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The potentiometric determination of nitrate and chloride in plant tissue

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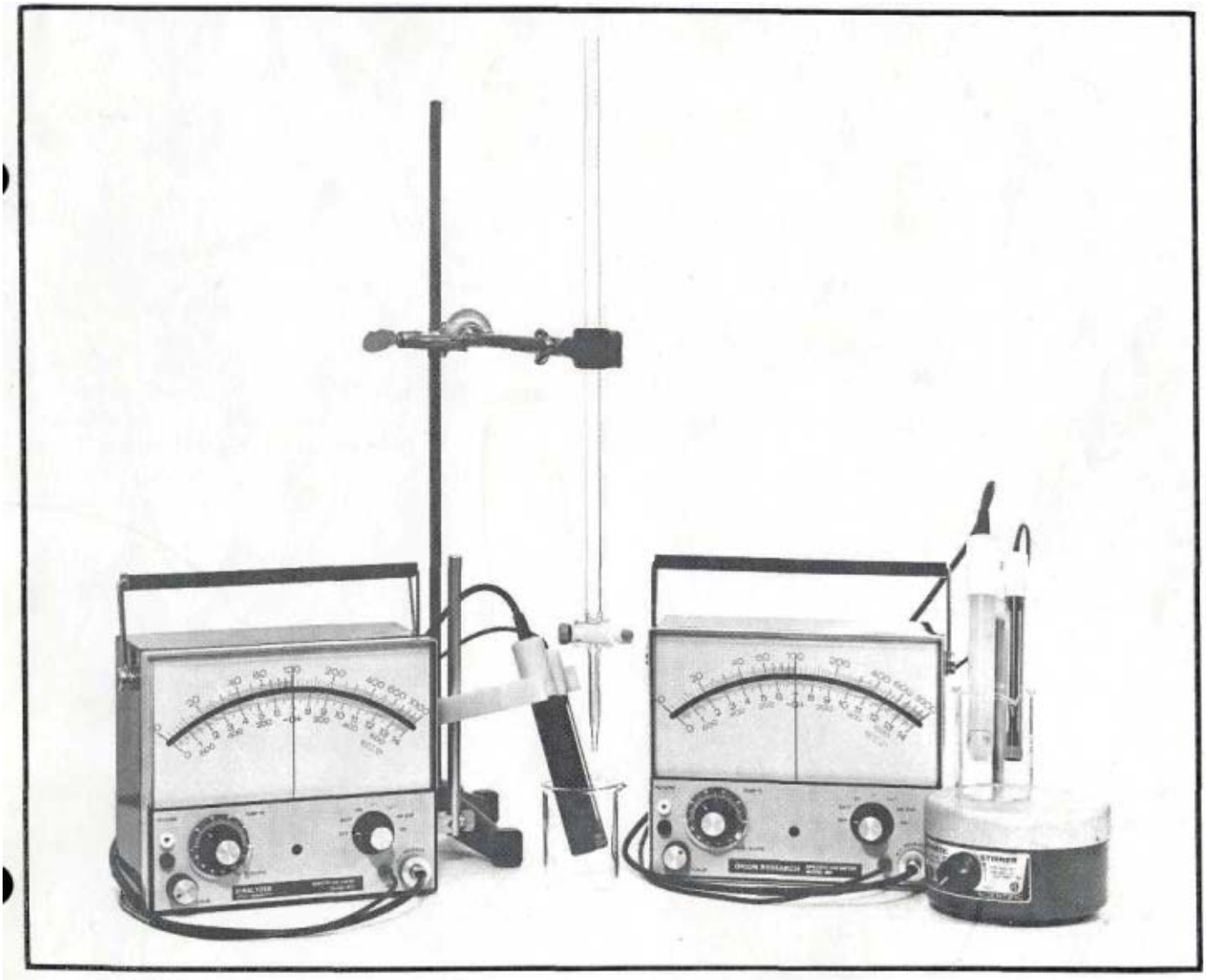

Abstract

Several extracting solutions were evaluated for their effectiveness in determining NO_3^- potentiometrically with a selective nitrate ion electrode, and the results were compared with a standard phenoldisulfonic acid method. The nitrate electrode proved to be highly satisfactory for determining NO_3^- in plant tissue, and is apparently as accurate as the phenoldisulfonic acid method when $Al_2(SO_4)_3$ +10 μg per ml NO_3^--N is the extracting solution.

Chloride did not interfere with NO_3^- determinations when the extract solution contained at least 25 $\mu g/ml$ NO_3^--N, even at tissue concentrations as high as 10 per cent Cl^-

Two chloride selective ion electrodes (a solid state and liquid membrane type) were evaluated for determining Cl^- in plant material. Direct potentiometric determination using the liquid membrane gave erroneous results with all extraction solutions tested. Equally unsatisfactory results were obtained when direct potentiometric readings were made with the solid state electrode using water as the extraction solution. A 0. IN HNO_3 extracting solution gave results which were more comparable with a standard Mohr method for Cl^- determination, but they were still erratic. The most accurate and sensitive potentiometric method for Cl^- was the solid state electrode to indicate an $AgNO_3$ potentiometric end point of plant tissue extracted with 0.1N HNO_3. The results of this method were obtained rapidly and in good agreement with the standard Mohr method.

Part I Nitrate Determination

In the past the determination of nitrate nitrogen (NO_3^--N) in plant tissue has been carried out by one or more of a large number of long and involved procedures. Recently, a nitrate selective electrode has been developed which greatly speeds up such determinations (5, 6, 8, 13, 16). Yet, to date, procedures for extraction and determination of NO_3^- in plant tissue using these electrodes have not been standardized (6, 13, 16).

The first portion of this bulletin compares various extracting solutions with a standard procedure for NO_3^- determination (phenoldisulfonic acid-PDS) in an effort to evaluate the effectiveness and efficiency of an Orion Nitrate Electrode in determining varying NO_3^- levels in plant tissue.

Experimental

Plant materials

Spinach petioles, spinach blades, and beet roots, two samples of each from low N fertilizer plots and two each from high N fertilizer plots, were used as the plant tissue samples.

The samples were lyophilized, then ground in a Wiley mill to pass a 20-mesh screen.

Oven dried snap bean tissue that was moderately low in NO_3^- was also used.

Reagents

Nitrate standards: A series of NO_3^- standards containing 10 to 100 μg NO_3^--N per ml derived from KNO_3 were prepared in 0.01 N K H_2PO_4 or 0.025 M $Al_2(SO_4)_3$ depending on the extracting solution to be used.

Extracting solutions: Distilled water, 0.025 M $Al_2(SO_4)_3$, and 0.025 M $Al_2(SO_4)_3$ + 10 μg NO_3^--N per ml were used as the extracting solutions.

Resins: Al and Ag resins were made up according to the procedures of Paul and Carlson (13) and were added to a distilled water extracting solution where noted.

Apparatus

An Orion Model 92-07 nitrate ion activity electrode and a single junction reference electrode, Orion Model 90-01, filled with saturated KC1, were used in conjunction with an Orion Model 401 Specific Ion Meter having expanded millivolt scale and direct read-out for monova-lent anion electrodes.

Procedure

Depending on the NO_3^- content of the plant tissue, 100 or 400 mg of tissue was weighed into a 125 ml flask, 50 ml of extracting solution was added, and the flask stoppered and shaken for 15 minutes by a standard wrist-action laboratory shaker. If resin was used, 1 ml of Al resin and/or 1.5 ml of Ag resin was added when the extracting solution was added to the sample. The sample was filtered through Whatman No. 31 filter paper into a 100 ml beaker and then read with the electrode.

A Teflon-coated magnetic stirrer was used to maintain constant stirring speed. This was most important in order to obtain repeatable results. Nitrate concentration was read directly on the red logarithmic scale of the Orion Model 401 Specific Ion Meter. The results were reported as parts per million (ppm) of NO_3^--N on a dry weight basis.

The phenoldisulfonic acid procedure for NO_3^- determination was run independently of the above according to the method of Greweling (9).

Results and Discussion

The extractant solutions had a direct effect on the results, being most pronounced with the spinach petioles (Table 1). When measuring petioles (samples 1 and 2), the electrode was in agreement with the PDS when $Al_2(SO_4)_3$ + 10 μg NO_3^--N per ml was the extracting solution, while all other extractants read lower. Sample number 3, high NO_3^- petiole tissue, was consistently measured lower by the electrode, regardless of extractant, compared with the PDS method. This difference could

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Table 1. Influence of extracting solution on nitrate determinations of plant tissue using an Orion Selective Ion Electrode

Plant material		Electrode: Distilled water	Al resin	Al & Ag resin	Al & Ag resin, same used in std.	$Al_2(SO_4)_3$*	$Al_3(SO_4)_3$* + 10 ugNO_3^--N/ml	Phenoldisulfonic acid
		Extracting solution						
		Per cent NO_3^--N in the tissue						
Spinach petiole								
1	0-N[1]	1.30	1.40	1.58	1.35	1.40	1.80	1.84
2	0-N	1.58	1.45	1.55	1.40	1.45	1.63	1.64
3	400-N	3.15	2.91	2.83	2.85	2.98	3.03	3.45
4	400-N	2.93	2.90	2.93	2.85	2.75	2.75	2.74
Spinach blade								
5	0-N	.24	.22	.23	.22	.21	.23	.19
6	0-N	.22	.17	.19	.17	.17	.18	.12
7	400-N	.62	.67	.63	.66	.63	.60	.57
8	400-N	.54	.55	.53	.54	.54	.53	.51
Beet root								
9	Low N	.13	.05	.05	.05	.06	.05*	.04
10	Low N	.18	.04	.05	.05	.08	.04*	.06
11	High N	.49	.45	.46	.45	.44	.44	.44
12	High N	.58	.53	.54	.53	.51	.52	.49

*No delay to read.

[1]Number refers to lbs/A of N fertilizer added before planting. Sample numbers 3 and 7 were fertilized with NH_4NO_3 and sample numbers 4 and 8 were fertilized with urea. Table beets and spinach from Project NY (G) 00306, *Factors affecting or regulating nitrate accumulation in plants.*

have been due to the larger accumulation of NO_3^- in this tissue resulting in reduced meter sensitivity, or to interferences from other sources causing a false high reading in the PDS method (9). Petioles generally contain greater amounts of NO_3^- and Cl^- than other plant parts.

With sample 4, both $Al_2(SO_4)_3$ extracting solutions gave readings similar to PDS, while the other extractants read 0.10 per cent to 0.18 per cent higher in NO_3^--N

In spinach blades (samples 5-8), which contained from about 0.18 per cent to 0.62 per cent NO_3^--N, the PDS method gave lower values than the electrode, $Al_2(SO_4)_3$ was closest to PDS in samples 5 and 6, while $Al_2(SO_4)_3 + 10\ \mu g\ NO_3^-$-N per ml was closest in samples 7 and 8. Values from distilled water and the Al + Ag resin extractants were consistently higher than the PDS method. Al resin alone gave high readings for samples 7 and 8. The Al^{+3} was used to lower the pH of the extract, thereby depressing the ionization of weak acids. The dissociated anions of these acids would interfere with NO_3^- readings by the nitrate electrode (6). Al^{+3} combined with the resin does not appear to be sufficient to accomplish this. However, $Al_2(SO_4)_3$ buffered the extracting solution at about pH 3 which depressed the ionization of the weak acids. It also seemed to minimize changes in ionic strengths caused by solutes from the plant tissue or the standards.

With a water extract, a false high reading was observed with beet samples (9 and 10) low in NO_3^-. This was probably due to organic anion interferences at such low NO_3^- levels (6, 13). The addition of a resin or $Al_2(SO_4)_3$ was sufficient at the low NO_3^--N level to eliminate this interference. Where the NO_3^--N levels were approximately 0.5 per cent (samples 11 and 12), all extractants gave similar readings except water which again gave slightly higher readings. Adding Al + Ag resin to the standards seemed to reduce the NO_3^- activity recorded in the extract.

The addition of Cl^- (2.5-10% on a dry weight basis) to snap bean tissue significantly increased the NO_3^- activity (Table 2). This increase was linear over each increment of added Cl^-. However, the effect of added Cl^- was completely overcome when NO_3^- (10 μg/ml) was added with the $Al_2(SO_4)_3$ extracting solution. When 9,375 ppm NO_3^--N was added to the tissue, additional Cl^- significantly decreased the amount of NO3- activity. Paul and Carlson (13) state that above 10 μg NO_3^--N per ml Cl^- interference is negligible even above 5 per cent tissue Cl^-, and its removal is not necessary. This was not found to be true with the snap bean extract (Table 2), where Cl^- added to the tissue increased the apparent NO_3^- activity even though the tissue contained 15 μg/ml of NO_3^--N. However, as levels NO_3^- were increased above 25 μg NO_3^--N per ml in the sample extract, interference due to Cl^- was overcome. For lower NO_3^- levels, Paul and Carlson (13) proposed the use of Ag resin to remove the Cl^-. They reported complete removal of Cl^- from plant tissue when an Ag resin was used. Our own results, however, indicate that Al + Ag resins do not compare as favorably with the PDS method as do an $Al_2(SO_4)_3 + NO_3$ extracting solution. Also, the addition of resin is time consuming and tends to "foul" the electrode. At this time, it appears that the addition of NO_3^- to the sample gives greater precision than removing the Cl^-

Table 2. The effect of the addition of chloride on the recovery of nitrate from snap bean tissue as determined by a nitrate selective electrode using $Al_2(SO_4)_3$ extracting solution[1]

Added NO_3-N[2] ppm	Added chloride[3] %					% recovery
	0	2.5	5	7.5	10	
	ppm NO_3-N					
0	1325a	1404b	1504c	1579d	1667e	–
1250[4]	2596f	2533f	2621f	2854g	2550f	102
3125	4437h	4375h	4513h	4416h	4500h	100
6250	7042i	7063i	7167i	7179i	7167i	94
9375	10167k	10042j	10002j	9958j	9917j	94

[1]Means not followed by the same letter were significantly different at odds of 19:1. Significance should be read across.
[2]Ppm NO_3^--N added is based on a dry weight basis of plant tissue.
[3]Percent Cl^- added is based on a dry weight basis of plant tissue.
[4]Equivalent to the addition of 0, 10, 25, 50, and 75 μg/ml NO_3^--N to the extract.

Baker and Smith (6) reported that in tests with distilled water standard solutions Cl^- interference was inversely proportional to the NO_3^- concentration, but it was not negligible at 10 μg per ml of NO_3^--N. Further, they stated that Cl^- interference was greater in $Al_2(SO_4)_3$ extracting solution—even with NO_3^- added in rather high quantities—than in distilled water. The discrepancy between their work and this work cannot be satisfactorily explained. Possibly, the heterogenous mixture obtained in our work when Cl^- and NO_3^- were added directly to plant tissue affected the NO_3^- activity as recorded from the electrode in quite a different manner than if the additions were made to distilled water solutions alone. Paul and Carlson (13) found that Ag resin added to tissue would remove some other interference besides Cl^- This was later thought to be a reduction of NO_3^- activity by the added Ag itself (6).

The NO_3^- added to snap bean tissue was almost completely recovered (Table 3). However, less recovery was observed at the lowest level of added NO_3^- than at the higher levels. In contrast, Myers and Paul (12) found less recovery at higher NO_3^- levels with soil extracts. They reasoned that the poor recovery was due to lower sensitivity of the electrode at high NO_3^- levels.

The results of the NO_3^- recoveries at the high NO_3^- levels as recorded in Table 2 were less than the data recorded in Table 3. This was due to a decrease in sensitivity of the Orion Specific Ion Meter (Model 401) at the high end of the instrument scale when reading in direct concentration. With the high NO_3^- concentration data in Table 3, standards were made up to 200 ppm instead of the usual 100 ppm; hence, the meter settings were scaled down when the higher NO_3^- activities were recorded. This led to almost complete recovery of added NO_3^-. In the case of the data of Table 2, additional standards did not have to be prepared; therefore, high NO_3^- activities were recorded by using the upper end of the scale on the instrument. This showed as a decrease in NO_3^- activity. Thus, for greatest accuracy when reading direct concentration, NO_3^- activities should fall well within the sensitivity range of the instrument.

Table 3. Nitrate recovery from low nitrate snap bean tissue using $Al_2(SO_4)_3$ extracting solution

Added NO_3^--N ppm	Expected	Found	Difference	Per cent recovery
	NO_3^--N recovery (ppm)			
0	1363	1363	0	
1250	2613	2500	– 113	96
2500	3863	3938	+ 75	102
6250	7613	7625	+ 12	100
12500	13863	13750	– 113	99
18750	20113	20000	– 113	99

For greater instrument sensitivity and ease of determination, the sample extract used should contain between 10 and 80 μg NO_3^--N per ml. For most tissue, this would be about 400 mg of dried tissue diluted in 50 ml of extractant solution. In the case of materials such as spinach petioles where the NO_3^- concentration is high, as little as 100 mg of tissue can be used. The same total NO_3^- concentration was found in any particular sample whether 100, 200, or 400 mg of tissue was used. On the other hand, if the sample extract contained less than 10 μg NO_3^--N per ml, determinations were unreliable because the standard curve was non-linear below this level. In this case, NO_3^- should be added to the sample.

Most plant extracts have an ionic strength in the range of 10^{-2} to 10^{-3} M, therefore the sample and standard solutions should be maintained at similar ionic strengths (1). By making the standards in a dilute salt solution or buffer, discrepancies in readings due to differences in ionic strengths between the standards and the plant tissue extracts are largely overcome. Also, when a buffer is used, differing NO_3^- concentrations in the samples or increasing KNO_3 concentrations in the standards have

no measurable effect on the activity coefficients (6), thus readings are unaffected.

Conclusions

The Nitrate Electrode proved to be a highly satisfactory method for NO_3^- determination in plant tissues when $Al_2(SO_4)_3 + 10 \mu g$ NO_3^--N per ml was the extracting solution. The procedure was faster and apparently as accurate as the phenoldisulphonic acid method. The addition of at least 10 μg NO_3^- per ml to the extraction solution was important for three reasons: (1) the standard curve is not linear below 10 μg NO_3^--N per ml, thus direct concentrations cannot be read below this level; (2) interferences from Cl^-, which are severe below this level, are largely alleviated; and (3) the time needed to take a reading is much reduced.

Almost complete recovery of NO_3^- from plant tissue was observed when $Al_2(SO_4)_3$ extracting solution was used. Chloride did not interfere with electrode determinations of NO_3^- when the NO_3^--N level in the $Al_2(SO_4)_3$ extracted solution was 25 μg/ml.

In general, for greatest precision, it was found best to scale the NO_3^- activities well into the range of the particular instrument being used.

Part II Chloride

The Cl^- concentration of plants has been found to vary from 0.3 per cent to over 10.0 per cent on a dry weight basis (13). Thus, a relatively rapid method that will give reliable results over the wide range of Cl^- concentrations is desirable.

Until recently, the two most common methods employed for Cl^- analysis were the Mohr method (14) and a potentiometric method utilizing an Ag-AgCl electrode.

The Mohr method involves titrating a charcoal filtered extract with $AgNO_3$ to the Ag_2CrO_4 end point in a pH range of 6-10 (10). This method is very tedious, time consuming, and the end point is extremely difficult to detect. The potentiometric titration using either laboratory made or commercial Ag-AgCl electrodes has been shown to be an accurate and sensitive method for the determination of Cl^- in plant materials (7). However, it is subject to redox potential errors in the presence of strong oxidizing substances (15).

Recently, La Croix et al. (11) determined the Cl^- concentration in plant material by potentiometric titration with a solid state chloride electrode (2) using 0.1N HNO_3, 2 per cent $Ca(NO_3)_2$, or boiling water as the extractants. The 0.1N HNO_3 extractant gave a sharp end point and accurate results. They also determined Cl^- by direct potentiometric determination using either 2 per cent $Ca(NO_3)_2$ or boiling water as extractants and observed extremely high and unreproducible Cl^- values.

In addition, a commercial liquid membrane chloride electrode has been introduced (3), but, to date, a method for its use in soil or plant analysis has not been documented.

This portion of the bulletin presents results of tests conducted to evaluate the effectiveness of the solid state and the liquid membrane chloride selective ion electrodes for the potentiometric determination of Cl^- in plant tissue extracts.

Experimental

Procedure

General: All working standards were prepared in the extracting solution being tested. A vigorous stirring with a magnetic stirrer was maintained for accurate sample reproducibility. With all determinations, 50 ml of extracting solution was added to 500 mg of plant tissue in a 125 ml flask. This mixture was stoppered, then shaken by a wrist-action shaker for 15 minutes. Chloride was then determined on the extract.

An Orion Model 401 Specific Ion Meter was used for the potentiometric determinations.

Mohr Method of Cl^- Determinations: This method was used as a standard of comparison. It consisted of extracting Cl^- from the plant tissue with water and 0.25 g activated charcoal. The mixture was then filtered through Whatman No. 31 filter paper into a white porcelain evaporating dish and titrated with 0.0282N $AgNO_3$ in the presence of 2 ml of 10 per cent K_2CrO_4 to an Ag_2CrO_4 end point.

Potentiometric Titration for Cl^-: An Orion 94-17 Solid State Chloride Electrode and 90-01 Single Junction Reference Electrode (filled with 0.0IN KCl saturated with $AgCl$) were used for potentiometric titration. The Cl^- was extracted with 0. IN HNO_3

The extract was titrated with 0.0282N $AgNO_3$ to a potentiometric end point predetermined on the millivolt (mv) scale of the Specific Ion Meter; i.e., reading the blank as 0. IN HNO_3

Direct Potentiometry-Solid State Chloride Electrode: The above electrodes were used for this determination. Distilled water or 0.1N HNO_3 was used as the extracting solution. The amount of Cl^- was determined by reading direct concentration on the meter or by using the mv scale. The meter was precalibrated with standards ranging from 30-1,000 ppm Cl^- as. $NaCl$ A reading was recorded after the meter needle became stable (20-30 seconds).

Direct Potentiometry-Liquid Membrane Electrode: The Orion 92-17 Liquid Membrane Chloride Electrode, and one of the following reference electrodes were used for this Cl- determination: (1) 90-01 Single Junction filled with 0.0IN KCl saturated with, $AgCl$ (2) 90-01 Single Junction with Orion 90-00-01 filling solutions, or (3) 90-02 Double Junction with 10 per cent KNO_3 used as outer filling solution.

Each of the following was used as extracting solutions: (a) 0.001N HNO_3, (b) 0.01N K H_2PO_4, (c) 0.025 M $Al_2(SO_4)_3$, (d) distilled water, and (e) charcoal treated distilled water extract. Readings were taken either direct in concentration or from the mv scale of the meter which was precalibrated with standards ranging from 30-1,000

ppm Cl^- as NaCl. A reading was recorded after meter drifting had stopped (usually 10-15 seconds). Each reference electrode was evaluated independently with the liquid membrane electrode on filtered and unfiltered extracts.

Results and Discussion

Only 90 per cent of the added Cl^- could be recovered if the plant tissue HNO_3 mixture was filtered (Table 4). However, if both extraction flask and filter paper were rinsed with the extraction solution, recovery was increased to 97-99 per cent. If Cl^- was determined on the unfiltered extract, its recovery was still higher.

The potentiometric titration method using the solid state electrode gave results that were comparable to the Mohr method (Table 5). This was in agreement with the report of La Croix et al. (11). The results showed that the two methods give practically identical results for low Cl^- values. However, at high values, Cl^- the potentiometric titration method yielded slightly higher readings. This may have been due to a loss of Cl^- by filtering the extract in the Mohr method (refer to previous paragraph and Table 4). It should be noted that filtration of the "Mohr extract" is necessary in order to remove added charcoal.

When HNO_3 was used as the extracting solution, direct potentiometric readings either on the mv scale or on the concentration scale produced results that exhibited variability between duplicates (Table 5) but which were in closer agreement to the Mohr and potentiometric titration procedures than that reported by La Croix et al. (11). However, they used distilled water as the extracting solution. In our study, when distilled water was used with the extracts, the results were much higher than those obtained by potentiometric titration (Table 6).

Also, direct potentiometric readings were highly variable between duplicates when the results were recorded from the mv scale. This variation was decreased when the concentration scale was used and when the extracting solution was either distilled water or HNO_3

Table 4. Recovery of chloride (as NaCl) from snap bean tissue as determined by potentiometric titration[1]

Sample number	Chloride added (mgm)	Filtered[2]		Filtered[3]		Unfiltered[4]	
		Found (mgm)	Recovery %	Found (mgm)	Recovery %	Found (mgm)	Recovery %
1	6.07	5.56	91.6	5.92	97.4	6.00	98.0
2	12.14	11.25	92.7	12.00	98.8	12.07	99.4
3	18.21	17.07	89.7	17.96	98.6	18.12	99.5

[1]Each entry is the average of two determinations.
[2]Filtered, not washed.
[3]Extraction flasks and filter paper each rinsed 3 times with 5 ml portions of 0.1N HNO_3.
[4]Extraction flask rinsed 3 times with 5 ml portions of 0.1N HNO_3.

Table 5. Comparison of two methods of chloride determination on mature table beet petiole tissue

Sample number	Mohr method[1]	Solid state electrode[2]		
		Potentiometric titration	Direct potentiometry	
			Millivolt scale	Concentration scale
		Per cent Cl^-		
1	0.32	0.32	0.31	0.40
2	0.37	0.35	0.57	0.54
3	1.85	1.96	2.46	1.95
4	4.14	4.16	3.72	3.52
5	4.43	4.48	4.32	3.78
6	7.57	7.67	7.02	6.87
7	7.70	7.66	7.20	6.99
8	10.03	10.27	9.90	10.20
Per cent variation from the mean:	0.3	0.8	7.3	4.3

[1]Extracting solution distilled water.
[2]Extracting solution 0.1N HNO_3.

Table beets from Project NY (G) 861, "Available phosphorus and potassium in the soil and response of vegetable crops."

Table 6. Chloride content in mature table beet petioles comparing direct potentiometry versus potentiometric titration method using the Chloride Solid State Electrode

Sample number	Potentiometric titration[1]	Direct potentiometry[2]	
		Millivolt scale	Concentration scale
		Per cent Cl^-	
9	0.30	0.72	0.60
10	1.09	1.50	1.20
11	1.98	2.46	2.67
12	3.76	4.32	5.16
13	4.40	6.30	6.54
14	7.04	9.30	9.60
15	8.65	12.48	13.08
16	8.70	12.42	11.76
Per cent variation from the mean:	1.0	6.6	1.9

[1]Extracting solution 0.1N HNO_3.
[2]Extracting solution distilled water.

Table beets from Project NY (G) 861, "Available phosphorus and potassium in the soil and response of vegetable crops."

The liquid membrane electrode in conjunction with all reference electrodes and extracting solutions produced results that were unreliable and erroneous compared with either the titration or Mohr methods. Meter stability and ample reproducibility were best when the Cl^- was extracted from the plant tissue with water and the recordings read from the concentration or millivolts scale. However, the results obtained were consistently much higher and in no way proportional to the Cl^- concentrations of samples as determined by either the Mohr or potentiometric titration procedures. At this time and under the conditions of this experiment, it appears that the liquid membrane electrode is unsuited for determining Cl^- in plant tissue extracts.

Conclusions

Potentiometric titration of a 0.1N HNO_3 plant tissue extract using a solid state chloride electrode gave results in complete agreement with the Mohr method. Recovery was best on an unfiltered extract, thereby apparently increasing the sensitivity of this method somewhat over the Mohr method.

Direct potentiometric determination of Cl^- was comparable to both the Mohr and potentiometric titration methods when HNO_3 was the extractant, but it did not agree with the potentiometric titration when water was used as the extracting solution.

The liquid membrane electrode produced readings that were erroneously high with all extracting solutions used and all reference electrodes tested.

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Editor's Note

This is a new series that replaces the former Research Circular series published by the New York State Agricultural Experiment Station at Geneva. It results from an intensive study made by a special committee, which recommended that all existing publication series be streamlined and modernized to better answer today's needs of both scientific and general audiences. It was thought important to identify each publication with its appropriate subject matter discipline, such as Biological Sciences, Food Sciences, or Plant Sciences, as well as with a departmental designation.