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Study on the Spectrophotometric Determination of Rare Earths with a New Chromogenic Reagent Dibromo-p-methyl-chlorosulfonazo(DBMCSA)

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Abstract: A new method for the determination of cerium subgroup rare earths was studied and reported in this paper. It was found that cerium subgroup rare earth elements react with DBMCSA in 0.6 mol/L hydrochloric acid medium to form stable blue complexes. The absorbances of equal amounts of cerium subgroup rare earths are close to each other at their maximum adsorptive wavelength (641 nm). Beer's law is obeyed for 0-20 μg of rare earths in 25 ml of solution. The method has been applied to the determination of the total amount of cerium subgroup rare earths in steel and cast iron samples with satisfactory results.

Keywords: Spectrophotometric determination, rare earths, dibromo-*p*-methyl-chlorosulfonazo (DBMCSA).

Introduction

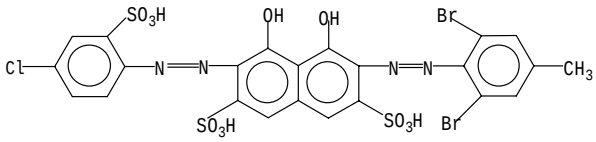
Determination of total amounts of rare earth elements is an important way for research and quality control in geology and metallurgy and in the application of rare earths. Spectrophotometry is widely used for this purpose for its simplicity and rapidity in analysis[1]. Chlorophosphonazo and arsenazo[2-4] type reagents are more frequently used as chromogenic reagents in the determination. But less attention has been paid to sulfonazo reagents, and only a few reagents have been reported. It was found that adding to the specific features shown by the above mentioned types of reagents, sulfonazo reagent have also the advantage of easy and simple to synthesize, thus leading to a cheaper price, and the advantage of their reaction with rare earths in high acidity medium[5]. Recently a new sulfonazo reagent dibromo-*p*-methyl-chlorosulfonazo has been synthesized in our laboratory. Its chemical name is 3-[(4-chloro-2-sulfon-benzene)azo]-6-[(2,6-dibromo-4-methyl-benzene)azo]-4,5-ihydroxyl-2,7-naphtyl disulfonic acid. The structure is as shown in Scheme 1.

It is a black powder, can be easily dissolved in water. Its solid and its water solution are very stable and it can be stored for at least half a year.

In this paper, the optimum conditions for the formation of DBMCSA-RE complexes are studied. In various acidic media such as hydrochloric, phosphoric, perchloric, sulfuric or nitric acid, it can react with rare earths to form stable blue complexes in a very wide rang of acid concentration with high sensitivity and good selectivity. Its tolerance for uranium and thorium is better than that of

chlorophosphonazo and arsenazo reagent. It is proved by experimental reasults that DBMCSA is a very good chromogenic reagent for cerium subgroup rare earths. The proposed method has been successfully employed to determine the total amounts of cerium subgroup rare earths in steel and cast iron samples without any masking reagents. The result obtained are satisfactor**y.**

Scheme 1



Experimental

Apparatus

Absorbances and absorption spectra were measured on a Beckman DU-7HS spectrophotometer with 1-cm cell.

Reagent

The standard stock solutions of rare earths are prepared as described previously[6] and the working standard solutions are prepared by diluting with hydrochloric acid (1+100) to 10 μg/ml. DBMCSA solution (0.1% w/v) is prepared by dissolving 0.100 g of DBMCSA in 100 ml of water. 6 mol/L hydrochloric acid solution. Other reagents used are of analytical grade.

Procedure

Transfer no more than 20 μg of lanthanum into a 25 ml calibrated flask and add 2.5 ml of 6.0 mol/L hydrochloric acid. Adjust the volume to about 15 ml with distilled water, then add 4.0 ml of 0.1% DBMCSA solution. Dilute to the mark with distilled water and mix well. Measure the absorbance at 641 nm with a 1.0-cm cell against a reagent blank.

Result and Discussion

Absorption spectra

Under the experimental conditions, the absorption spectra of the reagent and the DBMCSA-La complex were scanned. The absorption maximum of DBMCSA is at 533 nm, whereas the DBMCSA-La complex gives an absorption peak at 641 nm. The contrast of the two peaks is 108 nm, and can be obviously distinguished. So the absorption peak 641 nm is chosen as determination wavelength.

Effects of acids

Effects of various acids on the DBMCSA-La complex formation reaction were tested. It was found that the absorbances of the complex is almost unchanged in hydrochloric, phosphoric, perchloric, sulfuric or nitric acid medium in the following concentration range: HCl 0.48-1.44 mol/L, H_3PO_4 0.12-0.3 mol/L, $HClO_4$ 0.48-1.92 mol/L, H_2SO_4 0.48-1.44mol/L or HNO_3 0.06-0.48 mol/L, while in hydrochloric acid medium, the

absorbance of the complex is somewhat higher. Considering both the selectivity and the rate of reaction, an acidity of 0.4 mol/L hydrochloric acid in a total volume of 25 ml is chosen, corresponding to the addition of 2.5 ml of 6 mol/L hydrochloric acid to the reaction solution.

Effect of amount of reagent DBMCSA

In 25 ml of solution, the addition of 3.0-7.0 ml of 0.1% DBMCSA solution gives maximum and constant absorbance for 10 μg of lanthanum, thus an addition of 4.0 ml DBMCSA solution is recommended.

Reaction rate and stability of complex

The complex reaction is completed after 10 min under the optimum conditions, and its absorbance keeps stable at least for 24 h.

Calibration curve

A calibration curve was constructed in the usual way according to the procedure. Beer′s law is obeyed for 0-20 μg of lanthanum in 25 ml solution at 641 nm. The simple linear regression calibration equation is

$$A=0.0095+0.038C \qquad (C:\mu g/25\ ml)$$

with a correlation coefficient of 0.9999. The apparent molar absorptivity obtained is 1.4×10^5 $L\cdot mol^{-1}\cdot cm^{-1}$.

Effect of foreign ions

Solutions containing 10 μg of lanthanum and various amounts of 26 foriegn ions were prepared and the procedure was followed for the determination of lanthanum. The tolerance limits (5% error maximum) are as follows: NH_4^+(20); Na^+, Fe^{3+}, Zn^{2+}, Co^{2+}(10); Cu^{2+}(7); Ni^{2+}(6); Al^{3+}, Mn^{2+}, Mg^{2+}(5); Ti^{4+}, Bi^{3+}(2); Mo(VI)(1.5); Hg^{2+}, W(VI)(1); Gr^{3+}(0.5); V(V)(0.25); U(VI)*(0.12); Zr(IV)*(0.1); Th(IV)*(0.07); Ba^{2+}, Sr^{2+}, Pb^{2+}(0.001); citrate, $H_2C_2O_4$(100); CO_3^{2-}(10). most of the ions have no influence, but Ba^{2+}, $Sr^{2+}$and Pb^{2+} interfere.

* add 75 mg $H_2C_2O_4$

Color reaction with other rare earths

The reactions of DBMCSA with rare earths other than the cerium subgroup elements were also investigated. As shown in **Table 1**, under the conditions investigated, DBMCSA reacts with Eu, Gd, Tb and Dy to give much weaker complexes and there will be no complexing reaction beginning from the Ho. It can be seen also that the absorbances of its complexes with various cerium subgroup elements are very close. Hence, DBMCSA proves to be a very good chromogenic reagent for cerium subgroup rare earths.

Table 1 Absorbances and Molar Absorptivities of the DBMCSA-RE Complexes

RE	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
A	0.399	0.390	0.427	0.430	0.427	0.243	0.120	0.070
$\varepsilon\times10^{-5}L\cdot mol^{-1}\cdot cm^{-1}$	1.39	1.37	1.51	1.55	1.60	0.92	0.47	0.27
RE	Dy	Ho	Er	Tm	Yb	Lu	Y	
A	0.024	0.000	0.000	0.000	0.000	0.000	0.000	
$\varepsilon\times10^{-5}L\cdot mol^{-1}\cdot cm^{-1}$	0.0979	0.000	0.000	0.000	0.000	0.000	0.000	

Determination of the total cerium subgroup rare earths in steel and cast iron

Weigh accurately 0.500 g of steel and cast iron samples into a 100 ml beaker, add 15-20 ml of 6 mol/L hydrochloric acid. Concentrated nitric acid is added after the sample is dissolved by heating in order to oxidize the carbides. Transfer the solution into a 100 ml calibrated flask, wash the beaker and dilute with water to mark.

The rare earths bearing steel and cast iron obtained in our country contain mainly the cerium subgroup elements. Hence the method established in this paper can be successfully used to analyze these samples. Cerium subgroup rare earths in several steel and cast iron samples were determined by the proposed procedure. Lanthanum standard solution is used in this experiment to prepare the calibration curve and the results shown in **Table 2** are in good agreement with the certified values.

Table 2 Results for the Determination of Rare Earths in Steel and Cast Iron Samples

samples	referrence value(%)	found(%)	mean(%)	RSD(%)
cast iron	0.059	0.058 0.0599 0.0586	0.0591	0.76
(16-91-032)		0.0590 0.0594 0.0590		
cast iron	0.043	0.0430 0.0432 0.0434	0.0429	2.35
(20-19-036)		0.0428 0.0430 0.0422		
37-9 B-steel	0.154	0.155 0.157 0.157	0.157	0.81
		0.159 0.157 0.157		
10MnNbRE-1	0.0479	0.0477 0.0483 0.0477	0.0478	0.94
		0.0480 0.0469 0.0480		
10MnNbRE-3	0.0982	0.0977 0.0974 0.0986	0.0977	0.93
		0.0976 0.0974 0.0977		

Conclution

The method proposed is very simple and convenient for the direct determination of the cerium subgroup rare earths in steel and cast iron. The results are satisfactory.

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