

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 $\lambda_{ij} = \mu_{ij} = v_{ij}$. 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 Nair² 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.— $\mu_{ij} = \mu_i \mu_j$, independently of i and j . In this case we impose restrictions on the parameters λ_{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 Bose³ 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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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 S_2O_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

monoxide in terms of the equation $\text{SO} + \text{H}_2\text{S} = 2\text{S} + \text{H}_2\text{O}$. It was not practicable to suppress completely the decomposition of sulphur monoxide at the surface of silver sulphide, but by increasing the proportion of hydrogen sulphide to that of oxygen* used in the combustion of sulphur, the extent of the interaction between hydrogen sulphide and sulphur monoxide could be increased, as could be gathered from results obtained in a set of experiments:—

Ratio $\text{H}_2\text{S}/\text{O}_2$	Wt. S in mg.	Wt. H_2O in mg.	Ratio S/ H_2O
1.0	32.0	5.0	6.4
1.6	19.0	4.2	4.5
4.0	11.5	3.0	3.8

If the interaction between hydrogen sulphide and sulphur monoxide was the only reaction taking place at the catalyst surface, the ratio of sulphur to water would be 3.6. It has to be noted that the sulphur dioxide produced along with the monoxide during the combustion of sulphur, does not react with hydrogen sulphide at the surface of silver sulphide when phosphorus pentoxide is used as the desiccant for the two gases. Further work is in progress.

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*No accurate method that can conveniently be employed, is at present available for the determination of sulphur monoxide in the products of combustion. Conditions under which the sulphur was burnt were kept as constant as possible, and it was assumed that the sulphur monoxide produced was directly proportional to oxygen used in combustion. A method for the accurate determination of sulphur monoxide, based on its catalytic decomposition by silver sulphide, is now being developed in this laboratory.

A SENSITIVE METHOD FOR THE ESTIMATION OF COMMON VOLATILE TRIHALOGEN ANÆSTHETICS IN THE BLOOD AND TISSUES OF ANIMALS

FUJIWARA¹ in 1914 found that chloroform in the presence of alkali gives a pink colour with pyridine and that the method can detect chloroform in dilutions upto 1 in a million. Cole,² in 1926, utilised this method for determining the concentration of chloroform in the body tissues. Recently Daroga³ *et al.* have stabilised the colour produced by adding a little acetone. All these applications of Fujiwara reaction suffer from a drawback that the colour obtained is not quite clear due to the presence of protein in tissues and blood and that the colour of the blood interferes with the estimations. The present work is concerned

with a new method where the Fujiwara reaction has been employed to detect and estimate the common trihalogen volatile anæsthetics in the blood and other body tissues.

METHOD

5 c.c. of blood from an animal anæsthetised with chloroform or trichlorethylene are put in a 1½" diameter test tube containing 40 c.c. of distilled water and 5 c.c. of 0.05 per cent. saponin solution. The test-tube is fitted with a rubber cork through which pass two tubes, one as an entry for air and the other as an exit for it. The exit is bent twice at right angles and passed into another rubber cork with a condenser arrangement fitting to a similar test tube and containing 20 c.c. of pyridine. The exit tube dips into pyridine. The pyridine test tube is immersed in ice and ice water is circulated in the condenser which is fitted to it. The condenser exit is passed through rectified spirit which acts as a trap. Care is taken to see that all the connections are air-tight except the last exit. The blood is now air-distilled and the quantity of chloroform or trichlorethylene present in the blood is absorbed in pyridine. The current of air is passed for one and half hours and after this period the test tube containing the hæmolyzed blood is heated to about 80° C. by gentle heat, while the current of air is continued. After 2½ hours the apparatus is disconnected. The trap of rectified spirit is always tested for the presence of the anæsthetic. It is found that as long as the pyridine test tube and the condenser are properly cooled no anæsthetic could be detected in the trap. The pyridine in the test tube which now contains chloroform or trichlorethylene is taken for qualitative and quantitative estimations.

The pyridine containing the anæsthetic is diluted 1 in 4 with fresh pyridine. 5 c.c. of this solution are transferred to a long test tube containing 10 c.c. of 20 per cent. alkali [NaOH] and then lightly plugged with cotton wool. The test tube is now dipped into a boiling water bath for 1½ minutes and then cooled in ice. The coloured pyridine layer is transferred to another test tube and compared in a Leitz colorimeter with the colour produced by a standard solution of the anæsthetic prepared in pyridine. The concentration of the standard is usually 1.2 mg./100 c.c. The colour is stable for half an hour after removal if it is kept cold and no acid vapours are allowed to come in contact with it.

For estimating the anæsthetic in tissues, the tissue is finely minced and ground in a mortar and pestle, the whole operation being performed under acidified ice-cold water. The acid-water along with the suspended tissue is then transferred to a wide test tube and the procedure described above followed.

The method was standardised by estimating a known quantity of chloroform or trichlorethylene added to the blood. The following table shows some of the results obtained and the percentage variation between the actual quantities added and those that are estimated.

With this method the concentrations of chloroform in the blood of various animals