# Crystal Growth by Non-Aqueous Gel Diffusion

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The preparation of good quality single crystals by diffusion in aqueous silicate gels is a well established technique. [1] There is much less information on the use of non-aqueous gels for growing crystals of organic compounds. Desirju, Curtin and Paul [2] reported the use of a gel made from a dextran (Sephadex LH-20) with toluene and methanol to crystallise substituted quinhydrone complexes.

In trying to extend thier work we have found that the mixture of 3:1 toluene methanol used is too good a solvent to allow crystallisation of many of the metal complexes and organic electron donor-acceptor complexes which are of interest in our crystallographic laboratory. However, the solvent can be diluted with petroleum spirit without impeding gel formation. Using the technique described below have obtained single crystals suitable for x-ray measurements (size range 0.2-5.0 mm) from a number of systems. The structures of the pyrene complexes of 2,4,6-trinitroanisole [3] and 2,4,6-trinitrotoluene [4] have been determined on crystals grown in this way. Complexes of quinoline-2-carboxylic acid with Fe(II), Cu(II), Ce(III) and $UO_2^{2+}$ crystallised readily from the gel, we plan to determine the structures of some of these in the near future. We have also prepared crystals of α-Cu(oxine) and deep red crystals of a triclinic modification of $UO_2$ $(oxine)_2$ (Hoxine) which has not been reported previously. While we have used the technique so far only for complexes, the second example (below) shows how crystals of single substances might be grown by the diffusion of poor solvents into a gel phase containing the substance below saturation in a rich solvent.

The phenomena of Liesegang rings and of the growth of crystals with different habits in different zones of the gel, which are well known in silicate gels are also observed in the dextran gels. We feel that this technique has general utility and should be more widely known.

## Experimental

The following semi-micro scale technique gives adequate yields of crystals for crystallography(ca. 50 mg) with minimal use of the relatively expensive Sephadex LH20. Glass tubes of 5 mm bore and 10 cm long containing 4 cms of gel and 2 cms of supernatant liquid are closed at both ends with corks. When crystals appear the whole contents of the tube can be pushed out and dissected under a microscope. The crystals can be freed from traces of gel by washing with an appropriate non-solvent.

In a typical experiment the gel was prepared by mixing 0.5g of Sephadex LH20 with a solution of 50 mg of quinoline-2-carboxylic acid in 1.5 ml of a mixture of 60-80 light petroleum with toluene and methanol in the ratio 1:2:1. The gel set within one minute at 20°C. Next, 2.0 ml of a solution of anhydrous $CuCl_2$ in the same solvent were placed over the gel. The tube was corked and left vertical at room temperature. Green crystals appeared in the gel within hours and grew to 0.5 mm size over four days.

With the pyrene....2,4,6-trinitrotoluene system in the 1:2:1 solvent the supernatent trinitrotoluene diffused throughout the gel over 48 hours without crystal growth. The liquid phase was then removed and replaced by pure petrol. Orange crystals of the 1:1 complex grew throughout the gel over the next 24 hours.

Successful gel formation was obtained with ratios up to 4:1:1. Increasing the concentration of petrol reduced the solubility of both aromatic and hydrophilic compounds.While trial and error will optimise the solvent for any particular system the 1:2:1 solvent has proved generally useful.

**References**

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