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Crystal sensorics

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Abstract. The phenomena responsible for the dependence of the rate of nucleation, growth, and aggregation of crystals on the concentration and state of trace impurities in the supersaturated medium are discussed. Methods of increasing the sensitivity of the crystallisation to the presence of trace impurities are described. Data on diagnostic systems capable of detecting ultrasmall quantities of impurities from their effect on crystallisation are presented. The bibliography includes 210 references.

I. Introduction

In recent years the well known effects of impurities on crystallisation has stimulated the development of a new field of science: the crystal diagnostics of impurities. The term crystal diagnostics describes the detection, identification, and determination of the amount and state of molecular or colloidal impurities in liquid or in gaseous media from their effect on the crystallisation of a specially chosen substance: the crystallisant. At present crystal diagnostics are used in many laboratories throughout the world. The method now has its own theory and research methodology, and it can claim remarkable success in the determination of extremely small amounts of impurities, down to a few thousand and even hundreds of molecules. Thus we can assert that the foundations of a special field of knowledge (the sensitivity of crystallisation to the presence of small traces of impurities, i.e. crystal sensorics) have already been laid.

The recent developments in crystal sensorics can be attributed to two reasons. One is the unexpectedly large effect of some trace components on crystallisation,[1-3] which stimulated theoretical studies and led to a deeper understanding of the role of microcomponents. The second is the ever-increasing concern with the behaviour of trace components in ecological problems.[4, 5] The need to determine tens of thousands of different ions, complexes, isomers, conformers, and aerosol species present at concentrations down to 10^{-9} g cm^{-3} has been met only in the chemistry of the hydrosphere and of the atmosphere,[6, 7] and the best solution of these problems is not always clear.[8] In some cases a suitable solution has been provided by crystal sensorics. Thus, Kogan[9] determined small quantities (20 – 50 atoms cm^{-3}) of lead by using pyridine-2,6-dicarboxylic acid. Under certain conditions he found that in the condensation of this compound from a vapour containing lead the number of condensate particles was equal to the number of lead atoms.

In 1980 Ansorge and Maeyer[10] found that the reduction of silver nitrate by formaldehyde in a solution containing traces of protein can be controlled so that one silver microcrystal appears on each protein molecule. In this way they could estimate the amount of protein in the sample (approximately 10^6 molecules) from the number of Ag microcrystals. Lastly, in 1983 Kucher[11] used solid hydrazine to detect traces of aldehyde in the atmosphere. The conditions of the reaction were chosen to make the number of resulting hydrazone crystals proportional to the concentration of aldehydes. By counting the hydrazone crystals aldehydes in air could be detected at concentrations down to 10^{-9} g cm^{-3}. These studies[10, 11] led to the development of crystal-sensor diagnostic systems whose most important properties are listed below.

II. Fundamentals of crystal sensor action

It has been established experimentally that when a liquid (or gas) containing a microscopic component is supersaturated with respect to a crystallisant, crystallisation centres appear in its volume and grow, relieving the supersaturation.[2] On the other hand if the crystals are formed in large numbers they coalesce and grow together into aggregates. In the presence of trace components these processes follow paths different from those of the same processes in the pure liquid. As a result the kinetic parameters of the crystallisation (induction period, rate, number of crystals produced) and the morphological properties of the crystals (size, shape, and defect density) depend on the nature of the microcomponent.[12] The dependence is specific. If several trace components are present simultaneously in the system it is usually possible to choose the crystallisant and the crystallisation conditions which make the contribution of one of the trace components to the process predominant. Under these conditions by varying the crystallisation conditions we can ensure that the action of the trace component is selective and restricted either to the formation of the nucleation centres or to their growth and aggregation.

Experiments have also shown that if the trace component is sparingly soluble and is present in the medium (liquid, or gaseous) in amounts which make it supersaturated with respect to the trace

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component itself the concentration and state of the latter can be assessed from the kinetics of its spontaneous crystallisation.[13] It may therefore be useful to define the following limiting types of crystal sensor behaviour.

1. Impurity nucleation sensor action, i.e. the ability of the crystallisant to vary its rate of nucleation in response to the presence of the trace component.

2. Growth-related impurity sensor action, i.e. the ability of the crystallisant to vary its growth rate and surface features in response to the presence of the trace compound.

3. Impurity aggregation sensor action, i.e. the change in the rate of aggregation, size, and shape of the crystalline aggregates of the crystallisant under the influence of the trace component.

4. Spontaneous crystal sensor action, i.e. the ability of the trace component to vary the kinetic parameters of its spontaneous crystallisation and the properties of its crystals in response to changes in its concentration and state in the medium.

The sensor behaviour of any of these types can be characterised quantitatively by the functions $B_j(C, \Gamma)$, where B_j is the crystallisation parameter (or property of the crystal) which is sensitive to the trace component of concentration C and parameters of state Γ in the liquid. The simplest characteristics of the sensor behaviour could be the partial sensitivity factor A_j, the limit of detection Π, and the total sensitivity factor A:

$$A_j = B_{0j}^{-1}\left[C\frac{\partial B_j}{\partial C} + \Gamma\frac{\partial B_j}{\partial \Gamma}\right], \quad \Pi = \lim_{B_j \to B_{0j}} C, \qquad (1)$$

$$A = \sum_{j=1}^{n} A_j .$$

Here B_{0j} is the value of the parameter B_j in the absence of the trace component, and n is the number of crystallisation parameters and of properties of the crystals included in the diagnostic. Phenomena close to crystal sensor behaviour include catalysis with formation of a solid product, and photographic sensitivity. In the former case the crystallisant is formed in the medium by a chemical reaction, accelerated by the catalyst (trace component). In the latter the trace component is formed by a photochemical reaction.[14] In this respect both cases differ from the crystal sensor behaviour, in which the trace component and the crystallisant are both present in the medium initially.

III. Theory

The foundations of the theoretical studies of crystal sensorics include the models of condensation, crystal growth, and aggregation of colloids in a medium free from impurities (background models) and in the presence of trace component (working models). Most of the models are macrokinetic, with the nucleation and growth of the crystals expressed in terms of kinetic coefficients which require experimental determination.[15-18] Models in which the kinetic coefficients are expressed through the parameters of the molecular motion in the medium and on the surface of the crystals have also been developed.[19, 20]

The base model is the model of condensation in a dilute but slightly supersaturated vapour (or solution) in the presence of an impurity and of a carrier gas (to remove the heat of condensation), allowing for the formation of clusters of crystallisant and of impurity molecules and for their growth by the incorporation of free molecules or of other clusters.[21-26] The base models usually assume the existence of a critical size, below which the clusters can be treated as quasi-equilibrium formations. The probability of cluster formation is determined by the free energy of the formation, calculated quantum-chemically[27, 28] or estimated by processing data from molecular dynamics and from Monte Carlo calculations.[29-31]

Models of crystal growth include self-association and molecular adsorption processes, surface diffusion, surface clustering,[32-35] and interaction with growth steps.[36-38] The modelling of the aggregation allows for the successive addition of single microcrystals,[39-41] the equilibrium breakdown of the aggregated phase into fragments,[42-45] and the amalgamation of aggregates.[46-50] Recent developments have been reported in the numerical modelling of aggregation and fragmentation by the cluster dynamics and the Monte Carlo method,[51-55] and also analytical solutions of the kinetic balance equations describing the populations of aggregates.[56-60] The background models are the most generally used, the working models being confined to a small group of substances. Therefore the possibility of predicting the effect of the properties of the impurity and of the crystallisant on the rate of crystallisation is very limited at present.

IV. Basic relationships

1. Mechanism of the nucleation sensor action

In order to induce crystal sensor action we must generate a supersaturation with respect to the crystallisant in the diagnostic medium. In the supersaturated medium the molecules (or ions) of the crystallisant and the trace component combine to form clusters which grow by adding on single molecules or by the mutual aggregation of the clusters themselves.[61-72] The frequencies of the addition and removal of molecules vary irregularly with the size of the clusters (with a general trend for a decrease in the frequency of removal with increasing cluster size).[64] As a rule a cluster size can always be found for which the frequency of addition is smaller and that of removal is much greater than for both the smaller and the larger clusters. For example, in aqueous alkaline solutions of Fe(III) salts the critical cluster is the tetramer $[Fe(OH)_3]_4$,[65] whereas in solutions of 1,1′-diethyl-2,2′-cyanine chloride it is the pentamer.[72] When the number of molecules in the cluster is increased to $n = 500-1000$ regrouping can take place, and the structure of the cluster tends towards the structure typical of the macrocrystal.[61] After the rearrangement the properties of the cluster are indistinguishable from those of the massive body.[62, 63]

In a medium containing trace components heteroclusters containing molecules of both the crystallisant and the trace component can be formed. They grow, and become rearranged, in different ways from the homoclusters (consisting only of crystallisant molecules), as was established experimentally and by calculations.[73-79] In particular, heteroclusters are characterised by exchange reactions such as[80]

$$[Fe_6C(CO)_{16}]^{2-} + RhCl_3 \xrightarrow[80\%]{40\ ^\circ C,\ 2\ s} [Fe_5RhC(CO)_{16}]^{2-} + FeCl_3 .$$

No quantitative data on the kinetics of the growth of heteroclusters are yet available. Indirect information can be obtained from the frequency of the appearance of microcrystals: this involves the assumption that critical clusters are instantaneously converted into microcrystals. From the rate of appearance of the microcrystals we may conclude that in some cases the heteroclusters are formed many orders of magnitude faster than the homoclusters. Many solutions in which microcrystals are not formed even after several days in the absence of impurities produce crystal immediately when an impurity is added.[2] For example, in aqueous solutions an impurity of $PbCl_2$ accelerates the formation of K_4MnCl_6 microcrystals by more than 10^6.

Precise measurements have shown that the number of microdrops of water formed in a moderately supersaturated vapour containing ionised air molecules is proportional to the number of these molecules, the frequency of drop formation being at least three orders of magnitude greater than in the absence of ions.[76, 77] Atomic and molecular impurities have similar effects. Thus, if atomic lead ($10-100$ atoms cm^{-3}) is introduced into a stream of very pure saturated pyridine-2,6-dicarboxylic acid (dipicolinic acid) vapour, by cooling the vapour and measuring (after some time) the concentration of drops of the acid it can be shown[9] that if the supercooling is substantial each lead atom generates one drop of the acid (Figure 1). In a mixture of dilute $Fe_2(CO)_9$ vapour

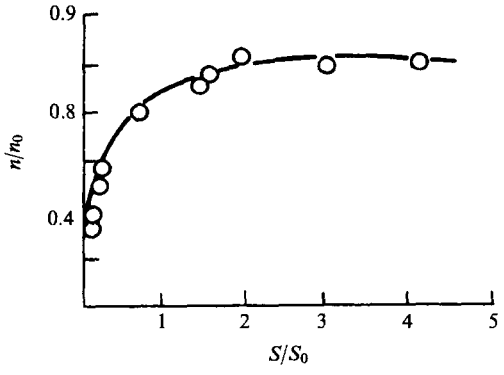


Figure 1. Dependence of the number of drops of dipicolinic acid in the vapour upon the supersaturation:[9] n and n_0 are the numbers of drops and of lead atoms in unit volume of the vapour, $S = [(C/C_\infty)-1]$ is the supersaturation of the vapour, C_∞ is the concentration of the acid in the saturated vapour, and S_0 is the reference supersaturation.

(10^3-10^{18} molecules cm^{-3}) and slightly supersaturated dioxyethyl sebacate (DES) vapour drops of DES are nucleated exclusively on the $Fe_2(CO)_9$.[78] This means that in this case the rate of formation of critical heteroclusters is 10^5 times higher than in homoclusters.

In all the cases mentioned so far the heteroclusters develop so rapidly that each molecule of the trace component becomes overgrown with crystallisant and is converted into a microscopic drop or crystal, and thus produces a large number of homoclusters of the crystallisant of critical size. In these cases the crystals decorate the molecules of the trace component. Decoration of the molecules takes place also during the crystallisation of silver in solutions of large aminoacid or protein molecules.[10] Thus, if $AgNO_3$ is added to a solution of DNA or of protein, and a reducer (formaldehyde) is then added, silver microcrystals are nucleated and grow only on the protein molecules.[81-83] These microcrystals are strongly bound to the protein and follow it during the electrophoretic separation.[10] Evidently the $AgNO_3$ and the formaldehyde are taken up by the protein like the Cu(II) and Ni(II) salts[84, 85] and small organic molecules.[86] In the bound state the $AgNO_3$ and the formaldehyde can interact and deposit silver on the parts of the protein molecule between the domains.[87]

However, cases of full predominance of the heteroclusters over the homoclusters are only seldom met. Often the two types develop with comparable speeds, and as a result the effect of the trace components on the nucleation is less marked, and confined to relatively high concentrations.

It has been established experimentally[88-94] that the effect of the trace components on the nucleation is selective. They can both accelerate and retard the process, and often similar compounds have different effects.[88] In particular, organic substances can affect the crystallisation of metals (Cu, Ni, Co, Fe, Ag, Au, Ru, Rh, Pt, Pd, Re, Sn, Te, In, Cd, Bi, Pb) from aqueous solutions by the reduction of their salts (for example, by borohydride).[89, 90] Compounds containing nitrogen and sulphur (thiocyanates, polysulphides, dithionates, thiocarbamide, dithiocarbamates, thioaminoacids, dithiols, thiazines) lower the rate of nucleation at concentrations of $10^{-4}-10^{-3}$ mol dm^{-3}, whereas other substances are effective only at concentrations of $10^{-2}-10^{-1}$ mol dm^{-3}. Under these conditions the mutual enhancement of the inhibitors' effects is non-additive.[91]

As was concluded by processing the results of Tsebul'skaya et al.,[94] in the crystallisation of nickel the rate of nucleation B_N depends on the concentration C of the impurity as described by the formula

$$B_N = B_{N,0}[1 - a(C/C_r)^{1/2}]^{-1}, \qquad (2)$$

where $B_{N,0}$ is the rate of nucleation in the absence of the impurity, a is an empirical parameter, and C_r is the critical concentration.

For an alkyldimethylamine impurity $a = -1$ and $C_r = (3.5 \pm 0.2) \times 10^{-4}$ mol dm^{-3}; for methionine, cysteine, thiocarbamide, 5-nitrobenzimidazole, and the tetraalkylammonium bromides $a = -1$ and $C_r = 10^{-5}-10^{-4}$ mol dm^{-3}, and C_r is independent of the length of the alkyl chain in the tetraalkylammonium molecules; for cetylpyridinium chloride $a = 1$ and $C_r = 5 \times 10^{-2}$ mol dm^{-3}.

It follows from formulae (1) and (2) that the limit of detection of these impurities from their influence on nucleation (assuming a minimum significance level of 5% in the difference between B_N and B_{N0}) is $\Pi = 2.5 \times 10^{-3}\ C_r = 10^{-8}-10^{-4}$ mol dm^{-3}. The sensitivity factor of the nucleation towards these impurities is $A_N = -0.5a(C/C_r)^{1/2}(B/B_{N0})^2$ if the influence of the impurities is determined exclusively by their concentration, i.e. if $\Gamma = 0$.

The rate of nucleation is also dependent on the presence of colloidal impurities. In some solutions impurity particles about 1 nm in diameter are known to behave as giant clusters which absorb the crystallisant and are rapidly converted into crystals. It has been reported[95-97] that if a polystyrene strip is immersed in a solution of $PdCl_2$ and $SnCl_2$ (0.1–1.0 g dm^{-3}) in hydrochloric acid, washed with water, and then transferred to a solution of $NiCl_2$ containing a reducing agent, nickel hemispheres (which can easily be developed and counted) are formed on the surface. The following processes are probably involved. In the initial solution in hydrochloric acid the reaction $SnCl_2 + PdCl_2 = Pd + SnCl_4$ produces colloidal palladium, deposited on the polystyrene surface as particles 0.3–1 nm in diameter. These are not removed from the surface by washing, and when the strip is immersed in a solution of $NiCl_2$ they grow by nickel deposition. After some time each colloidal particle of palladium is converted into a nickel hemisphere large enough to be easily counted. New nickel particles are not nucleated on the surface during this time, and the rate of nucleation is controlled exclusively by the palladium particles. A similar state of affairs is found in the crystallisation of copper and of many other metals.[89]

2. Growth sensor action

The effect of trace components on the growth of crystals depends on the relative energies of the interactions between crystallisant, trace component, and solvent molecules. If the trace component interacts with the solvent more strongly than with the crystallisant the effect is principally an acceleration of the growth by the salting-out of the crystallisant. With comparable interaction energies the predominant effect is contributed by the formation of solvated impurity–crystallisant complexes, which can both accelerate and suppress the growth. On the other hand, if the impurity interacts with the crystallisant more strongly than with the solvent, adsorption blocking of the surface by the impurity takes place, and usually suppresses the growth. Many workers have discussed these effects,[37, 98-120] but a generally valid dependence of the growth rate on the concentration and state of the impurity has not yet been formulated. It has been shown experimentally[105-107] that the growth of many salt crystals in weakly supersaturated solutions containing trace impurities is described by the isotherm

$$B_G = B_{G0}\left[Q + \frac{1-Q}{1+C/C_v}\right], \qquad (3)$$

where B_G and B_{G0} are the normal growth rate of the crystals with and without the impurity, Q is the maximum possible decrease in the growth rate under the influence of the impurity, and C_v is an empirical parameter, dependent on the supersaturation. From (1) and (2) we obtain

$$\Pi = \frac{C_v b}{1-Q-b}, \qquad A_N = \frac{Q-1}{(1+C/C_v)^2}\,\frac{C}{C_v}, \qquad (4)$$

where b is the smallest statistically significant relative deviation of B_G from B_{G0}. According to formula (4) the growth rate is

sensitive to the impurity at a concentration of the order of C_v. At lower concentrations the amount of impurity is too small (and at higher concentrations it is too great) to produce a significant change in B_G.

There is evidence[37, 105–110] that for many (and possibly for all) of the crystallisants special impurities can be found for which $Q \to 0$ (superinhibitors). For example, hydroxyethylene-1,1'-diphosphonic acid (for $C_v = 10^{-8}$ mol dm^{-3}) is a superinhibitor for calcite,[105] triethylenediaminetetramethylenephosphonic acid ($C_v = 10^{-6}$ mol dm^{-3}) for gypsum, and $CrCl_3$ ($C_v = 5 \times 10^{-7}$ mol dm^{-3}) for KH_2PO_4 and $NH_4H_2PO_4$.[109, 110]

An important example of inhibition is the cyanide retardation of the growth of AgHal crystals by iron and cobalt cyanides during the preparation of photographic emulsions.[111] The acceleration of the growth of crystals by an impurity has also been reported.[112–114]

If the crystal grows by the layer mechanism not only the normal growth rate (i.e. the rate of growth of a face at right angles to the surface) but also the parameters of the surface morphology of the crystal are sensitive to the impurity.[98–114] In layer growth the crystallisant is deposited on the surface of the crystal in successive layers.[37] It was experimentally found that molecules of the trace component deposited on the sides of the steps formed by the growth layers can suppress the attachment of molecules of the crystallisant to those steps (poisoning of the steps). Furthermore the adsorbed impurity can form a molecular fence on the faces, which inhibits the extension of the layers over the face (cut-off retardation of the growth).[98–101] This effect makes the surface morphology sensitive to the impurity. It was shown[109, 110] that the steepness of the growth hillocks on the faces of growing crystals of KH_2PO_4 is no less sensitive to the presence of $CrCl_3$ than is the normal growth rate (Fig. 2). At low supersaturations the faces have a complex morphology and the crystals grow very slowly. The growth rate becomes appreciable only at supersaturations in excess of some threshold value S_r. By processing published data[109, 110] it was shown that the threshold supersaturation S_r for KH_2PO_4 crystals is

$$S_r = S_0[1 + 1.1C/C_K], \tag{5}$$

where S_0 is the threshold supersaturation in the pure solution, and C and C_K are the concentrations of $CrCl_3$ and of the crystallisant in the solution. It follows from (1) and (5) that if the threshold supersaturation is used as the diagnostic criterion, a detection limit of $\Pi = 9.1 \times 10^{-7}\, bC_K$ can be achieved for chromium. For a claimed[109] significance level of the deviation of $b = 0.05$, $\Pi = 4.5 \times 10^{-8}\, C_K$. Even lower limits of detection can be reached by choosing a crystallisant for which crystal growth takes place through the formation of intermediate surface compounds incorporating the impurity. It was established that metal crystals grow faster under the influence of impurity–crystallisant complexes which transfer an electron.[115] For example, the crystals of a series of metals dissolved as their chlorides MCl_2 in the presence of an alkali M'OH and of a reducing agent RH grow as a result of the reaction[83, 116]

$$RH + 2M'OH + MCl_2 = ROH + H_2O + M + 2M'Cl\,. \tag{6}$$

The reducing agent and the chloride interact when adsorbed on the crystal faces. The M adatoms produced in this way combine to form surface clusters, and subsequently ultramicrocrystals, which arrange themselves in a layer as in the layer growth mechanism.[117–119] In the absence of the impurity the reaction (6) is slow. However, if a crystal of copper or nickel is treated (before growth) for 40 s with a 10^{-3} mol dm^{-3} solution of cetylpyridinium chloride (CPC), its growth is accelerated by a substantial factor as a result of a charge-transfer reaction within the complex:

$$RH + CPC + MCl_2 \to [RH(CPC)MCl_2] \xrightarrow{2M'OH}$$

$$\to ROH + H_2O + M + 2M'Cl + CPC\,. \tag{7}$$

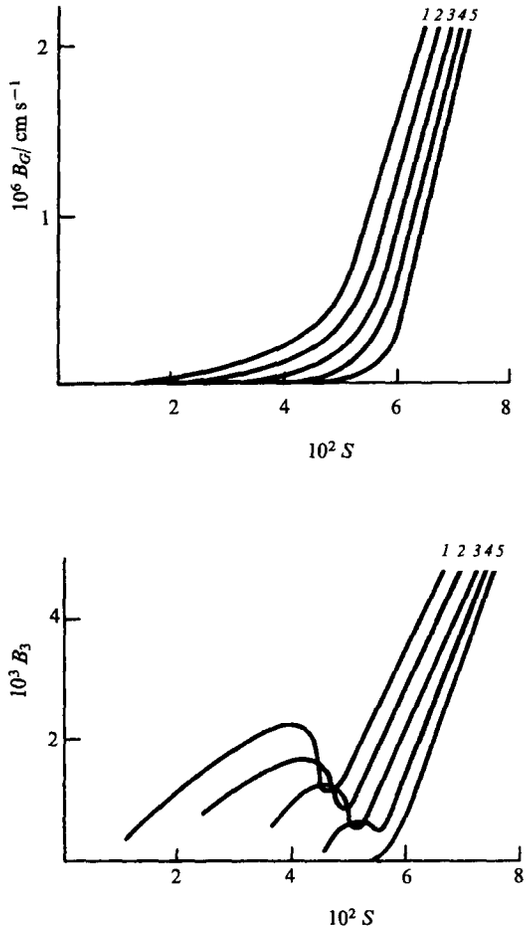


Figure 2. Dependence of the growth parameters of a KH_2PO_4 crystal on the supersaturation S for different contents of $CrCl_3$ in the solution.[109, 110] B_G is the normal growth rate, B_3 is the steepness of the growth hillocks; concentration of trace component: *1*) 0, *2*) 1.5, *3*) 3.3, *4*) 4.5, *5*) 6 ppm.

In reaction (7) the CPC acts as a catalyst, and the sensitivity of the crystal growth to this process can be maximised by choosing the most favourable conditions.

The action of trace components on faces with different surface morphologies is usually selective. As a result, the trace components can affect the habit of the crystals. Only $CdCl_2$, $MnCl_2$, $PbCl_2$, $ZnCl_2$, $HgCl_2$ influence the habit of NaCl crystals growing in an aqueous solution at low supersaturations: no other soluble chloride has any effect.[120] $CdCl_2$ and $ZnCl_2$ favour the formation of (111) faces instead of the more usual (100) for $\Pi = 5 \times 10^{-3}$ and 5×10^{-2} mol dm^{-3} respectively, but their analogue $HgCl_2$ produces (110) faces.[120]

3. Aggregation sensitivity

Crystalline aggregations are often formed as a result of collisions between the crystals. Thus, collisions can cause the crystals to merge, and finally to intergrow.[121–133] The most important manifestations of the effect of impurities on these process are the following.

1. Electrolyte impurities usually affect the coagulation threshold in accordance with the Deryagin–Landau–Verwey–Overbeek (DLVO) theory.[129] Low-molecular-mass electrolytes affect the properties of the electrical double layer, and therefore also the configuration of the aggregations and the radial distribution function of the crystals in the bulk of the aggregations.[134, 135] This effect is usually observed at electrolyte concentrations $C > 10^{-3}$ mol dm^{-3}.[129, 136]

2. Most trace impurities affect the aggregation as a result of specific adsorption.[134] For example, during the precipitation of

nickel by borohydride from an aqueous solution of $NiCl_2$ the primary Ni microcrystals (2–25 nm in size) are incorporated into spherical aggregations 100–200 nm in size if the solution contains alkylmethylamine oxide ($C = 5 \times 10^{-3}$ mol dm^{-3}) and 20–50 nm in size in the presence of 2-mercaptobenzimidazole or 6-methyl-2-thiouracil (5×10^{-4} mol dm^{-3}). On the other hand in a pure solution or in the presence of 6-methyluracil (5×10^{-4} mol dm^{-3}) aggregation of the microcrystals is not observed.[137]

In the crystallisation of $BaSO_4$ from an aqueous solution (37 °C, pH ~7)[128] in the presence of 1-hydroxy-1,1′-disulphonic acid the size of the aggregations decreases three-fold even for an impurity concentration $C = 2 \times 10^{-4}$ mol dm^{-3}, and in the crystallisation of AgI in the presence of $C_8H_{17}OC_6H_4 \cdot (OCH_2CH_2)_xOH$ ($x = 10-70$)[138] the same effect is reached for $C = 10^{-7}-10^{-8}$ mol dm^{-3}. If the impurity molecule is large enough it can be adsorbed on several crystals simultaneously.[139, 140] This effect was noted[141] in the flocculation of SKS-30ARK latexes and of polystyrene in the presence of polyethyleneimine (M = 4500) at a concentration $C = 4 \times 10^{-9}$ mol dm^{-3}. This type of adsorption has been observed only in aqueous gold and silver sols with microcrystals of about 50 nm.[142] In these sols aggregations containing $10-10^5$ microcrystals are formed within a few minutes of the addition of homo- and copolymers of aza-crown ethers (M = 55 000), in concentrations $C = 5 \times 10^{-6}-3 \times 10^{-5}$ mol dm^{-3}, irrespectively of the acidity of the sols. Measurements showed that the sol microcrystals had a negative charge, whereas the macromolecules were positively charged in an acid medium and uncharged in an alkaline medium. The similarity between the effects of the polymer in acid and in alkaline media suggests that charge neutralisation of the microcrystals does not play a major role in their mutual coupling, caused by the specificity of the adsorption. Conversely, in SiO_2, S, FeOOH, As_2S_3, and $CuFe(CN)_6$ sols the crown ethers induce aggregation only in an acid medium because of the charge neutralisation of the microcrystals. As a result the crown ethers affect only the gold and silver microcrystals in an alkaline medium. This observation suggests new diagnostic possibilities for crown ethers.

3. If the impurity macromolecule is much larger than the microcrystals it can act as an aggregation centre. In this case the microcrystals adhere to the impurity molecule and intergrow into a large aggregation long before homoclusters of the microcrystals are formed. The frequency of incorporation of the microcrystals is usually much greater on the large than on the small aggregations.[143] Therefore the overgrown impurity molecules rapidly grow into large particles from whose numbers the number of impurity molecules can be inferred. The reality of this interpretation has been demonstrated in a study[144] of the addition of a multitude of hydroxyapatite microcrystals to a molecule of DNA. Bacterial cells can be used as the aggregation centres in these studies:[145, 146] in the presence of biologically active impurities the bacteria add on microcrystals either selectively or in other ways.[146–148] For example, cells of *Bacillus sp. 1AC7* in an aqueous alkaline colloidal solution of gold can remove almost all the gold microcrystals in 1 h. By adding to the solution 2,4-dinitrophenol ($C = 10^{-6}$ mol dm^{-3}), gramicidin D (10^{-6} mol dm^{-3}), or pentachlorophenol (5×10^{-9} mol dm^{-3} most of the microcrystals can be removed from the surface of the cells. Increasing the concentration of these impurities by an order of magnitude removes the microcrystals completely.[146] Obviously, a colloidal solution of gold containing bacteria can be used as an aggregation sensor of the presence of pentachlorophenol offering a very low detection limit.

4. Spontaneous crystal sensor action

If the trace component undergoes a topochemical reaction with the crystals of the crystallisant it can be detected by the change in surface topology of the crystals. For example, if a crystal of fluoroapatite is introduced into a stream of water containing small quantities of H_3PO_4 its surface develops etch pits in which

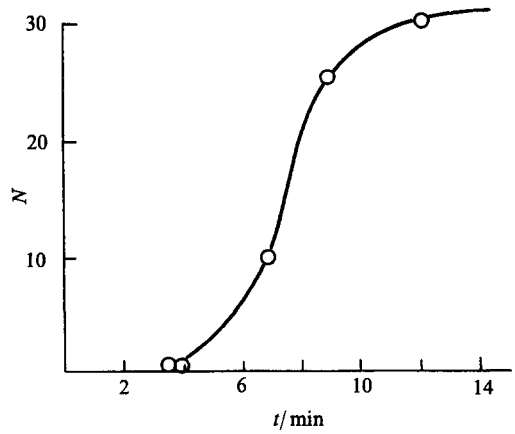


Figure 3. Rate of nucleation of microcrystals of sodium cyclophospate during the dehydration of $Na_3P_3O_9.6H_2O$.[152] Humidity of the air 26%; temperature 40 °C; N is the number of microcrystals on the (100) faces of the initial monocrystal ($F = 3$ mm^2).

$Ca(H_2PO_4)_2$ microcrystals are subsequently formed.[149–151] At the contact between a monocrystal of cyclophosphate ($Na_3P_3O_9 \cdot 6H_2O$) and moist air microcrystals of anhydrous cyclophosphate are produced on the crystal faces at a rate shown in Fig. 3.[152] The rate of nucleation of cyclophosphate crystals is sensitive to the water content of the air.

Monocrystals of fluoroapatite and of cyclophosphate hexahydrate also can be used as sensors for the presence of impurities. They should offer an enhanced sensitivity for the microcomponent if their surface morphology is determined by a microscopic method after a lengthy exposure to a stream of the medium under study. In this approach the long exposure and the small size of the morphological elements compensate for the low concentration of the trace component. Changes in morphology are revealed unambiguously if the size d of the new surface elements exceeds the resolution of the microscope and their number n is large enough. This requirement can be expressed as $d^2n > q$, where q is the minimum coverage of the surface by the new elements which can be identified unambiguously.[150] For an exposure time t and a growth rate of the topographic elements $B_G = B_{G0}C/C_K$ we have, for $d = B_G t$,

$$\Pi = (q/n)^{1/2} C_K / B_{G0} t, \tag{8}$$

where C_K is the solubility of the crystallisant. The new morphological elements are usually nucleated on active centres of the surface, so that the number n depends on the structural perfection of the monocrystal.[153–156] In monocrystals with a developed dislocation structure $n = 10^8-10^{10}$ cm^{-2}, and therefore a limit of detection $\Pi = (10^{-8}-10^{-7})C_K$ can be expected for the typical values $q = 10^{-6}$ and $B_{G0} t = 1$ cm.

Another method of revealing the trace component consists in localising its crystallisation on the surface of a specially provided collector and depositing on this surface the trace component from the largest possible volume of the medium.[157–161] The mass of the trace component removed from a volume V on a collector having a surface F is $\rho d^3 nF = CV$. Therefore if the condition $d^2n > q$ is obeyed we have

$$\Pi = \rho q^{3/2} \frac{F}{n^{1/2} V}, \tag{9}$$

where ρ is the content of the trace component in a unit volume of the reaction product.

If the reaction has a high activation energy, the process can be localised by heating the collector. Thus, in the pyrolytic reduction of silicon tetrachloride (activation energy 330 kJ mol^{-1}) or zirconium tetrachloride by hydrogen the product is collected quantitatively on the heated walls of the reactor.[157, 158] In the

pyrolysis of methylchlorosilane in a stream of hydrogen by a heated tungsten wire SiC was detected[159, 160] in 60–80% yield. TiC, NbC, HfC, BN, TiN, and TiB_2 have been obtained in a similar way.[158] An unusual method of localisation was reported by Givargizov.[161] If a single crystal of silicon heated to 1200 K is introduced into a stream of $SiCl_4$ vapour in H_2 carrier gas and a drop of molten gold is placed on the surface of the crystal the $SiCl_4$ is reduced on the drop surface and the resulting silicon dissolves in the gold. The drop becomes supersaturated in silicon, which crystallises at the contact surface with monocrystal. This produces a filamentary growth tipped with a drop of gold which collects $SiCl_4$ from the vapour. On the remainder of the monocrystal surface the reduction is negligibly slow. This technique was used to crystallise many trace components on collectors of various types.[161]

5. Selectivity of the effect of the trace component

The formation of excited and ionised forms of the trace component results in changes in the rate of crystallisation. This effect is observed as an acceleration of the crystallisation under the influence of an external ionising radiation.[162–165] The photolytic crystallisation of cadmium from the vapour of CdR_2 onto a silicon substrate was achieved by a preliminary exposure of the substrate to CdR_2 vapour followed by a brief irradiation with a laser beam (λ = 193 nm).[166, 167] If the substrate is not pretreated with the vapour, but is simply irradiated, crystallisation of cadmium is not observed. If the substrate, after being treated with vapour, is irradiated with a beam of irregular cross-section, the cadmium crystallises only on the illuminated part and its microcrystals are localised on an islet whose shape matches exactly the shape of the beam. Obviously, in this case the cadmium crystallisation centres are the radicals or ions adsorbed on the substrate.

Selective action has been observed[168] in metallic clusters of 2–10 atoms. Microcrystals of AgBr were irradiated as a layer with an Ag_n^+ ion beam, and after treatment with a reducing agent the microcrystals which had been reduced to silver were counted. The ion beam was produced in a mass spectrometer: it consisted of identical clusters accelerated to an energy of 8 eV per atom. The density of the beam and the exposure were chosen to produce at least 10 clusters for each microcrystal. It was found that after irradiation with a beam of Ag^+, Ag_2^+, or Ag_3^+ ions the microcrystals were not reduced. On the other hand irradiation with a beam of Ag_4^+ or with beams of larger clusters reduced 80% or more of the microcrystals.

In the crystallisation of metals by reaction (6) only the ultramicrocrystals of other metals, of given sizes, acted as crystallisation centres over a wide range of supersaturation.[89, 90] For example, in the crystallisation of nickel on polystyrene the crystallisation centres were particles of palladium (0.3–1 nm) or of silver (3–80 nm).

Alkyldimethylamine oxides do not affect the crystallisation of nickel, when present in solution in a molecular form, up to the micelle formation threshold, but they strongly retard the process when in the micellar form.[94] As reported,[94] near the micelle formation threshold the oxide lowers the rate of growth of nickel crystals from 1.7 ± 0.2 to 1.7×10^{-3} nm s^{-1}. Clearly, the microcrystals remain most of the time within the micelles, and the former rate characterises the growth outside the micelle whereas the latter refers to growth within the micelle.

V. Methods of increasing the sensitivity

Crystal diagnostics are most conveniently carried out under conditions of minimum B_{0j} but maximum number and size of the crystals formed under the influence of the impurity [Eqn (1)]. This objective can be achieved by the following procedures.

1. Lowering the supersaturation of the medium

At low supersaturations crystallisation in the absence of impurities is characterised by a long induction period.[169–174] Therefore in the diagnosis of impurities the supersaturation is lowered to a level for which the diagnosis time is substantially shorter than the induction period. The induction period t_0 has been measured by several workers.[2, 169–174] All their measurements are consistent with the formula

$$t_0 = KN_0S^{-n}\frac{RT^2}{H}M\frac{\mathrm{d}\ln C_K}{\mathrm{d}T}\exp\left(\frac{E}{RT}\right), \qquad (10)$$

where K and n are empirical parameters, N_0 is the minimum number of crystals which can be reliably determined, S is the supersaturation, M is the mass of one mole of crystallisant, and E is the activation energy for the nucleation of the crystals.

As has been reported,[2, 169, 173] the parameter K increases upon changing from anhydrous substances to crystal hydrates and from salts of univalent metals to salts of multivalent metals, i.e. as the composition of the crystallisant becomes more complex. In $Cu(NO_3)_2 \cdot 3H_2O$, $Na_2S_2O_3 \cdot 5H_2O$, $MnCl_2 \cdot 4H_2O$, and $Cd(NO_3)_2 \cdot 4H_2O$ and in many other complex crystallisants the K value is so high that in the absence of impurities their crystallisation is suppressed up to very high supersaturations. These crystallisants can be used at fairly high as well as at low supersaturations.

2. Overgrowing the primary crystals

The size of the crystals is increased by lowering the supersaturation S of the medium until new crystals cease to be nucleated, and holding it at this level for a long time.[175] In this case the crystals which had been nucleated before the decrease in supersaturation grow to an easily detected size without a change in their number. In a study[176, 177] of the overgrowing of ultramicrocrystals of metals in supersaturated zinc vapour it was shown that the rate of overgrowing can be controlled by electrically charging the ultramicrocrystals, and that the growth is completely suppressed at high enough negative charges. This suggests new prospects of controlling the overgrowing (in either direction) without altering the supersaturation.

3. Multiplication of the crystals

It has been established that a single primary crystal can produce a multitude of secondary crystals by three mechanisms.

Relay crystallisation. If drops of the supercooled melt of crystallisant (amorphous particles) are added to a medium containing a primary crystal the latter crystallises the drops with which it comes in contact. This effect was observed in a layer of amorphous $Ca_3(PO_4)_2$ powder as the formation of a group of secondary crystals round each primary crystal upon heating the medium,[178, 179] and also in a study[180] of an aqueous emulsion of molten hexachloro-*m*-xylene. Fig. 4 shows the result of the contactless crystallisation of a melt of *p*-bromoaniline dispersed in water and supercooled by 30 °C.[181] The drops of the melt and the primary crystal were deposited on an inert substrate and were not in mutual contact, but as a result of the dendritic overgrowth of the primary crystal the dendrite branches reached the nearest drops and crystallised them.

It has been established that ultramicrocrystals of silver are formed as a latent image in layers of AgBr crystal exposed to light. Treating the layer with a reducing solution produces growth of the ultramicrocrystal.[182–185] At a low and negative redox potential of the solution each ultramicrocrystal grows until it occupies the whole of the AgBr crystal in which it had been nucleated, but it does not extend to the neighbouring crystals.[182] On the other hand at a high negative potential each primary ultramicrocrystal emerges from its mother crystal and reaches the surface of the neighbouring crystals, inducing their reduction. As a result each microcrystal is surrounded by a cluster of secondary crystals.[183]

Multiplication by a topochemical process. It has been noted that when primary AgBr crystals are added to a solution of KI saturated with AgBr, microcrystals of AgI are nucleated at the corners of these crystals.[185] Their growth is accompanied by the dissolution of the adjacent parts of the AgBr crystal. However, the

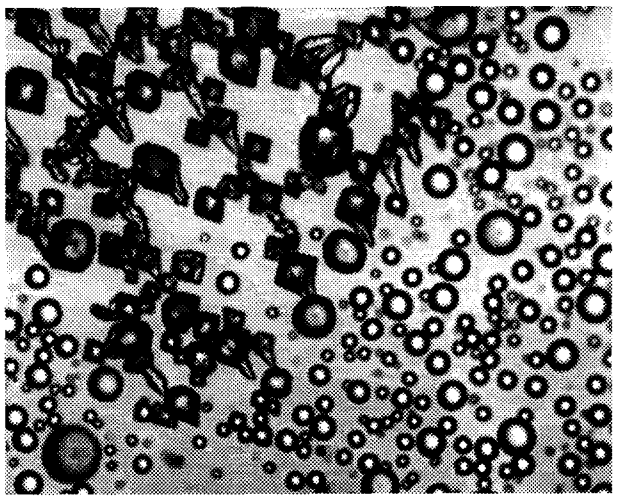


Figure 4. Relay crystallisation of a melt of *p*-bromoaniline dispersed in water (×20).[181]

microcrystals become separated from the mother crystals before reaching even one tenth of their size, and are replaced by new AgI microcrystals. In this way each primary crystal of AgBr generates hundreds of secondary AgI crystals. The same process is found in the interaction of fluoroapatite crystal with a mixture of sulphuric and phosphoric acid.[186]

Crystal showers. If a suspension of primary crystals is strongly stirred or irradiated with ultrasound the crystals can be broken down into a multitude of small fragments which grow to the size of the primary crystals as a result of overgrowth. This process has been observed in aqueous suspensions of $(NH_4)_2SO_4$, KCl, K_2SO_4, $CuSO_4 \cdot 5H_2O$, and $KAl(SO_4)_2 \cdot 12H_2O$.[187-190] A shower of secondary crystals is formed also by sliding a monocrystal of $MgSO_4 \cdot 7H_2O$ on a polished glass plate in a supersaturated solution of magnesium sulphate.[191]

VI. Diagnostic systems

Various systems based on nucleation and on growth sensor action have already been developed. Conditions suitable for the exploitation of aggregation sensor action have been formulated.[192, 193]

1. System for monitoring the concentration of carbonyl compounds

Fig. 5 shows a system developed for monitoring the concentrations of carbonyl compounds with $C = 10^{-7}-10^{-4}$ mol dm^{-3}. The system is prepared by depositing on an inert film an aerosol of a solution of the developer (a suitable hydrazide). After being dried the film is covered with a large number of microcrystals of the reagent.

The dried film acts as a crystal sensor. It is stored out of contact with the substance to be determined, and at the beginning of the experiment it is introduced into a stream of the gas to be analysed. After contact with the film the gas becomes supersaturated with the product, and ultramicrocrystals of the product are formed on the surface of the microcrystals of the reagent. The number of nucleated crystals is greater, the higher the concentration of the compound being monitored in the gas stream. The reagent is chosen so that the rate of nucleation is much smaller than the growth rate of the ultramicrocrystals. Therefore each nucleus grows over the whole volume of the mother microcrystal immediately after being nucleated, and the increase in the number of microcrystals of the product on the film is equal to the rate of nucleation. After being exposed to the flow the film is treated with a supersaturated solution of the product in order to overgrow the ultramicrocrystals to a conveniently detected size, ensuring that the supersaturation is kept below the level at which new crystals could be produced ($t \ll t_0$). When the crystals have been enlarged they are determined by counting them or by measuring any property which is dependent on their number. The sensitivity of the system increases when the drop size of the aerosol is decreased, the working area of the film is increased, and the supersaturation level used in the overgrowing is lowered. This system has been used to detect ketones, keto-esters, keto-acids, and other carbonyl compounds in gases and in solutions. 40 reagents offering a limit of detection of the carbonyl compound $II = 10^{-7}$ mol dm^{-3} have been found.[11]

2. Peptide visualisation system

The peptide visualisation system[81, 82] can be used to display and to determine amounts of protein down to 10^{-10} g. A layer of polyacrylamide gel[194] is deposited on a glass plate, and the solution of protein is admitted from the inlet side. The plate is then treated with a 0.1% solution of $AgNO_3$, and (after being washed) with a solution of formaldehyde (0.01–0.1%). Silver microcrystals are nucleated and grow on the protein molecules, which become decorated with silver.[82] The layer is examined by electrophoresis, and the localisation region of the protein is examined with a

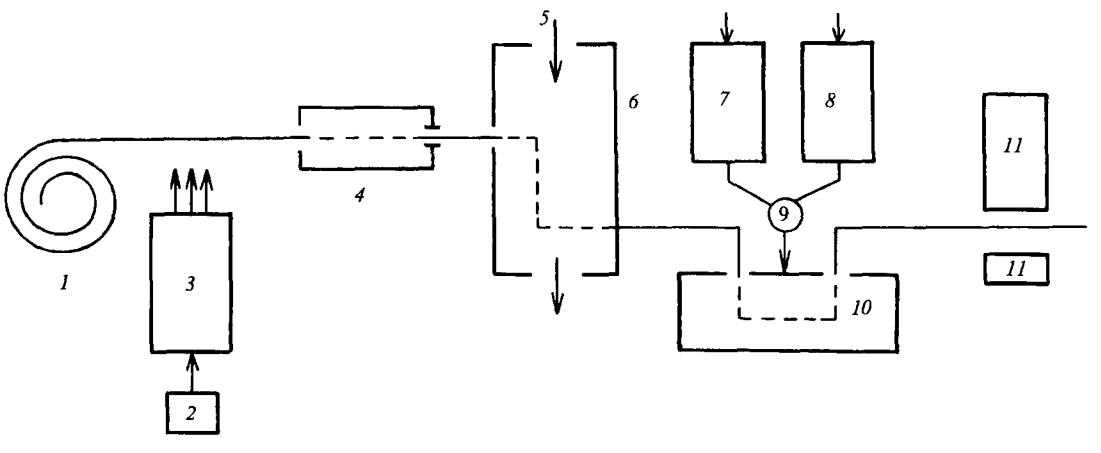


Fig. 5. System for monitoring the concentration of formaldehyde in a medium:[11] *1*) polymer film, *2*) methanolic solution of the hydrazide of *p*-hydroxybenzoic acid, *3*) aerosol generator, *4*) drying chamber, *5*) flow of gas (or liquid) containing formaldehyde, *6*) exposure chamber, *7*) aqueous solution of formaldehyde, *8*) aqueous solution of *p*-hydroxybenzoic acid hydrazide, *9*) mixer, *10*) chamber of contact of the film with the supersaturated solution of the hydrazone of *p*-hydroxybenzoic acid, *11*) photographic recording apparatus.

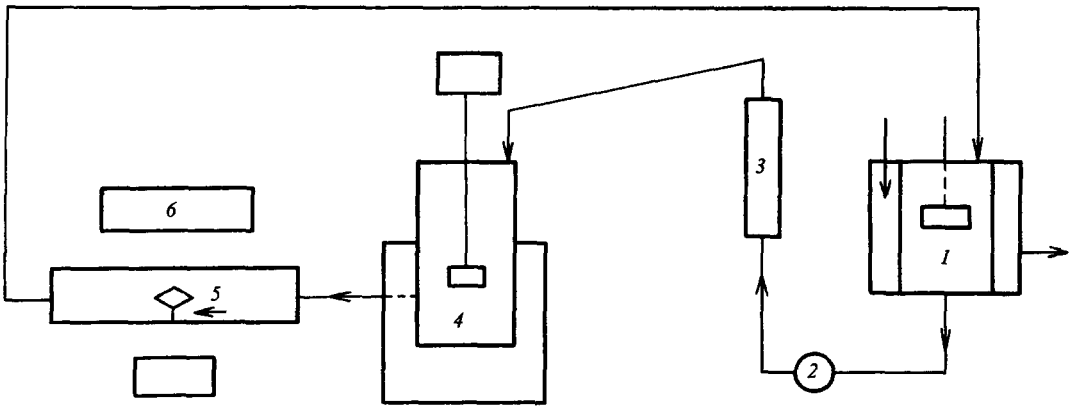


Figure 6. System for impurity diagnosis from the growth of crystals:[26] *1*) block for preparing a saturated solution of the crystallisant; *2*) pump; *3*) flow meter; *4*) cooling unit; *5*) growing crystal; *6*) block for monitoring the properties of the crystal *in situ*.

microphotometer. Occasionally the layer is treated, before the silver nitrate treatment, with a 0.01% solution of $KMnO_4$, which also stains the protein molecules with microcrystals of manganese dioxide.[81] A wide range of protein and DNA mixtures can be diagnosed from the position of the localisation region and from the intensity and nature of their coloration. The sensitivity is increased by treating the gel, after the formation of the silver microcrystals, with a mixture of iron cyanide and potassium bromide in order to convert the silver into AgBr. The AgBr is then converted into the sulphide by treating it with thiourea containing the ^{35}S radio-nuclide, which has a high specific radio-activity.[195, 196] In this case the localisation regions are delineated by autoradiography, which lowers the limit of detection of the protein by an order of magnitude.[83] Future improvements of the systems are expected to lower this limit still further.[82]

3. Growth systems

The basic system for monitoring the growth of crystals (Fig. 6) is designed for continuously recording the growth rate and the morphology of the growing faces.[29, 197] For β-methylnapthalene the growth rate is determined from the change in the interference colour of the crystals: this allows layers 2 nm thick to be determined.[198] By using the growing face of the crystal as one of the mirrors of a Michelson interferometer Rashkovich and Shekunov[199] were able to study the dynamics of the motion of layers more than 10 nm thick, and by including a Mach–Zehnder interferometer they lowered the thickness of the layer to 4 nm. Phase-contrast and reflection microscopy in conjunction with sensitive telephoto cameras and high-contrast video amplifiers allowed the *in situ* observation of the deposition of mono-molecular layers on the faces of calcium iodide, potassium hydrogen phthalate, and barium nitrate.[200–202] Other workers,[203] by including ellipsometry and low-angle scattering of synchrotron X-radiation, were able to demonstrate the effect of impurities on the composition and the crystal structure of the layers.

4. Autoradiographic system of detecting high-molecular-mass substances

The system relies on introducing into the molecule to be detected the ^3H, ^{35}S, ^{32}P, and ^{33}P radio-nuclides by isotope exchange or other methods.[204–206] The labelled substance is placed in contact with a layer of nuclear photographic emulsion which is then developed and examined in an electron microscope.[207–208] The system was used[209–210] for example, to detect DNA in aqueous solutions with a limit of detection $\Pi = 10^{-12}$ mol dm^{-3}. Under these conditions each molecule of DNA appeared in the field of the electron microscope as a circular conglomeration of silver microcrystals 0.4 μm in diameter.

VII. Conclusions

It has been established experimentally that crystal sensorics can offer a high sensitivity and selectivity in the detection of impurities. By using growth and aggregation sensor action a limit of detection of 10^{-9} mol dm^{-3} can be achieved. Intrinsic and nucleation sensor action give limits of 10^{-15} and 10^{-18} mol dm^{-3} respectively. These successes can be claimed even though crystal sensorics are a relatively new development: the theoretical foundations have been laid, but experimental data are still disconnected and incapable of answering the main question, i.e. of establishing the relationship between crystal sensorics and the nature of the impurity, the crystallisant, and the solvent. Working crystal sensorics systems offer an illustration of the problem rather than a scientifically well founded model. Very little use has been made so far of the fundamental methods of increasing the sensitivity (for example, crystal multiplication), and of the experimentally established special features of the crystallisation (for example, the transfer of the growing microcrystals into the volume of the micelles, or the formation of crystal islets on the illuminated substrate surface). Nevertheless recent progress in the use of crystal sensor systems strongly suggests that wide-ranging applications will be found in the near future.

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