

Laboratory Errors of Soil Analysis

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The total error variation of routine chemical-soil analyses was examined for its components attributable to operator, day, chemical treatment or digestion and instrumental measurement. The coefficient of variation (c.v.) fell below 8% in the case of pH, organic C, N, acid fluoride soluble P, exchangeable K, exchangeable Mg, total P and total Mn. Values of c.v. exceeding 10% were noted for 6N HCl extractions of K, Mg and Ca, as well as for exchangeable Ca. Instrument and day variations were relatively small and operator differences contributed only occasionally; chemical treatment was the major source of the total laboratory error.

Soil analysis for assessing the fertiliser requirements of *Hevea brasiliensis* can be made more precise if field sampling and laboratory analytical errors are adequately controlled. While such errors of leaf analysis have been studied by SHORROCKS (1962) and MIDDLETON *et al.* (1966), similar investigations on soil-chemical analysis have been limited. Recently, NG AND RATNASINGAM (1970) showed that there was considerable variation in nutrient contents within a 10-ha field on the same soil series, and that a sample of thirty random cores could achieve results for phosphorus, potassium, magnesium and calcium only within 20% of the mean values. To achieve a precision of 10% about 100 cores would be required. This sampling error also includes the analytical error in the laboratory, and although it is generally known that 'analytical error' is considerably less than 'sampling error,' its actual magnitude and composition have not been accurately ascertained for soil analysis of rubber plantings. It is important that this information is available in order to effect improvements complementary to those in field sampling, so that greater confidence can be gained in data used for manuring and soil characterisation.

The errors of laboratory analysis are both 'determinate' and 'indeterminate.' Soil analysis generally involves the actions of

an operator, procedures for treating samples and measurements on an instrument. Determinate errors comprise those arising from sub-sampling, processes such as heating, extraction, filtration, and finally from instrumental measurement. These can be estimated and reduced in magnitude. Indeterminate errors are highly subjective and more random; they include those due to operators of different temperament and to varying working conditions. An understanding of the various sources of error enables the identification of specific areas where improvements can be made.

EXPERIMENTAL

Materials

Top-soils (0 - 15 cm) and sub-soils (15 - 30 cm) of ten common soil series - Batu Anam, Munchong, Kuantan, Rengam, Sungei Buloh, Selangor, Segamat, Serdang, Malacca and Harimau - were oven-dried at about 60°C and mechanically ground to pass a 2-mm sieve.

Design of Experiment

A statistical design chosen to provide an estimate of the major errors attributable to operator, day of analysis, chemical treatment, digestion and instrument readings was used. Three operators analysed either

COMMUNICATION 577

the top-soil or sub-soil samples of the various soil series each day on four separate days (*i.e.* ten samples per day). The two depths of soil were allotted at random over the four days, and each operator carried out one digestion on each sample but made duplicate measurements with the same instrument on the final solution obtained.

The method estimates the digestion component of variation as the interaction between day and operator. Day-to-day and operator-to-operator variations are assumed to be real main effects, but their interaction is random, for it represents the varying day-to-day ability of the operator.

Table 1 shows the various sources of error in an analysis of variance for a particular depth of soil. The expectations of mean squares are given in the notation allotted to the different sources of variation. Excluding soil variation, the total test error can be divided into four major sources:

- Day - comprising days (*d*) and days \times soils (*ds*)
- Operator - comprising operator (*o*) and operators \times soils (*os*)

Digestion - comprising operators \times days (*od*) and operators \times days \times soils (*ods*)

Instrument - comprising duplicate readings

For any soil sample, these separate sources of error are additive and give the total laboratory error. The three operators and the four days were chosen to represent a random selection from the available set of operators and days. If the analysis is restricted to a particular operator or a given day, the total error will be smaller.

Instrument error was not measured in the determination of organic carbon because the sample solution was used in one titration and a duplicate reading was, therefore, not possible.

As experience had already shown, the greatest errors were associated with 6*N* HCl extractions, particularly for the digestion component; a further experiment was undertaken to study this source of variation for potassium, magnesium and calcium determination. Two filtrates were therefore taken from each of two digestions, and duplicate

TABLE 1. COMPONENTS OF VARIATION FOR EACH DEPTH OF SOIL

Source	Degree of freedom	Notation for component	Expectation of mean squares
Soil specimens (<i>s</i>)	9	σ_s^2	$\sigma^2 + 2 \sigma_{dos}^2 + 6 \sigma_{ds}^2 + 4 \sigma_{os}^2 + 12 \sigma_s^2$
Days (<i>d</i>)	1	σ_d^2	$\sigma^2 + 2 \sigma_{dos}^2 + 6 \sigma_{ds}^2 + 20 \sigma_{do}^2 + 60 \sigma_d^2$
Days \times soils (<i>ds</i>)	9	σ_{ds}^2	$\sigma^2 + 2 \sigma_{dos}^2 + 6 \sigma_{ds}^2$
Operators (<i>o</i>)	2	σ_o^2	$\sigma^2 + 2 \sigma_{dos}^2 + 4 \sigma_{os}^2 + 20 \sigma_{do}^2 + 40 \sigma_o^2$
Operators \times soils (<i>os</i>)	18	σ_{os}^2	$\sigma^2 + 2 \sigma_{dos}^2 + 4 \sigma_{os}^2$
Days \times operators (<i>do</i>)	2	σ_{do}^2	$\sigma^2 + 2 \sigma_{dos}^2 + 20 \sigma_{do}^2$
Days \times operators \times soils (<i>dos</i>)	18	σ_{dos}^2	$\sigma^2 + 2 \sigma_{dos}^2$
Duplicate readings	60	σ^2	σ^2
Total	119	—	—

If a component is negative, it is considered to be zero when calculating the sources of error.

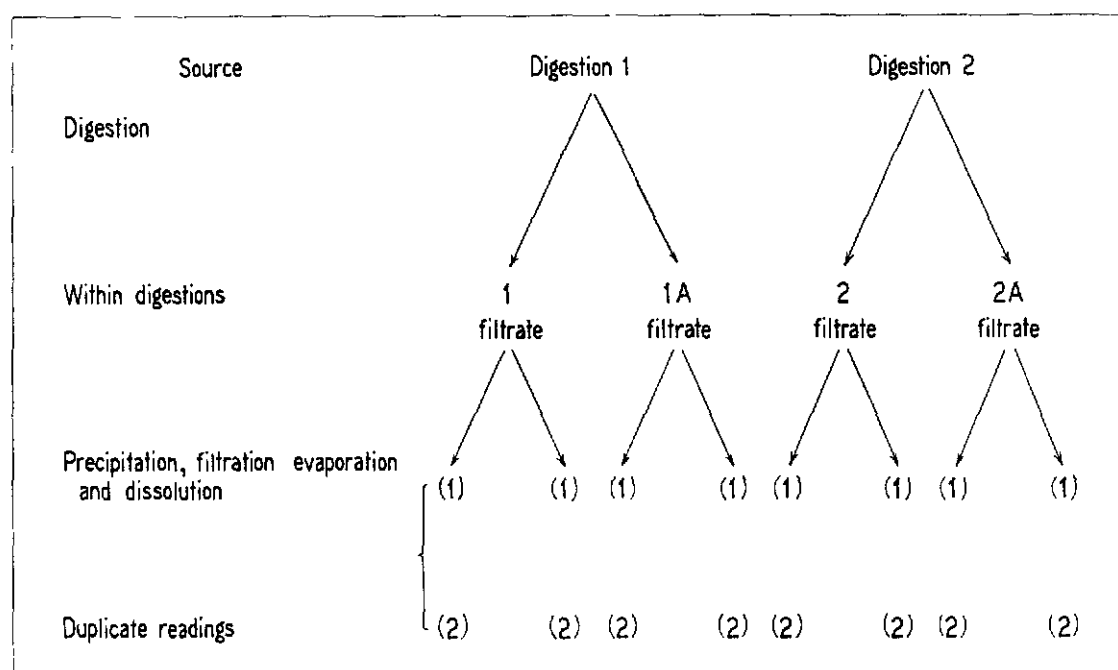


Figure 1. Plan of study of digestion variation in 6N HCl extraction.

measurements made on the final solutions obtained after removal of iron and aluminium by precipitation (Figure 1). The digestion components derived from the experiment on top-soil was assumed to be similar for sub-soil also in calculating the total error for these elements (Table 3).

Analytical Methods

The various determinations and analytical instruments used are outlined below.

pH. This was measured with a pH meter in a stirred suspension of 10 g soil and 25 ml water that was left to stand overnight.

Organic carbon. The rapid-titration method of Walkley and Black was used on 1 g of finely ground soil (72 mesh).

Nitrogen. A micro-Kjeldhal digestion procedure was followed, in which a 0.5 g sample was digested with sulphuric acid in the presence of potassium sulphate and potassium salicylate, with a selenium catalyst. The ammonium content in the digest was

determined colorimetrically by the indophenol-blue method on a Technicon Auto Analyzer.

Acid fluoride soluble P. The extraction followed the procedure of ARNOLD (1947) and the phosphate in the extract was determined by a molybdenum-blue method using ascorbic acid as reducing agent (NG, 1970).

Exchangeable cations. Soil (10 g) was continuously leached with 100 ml neutral normal ammonium acetate. The cations in the leachate were estimated directly: potassium on an EEL flame photometer and calcium and magnesium by a Techtron AA4 atomic absorption spectrophotometer.

Total phosphorus. Soil (2 g) was digested with 6 ml sulphuric-perchloric acid mixture and the phosphate determined automatically as described by NG (1970).

6N HCl extractable cations. Soil (2 g) was extracted with 20 ml 1 : 1 HCl on a steam bath for 1 hour. After filtration, iron and aluminium in solution were pre-

precipitated as hydroxides with ammonia, the filtrate evaporated to dryness and the residue treated with nitric acid and finally taken up with dilute hydrochloric acid. Potassium, magnesium and calcium were determined in the same manner as for exchangeable cations.

Total manganese. Soil (2 g) was digested with 5 ml each of nitric and sulphuric acids and manganese determined by the periodate method.

RESULTS

The laboratory errors (*Table 2*) can be grouped in increasing order for different elements as follows:

- 0 – 1% pH
- 1 – 3% Organic C, total P
- 3 – 5% N, exchangeable Mg
- 5 – 10% Acid fluoride soluble P, exchangeable K, 6N HCl extractable K, total Mn

TABLE 2. STANDARD DEVIATIONS AND COEFFICIENTS OF VARIATION OF TOTAL TEST ERRORS

Property	Horizon	Mean	Standard deviation	Coefficient of variation (%)
pH	Top-soil	4.577	0.0443	0.9669
	Sub-soil	4.603	0.0437	0.9485
	Top-soil + sub-soil	4.590	0.0431	0.9380
C (%)	Top-soil	1.286	0.0259	2.015
	Sub-soil	0.721	0.0200	2.777
	Top-soil + sub-soil	1.004	0.0224	2.230
N (%)	Top-soil	0.1221	0.0042	3.442
	Sub-soil	0.0709	0.0023	3.223
	Top-soil + sub-soil	0.0965	0.0033	3.413
Acid fluoride soluble P (p.p.m.)	Top-soil	8.691	0.4620	5.316
	Sub-soil	3.803	0.2544	6.688
	Top-soil + sub-soil	6.247	0.3691	5.908
Exchangeable K (p.p.m.)	Top-soil	49.87	3.172	6.360
	Sub-soil	38.22	2.078	5.436
	Top-soil + sub-soil	44.05	2.604	5.912
Exchangeable Mg (p.p.m.)	Top-soil	20.09	0.8036	4.001
	Sub-soil	10.11	0.3106	3.073
	Top-soil + sub-soil	15.10	0.6045	4.004
Exchangeable Ca (p.p.m.)	Top-soil	28.56	3.114	10.90
	Sub-soil	18.14	1.657	9.14
	Top-soil + sub-soil	23.35	2.392	10.24
Total P (p.p.m.)	Top-soil	357.3	12.81	3.586
	Sub-soil	316.3	7.79	2.464
	Top-soil + sub-soil	336.8	10.03	2.979
6N HCl extractable K (p.p.m.)	Top-soil	544.5	42.44	7.793
	Sub-soil	613.5	74.91	12.210
	Top-soil + sub-soil	579.0	54.83	9.469
6N HCl extractable Mg (p.p.m.)	Top-soil	280.2	32.66	11.65
	Sub-soil	342.8	64.33	18.76
	Top-soil + sub-soil	311.5	51.01	16.38
6N HCl extractable Ca (p.p.m.)	Top-soil	81.06	10.75	13.26
	Sub-soil	69.68	8.73	12.53
	Top-soil + sub-soil	75.37	9.45	12.54
Total Mn (p.p.m.)	Top-soil	106.8	6.931	6.492
	Sub-soil	99.1	7.242	7.310
	Top-soil + sub-soil	102.9	6.867	6.672

> 10% Exchangeable Ca, 6N HCl extractable Mg, 6N HCl extractable Ca

Except for carbon, acid fluoride soluble phosphate, 6N HCl extractable potassium and magnesium and total manganese, the coefficients of variation for top-soils were slightly greater than those for sub-soils. The greatest errors were incurred in the analysis of HCl extractable cations, indicating that such data should be interpreted with

care. The value of carrying out time-consuming routine tests by this method is questionable. The determination of exchangeable calcium also had a moderately large error.

Instrument errors and day-to-day variations are relatively smaller contributors to the total error, and are therefore less significant in laboratory practice (*Table 3*). Except for pH, nitrogen and total manganese, the digestion or chemical processes constitute

TABLE 3. COEFFICIENTS OF VARIATION (%) OF COMPONENTS OF TOTAL TEST ERROR

Property	Horizon	Total error	Day	Operator	Digestion	Instrument
pH	Top-soil	0.9669	0.5507	0.1411	0.5323	0.5731
	Sub-soil	0.9485	0.3836	0.2881	0.2991	0.7616
	Top-soil + sub-soil	0.9380	0.4946	0.2331	0.3551	0.6743
C (%)	Top-soil	2.015	1.168	0.492	1.566	—
	Sub-soil	2.777	0.957	1.799	1.886	—
	Top-soil + sub-soil	2.230	1.044	1.017	1.687	—
N (%)	Top-soil	3.442	1.916	0.735	2.478	1.221
	Sub-soil	3.223	1.009	1.207	1.811	2.152
	Top-soil + sub-soil	3.413	1.744	0.909	2.312	1.561
Acid fluoride soluble P (p.p.m.)	Top-soil	5.316	0	2.909	4.211	1.436
	Sub-soil	6.688	1.941	4.989	3.436	2.065
	Top-soil + sub-soil	5.908	0	3.573	4.398	1.669
Exchangeable K (p.p.m.)	Top-soil	6.360	2.615	3.363	4.578	1.161
	Sub-soil	5.436	1.991	1.388	4.750	1.049
	Top-soil + sub-soil	5.912	2.270	2.566	4.683	1.131
Exchangeable Mg (p.p.m.)	Top-soil	4.001	0	1.111	3.701	1.037
	Sub-soil	3.073	0	0.856	2.786	0.974
	Top-soil + sub-soil	4.004	0	1.003	3.723	1.078
Exchangeable Ca (p.p.m.)	Top-soil	10.903	0	0	10.604	2.535
	Sub-soil	9.137	0	5.513	6.712	2.835
	Top-soil + sub-soil	10.245	0	0	9.886	2.690
Total P (p.p.m.)	Top-soil	3.586	0	1.297	3.209	0.9363
	Sub-soil	2.464	1.418	1.020	1.420	1.0011
	Top-soil + sub-soil	2.979	0	1.140	2.577	0.9671
6N HCl extractable K (p.p.m.)	Top-soil	7.793	0	0	7.638	1.548
	Sub-soil	12.210	0	10.061	6.779	1.374
	Top-soil + sub-soil	9.469	0	5.996	7.183	1.455
6N HCl extractable Mg (p.p.m.)	Top-soil	11.65	0	8.183	8.251	0.885
	Sub-soil	18.76	0	17.490	6.744	0.723
	Top-soil + sub-soil	16.38	0	14.570	7.422	0.796
6N HCl extractable Ca (p.p.m.)	Top-soil	13.26	3.163	7.056	10.708	1.135
	Sub-soil	12.53	0	0	12.456	1.320
	Top-soil + sub-soil	12.54	2.389	4.186	11.516	1.220
Total Mn (p.p.m.)	Top-soil	6.492	1.170	4.900	3.457	2.197
	Sub-soil	7.310	3.480	5.297	2.632	2.517
	Top-soil + sub-soil	6.672	2.111	4.989	3.104	2.352

TABLE 4. SOURCES OF ERROR IN DIGESTION OF TOP-SOIL IN 6N HCl EXTRACTIONS

Property	Mean		Between digestions	Within digestions	Instrument	Total error	Total error ^a (excluding instrument)
6N HCl extractable K (p.p.m.)	521.9	s.d.	38.33	16.11	8.428	42.43	41.59
		c.v. (%)	7.35	3.09	1.61	8.13	7.97
6N HCl extractable Mg (p.p.m.)	267.7	s.d.	20.18	11.29	2.481	23.25	23.12
		c.v. (%)	7.54	4.22	0.93	8.69	8.64
6N HCl extractable Ca (p.p.m.)	59.28	s.d.	6.515	5.74	0.924	8.732	8.683
		c.v. (%)	10.99	9.68	1.56	14.73	14.65

^aThis column gives an indication of digestion variation based on one digestion, precipitation and filtration as pooled within a soil sample.

the major source of error, and it is in these operations that improvements have to be sought. This is particularly true for HCl extractions and exchangeable calcium, although operator errors cannot be wholly ignored. Table 4 shows that even after eliminating sources of error due to precipitation and filtration, a large error due to variations in digestion remains. The largest errors are associated with heating the samples during digestion and with the precipitation of iron and aluminium.

DISCUSSION AND CONCLUSIONS

The magnitude of the total analytical error is well within acceptable margins in routine soil analysis, except for the HCl extractions and exchangeable calcium. As the largest sources of error lie in the digestion of samples and in differences between operators, standard conditions of treating soil samples, using skilled and trained operators are important. The relatively small component of instrumental error underlines the advantages of instrumental analysis.

The rather large errors found in the determination of 6N HCl extractable cations are associated with variable conditions of extraction (e.g. temperature and duration of heating) and the loss of cations by absorption into the gelatinous precipitate of iron and aluminium hydroxides. Double pre-

cipitation, while feasible, would increase the time of analysis considerably and render the determination extremely slow and laborious. A more practical step appears to be to improve uniformity in conditions of extraction. In view of the relatively large errors, great care should be exercised in the interpretation of analytical data concerning 6N HCl extractable cations.

ACKNOWLEDGEMENT

We thank Dr J.W. Blencowe for valuable comments and staff of the Soil Analysis Section of the Analytical Chemistry Division and Statistics Section for help and co-operation.

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May 1971

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