by Hilditch and co-workers for cow milk fat3,10 are not, however, inconsistent (as judged by saponification equivalents and iodine values of residual ester fractions) with the presence of one or both of these acids in this fat. Indeed, Bosworth and co-workers11,12 tentatively claimed the presence of these acids in cow milk fat, a claim which seems to have been neglected by subsequent investigators.

Linoleic, linolenic and arachidonic acids are known to be essential in the nutrition of rats 13,14. The possibility of the physiological importance of eicosadienoic acid is of great interest. Work on the constitution of these acids is in progress.

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Chemistry Section, Animal Research Division, Department of Agriculture, Wellington, N.Z. Oct. 16.

Hilditch, "The Chemical Composition of Natural Fats" (London: Chapman and Hall, 1941), 60 ff.
Hilditch, Lea and Pedelty, Biochem. J., 33, 493 (1939).
Hilditch and Longenecker, J. Biol. Chem., 122, 497 (1938).
Hilditch and Redelty, Market 34, 640 (1939).

⁴ Hilditch and Pedelty, Analyst, **64**, 640 (1939). ⁵ Cramer and Brown, J. Biol. Chem., **151**, 427 (1943).

Baldwin and Longenecker, J. Biol. Chem., 154, 255 (1944).

'Mitchell et al., Ind. Eng. Chem. (Anal. Ed.), 15, 1 (1943).

⁸ Kraybill and Beadle, J. Amer. Chem. Soc., 66, 1232 (1944).

Shorland and de la Mare, Emp. J. Exp. Agric., in the press.

¹⁰ Hilditch and Paul, Biochem. J., 30, 1905 (1936).

21 Bosworth and Brown, J. Biol. Chem., 103, 115 (1933).

Bosworth and Sisson, J. Biol. Chem., 107, 489 (1934).
Burr and Burr, J. Biol. Chem., 86, 587 (1930).

14 Hume et al., Biochem. J., 34, 879 (1940).

Effect of Hydrogen Ion Concentration on Cation Exchange in Clay Salts

THE lyotrope series is usually observed in the exchange of cations from clays and permutites1,2. Deviations from this series have also been reported3.4. These have been attributed to the structural peculiarities of the clays² and variations in the hydration of cations4. Differences in the relative effects of Ba++ and Ca++ ions in the interaction of hydrogen clays with neutral salts and bases have been observed⁵ 6.7, depending on the prevailing pH of the system. Symmetry values3 of a number of clay salts against various electrolytes (chlorides) have been measured with and without adjustment of the pH of the system at a constant value by the addition of the requisite amount of hydrochloric acid. When a constant pH is not maintained, deviations from the normal lyotrope series often occur, especially in clays containing montmorillonite as judged from X-ray analysis. The deviations disappear when the symmetry values measured at a constant pH ranging from 6.0 to 7.0 are compared. At a constant pH between 3.0 and 5.0, all the cations examined give the same symmetry value, and the cation effect as envisaged in the lyotrope series altogether disappears.

At a low pH (3.0), hydrochloric acid alone gives a higher symmetry value than when used in conjunction with the salts. Al+++ ions are likely to be exchanged at this pH for the cations of the added salt. No appreciable exchange of aluminium at this pH would occur if hydrochloric acid alone were added10. The lower symmetry value observed in the presence of salts can be explained if one takes into

account the Al+++ ions exchanged for the cation

Further work is in progress.

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Jenny, Koll. Beih., 23, 429 (1926).
Wiegner, Trans. 3rd. Internat. Cong. Soil Sci., 3, 109 (1935).

Jenny, J. Phys. Chem., 36, 2217 (1932).
Schachtschabel, Koll. Beih., 51, 199 (1940).

⁵ Mukherjee, Mitra and Mukherjee, S., Trans. Nat. Inst. Sci. India, 1, No. 10, 227 (1937).

⁶ Mukherjee, S. K., and Ganguli, Ind. J. Agric. Sci., in the press. Mitra, Mukherjee, S. K., and Bagchi, Ind. J. Agric. Sci., 10, Part 2, 303 (1940).

⁸ Unpublished work of Mr. S. N. Bagchi.

Mukherjee and Chatterjee, J. Indian Chem. Soc., 12, 105 (1942).

16 Unpublished work of Dr. B. Chatterjee.

A Labour-saving Method of Sampling

If a fraction p of a population have the attribute A, then it is well known that if m members out of a sample of N have this attribute, the best estimate of

$$p$$
 is $\frac{m}{\widetilde{N}}$, and its standard error is $\sqrt{\frac{m(N-m)}{N^3}}$ or

$$p\sqrt{1-p}$$
. Supposing, therefore, that we want our

estimate of p to be correct within a standard error of 10 per cent of its value, we must count a sample containing 100(1-p) members with the attribute A. If we do not know p roughly beforehand we do not know how large to take our sample. For example, if we wish to estimate the frequency of a type of blood corpuscle, and count 1,000 blood corpuscles in all, we should get such values as 20 ± 1.3 per cent, or 1 ± 0.31 per cent. The former value would be needlessly precise for many purposes. The latter would not differ significantly from an estimate of 2 per cent.

The standard error is almost proportional to the estimated frequency if we continue sampling until a fixed number m of the minority with attribute Ahave been counted, and then stop. Supposing the total number in the sample is now N, we cannot use

 $\frac{m}{N}$ as an estimate of p. It can, however, be shown

that $\frac{m-1}{N-1}$ is an unbiased estimate of p, with

standard error very approximately $\frac{1}{N}\sqrt{\frac{m(N-m)}{N-1}}$,

or $p\sqrt{\frac{1-p}{m-2}}$, which is nearly proportional to p

when this is small. Thus to get a standard error of about 10 per cent of the estimate we should have to count until we had observed a number m of the rarer type A, which only varies from 102 when p is very small, to 72 when it reaches 30 per cent. If we were content with a standard error of 0.2p we could take a quarter of this value, and so on.