

THE USE OF N, N, N', N' TETRAKIS (2-HYDROXYPROPYL) ETHYLENEDIAMINE IN THE DETERMINATION OF THE R₂O₃ GROUP IN LIMESTONE

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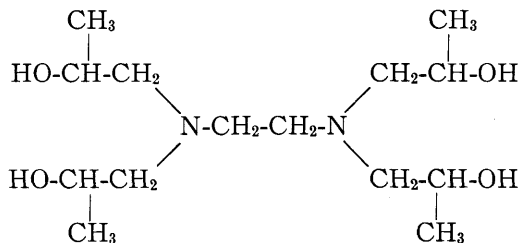
The separation of the R₂O₃ group from alkaline earth and alkali metal ions in the chemical analysis of limestone and dolomite is usually carried out by precipitating the former with ammonium hydroxide as a mixture of hydrous oxides. The coprecipitation of calcium and magnesium ions becomes negligible when a double precipitation procedure is followed. This technique, which is required for accurate analysis, takes from two to three hours per sample.

Various procedures other than that using ammonium hydroxide have been described in the literature for the separation of trivalent metal ions from divalent metal ions in solution. The "basic-acetate" method (Scott, 1939) has met with some success. The use of benzoic acid and ammonium benzoate (Kolthoff *et al.*, 1934) enables one to separate ferric, aluminum, and chromic ions from divalent metals quantitatively with negligible coprecipitation of the latter. Organic nitrogen compounds such as pyridine (Watters *et al.*, 1944), hexamethylenetetramine (Traub, 1946), and urea (Willard *et al.*, 1937) have also been used to effect separations as indicated above.

In a study being made by the authors of N,N,N',N' tetrakis (2-hydroxypropyl) ethylenediamine as a possible chelating agent, it was noted that ferric and aluminum ions were quantitatively precipitated in the presence of this reagent over a pH range of 6.0 to 6.5. In addition, it was found that ferric and aluminum ions were quantitatively separated from calcium and magnesium ions with negligible coprecipitation of the latter ions. This information indicated that the compound might be used as a precipitant for the R₂O₃ group in the analysis of limestone and dolomite.

EXPERIMENTAL PROCEDURE

Reagents. N,N,N',N' tetrakis (2-hydroxypropyl) ethylenediamine, produced by Wyandotte Chemicals Corporation and sold under the trade name of "Quadrol", was dissolved in distilled water and diluted to 1 liter. The quantity of "Quadrol" (29.2 grams) was sufficient to prepare a 0.1 molar solution. "Quadrol" is a tertiary amine alcohol with weakly basic properties. The compound is a viscous liquid, water white and infinitely soluble in water.



N,N,N',N' tetrakis (2-hydroxypropyl) ethylenediamine or "Quadrol"

Standard Iron Solution—7.0225 g. of analytical grade ferrous ammonium sulfate hexahydrate were dissolved in one liter of solution (1 ml. of standard solution = 1 mg. of iron).

Standard Aluminium Solution—1 g. of aluminum wire (spectrographic standard grade) was dissolved in hydrochloric acid and diluted to one liter (1 ml. of standard solution = 1 mg. of aluminum).

Standard Calcium Solution—24.9500 g. of analytical grade calcium carbonate were dissolved in hydrochloric acid and diluted to 500 ml. (1 ml. of standard solution = 20 mg. of calcium).

Standard Magnesium Solution—2.1105 g. of magnesium turnings, analytical reagent grade, were dissolved in hydrochloric acid and diluted to 500 ml. (1 ml. of standard solution = 4.2 mg. of magnesium).

TABLE 1
Determination of Iron (III) and Aluminum in Standard Solutions Using "Quadrol"

Amount of R_2O_3 in Standard Solution	Amount of R_2O_3 Precipitated by "Quadrol" pH = 6.0	Amount of R_2O_3 Precipitated by "Quadrol" pH = 6.5
0.0332 g	0.0336 g.	0.0335 g.
	0.0335	0.0337
	0.0331	0.0330
	ave: 0.0334 g.	ave: 0.0334 g.
0.0664 g	0.0660 g.	0.0662 g.
	0.0663	0.0667
	0.0667	0.0668
	ave: 0.0663 g.	ave: 0.0666 g.

TABLE 2
Determination of Iron (III) and Aluminum in Standard Solutions of Iron (III), Aluminum, Calcium, and Magnesium Using "Quadrol"

Amount of R_2O_3 in Standard Solutions*	Amount of R_2O_3 Precipitated by "Quadrol" pH = 6.0	Amount of R_2O_3 Precipitated by "Quadrol" pH = 6.5
0.0332 g.	0.0338 g.	0.0336 g.
	0.0336	0.0330
	0.0332	0.0338
	ave: 0.0335 g.	ave: 0.0335 g.
0.0664 g.	0.0668 g.	0.0670 g.
	0.0662	0.0665
	0.0670	0.0668
	ave: 0.0667 g.	ave: 0.0668 g.

*Standard solutions contained the equivalent of 0.0700 g. of MgO and 0.2800 g of CaO.

Procedure for R_2O_3 Analysis of Standard Solutions.—Ten milliliter aliquot parts of the standard iron and aluminum solutions were mixed and diluted to approximately 150 ml. with distilled water. Ten milliliter portions of 3 percent hydrogen peroxide were added to oxidize the iron to the ferric state, and the solution was slowly brought to a boil to remove the excess peroxide (Fouk *et al.*, 1952). After cooling the solution to room temperature, the standard "Quadrol" solution was added until the desired pH was attained. The pH was measured with a Photovolt line operated electronic pH meter. The solution was again brought to a boil and allowed to stand on a steam plate for 15 minutes. The precipitated hydrous oxides of aluminum and iron were then filtered (No. 41 Whatman filter paper) and washed with warm 1 percent ammonium nitrate

solution. After careful charring of the filter paper, the precipitate was ignited to constant weight at about 1000°C . This same procedure was followed in the analysis of solutions containing 20 ml. aliquot parts of each of the standard aluminum and standard iron and in the analysis of the solutions containing known quantities of aluminum, iron, calcium, and magnesium ions.

Procedure for R_2O_3 Analysis of Limestone and Dolomite.—The sample to be analyzed was thoroughly dried at 110°C , weighed, and ignited at 1000°C for one hour. The silicon dioxide was removed by the usual procedure, using a double dehydration with hydrochloric acid (Kolthoff *et al.*, 1952). After the silica was removed, the solution was diluted to approximately 200 ml. and treated

TABLE 3

A Comparison of the Chemical Analysis for R_2O_3 in Limestone and Dolomite Using Ammonium Hydroxide (Double Precipitation) and "Quadrol"

Sample Number	Per cent R_2O_3			
	Double Ppt'n with NH_4OH		Single Ppt'n with "Quadrol"	
	Mean (6 det.)	Ave. dev.	Mean (4 det.)	Ave. dev.
1	0.41%	$\pm 0.02\%$	0.40%	$\pm 0.02\%$
2	0.87	0.02	0.85	0.02
3	1.45	0.02	1.44	0.01
4	1.72	0.03	1.67	0.02
5	2.29	0.03	2.31	0.02
6	3.46	0.02	3.46	0.02
7	4.56	0.03	4.57	0.02
8	5.62	0.05	5.60	0.02

TABLE 4

A Comparison of the Chemical Analysis for R_2O_3 in Limestone Using Double and Single Precipitations with Ammonium Hydroxide

Sample Number ^a	Per cent R_2O_3	
	Double Ppt'n with NH_4OH^a	Single Ppt'n with NH_4OH^b
2	0.87%	1.40%
4	1.72	1.94
5	2.29	2.67
8	5.62	6.25

^aSample number and percentage values were taken from Table 3.
^bAverage of duplicate determinations.

with 3 percent hydrogen peroxide. The excess peroxide was removed by bringing the solution slowly to a boil. The solution was cooled to room temperature and ammonium hydroxide was added until its pH was raised to a value between two and three. The standard solution of "Quadrol" was then added slowly until a pH of 6.5 was reached. The solution was heated to boiling and allowed to stand on the steam plate for 15 minutes. The precipitated hydrous oxides were filtered, washed with warm 1 per cent ammonium nitrate, carefully charred, and finally ignited to a constant weight at about 1000°C . The filtrate was analyzed for its calcium and magnesium content.

RESULTS OF ANALYSIS

The results of the analysis of the standard solutions, using "Quadrol" as the precipitating agent, are reported in table 1 and in table 2. The amounts of R_2O_3 found in eight limestone and dolomite samples when "Quadrol" was used are listed in table 3. These are compared with those values found when the standard double precipitation method with ammonium hydroxide was used. Samples of limestone and dolomite, varying in iron and aluminum oxide content from less

than one half percent to over five percent, were selected for analysis. This wide range of R_2O_3 content was purposely selected to test the accuracy and precision of the procedure. The R_2O_3 content of four of the samples was measured using a single precipitation with ammonium hydroxide in order to determine the extent of the coprecipitation of calcium and magnesium. The results of these analyses are summarized in table 4.

After the separation of the R_2O_3 group with "Quadrol", the filtrate from each of the limestone and dolomite samples was analyzed for calcium and magnesium by the standard method. The amounts of calcium and magnesium found were in good agreement with those obtained when ammonium hydroxide was used as the precipitant for the R_2O_3 group.

DISCUSSION OF RESULTS

The results of the analyses as summarized in table 3 indicate that a single precipitation procedure for the R_2O_3 group ions with "Quadrol" compares very favorably with the standard double precipitation method required when ammonium hydroxide is used. The amount of coprecipitation of calcium and magnesium ions appears to be negligible during the "Quadrol" procedure. It is felt that at least three factors are contributing to this phenomenon.

1. The freshly precipitated hydrous oxides have a tendency to adsorb negative hydroxyl ions on their surfaces and, as a result, assume an overall negative charge. By operating at a pH of less than seven, the number of hydroxyl ions present in solution is reduced and the magnitude of the charge on the precipitate is reduced. This would decrease the attraction of the hydrous oxides toward positive ions in solution.

2. The positive "Quadrol" ion is large and bulky and when attracted to the surface of the charged precipitate would tend to block the approach of other positive ions, thus lowering the concentration of calcium and magnesium ions on the surface of the hydrous oxide.

3. Since the structure of "Quadrol" is similar to that of other chelating agents, it seems possible that some chelation of the calcium and magnesium occurs. Such action would tend to decrease the coprecipitation by reducing the effective concentration of these ions in solution. The chelation, however, appears to be of insufficient strength to prevent the precipitation of calcium as an oxalate. Therefore "Quadrol" does not interfere with the completion of the limestone or dolomite analysis.

The authors are of the opinion that a combination of all three factors is responsible for the favorable results found when "Quadrol" is used in the precipitation of the R_2O_3 group ions.

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