

NITRATE ION ELECTRODE METHOD FOR SOIL NITRATE NITROGEN DETERMINATION¹

Routine analysis of soil NO_3^- -N is common in soils research and soil testing laboratories. Where leaching does not remove nitrate from the soil, for example, in the semiarid areas of western Canada, the nitrogen soil test consists of measuring soil NO_3^- -N content by the phenoldisulfonic acid technique. This technique requires expensive reagents, and extracts must be filtered and evaporated to dryness before reagents for color development can be added.

The recently developed nitrate ion electrode could provide a suitable alternative technique for nitrate determination. It is claimed to be specific for the nitrate ion, and operates by the development of a potential across a thin layer of water-immiscible ion exchanger. The apparatus consists of a nitrate ion electrode², a calomel reference electrode, and a pH meter with an expanded millivolt scale. The technique is similar to pH measurement.

Soils were shaken with distilled water (1:5 or 1:10 soil-water ratio) for 30 min. Approximately 20 ml of supernatant were transferred to a 50-ml beaker. The electrodes were immersed, the mixture was stirred by a laboratory stirrer with a glass shaft and paddle (a magnetic stirrer gave less reliable results), and the potential in millivolts read within 15 to 30 sec, after drift had ceased. A calibration curve was obtained using standard nitrate solutions. The curve was prepared on semi-logarithmic paper with electrode potential on the linear axis, and nitrate concentration on the logarithmic axis (Fig. 1). The curve deviated from linearity below $0.5 \mu\text{g N/ml}$. Despite temperature compensation, some day-to-day changes occurred in the standard curve.

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²Model 92-07, Orion Research Inc., 11 Blackstone Street, Cambridge, Mass. 02139.

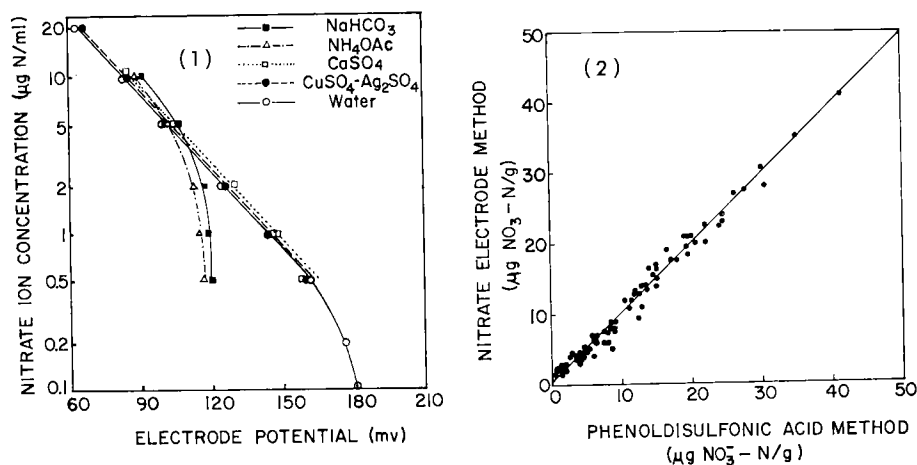


FIG. 1. Standard curves obtained with the nitrate electrode for nitrate in several soil-extracting solutions.

FIG. 2. Comparison of nitrate electrode and phenoldisulfonic acid methods for nitrate in 75 Saskatchewan soils.

Table 1. Effect of interfering ions on the determination of nitrate in two standard nitrate solutions (1 and 10 $\mu\text{g N/ml}$)

| Ion added and concentration | Nitrate present ($\mu\text{g N/ml}$) | |
|--|---|------|
| | 1.0 | 10.0 |
| | Nitrate measured ($\mu\text{g N/ml}$) | |
| No addition | 1.0 | 10.0 |
| Cl^- 0.1 meq/liter | 0.9 | 10.4 |
| 1 | 1.3 | 10.3 |
| 5 | 4.6 | 14.5 |
| HCO_3^- 0.1 meq/liter | 1.0 | 10.0 |
| 1 | 1.1 | 10.0 |
| 5 | 4.2 | 14.0 |
| NO_2^- 0.2 $\mu\text{g N/ml}$ | 1.0 | 10.0 |
| 2 | 1.3 | 10.0 |
| 10 | 3.5 | 12.8 |

Seventy-five soil samples were selected to cover a wide range of organic matter, $\text{NO}_3^- \text{-N}$ (0–40 $\mu\text{g N/g}$), CaCO_3 (0–20%) and salinity (2–65 mmhos/cm). Nitrate was determined by the Saskatchewan Soil Testing Laboratory using the phenoldisulfonic acid method on dilute $\text{CuSO}_4\text{-Ag}_2\text{SO}_4$ extracts.

Anions other than nitrate interfere with nitrate determination. Those causing the largest interference, such as ClO_4^- , ClO_3^- , I^- , are unlikely to be present in soils. Others, such as Cl^- , HCO_3^- , are common in soils and did interfere when present in sufficiently high concentration (Table 1). Sulfate and phosphate cause little or no interference. Nitrite interfered, the effects being more severe at low nitrate levels (Table 1), but ammonium seemed to have little or no effect.

Repeated determinations demonstrated the precision of the technique, standard deviations being very small (Table 2). We had difficulty in obtaining complete recovery of added nitrate in some soils (Table 2). Less than 90% was recovered in two soils initially high in nitrate. The reason for the poor recovery appeared to be the lower sensitivity of the instrument at high nitrate levels. Higher recoveries would be expected with a 1:10 soil-water extract. Using the phenoldisulfonic acid method, an average of 97% recovery was obtained from nitrate added to the same five soils.

Table 2. Precision of determination, and recovery of added nitrate from soils using the nitrate electrode, 25 $\mu\text{g N/g}$ added to each of five soils immediately before addition of water

| Soil | NO ₃ ⁻ - N (μg/g) | | | | |
|------|---|-------|---|------------|---------------------|
| | Soil only | | Soil plus added NO ₃ ⁻ - N | Difference | Percent Recovery |
| | Mean | S.D.* | | | |
| 15 | 2.0 | 0.0 | 27.5 | 25.5 | 102 |
| 1 | 5.2 | 0.1 | 30.0 | 24.8 | 99 |
| 34 | 12.5 | 0.0 | 37.0 | 24.5 | 98 |
| 10 | 17.8 | 0.2 | 39.5 | 21.7 | 87 |
| 78 | 31.2 | 0.4 | 52.5 | 21.3 | 85 |

*Five separate determinations on each soil-water extract.

Close agreement was found between soil nitrate by the nitrate electrode and phenoldisulfonic acid methods. In the 75 soils tested, the largest discrepancy was $3.1 \mu\text{g N/g}$, and the correlation coefficient was 0.991 ($P < 0.001$). The regression line, $y = 0.256 + 0.981x$, where y = nitrate by the electrode and x = nitrate by phenoldisulfonic acid, accounted for 98.2% of the total variance (Fig. 2).

The nitrate ion electrode was equally effective for nitrate in filtered or unfiltered soil extracts. Extracts of water, dilute CuSO_4 - Ag_2SO_4 and saturated CaSO_4 all gave similar results (Fig. 1), while 0.5 N ammonium acetate and 0.5 N NaHCO_3 proved unsatisfactory. In 2 M KCl, electrode potential did not change with nitrate concentration, and this extractant was thus unsuitable. No extractant proved superior to water. The possibility of soil nitrate measurements in 1:2 or 1:1 soil-water slurries was investigated. Low nitrate values were obtained, particularly in the 1:1 extract on high nitrate soils. This probably was caused by incomplete extraction, but increased concentration of interfering agents may have contributed.

In these tests, the major factor affecting the accuracy of the method proved to be interference by other anions. Nitrite, which occurs rarely in field soils, and then usually at low concentrations, should be of little importance. Where nitrite is expected or known to be present, the interference can be diminished by the use of sulfamic acid to destroy nitrite (1). Bicarbonate and chloride interference should be small in most arable soils. The method should be used with caution on known high-chloride soils (for example, Elstow Association) or on samples from depths exceeding 60 cm. If necessary, chlorides may be precipitated with silver sulfate (1).

While not as yet sufficiently accurate for exacting research use, the nitrate ion electrode technique appears to be suitable for soil testing and routine laboratory analysis of nitrate. The speed of the analysis is particularly attractive. With an experienced operator, using wide-necked extraction bottles for direct insertion of the electrodes, the rate of analysis should greatly exceed that of the phenoldisulfonic acid method.

1. BREMNER, J. M. 1965. Inorganic forms of nitrogen. pp. 1179-1237. In C. A. Black (ed.). Methods of soil analysis, part 2. Agronomy 9. Amer. Soc. Agron., Madison, Wis.

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