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Cu-EDTA-RE-EDTA SOLUTIONS.
USE OF THIOUREA AS IN SITU H₂S GENERATOR.**

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SUMMARY

A technique of homogeneous precipitation using the hydrolysis of thiourea as a H₂S source for the break up of Cu-EDTA chelate and copper sulfide precipitation is presented. The technique is simple and has some advantages for the recovery of the valuable products EDTA, copper and rare earths, avoiding the inconvenience of H₂S smell.

INTRODUCTION

In the individual rare earths (RE) fractionation by ion-exchange chromatography using a first cationic ion exchanger loaded with RE mixture associated to a second cationic ion exchanger loaded with Cu (II) ion, both columns are sequentially eluted with NH₄⁺ salt of the ethylenediaminetetraacetic acid (EDTA) solutions^{1/}. With this elegant and effective technique for fractionation of RE are obtained solutions contained Cu-EDTA and RE-EDTA complexes, great interest existing in the recovery of the valuable EDTA and RE products.

Recovery of EDTA in the presence of copper presents serious difficulty due to the strong stability of Cu-EDTA chelate over a wide pH range values, the copper ion being not precipitated by simply alkalization and the free EDTA acid being not precipitated by lowering the pH of solutions even at values lower than pH 1. In some RE fractions where the lanthanide concentration is low, the conventional precipitation of RE with oxalic acid is not attained. Mainly in case of such rarer lanthanides and, for this reason, of greater interest, as Lu, Yb and Tm (in one experiment in this laboratory there were 21 miligrams of Lu+Yb+Tm in 10 liters Cu-EDTA solution) render their recovery unsuitable. In such cases the break up of the Cu-EDTA complex is mandatory and only after this the EDTA crystallization and RE precipitation is possible.

Two methods are recommended for the recovery of EDTA from its Cu-EDTA solutions: 1) displacement and substitution of Cu⁺⁺ by Ca⁺⁺-ions, in solutions frankly alkaline, copper being precipitated and EDTA remaining in solution as Ca-EDTA; the filtrate is acidified to pH 1 for the EDTA crystallization. 2) disruption of the Cu-EDTA chelate with H₂S gas or Na₂S. Both techniques are troublesome. The first one requires a great excess of calcium ions, the final precipitate being considerably voluminous, the recovery of RE is laborious and has to be done in the presence of extraneous ion (calcium). With the second technique, when the precipitation of copper sulfide is done in the usual conditions the great solution volumes is markedly inconvenient. During the precipitation, filtration and acidification of the filtrate for EDTA recovery there is evolution of disagreeable smelling H₂S.

In this paper the technique of homogeneous precipitation using the hydrolysis of thiourea as a H₂S source for the break up of Cu-EDTA chelate and copper sulfide precipitation was

undertaken. This technique is simple and has some advantages and facilitated the recovery of the valuable products EDTA, Cu and RE.

THE STABILITY OF Cu-EDTA CHELATE

It is well known that the Cu-EDTA chelate is very stable. Schwarzenbach and Ackermann^{/2/} have found that the cupric ion-ethylenediamine-tetraacetate complex is very stable, presenting a log K value of 18.2. Plumb, Martell and Berworth^{/3/} reached the same conclusion through spectrophotometric studies. EDTA is a chelating agent with pronounced ability to chelate copper (II) ion over a broad pH range. Even at low pH value considerable amount of copper is complexed by the EDTA ligand and as a consequence the precipitation of the free EDTA from Cu-EDTA acidified solutions is unsuitable. At high pH values there is an insignificant amount of copper ion in equilibrium with the complex and again it is not possible to break up the Cu-EDTA complex by precipitating copper by alkalization of the copper versenate solutions.

Cu-EDTA COMPLEX DISRUPTION

A survey of the current literature have shown that only three possibilities exist for the Cu-EDTA complex break up for the recovery of EDTA and copper. The first one is the displacement and substitution of Cu(II) ion by Ca(II) ion, from frankly alkaline solution, copper being precipitated and EDTA remaining in the solutions as Ca-EDTA chelate. The filtrate is acidified to pH 1 for the recovery of EDTA by the crystallization of the free acid. This method has the inconvenient of using great excess of calcium ions and giving voluminous copper precipitate and, beside that, when lanthanides are present their recovery is laboriously done in the presence of calcium as extraneous ion.

A second alternative is the disruption of Cu-EDTA complex in frankly alkaline medium using an organic reductor like sucrose, raffinose, urea and gelatin. Wragreich^{/4/} obtained a yellow reddish brown cuprous oxide precipitate when Cu-EDTA solutions containing sucrose alkalized with NaOH were heated. The use of such technique for recovery of EDTA in the presence of PE will have the inconvenience of the lanthanide-sugar complex formed with the organic sucrose-type reductor used and, on the other hand, the crystallization of free EDTA in the presence of excess sugar is not known.

Finally the third possibility, yet in practice in some laboratories, is the disruption of Cu-EDTA chelate with gaseous H₂S or Na₂S. The precipitation of copper sulfide made in the usual conditions, mainly in the case of considerable great volumes, is not well suitable. The evolution of H₂S gas during the precipitation, filtration and acidification of the filtrate is annoying.

There is no doubt that the break up of the Cu-EDTA complex by the copper sulfide precipitation is the best alternative. In this paper the use of thiourea as a H₂S generator source for the precipitation of Cu₂S in the presence of RE was undertaken. The recommended technique is well fitted and advantageous for the recovery of EDTA, RE and also Cu from solutions proceeding from rare Earths fractionation, having no the inconvenience of H₂S liberation to the atmosphere, since all the H₂S generated by the hydrolysis of thiourea is consumed in the Cu₂S precipitation. The acidification of the filtrate for the precipitation of EDTA presents no H₂S smell as well.

THIOUREA AS H₂S SOURCE

Among the recommended compounds for use as H₂S generators, avoiding the direct use of hydrogen sulfide, are thioacetamide and thiourea, the first one being more spread out and used for analytical purpose. Several papers recommended the hydrolysis of thioacetamide for the metal sulfide precipitation. Armstrong^{/5/} advised its use for the sulfide precipitation of H₂S metals group. Thioacetamide was used as a source of H₂S by Hahn and Schellington^{/6/} and its hydrolysis in aqueous solutions have been studied^{/7/}. In acidic medium the hydrolysis of thioacetamide produces mainly acetamide and hydrogen sulfide while it seems that its hydroxide-catalyzed hydrolysis proceeds more rapidly than the acid-catalyzed hydrolysis^{/8/} giving H₂S. The use of thioacetamide as a reagent for separating several sulfide-forming elements from one another has been studied^{/9/}. The precipitation of several metals with the aid of thioacetamide, including copper as copper sulfide has been described^{/10, 11/}.

The utility of thiourea as a reagent for generating hydrogen sulfide in solution and its use for the precipitation of sulfide-forming elements has been studied^{/12-24/}. The commercial and ease availability of thiourea could renew this interest.

Thiourea is stable in aqueous solutions at room temperature and it is slowly decomposed by heating, H₂S being one of its decomposition products. This reagent, like thioacetamide can be applied for homogeneous in situ sulfide precipitation. Only a few papers have been published exploring this property of thiourea for analytical purpose. It was used for the cadmium and lead precipitation^{/25/}. Bauer and Wehling^{/26/} recommended its use for the precipitation of heavy metal sulfides, making the statement that the precipitation is quantitative and the obtained sulfides have stoichiometric composition. The same authors suggested the use of thiourea for separation of pairs like Cu-Co, Cu-As, Cu-Sn and Pb-Sb by controlled sulfide precipitation. Pollard^{/27/} precipitated iridium sulfide from perchloric acid that was separated from chromium.

In this paper we recommend the use of thiourea for the copper sulfide precipitation from Cu-EDTA solutions, the reagent being added at the warm slightly acid solution followed by alkalization with NaOH. The Cu-EDTA complex is easily disrupted and the cuprous sulfide precipitated. This technique allows the economical recovery of EDTA, Rare Earths and Copper from Cu-EDTA-RE-EDTA solutions proceeding from ion-exchange chromatographic rare earth fractionation at pilot plant scale. The copper sulfide is coarse, dense, easily settled down and filtered and the precipitation has the advantage of not smelling H₂S. All the values: EDTA, RE and Cu are recovered for re-use.

EXPERIMENTAL PART

REAGENTS.

Thiourea used was of commercial grade, without any previous treatment. Cu-EDTA-RE-EDTA solutions were proceeding from pilot plant fractionation of lanthanides by cationic ion exchange chromatographic technique using two columns system^{/28/}, copper used as retention metal. Elution of Cu and RE from the columns was attained with 15 g EDTA/l (ammonium salt).

GENERAL PROCEDURE

1. COPPER SULFIDE PRECIPITATION AND ITS RE-USE.

The recovery of copper from Cu-EDTA solutions is attained using thiourea by the following procedure: the eluted solution is acidified with HCl to pH 1-2 and warmed to 70-80°C and crystallized thiourea added slowly with stirring. The solution turned from blue to faintly green and at this moment ca. 2M NaOH is added, a slight excess to get a final ca. 0.1M NaOH concentration is recommended. The cuprous sulfide is immediately precipitated. Let the coarse Cu₂S settle down and observe the color of the solution: if it is yet bluish, add a little more thiourea and continue warming the solution for a few minutes for completion of the precipitation. Filter the precipitate and wash with little water. The Cu₂S can be dissolved with concentrate HNO₃ or dried and ustuled and dissolved with nitric or sulfuric acid for re-use as loading solution for the second chromatographic column.

2. CRYSTALLIZATION OF EDTA

The filtrate, practically colorless, containing sodium and rare earth versenates is acidified with HCl until pH 1 for the crystallization of free EDTA as usual. Filter the cool mixture, wash the EDTA crystals with dilute HCl solutions (pH 1) and dry the precipitate.

3. RARE EARTHS RECOVERY

The EDTA filtrate containing the lanthanides is treated with oxalic acid for the precipitation of RE. In special cases when the lanthanides content is low, the filtrate is percolated through a strong cationic ion exchanger column (H⁺ or NH₄⁺ form) for the preconcentration of RE. These are eluted with 1M (NH₄)₂SO₄, pH 1,0 - 2,5. The eluted solution is treated with oxalic acid or NaOH for the RE precipitation of oxalates or hydroxydes.

CONCLUSION

The technique here described and recommended for the disruption of Cu-EDTA complex using thiourea as H₂S source allowed the recovery and economical re-use of EDTA, Cu and RE from eluted solution proceeding from the ion-exchange fractionation of rare earths in the RE-Cu-Cationic exchanger-EDTA system. The method has being used routinely^{/28/} at pilot plant scale. The Cu₂S precipitate is coarse and dense, easily settled down and filtered. The technique avoided the inconvenience of H₂S evolution to atmosphere and its annoy smell.

Although the direct addition of thiourea to the Cu-EDTA-RE-EDTA solutions could be done, the experiments allowed to conclude that it is preferable to add the thiourea to the slightly acidified (pH 1-2) solutions, this facilitating the break up of Cu-EDTA chelate which completion is achieved by NaOH addition.

The excess of NaOH is not critical, the precipitation of cuprous sulfide being quantitative from free 0.08M NaOH on. The Cu₂S precipitation from Cu-EDTA solution was studied in the 0.08-0.5M NaOH range, no interest existing in using higher NaOH concentration. For the routine work final 0.1M NaOH is pointed out.

Several authors have studied and pointed out the use of other retention metals for substitution of copper, the most recommended being zinc, cadmium, nickel and iron. Spedding and col.^{/1/} advised the use of metals like iron, copper and nickel, and Powell^{/29/} suggested the use of zinc as retention ion for improving the efficiency of individual rare earth fractionation from ionic ion exchanges with EDTA as elutriant. The main reason for this is the difficulty of Cu-EDTA disruption and precipitation of free EDTA. This difficulty was overcome and the precipitation of Cu_2S facilitated with the use of thiourea for in situ H_2S generation as here described.

RESUMO

Este trabalho apresenta uma técnica para a precipitação homogênea de sulfato de cobre usando-se tiouréia como fonte geradora de H_2S , para a recuperação econômica dos constituintes de valor das soluções contendo os complexos de cobre-II e de lantanídeos-III com o ácido etilenodiaminotetraacético (EDTA). A técnica é simples e apresenta vantagens quanto à facilidade de recuperação dos produtos valiosos, permitindo a recuperação econômica do EDTA, do cobre e das terras raras e evitando a inconveniência do cheiro de H_2S quando se usa sulfidreto diretamente

RÉSUMÉ

Dans ce rapport on décrit une technique pour la précipitation homogène du sulfate du cuivre employant la thiouréie $(\text{NH}_2)_2\text{CS}$ comme fontaine génératrice du H_2S , par la recuperation économique des constituants de valeur de las solucions contenant des complexes du cuivre-II et du lantanides-III avec le acide (EDTA).

La technique est simple et present la vantage combien de la facilité du recouvrement des produits valables, permetran la recouvrement économique du EDTA, du cuivre et du terres rares evitand la incovenance du l'odeur du H_2S quand si a fette la usage du gas sulphidric directement.

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