

rough mirror images of each other. The extent and the pattern of the changes in hydrogen-ion concentration were found to vary considerably with the rate of mixing. Also, when the solutions contained a miscible organic solvent both the range of change in hydrogen-ion concentration and the sharpness of the change at the equivalence point were increased. For example, in an experiment in which 0.1 *M* barium chloride was added to a 50% ethanol solution of 0.1 *M* potassium sulfate the pH was 10.2 just before the equivalence point, and 6.5 just after.

We ascribe all such changes in hydrogen-ion concentration to the adsorption or desorption of hydrogen ions or hydroxide ions on the surface of the precipitates. The extent of the changes depends not only on the specific nature of the precipitate, but also on its state of subdivision, in other words its surface area. The different results observed with differences in rate of mixing and the greater changes caused by the presence of a miscible organic solvent may all be ascribed to differences in particle size and corresponding surface area.

This general effect is not only of theoretical interest but appears to be capable of practical application to analytical measurements. For example, by the use of a glass electrode as an indicator, we have been able to attain an accuracy of about 0.5% in the titration of sulfate with a standard barium solution.

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Biased Forest Stand Estimates Due to Sample Size¹

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There has been a tendency toward the use of small samples in American forest sampling for ecological purposes. Relatively few investigations have used sample plots larger than the 100 sq. m. (approximately 1/40 acre) recommended by Cain (1), and an entire state survey (Wisconsin) has been based on sets of two-tree samples, the "random pairs" of Cottam and Curtis (2). Recent comparisons of the precision and efficiency of various forest sampling procedures in the Great Smoky Mountains (3) illustrate a generally unrecognized small-sample bias, which may lead to important errors in stand estimates.

Cumulative distributions of sample basal area values for tenth-acre, fortieth-acre, and random-pair samples taken at the same random points in a spruce-fir stand are plotted on probability paper, on which a normal distribution would lie along a straight line (Fig. 1). The mean of the random-pair samples is considerably higher than the median and is an unreasonably high stand estimate, but the estimate based on fortieth-acre plots, which has the same sort of bias in lesser degree,

¹ Contribution from the Botanical Laboratory, The University of Tennessee, N. Ser. 154.

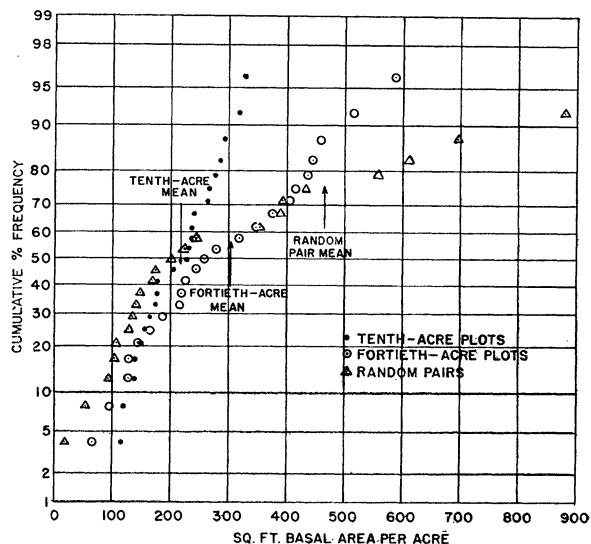


FIG. 1. Cumulative distributions of sample basal areas obtained from samples of different sizes, spruce-fir stand, Great Smoky Mountains. (The 24th point in each series is at infinity, and the 23rd point in the random-pair series lies off the graph, at 1680 sq. ft.)

is near enough to a reasonable range to be accepted in the absence of comparative data or detailed analysis.

The form of several small-sample curves, including those in Fig. 1, suggested a logarithmic transformation, which brought the data into satisfactory agreement with the normal distribution, as is evident from the chi-square test (Table 1). This transformation made possible the application of conventional statistical procedures to the small-sample data, and resulted

TABLE 1
CHI-SQUARE TESTS OF GOODNESS OF FIT TO A
NORMAL DISTRIBUTION

	χ^2	$\chi_{.95}^2$	Hypothesis of normal distribution
<i>Spruce-fir forest type, all-aged</i>			
Plots, tenth-acre (24)			
Data untransformed	1.00	3.84	Accepted
Plots, fortieth-acre (24, at the same points as above)			
Data untransformed	7.67	3.84	Rejected
Data transformed	1.33	3.84	Accepted
Plots, fortieth-acre (40, including the 24 above)			
Data untransformed	3.46	7.81	Accepted
Data transformed	2.79	7.81	Accepted
Random pairs (40, at the same points as above)			
Data untransformed	Very large	7.81	Rejected
Data transformed	3.57	7.81	Accepted
<i>Deciduous forest type, buckeye-basswood-sugar maple, all-aged</i>			
Plots, tenth-acre (25)			
Data untransformed	2.68	3.84	Accepted
Random pairs (39)			
Data untransformed	Very large	7.81	Rejected
Data transformed	.83	7.81	Accepted

TABLE 2
COMPARISON OF VARIOUS STAND ESTIMATES*

	Mean, untrans- formed data	Mean, trans- formed data	Median
<i>Spruce-fir forest type</i>			
Plots, tenth-acre	218.5	—	227.4
Plots, fortieth-acre	293.7	247.8	243.2
Plotless samples	203.5	—	207.0
Random pairs	422.6	240.4	206.5
<i>Deciduous forest type</i>			
Plots, tenth-acre	171.4	—	162.5
Plotless samples	165.8	—	157.5
Random pairs	238.0	154.0	169.5

* Expressed in square feet basal area/acre.

in the markedly improved agreement of stand estimates illustrated in Table 2. Medians are included to show their close agreement with each other and with the more reliable of the means. They offer a promising evasion of the labor of transformation if the utmost statistical efficiency (4) is not required.

It is evident that conventional statistical treatment of small samples (one-fortieth acre or less) yields biased stand estimates, at least in the Appalachian vegetation. In the examples cited, this bias was reduced or eliminated by a logarithmic transformation, which validated the use of standard statistical procedures with random-pair and other small-sample data.

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On the Metabolism of Reichstein's Substance S

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It is an established fact that there must be an adrenal precursor to urinary androsterone and etiocholanolone because these compounds are excreted by castrates. For theoretical reasons Dobriner (1) has postulated that this precursor might be 11-desoxy-17-hydroxy corticosterone (Reichstein's substance S) because this substance is known to be present in the adrenals and has no oxygen function at C-11.

A generous gift of substance S from the Glidden Co. has enabled us to perform some metabolic experiments in humans. Previously Conn (2) has administered 400 mg of substance S to human subjects and achieved a great increase in urinary 17-ketosteroids, but he gives no information about the nature of these steroids. With the aid of a somewhat modified chromatographic separation technique according to Zyg-

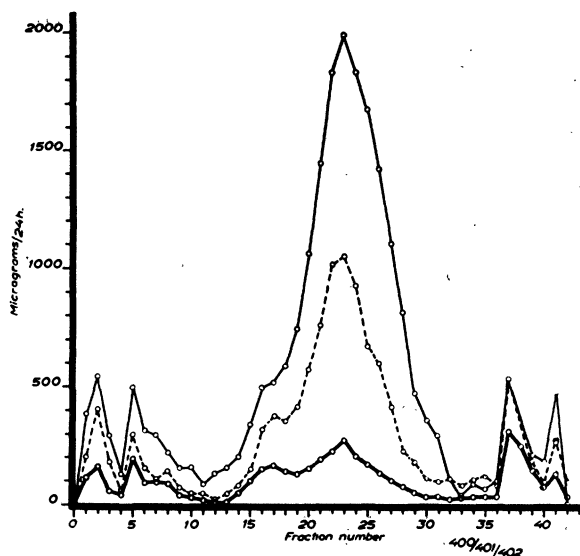


FIG. 1. Case P. T. ♀ Age: 50. Normal. Treated with 300 mg substance S-acetate per os. Heavy solid line: Before treatment (17-KS 4.4 mg/24 hr). Dash line: 1 day after treatment (17-KS 12.2 mg/24 hr). Light solid line: 2 days after treatment (17-KS 22.6 mg/24 hr).

muntowicz (3), we have registered the urinary excretion pattern of 17-KS before and after substance S was given to 4 patients and have analyzed the different fractions by infrared spectrography. First we gave 200 mg of substance S per os as the free alcohol but could not find any change in either the total amount of 17-KS or their relative amounts. In two cases, however, when we administered 300 mg of substance S as the monoacetate by the same route, we noticed in one case a small and in the other one a large increase in the 17-KS excretion. By infrared spectrography of the fractions in the 17-KS microchromatogram (Fig. 1) we made the following interesting observations. The tremendous increase in the fractions 18–30 is largely due to etiocholan-3 α -ol-17-one. Androsterone is present but in a very small amount compared to the etiocholanolone. It is not possible to say with certainty whether there is an increase in androsterone excretion or not. The total increase in 17-KS excretion above the mean value before the administration of substance S was 60 mg, which is 27% of what could be formed stoichiometrically from the given amount of substance S-acetate.

It is of course too early to draw any conclusions concerning the significance of these experiments, but they suggest that substance S might be the precursor of at least some of the etiocholanolone which has its source in the adrenals. Research is being continued.

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