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CATION-EXCHANGE COLUMN CALIBRATION FOR Sr AND THE REE BY EDTA TITRATION

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Abstract

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A rapid and inexpensive method for calibrating-cation exchange columns for Sr and the rare-earth elements (REE) is presented. The method involves a pH-sensitive complexiometric titration that gives precise information on elution peak shape.

1. Introduction

We present here a calibration scheme using EBT (Eriochrome Black-T®) and complexiometric titration of Sr and the rare-earth elements (REE) with ethylenedinitrilotetraacetic acid (EDTA) that has been modified to provide precise information on elution peak shape and position for cation-exchange columns. The accuracy of this calibration method is equivalent to that achieved with radioactive tracers but avoids the need to introduce them into the laboratory. The method has sensitivities in the μg range and is rapid, reproducible and inexpensive.

2. Method

2.1. Preparation of reagents

EDTA (ethylenedinitrilotetraacetic acid)
0.1 *M* solution:
- 29.21 g free EDTA acid
- 9.0 g NaOH
- heat and stir together
- dilute to 1 l of solution with H_2O

0.0002 *M*, 0.0001 *M*, 0.00005 *M* and 0.00001 *M* solutions:
- 2, 1, 0.5 and 0.1 ml (respectively) of 0.1 *M* EDTA
- dilute each to 1 l of solution with H_2O

TEA buffer (triethanolamine, pH ~ 7)
2 *M* solution:
- 298.38 g reagent grade TEA
- dilute to 1 l of solution with H_2O

1 *M* solution:
- 149.19 g reagent grade TEA
- dilute to 1 l of solution with H_2O

0.1 *M* solution:
- 100 ml 1 *M* TEA
- dilute to 1 l of solution with H_2O

EBT (Eriochrome Black T®)
stock solution:
- 0.2 g EBT powder
- 5 ml methanol
- 15 ml 1 *M* TEA stock solution

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working solution:
- 2.2 ml EBT stock solution
- 5 ml methanol
- 15 ml of 0.1 *M* TEA (dilute solution)

Mg-EDTA:
0.1 *M* solution:
- 2.0155 g MgO
- dissolve in 4 *N* HCl
- dry down to a grayish-white pad
- add to 500 ml 0.1 *M* EDTA solution

0.0005 *M* solution:
- 5 ml of 0.1 *M* Mg-EDTA solution
- dilute to 1 l with H_2O

NH_4Cl-NH_4OH buffer (pH ~ 10):
- 70 g NH_4Cl
- 570 ml reagent grade NH_4OH
- dilute to 1 l with H_2O

2.2. Direct titration for REE

(1) Load μg quantities of REE on column in the same manner as a sample. The amount of REE needed depends on the size of each collected fraction. 20–40 μg of REE will give good peak determination when divided into 10–15 aliquots of 1- or 2-ml size. Unfortunately, a test sample can not be loaded on the column simultaneously because the titration is not cation specific. The REE in the rock will interfere with the determination of peak shape and position by titration. However, based on hundreds of successful elutions and cross-checking with radiotracers, peak position and peak shape during actual sample elution reliably conform to those determined by titration in the absence of sample as long as the carrying capacity of the resin bed has not been overloaded during sample elution.

(2) Elute through column and collect aliquots to divide peak into enough segments to give peak shape information. Collection in 15 ml TFE (Teflon®) beakers is convenient for titration because the white background makes observation of the color change easier. The use of a stir-plate and a very small magnetic stir bar can be helpful.

(3) Add 5 drops of dilute EBT working solution directly to the aliquot off the column. All solutions will be pink in the low pH. Dilute EBT must be made up fresh to work properly. The stock solution has a shelf life of perhaps 1 month (Schwarzenbach and Flaschka, 1969) but the dilute working solution does not give accurate color changes if it is more than several days old.

(4) Titrate TEA into the solution to reach a pH of 7.0 ± 0.2. The pH is measured with a conventional digital pH meter fitted with a combination pH electrode. Use TEA with a molarity roughly matched to the normality of the eluting acid coming off the column. For example, 2 *M* TEA works well for REE being eluted with 4.0 *N* HCl or HNO_3, 1 *M* TEA works well for 2 *N* HCl or HNO_3 and 0.1 *M* TEA works well for ~ 0.2 *M* methyllactic acid. The EBT will be blue if no REE are present and purplish-blue, purple or pink depending on the amount of free REE in the beaker. If too much TEA was added, add enough HCl or HNO_3 to return to a pH of 7.0. Try not to let the pH of the solution rise above 9 because in basic solutions the indicator complex becomes too stable to be broken down by the EDTA (Schwarzenbach and Flaschka, 1969).

(5) While monitoring the pH and keeping it at 7.0, titrate 0.00001 *M* EDTA into the beaker until the color changes from pink to blue. Record amount of EDTA used. This is directly proportional to amount of REE present in solution (Fig. 1). Some adjustment of the concentration of EDTA and the number of drops of EBT used may be needed for the sensitivity of each individual's eye to the endpoint. The addition of 1 ml of deonized water to 1 ml or less of the eluted fraction prior to buffering has been found to enhance the color change. Sample REE elution curves are given in Figs. 2–4.

2.3. Substitution titration for Sr

(1) Load Sr on column as you would a sample. Like the REE titration, the Sr titration also is not cation specific so it cannot be performed in the presence of an actual rock sample. Fig. 3 shows a comparison between Sr peak position determined by titration in the absence of a rock

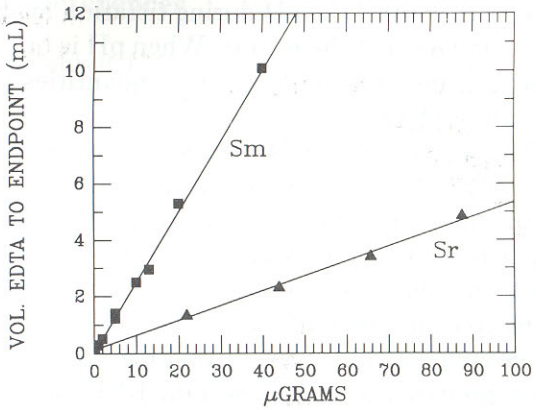

Fig. 1. Volume of 0.0001 *M* EDTA (Sm) or 0.0002 *M* EDTA (Sr) needed to reach the endpoint vs. the nominal concentration of Sm or Sr, showing the sensitivity of the titrations.

sample with Sr peak position determined by radiotracers in the presence of a rock sample. The peak positions agree to within 1–2 ml of eluant. The Sr titration is less sensitive than the titration for REE, either because of the kinetics of the substitution of Sr^{2+} for Mg^{2+} in the Mg-EDTA or the nonstoichiometry of the Mg-EDTA. Good results have been obtained on 200–400 μg Sr divided into 10–15 cuts of 2 ml each.

(2) Follow step (2) as for the REE titrations.

(3) Add 1 ml of 0.0005 *M* Mg-EDTA to the

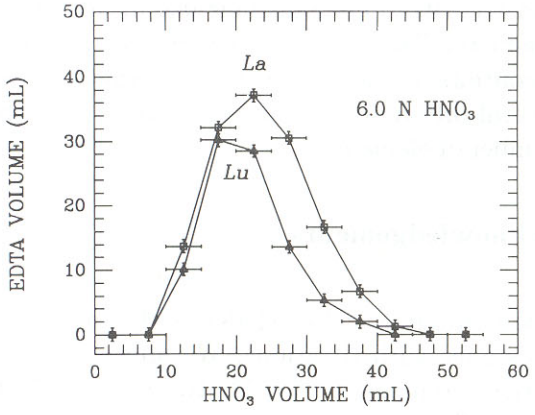

Fig. 2. Peak positions of 150 μg La and 250 μg Lu, eluted in 6.0 *N* HNO_3 on 1 cm×20 cm columns with Bio-Rad® AG*50*W X*8*, 100–200 mesh resin in H^+ form. Because La and Lu have similar distribution coefficients, the two peaks could not be resolved during a single elution and separate elutions were needed.

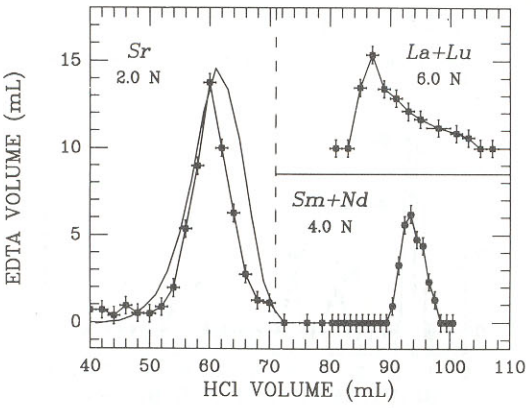

Fig. 3. Peak positions of 450 μg Sr, 44 μg (Sm+Nd) and 56 μg (Lu+La), eluted in 2.0 *N*, 4.0 *N* and 6.0 *N* HCl, respectively, on a 0.6 cm×20 cm column with Bio-Rad® AG*50*W X*8*, 200–400 mesh resin in H^+ form. Two elutions were performed with changeovers from 2.0 to 4.0 *N* at 70 ml and from 2.0 to 6.0 *N* at 80 ml, in order to separate either the REE as a group or the (Sm+Nd) group from Sr. The Sr peak position by titration is compared to peak position determined by using radioactive ^{85}Sr (*solid curve* without data points) with 60 mg or rock sample. Note the coincidence of peak position to within 1–2 ml. This shows the titration method can accurately calibrate columns in the absence of rock solution as long as subsequent elutions of rock solution do not overload the resin bed.

beaker. This provides a source of cations that exchange with aqueous Sr^{2+}. The titration is done on the Mg^{2+} freed up by the exchange.

(4) Add 5–7 drops of dilute EBT directly to the aliquot off the column.

(5) Titrate NH_4OH–NH_4Cl buffer into the solution to reach a pH of 10.0±0.2. The EBT will be a deep violet, bluish purple, or purplish blue if excess cations are present. It is difficult to mix up stoichiometric Mg-EDTA. Consequently, it is not unusual to have a slight purplish cast to the EBT even if no Sr is present. Since the goal of these procedures is peak determination and not accurate quantitative analysis, the small amount of EDTA (usually 0.5–0.8 ml) needed to take the solution to the endpoint in the absence of Sr can be considered "baseline" and is useful in getting the user's eye accustomed to the color change at the endpoint.

(6) While monitoring the pH and keeping it at 10.0, titrate 0.0001 *M* or 0.0002 *M* EDTA into

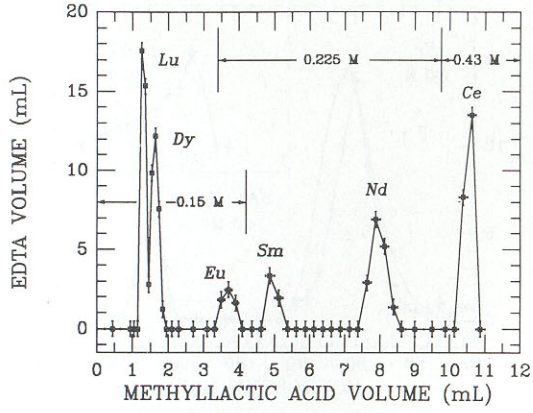

Fig. 4. Peak positions of 50–90 μg each of Lu, Dy and Eu and 25–30 μg each of Sm, Nd and Ce, eluted in 0.15 *M*, 0.225 *M* and 0.43 *M* 2-methyllactic acid in 0.25 cm×30 cm columns with Bio-Rad® AG*50*W X*4*, 200–400 mesh resin in NH_4^+ form. The elution was performed in three steps so that the following five groups could be collected separately from samples for mass spectrometry: Yb-Er-Dy; Gd; Eu-Nd-Sm; Ce and La. Step *1*: 0.15 *M* acid was eluted to determine Lu, Dy and Eu peaks positions. Step *2*: 0.225 *M* was eluted after 3.4 ml of 0.15 *M* so that Eu can be collected with Sm and Nd and can be kept separate from the heavier REE. Step *3*: after determination of the Nd peak position, 1 ml of 0.225 *M* acid was eluted to remove Pr, followed by the determination of the Ce peak position with 0.43 *M* acid.

the beaker until all traces of purplish tinge are gone from the EBT and it is a true "sky-blue" color. The amount of EDTA is directly proportional to the amount of Sr present in solution (Figs. 1 and 3).

3. Results

The calibration scheme uses direct titration for the REE and substitution titration for Sr. The key to achieving reproducible results in a variety of solutions for both titrations is to carefully control the pH during the titration. The color change of EBT is sensitive to pH as well as cation concentration (Schwarzenbach and Flaschka, 1969) and the working range for a complexiometric titration with the lanthanides is narrow (Lyle and Rahman, 1963). Thus, failure to control the pH during titration leads to degradation of the results. When pH is buffered, it is possible to titrate for μg quantities of Sr and the REE.

The amount of EDTA needed to complex Sr or the REE to the endpoint is a precise function of the amount of Sr or the REE present (Fig. 1). It is advisable to perform a series of blind tests on solutions of known concentration in order to calibrate one's eye to the color change at the endpoint and to ensure that reagents have been prepared properly. Several REE can be added at the same time and in different abundances, permitting their identification by both relative concentration and position. We use this technique routinely to calibrate nitric, hydrochloric and methyllactic acid cation-exchange columns that are used to separate elements prior to thermal ionization mass spectrometry. Figs. 2–4 present the results of calibrations for the different columns: group separation of the REE on nitric acid columns, separation of both (Sm+Nd) and (La+Lu) from Sr on HCl columns, and separation of individual REE on methyllactic acid columns.

The reader is directed to Kolthoff et al. (1969) and Schwarzenbach and Flaschka (1969) for detailed information on complexiometric titrations and their use in analytical chemistry. The latter is especially useful in that it contains numerous recipes for reagents and several different titration schemes for a large number of elements.

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