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**TECHNOLOGY OF URANIUM PURIFICATION. IMPURITIES DECONTAMINATION
FROM URANYL CHLORIDE BY EXTRACTION WITH TRI-n-OCTYLAMINE
IN THE PRESENCE OF THIOUREA AS COMPLEXING LIGAND.**

Alcídio Abrão

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TECHNOLOGY OF URANIUM PURIFICATION. IMPURITIES DECONTAMINATION
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ABSTRACT

The extraction of uranyl chloride by tri-n-octylamine (TOA) and its decontamination from several impurities with the aid of thiourea is investigated. The effect of thiourea as a complexing agent, giving rise to unextracted cationic species of several metallic ion and its consequence in the extraction of uranyl chloride from hydrochloric acid with TOA-benzene(xylene) is described. Also, the effect of an acidified thiourea solution for scrubbing the organic phase loaded with uranyl chloride is studied.

INTRODUCTION

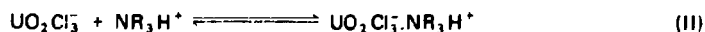
The long chain amines had shown to be excellent extractants for various inorganic and organic acids, and for a great number of anionic metallic complexes. Smith and Page⁽⁴⁴⁾ had indicated the association properties of high weight amines with acids. In a very simple way the amine protonation reaction can be written:



where R is an aliphatic or aromatic long chain group and A is a simple anion (like $FeCl_4^-$, $UO_2Cl_3^-$, $ZnCl_4^{2-}$)

Therefore, amines like tri-n-octylamine (TOA), tri-n-benzylamine (TBA) and methyl-n-octylamine (MDOA) had been used for the extraction of hydrochloric, sulfuric and hydrofluoric acids, and numerous organic acids, like acetic, formic and tri-chloroacetic, as well.

Although only a very few authors^(48,46,40) had added some doubts on the probable extraction mechanism, nowadays the more acceptable mechanism is the element transfer to the organic phase in the form of its anionic complex. Then, for instance, the extraction of uranium from hydrochloric acid may be explained by an ion association mechanism between the $UO_2Cl_3^-$ species and the protonated tertiary amine:



Similarly, the extraction of silver from dilute hydrochloric acid by a tertiary amine may be written:



(*) Presented in the Conference on Nuclear Power and Applications in Latin America. American Nuclear Society and Instituto Nacional de Energia Nuclear, Mexico, September 28 - October 1, 1975.

Of great importance, since are the simplest systems and more commonly found either in analytical chemistry or industrially, the chlorides, sulfates and, by last, the nitrates, have being the most investigated for amine extraction. A typical example is the extraction of UO_2^{++} ion for the pre-concentration of uranium from liquors of low grade minerals, or for its separation from many elements present as impurities. Uranium can be extracted from several dilute acids, as sulfuric, hydrochloric, phosphoric, acetic, oxalic, hydrofluoric, formic and maleic by long chain amines, as for instance with MDOA-xylene⁽³⁴⁾, or even extracted from dilute sulfate solutions⁽¹⁶⁾.

This paper is presented as a contribution to the selective solvent amine extraction of uranium from hydrochloric acid and its decontamination from several impurities.

OBJECTIVE

Let us assume the high weight amines as liquid anion exchangers, extracting only anionic species. In a previous paper⁽¹⁾ we described the use of thiourea (tu) as a complexing agent for metallic ions, transforming their simple cations in cationic complexes that, for this reason, no more can be extracted by the amines. The formation of several metallic complexes with thiourea that are partial or totally hindered to be extracted by long chain amines diluted in different diluents was previously described⁽¹⁾. Also we had shown the enormous possibility that this property offer to increase the separation systems in analytical chemistry and even, in some cases, the probable industrial applications.

In the two examples above mentioned, the reaction (II) should not be affected by the presence of thiourea, since it does not form complexes with the UO_2^{++} ion, therefore not avoiding the further extraction of uranium by amine. Or, probably, thiourea forms with the uranyl ion complexes so weak that anions like Cl^- and SO_4^{2-} could disrupt them in favor of the formation of extractable anionic species, like UO_2Cl_3 and $[UO_2(SO_4)_3]^{4-}$. As a consequence uranium continue being extracted by the amine. On the other hand the reaction (III) will be totally hindered, since immediately the formation of a very strong cationic $Ag(tu)_3^+$ complex occurs, for which the ion association with the amine cation is not allowed; silver, therefore, is not extracted.

This paper has a scope the investigation of the above mentioned property of thiourea forming cationic species with several metals, while uranium is not complexed, then allowing a further improvement for the uranyl chloride extraction by tri-n-octylamine.

REVISED BIBLIOGRAPHY

The interest for the extraction of acid and its metallic salts from aqueous solutions with long chain amines is in rapid expansion. Discussion of various parameters affecting the equilibrium extraction, as the type of extractant, acid or salt, nature of diluent and the influence of water in the organic phase, together with the composition dissociation or agregation, and the activity coefficients of the several complexes, as well many other informations, can be obtained from extensive revisions^(4,12,20,37).

Revisions made by Brown et al.⁽⁹⁾ and Coleman et al.⁽¹⁴⁾ had shown the properties of many amines types. Later, various compilations of experimental data for amines extraction of metals were published, specially for Pu⁽⁴⁵⁾, and also covering the extraction of many metallic salts^(37,33,13). In 1962, Coleman et al⁽¹³⁾ considered the N- and P- organic compounds as liquid ion-exchangers. Some more recent revisions summarized the use of amines for the fuel element reprocessing^(12,4,45).

For the explanation of metallic ions amine extraction the complex formation is assumed. The great majority of authors admit the formation of anionic complexes (2,3,5,6,8,10-12,14,15,17-19,21-23,28,29,31,35,39,41-43,47,49,50,52,53). The similarity between ion-exchange and extraction by amines is emphasized by many authors^(14,7,27,32,24,26).

Studies for the mechanism of amine extraction were published for indium^(47,31), iron⁽²¹⁾ and cobalt^(22,15) in chloride system. Good and Bryan⁽²¹⁾ mentioned the extraction mechanism and the nature of extracted species for Fe (III) and Co (III) for HCl amines systems. The extraction of Tc (VII) with various organic N-compounds is mentioned by Boyd and Barsen⁽⁵⁾, who believe in an ion exchange mechanism.

Since 1952 a great variety of amines and other organo-nitrogen compounds were studied at ORNL, Oak Ridge, Tenn., with the main scope to recover uranium, thorium and other valuable ions from minerals leaching liquors^(11,7,8,35). The Amex Process (amine extraction) was developed during that research and installed for the uranium production in several plants and also for other applications, from hydrometallurgical processes to analytical and radiochemistry applications.

Fundamental studies of the extraction process by amines, particularly for uranium, were made by Allen⁽²⁾, McDowell et al.⁽²⁸⁾, Carswell and Lawrence⁽¹¹⁾.

EXTRACTION OF URANIUM BY LONG CHAIN AMINES FROM HCl MEDIUM

One of the first references that uranium is extracted by long chain amines was made by Moore⁽³⁴⁾ in 1952.

In contrast with the extraction of uranyl ion from sulfuric medium, where relatively low SO_4^{2-} concentration is sufficient for the formation of anionic complexes, suitable for amine extraction, and, on the other hand, high concentration of sulfate compete with the extraction, this is very low for dilute chloride solutions (the extraction is still less efficient for the uranyl nitrate). The U (VI) extraction considerably increase with the increase of the NO_3^- or Cl^- concentration⁽²⁷⁾. The reason for this is a requirement of a reasonably high Cl^- or NO_3^- concentration to form the extractable anionic complexes.

Moore⁽³²⁾ used the uranium extraction from HCl with triisooctylamine (TIOA)-xylene for the separation of uranium from lanthanides and from thorium, since those elements do not form anionic chlorocomplexes. The profile extraction for UO_2^{2+} from HCl medium shows that the extraction is higher than 90% from 3M HCl and greater than 95% from 4M HCl. Moore also demonstrated that the equilibrium is rapid, attained in one minute.

The separation of U, Pa and Th is mentioned by Ichikawa et al.⁽²⁴⁾ as being much more efficient from HCl than from H_2SO_4 or HNO_3 . Moore⁽³²⁾ studied the extraction of U with TIOA-xylene and methylisobutylacetone. Excellent separation of U was reached from thorium, alkaline metals, earthalkaline metals, lanthanides, actinides, Zr, Nb, Ru and many other elements that do not form extractable chlorocomplexes. The same technique is applied for traces and macroquantities. Extracting U from 5M HCl, only Ru and Nb, of the fission products, are appreciably extracted. Nb can be scrubbed from the organic phase with 5M HCl. Ru remains in the organic phase when U is stripped with 0.1M HCl.

Laux and Brown⁽²⁶⁾ used TIOA-xylene for the quantitative separation of U from Zr in 4M HCl. Reynolds and Eldridge⁽³⁸⁾ used TBA-chloroform to extract U from 8M HCl prior the determination of ^{235}U by gamma-ray spectrometry. Ichikawa and Urano⁽²⁴⁾ mentioned that the extraction of U (VI) from HCl with a secondary amine (Amberlite LA-1) is superior than from other acids.

The uranyl chloride extraction in the presence of metallic chlorides as salting-out agents is done by Tikhomirov et al.⁽⁴⁶⁾ using tri-n-octylamine.

Moore⁽³²⁾ extracted U from hydrochloric medium at concentration starting from 2M HCl, when the U transfer to the organic phase is yet appreciable. For several reasons we had interest in

studying the uranium extraction with amine (TOA) from hydrochloric acid, but at lower acid concentration. For this purpose, experiments were done for the determination of the HCl threshold concentration at which U (VI) initiate to be extracted.

BEHAVIOR OF URANYL ION WITH THIOUREA

There is no indication in the current literature showing that UO_2^{++} ion forms complexes with thiourea. In the present paper we established that the extraction of uranyl ion from HCl, H_2SO_4 , and HNO_3 is not affected by the presence of thiourea. Also U (VI) is not stripped from the loaded organic phase by a solution of some composition as the aqueous phase but now containing thiourea and no U (VI).

Therefore the selectivity is considerable improved by the transfer of uranium from an aqueous phase containing thiourea, since several elements that form cationic complexes with it are not extracted by the amine⁽¹⁾, while uranium is well extracted.

An example of the most common elements present in uranium solutions is iron. This element, depending on the amine type, its diluent and the aqueous acid system used, is strongly extracted together U (VI). In the present contribution we demonstrated that iron is held by thiourea in the aqueous phase while U (VI) is extracted by TOA from HCl. The same was proved as true for Cu, Ag, Ru, Pb, Rh, Pt, Au, Hg, Ir, Os and Se, since they form stable cationic complexes with thiourea⁽¹⁾ and then are not extracted by the amine (Se is reduced to the elemental form).

EXPERIMENTAL PART

The experimental work was directed in such a way that initially only HCl was used for the extraction of U (VI) by TOA diluted in benzene or xylene. The elements preferably studied in the presence of U, due to their facility of anionic complex formation with HCl, were Fe, Cd, In, Zn, Cu, Co, Ag, Bi, Pb, Tl, Ru, Rh, Pd, Pt, Au, Hg, Sn, Sb, Ir, and Os.

REAGENTS

The tertiary tri-n-octylamine (TOA) was purchased from Koch-Light Laboratories Ltd., Englan.l, and used without further treatment. It was diluted to 5% (volume/volume) with xylene or benzene of PA quality. For the great majority of experiments the amine was used without being contacted with acids for preequilibrium. This was done only a few cases. In all experiments TOA was used as a fresh dilution, to avoid any aging effect.

Other reagents like acids, salts and thiourea were of analytical grade.

Uranyl solutions were prepared from U_3O_8 , UO_3 or ammonium diuranate (ADU) of high chemical purity. UO_2Cl_2 solutions were prepared by dissolution of ADU or UO_3 avoiding acid excess. Uranium was titrated by the dichromate-diphenylamine procedure after reduced with $SnCl_2$ and reoxidized with Fe (III)⁽³⁰⁾.

Radioisotopes used as tracers for the development of this work, with exception of ^{59}Fe , and ^{60}Co (supplied by Abbot Laboratories), were obtained by neutron activation of the metals or carbonates in the IEA-R1 Reactor. Natural radioisotopes, as ^{212}Pb , ^{212}Bi and ^{208}Tl were prepared from thorium chloride solution, by amine extraction.

EQUIPMENT

A gamma-ray single channel analyzer with a 2" NaI (TI) well type crystal, provided with recording unity, was used. A Hitachi - Perkin Elmer 139 model spectrophotometer with recording unity and a single beam atomic absorption Jarrel-Ash Co. spectrometer were used.

OPERATIONAL SCHEME FOR THE AMINE EXTRACTION EXPERIMENTS

As a standard procedure adopted for the great majority of experiments the aqueous and organic phases were agitated mildly, avoiding any energetic mixing. For the majority of experiments a (organic/aqueous) ratio of 1 was used, at room temperature. Laboratory experiments usually were done using centrifuge tubes provided with ground cap (15 ml capacity). When necessary, phase separation was done after centrifugation, using a small pipet with rubber bulb for transfer.

In a general way the amine extraction followed the sequence:

- 1) decontamination of several elements from uranium by their extraction from dilute hydrochloric acid ($< 0.5M$ HCl).
- 2) decontamination of several elements from uranium by U (VI) extraction from HCl $> 3M$, after addition of thiourea to the aqueous phase.
- 3) decontamination of some elements extracted together with uranyl chloride from HCl $> 3M$, using HCl-thiourea as scrubbing solution.

ANALYTICAL CONTROL

The analytical control for the extracted species or for the stripped elements were done by gamma-ray spectrometry, atomic absorption spectrophotometry or complexometric titration techniques, depending on the convenience in each case. Whenever possible radiotracer was used. Whenever possible the extracted species were determined directly in the organic phase; for atomic absorption measurements the organic phase was burned directly.

URANYL CHLORIDE EXTRACTION WITH TOA-XYLENE (BENZENE)

A work program was scheduled including many experiments for uranyl chloride extraction from HCl medium with TOA diluted with xylene or benzene. The following parameters were studied:

- 1) extraction time (extraction equilibrium).
- 2) threshold for HCl concentration at which U is extracted.
- 3) U concentration in the organic phase (organic phase capacity for UO_2Cl_2).
- 4) effect of the presence of thiourea on the U (VI) extraction.
- 5) stability of the organic phase loaded with uranium (aging effect).
- 6) molecular absorption spectra and selection of a maximum peak for the spectrophotometric determination of U directly in the organic phase.

To the uranyl chloride solution HCl was added to ascertain the desired acid concentration.

EQUILIBRIUM ATTAINMENT

The chemical equilibrium for metal extraction with amines from HCl is described to be rapid⁽⁵¹⁾. In the present paper, for each extracted species, firstly a check for the extraction velocity was made. In all cases we could demonstrate that the equilibrium was reached in less than one minute. Thus, all the extraction experiments were made by contacting both phases during one minute.

HCl THRESHOLD CONCENTRATION FOR U (VI) EXTRACTION

After the extraction and phase disengagement, the organic phase was transferred to the spectrophotometer cell and lectures done at 430 nm. For each experiment 10.713 mg U in 5 ml were used. Table I summarizes the results of UO_2Cl_2 extraction by TOA-xylene from different HCl concentrations. The results demonstrated that the U extraction is almost quantitative from 3M > HCl (one stage). The results for the UO_2Cl_2 -TOA-benzene system were approximately the same. Those results allow to choose one or other diluent for the amine in function of their physical characteristics, as for instance, benzene being preferable due to its lower B.P. (80°C) if it is desirable to separate the diluent by evaporation, or using xylene (B.P.139-144°C) when the loss, and consequently, a variation in concentration of the organic phase by evaporation of the diluent, should be minimized.

Tabla I

UO_2Cl_2 extraction by TOA-xylene
as function of HCl concentration.

HCl (M)	% U extracted
0.15	negligible
0.30	5.0
0.50	13.6
1.05	27.1
1.51	61.0
2.01	73.1
2.51	86.8
3.01	99.2
4.02	100.0

LOADING CAPACITY OF ORGANIC PHASE FOR URANIUM

For UO_2Cl_2 extraction performed at the operational conditions considered optimized, that is, at 4M HCl, (organic/aqueous) ratio 1, contact time one minute, room temperature, extractant 5% TOA-benzene or xylene, a saturation equivalent of 7.5 to 8.0 mg U per ml organic phase was encountered.

STABILITY OF THE URANIUM LOADED ORGANIC PHASE (AGING)

The UO_2Cl_2 loaded organic phase exhibited excellent stability during 24 hours, no turbidity or signals of alteration being observed. The stability was followed by measuring the absorbance of a same organic phase exposed to the sun light and kept at dark. After 48 hours signals of alteration were observed in the sample exposed to the solar light, with a probable reduction of the uranyl ion to U (VI).

These experiments allowed to conclude that the stability of the organic phase is good, at least during 24 hours in direct sun light, what is important from the analytical and industrial point of view.

EFFECT OF THIOUREA IN THE URANYL CHLORIDE EXTRACTION

The uranyl chloride extraction with TOA-benzene was repeated exactly in the same conditions, but now with addition of thiourea (100 mg for 0.5 – 10.0 mg U). It was demonstrated here that the presence of thiourea does not avoid the uranyl chloride extraction. The calibration curve was repeated for the new situation and the recorded spectra had depicted the same aspect and the same peaks as in the absence of thiourea.

MOLECULAR ABSORPTION SPECTRUM FOR UO_2Cl_2 -TOA-BENZENE (XYLENE)

The centrifuged organic phase was transferred to 1,00 cm quartz cell. When necessary it was filtered through a filter paper of high porosity (S&S black ribbon) wetted with the diluent. The molecular spectrum of uranyl chloride in the amine phase was recorded against an organic phase that extracted an aqueous solution of same chemical composition of the uranyl chloride one, but without uranium.

The maxima observed for the UO_2Cl_2 - TOA-xylene and UO_2Cl_2 - TOA-benzene are practically the same: 405, 413, 417, 426, 430, 444, 460, 476 and 493 nm. These results will be used for the uranium determination directly in the organic phase.

DECONTAMINATION OF URANIUM IMPURITIES. TRI-n-OCTYLAMINE EXTRACTION OF UO_2Cl_2 FROM HCl USING THIOUREA AS COMPLEXING AGENT

In the present work great emphasis was given to the U(VI) extraction from other normally accompanying elements. For this the enormous versatility exhibited by the high weight amines was investigated. TOA was chosen as the tertiary representative amine, diluted in benzene or xylene. Preferably the extraction of U(VI) was made from hydrochloric acid.

In a previous paper the complexing effect of thiourea on several elements was studied⁽¹⁾. In the present contribution the complexing properties of thiourea was explored for the decontamination of several elements from uranium by the extraction of uranyl chloride with TOA-benzene after the addition of thiourea to the aqueous phase. A scrub acid solution containing thiourea enhanced still more the decontamination of uranyl chloride in the organic phase.

Briefly, the separation of U(VI) from several contaminants was accomplished by several alternatives:

- 1) Through the extraction of various elements that are well extracted by TOA from dilute (0.25 – 0.50M) HCl. Included in this group are Cd, Pb, In, Bi, Zn, Sn, Ag, Sb, Ru, Pd, Pt, Au, Tl, Hg. U is not extracted and is maintained in the aqueous phase, since at low chloride concentration it does not form anionic complex.
- 2) Extracting the uranyl chloride from HCl medium of such concentration (2M) that elements like Cu, Co and Ni are not extracted by the amine.
- 3) Retaining the elements that form cationic species in the aqueous phase by addition of thiourea and then extracting the UO_2Cl_2 with the amine.

- 4) Extracting the uranyl chloride and those elements that are coextracted by the amine in the same conditions but that can be decontaminated by scrubbing the organic phase with acidified thiourea solution. The contaminants are removed while uranium is still in the organic phase.

SOME APPLICATIONS

1 – Separation of Cadmium from Uranium

This separation has considerable interest in the uranium chemistry, since the decontamination of cadmium (high cross section for thermal neutrons) is imperious and allows its determination from U. Also Cadmium appears in irradiated uranium as fission product (^{115m}Cd). It can be separated from uranium by its extraction with TOA-benzene, only Cadmium being extracted from dilute HCl. The results of some experiments are depicted in Table II.

Table II

Decontamination of Cadmium from Uranium by TOA-benzene.

HCl (M)	U (mg)	U extracted	Cd (mg)	% Cd ext.	(O/A)
0.17	10.7	nihil	9.34	99	1
0.25	10.7	nihil	9.34	99	1
0.25	500	traces	9.34	99	3
0.25	500	traces	4.67	99	5
0.25	1000	traces	4.67	99	3
0.20	10000	traces	1.0	88	5

Uranium was tested in the raffinate by the ferrocyanide reaction. Cadmium was determined by atomic absorption spectrometry burning directly the organic phase⁽³⁶⁾, or, alternatively, stripping the Cd with ammonium carbonate and determining it via polarography.

2 – Separation of Cd and Fe from U

It was possible to separate Fe and Cd from U, extracting first Cd with TOA-benzene from 0.25M HCl. Cd is quantitatively extracted, accompanied by traces of U (VI) and Fe (III), both removed by scrubbing the organic phase with 0.25M HCl. Removed the cadmium, the separation of Fe is done using one of the alternatives:

- increasing the acid concentration to 0.5M HCl and extracting Fe (III) (3-4 extraction stages are required in this case) and scrubbing the organic phase with 0.5M HCl to strip any extracted uranium.
- adding thiourea, warming up the solution, cooling again to room temperature, ascertaining the acidity to 3-4M HCl and extracting the uranyl chloride. Iron, complexed by thiourea, remained in the aqueous phase.

Our experience had proved that it is more practical to complex iron with thiourea and then extracting uranyl chloride. In a laboratory experiment using 5 g of U and 5 mg of Fe the

complexation with thiourea was done at room temperature, waiting 20 minutes, extracting with TOA-benzene. Approximately 98.5% Fe were retained in the raffinate.

3 – Separation of Silver from Uranium

The separation of silver from uranyl salts has great interest since is desired to know the small quantities of Ag as uranium contaminant and for its determination as fission products (^{109m}Ag , ^{111}Ag , ^{112}Ag , ^{113}Ag and ^{114}Ag). Experiments using 20 g U were performed extracting the uranyl chloride after addition of approximately 100 mg of thiourea. ^{110m}Ag was used as tracer. Silver was quantitatively retained in the aqueous phase (raffinate).

DISCUSSION

The extraction of anionic complexes by long chain amines has enormous flexibility when factors like the class of amine, its diluent, the modification of the organic phase by addition of certain compounds, the composition of the aqueous phase and its modification by the presence of complexing agents are considered. In this paper only a tertiary amine was used (TOA), diluted at 5% with benzene or xylene. The aqueous phase was restricted to the Cl^- system (hydrochloric acid or its salts as salting-out agents). Hydrochloric acid medium was more extensively used since it is well known its strong tendency for the formation of anionic complexes. Finally, a very interesting complexing ligand was choose: thiourea, exploring its properties of forming cationic complexes, not extracted by the amine. Thiourea was used also as scrubbing solution, removing several anionic complexes extracted by the amine by their conversion to cationic species, not retained by the organic phase.

In a previous paper it was demonstrated⁽¹⁾ that those elements that form strong cationic complexes with thiourea are not extracted by the amine. Ag, Tl-III, Hg, Cu, Au, Pd, Pt and Ru are in this group. For elements that form with thiourea cationic complexes only moderately stable the extraction is only partially hindered by the amine: Pb, Sb and Tl-I are in this group. Finally, for elements that form weak complexes with thiourea, the cationic species are disrupted when the amine extraction is involved, the chlorocomplexes being extracted. Cd is a typical example.

In conclusion, exploring the extraction of various elements from dilute HCl (U-VI is not extracted) or extracting the uranyl chloride from moderately concentrated HCl solutions (3-4M HCl) and adding thiourea as complexing agent, decontamination of several elements are accomplished. Again, using the thiourea as acidified scrubbing solution is a suitable alternative to remove some elements coextracted with uranyl chloride.

RESUMO

Estudou-se a extração de cloreto de urânio por tri-n-octilamina (TOA) e sua descontaminação de várias impurezas com o auxílio de tiouréia. Descreve-se o efeito da presença de tiouréia como agente complexante, formando espécies catiônicas com vários íons metálicos e sua consequência na extração do cloreto de urânio em meio ácido clorídrico com TOA-benzeno (xileno). Estudou-se também o efeito de uma solução ácida de tiouréia como lavagem da fase orgânica carregada com cloreto de urânio.

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