MORIN IDENTIFICATION OF THORIUM IN RARE EARTH ELEMENTS

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ABSTRACT

Morin (3,5,7,2′,4′-pentahydroxy flavanol) has been used as an organic reagent for detection of several trace ions with which it forms colored and fluorescent complexes. Morin forms fluorescent compounds with Al(III), Pb(II), Cd(II), Sn(II,IV), Mg(II), Be(II), In(III), Ga(III), Sc(III), Zn(II), Ca(II), Rare Earths(III), Nb(V), Ta(V), Zr(IV) and Th(IV). The following elements give only nonfluorescent dark spots over a filter paper impregnated with morin: Cu(II), Fe(III), Ag(I), Hg(I,II), Bi(III), Cr(III), Mn(II), Co(II), Ni(II), Ti(IV) and U(VI).

A survey of the literature revealed that only Zr(IV) reacts with morin in strong acid medium. Morin reacts with the other elements above mentioned in slightly acid or alkaline media, including Al(III). The aluminum morinate, once formed from neutral, slightly acidic (acetic acid) or alkaline media resists the treatment of hydrochloric acid.

In the present investigation the writer reports his finding that the reaction of thorium with morin is effective in high acid concentration (hydrochloric acid). Using a spot test on a morin impregnated filter paper it is possible to detect 0.1 ug of Th with a limit of dilution of 2:1.000.000. Using a natural rare earth elements mixture from monzite sand it is possible to recognize 0.3 ug Th with a ratio of (Th/REE) = 3:1.000.000. The test can be applied to rare earths solutions with concentration ranging from 30 to 300 g R_2O_3/L.

INTRODUCTION

Morin (3,5,7,2′,4′-pentahydroxy flavanol) has been used as an organic reagent for detecting several ions by ultraviolet fluorescence [1]. Well documented is its use as a reagent for the identification of traces of aluminum, to which it reacts in neutral or acetic acid solution to give rise to an intense yellow-green fluorescence under the ultraviolet light. The fluorescence of aluminum-morin compound is claimed to be due to the formation of a colloidal species of the complex aluminum salt of morin [2] or to an adsorption compound of morin with alumina. It is also reported that zinc react with morin on a filter paper giving a bright spot and that lead(II), cadmium(II), tin(II) , tin(IV) and magnesium(II) give fluorescent spots. The following elements give only nonfluorescent dark spots[1]:Cu(II), Fe(III), Ag(I), Hg(I), Hg(II), Bi(III), Cr(III), Mn(II), Co(II), Ni(II).Beryllium(II) [3], indium(III), gallium(III), thorium(IV) and scandium(III) salts [4] also form fluorescent compounds with morin. The pH of the system has strong influence in the correspondent reactions [5].

Morin gives with aluminum in neutral or acetic solution a strong green fluorescence whose identification limit is, according to Feigl [6] 0.005 ug and concentration limit as low as 1:10.000.000. Galium(III), indium(III), beryllium(II), thorium(IV), scandium(III) and zirconium(IV) give a similar fluorescence.

Beryllium(II) can be determined with morin, in a reaction that is is sensible, and specific under determined conditions, e.g., after addition of ammoniacal solution of EDTA [7,8].

Morin gives with gallium(III) a fluorescence that is not quenched with sodium fluoride, unless the gallium concentration is extremely low (diference from aluminum) [9].

Indium reacts with morin giving a fluorescence similar to aluminum and gallium that resists the action of fluoride (also diference with aluminum) [4].

Morin in weakly acid (acetic acid-acetate) solution reacts with aluminum(III), scandium(III), beryllium(II), gallium(III), and indium(III) to give compounds that show strong fluorescence under the ultraviolet light. Scandium is said to give a fluorescence in weak mineral acid solution [4]. On the other hand the rare earths show a weak fluorescence.

Test of aluminum with morin was reported [10,11].

Some water-insoluble metal hydroxides give rise the strong fluorescence when treated with an ethanol or acetone solution of morin. Tin(II) and tin(IV) hydroxides obtained by treatment of the correspondent chlorides with dilute ammonium hydroxide when contacted with the morin solution develops intense green fluorescence. The compounds when treated with hydrochloric acid no more fluoresce. This behavior is a commonplace for about the totality of the colorless metal hydroxides [11].

A test for tin with morin is recommended by Feigl [12].

Morin, with tin(IV) after reduction to tin(II) with ammonium sulfide and addition of one drop of 5%H_2O_2, on a filter paper treated with NH_3,gives a yellow-green fluorescence under the ultraviolet light [13, 14].

Titanium(IV) as titanyl sulfate ($TiOSO_4$) reacts with morin in acid medium giving a dark brown-reddish spot that does not fluoresce [15].

Zirconium(IV) forms an acid-resistant, bright strong green fluorescence compound with morin. Its stability toward hydrochloric acid is remarkable, even if concentrated acid is used [16].

Charlot[17] recommended the test for identification of zirconium with morin in strong hydrochloric acid (10M) and claims that no other ion give rise to fluorescence in the same conditions. He reported also that thorium(IV), antimonium(III) and antimonium(V) give only a brown color that fade slowly and tin(IV) does not give the reaction in 2M HCl medium [17].

Charlot [17] also reported that tin(IV) gives a green fluorescence with morin in acetic medium and that germanium(IV), gallium(III) and indium(III) give the same reaction.

In strongly basic solution, e.g.,1M NaOH, morin becomes nearly a specific reagent for beryllium.Aluminum, gallium, and indium no longer react in strongly basic medium. Zinc, however, fluoresces, but cyanide prevents its interference. Lithium fluoresces very weakly. Calcium can be prevented from interfering by addition of pyrophosphate [18].

Several reports describing the use of morin in chemical analyses have been published. Morin can be used for the titration of gallium and indium [19]. The determination of aluminum by its fluorescence with morin has been described [20].

The reaction of beryllium with morin in sodium hydroxide solution is the basis of a very sensitive fluorometric method for the determination of beryllium [8].

Sill and Willis [21] studied the use of morin in the determination of minute quantities of metals and have given the conditions for the determination of submicrogram quantities of thorium. The proper choice of buffer and complexing agent is important in this method where a pH of 11 is used.

Morin is strongly recommended for the fluorometric determination of aluminum at pH 3-4 or 5-6 [22].

Morin have been used as a reagent for the determination of zirconium in sea water [23].

Some of the rare earth hydroxides and also scandium hydroxide are sufficiently soluble in excess of sodium hydroxide to yield a distinct yellow fluorescence with morin. Scandium, like aluminum, beryllium, gallium and some other metals react similarly with morin in neutral or faintly acid solution resulting in the formation of a fluorescent complex [18]. Fleck [24] has made a spectrofluorometric study of morin chelates of lanthanum.

Both niobium [25,26] and tantalum [27] in the presence of H_2O_2 form fluorescent complexes with morin which are used in the analyses for these elements.Tungsten may be determined by the formation of a fluorescent compound with morin [28].

Complex formation of uranium(VI) with morin is scarcely reported in the technical literature. Sill and Willis [21] mention that uranium forms with morin a brownish yellow complex.

Feigl [12] claims that the aluminum-morin complex once formed resits the treatment with 2M HCl and that besides aluminum, only the zirconium-morin compound resists such acid treatment. Charlot [16,17] also claims that zirconium reacts with morin in strong hydrochloric acid and that no other ion give rise to fluorescence in this condition.

In this paper the writer would like to report that the fluorescent compound formed by thorium(IV) with morin also resists the treatment with 2M HCl or higher concentration , while the species formed by rare earth elements and morin do not fluoresce in the acid solution.

Both zirconium(IV) and thorium(IV) give rise to the fluorescent compounds when their acidified solutions react with morin. On the other hand, as it is well known, metals like aluminum, beryllium, indium, gallium, magnesium, and scandium [4,18] do not react with morin in acid media. In the present investigation the author confirmed that the rare earth elements give fluorescent compounds with morin from neutral or slight acid (acetic acid) medium, but they do not resist hydrochloric acid treatment as zirconium and thorium neither are they formed when the analyte solution is fairly acid.

The reaction of thorium with morin in acidic solution giving a strong fluorescent compound under the ultraviolet light is the basis for a spot test highly effective for the identification of thorium in rare earth elements.

EXPERIMENTAL

Reagents

1.Morin - (3,5,7,2´,4´-pentahydroxyflavone), British Drug Houses (BDH) Ltd., was used without further purification. Solution of morin 0.01% in 95% ethanol was used in the procedure.

2.Water - the water used in the preparation of solutions was demineralized.

3. Thorium chloride - A stock solution of thorium containing 2,55 gram of ThO_2 per liter was prepared. The solution was standardized gravimetricaly via thorium oxalate and ignited to thorium oxide. To all diluted solutions some drops of hydrochloric acid was added to avoid hydrolysis.

4. Solutions of rare earth chlorides of lanthanum, neodymium and praseodymium were preparad by dissolution of the correspondent pure oxides (IPEN/CNEN/S.Paulo) with hydrochloric acid. Solutions of thullium, europium, ytterbium (Polyscience Inc., USA) and lanthanum (Carlo Erba) chlorides were preparared by dissolving

the commercially available salts in deionised water . The rare earth content was determined gravimetrically in these solutions by precipitating the oxalates which were ignited (800°C) to oxides.

A natural mixture of the rare earths chlorides with the same composition as the monazite lanthanides was supplied by Nuclemon Minero Quimica Ltda., S.Paulo.The rare earths in this sample were precipitated as oxalate from a hydrochloric acid medium, filtered, washed with dilute oxalic acid, and ignited (800°C)to the oxide. Aliquots of this oxide were dissolved with hydrochloric or nitric acid when required and diluted as necessary.

5. Morin impregnated filter paper. Analytical filter paper of medium porosity was impregnated with 0.01% morin ethanolic solution and air dried. The dried paper was then treated with one drop of tri-n-octylphosphine oxide (TOPO) of 19.3 g/L(0.05M) in xylene and dried again. This treated paper was used for the spot test of thorium.

6. All other chemicals were reagent grade and used as received.

Procedure

Pure solutions of thorium chloride were acidified with hydrochloric acid, in a concentration ranging from 0.1 to 10 M . One drop of the thorium solution was deposited over the Morin-TOPO impregnated filter paper. The paper was then observed under the ultraviolet light,and an intense yellow-green fluorescence was noted. The fluorescence does not fade, but on the contrary, lasts a long time. For thorium solutions near the identification limit(0.1 ug Th)it is advised to wait one to five minutes for the spot be well formed and then observed under the ultraviolet light. Those filter papers with the spot of thorium can be stored for several months and then wet with 2M HCl and observed again their fluorescence under the ultraviolet light.

To identify thorium in pure rare earth solutions or in a mixture of rare earth elements , add one drop of the acidified solution with hydrochloric acid over the Morin-TOPO treated *filter paper* and after one to five minutes wash the paper with 2M HCl solution and then examine under the ultraviolet light. An alternative procedure is to dry the paper after the addition of the analyte and then to wet the paper with 2M HCl solution and finally examine under the ultraviolet light.

DISCUSSION

In this paper the author confirms his finding that thorium reacts with morin in frankly acid medium and develops an intense yellow-green fluorescence, similar to that of zirconium (hafnium) and aluminum. The reaction of thorium with morin is very sensitive with low limits of identification and dilution. The fluorescence of thorium-morin complex is explored for the identification of thorium in rare earth elements without prior separation.

Feigl [12] claimed that only aluminum-morin complex after formed resists the treatment with 2M HCl, and that besides aluminum, only zirconium compound resists such acid treatment. Charlot [16,17] reported that zirconium forms an acid-resistant fluorescent compound with morin and no other ion give rise to fluorescence in the same conditions. More, Charlot [17] stated also that Th(IV), Sb(III), Sb(V) give only a brown color with morin that fade slowly. Sill and Willis [21] reported the determination of minute quantities of metals with morin, including thorium, but this ion was analysed by complexing with morin at high pH. Again Sill[29] reported the determination of thorium in biological material with morin as a reagent in the range of $2\times10^{-6}\%$ in bone ash to $2\times10^{-10}\%$ in blood after the separation of thorium.

A thorium-morin method for fluoride analysis depends on the reduction of the fluorescence of this complex on the addition of fluoride [30].

Morin was also used as a fluorescence indicator in the complexometric titration of microgram amounts of thorium with Complexon-III or oxalic acid at pH 1-3, with a good sensitivity and specificity [31]; the method was applied to the determination of thorium in tungsten wire, after separation as the fluoride [32].

For sulfate in natural waters, quenching of the thorium-morin complex fluorescence was a sensitive method, but subject to interference by phosphate, fluoride, several cations and some organic compounds [33,34].

Sill and Willis [21] reported that thorium produce a very sensitive greenish yellow fluorescence with morin in alkaline solution containing ethylenedinitrilo-tetraacetic acid (EDTA) and that zirconium, yttrium, scandium, lanthanum and lithium also produce fluorescent complexes but at lower sensitivity.These authors mentioned also that thorium-morin rection at pH 2 is prevented completely even by small quantities of sulfate. They considered also that one of the most sensitive chemical procedure available for thorium appears to be the spectrophotometric one using morin at pH 2, which is capable of determining about 0.2 ug of thorium in a 50 ml volume.

Thorium has been shown to produce two complexes with both morin and its isomer quercetin [21] from weak acid solutions. Sill and Willis also reported that the determination of thorium using morin in the presence of rare earths presents special problems.

One of the most sensitive chemical procedure available for the determination of thorium is the spectrophotometric method using morin [35].

The reaction of thorium with morin in alkaline or dilute acid solutions is well known and has been used for the determination of thorium [35,36,37,21] and for the titrimetric determination of fluoride with thorium [38]. The thorium-morin system in dilute acid medium was throughly studied by Fletcher and Milkey [35,37].

Therefore, a survey of the literature covering thorium-morin complexation shows that the reaction is effective in alkaline or slight acid medium. In the present paper the writer reports his finding that the reaction of thorium with morin is effective in high acid concentration (hydrochloric acid was preferentially used; nitric acid oxidizes the morin reagent).Thorium can be identified straightforward in acidified rare earth solutions.

Summarizing, contrastive with the literature,thorium can be detected directly in the presence of rare earth elements from frankly hydrochloric acid solution by a spot test on a Morin-TOPO impregnated filter paper. The limit of detection is 0.3 ug Th and the limit of concentration is 3:1.000.000 (3 p.p.m.).For lower concentration of thorium it is mandatory its separation from the rare earths using for instance an ion exchange separation technique, e.g., colection onto an anionic ion exchanger from nitric acid. Danon [39,40] reported a quantitative separation of thorium from lanthanum, neodymiumm, samarium, europium, and yttrium using 5 to 8M nitric acid. Fritz and Garralda [41] also reported a quantitative retaintion of thorium by an anion exchange column from 6M nitric acid, with excellent separation of thorium from aluminum, rare earths, iron, uranium, zirconium and other elements.The selective separation of thorium from rare earths and other elements can be made using a liquid-liquid solvent extraction technique. For instance, Ross and White [43] were able to perform such a separation extracting thorium with tri-n-octylphosphine oxide (TOPO) from acidic chloride or nitrate solutions and using cyclohexane as diluent. These authors recommended the extraction of thorium from 1 to 3 M HNO_3 or 4.5 to 7M HCl as optimum conditions for the separation.

Limit of Identification and Dilution

Working with pure thorium solution and using one drop of analyte over the Morin-TOPO impregnated filter paper it is possible to recognise 0.1 ug Th under the ultraviolet lamp. In this situation it is recommended to observe the test five minutes after or alternatively, after drying the paper ($60-80^{o}C$) and wetting with 2M HCl solution. Usually the thorium-morin spot has the shape of a ring when the Morin-TOPO filter paper is used. The limit of dilution is 2:1.000.000.

Using the natural mixture of rare earth elements from monazite sand, after purification by precipitating the oxalates as described, it was possible to detect 0.3 ug Th with a ratio of (Th/REE) = 3:1.000.000 (3 p.p.m.). For solutions of rare earth elements of low thorium content it is also recommended to wait about five minutes after dropping the analyte over the Morin-TOPO paper and treating with some drops of 2M HCl before observation under the ultraviolet light. Alternativelly the filter paper can be dried and then wet with 2M HCl solution and finally observed under the ultraviolet light.

For the present work solutions of pure rare earths and mixture of rare earths were used with concentration ranging from 30 to 300 g R_2O_3/L. All solutions were acidified with hycrochloric acid.

Interferences

If the thorium-morin reaction is performed in acid medium, especially hydrochloric acid, the most ions that can follow thorium do not interfere, including yttrium and the lanthanides, aluminum, zinc, gallium, beryllium, indium, magnesium, calcium, lithium and others. The only elements that react with morin in frankly acidic media are titanium(IV),uranium(VI), both of them yielding nonfluorescent brown-reddish compounds, and zirconium (and hafnium of course). Thorium and zirconium(hafnium) are very ease and simply detected in rare earth elements solutions using the spot test with Morin-TOPO impregnated filter paper. Although titanium(IV) and uranium(VI) morinates do not fluoresce in hydrochloric acid, their formation consume the morin and the intense color interferes in the visual observation of the thorium fluorescence.

The uranium(VI)-morin spot, initially brown reddish, after treatment with 2-10 M HCl solution turns yellow and, when the amount of uranium is high, it precludes the observation of the thorium-morinate fluorescence.

To confirm the presence of thorium together with zirconium it is required their separation, for instance, with the conventional oxalate precipitation, the rare earth elements themselves serving as a carrier for the thorium. Sandell [43] has reported that thorium can be separated from titanium, zirconium, uranium,iron and most metals, except the rare earths, by precipitation with oxalic acid in dilute mineral acids.

Therefore, if it is known that the rare earth analyte did not pass an oxalate precipitation it is recommended to obtain the oxides via oxalates and then the rare earth solution to be tested with morin.

Zirconium can be confirmed in the oxalate filtrate after convenient treatment, using for instante the rare earth as carrier and colecting the zirconium as hydroxide and then analised through the Morin-TOPO impregnated filter paper.

Quadrivalent cerium interferes seriously by oxidizing the morin reagent, but this ion can be easily reduced to Ce(III) by addition of hydroxylamine hydrochloride or hydrogen peroxyde.

Sulfate, oxalate, fluoride,and phosphate are the main anions interference. The interference of sulfate in the formation of the thorium-morin complex probably is caused by the formation of sulfate complex species with thorium [35,37].Based on these interactions a sensitive fluorometric method for the determination of sulfate was developed [44].The reaction of thorium-morin was used also for the titrimetric determination of fluoride with thorium [38]

Thorium morinate fluorescence stability

As was mentioned hitherto the aluminum (III), zirconium(IV) and thorium(IV) morinates resist the treatment with 2M HCl solution. The author would like to add here another significative feature concerning these fluorescent compounds. After treated with hydrochloric acid, both zirconium and thorium morinates, continue to fluoresce for a long time, while the aluminum morinate does not fluoresce one hour after treated with 2M HCl. The fluorescence of thorium morinate was followed up for two months and still it does fluoresce, that is, the thorium-morin complex remained stable for at least two months.

ACKNOWLEDGMENT

The author is grateful to Nuclemon Minero Quimica Ltda, São Paulo, for supplying several rare earths samples.The author acknowledges his colleague Carlos Octavio de Freitas for the critical reading of the manuscript.

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