THE FLAME SPECTROPHOTOMETRIC DETERMINATION OF POTASSIUM, SODIUM, CALCIUM AND MAGNESIUM IN COCONUT WATER

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The use of coconut water analysis as a guide to the nutrition of the coconut palm was first investigated in Ceylon by Salgado (1, 2). His work has been confined mainly to potassium estimations and shows that the uptake of potassium, as measured by the concentration in the coconut water, is related to the degree of response to potassic fertilizers and to the yield of coconuts in Ceylon. Cassidy (3) has also attempted to relate the potassium content of the nut water with the poor condition of palms in Fiji, but came to the conclusion, based on Salgado's figures, that potassium deficiency was not likely to be a factor in their decline.

Coconut water provides a unique sampling medium in that nuts are easily collected on the ground under individual palms and representative samples of large areas can be taken during the normal harvesting and production procedures. Leaf analysis would involve climbing the palms to cut off fronds, and to obtain representative leaf samples would be a slow and laborious task. It is thought that a system of co-ordinated soil and coconut water analysis may be useful in the diagnosis of the many coconut nutrition problems of Papua and New Guinea.

Salgado (2) used the rather time consuming gravimetric cobaltinitrite method without preliminary treatment for the determination of potassium in routine samples. However, he suggested that the use of flame photometric methods carried out directly on coconut water would be more expeditious for large scale routine analysis. The purpose of the present investigation was to determine whether such methods were sufficiently accurate and precise, not only for the estimation of potassium, but for the other cations in coconut water.

Materials and Methods.

Samples of coconut water, preserved from excessive fermentation by the addition of formaldehyde (1 ml. per 100 ml. sample) were filtered and diluted ten times with distilled water for the estimation. The purpose of the dilution was to bring the concentrations of the cations to within a more accurate range of the instrument and for the convenience of interference and recovery studies.

The instrument used was a Beckman Model D.U. Spectrophotometer with photomultiplier attachment, and oxygen-acetylene flame accessory.

A series of nut water samples taken from Baibara, Papua, and New Ireland, on various soil types, was analysed in a trial run to find the range of concentrations likely to occur during routine work. No allowances were made for interferences or other inaccuracies in the flame method. The results are listed in Table 1. They indicate that the range of concentrations is very wide for all cations. The average concentrations given by Salgado (2) are 32 milli-equivalents per litre for potassium, 4.8 for sodium and 14.3 for calcium. Magnesium is reported to be present in much smaller amounts than calcium. It is apparent from some of the values obtained here that the part played by sodium may be important as it can replace potassium as the dominant cation in the nut water.

Stock standard solutions were made up as follows :—

1. *Potassium.* 100 milli-equivalents per litre. Dissolve 7.456 g. dried A.R. potassium chloride in distilled water and make to one litre.
2. *Sodium.* 100 milli-equivalents per litre. Dissolve 5.846 g. dried A.R. sodium chloride in distilled water and make to one litre.
3. *Calcium.* 25 milli-equivalents per litre. Dissolve 1.251 g. dried calcium carbonate in 25 ml. NHCl. and dilute to one litre with distilled water.
4. *Magnesium.* 50 milli-equivalents per litre. Dissolve 0.61 g. cleaned magnesium ribbon in 50 ml. NHCl. and make to one litre.

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TABLE 1. APPROXIMATE CONCENTRATION OF CATIONS IN NUT WATER FROM VARIOUS SOIL TYPES OF PAPUA AND NEW GUINEA.

Sample No.	Potassium m.e./litre	Sodium m.e./litre	Calcium m.e./litre	Magnesium m.e./litre
Baibara A	71.5	7.0	16.0	18
B	55.0	20.5	16.0	18
C	69.0	2.4	16.3	14
D	71.6	6.5	18.0	19
E	78.0	8.2	10.0	14
F	53.7	5.6	8.0	9
New Ireland 1	70.4	21.6	11.5	16
2	65.8	14.0	15.3	19
3	67.2	5.6	13.3	14
4	11.5	39.8	20.3	14
5	65.8	3.0	16.0	16
6	70.4	3.2	15.3	12
7	5.1	67.3	12.0	2
8	5.8	68.4	12.5	3
9	14.1	61.8	12.5	9

The calcium and magnesium solutions were standardized by titration with E.D.T.A. using the method of the U.S. Salinity Laboratory for calcium and magnesium in irrigation waters (4).

These stock solutions were diluted to make up the standard solutions for the flame photometric determinations, the details being set out in Table 2, together with the instrument settings and wave lengths used. Typical calibration curves obtained for the various cations are shown in Figures 1 to 4. Little difficulty was experienced in the estimations except for magnesium, where the sharp arc line at 285.2 milli-microns was used. With the photomultiplier at full sensitivity there were large fluctuations of the meter needle and also a high background reading. Following on the work by Knutson (5), an increased ratio of acetylene to oxygen was used, and more sensitivity was achieved. However, the accuracy of this determination is probably not better than ± 5 per cent.

The flaming of the diluted coconut water samples was carried out after the original solutions had been filtered through two

TABLE 2. FLAME SPECTROPHOTOMETER INSTRUMENT SETTINGS.

Element Determined	Range of Concentration m.e./litre	Slit Width m.m.	Oxygen Pressure lb.p.s.i.	Acetylene Pressure lb.p.s.i.	Wave Length used millimicrons	Phototube
Potassium	0-10	0.10	10	3	770	Red Sensitive.
Sodium	0-10	0.05	10	3	590	Blue Sensitive with photomultiplier.
Calcium	0-2.5	0.04	10	3	423	Blue Sensitive with photomultiplier.
Magnesium	0-5	0.05	8	5	285	Blue Sensitive with photomultiplier.

Whatman No. 5 filter papers, and diluted ten times. The standard oxy-acetylene burner worked satisfactorily for these samples although after many estimations there was a tendency for an incrustation to form on the burner tip due to the organic matter present in the coconut water. Test samples containing 1 per cent. of formaldehyde gave no difference in the emission of the coconut water solutions. The dilution errors involved in adding formaldehyde to the original solutions have been neglected throughout all the determinations.

Experimental Results.

In estimating the accuracy of these flame photometric methods, the effects of the cations, anions and organic matter on the flame emissions at the particular wave lengths and instrument settings were investigated. Recoveries of cations (Table 3) showed that the potassium estimation was highly accurate; the sodium recoveries being consistently slightly high while the magnesium recoveries varied but in the main were low. As was expected the calcium recoveries were low due to the depressing effect of the other ions present.

For the investigation of the anion and organic matter interference on the emission of the cations, 10 ml. samples of undiluted coconut water were passed through columns of the cation exchange resin Amberlite IR-100(H). The cations were completely sorbed, the effluents giving no emission for the four cations. The cations were then released by passing 3N hydrochloric acid through the columns until no trace of the cations was found in the eluate. The acid solutions were evaporated to dryness and the chlorides dissolved and made to a volume of 100 ml. The evaporated solution showed no trace of organic matter, indicating no adsorption on the resin.

A similar series of 10 ml. samples of coconut water was treated in the same way but instead of making the solutions of chlorides to volume, the calcium was precipitated as calcium oxalate. The precipitate was centrifuged, washed, and dissolved in a small amount of dilute hydrochloric acid and made to volume.

The results of the flame estimations for these two series of samples, together with the diluted original solutions are shown in Table 4. The emission of potassium, sodium and magnesium are relatively unaffected by the organic matter and the anions present in the coconut water. Results show the large negative effect on the flame emission of calcium by the anions and organic matter. However, the positive effect of the other cations largely offsets this effect and in most cases the results obtained for the diluted original solution of a varied series of samples are not widely divergent from the calcium result determined after separation as calcium oxalate.

The effects of added cations on the emission of the cation to be determined are shown in Tables 5 to 8. The experimental results show that apart from a slight enhancement of the potassium flame by increased sodium, only the emission of calcium is markedly affected. There is a large positive effect by potassium and a smaller but significant positive effect by sodium. Magnesium, however, decreases the flame emission considerably. The interfering cations were added singly and in concentrations which could be expected in this type of sample.

When many coconut water samples are being received for analysis it is often necessary to store them for several weeks before the analysis can be carried out. An investigation was made to show the effect of storage and deterioration of the sample on the analysis figures. Results which are listed in Table 9 show that there is no great effect despite fermentation and heavy discolouration of samples after storing for three months with formaldehyde added. There is a tendency for the increase in concentration of potassium, calcium and magnesium with a slight opposite effect for sodium.

Discussion.

The estimation of the four principal cations in coconut water can be carried out in a rapid manner, up to 100 samples being analysed in a day and so far over 1,000 samples of nut water have been analysed for the four cations. A complete study of the variation of cation content in coconuts from the same palm and from palms in the same area has not yet been made but indications are that cations can vary considerably between palms in the same vicinity. It is likely, therefore, that sampling variations will be much greater than errors involved in the estimations, with the possible exception of calcium, unless the bulking of many samples

TABLE 3. RECOVERIES OF ADDED CATIONS, m.e./litre.

Sample No.	Potassium added	Potassium found	Per Cent. Recovery	Sodium added	Sodium found	Per Cent. Recovery	Calcium added	Calcium found	Per Cent. Recovery	Magnesium added	Magnesium found	Per Cent. Recovery
1	0	1.12	....	0	5.38	....	0	0.99	....	0	0.72	....
1	2.50	3.70	103	2.50	7.90	101	1.00	1.83	84	1.00	1.72	100
1	5.00	6.10	100	....	....	....	2.00	2.54	78	2.00	2.77	103
2	0	4.30	....	0	3.70	....	0	1.53	....	0	0.91	....
2	2.50	6.79	100	2.50	6.30	104	1.00	2.32	79	1.00	1.86	95
2	5.00	9.28	100	5.00	9.00	106	....	....	....	2.00	2.90	100
3	0	2.81	....	0	4.40	....	0	1.50	....	0	1.00	....
3	2.50	5.34	101	2.50	7.00	104	1.00	2.31	81	1.00	1.90	90
3	5.00	7.70	98	5.00	9.60	104	....	....	....	2.00	2.90	95
4	0	3.03	....	0	3.30	....	0	0.71	....	0	0.67	....
4	2.50	5.53	100	2.50	5.96	106	1.00	1.62	91	1.00	1.60	93
4	5.00	7.97	99	5.00	8.52	104	2.00	2.43	86	2.00	2.49	91

TABLE 4. ANION AND ORGANIC MATTER INTERFERENCE ON DETERMINATION OF CATIONS IN COCONUT WATER.

(Concentration in m.e./litre, diluted solution.)

Sample No.	Potassium found		Sodium found		Calcium found			Magnesium found	
	(1)	(2)	(1)	(2)	(1)	(2)	(3)	(1)	(2)
59	1.96	1.96	5.00	5.00	0.80	1.03	0.89	2.1	2.1
88	2.34	2.34	4.63	4.50	1.56	1.68	1.56	2.0	1.8
91	1.28	1.28	6.00	5.88	1.21	1.42	1.25	2.1	2.0
131	7.10	6.96	0.61	0.58	1.06	1.18	....	1.9	1.7
132	6.80	6.67	1.36	1.36	1.18	1.36	1.21	1.7	1.6
145	7.54	7.70	0.58	0.61	1.21	1.25	1.15	1.3	1.1
171	2.70	2.70	5.31	5.17	0.68	0.88	0.74	1.0	1.0
177	3.21	3.21	4.16	4.16	0.80	1.00	0.80	1.0	1.1
182	3.04	3.04	4.22	4.16	0.95	1.18	1.00	1.4	1.3
188	3.50	3.50	2.40	2.40	1.12	1.27	....	1.4	1.4

(1) Original solution, diluted ten times. (2) Free of organic matter, all anions as chlorides. (3) Calcium, free from other cations.

EFFECT OF ADDED CALCIUM ON ESTIMATION OF POTASSIUM, SODIUM AND MAGNESIUM.

Sample	Potassium found, m.e./litre			Sodium found, m.e./litre			Magnesium found, m.e./litre		
	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)
1	1.13	1.14	1.11	5.35	5.30	5.35	0.70	0.72	0.75
2	4.23	4.23	4.23	3.74	3.76	3.73	0.91	0.98	0.98
3	2.85	2.80	2.78	4.38	4.40	4.44	1.04	1.07	1.04
4	3.00	3.01	3.03	3.24	3.30	3.33	0.67	0.60	0.63

(a) No Calcium added. (b) Calcium concentration increased by 1.0 m.e./litre. (c) Calcium concentration increased by 2.0 m.e./litre.

TABLE 6. EFFECT OF ADDED POTASSIUM ON ESTIMATION OF SODIUM, CALCIUM AND MAGNESIUM.

	Sodium found, m.e./litre			Calcium found, m.e./litre			Magnesium found, m.e./litre		
	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)
1	5.32	5.35	5.32	0.97	1.09	1.16	0.85	0.80	0.75
2	3.76	3.78	3.80	1.50	1.62	1.70	0.98	0.88	0.91
3	4.52	4.48	4.50	1.51	1.63	1.78	1.10	1.14	1.14
4	3.42	3.43	3.42	0.72	0.77	0.80	0.60	0.63	0.65

(a) No Potassium added. (b) Potassium concentration increased by 2.5 m.e./litre. (c) Potassium concentration increased by 5.0 m.e./litre.

TABLE 7. EFFECT OF ADDED SODIUM ON ESTIMATION OF POTASSIUM, CALCIUM AND MAGNESIUM.

Sample	Potassium found, m.e./litre			Calcium found, m.e./litre			Magnesium found, m.e./litre		
	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)
1	1.14	1.15	1.18	0.99	1.06	1.09	0.70	0.72	0.70
2	4.28	4.38	4.37	1.50	1.56	1.60	0.91	0.88	0.88
3	2.78	2.81	2.90	1.51	1.57	1.64	1.00	1.07	1.14
4	2.99	3.05	3.07	0.71	0.72	0.75	0.67	0.63	0.67

(a) No Sodium added. (b) Sodium concentration increased by 2.5 m.e./litre. (c) Sodium concentration increased by 5.0 m.e./litre.

TABLE 8. EFFECT OF ADDED MAGNESIUM ON THE ESTIMATION OF POTASSIUM, SODIUM AND CALCIUM.

Sample	Potassium found, m.e./litre			Sodium found, m.e./litre			Calcium found, m.e./litre		
	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)
1	1.13	1.12	1.13	5.15	5.17	5.20	0.96	0.88	0.78
2	4.23	4.27	4.28	3.69	3.74	3.69	1.48	1.37	1.22
3	2.78	2.73	2.72	4.43	4.30	4.31	1.50	1.37	1.27
4	2.99	2.97	2.99	3.27	3.27	3.30	0.71	0.61	0.56

(a) No Magnesium added. (b) Magnesium concentration increased by 1.0 m.e./litre. (c) Magnesium concentration increased by 2.0 m.e./litre.

TABLE 9. CHANGES IN CATION CONTENT AFTER STORAGE FOR THREE MONTHS.

(Concentration in m.e./litre, undiluted nut water.)

Sample No.	Potassium found		Sodium found		Calcium found		Magnesium found		Colour.
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	
64	26.0	27.9	51.5	50.0	7.7	8.3	8	10	Clear.
58	17.2	18.5	45.6	44.2	9.2	9.8	12	13	Clear.
101	37.0	39.0	30.0	30.1	12.7	13.6	17	18	Clear.
112	21.9	23.4	45.6	44.2	9.5	10.0	13	15	Clear.
98	27.8	27.9	31.2	30.1	10.9	11.5	8	9	Yellow.
75	21.9	22.7	50.0	48.7	10.6	11.5	16	14	Yellow.
36	41.2	41.2	37.4	36.1	7.7	7.7	15	13	Brown.
33	27.0	27.0	41.5	41.6	10.6	10.0	20	22	Brown.
19	22.8	24.3	48.8	48.7	7.1	7.4	12	13	Brown.
89	29.5	30.4	41.5	50.0	10.6	11.5	11	13	Brown.
67	35.0	37.1	44.2	44.2	11.5	12.1	16	16	Yellow-Brown.
83	23.5	22.8	45.6	44.2	4.3	4.6	9	10	Yellow.

(a) Original Estimation. (b) Estimation after three months' storage.

TYPICAL CATION CALIBRATION CURVES.

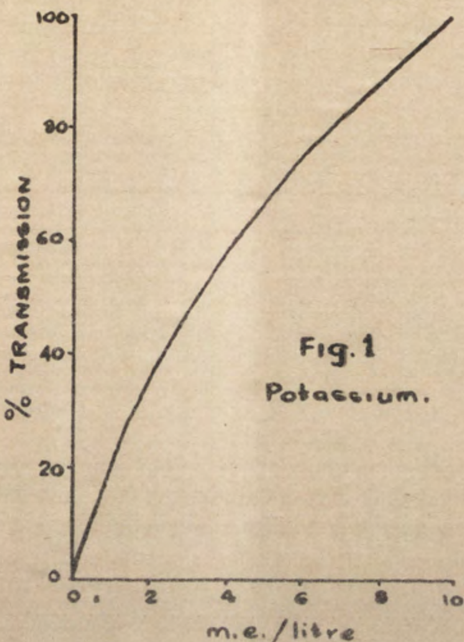

Fig. 1
Potassium.

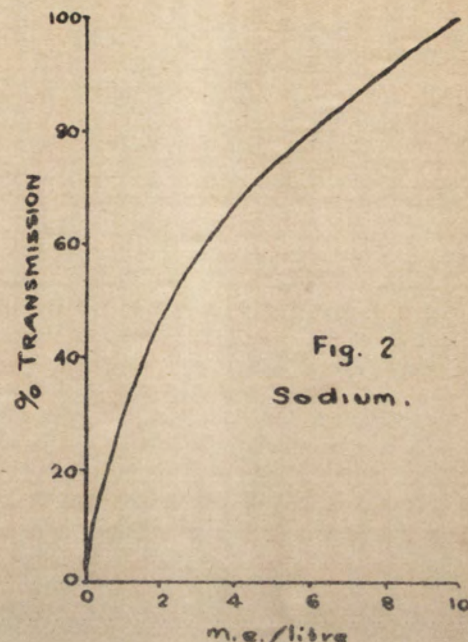

Fig. 2
Sodium.

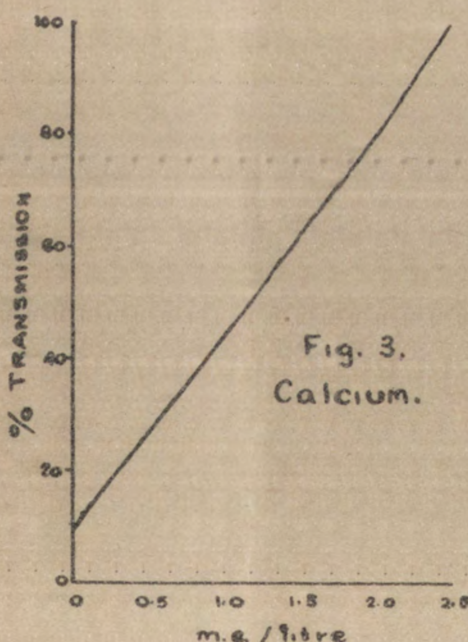

Fig. 3.
Calcium.

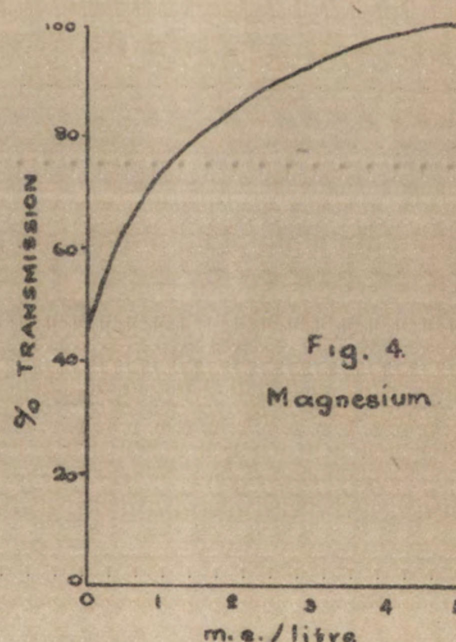

Fig. 4.
Magnesium

together is used. It is proposed to investigate the E.D.T.A. titration method for calcium and magnesium as this is likely to be more accurate for calcium and magnesium.

The anion content of coconut water consists chiefly of the chloride, sulphate, phosphate and nitrate radicles, and further work on their estimation is contemplated. Surveys of the main coconut producing areas in Papua and New Guinea are being undertaken and samples of soil, coconut water and other plant material are taken from areas of varying production and decline. Nut water analysis is also being used in conjunction with coconut fertilizer trials in order to measure the uptake of nutrients as determined by the concentration in the coconut water. So far, potassium estimations of soil and nut water show that the potassium status of the soil on many plantations is very low, and that the low potassium content in the nut water is accompanied by a high sodium content.

Summary.

A method is described for the rapid routine analysis of the principal cations in coconut water using the Beckman D.U. Spectrophotometer with flame attachment. The method is accurate for the estimation of potassium and sodium. The calcium estimation suffers from cationic and anionic interference, and the magnesium method is rather insensitive for accurate work. Coconut water analysis is being used to study coconut nutrition problems in Papua and New Guinea.

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