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MODIFICATION OF THE ALKALINE PERMANGANATE METHOD FOR ASSESSING THE AVAILABILITY OF SOIL NITROGEN IN UPLAND SOILS[1]

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ABSTRACT

The alkaline permanganate digestion method has been widely used for assessing the available nitrogen pool in soils. We report that simple laboratory experiments have shown that the standard method does not include nitrate and nitrite, but that a simple modification, involving the use of Devarda's alloy, allows inclusion of nitrate and nitrite. This modification is desirable if the method is to be used for assessing available nitrogen in tropical upland soils that experience pronounced wet and dry seasons. Results with soil on our experimental farm showed that the nitrate content of the soil contributed 10 to 40 percent of the available nitrogen assessed by the modified method.

INTRODUCTION

The alkaline permanganate digestion method has been widely used for assessing the available nitrogen pool in soils, especially in India (Truog 1954; Subbiah and Asija 1956; Kresage and Merkle 1957; Tamhane and Subbiah 1962; Bajaj et al. 1967; Stanford and Legg 1968; Singh and Tripathi 1970; Ranganathan et al. 1972). This method was originally developed for estimating the easily oxidizable organic nitrogen fraction in organic manures and fertilizer (AOAC 1930); its adoption for soil studies followed the demonstration of fair correlations between the amounts of nitrogen extracted by this technique and the mineralizable nitrogen contents of soils (Subbiah and Asija 1956; Boswell et al. 1962; Kresge and Merkle 1957; Herlihy 1972; Stanford 1978; Sahrawat 1978) and nitrogen uptake and yield of different crops, including rice (Munson and Stanford 1955; Kresge and Merkle 1957; Bajaj et al. 1967; Stanford and Legg 1968; Rajamannar et al. 1970; Ranganathan et al. 1972; Sahrawat 1978). Other studies have indicated that the method gives good correlation with the response of rice to applied fertilizer nitrogen (Bajaj et al. 1967; Rajamannar et al. 1970; Sahrawat 1978).

In some studies however, and especially with upland crops, the poor performance of the alkaline permanganate method for assessing available soil nitrogen has also been reported (for example, see Olson et al. 1960; Peterson et al. 1960; Keeney and Bremner 1966). Additionally, closer relationships were obtained for paddy rice than for upland wheat, when the soil test values were correlated with nitrogen uptake or the percent response to fertilizer nitrogen (Bajaj et al. 1967). The reasons for these variable results do not appear to have been investigated.

Although it is clear that alkaline permanganate releases nitrogen from the soil organic nitrogen pool by both oxidation and hydrolysis (Stanford 1978), the chemistry of the method is not clearly understood (Bremner 1956*b*). One aspect that has received little attention is the fact that the method appears to estimate only the ammonium-N released from the soil organic matter by alkaline permanganate in addition to ammonium-N already present in the soil. No report has been made of the recovery of nitrate by this method. There is, in fact, good reason for expecting that nitrate- and nitrite-N would not be included in the available pool that is estimated by the alkaline permanganate method, because this has an oxidizing action and therefore would not be expected to reduce nitrate-N to ammonium-N. In upland soils in the seasonally dry tropics, as well as elsewhere, appreciable concentrations of nitrate-N may accumulate. It was therefore expected that the poorer relationships for upland crops (grown on soils containing nitrate), than paddy rice (in which nitrate would be largely lost by denitrification), may be due to inability of the alkaline permanganate method

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to include soil nitrate-N. Experiments were therefore undertaken in the laboratory to examine the extent that nitrate may be included in this method, especially by the use of simple modifications to ensure its reduction to ammonium, for example, by the use of Devarda's alloy.

MATERIALS AND METHODS

Standard alkaline permanganate method

The standard alkaline permanganate method used for determination of soil-available nitrogen was essentially that described by Subbiah and Asija (1956). A subsample of 20 g soil (<2 mm) was transferred to a 800-ml Kjeldahl digestion flask, to which were added 100 ml of 0.32% $KMnO4$ solution, 100 ml of 2.5% $NaOH$ solution, and 20 ml of water. The flask was connected to a standard macro-Kjeldahl distillation unit, and 75 ml of the distillate was collected in 25 ml of boric acid indicator mixture; the indicator used was bromocresol green and methyl red, and the absorbed ammonia was titrated with 0.05 *N* H_2SO_4 to calculate available nitrogen content of the sample (Bremner 1965*a*).

Modification alkaline permanganate method to include nitrate

To determine the recovery of nitrate-N by this method, 1.5 g of Devarda's alloy was added to the distillation flask in addition to alkaline permanganate. Modification 1 involved addition of Devarda's alloy with the other reagents before distillation. Modification 2 involved distillation as in the standard method until 50 ml of distillate was collected, then addition of Devarda's alloy followed by further distillation until another 25 ml was collected; this two-stage distillation was adopted because the action of Devarda's alloy (added to reduce nitrate to ammonium) appeared to interefere with the oxidization of organic nitrogen by alkaline $KMnO_4$.

For comparisons of the modified 2 and unmodified (standard) methods, appropriate controls were conducted; it was established that the addition of water and the brief cessation of digestion after collection of 50 ml distillate caused no significant change in the amount of distillable nitrogen.

Experiments with solutions

For recovery of nitrogen in aqueous solutions, known amounts of amino-, NH_4^+-, NO_2^--, and NO_3^--N were added and distilled with the alkaline permanganate as described above. The amino acids used for recovery studies were aspartic acid, valine, lysine monohydrochloride, leucine, and glutamic acid (Fisher Scientific Co., Chicago, Illinois). The amounts of nitrate-N (as KnO_2), nitrite-N (as $NaNO_2$), and amino acid-N added for these recovery experiments were in the range of 1000 to 2500 μg N. All the analyses were done at least in duplicate.

Experiments with soils

The efficiency of the standard and modified methods for recovering nitrate was determined by comparing the difference in the amount of native soil nitrogen distilled by each method, and also by comparing the recovery of nitrate-N added to the soils. The latter was achieved by adding up to 4000 μg nitrate-N (200 μg N/g soil) to the flask after addition of soil, but before addition of reagents, and then distilling by either the standard or modified method as described previously. For the soil studies, the soil samples were selected to provide a wide range in nitrate-N content. The soil samples belong to the orders Alfisols and Vertisols; these samples were collected from experimental fields, of different land use and fertilization history, at ICRISAT Center, at Patancheru near Hyderabad India. The soil samples wereair-dried and ground to pass through a 2-mm sieve before use. None of the soil samples contained any measurable amounts of nitrite-N.

RESULTS

Solutions

The preliminary studies, carried out with solutions of pure salts, showed that 80 to 95% of the amino acid N and 95% of NH_4^+-Ncould be recovered when the standard alkaline permanganate distillation method was employed (Table 1). However, very little NO_2^--N, NO_3^--N, or urea-N were recovered.

Devarda's alloy is a common reducing agent employed for reduction of nitrite and nitrate to ammonium, which then be distilled with alkali (Bremner 1965*a*). The use of the simple modification (1) of the alkaline permanganate method—involving the addition of Devarda's alloy with the alkaline permanganate—did not affect the recovery of ammonium or of small amounts of nitrate- or nitrite-N, but it caused a significant reduction in the proportion of amino acid-N that was recoverable as ammonium on distillation (Table 1). The cause of the lower recovery of amino acid-N would seem to be the fact that the reductive capacity of Devarda's alloy and the oxidative capacity of permanganate neutralize each other to a certain extent. The second modification (2)—distillation of the solutions with alkaline $KMnO_4$ before the addition of Devarda's alloy—resulted in good recoveries (96%) of amino acid-N, NO_3-N, NO_2-N, and NH_4-N (Table 1); however, again, urea-N was not recovered.

Soils

Comparison of the amounts of N extracted by the standard method and the modified method (2) show that there is an appreciable difference between the values of available N extracted by these two methods (Table 2). The mean difference in available-N by the two methods is 26.0 ppm, and this difference is very similar in magnitude to the mean nitrate-N content of the soil samples (27.1 ppm). By assuming that the difference between the two methods is due solely to the lack of the inclusion of NO_3-N or NO_2-N by the standard method, it may be estimated that the addition of Devarda's alloy in the modified method leads to a mean recovery of the native soil nitrate-N of 96%. This is in agreement with the recoveries (97%) of nitrate-N from pure solutions (Table 1). The nitrate-N content of the soils used in this study on average contributed about 21% (range 10 to 44%) of the available N as assessed by the modified method.

To verify suggestion that the difference between the N determined by the two methods represented the nitrate-N that could be recovered only by use of the modified method, recoveries of added nitrate were determined by both methods. The results (Table 3) show clearly the nitrate is not recovered to any extent by the standard method, but that there is almost complete recovery by the modified method, when nitrate is added in moderate amounts to both Alfisols and Vertisols; recoveries were greater than 99% and 94% when 50 and 100 ppm nitrate-N were added.

DISCUSSION

Nitrates are not included in the available N pool when the alkaline permanganate method is used for determination of available soil N (Tables 2 and 3). This may not be of importance for a wetland soil where nitrate is unlikely to be present, due to losses by denitrification. But nitrate may accumulate in appreciable amounts in upland soils, and it may contribute significantly to a soil's pool of available nitrogen. For example, in the soils used in the study, nitrate-N in the soil was equivalent to 14 to 75% of the available-N assessed by the standard alkaline permanganate method, and it contributed 10 to 40% of the available-N assessed by the modified (2) method.

Nitrate accumulation may be appreciable in upland soils of the seasonally dry tropics, especially just after the commencement of the rainy

TABLE 1

Recovery of different forms of N *on treating pure solutions of specified compounds with the standard and modified alkaline permanganate digestion and distillation methods*

Form of N	Compound added	% recovery[a] by		
		Standard[b] method	Modified method[c]	
			1	2
Amino acid	Asparatic acid L	93	6	91
	Leucine, DL	94	13	96
	Glutamic acid L	95	17	94
	Lysine monohydrochloride, L	80	20	82
	Mean	91	14	91
Urea	Urea	2	4	4
Ammonium	$(NH_4)_2SO_4$	95	96	96
Nitrate	$NaNO_2$	1	96	96
Nitrate	KNO_3	1	97	97

[a] Based on addition of 2500 μg N in solution as specified compounds.

[b] No alloy added.

[c] Devarda's alloy added with $KMnO_4$ (1) or after distillation of 50 ml distillate and before final dilution of 25 ml distillate (2).

TABLE 2

Comparison of the available N *content of soils and different nitrate-*N *contents, as assessed by the standard and modified (2) alkaline permanganate methods*

Soil		Available-N, ppm		Difference, ppm	Nitrate-N content of soil, ppm	Apparent recovery of nitrate-N, %
Order	Field	Standard method	Modified method			
Alfisol	a	63	112	49	50	98
	b	73	83	10	11	91
	c	177	202	25	26	96
Vertisol	d	64	77	13	15	87
	e	67	79	12	12	100
	f	77	90	13	14	93
	g	81	90	9	9	100
	h	85	124	39	41	95
	j	85	138	53	53	100
	k	114	151	37	40	93
	Mean	88.6	114.6	26.0	27.1	95.3

TABLE 3

Recovery of nitrate added to soil by the standard and modified (2) alkaline permanganate methods

Soil order	Nitrate-N added, ppm	Avilable N content, ppm, as assessed by		Recovery % of nitrate-N added	
		Standard method	Modified method	Standard method	Modified method
Vertisol	0	81	99	–	–
	10	81	109	0	100
	25	81	124	0	100
	50	81	149	0	100
	100	82	193	1	94
	125	80	218	−1	95
	150	81	231	0	90
	200	81	277	0	89
Afisol	0	116	127	–	–
	10	115	137	−1	100
	25	116	152	0	100
	50	117	176	1	98
	100	116	222	0	95
	200	118	307	2	90

season. This accumulation results from the flush of microbial activity that occurs on rewetting of a soil after severe dessication, such as that due to the very hot dry season that precedes the rainy season. When comparing the "available N" contents of soils that have been collected at different times, it is thus important to include nitrate-N. Failure of the standard method used by earlier workers to include variable amounts of nitrate would seem to be one possible reason why poorer correlations were obtained for upland crops than for paddy rice (Bajaj et al. 1967). Under paddy, the nitrate would be lost by denitrification, and therefore there is no need to measure it.

Although the suggested modification results in measurement of most of the nitrate, it may not recover all. Nitrate recoveries were almost quantitative for solutions (>97%), and for soils where moderate amounts of nitrate-N (<50 ppm) had been added. But, if higher amounts of nitrate-N (>100 ppm) were added to soil, recoveries were lower (<95%); the addition of larger amounts of Devarda's alloy improved the recoveries. The reasons for these effects are not known, and require further study. Nevertheless, as nitrate is at most only a subdominant component of the total available N, some loss of accuracy can be tolerated. For the present, the modified method (2) has improved the effectiveness of the alkaline permanganate method, so that it should provide an improved estimate of the available N pool for upland soils, as well as paddy soils.

The only alternative vision of this method that is better for upland soils involves two measurements rather than one. The standard alkaline permanganate method provides an index of the "readily mineralizable N" over the life of a crop; this soil, or preferably the soil profile, to indicate also the amount of "instantly available" N in the soil.

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