2. It is believed that the new values here reported are more accurate than those heretofore available in the literature for the following reasons: (*a*) the purities of the various metals worked with have been greater than those formerly used; (*b*) a calorimeter capable of a higher degree of accuracy, of modern type and adiabatic in operation was used; (*c*) a new method of procedure was employed for determining the completeness of oxidation of samples; the operation of the accessory apparatus devized made it possible to weigh with accuracy the metallic oxide formed and thus furnish a direct check upon the completeness of oxidation in each case; (*d*) while metals of a very high degree of purity have been obtained for samples, special interest is connected with some of the samples because heretofore they have been available only in impure form; the list includes cerium, cadmium, lanthanum and tantalum; also, the values of these elements have been reported heretofore in each case by only one investigator.

3. Beryllium has been only partially oxidized. It is believed, however, that owing to the method of checking by weighing the oxide formed, acceptable results have been secured.

4. All values here determined have been obtained by the direct method.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

A NEW ORGANIC REAGENT FOR THE DETECTION OF NITRATES AND PERCHLORATES

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RECEIVED JULY 7, 1924 PUBLISHED DECEMBER 13, 1924

In some recent work[1] it was noticed that the nitrate of α-phenyl-β-diethylaminoethyl-*p*-nitrobenzoate was fairly insoluble. On account of the interest in finding a suitable reagent for precipitating nitrates it was thought to be desirable to determine the solubilities of the nitrate and of other common salts with considerable accuracy.

The only organic reagent now in common use for the determination of nitrates is nitron.[2] It gives a highly insoluble salt with nitric acid (0.0099 g. of nitron nitrate per 100 cc.) and also with perchloric acid (0.0082 g. of nitron perchlorate in 100 cc.). The two objections to the general use of nitron are, first, many anions interfere on account of giving slightly soluble salts and second, its solutions are not particularly stable.

Rupe and Becherer[3] have recently advocated di-(α-naphthylmethyl)-amine as a reagent for nitrates, as the salt with nitric acid is exceedingly

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[1] Marvel and du Vigneaud, THIS JOURNAL, **46**, 2095 (1924).

[2] Cope and Barab [THIS JOURNAL, **39**, 504 (1917)] give a good bibliography on nitron.

[3] Rupe and Becherer, *Helvetica Chim. Acta*, **6**, 674, 885 (1923).

insoluble. However, this is apparently not a specific reagent, as only the acetate, sulfate and phosphate are easily soluble. No quantitative data are given except for the solubility of the nitrate.

As will be shown in the experimental part of this paper, the new reagent gives precipitates which are not nearly as insoluble as those obtained with either of the reagents named above. However, since the reagent seems to be more specific for the nitrate and perchlorate ions, it may be of some use in analytical procedures.

Experimental Part

The reagent was prepared by dissolving 3 g. of the hydrochloride of the amine in 10 cc. of water. When 0.5 cc. of this reagent and 3 drops of dil. hydrochloric acid were added to 5 cc. of approximately 0.1 *N* solutions containing the anions, chloride, bromide, chlorate, iodate, sulfate, carbonate, acetate, borate, arsenite, arsenate, acid phosphate and thiosulfate, no precipitate was formed. A crystalline precipitate was obtained when an iodide, oxalate, perchlorate, nitrate or nitrite was similarly treated. The precipitate obtained from the nitrite was identical with that from the nitrate as shown by melting-point and mixed-melting-point determinations. The nitric acid undoubtedly is formed by the decomposition of the nitrous acid. In neutral solution nitrites do not give an immediate precipitate with the reagent. Bromates give an oily material in acid solution but no reaction in neutral solution. Thiocyanates and dichromates give oily precipitates in either acid or neutral solutions. When a 0.01 *N* solution of an iodide or a 0.014 *N* solution of an oxalate is used, no salt is precipitated by this reagent.

Table I shows the results of treating 5 cc. of nitrate solution with 0.5 cc. of the reagent at 15°.

Table I

Delicacy of the Nitrate Test

Nitrate solution *N*	No acid	Two drops of dil. hydrochloric acid	Three drops of dil. hydrochloric acid
0.1	Immediate ppte.	Immediate ppte.	Immediate ppte.
.01	Ppte. in about 30 min.	Ppte. in about 1 hr.	Ppte. in about 1 hr.
.0075	Ppte. overnight	Ppte. overnight	Ppte. overnight
.005	Ppte. overnight	Ppte. overnight	No ppte.
.0025	No ppte.	No ppte.	No ppte.

Solubility of the Nitrate.—The exact solubility of the nitrate[4] was determined by treating 100 cc. of water with an excess of the salt and shaking the mixture in a thermostat at 25°. After several days the solution was allowed to settle and two 10cc. samples of the supernatant solution were removed, evaporated to dryness on a water-bath and dried to constant weight at 100°. The residue in each case weighed 0.0310 g.

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[4] For the properties of the nitrate, see Ref. 1.

On account of the solubility of the precipitate, accurate quantitative results could hardly be expected. Two analyses of sodium nitrate (ordinary C.P. grade) showed errors of —0.47% and —0.73% of nitrate, respectively.

Properties of the Perchlorate.—The pure perchlorate of the base was prepared by dissolving the hydrochloride in water and treating this solution with an excess of potassium perchlorate solution. The perchlorate separated in a rather gummy mass from the concentrated solution but gradually crystallized. It was recrystallized from alcohol, giving light yellow crystals; m. p., 144°. Further crystallization did not change the melting point.

Anal. (Kjeldahl). Subs., 0.5000: 23.1 cc. of 0.0966 *N* HCl. Calc. for $C_{19}H_{22}O_4N_2.HClO_4$: N, 6.33. Found: 6.26.

The solubility of the perchlorate was determined in the manner described for the nitrate and found to be 0.0296 g. in 25 cc. at 25°. The perchlorate should not be heated above 100°.

The delicacy of the perchlorate test is indicated in Table II.

TABLE II

DELICACY OF THE PERCHLORATE TEST

Perchlorate solution *N*	No acid	Three drops of concd. hydrochloric acid
0.01	Cloudy at once Crystalline ppte. in three hours	Cloudy at once Crystalline ppte. in three hours
.005	Cloudy at once Ppte. overnight Crystalline after two days	Cloudy at once Ppte. overnight Crystalline after two days
.0025	Cloudy at once Ppte. overnight (15°) Crystalline after one week	Faint cloudiness Crystalline after one week
.001	Cloudy but no definite ppte.	No change

Summary

1. α-Phenyl-β-diethylaminoethyl-*p*-nitrobenzoate forms quite insoluble salts with nitric and perchloric acids. Using the hydrochloride of the amine as a reagent, a nitrate may be detected in a 0.005 *N* solution and a perchlorate may be detected in a 0.0025 *N* solution.

2. Most of the anions including nitrites and chlorates do not interfere with the use of this reagent, while iodides, oxalates, thiocyanates and dichromates do.

3. The solubilities of the nitrate and of the perchlorate of the reagent have been determined.

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