

definitely. However, by making reasonable assumptions, one can calculate that the heat would be enough to raise the temperature on the order of 0.5° F. per day if there were no loss. If heat could not be dissipated so quickly from the interior of the pile, the temperature would rise and the reaction would be accelerated. Because of uncertainties of the calculation and the variations in heat transfer conditions possible, an exact point at which rising temperature of the pile would be encountered cannot be determined. For this fertilizer in a large pile, 266° F. (130° C.) would be in the uncertain range. It would consequently be safer to make a practice of cooling it below 212° F. (100° C.) before storing.

#### Effect of Organic Matter

A set of three fertilizers was made on a laboratory scale. These were basically 8-7-4's, with such additional plant food as the filler contained. The

filler amounted to 580 pounds per ton of a fertilizer. In one it was inorganic, a mixture of sand and expanded vermiculite, in another it was cottonseed meal, and in the third it was activated sewage sludge. The fertilizers with the organic fillers consistently evolved more gas than the straight inorganic one. Nevertheless, the inorganic one gave prompt spontaneous ignition when heated to 468° F. (242° C.), while neither of those with organic filler ignited spontaneously even when heated to 545° F. (285° C.), the highest convenient temperature.

These tests were made on well ammoniated fertilizers. The work of Hardesty and Davis (2, 3) has shown that underammoniated fertilizers containing organic material can heat spontaneously, even starting at room temperature, to such a degree that they ignite. Moreover, the test conditions were unsuitable for showing the spontaneous heating due to oxidation of organic matter. Thus, even though

these fertilizers did not show a sudden, sharp ignition like the inorganic ones, they would be subject to spontaneous heating and possible destruction if placed in pile storage while hot.

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## PLANT ANALYSES

### Rapid Determination of Nitrate and Nitrite in Plant Material

Because of its rapidity and simplicity, this modification of the Nelson, Kurtz, and Bray method is well adapted for measuring day-to-day changes in nitrate or nitrite or for other applications in which the basic plant material remains essentially constant. Modifications suggested are use of copper and slightly more reagent powder, and allowance of more latitude in the time schedule of operations.

**A** MODIFICATION of the Nelson, Kurtz, and Bray (2) method for the determination of nitrate and nitrite determines nitrite by diazotization of sulfanilic acid and coupling with 1-naphthylamine to form a red dye. Nitrate must be reduced to nitrite for this analysis. The modifications suggested are the use of copper, the use of slightly more reagent powder, and the allowance of more latitude in the time schedule of operations than was proposed by the original authors.

#### Procedure

For determination of nitrate in the absence of nitrite, an aqueous extract of plant material is made, usually at the ratio of 1 gram of fresh or 0.1 gram of dried plant material to 20 ml. of water. To 1 ml. of this extract are added 9 ml. of 20% acetic acid solution containing

0.2 p.p.m. of copper as copper sulfate. By the use of a measuring scoop, 0.8 gram (between 0.6 and 1.0 gram) of the powder described by Nelson, Kurtz, and Bray (2) is added. This powder is an intimate mixture of 100 grams of barium sulfate, 75 grams of citric acid, 10 grams of manganous sulfate dihydrate, 4 grams of sulfanilic acid, 2 grams of powdered zinc, and 2 grams of 1-naphthylamine. The sample is then shaken for about 15 seconds, and is similarly shaken 3 minutes later. After 3 minutes more the sample is shaken for the third time and is centrifuged for 3 minutes at 1000 × G. The supernatant solution is poured through a small loose plug of borosilicate glass wool, the light absorbance is measured at a wave length of 520 mμ, and the amount of nitrate is calculated from a standard curve. The time between shakings is relatively unimportant; it can be halved or doubled with little

change in results. Usually the powder is added to eight sample tubes in succession, the tubes are shaken successively by hand at 3-minute intervals, and all eight tubes are centrifuged simultaneously.

The same procedure may be used for the determination of nitrite in the absence of nitrate, but if nitrite is to be determined in the presence of nitrate, the zinc, manganese sulfate, and cupric sulfate should be omitted.

The determination of nitrate in the presence of nitrite requires two runs, one with the zinc, manganese sulfate, and cupric sulfate and the other without these substances. Different standard curves must be made for nitrate and nitrite, as not all of the nitrate originally present appears as nitrite after the reduction (Figure 1).

The water should be as free from copper as is possible, because the final

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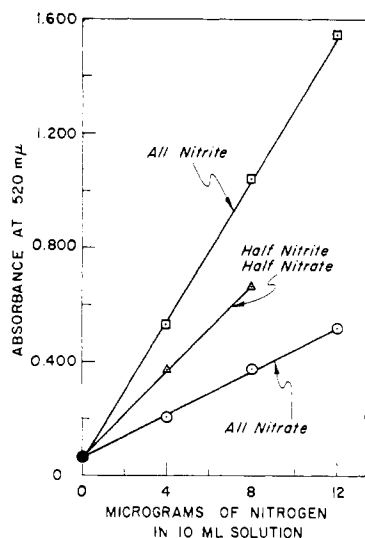


Figure 1. Standard curves for nitrate, nitrite, and a mixture of nitrate and nitrite

10 ml. of test solution must not contain more than 1.25 p.p.m. of copper. The water used in this work has been tested several times by the dithizone (3) method and has consistently been shown to contain less than 0.002 p.p.m. of heavy metals. Further, the electrical conductivity of the water was never higher than could be accounted for by dissolved carbon dioxide in equilibrium with the atmosphere. Water of this purity was obtained either by ion exchange with Rohm and Haas Amberlite MB-3 resin or by distillation in a borosilicate glass still. Water from these two sources gave identical results.

Standard potassium nitrate, potassium nitrite, and calcium nitrate samples, without plant material, were analyzed by this method, but with variation in the amount of copper used in the powder mixture.

### Results and Discussion

The reduction of nitrate to nitrite in this method is dependent upon small amounts of copper salts. As is shown by Figure 2, maximum color is developed when the 10 ml. of test solution contain between 1.5 and 12.5  $\gamma$  of copper. This is apparently a specific requirement for copper, in that cupric sulfate and cuprous chloride were equally effective at several concentrations, while individual applications of several other salts (cobalt chloride, potassium dichromate, sodium tungstate, ceric sulfate, tin chloride, and ammonium molybdate at concentrations of 0.1  $\mu$ mole in the 10 ml. of solution, and 0.01, 0.1, and 1.0  $\mu$ mole of ferrous sulfate) were completely

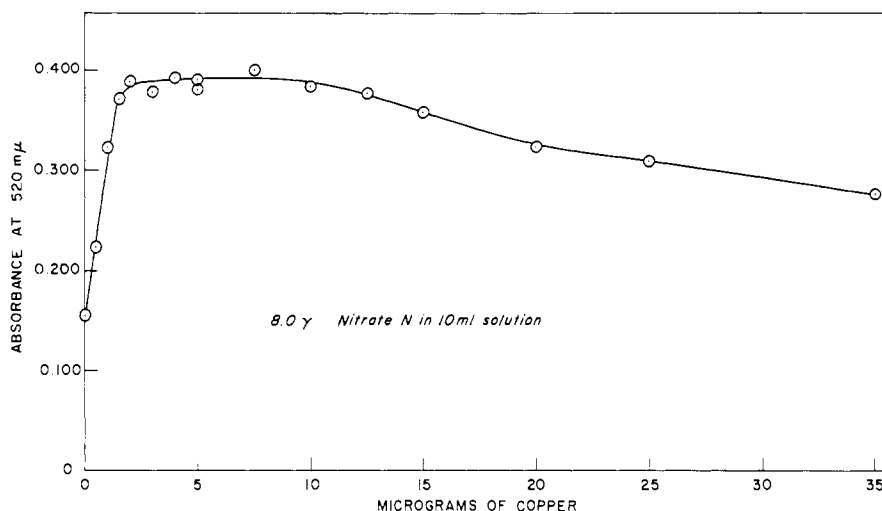


Figure 2. Dependence of nitrate determination on presence of copper

Table I. Recovery of Nitrate and Nitrite Added to Plant Leaf Material

Sample	Originally Present, $\gamma$	Added, $\gamma$	Total Found, $\gamma$	Recovery, % of Added
Nitrate Nitrogen				
Corn 1	1.80	4.00	6.08	106
Corn 2	1.46	4.00	5.28	96
Magnolia	1.23	4.00	6.10	122
Soybean 1	6.02	4.00	9.80	94
Nitrite Nitrogen				
Corn 1	0.05	4.00	4.00	99
Soybean 2	0.08	4.00	3.95	97
Soybean 3	0.10	2.00	2.25	108

ineffective in producing the required color.

This copper requirement was not found by the original investigators, presumably because their distilled water contained traces of copper from a defective tin-lined copper still.

More than the 12.5  $\gamma$  of copper interferes with the determination of nitrite as well as of nitrate, but below this amount copper seems to have no other effect than that upon the reduction of nitrate.

Table I shows that nitrate and nitrite can be recovered after being added to plant material. Table II compares the results of this modified method to those obtained by the more accurate method of Johnson and Ulrich (7) for nitrate determination. The differences between the values obtained with the two methods are in the order of 10% for corn leaf samples containing more than 10 p.p.m. of nitrate nitrogen on a dry weight basis. Samples containing less nitrate than this cannot usually be analyzed with ac-

Table II. Nitrate Determination in Corn Leaf Tissue by Two Methods

Sample	P.P.M. Nitrate Nitrogen Found (Dry Weight Basis)	
	Modified Nelson, Kurtz, and Bray method	Johnson and Ulrich method
A	115	124
B	507	472
C	700	630

curacy because the total quantity of plant material must be kept low to avoid interference with the analysis.

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