A SYSTEM OF ROUTINE FOLIAR ANALYSIS OF SUGAR CANE MAJOR AND TRACE ELEMENTS

By A. C. LONG

Rhodesia Sugar Association Experiment Station, Chiredzi, Rhodesia

Abstract

A system of routine foliar analysis of sugar cane for N, P, K, Ca, Mg and S is discussed which, together with subsequent field soil analysis, is used as criteria for fertilizer recommendations on the estates and privately-owned sugar farms in the Rhodesian Lowveld.

The sampling techniques and analytical methods described are reasonably rapid, economical and accurate. Furthermore, they do not require highly skilled analysts and our staff have been trained in a comparatively short time to perform these operations reliably. Briefly, after semi-micro H_2SO_4/H_2O_2 digestion, aliquots are taken for: N by micro-distillation of NH_3 and titration with standard H_2SO_4; P by Vanando-Molybdenum complex colorimetry; K, Ca, Mg by atomic absorption; and S by tube furnace in a stream of oxygen at 1 000°C with titration of resultant H_2SO_4 with standard sodium borate.

The method for Fe, Mn, Zn, Cu, Ni and B is briefly discussed.

Introduction

When planning our foliar analysis service it was resolved that methods should be rapid and economical, in view of the fact that we envisaged a throughput of around 500 samples a month. In particular, it was decided that Micro-Kjeldahl technique would be used to save high initial capital cost and large consumption of reagents.

This paper gives a brief account of our procedure from sampling to analytical methods.

Sampling

Top visible dewlap leaves are taken by a trained team at age 5 months ± 2 weeks. The number of leaves per field and exact sampling pattern vary somewhat with acreage but, in general, the aim is to take about 100 leaves per field. The leaves are returned to the laboratory in plastic bags to avoid contamination. The centre of gravity of the bundle is then found, and from this point 20 cm towards the leaf tip is removed as a sub-sample. After extraction of the mid-rib the sample is dried at about 95°C and milled in a Wiley mill.

We recently carried out an investigation into the effect on foliar nutrient levels of various sampling times throughout the day. Each time three different sets of leaves were taken from the same field, so that the triplicate analyses are not actually the same sample. We feel, therefore, that Table I is a good indication of our reproducibility on any given field

TABLE I

Reproducibility of Sampling and Analytical Procedure

Time	% N		% P		% K		% Ca		% Mg	
		Mean		Mean		Mean		Mean		Mean
6 a.m. — 1	2,22		,25		1,48		0,22		0,17	
2	2,20	2,21	,25	,25	1,48	1,48	0,22	0,22	0,17	0,18
3	2,22		,24		1,48		0,23		0,19	
8 a.m. — 1	2,21		,23		1,43		0,23		0,18	
2	2,27	2,25	,24	,24	1,43	1,45	0,23	0,23	0,18	0,18
3	2,27		,25		1,48		0,23		0,19	
10 a.m. — 1	2,11		,24		1,43		0,24		0,18	
2	2,22	2,20	,24	,24	1,48	1,45	0,24	0,24	0,17	0,18
3	2,26		,25		1,43		0,25		0,17	
12 noon — 1	2,20		,24		1,52		0,24		0,18	
2	2,22	2,21	,25	,25	1,52	1,54	0,24	0,24	0,18	0,18
3	2,21		,25		1,57		0,24		0,17	
2 p.m. — 1	2,19		,25		1,62		0,24		0,16	
2	2,14	2,16	,24	,25	1,66	1,65	0,21	0,23	0,15	0,15
3	2,15		,25		1,66		0,24		0,14	
4 p.m. — 1	2,07		,24		1,75		0,22		0,14	
2	2,10	2,11	,25	,25	1,66	1,66	0,21	0,21	0,15	0,15
3	2,16		,26		1,57		0,21		0,16	

(both as regards sampling and analytical procedure).

Digestion with hydrogen peroxide/sulphuric acid

0,25 g of dried sample is weighed into 150 × 18 mm Pyrex test tubes in batches of 24, including a reagent blank and two check samples from previous day. 3 ml of A.R. sulphuric acid is then added to the tube, the sample being wetted by gentle agitation and allowed to stand for five minutes (minimum). 2 ml of 30% hydrogen peroxide A.R. are then added dropwise very cautiously (very small drops), allowing frothing to subside after each drop and never allowing frothing to rise more than about one-third of the height of the tube. After each drop gentle agitation is continued until the next drop is introduced. Only by scrupulously observing this procedure can loss of N be avoided and, although time-consuming, the procedure cannot be hurried (Samuels 1969).

We found that high amounts of Se catalyst interfered with phosphorus determination occasionally. We are now using our own selenised powder made up by adding 1 g selenium dioxide to 500 g A.R. sod. sulphate anhydrous and thoroughly mixing on a shaking machine. We now add 1 g of this powder to each tube and place them on a Gallenkamp Micro-Kjeldahl Digestion Stand (catalogue number NR 510) holding 24 tubes. This stand has two heater elements which heat bottom and sides of the tube either simultaneously or independently. Switches give: (1) gentle bottom/high top heat to drive off water without refluxing; (2) finally, high bottom/high top heat to complete digestion; (3) or variations of the above as required. Digestion takes about one hour by which time digest should be colourless or nearly so. After initial digestion for about half-an-hour a further 2 ml of A.R. sulphuric acid is introduced into tubes washing down any carbon, etc., adhering to walls. Heat is now turned up to maximum, as and when conditions dictate, to complete the digest. The digest is now allowed to cool somewhat and is transferred quantitatively to 50 ml volumetric flasks and made up to volume. A little insoluble matter will remain at the bottom of the flasks; this is dehydrated silica and does not interfere. Filtering is not normally necessary, the supernatant being taken. Aliquots are now taken as detailed below.

Photometric determination of phosphorus

Introduction

This is merely an adaptation of the classical phosphovanadomolybdate colorimetric method to suit the above digest. The molybdenum blue method in our hands has proved quite unreliable despite perseverance with various reducing agents and scrupulous attention to timing of colour development. It was finally abandoned in favour of the above which gives excellent reproducibility even in unskilled hands.

Instrumentation

Unicam S.P. 600 Series 2 Spectrophotometer using 1 cm cells at 420 millimicrons. The procedure could easily be adapted for Spekker absorptiometer or simple colorimeter with filters.

Reagents

Vanadium molybdate reagent

Dissolve 40 g ammonium molybdate in approximately 200 ml dist. water. Dissolve 1 g ammonium meta-vanadate A.R. in 200 ml dist. water and 200 ml conc. nitric acid A.R. Add the ammonium molybdate solution to the vanadate solution while stirring and finally make up to 1 litre. Store in a dark place.

Solution A

40 ml conc. sulphuric acid A.R. and 10 g sod. sulphate anhydrous A.R. made up to 1 litre with water. This solution is used in the standards only to match the acid and salt concentration in the samples.

Stock phosphate solution (12,5 ppm)

Dissolve 0,054 9 g KH_2PO_4 oven-dried in dist. water and make up to 1 litre.

Procedure

1. Take a 5 ml aliquot of the above digest into a 50 ml beaker and make to 15 ml with dist. water.
2. Add 4 ml vanadium molybdate reagent and stir.
3. After minimum 10 mins. to develop colour read at 420 millimicrons on spectrophotometer. Prepare a reagent blank from the digest blank and subtract this absorbance from the sample reading.

Standards

1. Pipette 2, 3, 4, 5 ml of 12,5 ppm P solution into 50 ml beakers. Make all volumes to 5 ml with dist. water. These standards represent 0,10, 0,15, 0,20, 0,25% P.
2. Add 10 ml solution A to each standard.
3. Colour up in exactly the same way with vanadium molybdate reagent and read the absorbances in series with the samples. Prepare a "standard" blank in exactly the same way using dist. water instead of stock phosphate solution. Subtract this blank from the standard absorbance. That is to say, standards and samples are both read against dist. water — the reagent blank being subtracted from the samples and the "standard" blank from the standards.
4. Standard curve has been found to be always linear and almost exactly reproducible from day to day. Thus, after checking for a few days that procedure is satisfactory, it is only usually necessary to prepare two standards daily — say, 0,15 and 0,25% P.

Determination of nitrogen by micro distillation

Introduction

Attempts were made to evolve a colorimetric method for nitrogen on the above digest using Nessler's reagent. Good reproducibility could not be obtained despite various methods of preparing the reagent and careful adjustment of pH. We were left with the impression that Nessler's reagent, however carefully prepared, is most unreliable and, in any case, is known not to remain stable for very long.

Careful attention was also paid to timing of colour development but no improvement was observed. The method was finally abandoned for a micro distillation of the digest into a boric acid-indicator solution.

Instrumentation

The use of the Metrohm Multi Dosimat motor driven burette (manufactured by Metrohm AG Switzerland) for titrating the ammonia from the distillation greatly enhances the accuracy and reproducibility of this determination. It is expensive (about R$300 in Rhodesia) but vastly superior to the best conventional micro-burette obtainable. One short touch of the remote control button delivers 0,01 ml which is read off a visual digital counter. At the touch of another button the instrument automatically zeroes. Furthermore, the instrument has the advantage of complete interchangeability of the piston/reservoir assembly enabling one to use it immediately, without cleaning, for another titration.

Steam distillation apparatus

Any of the classical semi-micro distillation units can be used — e.g. the Markham, Hoskins or Parmas and Wagner apparatus. We use the apparatus described by Bremner (1965 p. 1196). Minor variations in specification may well be important and we are grateful to S.A.S.A. Experiment Station for the loan of their apparatus as a prototype for manufacture. It consists essentially of a 100 ml Pyrex Kjeldahl flask with ground glass joints to be used as the distillation apparatus attached by spiral steel springs and glass hooks. Steam is generated in a 5 litre flask and passes via a trap down an internal glass tube to discharge below the sample level, and thence via another trap to a Liebig condenser. A ground-glass plug is incorporated in the steam delivery tube to discharge steam to waste when not distilling.

Notes on operation of distillation apparatus

1. A variable transformer coupled to the heating mantle of the boiling flask facilitates the production of exactly the right quantity of steam which should be adjusted to collect approximately 30 ml of distillate in four mins.
2. Ideally, the flow of cold water through the condenser should be such that the temperature of the distillate does not exceed about 22°C. This is not always possible with our very high ambient temperatures but, nevertheless, our reproducibility is good (standard deviation <3% at values around 2,00% N).
3. A small amount of H_2SO_4 will trap any ammonium in the boiling flask water.

Reagents

1. Chlorazol sky blue-boric acid indicator*
   This is made up as follows:
   (a) Dissolve 0,20 g chlorazol sky blue in 100 ml H_2O.
   (b) Dissolve 0,08 g methyl red in 200 ml ethanol.
   (c) Take 10 ml of (a) and 20 ml of (b) and make up to 100 ml with 2% boric acid.
   Use 5 ml per sample and titrate to a standard purple colour made up as follows:
   Mix 10 ml of (a) and 20 ml of (b) and pipette 5 ml of this mixture into a 100 ml Erlenmeyer flask. Then add 25 ml of 9,07 g.p.l. potassium di-hydrogen phosphate solution. The resultant colour represents the end-point.
2. 0,014 28 N H_2SO_4: prepared by diluting 142,8 ml of 0,1 N H_2SO_4 to 1 litre. (1 ml = 200 micro-grammes N.)
3. 1 N NaOH solution: (i.e. 40 g.p.l.).

Procedure

1. Pipette 5 ml of boric acid-indicator solution into a 100 ml Erlenmeyer flask and place the flask below the condenser so that the tip is about 2 cm above the solution level.
2. Transfer a 10 ml aliquot from the above digest (including the reagent blank), add 10 ml of 1 N NaOH solution from a tilting measure. Place flask on to distillation apparatus (two small springs are hooked on to the flask to prevent its blowing off), place ground glass plug in steam discharge orifice and commence distillation. As soon as distillate appears at tip of condenser set timer for four minutes and distil for this period (approximately 30 ml should have distilled over).
3. Place Erlenmeyer flask on magnetic stirrer and titrate from green to purple colour, matching the end-point with the standard colour prepared. Subtract the blank titration from all sample titrations.
   Ml titration × 0,4 = % N (for 10 ml aliquot of above digest).

Determination of K, Ca and Mg by atomic absorption spectrophotometer

Introduction

All the above elements are satisfactory by atomic absorption but the $SO_4^=$ concentration tends to depress absorbance on K and the curve flattens somewhat at concentrations corresponding to 1,0 - 1,2% K.

In accordance with standard practice we at one time used lanthanum alone to counteract the interference of phosphorus on Ca and Mg. Strontium cannot, of course, be used because of the insolubility of strontium sulphate. However, we did not get good reproducibility generally using lanthanum for some reason not yet determined. E.D.T.A. is the other alternative for calcium but it is known that phosphorus interference on Mg is actually increased in the presence of Ca when E.D.T.A. is used (Robinson 1966). Nevertheless, we found that E.D.T.A. enhanced the rather marginal sensitivity of Ca and gave more stable conditions. We therefore decided to use E.D.T.A. and to correct the interference of phosphorus on Mg by adding to the standards an amount of phosphorus equivalent to that present in

* Details of indicator supplied by R. A. Wood, South African Sugar Association Experiment Station, Mount Edgecombe.

the leaf, which is fairly constant at 0,20-0,25% P. This procedure gave fairly good reproducibility but we later found that the addition of both lanthanum and E.D.T.A. gave the best results.

Instrumentation

A Unicam SP 90 with recorder is used throughout.

Reagents

Lanthanum nitrate 2%
E.D.T.A. (di-sodium salt) 0,5%
Sodium sulphate (anhydrous) A.R.
Conc. sulphuric acid A.R.
Phosphoric acid A.R. 0,15%.

Procedure

Take a 5 ml aliquot from the above digest into a 50 ml beaker and add 5 ml lanthanum nitrate 2% and 5 ml E.D.T.A. 0,5%. This solution is atomised direct for K, Ca, Mg. Subtract reagent blank absorbance from all sample readings.

Preparation of standards

1. Make up the following stock solutions:
   500 ppm K . . . . . 0,953 4 g KCl/litre
   50 ppm Ca . . . . . 0,124 9 g $CaCO_3$/litre
   50 ppm Mg . . . . . 0,050 0 g Mg metal litre
   (Use minimum amount of HCl to dissolve the $CaCO_3$ and Mg)
   These solutions keep for some months at least.
2. Take aliquots given below into 100 ml vol. flasks:

Std.	*Ca and Mg*	*K*
I	3 ml ≡ 0,09%	2 ml ≡ 0,60%
II	5 ml ≡ 0,15%	3 ml ≡ 0,90%
III	10 ml ≡ 0,30%	4 ml ≡ 1,20%
IV	15 ml ≡ 0,45%	5 ml ≡ 1,50%

   Add in this order:
   Make to approx. 45 ml with H_2O.
   Add 2,5 ml 0,15% phosphoric acid.
   Add 0,66 g sodium sulphate (anhydrous).
   Add 30 ml 2% lanthanum nitrate.
   Add 30 ml 0,5% E.D.T.A.
   and make up to the mark with de-ionised water. These standards are stable for approximately three days. They definitely deteriorate with age. This also applies to the sample digest solutions and in practice we never keep them more than two days.
3. Prepare a "standard" blank in exactly the same way as the standards but substituting water for the above aliquots. Read standards and samples against water and subtract standard blank from standard readings and reagent blank from sample readings.

Determination of sulphur on tube furnace

Introduction

The author has done a considerable amount of investigational work on the determination of sulphur on a tube furnace at 1 000°C-1 200°C (depending on the material). As a result of this, a very satisfactory method was evolved for products very low in organic matter and high silica (mainly mine products). Briefly, the method involves heating in a stream of oxygen in the above temperature range, converting all sulphur to SO_2 which, on bubbling through weak hydrogen peroxide solution, is oxidised to SO_3 and hence forms H_2SO_4. This is titrated against standard sodium borate using a suitable indicator. There is also another furnace method in use (mainly in the USA) in which iodine is liberated from a KIO_3/KI solution and the iodine reduced with the evolved SO_2 (Rice-Jones 1953). The method is rather complicated (particularly in unskilled hands) because only a very slight excess of liberated iodine can be allowed in the bubbler and this is controlled by the slow addition of standard KIO_3 as the SO_2 reduces the slight excess iodine (using starch indicator). Furthermore, there is the additional complication that some SO_3 may be formed in the furnace and this will not reduce iodine; thus necessitating a set of physical conditions favouring the production of SO_2 (e.g. temperature, oxygen flow, rate of cooling of evolved gas, size of sample, etc.). In the above-mentioned H_2SO_4 titration these problems are eliminated.

It was natural, therefore, that we should turn our attention to evolving a furnace method for sulphur on plant material. It was realised, of course, that all, or most of, the organic matter would have to be burnt off prior to insertion of the sample in the tube furnace. It was also realised that some pre-treatment would be required to avoid loss of sulphur during this ashing process. Various oxidising agents were tried, e.g. HNO_3/bromine, Eschka's mixture (MgO/Na_2CO_3) etc., without success.

In the classical gravimetric method for plant material (which we used but which is rather tedious and time-consuming) the sample is wetted with saturated magnesium nitrate solution, heated on a hot-plate at about 180°C until evolution of nitrous

TABLE II

Operating Parameters on S P 90

Element	Wavelength Å	Air l.p.min.	Acetylene l.p.min.	Lamp Current milliamps	Slit Millimeters	Burner Height cm	Scale Expansion
K	7 665	5,5	1,4*	20	0,05	0,8	Nil
Ca	4 227	5,5	1,6+	10	0,05	1,0	X2.
Mg	2 852	5,5	1,6+	4	0,05	0,8	Nil

* Lean flame — i.e. Oxidising
\+ Slightly rich flame — i.e. Reducing
× Burner must be angled to reduce sensitivity

fumes has ceased, ashed at 500°C, dissolved in HCl, filtered and bulked to about 200 ml, pH adjusted and $BaCl_2$ added to precipitate sulphur as $BaSO_4$, which is filtered and weighed. We therefore thought it likely that this pre-treatment with magnesium nitrate would be suitable for the tube furnace determination. Such proved to be the case. The only drawback is the substantial increase in bulk due to the remaining magnesium oxide necessitating the use of rather large boats and rather small sample weight (0,5 g) for the levels of S in our samples (about 0,20%). We are not yet entirely satisfied with our standard deviation on the furnace nor our furnace checks with the gravimetric method. Nevertheless, it is not an easy, or particularly accurate analysis, even when done gravimetrically by skilled personnel. We therefore consider the following preliminary results encouraging. They are presented incomplete at this stage as further test work must be done before we would feel justified in adopting this as our standard procedure.

TABLE III

Comparison of Sulphur Results by Gravimetric and Furnace Methods

Sample No.	Gravimetric % S	Furnace % S
1	0,22 0,22 } Mean 0,22	0,23 0,22 0,20 0,22 0,27 (?) } Mean 0,23
2	0,28 0,27 } Mean 0,28	0,26 0,29 0,29 0,29 0,32 (?) } Mean 0,29
3	0,27 0,25 } Mean 0,26	0,27 0,26 } Mean 0,27
4	0,23 0,22 } Mean 0,23	0,20 0,23 0,21 0,18 0,27 (?) } Mean 0,22
5	0,26 0,28 } Mean 0,27	0,26 0,30 } Mean 0,28
6	0,26 0,23 } Mean 0,25	0,28 0,26 } Mean 0,27

Instrumentation

The Gallenkamp twin tube furnace FS 235 (1 200°C maximum) tube bore 3,8 cm length 30 cm (i.e. size 1) was used. The fused silica work tubes are not supplied with the furnace and were manufactured by a Johannesburg glassworks. The design is shown in the diagram below (Figure 1).

The advantage of this design is that the oxygen is heated somewhat while passing between the inner and outer tube before coming in contact with the sample. The oxygen is passed through soda-lime

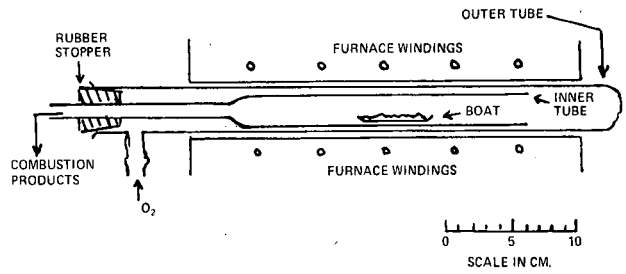

FIGURE 1: Work tube arrangement in furnace for sulphur determination.

and magnesium perchlorate prior to entry into the tubes to remove any CO_2 and H_2O. For plant material we have found that a temperature of 1 000°C is adequate. 90% of the S is in the form of cysteine and methionine (Allway and Thompson 1966). The oxygen flow is not very critical but should not be excessive — it is <1 litre/min on our flowmeter. We have found 10 mins combustion to be adequate. The tubes and bubblers from the Leurquin micro nitrogen apparatus make excellent absorption vessels. (Quickfit No. 11 MC 44 MC).

Reagents

Mixed indicator
Mix equal parts of methyl red (0,1% in alcohol) and methylene blue (0,1% in alcohol).
Sodium borate
2,120 g.p.l. A.R.
Saturated magnesium nitrate
Dissolve 960 g $Mg(NO_3)_2.6H_2O$ A.R. in 1 litre water (It should not contain more than 0,01% SO_4).
Hydrogen peroxide
30 ml of 100 vol. (30%) in $2\frac{1}{2}$ litres.

Procedure

1. Weigh 0,5 g fine-milled sample into a fused silica crucible (approximately 5 cm dia. × 3,5 cm deep) add exactly 3 ml saturated magnesium nitrate solution and agitate and stand for a few minutes to ensure complete wetting of particles. This amount of magnesium nitrate is adequate for our sulphur levels but higher levels may well require more.
2. Place crucibles on hot plate (not > 180°C). After evaporation of H_2O is finished nitrous fumes will be evolved and sample will rise into a spongy mass.
3. When all reaction is complete (about 20 mins) transfer while hot to muffle furnace and ash at 500°C — it is convenient to do this overnight.
4. Remove from muffle, break up mass of sample and MgO, and transfer with a small brush into a suitable boat (previously ignited) — about 9 × 1,5 × 1,2 cm will conveniently contain the material.
5. Transfer to tube furnace at 1 000°C, adjust oxygen flow and absorb combustion gases for 10 minutes.
6. Add a few drops of mixed indicator and titrate with a micro burette (or, better, the

Metrohm Dosimat Motor Burette) from magenta to greyish-green (pure green is over-titrated) 1 ml of 2,120 g.p.l. sodium borate — 0,04% C (0,5 g sample).

7. Always run a blank with 3 ml saturated magnesium nitrate and deduct blank titration from sample titration. It is good practice to include one or two samples from the previous batch as checks.
8. It is necessary, if the Leurquin tubes are used as absorption vessels, to transfer the contents to a suitable flask for titration. Also, the inner furnace tube and associated tubing (which should be as short as possible) must be washed into the flask with water to recover any small amount of SO_2 dissolved in moisture in the tubes. The furnace tube should be allowed to cool adequately before doing this otherwise it tends to deteriorate after a few weeks' use. It is convenient to have two sets of inner tubes and associated tubing so that while the next pair of samples is in the furnace the titration of the previous pair may be performed.
9. No sulphur contamination from the rubber stopper has been observed by the author during ± 1 000 determinations on mine products (some very low in S) despite the fact that the stopper tends to get very hot. Trouble has been experienced with heat transference from the furnace tubes to the polythene tubes at the point of contact. This was overcome by using a short length of Teflon tubing in contact with the tubes. Teflon cannot be used over the whole length as it is not flexible enough.

Determination of trace elements (Fe, Mn, Zn, Cu, Ni, Na)

Introduction

These determinations will only be described very briefly since they present no particular difficulty on atomic absorption. The only controversial matter is the decision as to what acid will be used to dissolve the metals in the ash. After many years' experience in heavy metal analysis by A/A, the author has come to the conclusion that nitric acid is the best medium except where there are special contra-indications. Hydrochloric acid and aqua regia have been used — sulphuric acid is to be avoided, if possible, as, in general, it depressed absorbance.

Procedure

Briefly, 5 g of sample are ashed in fused silica dishes at 550°C. 15 ml of 50% nitric acid is added, boiled for about a minute, cooled and transferred quantitatively to 50 ml vol. flasks, then made up to volume with de-ionised water. Filtering is not necessary, the supernatant being atomised direct from the flask after the insoluble matter has settled. The wavelengths are: Fe 2480Å; Mn 2795Å; Zn 2140Å; Cu 3247Å; Ni 2320Å; Na 5890Å. Care must be taken when setting the monochromator for Fe, Zn and Ni as there are several strongly emitting lines in the vicinity of the above wavelengths which do not absorb at all. The Ni line at 2320Å is actually a doublet when scanned and the one peak does not absorb; furthermore, a good monochromator is necessary to resolve these peaks and our instrument is somewhat lacking in this respect. A blank should be run using 15 ml of 50% nitric acid made up to 50 ml with de-ionised water. The risk of contamination at these low levels is ever-present and all glassware, etc., should be scrupulously cleaned.

Standards

Three standards are prepared by first transferring the following to three 100 ml vol. flasks: 15 ml Conc. HNO_3; 0,02 g Mg metal; 0,04 g $CaCo_3$; 0,10 g KH_2PO_4 (all A.R. grade). Aliquots of stock solutions are then added as shown in Table IV and the flasks made to volume with de-ionised water. These standards are stable for some months and satisfactory for all elements except Zn which, owing to some inter-element interference, deteriorates rapidly. It is necessary, therefore, to make up separate Zn standards by pipetting 5, 10, 20 ml of Zn stock solution, adding 15 ml of conc. HNO_3 and making up to 100 ml with water. These standards are then equivalent to 10, 20, 40 foliar ppm respectively. Whatever Zn interference occurs in the mixed standards, it does not appear to occur in the samples, for these pure Zn/HNO_3 standards give good results which have been checked independently (as, indeed, have the other elements).

TABLE IV

Showing Stock Trace Element Solutions and Aliquots for Standards

		MIs %			≡ Foliar ppm		
Stock	ppm	I	II	III	I	II	III
Fe	100	5	10	20	50	100	200
Mn	100	2	5	10	20	50	100
Zn	20	5	10	20	See Last Paragraph of methods		
Cu	10	5	10	20	5	10	20
Ni	10	2	5	10	2	5	10
Na	1 494	1	2	4	150	300	600

Determination of boron

Introduction

We use a curcumin/ethanol colorimetric procedure, the advantage over other methods being that it avoids the use of concentrated sulphuric acid. The method has been in use for some considerable time at the Department of Chemistry and Soil Science, Salisbury (Fenner 1970).

Reagents

Curcumin/oxalic acid
0,04 g curcumin and 5 g oxalic acid in 100 ml 95% ethanol.
Hydrochloric acid
0,2 N (A.R.)

Procedure

1g sample is ashed at 550°C in fused silica dishes, the ash dissolved in 0,2 N HCl, transferred quanti-

TABLE V

Reproducibility of Analytical Procedures

	N	P	K	Ca	Mg
No. of Det.	29	33	30	20	20
Range: Lowest %	1,26	0,12	1,05	0,31	0,09
Highest %	1,32	0,14	1,13	0,36	0,10
Mean Value %	1,29	0,13	1,09	0,34	0,09
Std. Deviation	±0,024	±0,0025	±0,021	±0,015	±0,005
C. V. %	1,86	1,60	1,93	4,41	5,67

tatively to graduated 50 ml polythene beakers and made to 50 ml with 0,2 N HCl. A 1 ml aliquot is now transferred into fused silica dishes, 4 ml of curcumin/oxalic acid solution added and mixed by rotation. The dishes are now evaporated to dryness on a water bath 55°C ± 3°C, then baked at the same temperature for 15 minutes. 25 ml ethanol 95% is now added and the contents well titurated with polythene covered rod. The solution is then filtered through previously leached (twice with dil. HCl — 1 part acid to 4 parts de-ionised water — and twice with de-ionised water) into a 25 ml polythene stoppered container.

Standards

Standards are prepared in exactly the same way by taking 1 ml of 0,5, 1,0, 1,5 ppm B which are equivalent to 25, 50, 75 ppm foliar B. A blank is always run and standards and samples read against it at 540 millimicrons.

Boron levels in some areas may necessitate the use of a lower range of standards.

Discussion on the system as a whole

The object of the foliar analysis of sugarcane is to check on the nutritional status of the field. It is imperative that all the foliar samples are taken at the same age (in our case ± 5 months) since levels of nutrients vary considerably during the crop life and varietal differences are also quite marked. The results of any year's foliar analysis are generally too late to correct any deficiencies observed in that crop (although occasionally, perhaps, this might be of benefit). The results are, however, extremely useful when used in conjunction with soil analysis samples taken routinely at the time of cutting (usually about 12 months under our conditions). Accordingly, we correlate foliar and soil analysis when making fertiliser recommendations. The above system is rapid, economical and reasonably accurate.

An evaluation of analytical variability was carried out recently: over 30 separate digests were made on different days from the same sample. These were analysed in the standard manner, giving the results shown in Table V.

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