction. On the other hand, too high concentration of organic acid would bring problem for the analysis by ICP-MS. Therefore this was that the concentration chosen to implement the extraction procedure. Figure 3 shows that the highest amount of La was extracted when the different soil-solution ratio of 1/10 was chosen.

Extraction of REEs

Total REE contents in soils varied widely across sites especially for light REEs, as shown in Table IV. Soil 1 has the highest concentration of REEs. It may attribute to the fact that soil 1 is a new cultivated land soil. The leaching down of metals has been limited and metals inherited from the parent materials dominate the soil properties. Therefore, the total REE contents in surface soil is higher comparing with other soils.

The extraction percentages for different soils are summarized in Table V. Extractable REEs in soils comprised roughly from 1.72% to 26.7% of the total. When the differences among soils were considered, it was observed that soil 4, 9 and 10 had low extractable REEs while others had higher ones. The most reasonable explanation is that soil 4, 9 and 10 were collected from north China, which developed in a humid frigid-temperature zone and normally had higher proportion of organic matter. Of the organic matter high molecular organic compounds are predominant, such as humic-acid which is about twice as much as fulvic acid[13]. The high molecular organic compounds have weak chemical activity, and are not liable to be resolved to release REEs. Soil 1 and 2 were red soils collected from South China in subtropical climates with abundant precipitation. These soils generally have low pH values. Under this condition, the REE activity is intensified. Mineral and organic bound REEs are easier to be released. Soil 1, 5, 6, 7 and 8 were calcareous soils with high content of carbonates. During extraction REEs associated with carbonates were released by malic-citric acid, leading higher proportion of extractable REEs. The results showed a general tendency that the extractability of REEs for different soils decreases gradually from Southern China to Northern China.

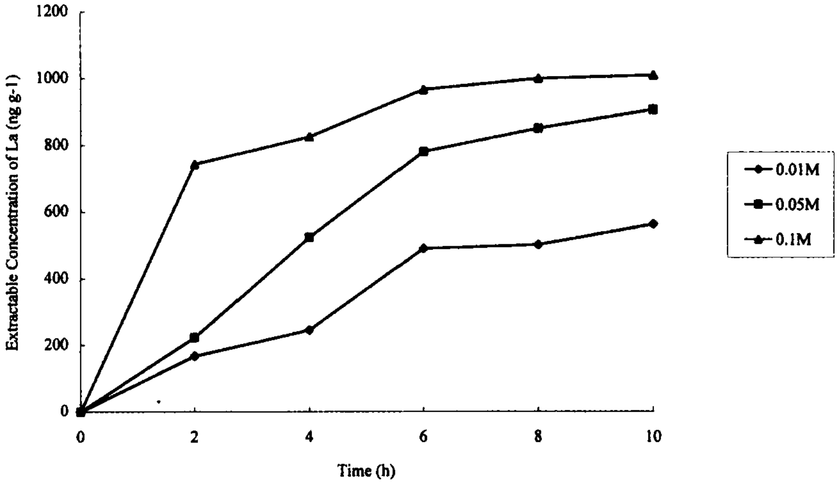

FIGURE 1 The effect of extraction time on extractable La for different acid concentration

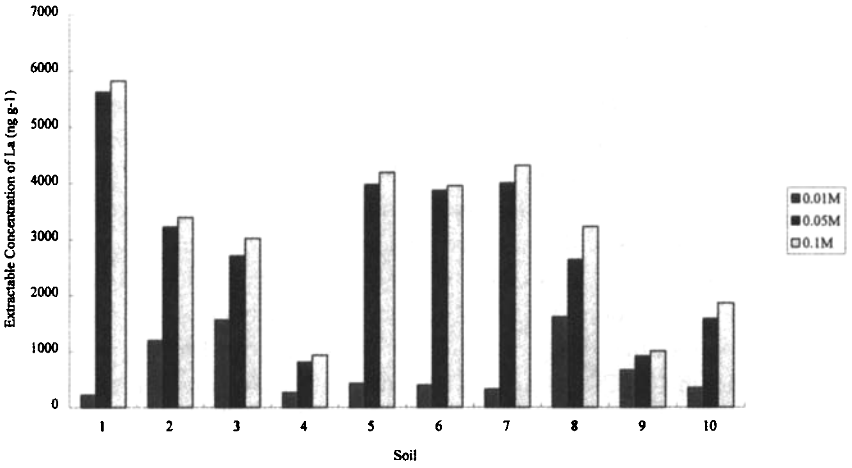

FIGURE 2 Concentration of La extracted by different concentration of malic-citric acid

Correlation of REEs between plant and soils

Correlation analysis was conducted between the REEs in soil extracted with malic-citric acid and the concentration of REEs in plant. The results are listed in

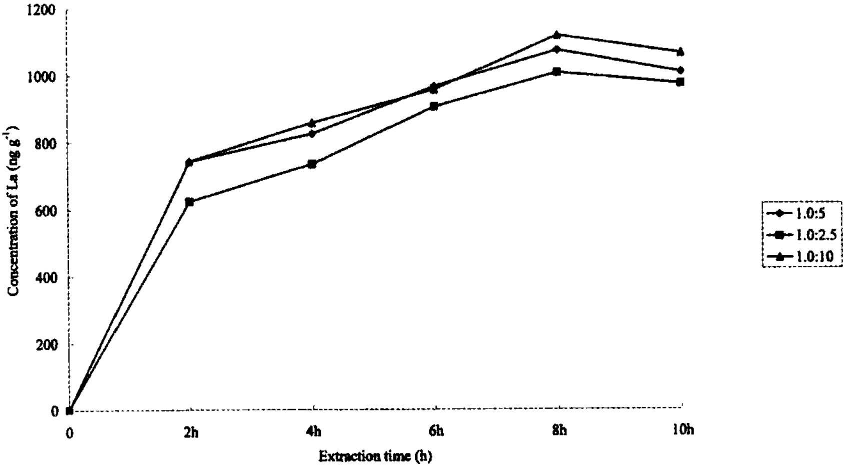

FIGURE 3 The effect of extraction time on extractable La with different soil-extractant ratios

Table VI. High correlation coefficients were obtained, which ranged from 0.7153 to 0.9635. These results suggest that malic-citric acid extractable REEs could be used as a predictor of plant-available REEs in soils.

Mehlich-3, DTPA, EDTA and CH_3COOH extraction procedures are commonly employed to estimate the plant-available forms of micronutrients in soil [14, 15]. A comparison for the correlation coefficients between the extractable REEs and REEs in plants was carried out among 0.1M malic-citric acid, 0.05M DTPA, 0.05M EDTA, Mehich-3 extractants and the total content of REEs in soil. The results are listed in Table VI. For most of the REEs, total contents of REEs in soils correlated poorly with the concentrations in plants, which is in agreement with previous report [7]. This could be interpreted by the general consideration that only limited fraction of the total REEs in soils is available to plant uptake and it is therefore that total content of REEs in soils can hardly predict plant uptake. REEs in CH_3COOH and DTPA extractants also correlated poorly with REEs concentration in plant for most of the REEs. In previous work, significant positive correlation coefficients were obtained between the contents of REEs in CH_3COOH extractant and REEs in leaves of corn. However the correlation existed only for some of the REEs. Also the soils were all calcareous soils collected in the limited range with similar physico-chemical properties. It may not be suitable for different types of soil. Although Mehlic-3 and EDTA resulted in acceptable predictions for REEs, malic-citric acid is the best extractant for prediction of plant-available REEs.

TABLE IV Total REE content in soils

Soil no.	*Concentration (ug/g)*														
	Y	*La*	*Ce*	*Pr*	*Nd*	*Sm*	*Eu*	*Gd*	*Tb*	*Dy*	*Ho*	*Er*	*Tm*	*Yb*	*Lu*
1	41.9	53.4	146.8	10.42	31.5	5.7	1.0	5.1	1.05	5.5	1.1	2.6	0.40	1.6	0.60
2	22.7	38	114.1	9.4	33.1	4.9	1.8	6.5	0.61	4.5	0.7	1.98	0.43	1.93	0.68
3	24.13	36.81	70.36	8.38	30.91	5.62	1.15	5.34	0.76	4.54	0.80	2.17	0.33	2.21	0.41
4	17.2	38.2	100	10.3	30.1	5.1	1.3	4.3	0.6	3.1	0.65	1.4	0.34	1.2	0.33
5	15.58	20.67	44.52	4.96	16.83	4.06	1.12	4.72	0.69	3.55	0.71	1.79	0.34	2.24	0.47
6	19.8	30.37	60.24	7.11	25.69	4.27	1.3	5.07	1.01	3.67	0.85	2.66	0.25	2.49	0.26
7	24.71	35.36	84.7	8.32	28.69	5.21	1.19	5.11	0.74	4.3	0.81	2.05	0.32	2.15	0.45
8	15.55	17.96	37.04	5.02	19.19	3.48	0.79	3.29	0.52	3.37	0.65	1.72	0.25	1.7	0.32
9	28	42.5	87.6	8	27.8	5.9	1.4	5.6	0.68	4.9	0.81	1.87	0.34	2.1	0.45
10	24.58	37.05	81.65	9.71	30.53	6.48	1.3	5.71	0.79	4.65	0.85	2.36	0.32	2.55	0.36

TABLE V Percentage of extracted REEs by 0.1 M malic-citric acid

Soil no.	*Extractable REEs (%)*														
	Y	*La*	*Ce*	*Pr*	*Nd*	*Sm*	*Eu*	*Gd*	*Tb*	*Dy*	*Ho*	*Er*	*Tm*	*Yb*	*Lu*
1	10.28	10.89	11.80	16.77	21.83	24.15	31.09	25.52	16.64	16.49	14.06	16.44	14.09	16.46	7.95
2	24.36	18.91	15.58	13.43	17.37	24.77	17.92	17.23	23.88	17.91	21.31	21.83	13.32	17.19	7.12
3	24.57	8.20	10.23	12.30	14.26	18.79	15.29	19.38	21.94	21.26	23.76	26.71	25.56	22 87	18.86
4	3.00	2.42	1.72	2.40	3.25	3.74	3.84	4.10	4.625	5.60	4.40	7.58	4.20	7 22	3.07
5	24.87	20.27	20.94	22.35	24.24	20.52	16.25	17.51	16.55	18.60	17.23	19.16	14.76	11.62	8.67
6	21.86	13.00	11.84	13.80	14.96	17.83	12.9	14.47	11.58	16.62	13.88	11.65	17.15	9.18	17.60
7	14.47	12.17	9.21	13.14	13.29	14.36	15.26	15.32	15.10	13.92	14.20	13.20	12.09	11.55	7.26
8	21.12	14.85	9.64	16.33	16.92	21.08	20.00	20.13	18.68	15.58	14.35	16.05	14.28	13.3	10.68
9	5.11	2.35	2.04	3.78	4.61	4.34	4.38	4.81	6.47	5.10	5.34	8.43	6.67	5.27	3.77
10	12.43	5.02	5.04	6.06	7.83	7.72	8.31	7.73	9.39	10.05	10.48	10.88	11.60	8.90	9.43

TABLE VI Correlation coefficients (r) between extractable REEs in soils and REE concentration in plants (n=10)

Element	*LMWOAs*	*CH_3COOH*	*DTPA*	*EDTA*	*Mehlich-3*	*Total content*
Y	0.8437†	0.2848	0.24106	0.67299*	0.84088†	0.2031
La	0.7214*	0.6361*	0.33329	0.66821*	0.49290	0.4661
Ce	0.8443†	0.2141	0.43915	0.68313*	0.60697	0.5695
Pr	0.8121†	0.2003	0.38361	0.59761	0.52041	0.0408
Nd	0.8062†	0.4116	0.32012	0.60171	0.58035	0.5195
Sm	0.8746†	0.3506	0.38276	0.6387*	0.66158*	0.1530
Eu	0.9635†	0.3746	0.12057	0.55426	0.61656*	0.6392*
Gd	0.7401*	0.2865	0.43627	0.62806	0.67866*	0.1031
Tb	0.7815†	0.4106	0.26889	0.62757	0.46212	0.3090
Dy	0.8098†	0.6031	0.54465	0.61209	0.79451†	0.0688
Ho	0.7516*	0.5836	0.41548	0.61886	0.60173	0.2118
Er	0.7468*	0.3957	0.57100	0.66861*	0.75032*	0.1950
Tm	0.7153*	0.2787	0.39677	0.34372	0.46366	0.0540
Yb	0.8856†	0.6410*	0.59024	0.61661*	0.78663†	0.0662
Lu	0.9193†	0.4810	0.19688	0.64789*	0.78908†	0.0917

*. Significant at 0.10 probability level.

†. Significant at 0.050 probability level.

CONCLUSION

In this paper a single extraction procedure for the determination of the readily available REEs in soils is presented. Malic-citric acid extractable REEs have significant correlation with REEs in plant. We may infer from the results that REEs extracted by malic-citric acid may be considerably similar to the plant available part of REEs. Most importantly LMWOAs might have potential as a general extractant to predict plant bioavailability of trace elements based on the rhizosphere-mimetic extraction.

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