



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  $1000^\circ\text{C}$ . 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  $110^\circ\text{C}$ , weighed, and ignited at  $1000^\circ\text{C}$  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 <sup>a</sup>	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

<sup>a</sup>Sample number and percentage values were taken from Table 3.  
<sup>b</sup>Average 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  $1000^\circ\text{C}$ . 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.

#### LITERATURE CITED

- Foulok, C. W., H. V. Moyer, and W. M. MacNeven. 1952. Quantitative Chemical Analysis. Ed. 1. McGraw Hill Co., New York.
- Kolthoff, I. M., V. A. Stenger, and B. Moskovitz. 1934. A benzoate method, a new procedure for the separation of iron, aluminum and chromium from the other ions of the third group and the alkaline earth ions. Jour. Amer. Chem. Soc. 56: 812.
- , and E. B. Sandell. 1952. Textbook of Quantitative Inorganic Chemistry. Ed. 3. Macmillan Co., New York.
- Scott, W. W. 1939. Standard Methods of Chemical Analysis. V. 1. Ed. 5. D. Van Nostrand Co., New York.
- Traub, K. W. 1946. Hexamethylenetetramine in the separation of titanium and columbium. Ind. Eng. Chem. Anal. Ed. 18: 122.
- Watters, J. I., and I. M. Kolthoff. 1944. Determination of manganese after oxidation to trihydrogen pyrophosphatomanganate—use of pyridine to separate iron, chromium, vanadium, and cerium from manganese. Ind. Eng. Chem. Anal. Ed. 16: 187.
- Willard, H. H., and N. K. Tang. 1937. Quantitative determination of aluminum by precipitation with urea. Ind. Eng. Chem. Anal. Ed. 9: 357.