RHYTHMIC PRECIPITATES.

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In the experiments on the diffusion of electrolytes in jellies, the author has found some new examples of rhythmic precipitates. In this communication the obtained results is reported briefly. The formations of rhythmic precipitates have been observed in the following cases: oxalates of calcium and strontium, copper hydroxide, and lead chromate in silica gel, and silver chromate in gelatine gel. The last mentioned case is, of course, the best known example of the rhythmic precipitate, yet it is described here because the author succeeded in making more beautiful and more sharp layers of silver chromate than ever obtained.

Calcium Oxalate in Silica Gel. To 5 c.c. of sodium silicate solution (density, 1.06) add 5 c.c. of a mixture of acetic and oxalic acid solutions (0.5 N., ratio of two acids: 1:1 or 1:3). This silica gel set in one night. Now ca. 5 c.c. of calcium chloride solution (10 to 25% solution) are poured on the gel. The banding readily forms which has an appearance like the opal. Clear spaces between bands are so narrow that the banding can better be seen by the transmitted light. Too large or too small quantity of oxalic acid prevents the formation of calcium oxalate band.

Strontium Oxalate in Silica Gel. To 5 c.c. of water glass solution (1.06) add equal volume of the mixed acid above described, and 0.01 –0.02 gr. of potassium citrate. After setting the gel put 5 c.c. of 25% strontium nitrate solution on it. About a week later, the formation of the banding of strontium oxalate is found. When the solution of strontium nitrate is poured on the silica gel containing the soluble oxalate or oxalic acid only, no strata is formed. It has previously been found by Hatschek(1) that the addition of material indifferent to the reaction system often causes the formation of bands. It is moreover known that citrate of potassium or sodium accelerates the formation of nucleus of the crystals. If the jelly contains citrate the nucleus formation will be accelerated and, accordingly, the formation of strata will become easier. By adding a small quantity of potassium citrate to the mixture before setting, the author has found the formation of dense, white banding of strontium oxalate.

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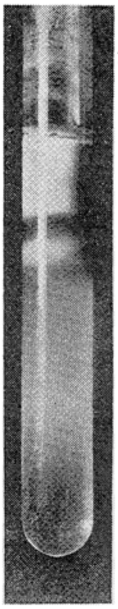
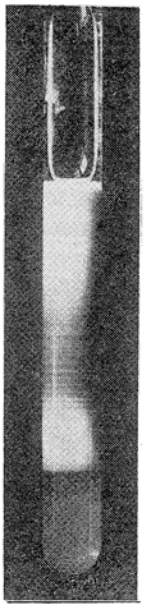
(1) Hatschek, *Kolloid Z.*, **27** (1920), 225; *Biochem. J.*, **14** (1920), 418.

The formation of periodic precipitate of barium oxalate in silica gel could not be observed whether the citrate was added or not. Without the addition of citrate the barium oxalate grows as beautiful dentrites or plumes. The addition of small amount of glucose gives the crystal of silky lustre and the crystals become larger. In the lower part of the test-tube grow crowds of thin long plates, composed of many needles just like asbestus, and each plate often measures more than 3–4 mm. When citrate is added in the silica gel, the dentrites or plumes are not formed but many small globules and crystals form. At the lower part of the test-tube considerably large well-defined crystals of barium oxalate are formed. It measures often 2–3 mm. long.

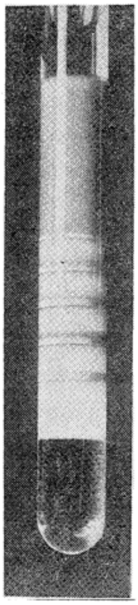
Copper Hydroxide in Silica Gel. To 5.5–6 c.c. of sodium silicate solution add 5 c.c. of 0.5 N. acetic acid. After setting the basic gel put 0.5 N. copper sulphate solution as outer electrolyte. Two or three large thick bluish white layers are formed. Besides, in the lower part of the test-tube faint layers are also formed. These precipitates are probably copper hydroxide. Fig. 1 is the photograph of it.(2)



Copper hydroxide
in silica gel
Fig. 1.



Lead chromate
in silica gel
Fig. 2.



Silver chromate
in gelatine gel
Fig. 3.

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(2) The photographs were kindly taken by Mr. N. Asada, for which the writer expresses his hearty thanks.

Lead Chromate in Silica Gel. In 5 c.c. of sodium silicate solution dissolve 0.01–0.005 gr. of potassium chromate as inner electrolyte and 0.03–0.05 gr. of glucose. To this solution add an equal volume of a half normal solution of acetic acid. After setting 10% lead nitrate solution is poured on the gel as outer electrolyte. Ten or more days later, we find that many thin and crowded bands were formed. If too much potassium chromate are added, the dentrites are also formed simultaneously, and if too little, the bands become very vague.

It is said that lead chromate precipitates in bands in agar-agar gel but not in gelatine and in silica gel. In the author's experiment, however, the periodicity has also been observed in silica gel. In the periodic precipitates of mercuric iodide in silica gel H. N. Holmes(3) has found that the presence of glucose in the gel makes the bands very much sharper. In the same manner, the author has found that the addition of glucose makes the periodic structure of the lead chromate much sharper. In this case, two periodicities exist just as the case of silver chromate banding in gelatine containing small amount of soluble chlorides. Larger periodicity is easily recognised while smaller one is often difficultly observable without using a magnifying glass. At the lower part of the tube, however, both can easily be recognised with the naked eyes. It is interesting that in this case the upper part of the jelly is coloured yellow, the subsequent layer orange and the lower brown. Under this part the banding appears and the lowermost part becomes yellow again. It seems that such colour change is caused by the size of crystals formed. The photograph is shown in Fig. 2.

Silver Chromate in Gelatine Gel. Banding of silver chromate in gelatine gel was first found by R. E. Liesegang(4) and since then, many papers have been published on this subject. It is known that silver chromate does not deposit in bands in pure agar-agar gel, while S. C. Bradford(5) succeeded in making bands in agar gel by addition of small amount of potassium citrate. According to Bradford, the existence of salts of polyvalent acids such as citrates increases, generally, the metastable limit of crystallization of silver chromate or dichromate, and accordingly, the deposited crystals will be smaller in size. And this condition favors the formation of banding.

In the case of gelatine jelly, the banding appears without the addition of any indifferent substance, though the formed silver chromate is

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(3) See, Alexander, "Colloid Chemistry," Vol. I (1926), p. 803.

(4) Liesegang, *Naturwiss. Wochenschr.*, **11** (1896), 353.

(5) See, Alexander, "Colloid Chemistry," Vol. I (1926), p. 790.

fairly coarse. So, for the same reason, if citrate is added in the inner electrolyte, more beautiful and sharper layers of very fine crystals may be expected. The experiment has been conducted as follows.

Let 0.2 gr. of gelatine swell in 10 c.c. of water and then dissolve by warming on a water bath and filter, if necessary. Then add 0.01 gr. of potassium dichromate and 0.02 gr. of potassium citrate. After setting completely, 5 c.c. of 15% silver nitrate solution are poured on the gel and stand it in a dark cold place. The banding is obtained which is more beautiful and sharper than usual (Fig. 3).

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