2. Studies on the Method of Batch Analysis

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INTRODUCTION

Among the methods available for the control of the composition of batch charged daily to the tank furnaces of a glass factory, the main stress should be laid upon the method of routine analysis capable of giving the results as promptly as possible which is, at the same time, accurate enough to meet the purpose. A couple of papers treating simply the method of batch analysis[1][2] have already been published, however, to the best of authors knowledge, such report as touching the complete course of analysis running through from the method of sampling has not been given out yet. Assuming the batch producing bottles in a factory as an example, the authors have devoted themselves to establish statistically rational ways of sampling and dividing as well as the rapid, still precise method of routine analysis. These procedures have then been transfered to the daily practice of the batch analysis in the factory in order to work out the precision of the results and to estimate the time necessary to carry on the whole steps.

I. METHOD OF ANALYSIS

(1) Method of Sampling of Gross Sample

The batch taken up as the object of the present investigations was that used for the production of flint containers composed of the mixture of silica sand, soda ash, lime, some refining agents and cullet. If cullet be excluded, the remaining powder was so fine as to pass through 10 mesh Tyler's standard sieve completely. In Fig. 1, curve I shows the distribution of grain size of the batch after screening through 10 mesh sieve. Cullet was the self production whose mean size was found to be about 2 cm., containing 4 cm. pieces as the maximum. The amount of cullet dust passing through 10 mesh sieve was confirmed to be so small as 0.02 to 100 parts of cullet. For the present case the daily charge of batch into the tank was 32 tons. After passing through the mixer, conveyor and hopper the batch is, as usual, piled up before the dog-house and is being ready for charge, whence the sample for analysis was scooped up.

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Fig. 1.

Passed
I : 10 mesh sieve (Tyler)
II : 30 mesh sieve
III : 60 mesh sieve

Maximum diameter of particles
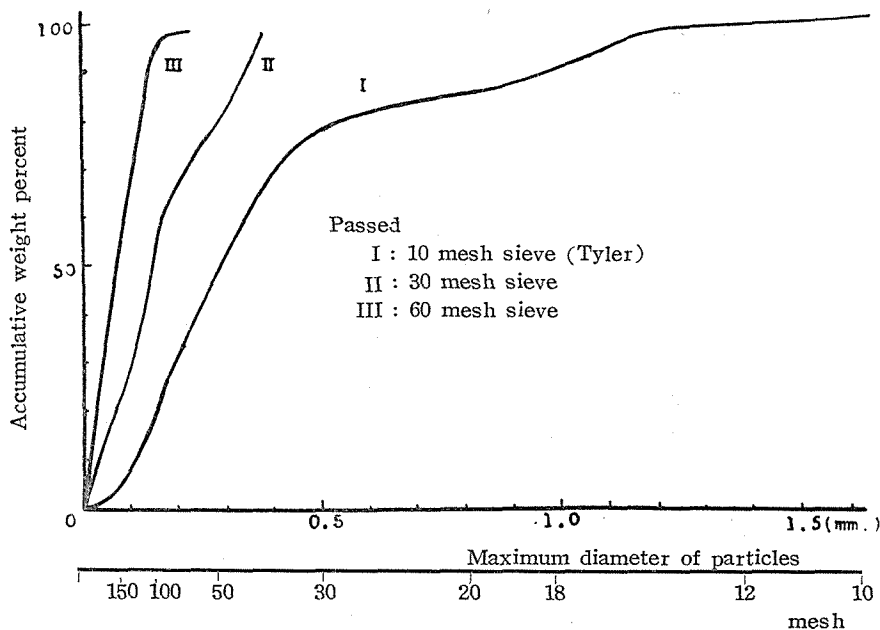
The shovel of about 2 kg. capacity as shown in Fig. 2 was used for this purpose, namely, in every 15 minutes it was ducked into the pile of batch and after scooping it up and levelling the surface by a rod the content was discharged alternatively into one of the two boxes marked previously A and B. Hence the total amount of samples came up to 192 kg. per day and of these each 96 kg. was contained separately in the boxes A and B.
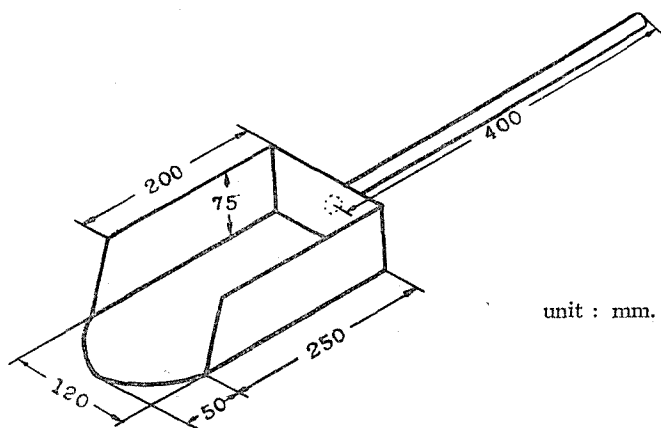
unit : mm.

Fig. 2.

(2) Deviding the Gross Sample into the Sample for Analysis

The content of each box was screened through 10 mesh sieve in order to exclude

the cullet. The schedule for dividing the large size samples into available for chemi‑
cal analysis is given in Fig. 3.

For this purpose two riffle sample dividers, large and small in size, were used,
in which the distance between the dividing walls, appearing in photo-reproduction of
smaller one in Fig. 4, are respectively, 5 and 10 mm. according to the size of divider.

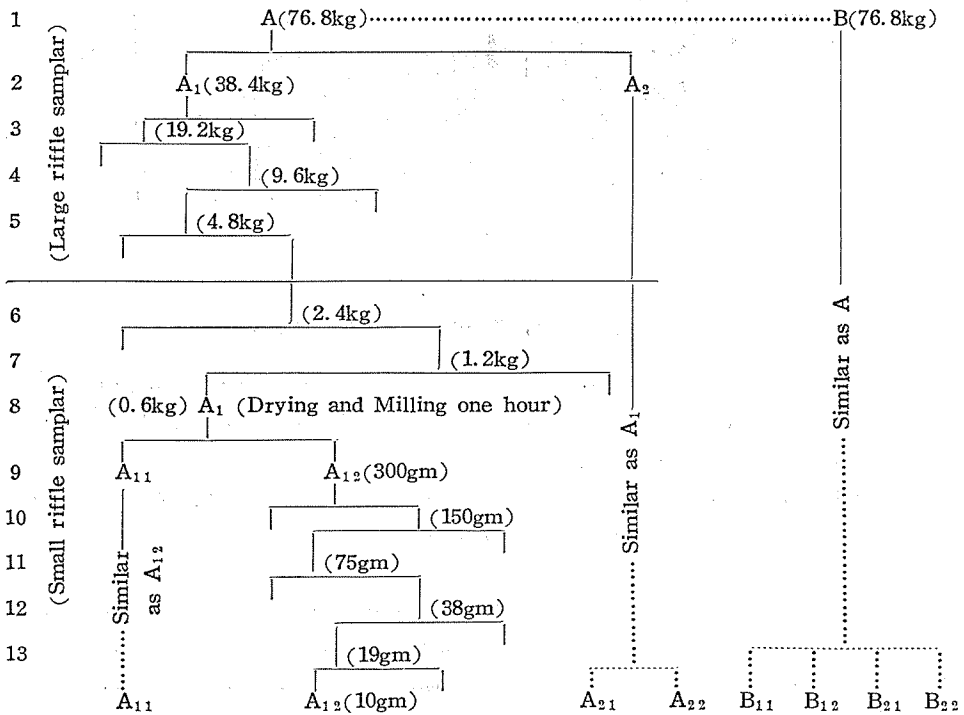As indicated in Fig. 3 the box A is firstly halved.

Fig. 3.

Then, rejecting half an amount in each step the halving from A_1 and A_2 is repeat‑
ed until the sample size will be reduced to 600 g. According to the two categories
of sample size, namely, from 76.8 to 2.4 kg. and from 2.4 to 0.6 kg., the larger and
smaller riffle divider is to be used. The so obtained 600 g. sample is firstly dried
for two hours at 200°C in a dryer and, after cooling down, milled until the whole
contents pass through 60 mesh sieve. Then it is mixed thoroughly by the mixer of
an inclined eccentric cylinder type such as appeares in Fig. 4 for five minutes under
6 r.p.m. Six consecutive dividing again follows until the amount will be reduced to
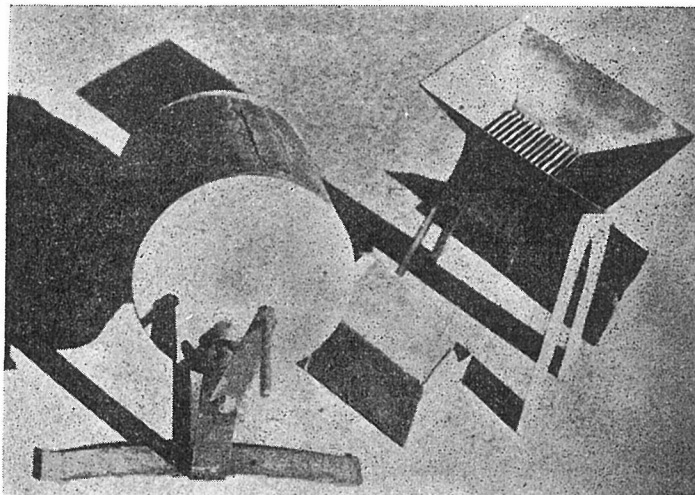10 g. which is to be subjected to chemical analysis.

Fig. 4.

(3) Simplified Routine Chemical Analysis

In order to separate the sample into three components, wathe soluble, acid soluble and residue which will be named hereafter, respectively, as soda ash, lime and sand the following procedure was used :

Estimation of Soda Ash.   The sample of about 10 g. is dried at 200–210°C for an hour, weighed out exactly, transfered to beaker, added by 100 c.c. of water from a pipette and then the content is kept at 40–50°C for five minutes.   The solution in agitated thoroughly by a glass rod and allowed to stand until all residues set to the bottom of beaker.   From the filtrate of clear liquid 10 c.c. is pipetted out and titrated with 0.3 N hydrochloric acid solution using methyl orange as an indicator.   The a-mount of soda ash is calculated from the results. The loss by evaporation during the manipulations should be made up by adding distilled water to exactly the same weight as the preceding value.

Estimation of Lime.   The residue is transferred to 200 c.c. beaker together with all solutions surplus of preceding procedure.   The lime in residue is dissolved by 20 c.c. of exactly standardized ca. 4 N solution of hydrochloric acid added by pipette. In order to expel out carbon dioxide the solution is kept warm at 40–50°C for 5 minutes and stirred occasionally. The solution, being at room temperature, is transferred to 100 c.c. burette in order to titrate 10 c.c. of 0.2 N Na_2CO_3 solution. From the consumption of the solution the amount of lime is worked out. The loss by evaporation should be made up as before.

Estimation of Sand.   The weight of dried sample substracted by that of the sum of lime and soda makes the value of sand.

II. THEORETICAL BACKGROUND OF THE METHOD ANAIYSIS

The method of analysis stated above has been drawn up in order that the precision of the overall procedure remains within the measure of 0.1 % in standard deviation.

According to the law of additivity of variance the variance σ^2 of the overall procedure is expressed by

$$\sigma^2 = \sigma_S^2 + \frac{\sigma_{R1}^2}{2} + \frac{\sigma_{R2}^2}{4} + \frac{\sigma_M^2}{4}$$

in which σ_S^2 is the variance in sampling, σ_{R1}^2, the value in the first step of dividing, namely, from 76.8 kg. to 600 g., σ_{R2}^2 the same corresponding to the second step, namely, from 600 g. to 10 g., and σ_M^2 the variance in the chemical analytical procedure.

The following experiments have been carried out in order to know in advance whether the method of analysis given above is precise enough for keeping the value of σ within the limit of 0.1 %.

(1) Precision of Analytical Method

The variance σ_M^2 in the analytical procedure was evaluated from the results of analysis of the mixture in ratio by weight of $2:1:7$ of the pure chemicals, of which sand had previously been treated by hydrochloric acid to dissolve out the acid soluble impurities.

The results of 15 analyses are consolidated in Table 1.

Table 1. Results of chemical analysis.

Sample No.	Wt. of Na$_2$CO$_3$ in Sample (g.)	Na$_2$CO$_3$ Value Analysed (g.)	Diff.	Wt. of CaCO$_3$ in Sample (g.)	CaCO$_3$ Value Analysed (g.)	Diff.
1	2.0005	2.0028	+0.0023	1.0015	0.9977	−0.0038
2	2.0018	2.0038	+0.0020	0.9994	0.9956	−0.0038
3	1.9990	2.0017	+0.0027	1.0010	1.0000	−0.0010
4	1.9995	1.9998	+0.0003	0.9985	0.9967	−0.0018
5	1.9992	1.9989	−0.0003	0.9996	0.9996	0.0000
6	2.0010	2.0008	−0.0002	1.0064	1.0070	+0.0006
7	2.0022	2.0025	+0.0003	0.9959	0.9930	−0.0029
8	2.0001	2.0008	+0.0007	0.9997	1.0025	+0.0028
9	1.9996	1.9993	−0.0003	0.9988	0.9990	+0.0002
10	1.9995	1.9993	−0.0002	0.9995	0.9995	0.0000
11	1.9942	1.9952	+0.0010	1.0010	1.0005	+0.0004
12	2.0002	1.9993	−0.0009	1.0018	1.0030	+0.0012
13	2.0019	2.0017	−0.0002	1.0025	1.0050	+0.0025
14	1.9976	1.9969	−0.0007	1.0012	1.0010	−0.0002
15	1.9968	1.9961	−0.0007	0.9994	1.0000	+0.0006
Total	29.9931	29.9989	+0.0058	15.0053	15.0001	−0.0052
Mean (%)	19.9954	19.9993	+0.0039	10.0035	1.0000	−0.0003

From these values the expected values of the average of differences between the original amount and analytical data and the unbiased varianses have been calculated and are given in Table 2.

Table 2. Precision of chemical analysis.

	Soda ash	Lime	Silica
Expected value of the average of difference (x) %	+0.0039	−0.0035	+0.0004
Unbiased variance of the difference (u^2) %	129.7×10^{-6}	401.5×10^{-6}	264.8×10^{-6}
Root of unbiased variance (u) %	0.011	0.020	0.016

The facts that the deviations of analytical data from real value, being represented by the expected value of the average of differences, are smaller than 0.004 %, and the root of variance, u, being equivaent to σ_M, are also lower than 0.02 % prove that the accuracy of the amalytical method is satisfactory for keeping the value of σ within the limit of 0.1 %.

(2) Setting up the Method of Dividing

The introduction of the milling process particulary when the sample size is reduced to about 0.6 kg as shown in Fig. 3 is based on the following experimental facts.

From the raw materials now currently used for the production of bottles in a factory the batch of 640 g. was prepared by mixing the soda, lime and sand in proportion by weight of $2:1:7$. The mixture was then subjected to the procedure of mixing and dividing as given above until, however, the sample size was reduced to, respectively 1, 10, 40 and 80 gs. and the comparative chemical analysis of these samples has been carried out. The analysis was repeated eight times for each species, in which the method adopted was in the measure as given above.

The results are tabulated in Table 3.

Table 3, Influence of the weight of sample.

Wt. of Sample	Sample No.							
	1	2	3	4	5	6	7	8
1g.	18.69	18.40	18.34	18.78	19.34	19.24	18.81	19.18
10g.	19.31	19.78	19.28	19.85	19.70	19.80	19.44	19.54
40g.	19.49	19.33	19.38	19.49	19.42	19.25	19.33	19.45
80g.	19.41	19.51	19.38	19.44	19.28	19.37	19.22	19.42

From these data the unbiased variances and the confidence limits (confidence

coefficient 98 %: a = 99 %, β = 99 %) in connection with different sample weights have been worked out, whose results are represented by curves in Fig. 5.

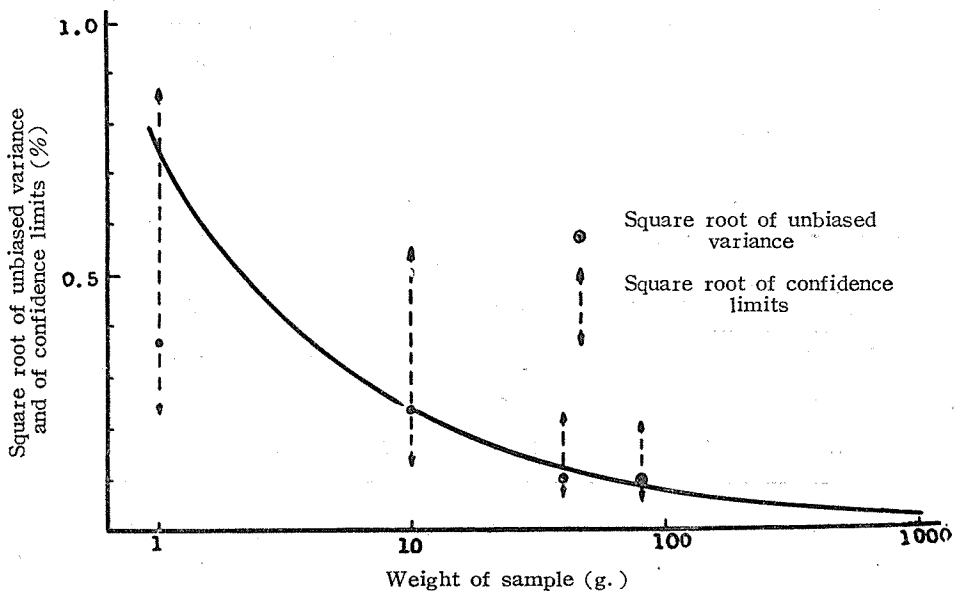Weight of sample (g.)

Fig. 5

It is well known that there exists a relation $\sigma_b{}^2 = \dfrac{\sigma_a{}^2}{w_b/w_a}$, which connects the sample weight w_a, w_b and the corresponding variances $\sigma_a{}^2$ and $\sigma_b{}^2$.

The thick likne in the figure represents above relation taking w_a=10 g as standard. Although the point corresponding to σ_b for w_b=1 g. is located at some distances from the curve the other ones representing, namely σ_b for w_b=40, 80 g. find themselves almost exactly on the curve.

As has been stated before, the law of additivity of variance suggests that it is desirable to keep the value of σ_{R1}, around the limit of 0.03 % in order to guarantee the value of σ of about 0.1 %. The curves in Fig. 5 indicate clearly that it would be difficult to keep σ_{R1} in the range of 0.03 % if the dividing were kept on further. This is the reason why the first group of dividing process was broken up at the sample size of 640 g.

(3) Determination of Particle Size

It has been proved that the precision of analysis would fall appreciably if the process of dividing were continued further beyond the sample size of 640 g. leaving the grain size as it is and such large amount as 640 g. is, obviously, inconvenient to subject directly to chemical analysis. In order to carry on the dividing to an amount convenient for analysis, viz. about 10 g., without giving any influence on the precision of analysis it is desirable to reduce the grain size by milling at this stage.

The experiments have, therefore, been performed in order to find out the proper fineness of batch for such purpose.

A pair of 640 g. batch prepared as before were milled separately in a pot mill until they pass through, respectively 30 and 60 mesh. The six consecutive dividing were then carried on with these samples and two sets of samples, each consists of weight 10 g. samples were submitted to the analysis of soda.

In Table 4 are given the results.

Table 4. Results of the analysis of soda.

Particle size Passed	Sample No.							
	1	2	3	4	5	6	7	8
10mesh	19.31	19.78	19.28	19.85	19.70	19.80	19.44	19.54
30mesh	18.05	17.99	18.15	17.96	18.01	18.02	18.07	18.08
60mesh	18.63	18.64	18.66	18.64	18.67	18.67	18.70	18.69

The distribution of grain size of the milled samples appears in Fig. 1 as curve II and III.

From the date the unbiased variances and the confidence limits of variance (confidence coefficient 98 % : a = 99 %, β = 99 %) have been calculated.
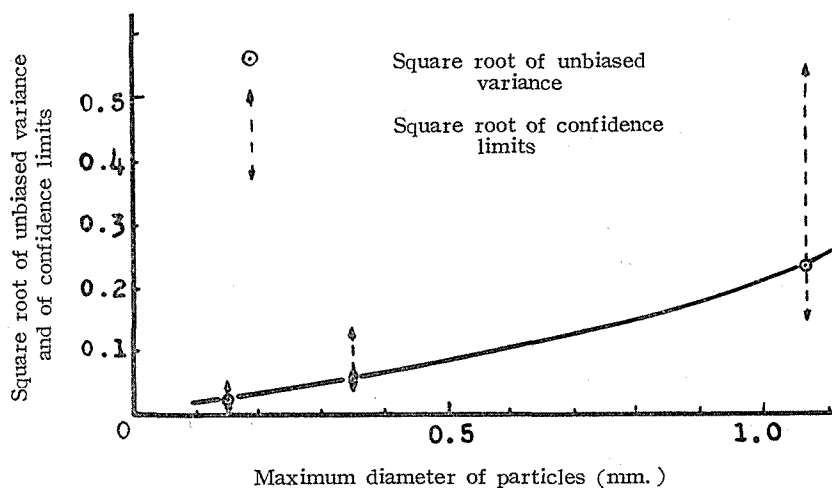

Fig. 6. Relation between the grain size and the unbiased variance.

The curve in Fig. 6 which reproduces the change of unbiased variance and of confidence limit with grain size indicate that the dividing may be carried on to 10 g. sample without reducing the precision beyond the limit of σ_2 = 0.03 % if the grain size be reduced to such degree as to pass through 60 mesh sieve.

(4) Influence of the Intermixing of Cullet

Hunt[1] has pointed out the influence of powdered cullet on the results of analysis and, considering it as being a cause of errors suggested a method for excluding this kind of error.

For present case, however, the authors have confirmed that the amount of inter-mixing of fine powder of cullet was so small as negligible and the Hunt's method has not been used.

III. ANALYSIS OF BATCH FLOWING CONTINUOUSLY IN FACTORY

Using the pure chemicals as the first step and then the raw materials currently used in a factory the authors have devoted to establish the statistically correct method of batch analysis. In these cases the values of variances, $\sigma_M{}^2$, $\sigma_{R^2}{}^2$, could be evaluated from the results of analysis. For the purpose, however, of introducing these methods into the factory practice with the confidence that the results are supported by the sound statistical backgrounds, the expected values of $\sigma_S{}^2$, $\sigma_{R1}{}^2$ and σ^2 should be esti-mated from the data obtainable during the daily running. Hence the authors have tried to find out the values of σ^2, $\sigma_S{}^2$ and $\sigma_{R1}{}^2$, from these methods to the factory operation during 10 days as the tentative measure before the sampling and dividing

Table 5. Analysis of soda.

Lot No.	Date		X_{11}	X_{12}	$\overline{X}_1$	R_1	X_{21}	X_{22}	$\overline{X}_2$	R_2	$\overline{X}$	R_3	$\overline{\overline{X}}$	R_4
I	20	B	21.34	21.39	21.365	0.05	21.40	21.24	21.320	0.16	21.343	0.045	21.377	0.067
		A	21.44	21.51	21.475	0.07	21.36	21.33	21.345	0.03	21.410	0.130		
II	21	A	21.40	21.36	21.380	0.04	21.42	21.46	21.440	0.04	21.410	0.060	21.369	0.082
		B	21.08	21.15	21.115	0.07	21.54	21.54	21.540	0.00	21.328	0.425		
III	22	A	21.62	21.61	21.615	0.01	21.63	21.57	21.600	0.06	21.675	0.015	21.552	0.247
		B	21.46	21.45	21.455	0.01	21.38	21.42	21.400	0.04	21.428	0.055		
IV	23	A	21.56	21.61	21.585	0.05	21.54	21.51	21.525	0.03	21.555	0.060	21.537	0.037
		B	21.89	21.85	21.870	0.04	21.12	21.21	21.165	0.09	21.518	0.705		
V	24	A	21.69	21.76	21.725	0.07	21.45	21.49	21.470	0.04	21.598	0.255	21.702	0.207
		B	21.85	21.82	21.835	0.03	21.78	21.77	21.775	0.01	21.805	0.060		
VI	25	A	21.60	21.69	21.645	0.09	21.72	21.72	21.720	0.00	21.683	0.075	21.677	0.013
		B	21.60	21.68	21.640	0.08	21.74	21.66	21.700	0.08	21.670	0.060		
VII	26	A	21.88	21.84	21.860	0.04	21.91	21.91	21.910	0.00	21.885	0.050	21.947	0.123
		B	21.98	21.97	21.975	0.01	22.02	22.06	22.040	0.04	22.008	0.065		
VIII	27	A	21.40	21.35	21.375	0.05	21.44	21.45	21.445	0.01	21.410	0.070	21.385	0.050
		B	21.24	21.27	21.225	0.03	21.45	21.48	21.465	0.03	21.360	0.210		
IX	28	A	21.94	21.90	21.920	0.04	21.53	21.63	21.580	0.10	21.750	0.340	21.873	0.245
		B	22.02	22.08	22.050	0.06	22.12	22.16	22.140	0.04	22.095	0.090		
X	29	A	22.12	22.02	22.070	0.10	22.09	22.05	22.070	0.04	22.070	0.000	22.159	0.178
		B	22.21	22.14	22.175	0.07	22.34	22.30	22.320	0.04	22.248	0.145		
Total						1.01				0.88		2.915	216.578	1.249
Mean						0.051				0.044		0.146	21.658	0.125
L.C.L.						0				0		0	21.423	0
U.C.L.						0.167				0.144		0.477	21.893	0.408

procedures will have been mechanized.

As an example the results of soda-analysis are summarized in Table 5. In the Table the data, for example, of lot No. 1 (Dec. 20 th) A_{11}, A_{12}, A_{21}, A_{22}, corresponding the notations in Fig. 3 are, respectively 21.34, 21.39, 21.40 and 21.24 %, and it is the same with respect to the results obtained from the gross sample B. Further ; $\overline{X}_1$ is the average of X_{11} and X_{12}, R_1 the range, $\overline{X}$ is the average of $\overline{X}_1$ and $\overline{X}_2$, R_3 the range, $\overline{\overline{X}}$ is the average of $\overline{X}_{(A)}$ and $\overline{X}_{(B)}$ and R_4 is the corresponding range.

Fig. 7 is the control charts of R_1, R_2, R_3 and R_4 corresponding to the batch components of soda ash.
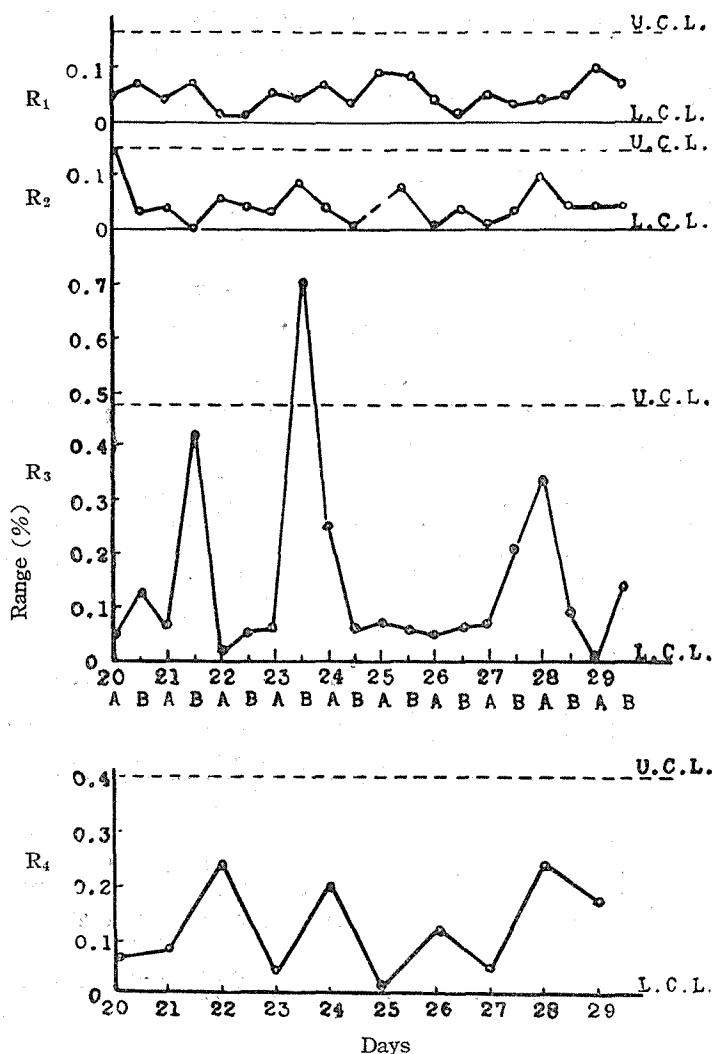

Fig. 7. Control chart.

It will be seen that the values of R_1, R_2, R_3 and R_4 are respectively within U.

C. L. if one of them may be rejected, which indicates that the whole procedure, from sampling to chemical analysis, is almost in statistically controlled state. The control limits have been worked out by the relations, U. C. L. ; 3.27 $\overline{R}$, L. C. L. ; O, in which $\overline{R}$ is the average of R.
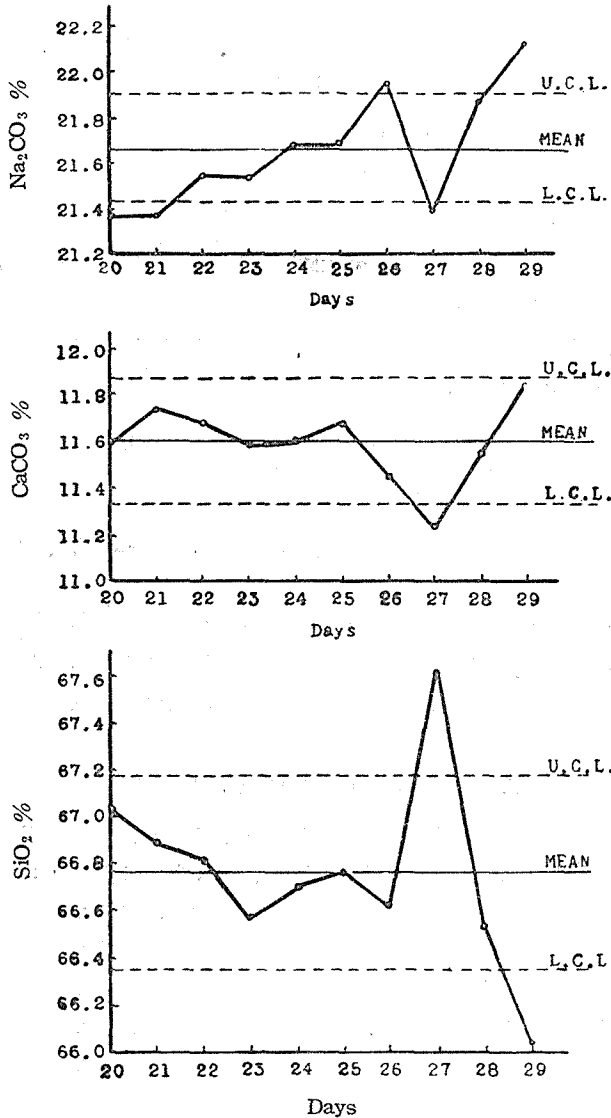

Fig. 8. Daily change of average.

In Fig. 8 is given the daily change of the value of $\overline{\overline{X}}$, namely, the expected values of the average of the components, soda ash, lime and sand in 32 tons charged during a day.

The broken lines in the figure indicate the control limits of the average values

corresponding to each components which have been calculated by

$$\text{U. C. L. : } \overline{\overline{X}} + 1.88 \ \overline{R_4}$$

$$\text{L. C. L. : } \overline{\overline{X}} - 1.88 \ \overline{R_4}, \text{ where } \overline{R_4} \text{ is the average of } R_4.$$

IV. RECISION OF ANALYTICAL METHOD

The expected values $\hat{\sigma}$, $\hat{\sigma}_S$, $\hat{\sigma}_{R1}$, $\hat{\sigma}_{R2}$ aud $\hat{\sigma}_M$ corresponding, respectively, to σ, σ_S, σ_{R1}, σ_{R2} and σ_M can be found out using following relations.

$$\hat{\sigma}^2 = (\overline{R_4}/d_2)^2$$

$$\hat{\sigma}_{R2}^2 + \hat{\sigma}_M^2 = (\overline{R_2}/d_2)^2$$

$$\hat{\sigma}_{R1}^2 = (\overline{R_3}/d_2)_2 - (\hat{\sigma}_{R2}^2 + \hat{\sigma}_M^2)/2$$

$$\hat{\sigma}_S^2 = (\overline{R_4}/d_2)^2 - (\hat{\sigma}_{R1}^2/2) - (\hat{\sigma}_{R2}^2 + \hat{\sigma}_M^2)/4,$$

in which the coefficient $d_2 = 1.128$[3].

In Table 6 are given the varience and standard deviation of the results of analysis of soda ash, lime and sand.

Table 6. Precision of analytical method.

	Variance and standard deviation %									
	$\hat{\sigma}^2$	$\hat{\sigma}$	$\hat{\sigma}_S^2$	$\hat{\sigma}_S$	$\hat{\sigma}_{R1}^2$	$\hat{\sigma}_{R1}$	$\hat{\sigma}_{R2}^2$	$\hat{\sigma}_{R2}$	$\hat{\sigma}_M^2$	$\hat{\sigma}_M$
Soda ash	0.0121	0.1098	0.0037	0.0608	0.0157	0.125	0.0017	0.041	0.0001	0.011
Lime	0.0163	0.1277	0.0030	0.0548	0.0215	0.147	0.0095	0.097	0.0004	0.020
Silica	0.0370	0.1922	0.0192	0.1400	0.0305	0.174	0.0100	0.100	0.0003	1.016

V. RESULTS OF TIME STUDY

The time necessary for carrying on each step, from the sampling out of batch into the boxes A and B to the chemical analysis, was found to be :

(1) Dividing the gross sample of 76.8 kg. to 600 g.   1 hr.

(2) Drying the 600 g. sample   2 hr.

(3) Milling of raw batch   1 hr.

(4) Dividing from 600 g. to 10 g.   0.5 hr.

(5) Drying 10 g. sample   1 hr.

(6) Chemical analysis   1.5 hr.

Some of the above procedures can be carried out at a time to some extent. The total time necessary for carrying out the batch analysis by two operators was found to be about 13 hours. If only two final samples, each from A and B, were analysed the time necessary would be reduced to about 8 hours, although, at the same time, the precision would be lowered, for example, to $\sigma = 0.15$ % for water soluble component.

SUMMARY

1. The method of analysis to estimate the average batch composition of daily chargh in a factory with the precision of 0.1 % was established.

2. The statistical backgrounds for each step of above analytical procedure, the sampling, dividing and chemical analysis have been discussed in detail.

ACKNOWLEDGMENT

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