USE OF WESTPHAL BALANCE IN SEDIMENTATION ANALYSIS

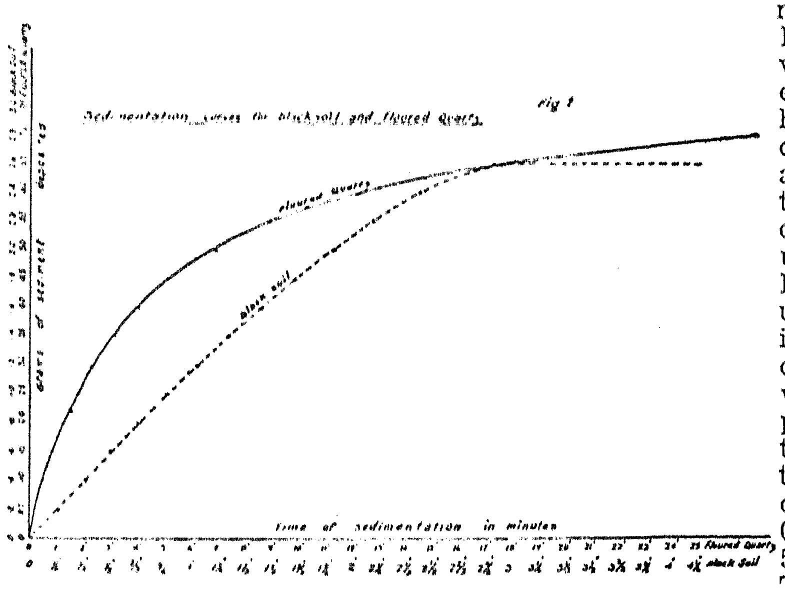
Oden[1] devised an accurate method of soil classification on the basis of continuous particle size-distribution curves.

The author has now adapted the Westphal Balance for the mechanical analysis of soils on Oden's principle. The weighted sinker of the balance is replaced by a mica pan weighted with a steel wire at the centre. The movement of the beam, and therefore of the pan, is restricted to 2 mm. from the horizontal.

To start with the pan is kept under the pure liquid upto a known depth (20 cm.). The rider is placed immediately above the knife-edge carrying the pan. Then the balance is brought to a horizontal position with the movable weight at the other end. The rider is shifted through one division towards the central knife-edge. The liquid is carefully replaced by the soil suspension up to the same depth of the liquid, and the time taken for the beam to assume the horizontal position noted with a stop-watch. The rider is shifted rapidly through another division in the same direction, and the time taken for the beam to regain the horizontal position is again noted. This operation is repeated till the sedimentation is complete.

The shifting of the rider through equal divisions is equivalent, as in Oden's sedimentation balance, to counter-balancing with a number of weights of equal masses. The mass of sediment deposited on the pan at any given position of the rider when the beam of the balance is horizontal is given by $W = R\frac{N}{M}$ where

W = mass of sediment deposited on the pan,
N = division at which rider is at that instant,
M = number of equal divisions into which the beam, between the two knife-edges, is divided,
R = mass of rider.



The sedimentation or accumulation curves for black soil and quartz flour are thus obtained by plotting the data as illustrated in the following figure. From these the distributive curves can be derived graphically or mathematically.

A detailed paper embodying the technique and results for other samples will be published elsewhere.

In conclusion I express my thanks to Prof. C. Mahadevan for his keen interest in the work.

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June 21, 1947.

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[1] Oden, S., *Int. Mitt. Bodenk.*, 1915, **5**, 257.

PHOTOCHEMICAL AFTER-EFFECT IN THE DECOMPOSITION OF HYDROGEN PEROXIDE BY POTASSIUM FERROCYANIDE

It has been reported that the illumination of aqueous potassium ferrocyanide results in the formation of appreciable quantities of the aquo-salt (II), potassium aquopentacyanoferrite, and this brings about rapid decomposition of hydrogen peroxide in the dark as measured by the photochemical after-effect.[1] The photo-formation of the aquo-salt (II) from ferrocyanide is a reversible reaction. It has also been suggested that the aquo-salt (II) is in itself light-sensitive, and is decomposed by light in a short time. It undergoes slow and complicated changes on standing in the dark in the presence of air finally producing ferrocyanide, ferricyanide and ferric hydroxide. The same reactions take place on heating but relatively rapidly.

The validity of these conclusions has been experimentally tested. It has been possible to reproduce the photochemical after-effect in this reaction in the dark by using minute quantities of pure sodium aquopentacyanoferrite (II) with the unilluminated solutions of ferrocyanide. Pure aquo-salt (II) was prepared in the laboratory by the method of Hofmann,[2] and varying quantities of this substance were mixed with the usual amounts of ferrocyanide and hydrogen peroxide in the dark. The rate of decomposition so obtained is of the same order as the photochemical after-effect. It was further discovered that a minimum concentration of ferrocyanide is essential for keeping the unimolecular rate at a constant value. With lower concentrations of the ferrocyanide, the unimolecular velocity constant goes on decreasing from the beginning to the end of the decomposition. The same behaviour is observed when the ferrocyanide is not used, but decomposition of hydrogen peroxide takes place in the presence of the aquo-salt (II) alone. In the following experiments (40° C.), pure aqueous hydrogen peroxide (N/6) was used with 0·0025 gm. of the sodium aquo-salt (II) in 50 c.c. of the reaction mixture in the dark. The velocity constant, K, has been calculated by the usual equation $K = 1/t \log a/a-x$, where t represents time in minutes, a the initial concentration of hydrogen peroxide in terms of c.c.s of potassium permanganate, and x the change in time t.

TABLE I
Without Ferrocyanide

t (*minutes*)	$a-x$	$K'\cdot 10^4$
0	16·20	..
20	11·90	67
39	10·00	54
64	8·75	42
90	7·90	35
129	7·15	28

TABLE II
Ferrocyanide = M/1066·7

t (*minutes*)	$a-x$	$K'\cdot 10^4$
0	20·10	..
7	16·50	122
21	14·00	75
41	11·70	57
77	9·00	45
132	6·60	36
195	5·20	30
201	4·00	24

TABLE III
Ferrocyanide = M/533·3

t (*minutes*)	$a-x$	$K'\cdot 10^4$
0	19·60	..
10	15·15	112
17·5	12·75	107
42	8·05	92
62	4·65	96
90·5	2·35	102

TABLE IV
Ferrocyanide = M/320

t (*minutes*)	$a-x$	$K'\cdot 10^4$
0	19·10	..
7	14·10	188
17	10·30	158
41	4·40	156
64·5	1·35	179

These results show that the effect of concentration of the aquo-salt (II) is determined by the concentration of ferrocyanide in the reaction mixture. The results of experiments performed by using a constant amount of unilluminated ferrocyanide (M/320) and varying quantities of the sodium aquo-salt (II) in 50 c.c. of the reaction mixture are summarised below:—

TABLE V

Sodium aquo-Salt (gm $.10^{-4}$)	$K\cdot 10^4$ (Average value)
0·5	5·5
1·0	11·5
5·0	44·5
10	66·8
20	159
25	170
30	215
50	345
100	581

It is clear that the photochemical after-effect can be reproduced in the dark by suitably choosing the concentrations of the ferrocyanide and the aquo-salt (II). A complete similarity in the course of the after-effect by light and by the aquo-salt (II) added in the dark to $K_4Fe(CN)_6$-H_2O_2 mixture becomes obvious. This reaction is highly susceptible to traces of impurities, for in parallel experiments there occur sometimes variations of more than 20 per cent., which cannot be ascribed to errors in manipulation but can only be accounted for by impurities in the air of the laboratory.[3]

It was suggested by the author[4] that the primary oxidation process

$$2\,K_3Fe(CN)_5H_2O + H_2O_2 \rightarrow 2\,K_2Fe(CN)_5H_2O + 2KOH + \text{Energy}$$

is responsible, by virtue of the liberated energy, for the decomposition of a large number of hydrogen peroxide molecules. The aquo-salt (III) so formed is instantly reduced to aquo-salt (II) by the ferrocyanide and the system $Fe(CN)_5H_2O''' \rightleftharpoons Fe(CN)_5H_2O''$ continues to decompose hydrogen peroxide at a constant rate. It follows, therefore, that the aquo-ferrate (III) in the presence of ferrocyanide should be capable of reproducing almost quantitatively the results obtained with aquo-ferrite (II). This point has been fully substantiated by employing suitable concentrations of pure sodium aquo-pentacyanoferrate (III) obtained by Hofmann's method. In 50 c.c. of the reaction mixture, 0·0025 gm. of the violet aquo-salt (III) was used.

TABLE VI
Without Ferrocyanide

t (*minutes*)	$a-x$	$K'\cdot 10^5$
0	16·40	..
22	16·20	24
48	12·00	283
74	7·00	500
94	4·65	582

These results show that sodium aquopentacyanoferrate decomposes hydrogen peroxide in presence of ferrocyanide in the same manner as the aquo-ferrite (II). Moreover, the course of the decomposition in presence of relatively smaller amounts of ferrocyanide is similar to