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9. ABSTRACT

An evaluation of the performance of a nitrate-specific ion electrode in presence of interfering anions. This was done by adding known amounts of interfering anions to standard nitrate solutions and then estimating the amount of nitrate measured by the electrode. The following anions commonly found in tropical and arid soils, irrigation waters, fertilizers, and pesticides significantly interfered with electrode sensitivity: NO_2^-, Cl^-, HCO_3^-, and SO_4^{2-}. The magnitude of interference from these anions was large in the lower concentration range of nitrates (less than ppm NO_3-N). There was a slight change in the nitrate standard curve with time, and so the electrode should be calibrated for each set of readings taken at different times or days. In between actual use, the prepared electrode can best be stored in a very dilute NO_3^- solution and preserved with 0.02 ppm phenyl mercuric acetate solution. $CuSO_4$ solution (0.02N) was shown to be an effective NO_3^--extracting solution for the electrode method in the soils studied. A high correlation coefficient (r^2 = 0.996) was obtained when the electrode procedure was compared with the steam distillation method for soil nitrate analysis. Thus in soils with high soluble salts the nitrate electrode can be successfully employed for nitrate analysis if proper precautions are taken to avoid or compensate for the anion interference.

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ADAPTABILITY OF NITRATE SPECIFIC ION ELECTRODE FOR NITRATE ANALYSIS IN TROPICAL SOILS

V. Balasubramanian[1/] and Y. Kanehiro[2/]

INTRODUCTION

The literature on soil nitrate analysis reveals numerous colorimetric and distillation methods for NO_3^- determination in soil and plant extracts. Many such methods are time consuming and complicated, and they require special equipment and chemicals.

In the past decade, several selective ion electrodes have been introduced as a quick means of determining specific ions in solutions. The nitrate electrode is one such introduction that has gained wide usage in recent years. Many workers claim that this electrode procedure for nitrate analysis is simple, easy, and rapid with no appreciable loss in accuracy (3-8). The question of anion interference on NO_3^- electrode is very important for the successful employment of this method for nitrate analysis in tropical

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and arid zone soils which may contain large amounts of soluble salts. Another source of these interfering anions in such soils is the irrigation water which is often high in Cl^- and HCO_3^- ions (9). Hence this work was taken up to investigate the following aspects in detail:

1. Anion interference in nitrate electrode
2. Nitrate standard curve vs. time.
3. Storage of nitrate electrode.
4. Extraction of NO_3^- for electrode process.

MATERIALS AND METHODS

General - The apparatus used consisted of the Orion Nitrate Specific Ion Electrode, Model 92-07, a calomel reference electrode, and a Beckman Expandomatic pH meter.

Interference - The interference work was concentrated on anions, such as Cl^-, HCO_3^-, NO_2^-, and SO_4^{2-}, which are frequently encountered in soils and irrigation waters or added to soils through fertilizers and pesticides. The interfering anions at concentrations from 1 to 1000 ppm were added to pure nitrate solutions of known composition, and then the nitrate concentration was measured by the electrode.

Electrode Calibration - The electrode was calibrated using the calibration-curve technique with standard nitrate solutions which were preserved with 0.02 ppm phenyl mercuric acetate. The calibration procedure was repeated daily to find out the effect of time on standard curves.

Extraction of Nitrate for Electrode Method - Different extracting agents (distilled water, 0.02 N $CuSO_4$, 0.02 N Na_2HPO_4, and 2 N KCl) were used to extract nitrate from various surface soils. Fifty ml of the extractant were added to 10 g soil (oven-dry basis) and shaken for 1 hour, and the clear

supernatant solution was used for nitrate measurement. The soil extract with KCl was used only for the steam distillation method (2) because the Cl^- concentration in that solution was too high to be employed for the electrode procedure. In all other extractants nitrate was estimated by the electrode. The NO_3^- values obtained with the electrode using various extractants were compared with those obtained from 2 N KCl by the steam distillation method.

RESULTS AND DISCUSSION

Interference - The measured potential for a nitrate solution containing interfering ions is given by the equation

$$E = \text{Constant} - 2.3 \frac{RT}{F} \log (A_{NO_3^-} + K_x C_x^{1/n})$$

where $A_{NO_3^-}$ is the nitrate ion activity, K_x is the selectivity constant of interfering anion at a concentration C_x with a charge n. The percentage interference may be calculated as follows:

$$\text{Percentage interference} = \frac{100\ K_x C_x^{1/n}}{A_{NO_3^-}}$$

The common interfering anions occurring in soils and having significant selectivity constants are NO_2^-, HCO_3^-, Cl^-, and SO_4^{2-}. The results in Tables 1 and 2 indicate that the above anions seriously interfered with nitrate measurement by the electrode. For a particular concentration of interfering anion, the magnitude of interference increased with decreasing contents of nitrate in the solution; solutions having less than 10 ppm NO_3-N were affected seriously. The interference from Cl^- was higher than that from HCO_3^-, both enhancing the measured NO_3^- values over and above the expected values. This confirms the observation of Myers and Paul (6), but the HCO_3^- interference con-

Table 1. The effect of various amounts of interfering anions on the electrode measurement of nitrate*

Interfering anions added, ppm	Cl^- as NaCl			HCO_3^- as $NaHCO_3$			SO_4^{2-} as Ag_2SO_4		
	1 ppm	10 ppm	100 ppm	1 ppm	10 ppm	100 ppm	1 ppm	10 ppm	100 ppm
0	1.00	10.0	100.0	1.00	10.0	100.0	1.00	10.0	100.0
1	1.00	10.0	100.0	0.95	10.0	99.5	0.96	9.7	100.0
10	1.35	9.7	102.0	0.97	10.2	100.0	0.71	0.5	100.0
100	3.20	11.0	112.0	1.18	10.4	100.0	0.61	8.6	92.0
500	5.20	12.2	114.0	1.95	10.6	100.0	0.61	7.3	93.0
1000	8.00	13.1	114.0	2.20	10.5	99.0	0.61	6.7	89.0

*NO_3-N measured by the electrode at levels of 1, 10, and 100 ppm NO_3-N.

Table 2. Interference of nitrate in nitrate measurement by the electrode in a 10 ppm NO_3-N standard solution

Nitrite (NO_2^-) added, ppm	0	1	10	100	500	1000
NO_3-N measured, ppm	10	9.8	10.8	19.5	40	62

tradicts the results of Oien and Selmer-Olsen (7). The interference from SO_4^{2-} was of a different type in that it depressed the activity of NO_3^-. This may be attributed to the ionic strength effect as discussed below.

The data in Table 2 show the interference of NO_2^- on the nitrate electrode. When large amounts of NO_2^- were present (100 ppm and greater), the magnitude of interference became large. At the greatest level of NO_2^- (1000 ppm), the original 10 ppm NO_3-N was found to erroneously read 62 ppm. Therefore, care should be taken to see that nitrite is not present in solutions used for this method.

The valency effect of the cations accompanying the interfering anions on sensitivity of nitrate electrode is shown in Table 3. As the valency of cations accompanying the interfering anions increased, the magnitude of anion interference on nitrate electrode decreased. This may be caused by the depressing effect of increased ionic strength (due to increased cation valency).

Since SO_4^{2-} possesses the lowest selectivity constant for interference, it was selected to study the ionic strength effect on electrode sensitivity. It will be noticed in Table 4 that the measured NO_3^- concentrations of a standard 10 ppm NO_3-N solution decreased with increasing ionic strength; in the case of $CuSO_4$ this decrease was stabilized at the ionic strength of 207.14×10^{-4}. According to Adams (1), ion pairing with SO_4^{2-} is slight with univalent cations but extensive with multivalent cations. Thus it is probable that the reduction in the measured ionic strength due to ion pairing with SO_4^{2-} would be considerably higher in the $CuSO_4$ system than in the Na_2SO_4 solution. This might be the reason for the continued depression of NO_3^- activity with increasing SO_4^{2-} concentration in the Na_2SO_4 system as compared to the $CuSO_4$ solution.

Table 3. The effect of ion valency on nitrate determination by the electrode method*

Interfering anions added, ppm	Increasing cation valency		
	Cl^- as NaCl	Cl^- as $BaCl_2$	Cl^- as $AlCl_3$
0	10.0	10.0	10.0
1	10.0	9.5	9.7
10	9.7	9.3	9.5
100	11.0	10.0	10.4
500	12.2	10.6	10.9
1000	13.1	12.0	11.5

*NO_3-N measured by the electrode at 10 ppm NO_3-N level.

Table 4. The effect of ionic strength on sensitivity of NO_3^- electrode

Concentration of sulfate in the solution, N	$CuSO_4$		Na_2SO_4	
	I* X 10^{-4}	Measured NO_3-N, ppm	I* X 10^{-4}	Measured NO_3-N, ppm
0.000	7.14	10.0	7.14	10.0
0.001	27.14	8.5	22.14	9.4
0.005	107.14	8.0	82.14	8.6
0.010	207.14	7.7	157.14	8.5
0.020	407.14	7.8	307.14	8.0
0.030	607.14	7.8	457.14	7.8
0.040	807.14	7.7	607.14	7.7
0.050	1,007.14	7.8	757.14	7.4

*I = Calculated ionic strength assuming 100% ionization and no ion pairing.

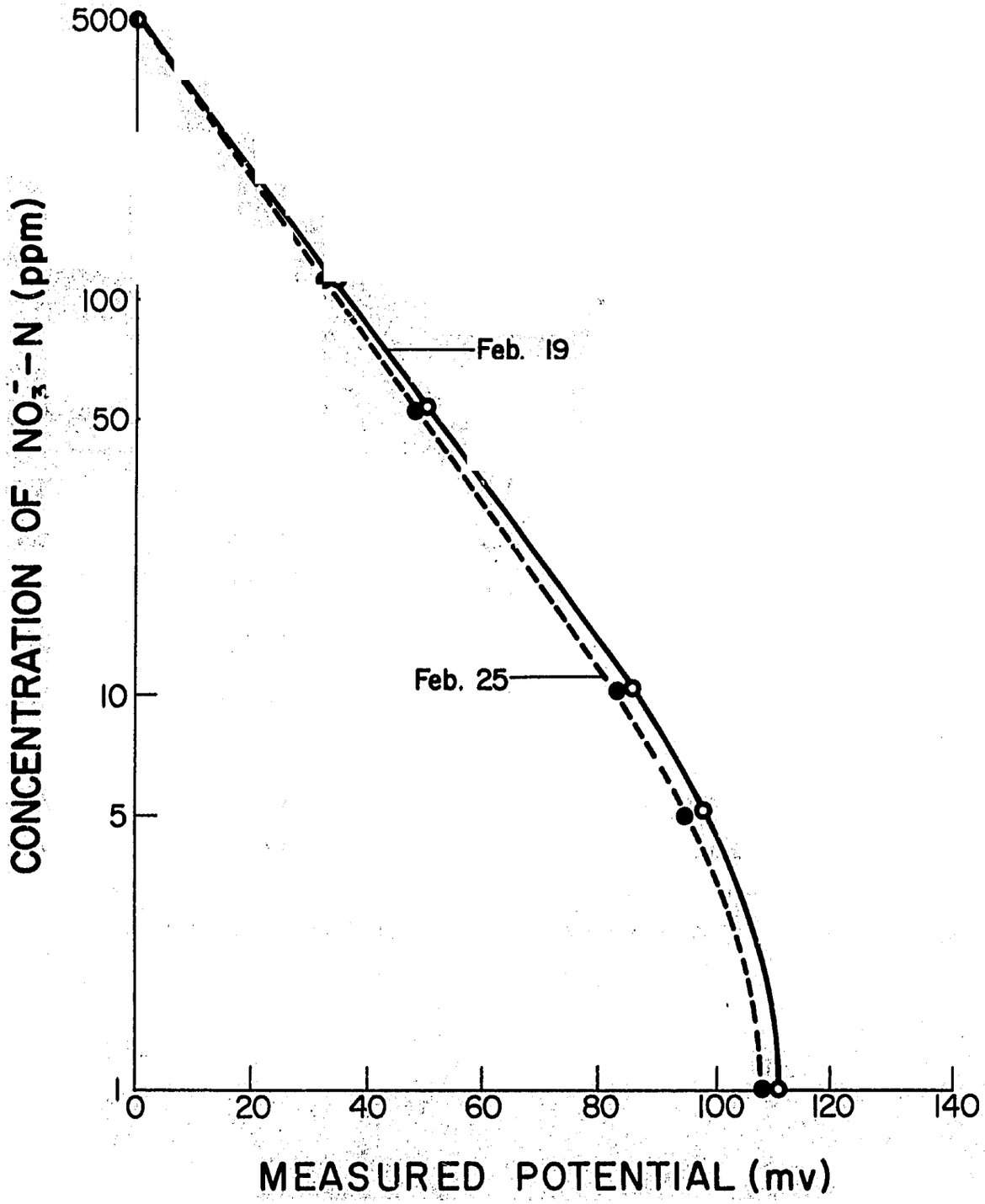

Figure 1. The effect of time on nitrate standard curve.

Effect of Time on Nitrate Standard Curve - The electrode should be calibrated with standard nitrate solutions; for each extractant a separate standard curve should be prepared. If the readings are plotted on a semi-log paper with NO_3^- concentrations on the log scale and measured millivolts on the normal scale, a straight line relationship is obtained. However, in the presence of interference, the curve deviates from linearity. For instance, when an irrigation water containing 250 ppm of Cl^- was used to prepare standard solutions, the deviation of the curve from linearity was very much pronounced in the lower concentration range of nitrates (Figure 1). It was also noticed that there was a shift in the nitrate standard curve with time (Figure 1). The curves constructed on two different dates showed a lateral displacement. Therefore, the electrode should be calibrated for each set of readings taken at different times or days.

Storage of Nitrate Electrode - When not in use, the nitrate electrode was separated from the reference electrode and stored in a very dilute nitrate solution (0.2 to 0.3 ppm NO_3-N) containing 0.02 ppm phenyl mercuric acetate as a preservative (9). It was found that there was no detectable increase in the NO_3^- concentrations of the solution (due to electrode leakage) in which the electrode was stored for several weeks. This is contrary to the observation of Mack and Saunderson (4) who reported excessive electrode leakage during storage. With the kind of storage as mentioned above, the performance of the nitrate electrode was observed to be good for longer periods of time (4 to 6 weeks). This suggests that the electrode need not be stored in a very concentrated NO_3^- solution as speculated by Mack and Saunderson (4).

Extraction of NO_3^- for Electrode Method - The electrode compared very well with the steam distillation method for nitrate analysis. When 11

Table 5. Determination of NO_3-N (ppm) in various soil extracts by two methods

Soil series	Electrode method			Steam distillation method
	Distilled water extract	0.02N $CuSO_4$ extract	0.02N Na_2HPO_4 extract	2N KCl extract
Molokai silty clay	8.4	6.8	4.8	5.2
Waimea fine sandy loam	24.8	25.0	18.0	25.6
Wahiawa silty clay	1.5	1.8	0.7	2.8
Akaka silty clay	45.5	47.0	60.0	50.7
Hilo silty clay loam	34.5	42.0	41.0	41.4
Honokaa silty clay loam	22.9	22.3	22.4	21.5
Maile silty clay loam	80.0	80.0	83.4	78.3
Kawaihae stony loam	2.4	1.6	1.7	1.6
Waikaloa fine sandy loam	46.2	45.0	45.8	45.9
Lualualei clay	12.1	12.3	10.2	12.1
Pahala fine sandy loam	79.5	78.0	73.8	74.2
Correlation with the steam distillation method (	0.984	0.996	0.984	---
C. V. for absolute di ences between the ele and the steam distill methods (%).	7.19	3.95	9.95	

different surface soils were measured for nitrate by the electrode in various soil extracts and compared with the steam distillation method (KCl extract), very high correlations (r^2 = 0.984 to 0.996) were obtained (Table 5). Of the three extractants tried, 0.02 N $CuSO_4$ gave the highest correlation (r^2 = 0.996) and thus was shown to be an effective nitrate extracting solution for the electrode method in the soils studied. This high correlation of the electrode method ($CuSO_4$ extractant) with the steam distillation method (KCl extractant) is shown in Figure 2. Moreover the $CuSO_4$ extract gives a clear supernatant solution in about 1 hour after shaking, facilitating the direct determination of NO_3^- in the supernatant solution without any necessity for filtration. The percentage coefficient of variability for absolute differences between the electrode and the steam distillation methods is minimum for $CuSO_4$ extractant.

CONCLUSIONS

Anion interference in the nitrate electrode method was found to be significant. The electrode can be used for NO_3^- analysis in soils containing large amounts of soluble salts if proper precautions are taken to avoid or compensate for the anion interference. This method is highly useful when rapid determinations of nitrates are required in a large number of samples or in routine nitrate analysis. In between actual use, the electrode can best be stored in a very dilute nitrate solution to which phenyl mercuric acetate is added as a preservative.

SUMMARY

The performance of a nitrate-specific ion electrode in presence of interfering anions was evaluated in this study. This was done by adding known

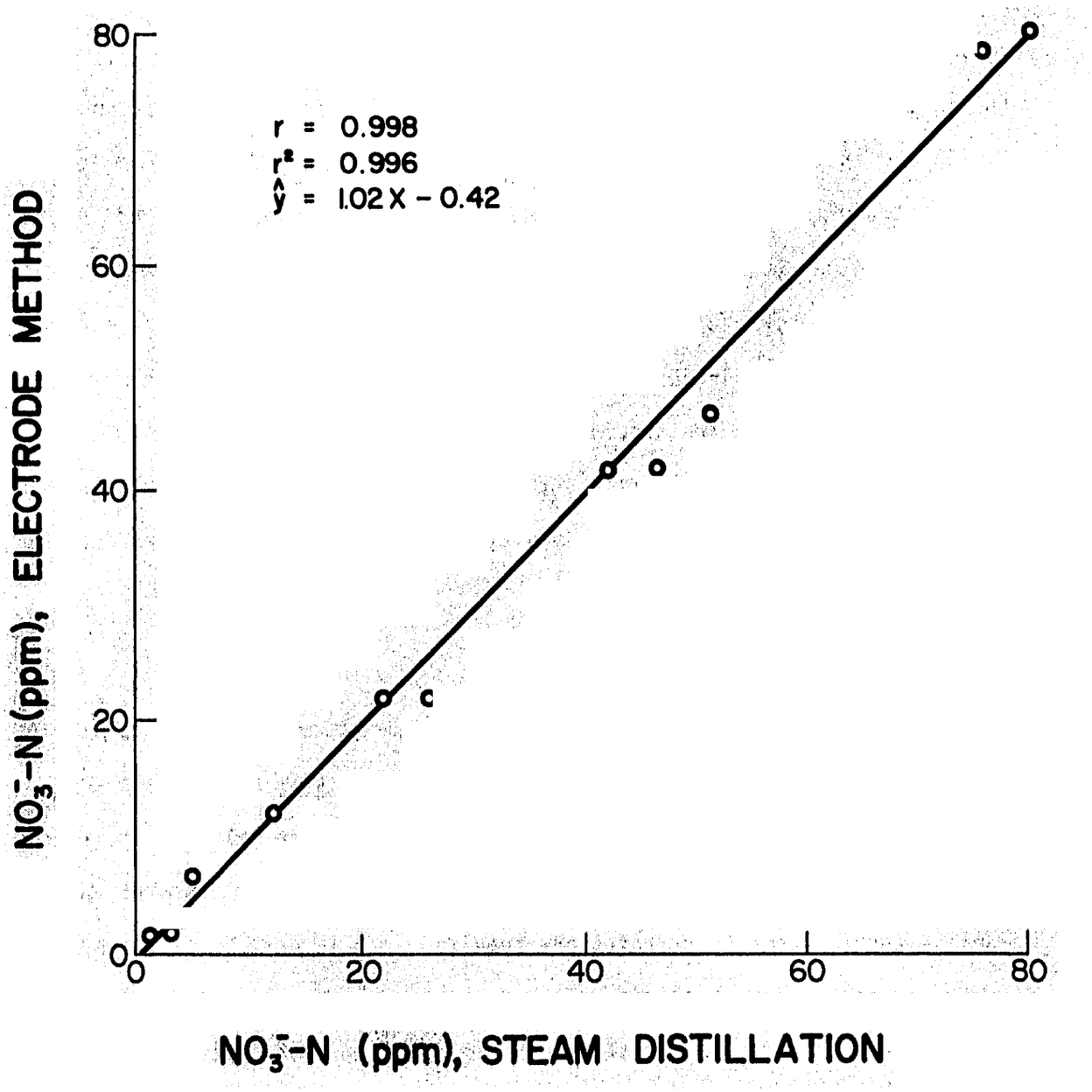

Figure 2. Comparison of methods for nitrate analysis: electrode method vs. steam distillation method.

amounts of interfering anions to standard nitrate solutions and then estimating the amount of nitrate by the electrode. The following are the anions which significantly interfered with electrode sensitivity and which are commonly found in tropical and arid soils, irrigation waters, fertilizers and pesticides: NO_2^-, Cl^-, HCO_3^-, and SO_4^{2-}. The magnitude of interference from these anions was large in the lower concentration range of nitrates (less than 10 ppm NO_3-N). There was a slight change in the nitrate standard curve with time, and so the electrode should be calibrated for each set of readings taken at different times or days. In between actual use, the prepared electrode can best be stored in a very dilute NO_3^- solution (0.2 to 0.3 ppm NO_3-N) and preserved with 0.02 ppm phenyl mercuric acetate solution. $CuSO_4$ solution (0.02 N) was shown to be an effective NO_3^--extracting solution for the electrode method in the soils studied. A high correlation coefficient (r^2 = 0.996) was obtained when the electrode procedure was compared with the steam distillation method for soil nitrate analysis. Thus in soils with high soluble salts the nitrate electrode can be successfully employed for nitrate analysis if proper precautions are taken to avoid or compensate for the anion interference.

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