working curve; then measure the emission intensity of the unknown. Correct the data for background. Determine the cation concentration in the unknown by comparison with the working curve.

37Q APPLICATION OF ION EXCHANGE RESINS

37Q-1 The Separation of Cations

The application of ion-exchange resins to the separation of ionic species of opposite charge is discussed in Section 30D. Directions follow for the ion-exchange separation of nickel(II) from zinc(II) based on converting the zinc ions to negatively charged chloro complexes. After separation, each of the cations is determined by EDTA titration.

Discussion

The separation of the two cations is based on differences in their tendency to form anionic complexes. Stable chlorozincate(II) complexes (such as \( \text{ZnCl}_2^- \) and \( \text{ZnCl}_4^{2-} \)) are formed in 2 M hydrochloric acid and retained on an anion-exchange resin. In contrast, nickel(II) is not complexed appreciably in this medium and passes rapidly through such a column. After separation is complete, elution with water effectively decomposes the chloro complexes and permits removal of the zinc.

Both nickel and zinc are determined by titration with standard EDTA at pH 10. Eriochrome Black T is the indicator for the zinc titration. Bromopyrogallol Red or murexide is used for the nickel titration.

PREPARATION OF SOLUTIONS

2. pH-10 buffer. See Section 37E-1.
4. Bromopyrogallol Red indicator (sufficient for 100 titrations). Dissolve 0.5 g of the solid indicator in 100 mL of 50% (v/v) ethanol.
5. Murexide indicator. The solid is approximately 0.2% indicator by weight in NaCl. Approximately 0.2 g is needed for each titration. The solid preparation is used because solutions of the indicator are quite unstable.

PREPARATION OF ION-EXCHANGE COLUMNS

A typical ion-exchange column is a cylinder 25 to 40 cm in length and 1 to 1.5 cm in diameter. A stopcock at the lower end permits adjustment of liquid flow through the column. A buret makes a convenient column. It is recommended that two columns be prepared to permit the simultaneous treatment of duplicate samples.

Insert a plug of glass wool to retain the resin particles. Then introduce sufficient strong-base anion-exchange resin (Note) to give a 10- to 15-cm column. Wash the column with about 50 mL of 6 M \( \text{NH}_3 \), followed by 100 mL of water and 100 mL of 2 M HCl. At the end of this cycle, the flow should be stopped so that the liquid level remains about 1 cm above the resin column. At no time should the liquid level be allowed to drop below the top of the resin.
PROCEDURE

Obtain the unknown, which should contain 2 to 4 mmol of Ni\(^{2+}\) and Zn\(^{2+}\), in a clean 100-mL volumetric flask. Add 16 mL of 12 M HCl, dilute to the mark with distilled water, and mix well. The resulting solution is approximately 2 M in acid. Transfer 10.00 mL of the diluted unknown onto the column. Place a 250-mL conical flask beneath the column, and slowly drain until the liquid level is barely above the resin. Rinse the interior of the column with several 2- to 3-mL portions of the 2 M HCl; lower the liquid level to just above the resin surface after each washing. Elute the nickel with about 50 mL of 2 M HCl at a flow rate of 2 to 3 mL/min.

Elute the Zn(II) by passing about 100 mL of water through the column, using the same flow rate; collect the liquid in a 500-mL conical flask.

Titration of Nickel

Evaporate the solution containing the nickel to dryness to eliminate excess HCl. Avoid overheating; the residual NiCl\(_2\) must not be permitted to decompose to NiO. Dissolve the residue in 100 mL of distilled water, and add 10 to 20 mL of pH-10 buffer. Add 15 drops of Bromopyrogallol Red indicator or 0.2 g of murexide. Titrate to the color change (blue to purple for Bromopyrogallol Red, yellow to purple for murexide).

Calculate the number of milligrams of nickel in the unknown.

Titration of Zinc

Add 10 to 20 mL of pH-10 buffer and 1 to 2 drops of Eriochrome Black T to the eluate. Titrate with standard EDTA solution to a color change from red to blue.

Calculate the mass of zinc in the unknown in milligrams.

37Q-2 Determination of Magnesium by Ion-Exchange Chromatography

Discussion

Magnesium hydroxide in milk of magnesia tablets can be determined by dissolving the sample in a minimum of acid and diluting to a known volume. The excess acid is established by titrating several aliquots of the diluted sample with standard base. Other aliquots are passed through a cation exchange column, where magnesium ion is retained and replaced in solution by a chemically equivalent quantity of hydrogen ion:

\[
\text{Mg}^{2+} + 2\text{H}^+_\text{res} \rightarrow \text{Mg}^{2+}_{\text{res}} + 2\text{H}^+
\]

The acid in the eluate is then titrated; the difference between the volumes of base needed for the two series of titrations is proportional to the magnesium ion in the sample. Thus,

\[
\text{net mmol H}^+ = 2 \times \text{mmol Mg}^{2+}
\]
PROCEDURE

Step 1. Prepare approximately 1 L of 0.05 M NaOH. Standardize this solution against weighed portions of dried primary-standard potassium hydrogen phthalate (KHP); use about 0.4-g (to the nearest 0.1 mg) samples of KHP for each standardization.

Step 2. Record the number of tablets in your sample. Transfer the tablets to a clean 500-mL volumetric flask (Note 1). Dissolve them in a minimum volume of 3 M HCl (4 to 5 mL/tablet should be sufficient). Then dilute to the mark with distilled water.

Step 3. Titrate the free acid in several 15.00-mL aliquots of the dissolved sample; phenolphthalein is a satisfactory indicator.

Step 4. Condition the column with about 15 mL of 3 M HCl (Note 2), followed by three 15-mL portions of distilled water. Never permit the liquid level to drop below the top of the column packing.

Step 5. Charge each column with a 15.00-mL aliquot of the sample. Elute at a rate of about 2 to 3 mL/min. Wash the column with three 15-mL portions of water. Collect eluate and washings in a conical flask. Repeat this step with additional aliquots of the sample (Note 3).

Step 6. Titrate the eluted samples (and washings) with standard base. Correct the total volume for that needed to titrate the free acid, and calculate the mass of Mg(OH)\textsubscript{2} in milligrams in each tablet.

Notes

1. The sample will dissolve more quickly if the tablets are first ground in a mortar. If you choose this alternative, you will need to know (a) the total mass of your tablets and (b) the mass of ground sample that you transfer to the volumetric flask.

2. The volume of the sample aliquots and the volume of base used in the several titrations must be measured carefully (to the nearest 0.01 mL). All other volumes can and should be approximations only.

3. A 25-mL buret packed to a depth of about 15 cm with Dowex-50 cation exchange resin makes a satisfactory column. Reconditioning after 4 or 5 elutions is recommended.

GAS-LIQUID CHROMATOGRAPHY

As noted in Chapter 31, gas-liquid chromatography permits the analyst to separate the components of complex mixtures. The accompanying directions are for the determination of ethanol in beverages.

37R-1 The Gas-Chromatographic Determination of Ethanol in Beverages\textsuperscript{15}

Discussion

Ethanol is conveniently determined in aqueous solutions by means of gas chromatography. The method is readily extended to measurement of the proof of alcoholic beverages. By definition, the proof of a beverage is two times its volume percent of ethanol at 60°F.

\textsuperscript{15}Adapted from J. J. Leary, J. Chem. Educ., 1983, 60, 675.