Brazilian Journal of Experimental Design, Data Analysis and Inferential Statistics

Federal University of Rio de Janeiro

BJEDIS, Rio de Janeiro, Special Edition, v. 01, 2021, Page:130

DOI: https://doi.org/10.55747/bjedis.v1i1.48412

E-ISSN: 2763-6925

Special Edition **Received 01/27/2021. Revised 02/03/2021. Accepted 03/16/2021. Published 05/13/2021.**

A Case Study of an Experimental Design to Laboratory Process Improvement.

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Abstract: In a chemical analysis laboratory it is extremely important to identify and quantify the contribution of the stages of the analytical process in the final variability of the results, thus facilitating the directing of efforts in the search for continuous improvement. In this type of laboratory, the improvement corresponds to the reduction of variability, which guarantees greater reliability of the analytical results, and one of the ways to achieve this reduction is to carry out an experiment. In this work, a practical example of a chemical industry will be presented in which the experiment allowed to quantify the contribution of the steps: (I) preparation of the samples, (II) of the different technicians and (III) the measurement itself. An experiment with random factors and a hierarchical factor (nested factor) was used and the results were analyzed using an ANOVA. From the analysis of the results, it was identified that the major contributor to the final variability was the preparation of the samples. Efforts were directed at this stage, with a review of the procedure and training of technicians, which provided a general improvement in the reliability of the analytical results. With a second similar experiment it was possible to prove the effectiveness of the improvement actions.

Keywords: Design of Experiment; Variability Reduction; Chemical Analyses, Analytical Laboratory; Continuous Improvement.

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1. INTRODUCTION

The laboratory within an industry is of fundamental importance to control and improve the stages of the production process, in addition to ensuring the quality of the products generated. The bauxite refining industry is no different.

In the process control of bauxite refining, as in any other process, it is extremely important to reduce variability. For this, it is desirable to know the contribution of all the process and laboratory variables that make up the product's variability, thus it is possible to identify the greatest opportunities for reducing variability and consequently production costs.

Usually in the process control they emphasize only the variability of the analytical process, leaving aside other steps that also contribute to the final variability. Within the laboratory, the variability of the resampling and sample preparation steps (quartering, crushing and spraying), its sums to the variability of the analytical process and consequentially to the production process.

What is usually found is that when an analytical result is not favorable to the production personnel, the laboratory is questioned as to the reliability of these results, as if the analysis step were the only one responsible for the variability of the process.

The ideal is to know the variability of each stage of the process, from sampling to the analysis of the sample, including initial quartering, crushing, some secondary quartering and spraying. Each step is a process and according to [1] and [2], based on the second principle of Statistical Thinking, every process has variability, and if the variance is a quadratic operator, it will be added and never subtracted, thus, the final variability it will always be greater than that of each stage individually.

Also, according to the authors [1] and [2], the third principle of Statistical Thinking, the knowledge of the causes and the reduction of variability is what makes the difference between a good professional and a mediocre one. Thus, any effort to know the contribution of each step of the sampling process, sample preparation and analysis is extremely important, since efforts can be focused on improving the process of that step that has the greatest contribution to the final variability, providing greater reliability for the laboratory results.

The process of preparation and analysis of bauxite samples, which is the object under study, consists of, after collecting the sample, grinding, quartering and spraying. An aliquot of this sample is mixed with a NaOH solution under previously defined conditions (sample mass, concentration and volume of the caustic solution) and a digestion of this mixture is performed with time and temperature defined in procedure. After this stage, the material is filtered and the contents of available alumina, reactive silica, among others, are analyzed.

With this study it is possible to obtain gains for the company, which are incalculable, since the decisions to control the production process are more correct, contributing to significantly reduce losses and, consequently, production costs.

There are several techniques proven to be effective for this study, such as complete (2^K) and fractional (2^{K-P}) factorial experiments, among others. It was decided to use the classic experiment planning model proposed by [3] for the ease of execution for this case, in addition to being a proven technique.

In this paper was presented a practical situation where was used an application of a Design of Experiments (DOE) and the statistical technique applied in this case was an ANOVA with a nested factor and considering all factors as random factors. This is a common situation in a mining laboratory but normally by lack of knowledge they do not apply more sophisticated ANOVA like showed in this paper. This technique should be used as an example not only for bauxite but for different ores because this is a universal and robust statistical technique. The objective of this work was the identification of opportunities for improvement in the analytical process with the reduction of variability through an experiment (DOE - Design of Experiment); and other objectives were evaluated: I) If there is a difference between the sub samples obtained in the process of quartering / spraying; II) If there is a significant difference between laboratory analysts and III) If there is a significant effect of the Sample and Technician interaction.

2. EXPERIMENT

To carry out the experiment, 3 samples of bauxite (A_i) with alumina contents very different from each other were selected to cover a wider range of variation and allow the conclusions to be valid for the entire range of the experiment. For the initial sample preparation, which consists of crushing and quartering, only one technician was assigned. The intention of assigning only one person to the activity was to reduce the variability of the experiment, reducing a source of variation and making it a little less complex.

Still in the initial preparation, following the company's procedure, each of the 3 samples was ground, homogenized and quartered, producing 4 sub-samples, totaling 12 sub-samples, called $B_{j(i)}$. This step can be seen in Figure 1.

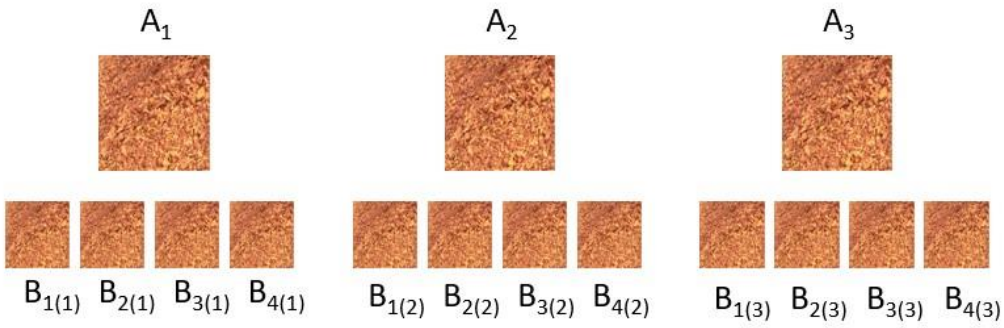

*Figure **1** – Initial sample preparation.*

Each of the 12 sub-samples ($B_{j(i)}$) was homogenized and divided into two equal parts, totaling 24 sub-samples, thus completing the preparation.
Two technicians (C_k) were randomly chosen from among the possible ones that dominate the analytical technique and 12 sub-samples ($B_{j(i)}$) were designated for each one.
In a random way, each technician analyzed the 12 sub-samples in duplicate, totaling 48 experiments.

2.1. Experiment Modelling

The experiment model defines the entire structure of the ANOVA – Analysis of Variance [3] from the calculations, to the definition of the control factors, their levels and the type of factor.

2.1.1 Control Factors

Based on the knowledge of the bauxite analysis process, the main variables (or control factors) that impact on the quality of the result were chosen. For each control factor, the number of values tested (levels) was based mainly on the time and resources available in the laboratory.
The control factors, the type and the respective levels defined were:
A_i = Samples; 3 levels; Random factor;
$B_{j(i)}$ = Sub samples; 4 levels; Random and hierarchical factor to the Samples factor (A_i);
C_k = Technicians; 2 levels; Random factor;
Analysis repetitions = 2;
Response variable = Al_2O_3 available;
Significance level of the experiment (α) = 5%.

2.1.2. Experiment Structural Model

Each experiment needs a model to represent it and define the entire experimental structure, including the calculations. For this experiment the structural (qualitative) model was:

$$X_{ijkl} = \mu + A_i^{(R)} + B_{j(i)}^{(R)} + C_k^{(R)} + AC_{ik}^{(R)} + Z_{l(ijk)}^{(R)}$$

As the Sub Samples depend on the respective Samples, this particularity was represented by a hierarchical factor in the model, in the case $B_{j(i)}$; thus, it is not possible to test the interactions with this control factor, that is, the interactions AB_{ik}, BC_{jk} and ABC_{ijk}.

In order to have an exact estimate of the variance of each factor, it was defined that all factors in the model would be considered as Random factor – represented by the symbol (R) above each factor in the model, and as a consequence of this, the conclusions about each factor can be extended to other levels of the factor that was not tested in the experiment.
With the disadvantage of this fact, is that the F test is calculated in an unconventional way, and to define the denominator of the F test, the algorithm presented in [3] was used.

2.1.3. ANOVA Table

The hypotheses to be tested in this experiment are:

$H_0: [\sigma_A^2] = 0$, it means that there is no significant difference between the samples in relation to the alumina content;
$H_0: [\sigma_B^2] = 0$, it means that there is no significant difference between the sub-samples in relation to the alumina content;
$H_0: [\sigma_C^2] = 0$, it means that there is no significant difference between the technicians in relation to the alumina content;
$H_0: [\sigma_{AC}^2] = 0$, it means that there is no significant effect of the interaction between samples and technicians on the alumina content;

The table structure and ANOVA calculations are shown in Table 1.

Hypothesis	SV	DF	SS	MS	F_{obs}	F_{crit}	P-value	Decision
$\boldsymbol{H_0: [\sigma_A^2] = 0}$	A_i	i – 1		SS_A/DF_A	MS_A/MS?	$F_{(5\%;\ DFA;DF?)}$		
$\boldsymbol{H_0: [\sigma_B^2] = 0}$	$B_{j(i)}$	(j – 1) * i		SS_B/DF_B	MS_B/MS?	$F_{(5\%;\ DFB;DF?)}$		
$\boldsymbol{H_0: [\sigma_C^2] = 0}$	C_k	k – 1		SS_C/DF_C	MS_C/MS?	$F_{(5\%;\ DFC;DF?)}$		
$\boldsymbol{H_0: [\sigma_{AC}^2] = 0}$	AC_{ik}	(i – 1) * (k – 1)		SS_{AC}/DF_{AC}	MS_{AC}/MS?	$F_{(5\%;\ DFAC;DF?)}$		
Residues	$Z_{l(ijk)}$	Diference						
	Total	ijkl-1						

Table **1** – ANOVA table.

Where:
Hypothesis: Hypotheses to be tested;
SV = Source of Variation;
DF = Degrees of Freedom;
SS = Sum of Squares;
MS = Mean Squared;
Fobs = Observed F Value;
Fcrit = Critical Value;
P-Value = Probability of the observed F value;
Decision = If the tested hypotheses was rejected or not.
Due to the fact that the control factors are considered random, it was necessary to calculate the Fobs according to the algorithm defined by Bennet and Franklin (1954) presented in Table 2.

*Table **2** – Algorithm to define the F test.*

Hypothesis	SV	i, 3 Random	j, 4 Random	k, 2 Random	l, 2 Random	E[QM]	F test
$\boldsymbol{H_0: [\sigma_A^2] = 0}$	A_i	1	4	2	2	$1[\sigma^2_Z] + 8[\sigma^2_{AC}] + 4[\sigma^2_B] + 16[\sigma^2_A]$ = $1[\sigma^2_Z] + 8[\sigma^2_{AC}] + 4[\sigma^2_B]$	$QM_A/(****)$
$\boldsymbol{H_0: [\sigma_B^2] = 0}$	$B_{j(i)}$	1	1	2	2	$1[\sigma^2_Z] + 4[\sigma^2_B]$ = $1[\sigma^2_Z]$	QM_B/QM_R
$\boldsymbol{H_0: [\sigma_C^2] = 0}$	C_k	3	4	1	2	$1[\sigma^2_Z] + 8[\sigma^2_{AC}] + 24[\sigma^2_C]$ = $1[\sigma^2_Z] + 8[\sigma^2_{AC}]$	QM_C/QM_{AC}
$\boldsymbol{H_0: [\sigma_{AC}^2] = 0}$	AC_{ik}	1	4	1	2	$1[\sigma^2_Z] + 8[\sigma^2_{AC}]$ = $1[\sigma^2_Z]$	QM_{AC}/QM_R
Residues	$Z_{l(ijk)}$	1	1	1	1	$1[\sigma^2_Z]$	

The algorithm was unable to find the denominator for the F test of the A_i factor, so it is necessary to perform an approximate F test for this factor, which is nothing more than a linear combination between the MS for both the numerator and the denominator of the F test, as described in [3].

The approximate F test for the factor A_i is obtained by the expression: *[QMA + QMR] / [QMB + MQAC]* and the respective degrees of freedom are:

$$GL_{Numerator} = \frac{(QMA + QMR)^2}{\frac{(QMA)^2}{GL_A} + \frac{(QMR)^2}{GL_R}}$$

$$GL_{Denominator} = \frac{(QMB + QMAC)^2}{\frac{(QMB)^2}{GL_B} + \frac{(QMAC)^2}{GL_{AC}}}$$

3. RESULTS ANALYSIS

The analytical results of %Al2O3-available obtained through automatic titration are not presented due to the confidentiality contract with the client. After the execution of the experiment and the application of ANOVA, the results are shown in Table 3.

*Table **3** – ANOVA experimental results.*

Hypothesis	SV	DF	SS	MS	F_{obs}	F_{crit}	P-value	Decision
$\boldsymbol{H_0}: [\boldsymbol{\sigma_A^2}] = \mathbf{0}$	A_i	2	892.95	446.48	377.71	4.10	0.000	Reject
$\boldsymbol{H_0}: [\boldsymbol{\sigma_B^2}] = \mathbf{0}$	$B_{j(i)}$	9	9.42	1.05	3.94	2.18	0.002	Reject
$\boldsymbol{H_0}: [\boldsymbol{\sigma_C^2}] = \mathbf{0}$	C_k	1	22.82	22.82	167.83	18.51	0.006	Reject
$\boldsymbol{H_0}: [\boldsymbol{\sigma_{AC}^2}] = \mathbf{0}$	AC_{ik}	2	0.27	0.14	0.51	3.28	0.604	Not Reject
Residues	$Z_{l(ijk)}$	33	8.76	0.26				
	Total	47	934.23					

All three control factors were tested for heteroscedasticity (different variances) using the Levene test and none of them showed a significant difference between the variances of the levels of each factor.

The model's explanation coefficient, R^2, was 0.991, showing a model that explains the experimental variation. For a future comparison of the variability (before and after), an estimate of the standard deviation of the experimental data (√QMR) was obtained, which is ± 0.515%.

With a significance level of 5%, it can be said that there is a significant difference between the samples (A_i) in relation to the alumina content. It was already expected, because 3 samples were chosen purposely very different from each other, so that the test conclusions can be valid for practically the whole possible range of routine samples. There was also a significant difference (at 5%) between the sub-samples that were prepared and quartered, within each sample ($B_{j(i)}$); which shows that there is a significant variation during sample preparation.

There was also a significant difference between technicians (Ck), which shows a great opportunity for improvement in the analytical process. The Technician * Sample interaction was not rejected (p-value 0.604), which leads to the conclusion that technicians do not produce significant variation with any particular sample.

Since the ANOVA rejected the null hypothesis, but does not show where are the differences, it is possible to check it by the use of different techniques, in this case we choose the Box Plot. A visualization of this Sample * Technician interaction using Box Plot can be seen in Figure 2.

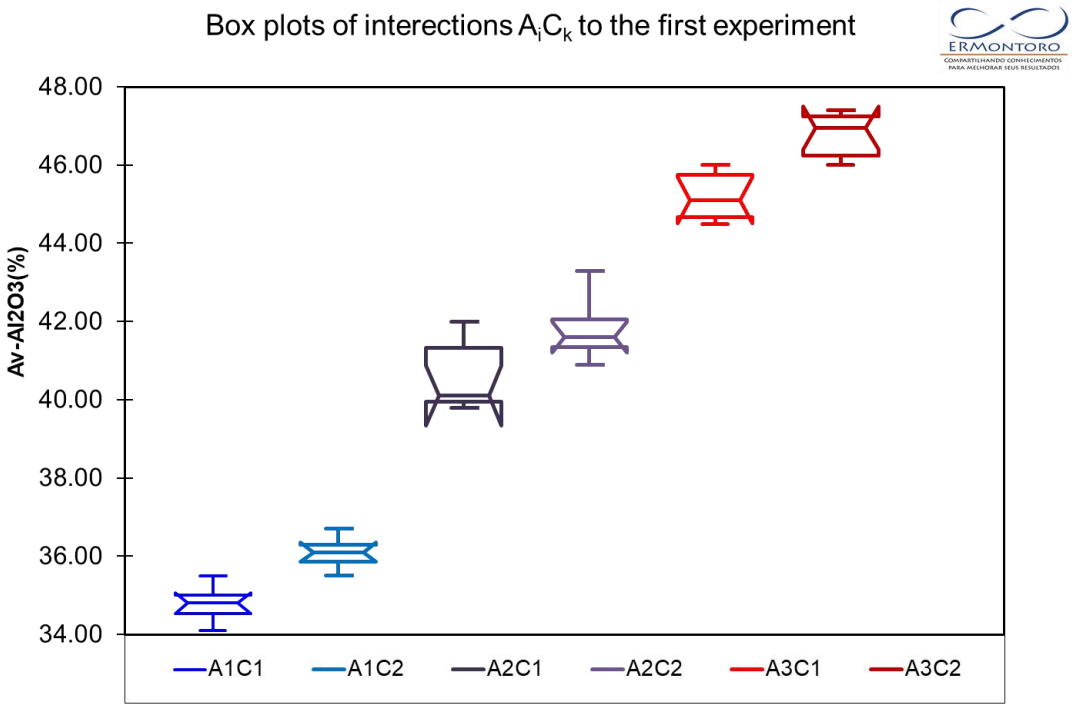

*Figure **2** – Box plot of the Sample*Technician initial experiment.*

From Figure 2, it is possible to see a clear tendency for Technician 2 to produce greater results than Technician 1 in all samples; clearly there are opportunities for improvement in performing the analytical procedure.
The variance estimate for each control factor was made using the variance components method, as presented in [3]. The drawback of this method is that it can sometimes it obtained an estimate of negative variance, which is not reasonable because by definition, variance is non-negative. Still according to the author [3], there are some ways to work with these cases, one of which is to assume the negative variance estimate as zero, keeping the others intact.
The estimates of the variance components were obtained from the expressions of the E[MS] in Table 3 and the respective mean squares (MS) of the ANOVA table, treating them in a system of equations. Solving this system, it is possible to obtain the following estimates presented in the Table 4.

*Table **4** – Variance components estimative.*

Component	Variance Estimative	Standard Deviation
Samples (A_i)	27,84	±5,28
Sub Samples ($B_{j(i)}$)	0,198	±0,44
Technician (C_k)	0,935	±0,97
Sample*Technician (AC_{ik})	-0,015	
Residues ($Z_{l(ijk)}$)	0,26	±0,51

Based on the analysis of the experiment, training work on the analytical procedures was carried out with the laboratory technicians, both in preparation and analysis.
After a while, the same experiment was repeated, with the same samples to assess the effectiveness of the training carried out with the technicians. ANOVA results are shown in Table 5.

*Table **5** – ANOVA results for the second experiment.*

Hypothesis	SV	DF	SS	MS	F_{obs}	F_{crit}	P-value	Decision
$H_0: [\sigma_A^2] = 0$	A_i	2	795.009	397.50	4380.19	9.55	0.000	Reject

$H_0: [\sigma_B^2] = 0$	$B_{j(i)}$	9	0.157	0.017	0.30	2.18	0.971	Not Reject
$H_0: [\sigma_C^2] = 0$	C_k	1	0.010	0.018	0.14	18.51	0.745	Not Reject
$H_0: [\sigma_{AC}^2] = 0$	AC_{ik}	2	0.147	0.07	1.25	3.28	0.300	Not Reject
Residues	$Z_{l(ijk)}$	33	1.937	0.06				
	Total	47	797.113					

The model's explanation coefficient, R^2 was 0.998, which demonstrates that in this second test, the model also explains the experimental variability.

The estimative of the standard deviation of the experimental results of the second experiment was ± 0.242, which compared to the first experiment (± 0.515), achieved a significant reduction in the variability of about 50%.
The null hypotheses were not rejected with a significance level of 5%, except for the hypothesis of difference between samples (Ai), but this was already expected for the same reason exposed in the first test.
The Box Plot comparing each technician within each sample can be seen in Figure 3, in which there is a significant improvement, as there is no trend for any technician.

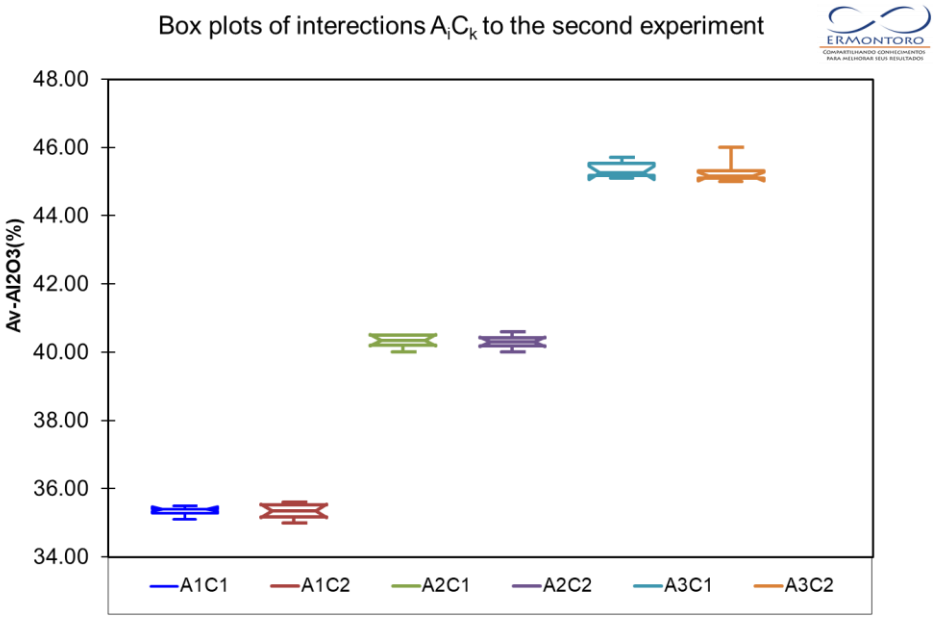

*Figure **3** – Box plot of the Sample*Technician second experiment*

The estimates of the variance components for the second experiments are shown in Table 6.

*Table **6** – Variance components estimative (second experiment)*

Component	Variance Estimative	Standard Deviation
Samples (A_i)	27,84	±5,28
Sub Samples ($B_{j(i)}$)	0,198	±0,44
Technician (C_k)	0,935	±0,97
Sample*Technician (AC_{ik})	-0,015	
Residues ($Z_{l(ijk)}$)	0,26	±0,51

The effectiveness of the training was verified by reducing the variability presented in Table 7, comparing the variances of the control factors of the two experiments.

*Table **7** – Variance estimative comparison between first and second experiment.*

Component	First Experiment		Second Experiment	
	Variance Estimative	Standard Deviation	Variance Estimative	Standard Deviation
Samples (A_i)	27,84	±5,28	24,85	±4,98
Sub Samples ($B_{j(i)}$)	0,198	±0,44	-0,011	
Technician (C_k)	0,935	±0,97	0,006	±0,08
Sample*Technician (AC_{ik})	-0,015		-0,007	
Residues ($Z_{l(ijk)}$)	0,26	±0,51	0,06	±0,24

The reduction in the standard deviation of Technicians (C_k) was about 10 times.

For the Sub Samples factor ($B_{j(i)}$), which represents the sample preparation step, it was not possible to compare the standard deviation directly, as the variance estimate of the second experiment showed a negative value.

According to [3], an additional experiment could be performed to estimate the variance of this control factor only ($B_{j(i)}$). In this case, an additional experiment was not carried out, as it was judged by the monitoring of the sample preparation activity that the procedure was being strictly followed, in addition to the fact that the variability was reduced (from 0.198 to -0.011 in the second experiment).

4. CONCLUSIONS AND RECOMMENDATIONS

Complaints from customers about the variability of results generated distrust of the laboratory and the laboratory team could not say which were the main contributors to the final variability. This complaint was really well founded, which generated an uncomfortable situation within the company.

It was proposed to carry out an experiment to quantify the contribution of the laboratory process stages to the final variability, and after the experiments were carried out, the laboratory regained the trust of his customers, additionally the morale of the technicians was restored.

Corrective actions, including the training of technicians, proved to be effective in reducing variability, providing greater reliability of the laboratory's results to customers.

The strength of the design of experiments was evident, the gains that are generated with this technique are the reduction of costs, greater analytical reliability, better and more correct decisions.

The improvements achieved were proven through the design of experiments, which proved to be a quite simple execution and effective statistical technique for used in any industry.

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