

**AN EVALUATION OF AUTOMATED AND MANUAL METHODS FOR  $\text{NH}_4\text{-N}$   
ANALYSIS IN THE DETERMINATION OF CATION EXCHANGE CAPACITY OF SOILS\***

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**Y.P. Kalra and D.G. Maynard**

Northern Forest Research Centre  
Canadian Forestry Service  
Edmonton - Canada

**PUBLICATIONS  
NORTHERN FORESTRY CENTRE  
5320 122 STREET  
EDMONTON, ALBERTA  
T6H 3S5**

**ABSTRACT**

Cation exchange capacity (CEC) is an important and commonly used measurement in the analysis of soils. One of the most widely used methods for CEC involves saturation of the exchange sites with  $\text{NH}_4$  (as 1.0 N  $\text{NH}_4\text{OAc}$ , pH 7.0), followed by the displacement of the  $\text{NH}_4$  by another salt solution and the determination of  $\text{NH}_4$  in the resulting extract. Twenty soil samples from nine countries (including Labex round 85-1 soil samples) were analyzed. The samples varied in their textures and organic matter content. Two automated methods of  $\text{NH}_4$  determination were compared with the traditional macro-Kjeldahl technique. The two automated methods tested were the colorimetric (AutoAnalyzer) and the distillation (Kjeltec) procedures. The CEC of the soils ranged from 1.33 to 123 meq  $100\text{ g}^{-1}$  ( $\text{cmol kg}^{-1}$ ). There were no significant differences among the three methods tested; therefore, any one of the techniques can be used for the determination of  $\text{NH}_4$  for CEC. The advantages and disadvantages of these methods are discussed.

**I Introduction**

Cation exchange capacity (CEC) is an important and commonly used measurement in the analysis of soils. It is a measure of the quantity of readily exchangeable cations neutralizing negative charge in the soil (Rhodes, 1982). To a large degree, CEC determines the level of soil fertility (Wilde et al., 1979). One of the most widely used methods for CEC (Atkinson et al., 1958) involves saturation of the exchange sites with an index cation (such as  $\text{NH}_4$  using 1.0 N  $\text{NH}_4\text{OAc}$ , pH 7.0), followed by the displacement of the  $\text{NH}_4$  by another salt solution and the determination of  $\text{NH}_4$  (that had been adsorbed by the soil) in the resulting extract. It is most frequently determined by the Kjeldahl distillation technique (Chapman and Pratt, 1961; Jackson, 1958). The literature on the conventional Kjeldahl determination is voluminous.

Automated colorimetric methods have been used by several investigators for the determination of  $\text{NH}_4$  in Kjeldahl digests of soils (Schuman et al., 1973; Skjemstad and Reeve, 1976) and in solutions containing widely differing amounts of organic and inorganic compounds (Johnson and Edwards, 1979; Verry and Timmons, 1977; White and Gosz, 1981).

An automated distillation-titration method utilizing the Kjeltec Auto 1030 Analyzer, based on the Kjeldahl procedure, has been used for the determination of nitrogen in plant samples. However, this technique has not been evaluated for  $\text{NH}_4$  analysis in the  $\text{NaCl}$  leachates for the determination of CEC (Ola Hult, Technical Manager, Tecator AB, Högånäs, Sweden: personal communication, 1985).

The present study was undertaken to compare the automated colorimetric method and the automated distillation and titration method against the

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conventional Kjeldahl procedure for  $\text{NH}_4\text{-N}$  analysis to determine CEC of soils.

## II Materials and Methods

### a. Soils

Twenty soil samples were used for this investigation (Table 1). They were selected to obtain a range in pH, organic carbon content and texture. Samples 1-17 had been used earlier for inter-laboratory check sample studies carried out by different organizations as shown in Table 1. The last three samples (No. 18-20) were air dried, ground to pass through a 2-mm sieve and mixed thoroughly.

### b. Soils Characterization

The pH was determined on a soil paste (US Salinity Laboratory Staff 1954). Organic carbon was determined by the Walkley-Black titrimetric wet oxidation method (Greweling and Peech, 1965). Particle-size analysis was performed by the Bouyoucos hydrometer sedimentation technique (Day, 1965). These properties of the soils are presented in Table 2.

### c. Extraction

The extraction was performed according to the procedure given by Atkinson et al. (1958). Approximately 50 ml of 1.0 N  $\text{NH}_4\text{OAc}$  (pH 7.0) were added to a 25.0 g soil sample (10.0 g organic soil) in a 250 ml beaker. After stirring, the samples were allowed to stand overnight. Samples were filtered with gentle suction through a Nalgene Buchner funnel (Whatman #42 filter paper, 7.0 cm). Small portions of  $\text{NH}_4\text{OAc}$  solution were used for leaching, draining well between each addition. The leachate (approximately 250 ml) was discarded. Excess  $\text{NH}_4\text{OAc}$  from  $\text{NH}_4$ -saturated soil was leached with 200 ml 95%  $\text{C}_2\text{H}_5\text{OH}$ , using small volumes. The leachate was discarded. The alcohol-washed soil was leached with 10% acidified NaCl solution (0.005 N with respect to acidity) in increments. The leachate was washed into a 250 ml volumetric flask, made up to volume with NaCl and mixed well. All the extractions were done in triplicate.

### d. Chemical Analysis

Ammonium-N in the leachate was determined by the Kjeldahl procedure, Auto-Analyzer technique, and Kjeltac 1030 Auto Analyzer.

Kjeldahl Method: The NaCl leachate (100 ml) was transferred to an 800 ml Kjeldahl flask and diluted with approximately 300 ml water. After the addition of 10 ml 40% NaOH solution, the  $\text{NH}_3$  liberated by distillation was collected in approximately 25 ml of 4% boric acid solution containing N-point indicator. The resulting  $\text{NH}_4\text{H}_2\text{BO}_3$  was titrated with standard  $\text{H}_2\text{SO}_4$  to a pink end point.

AutoAnalyzer Technique: The NaCl leachate was diluted 10 times. A set of 5, 10, 15, 20, 25, 50, 75 and 100 ppm  $\text{NH}_4\text{-N}$  (as  $(\text{NH}_4)_2\text{SO}_4$ ) were prepared. Ammonia was determined by a Technicon AutoAnalyzer. The flow diagram of the AutoAnalyzer and the manifold are shown in Figure 1. The set up was similar to that of Technicon Instrument Corporation Industrial Method 154-71W (1973).

Kjeltac Auto 1030 Analyzer Technique: The alkali pump was adjusted to deliver 10 ml 40% NaOH solution (Tecator, 1985). An aliquot (100 ml) of the NaCl leachate was transferred to the distillation vessel. The distilled  $\text{NH}_3$  was collected into 25 ml 1% boric acid solution containing a mixed indicator methyl red and bromo-cresol green. The titration was performed with standard HCl.

### III Results and Discussion

Cation exchange capacity is dependent on soil organic matter and texture. In mineral soils, the clay fraction is largely responsible for cation exchange properties. Therefore, mineral soils were selected to obtain a range in pH (4.8-10.3), organic carbon content (0.14-6.9%), and texture (5-69% sand, 3-68% silt and 18-79% clay). In addition, an organic soil (pH 3.5, organic carbon 48%) was also used.

The CEC of the soils ranged from 1.33 to 123 meq 100 g<sup>-1</sup> (Table 3). In Table 3, the standard deviations show good precision in all the three methods. Although there was a wide range in the coefficient of variation values for Kjeldahl (0.6-21.2), AutoAnalyzer (0.9-26.8) and Kjeltec system (0.4-17.1), most of the values were less than 5%. It must be pointed out that the triplicate analyses were on three different sub-samples of each soil. Therefore, some of the variation between replicates is probably due to the natural variability found in soils.

There was no significant difference in the CEC (Table 4) among the three methods ( $P < 0.05$ , two-way ANOVA, SAS Institute Inc., 1985). The three methods were not affected by the various soil types, over a wide range of pH's, CEC, organic carbon and texture. Similarly, automated methods have been reported to give results that do not differ significantly from the accepted Kjeldahl method on water samples (American Public Health Association 1985).

The Kjeldahl procedure is a reliable technique that has provided excellent reproducibility over time for N determination (Bremner and Mulvaney, 1982). The limitations are that it is a cumbersome, time- and labor-intensive technique that can be subject to serious error during certain steps of the analytical procedure.

The AutoAnalyzer is a simple, easy-to-operate instrument. It permits an automated uniform mixing of small precise volumes of the sample solutions and reagents. The technique is very sensitive (set up in Fig. 1 for 0-0.14 ppm NH<sub>4</sub>-N). The reduction in the amounts of glassware and reagents required lowers the cost of analysis. Since the analyses can be performed rapidly (40 samples/hr), it enables the laboratory a high sample throughput in routine operation. The instrument does not need the operator to be there constantly. The limitation of the technique is that the time required for set-up and cleanup procedures is greater than the other two techniques. Generally, NH<sub>4</sub> in soil extracts has been determined in a two-step procedure involving distillation and colorimetric techniques (Bremner and Mulvaney, 1982; Kempers, 1974). In our investigation NH<sub>4</sub> was determined by the AutoAnalyzer directly in the NaCl leachates, thus eliminating the distillation step. Similarly, NH<sub>4</sub>-N in 2 M KCl soil extracts has been analyzed directly rather than in distillates by the AutoAnalyzer (Keeny and Nelson, 1982).

The Kjeltec Auto 1030 Analyzer is a part of the Kjeltec Auto Systems. It has been used for fast and automatic distillation, titration and calculation for the determination of protein in plant samples. It uses microcomputer technology for instrument control and for data processing. Receiving solution (H<sub>3</sub>BO<sub>3</sub>) is dispensed automatically into the titration vessel. Similarly, a preset volume of 40% NaOH solution is pumped into the sample. Titration with a standard HCl solution following the distillation step is performed automatically; a dual photocell system continually sensing the color of the indicator. After completion of the analysis cycle, the instrument is reset automatically for the next sample. Also, the distillation residues are automatically evacuated. This eliminates the handling of hot caustic solution, thus ensuring maximum operator safety. Automatic titration eliminates the subjective error of obtaining the end point manually in the Kjeldahl method. The technique requires two minutes for distillation, titration and presentation of results. The measuring

range is 1-160 mg N with a recovery of 99.5-100% (Hjalmarsson and Mindel, 1981). A water saving system reduces the cost of operation compared to the Kjeldahl system. Although in the Kjeldahl method there is a likelihood of  $\text{NH}_3$  loss if the flask is not connected to the distillation set up immediately after the alkali addition, we did not experience this problem. Moreover, this problem is eliminated in the Kjelttec system as the alkali is added in a closed system. A limitation of the Kjelttec technique is that the operator has to be present with the equipment as in the Kjeldahls procedure.

Both the AutoAnalyzer and Kjelttec methods are suitable for routine measurements of CEC of soils over a wide pH, organic C and textural ranges. They are rapid, precise, safe and accurate. Experience in our laboratory has shown that it is possible to perform 250 and 125 analyses by the AutoAnalyzer and Kjelttec techniques, respectively, in a normal working day compared to only 45 analyses by the Kjeldahl method. In addition, both automated systems are compact and, therefore, require less space than the macro- Kjeldahl unit. The Kjelttec technique would be preferred for smaller workloads of soil high in CEC while the AutoAnalyzer is preferred for larger workloads.

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Table 1. Soil samples selected for the present study.

No. Sample		Reference	
1	CSSC 9	Canada Soil Survey Committee, Ottawa, Ontario, Canada	McKeague et al. (1978)
2	CSSC 13		
3	WEALA 1	Western Enviro-Agricultural Laboratory Association, Edmonton, Alberta, Canada	Kalra and Peters (1981)
4	WEALA 3		
5	WEALA 6		
6	Utah 1	Utah State University, Logan, Utah, USA	James (1984) *
7	Utah 2		
8	Utah 3		
9	WEALA Research 1		Sandberg (1984)**
10	WEALA Saskatchewan 2		
11	Labex 11 (Syria)	Laboratory Exchange Program, Wageningen, the Netherlands	Pleijssier (1985)
12	Labex 14 (Malaysia)		
13	Labex 15 (Hungary)		
14	Labex 17 (Kenya)		
15	Labex 23 (France)		
16	Labex 26 (Brazil)		
17	Labex 28 (Netherlands)		
18	Kananaskis Provincial Park, Alberta, Canada		
19	Banff, Banff National Park, Alberta, Canada		
20	Mt. Norquay, Banff National Park, Alberta, Canada		

\* D.W. James, Utah State University, Logan, Utah, USA (Personal communication).

\*\* P. Sandberg, Alberta Soil and Feed Analysis Ltd., Lethbridge, Alberta, Canada (Personal communication).

Table 2. Some characteristics of the soils used.

Sample No.	pH (water)	Organic carbon	Sand 0.05-2.00 mm	Silt 0.002-0.05 mm %	Clay 0.002 mm	Textural class
1	8.3	0.20	48	29	23	L
2	3.5	48.0	-	-	-	organic
3	8.1	2.01	21	38	41	C
4	6.1	0.50	40	40	20	L
5	5.3	6.97	34	46	20	L
6	5.5	2.90	36	38	26	L
7	7.4	2.38	18	48	34	SiCL
8	7.6	1.45	14	34	52	C
9	7.4	1.57	38	30	32	CL
10	8.0	3.09	68	14	18	SL
11*	7.8	0.14	29	34	34	CL
12	4.8	0.34	62	3	35	SCL
13	10.3	0.26	43	27	29	CL
14	7.9	1.71	5	15	79	C
15	8.0	1.85	35	33	32	CL
16	4.9	0.20	69	5	26	SCL
17	6.8	0.20	14	68	19	SiL
18	7.1	2.31	46	36	18	L
19	7.8	-	-	-	-	-
20	7.5	5.30	37	42	21	L

\* Samples 11-17: Median-1 values as given in a report by Pleijsier (1985). This median is the "half-way value" i.e., the number of laboratories reporting a lower value than the median equals those reporting higher values.

Table 3. The mean\*, standard deviation and coefficient of variation of cation exchange capacity of soils\*\*.

Sample	Kjeldahl			AutoAnalyzer			Kjeltec		
meq 100 g <sup>-1</sup>									
1	14.3	0.67	(4.7)	14.1	0.97	(6.9)	14.2	0.48	(3.3)
2	123	3.33	(2.7)	123	7.72	(6.3)	124	4.85	(3.9)
3	32.9	1.13	(3.4)	32.5	0.97	(3.0)	32.3	0.92	(2.9)
4	9.73	0.18	(1.9)	9.39	0.22	(2.3)	9.60	0.32	(3.4)
5	36.0	0.22	(0.6)	38.4	1.11	(2.9)	37.1	1.34	(3.6)
6	18.0	0.40	(2.2)	18.0	0.23	(1.3)	18.1	0.52	(2.9)
7	22.4	0.16	(0.7)	22.5	0.23	(1.0)	22.1	0.09	(0.4)
8	29.3	1.29	(4.4)	29.8	1.24	(4.2)	29.6	1.11	(3.8)
9	19.4	0.29	(1.5)	19.2	0.59	(3.1)	19.5	0.19	(1.0)
10	20.9	0.40	(1.9)	20.7	0.59	(2.8)	21.0	0.48	(2.3)
11	13.2	0.63	(4.8)	12.9	0.22	(1.7)	13.1	0.63	(4.8)
12	2.36	0.23	(9.6)	2.62	0.21	(7.9)	2.52	0.43	(17.1)
13	8.84	0.31	(3.5)	8.62	0.59	(6.9)	8.76	0.28	(3.2)
14	77.3	6.80	(8.8)	76.8	0.66	(0.9)	73.8	3.18	(4.3)
15	16.0	0.15	(0.9)	15.4	0.67	(4.3)	15.9	0.24	(1.5)
16	1.24	0.26	(21.2)	1.55	0.42	(26.8)	1.21	0.09	(7.1)
17	9.60	0.31	(3.2)	9.26	0.39	(4.2)	9.48	0.18	(1.9)
18	10.6	1.36	(12.7)	10.2	1.78	(17.6)	10.6	1.03	(9.8)
19	61.9	1.07	(1.7)	62.3	2.41	(3.9)	61.3	1.01	(1.6)
20	23.8	1.04	(4.4)	23.1	0.66	(2.9)	23.7	1.18	(5.0)

\* All results are the average of three replicates.

\*\* meq 100 g<sup>-1</sup> = cmol kg<sup>-1</sup>.



Table 4. Two-way analysis of variance (SAS Institute Inc. 1985)

Source	DF	ANOVA SS	F Value	Significance
Sample.Treatment	38	34.55720111	0.30	NS*
Sample	19	146061.01591722	2496.14	...**
Treatment	2	1.33848778	0.22	NS

Means with the same letter are not significantly different.

SNK#	Grouping	Mean	N	Treatment
	A	27.5567	60	1
	A	27.5397	60	2
	A	27.3658	60	3

\* Not significant

\*\*  $P < 0.001$

# Student-Newman-Keuls test for variable.

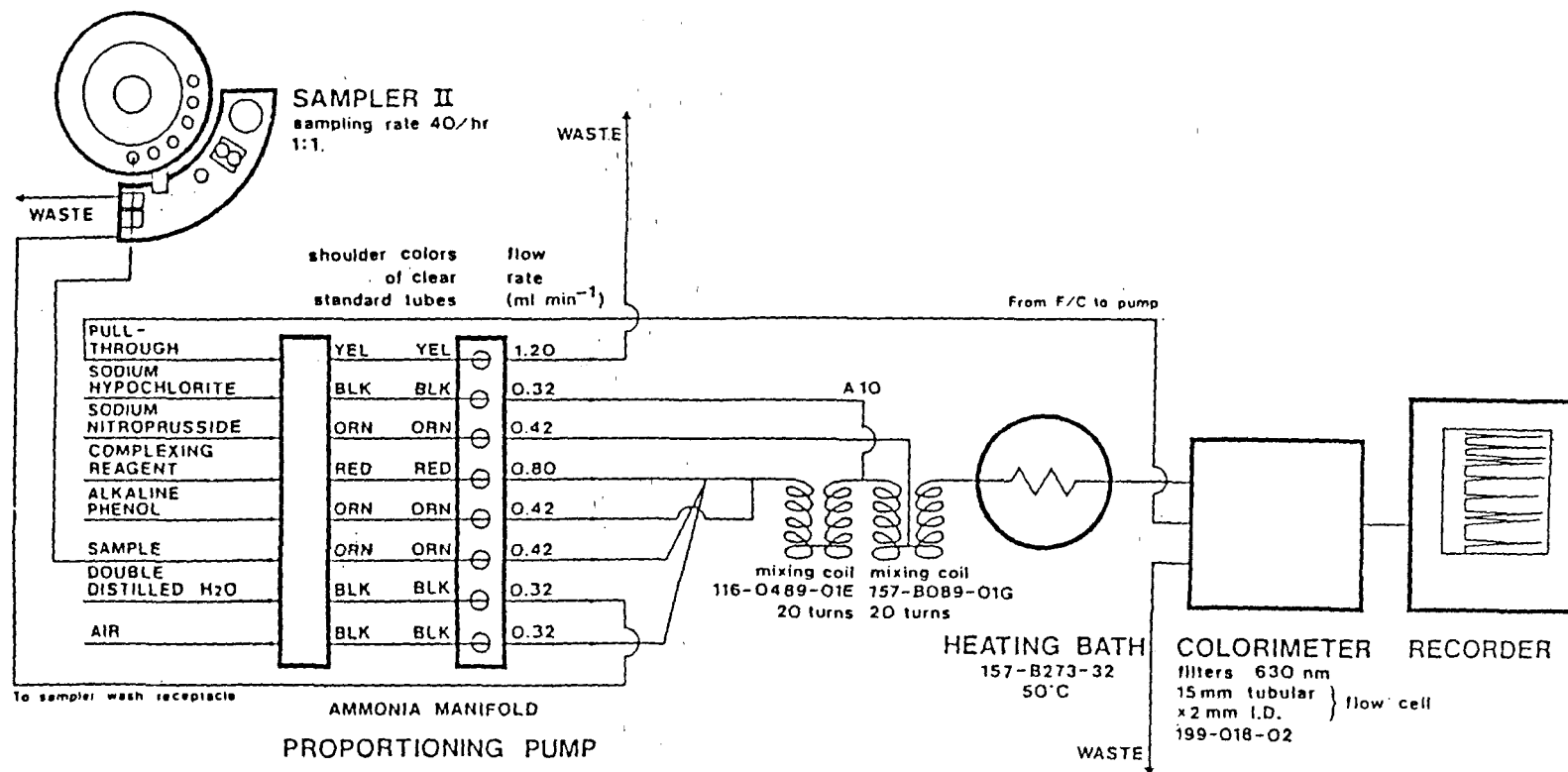


Figure 1. Flow diagram for the determination of NH<sub>4</sub>-N in NaCl leachates by AutoAnalyzer