

Determination of Nitrates in Saline Minerals

By LAURA E. REICHEN and JOSEPH J. FAHEY

CONTRIBUTIONS TO GEOCHEMISTRY

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*A quantitative method of analysis
based on the stoichiometric relation
of the nitrates to the magnesium oxide
that is formed when a sample is heated
to 700°C in the presence of an excess
of magnesium sulfate*



UNITED STATES DEPARTMENT OF THE INTERIOR

STEWART L. UDALL, *Secretary*

GEOLOGICAL SURVEY

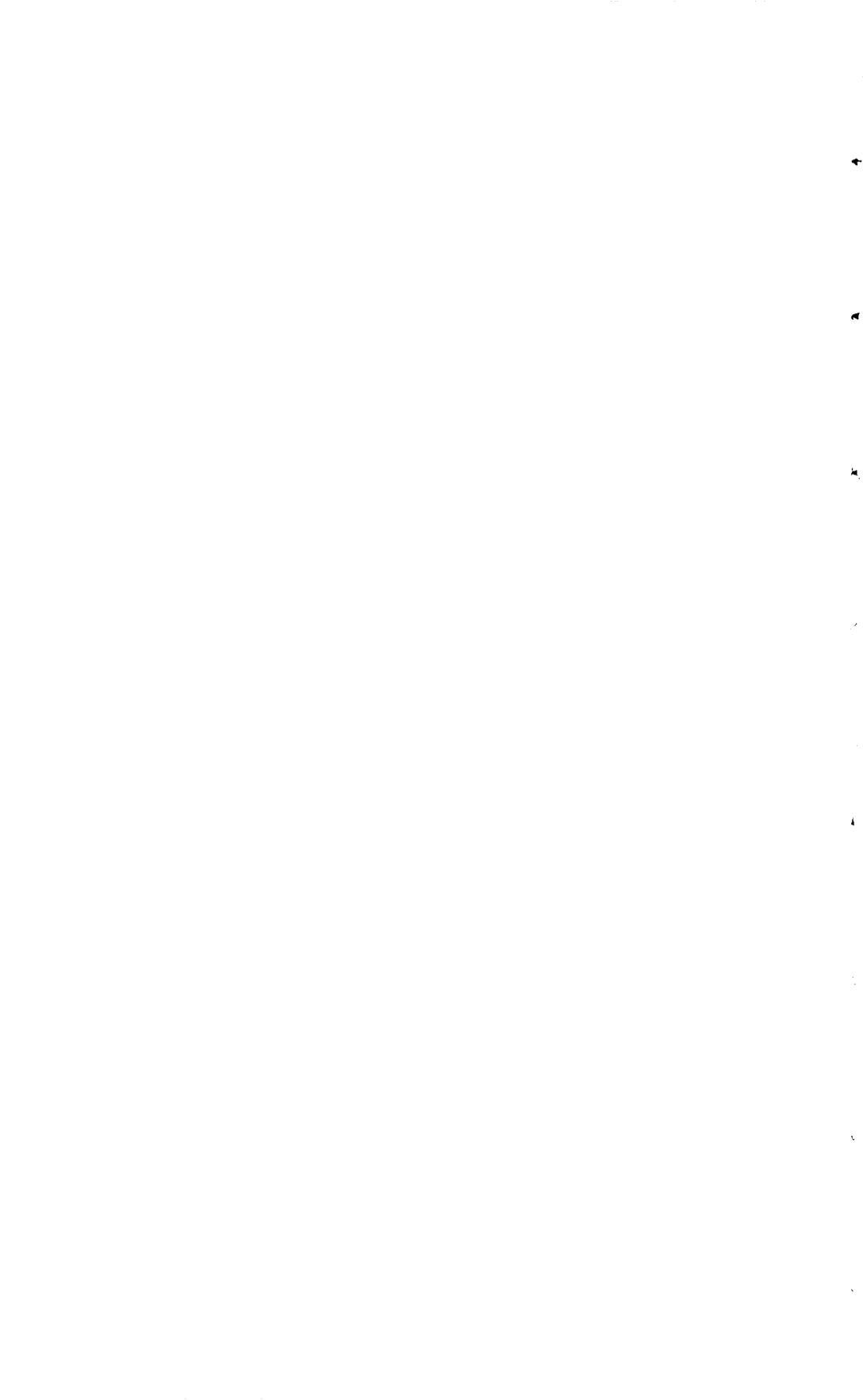
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DETERMINATION OF NITRATES IN SALINE MINERALS

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Abstract

The alkali nitrate is heated in the presence of magnesium sulfate for 40 minutes at 600°C, whereby magnesium oxide is produced in stoichiometric relation to the N₂O₅ present. The amount of magnesium oxide is measured by titration with sulfuric acid, and the equivalent N₂O₅ is calculated.

INTRODUCTION

When an aqueous solution of sodium nitrate and magnesium sulfate is evaporated to dryness and the residue heated to 600°C, magnesium oxide is formed: $2\text{NaNO}_3 + \text{MgSO}_4 \rightarrow \text{MgO} + \text{N}_2\text{O}_5 + \text{Na}_2\text{SO}_4$. As is shown by the equation, the magnesium oxide bears a stoichiometric relation to the nitrate in the sample. A careful search of the literature revealed no previous reference to this relation.

If a lake water is concentrated by evaporation it deposits its saline constituents. These minerals consist mostly of chlorides, nitrates, sulfates, carbonates, bicarbonates, and borates of sodium, potassium, calcium, and magnesium. Of these saline minerals, the only ones which need be considered in this procedure are those that are soluble in water, as all the others are easily separated from the nitrates by a water leach.

PROCEDURE

Prepare the following reagents:

MgSO₄: 10 percent solution

Standard H₂SO₄: 0.1 N

Standard NaOH: 0.1 N

Ag₂SO₄: Hot, saturated solution (about 1.5 percent)

Take a sample of such size that no more than 250 mg of N₂O₅ is present. (A full 50-ml burette of 0.1 N H₂SO₄ for the titration

of MgO is equivalent to 270 mg N_2O_5 .) Treat the sample in a small beaker with 25 ml of water at room temperature, filter, and wash into a porcelain dish. This removes all insoluble material from the readily soluble nitrate of the sample.

Add a drop of methyl red and neutralize carefully, making the final adjustment with dilute sulfuric acid or sodium hydroxide so that the solution is *exactly* neutral. If the sample contains carbonate, sweep carbon dioxide-free air through the system during neutralization until it is free of carbon dioxide.

If chlorides are present, gradually add hot silver sulfate solution, while stirring, directly to the nitrates in the dish until the silver chloride precipitate coagulates and no more precipitate forms. Digest briefly on the steam bath until the precipitate settles; it is not necessary to filter off the silver chloride.

Add 10 ml of the magnesium sulfate solution to the neutral alkali nitrate and evaporate to complete dryness so that there will be no spattering or decrepitation when the dish is heated over a flame. Heat the dish over a flame—being careful not to exceed 600°C —until no more gases seem to be coming off so that the muffle furnace will not be attacked unduly by the fumes. Heat at 600°C for 40 minutes in muffle. Add a calculated excess of standard sulfuric acid to the cooled dish and heat on the steam bath to dissolve the magnesium oxide. Titrate the excess sulfuric acid with standard sodium hydroxide using methyl red indicator. Calculate the percent N_2O_5 from the magnesium oxide which reacted with the sulfuric acid (1 ml 0.1 N H_2SO_4 \approx 0.002016 g MgO \approx 0.005401 g N_2O_5).

DISCUSSION AND RESULTS

The optimum temperature for the formation of magnesium oxide, stoichiometrically equivalent to the nitrate of the sample, is 600°C . At 700°C , magnesium sulfate alone produces a few milligrams of magnesium oxide, and below 600°C the nitrate-magnesium oxide reaction is incomplete. At 500°C , 98 percent of the nitrate present reacts with the magnesium sulfate to produce magnesium oxide; at 400°C , about 93 percent reacts, and at 300°C only 64 percent reacts.

The stoichiometric relation of the magnesium oxide formed to the nitrate present in the sample was demonstrated by using sodium nitrate, potassium nitrate, and known volumes of standard nitric acid (table 1). The nitric acid was neutralized with sodium hydroxide before the addition of the magnesium sulfate. An excess of about 1 g of magnesium sulfate was added before evaporation.

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TABLE 1.—*Determination of nitrates, in grams*

Source	MgO equivalent to NO ₃ taken	MgO found	N ₂ O ₅ taken	N ₂ O ₅ found
HNO ₃ -----	.0040	.0041	.0108	.0110
	.0040	.0041	.0108	.0110
	.0403	.0404	.1079	.1082
	.0403	.0409	.1079	.1096
	.0806	.0806	.2159	.2159
KNO ₃ -----	.0403	.0401	.1079	.1074
	.0403	.0400	.1079	.1072
	.0806	.0813	.2159	.2178
NaNO ₃ -----	.0040	.0037	.0108	.0099
	.0403	.0399	.1079	.1067
	.0806	.0805	.2159	.2157
Humberstonite ¹ -----	.0341	.0340	.0914	.0910

¹ Ericksen, G. E., Fahey, J. J., and Mrose, M. E., 1967, Humberstonite, Na₇K₃Mg₂(SO₄)₆(NO₃)₂·6H₂O:—A new saline mineral from the Atacama Desert, Chile [abs.]: Geol. Soc. America Program 1967—Ann. Mtgs., Nov. 20–22, 1967, New Orleans, La., p. 58.

Determining the magnesium oxide by filtering and weighing is difficult because it sticks so tenaciously that the dish cannot be scrubbed clean. Also, the magnesium oxide contains a small amount of magnesium sulfate in spite of all attempts to wash it out. The magnesium oxide is best measured by dissolving it in a known volume of standard sulfuric acid and titrating the excess acid with standard sodium hydroxide.

The solution must be neutralized with sulfuric acid before evaporation; any carbonates or bicarbonates present will be converted to sulfates and, as such, will not interfere. The alkali chlorides react with magnesium sulfate and produce magnesium oxide stoichiometrically. Either the total magnesium oxide from the nitrate and the chloride can be measured and a correction made for the chloride present, or the chloride can be inactivated by precipitation with silver sulfate. It is not necessary to filter off the precipitated silver chloride.

Although nitrites do not occur as minerals, and therefore are not listed as interfering substances, they react with magnesium sulfate stoichiometrically, as do nitrates, and thus could be quantitatively measured. Sodium iodate does not react with magnesium sulfate to form magnesium oxide, but it is decomposed below 600°C and would interfere in the determination of nitrates.

Sodium borate was used to simulate the soluble alkali borates (borax, tinalconite, and kernite). It was heated to 600°C with magnesium sulfate and then allowed to cool to room temperature;

all the salts present were soluble in water, indicating that no magnesium oxide was produced. However, when standard sulfuric acid is added and back titrated with standard sodium hydroxide, it is found that sulfuric acid, equivalent to as much as 2 mg of magnesium oxide, reacted with the sample. This is equivalent to as much as 5 mg of nitrate. The error is not dependent on the amount of sodium borate present. Many determinations have shown that sodium borate does not cause erroneous results if 5 mg or more of nitrate is present in the sample.