

Comparison of Three Methods for Determination of Total Nitrogen in Fertilisers for Hevea

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Total nitrogen in twelve fertilisers was determined by three methods. Coefficients of variation obtained from replicate analysis showed that the modified comprehensive nitrogen method produced the most precise results. The method is suitable for determining total nitrogen in fertilisers containing unknown nitrogen sources and a large proportion of chloride to nitrate.

Application of fertilisers to increase growth and sustain yield during the immature and mature phases of rubber is an established practice since the early sixties. In all fertilisers for rubber, the source of nitrogen is from ammonium sulphate, ammonium nitrate and urea¹. Other sources like ammonium chloride and calcium ammonium nitrate or 'nitro-chalk' have been reported but their usage is not common.

Chemical analysis to ensure that the nutrient content of fertilisers agrees to specifications are carried out by many laboratories. Poon² reviewed the analytical methods used by Malaysian laboratories. For analysis of total nitrogen, most laboratories use the classical Kjeldahl digestion method with sodium sulphate-selenium mixture as catalyst and concentrated sulphuric acid-salicylic acid. Some laboratories determine the total nitrogen content by measuring the concentration of ammoniacal nitrogen after distillation or by colorimetry. The ammoniacal nitrogen comes from the hydrolysis of urea by the urease enzyme technique or the reduction of nitrate by the Devarda method. This method has been preferred, especially when the source of nitrogen is known.

In this paper, the total nitrogen content in twelve fertilisers are reported. The results obtained by the Association of Official Agricultural Chemist (AOAC)³ modified comprehensive nitrogen method was compared with those obtained by the two analytical methods commonly used in Malaysian laboratories.

MATERIALS AND METHODS

Representative samples were taken from twelve 50 kg bag containing five mixtures and seven compound fertilisers, ground to homogeneous powder and kept in air-tight containers. Each of the ground samples was then sub-sampled for the determination of total nitrogen by the methods described below.

Methods I and II follow the procedures adopted by the Rubber Research Institute of Malaysia⁴ while *Method III* is similar to the modified comprehensive nitrogen method of AOAC.

Method I. About 0.25 g fertiliser was weighed and transferred to a 50 ml Kjeldahl flask. Into the flask was added 10 ml of 5% (w/v) salicylic acid in concentrated sulphuric

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acid and the mixture was swirled gently to ensure thorough mixing. Subsequently, 1 g sodium thio-sulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) was introduced and the contents digested at low heat until frothing ceased. The flask was removed and 2 g sodium sulphate-selenium mixture (Na_2SO_4 to Se ratio of 100:1) was added. The content was heated at boiling temperature for about 1 h until a clear solution was obtained. After allowing to cool for a few minutes, 10 ml of distilled water was added to prevent solidification. The digest was transferred to a 100 ml standard flask and made to volume.

A suitable aliquot of the digest was pipetted into a Hoskin distillation apparatus, 15 ml of 30% (w/v) sodium hydroxide solution added and the ammoniacal nitrogen distilled into 50 ml of 0.1 M hydrochloric acid. The excess acid was titrated against 0.1 M sodium hydroxide solutions using methyl red-methylene blue mixed indicator. A similar digestion without fertiliser was carried out. From the concentration of ammoniacal nitrogen in both the sample and blank digests, the total nitrogen in the fertilisers was determined.

Method II. This method of determining total nitrogen incorporates the procedures for the determination of ammoniacal nitrogen, nitrate nitrogen and urea nitrogen.

About 20 ml distilled water was added to 0.5 g fertiliser in a 100 ml volumetric flask. The suspension was shaken to ensure complete dissolution of all nitrogenous compounds, pH adjusted to 7.0 with methyl purple (if necessary) and made to volume with water. To 20 ml of the sample solution in a 50 ml conical flask, 0.2 g urease powder was added and the content incubated at 37°C for 3 h. Upon cooling, the content was introduced into a Hoskin distillation apparatus and this was followed by

addition of 1 g Devarda alloy and 15 ml of 30% sodium hydroxide solution. The ammoniacal nitrogen was distilled into 50 ml of 0.1 M hydrochloric acid and determined as described earlier. A similar determination without fertiliser was carried out. Total nitrogen in the fertiliser was obtained after adjusting for the blank analysis.

Method III. Into a 100 ml Kjeldahl flask was introduced 0.25 g fertiliser, 0.6 g chromium powder and 18 ml distilled water. The suspension was shaken gently to dissolve all nitrogenous compounds and 3.5 ml concentrated hydrochloric acid was added. The flask was placed on a preheated heater (previously adjusted to bring 250 ml water at room temperature to boil in about 5 min) and allowed to boil for 3 to 5 min. The flask was removed from the heater and the content was allowed to cool. About 6 g anhydrous sodium sulphate (Na_2SO_4) together with 0.3 g anhydrous copper sulphate (CuSO_4) and 10 ml concentrated sulphuric acid were added and the content was again heated on a heater (pre-set at 5 min boil test) until dense white fumes in the flask had cleared. If excessive foaming in the bulb of the flask occurred, the heating temperature was adjusted. The heating process took about 1 to 2 h.

The flask was removed from the heater. After about 5 min, a few millilitres of distilled water was added (to prevent solidification). After cooling, the content was transferred into a 100 ml flask and made to volume. A suitable aliquot of the digest was pipetted into a Hoskin distillation apparatus, 15 ml of 30% sodium hydroxide solution was added and the ammoniacal nitrogen distilled into 50 ml of 0.1 M hydrochloric acid. The excess acid was titrated against a 0.1 M sodium hydroxide solution using methyl red-methylene blue mixed indicator. A similar digestion without the fertiliser was carried out. From both the

sample and blank digests, the total nitrogen content in the fertiliser was determined

Determination of total nitrogen in each of the fertilisers by any of the above methods was done in six replicates. In each replicate, a sub-sample was used. The total nitrogen content was expressed as percentage of dry material (oven-dried)

RESULTS AND DISCUSSION

In the twelve fertilisers, the total nitrogen content as specified by the manufacturers ranged from 8.4% to 24.9% (Table 1). Compound fertilisers like Nitro-B, Nitro-G, Nitro-Y, CCM 55 and CCM 65 contained a significant amount of nitrate nitrogen with values ranging from 3.5% to 7.9%. The

TABLE 1 COMPOSITION OF FERTILISERS

Fertilisers	Nutrient Composition (%) ^a				Cl NO ₃ ratio ^c
	N	P ₂ O ₅	K ₂ O	MgO	
Mag X	8.4 (T) ^b	14.4	7.2	2.1	—
Mag Y	10.7 (0.3)	10.4	7.2	2.1	—
Mix X	9.2 (T)	15.1	8.4	—	—
Nitro-B	12.0 (3.5)	12.0	17.0	2.0 + TE	0.49
Nitro-G	15.0 (5.2)	15.0	15.0	—	0.44
Nitro-Y	15.0 (3.5)	15.0	6.0	4.0	0.22
CCM 25	14.0 (7.9)	13.0	9.0	2.5	0.23
CCM 45	12.0 (3.9)	12.0	17.0	2.0 + TE	1.01
CCM 55	15.0 (7.4)	15.0	6.0	4.0	0.22
CCM 65	15.0 (4.8)	15.0	15.0	—	0.47
UU 99	16.3 (T)	20.9	11.2	3.3	—
UU 77	24.9 (T)	11.9	13.3	—	—

RRIM mixtures: Mag X, Mag Y and Mix X

Compounds: Nitro-B (nitrophoska blue), Nitro-G (nitrophoska green), Nitro-Y (nitrophoska yellow),

CCM 25, CCM 45, CCM 55 and CCM 65

Urea based mixtures: UU99 and UU77

^aComposition of fertilisers are as specified by the suppliers

^bValues within brackets are nitrate nitrogen in percentage

^cRatio based on weight and determined by ion chromatography

TE: Trace element

T: Trace amount

TABLE 2. MEAN TOTAL NITROGEN CONTENT OF TWELVE FERTILISERS DETERMINED BY THE THREE METHODS

Fertilisers	Nitrogen content (%)			Difference between methods
	Method I	Method II	Method III	
Mag X	8.57 (3.36)	8.45 (1.24)	8.25 (4.18)	
Mag Y	10.30 (2.68)	10.10 (1.08)	10.10 (1.53)	
Mix X	9.05 (3.81)	8.83 (3.48)	9.08 (4.59)	
Nitro-B	11.53 (5.50)	11.45 (2.75)	11.70 (2.48)	
Nitro-G	14.02 ^b (1.23)	14.85 ^a (1.26)	15.02 ^a (0.89)	***
Nitro-Y	14.63 (6.77)	14.48 (4.93)	14.62 (2.72)	
CCM 25	13.42 ^b (4.20)	13.95 ^a (2.11)	13.33 ^b (2.71)	*
CCM 45	12.62 ^b (1.77)	13.37 ^a (1.02)	13.40 ^a (1.77)	***
CCM 55	14.95 (3.07)	14.78 (2.20)	14.85 (3.12)	
CCM 65	13.40 ^b (1.63)	13.97 ^a (0.58)	13.67 ^b (2.15)	**
UU 99	15.77 ^a (1.99)	13.23 ^b (3.78)	15.55 ^a (3.32)	***
UU 77	24.77 ^a (4.17)	22.26 ^b (6.60)	23.87 ^a (5.38)	*
Mean	13.59 (3.97)	13.31 (3.99)	13.62 (3.65)	

Means with different superscripts (a,b) in the same horizontal column are significantly different from each other at: * P < 0.05; ** P < 0.01; *** P < 0.001

Values within brackets are coefficients of variation

mixtures contained very little or no nitrate nitrogen as the nitrogen is in the form of ammoniacal or urea nitrogen. The principal source of nitrogen in mixtures Mag X, Mag Y and Mix X is known to be ammonium sulphate while that of UU 99 and UU 77 is granular urea.

Mean total nitrogen contents determined by the three methods are shown in Table 2. Coefficients of variation (CV) obtained from

replicate analysis of each of the fertilisers lie within the ranges 6.77% - 1.23%, 6.60% - 0.58% and 5.38% - 0.89% for Method I, Method II and Method III, respectively. Nitrogen values in Nitro-Y by Method I had the highest CV (6.77%). This was also the case for UU 77 by Method II and Method III (6.60% and 5.38%, respectively). For all fertilisers, the combined CV values increased in the following order: Method III (3.65%) < Method I (3.97%) < Method II (3.99%). This

suggests that *Method III* gave more precise results than the other two methods.

With the exception of Mag X, Mag Y, Mix X, Nitro-B, Nitro-Y and CCM 55, there are differences in nitrogen values determined by the three methods. Samples exhibiting the most significant difference (at $P < 0.001$) were Nitro-G, CCM 45 and UU 99.

Examination of nitrogen values in UU 99 and UU 77 showed that *Method II* gave consistently lower results when compared with those obtained by *Method I* and *Method III*. In *Method II*, urea nitrogen is hydrolysed by the urease enzyme to ammoniacal nitrogen which is subsequently determined by distillation and acid-base titration. The lower results could be attributed to the effectiveness of the urease enzyme in the presence of other fertiliser components. Excess freshly prepared urease enzyme was added, but this did not appear to increase the nitrogen values. The presence of nitrogen in forms other than urea nitrogen, ammoniacal nitrogen and nitrate nitrogen could also lead to lower results as the nitrogen could not be determined by *Method II*.

Comparatively, nitrate containing compound fertilisers like Nitro-G, CCM 45 and CCM 65 tend to have lower total nitrogen values by *Method I*. In particular, the nitrogen content of Nitro-G and CCM 45 was about 94.0% of that determined by *Method II* and *Method III*. Wall and Gehrke⁵ found that the chloride content in fertilisers could affect the nitrogen values determined by *Method I* in which sulphuric-salicylic acid was used. In samples with chloride:nitrate ratios > 0.75 (w/w), it was shown that the nitrogen values were 94.1% – 99.1% of those determined by the comprehensive nitrogen method of AOAC³. The chloride:nitrate ratios of Nitro-G, CCM 45 and CCM 65 were found to vary from 0.44 to 1.01; with CCM 45 having the highest value.

Based on these observations, it is important to note that *Method I* is not suitable for fertilisers with a large proportion of chloride to nitrate. Not only lower values are obtained, but the precision of the analytical results can also be affected.

Total nitrogen determined by the three methods is linearly correlated with one another with correlation coefficients (r) higher than 0.97 (*Table 3*). The slopes of the linear regression equations vary from 0.84 to 1.13 and give an overall mean of 0.99. These results indicate that the total nitrogen content determined by the three methods is very close and in good agreement.

The results showed that all three methods can be used for the determination of total nitrogen in fertilisers. *Method II* is simple and enables rapid determination if the nitrogen sources are known to be ammoniacal, urea or nitrate nitrogen. Since all fertilisers for *Hevea* contain one or more of these forms of nitrogen, *Method II* is the most preferred method when compared with *Method I* and *Method III*.

Where the nitrogen sources are not known as in the case of compound fertilisers, most laboratories are in favour of *Method I* for total nitrogen determination. This preference stems from the fact that the method has been established and in use for a long time. Errors in analytical results were seldom encountered or reported as most of the fertilisers have chloride:nitrate ratios well below 0.75. The evidence comes from the observation that only one out of twelve fertilisers given in *Table 1* had a high chloride:nitrate ratio exceeding 0.75. Furthermore, the inhibitive effect of chloride, if there is, is either not detected or overlooked.

The use of *Method III* for the determination of total nitrogen in fertilisers is not common in Malaysian laboratories. One of the important reasons is the relative lack of information on

TABLE 3. LINEAR REGRESSION EQUATIONS AND CORRELATION COEFFICIENTS BETWEEN TOTAL NITROGEN VALUES

Methods Y vs X	Regression equations	Correlation coefficients (r)
I vs II	$Y = -1.404 + 1.126X$	0.97***
I vs III	$Y = -0.465 + 1.038X$	0.99***
II vs I	$Y = 1.960 + 0.836X$	0.97***
II vs III	$Y = 1.368 + 0.882X$	0.98***
III vs I	$Y = 0.693 + 0.945X$	0.99***
III vs II	$Y = -0.880 + 1.083X$	0.98***

***Significant at $P < 0.001$

the test method for routine determination. Despite the adoption of the method by AOAC as official first action, its application to the determination of total nitrogen in a wide variety of fertilisers in Malaysia has not been studied. The results presented in this study showed that *Method III* is comparable if not better than *Method I* and *Method II*. Precision of analysis was good with mean CV value lower than the other methods. In a collaborative study covering eleven nitrogenous fertilisers, Rexroad and Krause⁶ also found that results obtained by *Method III* were equal in accuracy and precision to the official method using mercury as the metallic oxidative catalyst. A critical review of methods of fertiliser analysis by Sweeney *et al.*⁷ described *Method III* as a mercury free method for accurate determination of total nitrogen. Additionally, *Method III* uses chromium metal which is less toxic than selenium that is used in *Method I*. Considering the various aspects, *Method III* should be the preferred method in the determination of total nitrogen, especially when the nitrogen sources are not known and if there is chloride interference.

CONCLUSION

Total nitrogen in fertilisers for rubber can be determined by any one of the methods described since the sources of nitrogen are nitrate nitrogen, ammoniacal nitrogen and urea nitrogen and the chloride to nitrate ratio in most samples is below 0.75. For fertiliser samples containing nitrogen of unknown sources, *Method III* is to be preferred as it gives more accurate and precise results. In addition, the method is less susceptible to chloride interference.

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