

## LETTERS TO THE EDITOR

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## QUASI-LATIN SQUARES IN EXPERIMENTAL ARRANGEMENTS

IN the thesis submitted by the author in 1943 to the Calcutta University, it was shown how the Design of Experiments consists of the Fundamental problem together with the problem of Balancing and the Construction of designs. Every experimental design is a mathematical solution to a combinatorial problem directly deducible from the mathematical model set up by the necessary balance and other requirements such as the block size, number of replications, cost of experimentation, etc., required by the experimenter. Two types of designs called as 'The partially balanced design' and 'The Intra- and Inter-group balanced design', gave a variety of designs in the case of incomplete block designs. These two systems, also, gave balanced or partially balanced confounded designs in the case of general factorial experiments, asymmetrical or symmetrical. It is proposed to extend these ideas to Quasi-Latin squares which are suggested by Fisher's requirement of the 'local control' by which the efficiency of an experimental design may be enhanced by minimising the error without increasing the number of replications. These were first introduced by Yates<sup>1</sup> in the case of incomplete block designs.

**The Fundamental Problem.**—The most general set up consists of  $v$  treatments denoted by  $T_1, T_2, T_3 \dots T_v$  tested in  $n$  lattice square arrangements of  $s^2$  cells each, such that the  $i$ -th treatment is replicated  $r_i$  times and the treatments  $T_i$  and  $T_j$  appear together in columns and rows combined  $\lambda_{ij}$  times and in squares, on the total  $\mu_{ij}$  times. The parameters are connected by the following relationships:—

$$\lambda_{ii} = 0$$

$$\lambda_{ij} = \lambda_{ji}, \mu_{ij} = \mu_{ji}$$

$$\sum r_i = n s^2$$

$$2(s-1)r_i = \sum_j \lambda_{ij}$$

$$r_i(s^2-1) = \sum_j \mu_{ij}$$

— **Analysis of the General Design.**—Using the methods of analysis developed in the above thesis we get the estimating equation as,

$$Q_i = r_i(s-1)^2 t_i - s \sum_j \lambda_{ij} t_j + \sum_j \mu_{ij} t_j$$

where  $t_i$  estimates the effect of the treatment  $T_i$ , and

$Q_i = s^2$  (sum of observations of the  $i$ -th treatment)

—  $s$  (sum of row and column totals in which the  $i$ -th treatment occurs)

+ the weighted sum of square totals the weights being number of times the  $i$ -th treatment occurs in a square.

From these set of equations, we can test the significance of any estimable linear expression of the treatment effects by comparing it against its estimated standard error. The estimates of linear expressions being linear functions of  $Q_i$ , their standard errors, ultimately, depend on the following results. Let  $Q_i$  be gathered from  $m_i$  lattice squares the contribution from the  $j$ -th square being  $q_{ij}$ .

$$Q_i = \sum_j q_{ij}$$

$$V(Q_i) = \sum_j V(q_{ij})$$

$$V(q_{ij}) = r(s-2s+r)^2 + (s-r)^2 2r + (s-r)^2 + r(r-1)(r-2s)^2$$



when the  $i$ -th treatment occurs  $r$  times in  $j$ -th lattice square.

$$\text{Cov}(Q_i Q_m) = \sum \text{Cov}(q_{ij} q_{mj}).$$

The most general expression for the covariance has been found out but is not given here due to lack of space. There are two types of designs which appear to be fruitful.

**Type 1.**—Let  $s\lambda_{ij} - \mu_{ij} = v_{ij}$ . We impose restrictions on  $v_{ij}$  similar to that of the partially balanced design (it may be noted that the second system of parameters introduced by Bose and Nair<sup>2</sup> are restrictions on the parameters  $v_{ij}$ ) or the Intra- and Inter-group balanced design of the incomplete blocks. Thus we get two subtypes in type 1.

**Type 2.**— $\mu_{ij} = \mu$   $i \neq j$ , independently of  $i$  and  $j$ . In this case we impose restrictions on the parameters  $\lambda_{ij}$ . We get two subtypes by allowing the parameters to satisfy the conditions of the partially balanced or the Intra- and Inter-group balanced design of the incomplete block designs.

Various methods of construction of the designs such as the geometrical and the method of differences developed by Bose<sup>3</sup> and used by the author have been found out and a full list of practically useful designs will be given in an elaborate paper to be published shortly. Also the Quasi-Latin squares used for double confounding in factorial experiments, the necessary and the sufficient condition for which has been given by the author in the work referred to, come out as special cases.

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October 4, 1943.

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1. Yates, *Technical Communication* 35, *Imp. Bureau Soil Science*.
2. Bose and Nair, *Sankhya*, 4, 337-72.
3. —, *Ann. of Eugen*, 9, 358-99.

### CATALYSIS OF THE INTERACTION BETWEEN HYDROGEN SULPHIDE AND SULPHUR DIOXIDE BY SILVER SULPHIDE

In the course of an investigation on the influence of moisture on the interaction between hydrogen sulphide and sulphur dioxide ( $2 \text{H}_2\text{S} + \text{SO}_2 \rightarrow 2 \text{H}_2\text{O} + 3 \text{S}$ ), it was noticed that the reaction between the two gases occurred only to a small extent at the surface of pure silver powder but that the reaction was highly autocatalytic, owing to the production of silver sulphide, which vigorously catalysed the union. For instance, in a representative experiment where the volume of the gases was kept constant (the reaction vessel being in an air thermostat at  $32^\circ.5 \text{C.}$ ) the fall in pressure due to interaction at the surface of silver was only 13 mm. during the first 70 minutes and the silver gradually acquired a dark colour, owing to the formation of silver sulphide. During the next 20 minutes, however, owing to the catalytic effect of silver sulphide, the fall in pressure was 103 mm.

The progressive formation of water during the above reaction greatly enhanced the auto-

catalytic nature of the reaction, the activity of silver sulphide being proportional to the vapour pressure of water in the system. Using a hygrometer (mixture of suitable hydrate and its anhydrous form, e.g., oxalic acid, barium bromide) the vapour pressure of water in the reaction vessel could be controlled and the effect of moisture on the catalytic activity of silver sulphide studied. When phosphorus pentoxide was used as the desiccant, the silver sulphide was inactive.

To catalyse the union of the two gases at the surface of glass, a very much higher vapour pressure of water was found to be necessary, than in the case of silver sulphide. The kinetics of the reaction between sulphur dioxide and hydrogen sulphide, as catalysed by silver sulphide could, therefore, be conveniently investigated in a glass apparatus, wherein the vapour pressure was kept sufficiently low with the aid of an appropriate hygrometer, so that while no detectable reaction took place at the surface of glass, the catalytic activity of silver sulphide was adequate.

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### CATALYTIC ACTIVITY OF SILVER SULPHIDE

SILVER SULPHIDE, which had been found by one of us to catalyse the union between hydrogen sulphide and sulphur dioxide, was noticed to have an equally remarkable catalytic effect on the decomposition of sulphur monoxide (and its polymer  $\text{S}_2\text{O}_2$ ). The monoxide, prepared by the combustion of sulphur in carefully dried oxygen under a pressure of 5 mm. of mercury, was passed over silver sulphide and found to undergo rapid decomposition as indicated by the increase in weight of the sulphide, due to sulphur deposition. In one series of experiments, wherein the same sample of silver sulphide was used as catalyst, the sulphur produced by decomposition of the monoxide was 30.5, 22.4 and 20.0 mg., the corresponding volumes of oxygen employed in the combustion of sulphur being 195, 210 and 250 c.c. A noticeable fall in efficiency of the sulphide occurred as the catalyst got covered by sulphur. In another experiment, when a fresh sample of catalyst was used, the weight of sulphur deposited was 265 mg. when 4 litres of oxygen were employed for combustion.

Silver sulphide was also found to rapidly catalyse the reaction between hydrogen sulphide and sulphur monoxide, even when both the gases had been carefully dried over phosphorus pentoxide. As in the previous experiments, the sulphur liberated during the reaction, was determined by measuring the increase in weight of the silver sulphide. Water formed, was absorbed in a phosphorus pentoxide tube and weighed. As was to be expected, two reactions took place simultaneously at the surface of the catalyst—the decomposition of sulphur monoxide and the reaction between hydrogen sulphide and sulphur