

## Monodisperse colloids of transition metal and lanthanide compounds

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**Abstract** – Monodisperse colloids are regularly shaped particles, often spheres, all of nearly the same size. Monodispersity is achieved by creating a short period of nucleation, after which no new particles are formed, but the particles continue to grow. Examples which have been known for a long time include gold sols, sulfur sols, and polymer latices. Recently, conditions have been found to prepare monodisperse colloids of metal hydroxides and oxides.

Monodisperse powders are not necessarily good ceramic precursors, because the packing density of uniform spheres is low. The correct proportion of large and small particles to create a high packing density could be preferable. Hence it is desirable to control the growth of monodisperse colloids so that particles of a particular size can be produced. To control the size of the particles it is necessary to control the length of the growth time relative to the nucleation period.

Monodisperse hydroxides of trivalent transition metal ions and of lanthanide ions have been produced by thermally forced hydrolysis of aqueous solutions. Calcination of these colloids can lead to oxide particles of the same spherical shape. This approach is limited, however, because the only controllable variables are the temperature, time, and initial conditions.

More flexible is the generation of a critical reagent by a chemical reaction. Various monodisperse hydroxides and carbonates have been formed by the thermal hydrolysis of urea. This is an example of homogeneous precipitation, a procedure widely used in analytical chemistry to obtain precipitates of desirable properties. By introducing this additional homogeneous chemical reaction, further control of the systems can be obtained. Some examples include coprecipitation to obtain potential catalyst precursors of precious metals on alumina, coprecipitation to generate powders for high-temperature superconducting materials, and preparation of monodisperse lanthanide oxides for various applications.

### INTRODUCTION

Colloids are particles dispersed in a solvent which are much larger in size than the molecules of the solvent. Dispersions of a solid in a liquid are termed 'sols'; dispersions of a liquid in a liquid are termed 'emulsions' (ref. 1). Monodisperse colloids are dispersions in which the size distribution of the colloidal particles is very narrow. Many but not all monodisperse colloidal particles are spheres, for which a single parameter, the radius or diameter, can be used to describe the size. Colloidal particles are generally considered to lie within the size range of 1 nm to 1  $\mu$ , although larger particles can display colloidal properties.

Monodisperse colloids have a number of advantages in a variety of applications. Because their size distribution is narrow and known, they can be used for the calibration of measurement devices. Their properties are reproducible and can be used more conveniently for the testing of theories. In addition, they confer practical processing advantages. For example, in the production of pigments control of size can lead to control of the optical properties of the particles. In the production of ceramic products, the uniform packing of monodisperse spheres can lead to significantly lower sintering temperatures (ref. 2). The packing of monodisperse spheres is not necessarily the best way to obtain a dense ceramic green body, however, for close-packed spheres still only occupy a volume fraction of 0.74. To increase the packing density and thus reduce the shrinkage which occurs on firing a ceramic green body, a controlled distribution of particle sizes is preferred. Hence it is desirable to be able to control the growth of colloidal particles in order to produce a range of particle sizes.

Monodisperse colloids have been prepared for various substances, beginning with the monodisperse gold sols discovered by Zsigmondy early in this century. Some examples of these are listed in Table 1. They include the commercially important silica sols and polymer latices which are produced in large quantities. In the last twenty years a number of different metal salts have been prepared as monodisperse particles, especially through the efforts of Matijevic and his co-workers (refs. 3-5).

TABLE 1. Examples of monodisperse colloids

Substance	Method	Ref.
Au	Reduction of Au salts	6
S	Oxidation of sulfide	7
SiO <sub>2</sub>	Dehydration silicic acid	8
latices	Emulsion polymerization	9
hydroxides	Hydrolysis metal ions	3
oxides	Hydrolysis alkoxides	10
sulfides	Homogeneous precipitation	11

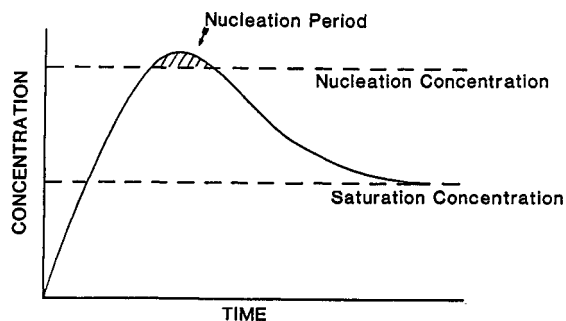


Fig. 1. The LaMer diagram illustrating the time dependence of the concentration required for monodispersity.

## PRINCIPLES

The principles by which monodisperse colloids can be prepared are readily presented in a diagram due to LaMer (Fig. 1) (ref. 12). The concentration or concentration product of the species which is to precipitate increases due to some chemical or physical process. At some degree of supersaturation, nucleation occurs, either heterogeneously on impurity centres or homogeneously through spontaneous nucleation. The growth of these nuclei causes the concentration to fall below the nucleation concentration, after which no more particles are created. The particles continue to grow, however, until the concentration falls to the saturation concentration.

The requirements for monodispersity are evident from the LaMer diagram:

- (i) The rate of nucleation must high enough so that the concentration does not continue to climb. Instead, a burst of nuclei are created in a short period.
- (ii) The rate of growth of these nuclei must be fast enough to reduce the concentration below the nucleation concentration quickly. In this way only a limited number of particles are created.
- (iii) The rate of growth must be slow enough, however, that the growth period is long compared with the nucleation period. This usually narrows the size distribution which has been the result of the finite nucleation period.

Overbeek (ref. 13) has observed that if the growth of the particles is controlled by diffusion, the size distribution narrows as the particles grow. If the rate determining step for particle growth is determined by reactions on the surface of the particles, then the absolute width of the size distribution remains constant, but of course the relative width would decrease as the particles grow larger. Only if the growth is controlled by a rate determining step which depends on the volume of the particle does the relative width of the size distribution which existed at the end of the nucleation period remain constant. Thus the usual growth kinetics would lead to monodisperse distributions if the particles are created in a single, short nucleation period. Various physical and chemical strategies have been employed to create these conditions. One is to separate the nucleation and growth processes, for example by seeding or by initiating nucleation with a separate chemical reaction. Another strategy is to extend the growth period by providing a reservoir of monomer molecules available for growth. Both chemical and physical reservoirs can be used.

## PHYSICAL CONTROL

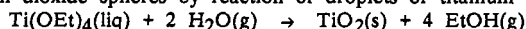
### Seeding

The first monodisperse colloids were gold sols grown by Zsigmondy (ref. 6) by seeding with gold nuclei. Small gold particles of about 3 nm in diameter were formed by reduction of a solution of a Au(III) salt with red phosphorus. Addition of a quantity of this gold seed sol to another solution of Au(III) with a different reducing agent such as formaldehyde caused the seed particles to grow to 20–50 nm in diameter. The number of gold particles produced was directly proportional to the volume of the seed sol added, showing that no further nucleation occurred.

Seeding is also used for the growth of monodisperse polymer latices. It is a reliable method when it can be applied and is particularly useful for growing larger particles than those which can be obtained in a single step process.

### Aerosols

An aerosol is a dispersion of a solid or liquid in a gas. If a reactive liquid is formed into droplets of uniform size in an atmosphere of a second, gaseous reagent, diffusion of the gas into the liquid can lead to formation of monodisperse, spherical aerosol of product. This technique has been used, for example, for the formation of titanium dioxide spheres by reaction of droplets of titanium alkoxides with water vapor (ref. 4).



Alkoxides are known for a wide range of metal ions (ref. 14); this method is consequently of some

generality. The particle size and size distribution are determined by the size of the aerosol droplets; particles of micron size and larger can be obtained.

Other applications of aerosol techniques include solvent evaporation by freeze drying, spray drying, or spray pyrolysis (ref. 15).

### Emulsions

Emulsions are dispersions of a liquid in a liquid. Highly monodisperse polymer latices are formed by emulsion polymerisation. In this process the nucleation step occurs as a single event by free radical initiation of polymerisation. The growth period is sustained by a large monomer reservoir which determines the ultimate size of the particles. The spherical shape is determined by the surface forces of the emulsion.

Inorganic materials have also been made by reactions of salts dissolved in the aqueous phase of water/oil microemulsions (ref. 16). Ultrafine metal powders of several nm diameter have been prepared by reduction of salts of the platinum metals and various chloride, carbonate, and oxide salts have been produced. Clearly a requirement of this method is that one of the reagents must be soluble in the organic phase. Control of the product size depends on control of the microemulsion structure.

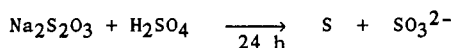
### Sol-gel processes

Monodisperse colloids can be amorphous, crystalline, or polycrystalline. If the solvent of a stable sol is removed, a gel may form which allows ordered aggregation of the sol particles (refs. 17 & 18). Monodisperse polycrystalline aggregate particles have been formed in this way (ref. 19). The particles can grow by the mechanism of Ostwald ripening in the gel, in which larger particles grow at the expense of the greater solubility of smaller ones.

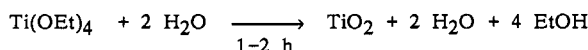
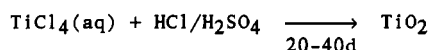
## CHEMICAL CONTROL

### Rate control

For some systems it is possible to find particular conditions such that the rates of concentration increase, nucleation, and particle growth are so balanced that monodisperse particles are formed. These conditions were found for the disproportionation of millimolar solutions of thiosulfate which lead to the formation of monodisperse sulfur sols (ref. 7).



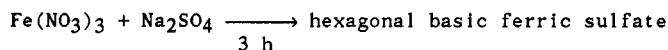
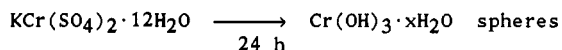
Similarly, slow ageing of 0.1 M acidic solutions of  $\text{TiCl}_4$  at  $98^\circ\text{C}$  gave monodisperse  $\text{TiO}_2$  spheres of 1–3  $\mu$  diameter (ref. 20), while hydrolysis of  $\text{Ti}(\text{OEt})_4$  in ethanol solution produced  $\text{TiO}_2$  of 0.1–1  $\mu$  in minutes to hours (ref. 21).



Clearly, finding the right conditions to achieve the appropriate balance of rates is difficult. This method requires considerable empirical searching and probably cannot be considered of general applicability.

### Thermal hydrolysis

The hydrolysis of aqua metal ions is endothermic and therefore is increased at higher temperatures. Aging a millimolar solution of potassium chromium alum at  $80^\circ\text{C}$  for a day enabled Demchak and Matijević (ref. 20) to obtain monodisperse spherical particles of chromium(III) hydroxide. Subsequently, monodisperse hydrous oxide sols of many other metal ions have been prepared (ref. 21). The specific conditions employed are critical; different anions lead to different particle shapes or to no particles at all. In some cases only dilute solutions can be used; in other instances concentrations up to tenths molar are successful.

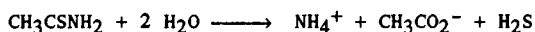


Since the acidity of the trivalent metal ions is about the same for all of the transition metal and main group metals, it is possible to coprecipitate mixtures of these metals. Thus rhodium(III) can be co-precipitated with aluminium(III) to yield monodisperse spheres of rhodium incorporated in an alumina lattice (ref. 22). It is not yet known whether such particles can form active catalysts. It is not possible to coprecipitate divalent and trivalent aqua transition metal ions because of their different hydrolysis equilibria. Neither can the lanthanides be coprecipitated with the trivalent transition metal ions, but thermal hydrolysis can be used to obtain monodisperse crystalline particles of some lanthanide metal ions (ref. 22).

Some mechanistic principles may emerge from further studies of these hydrolysis reactions, but the variety of complex equilibria and kinetics lability of the various metal ions suggests that conditions appropriate for each metal ion may have to be found.

### Homogenous precipitation

Further control over the precipitation process can be achieved by homogeneous precipitation. In this procedure a critical reagent is generated by an independent chemical reaction. The critical reagent is generated homogeneously throughout the solution, which allows quite insoluble materials to be precipitated in a controlled manner. An early example of homogeneous precipitation for the generation of monodisperse particles was the preparation of sulfide sols through the hydrolysis of thioacetamide (ref. 11).



Similarly, hydroxides and carbonates can be precipitated by the hydrolysis of urea (ref. 23). Figure 2 illustrates some europium(III) carbonate particles prepared in this manner (ref. 22).

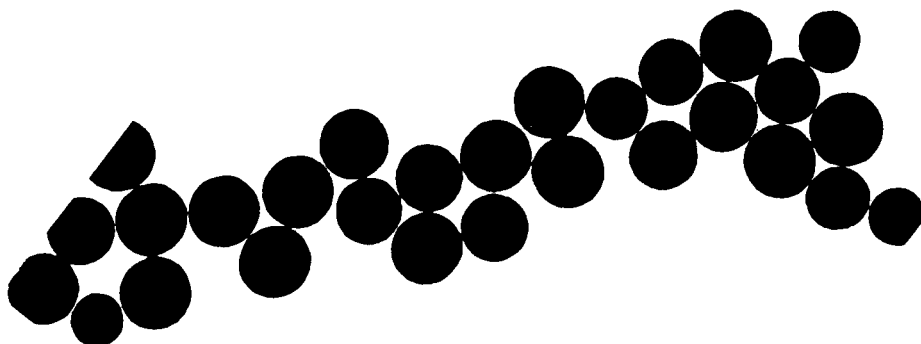
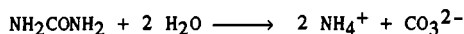


Fig. 2. Europium carbonate particles formed through hydrolysis of urea.

Homogeneous precipitation has been a well-known analytical chemistry practice for many years. Table 2 lists a number of different salts which have been homogeneously precipitated for analytical purposes (refs. 24 & 25). Coordination chemists should have no difficulty in extending this list to include many other complexes and reactions which could be used for this purpose. Two additional challenges are to select those which are of scientific or commercial significance and to establish, if necessary, the conditions required for the growth of monodisperse particles in reasonable quantities.

TABLE 2. Analytical precipitation from homogeneous solution.

Precipitate	Reagent
Hydroxides (Al, Ga, Th, Fe <sup>III</sup> , Sn, Zr) (Ti)	Urea Acetamide
Carbonates (Ln, Ba, Ra)	Urea Trichloroacetate
Phosphates (Zr, Hf)	Trialkylphosphate
Sulfate (Ca, Sr, Ba, Pb)	Dimethylsulfate Persulfate-thiosulfate
Oxalate (Ln, Mg, Ca, Zn)	Dialkyloxalate
Sulfide (As, Sb, Bi, Sn, Pb, Hg, Mn, Cu, Cd)	Thioacetamide
Chromate (Ag, Pb, Ba, Ra)	Urea-dichromate
Dimethylglyoxime (Ni)	Urea-metal chelate

## CONTROL OF SIZE

Although many different examples of monodisperse particles are known, in only a relatively few cases have different size particles been obtained by design. Seeded growth procedures can be successful because the growth medium can be controlled differently from the nucleation process. Thus Zsigmondy obtained different size gold sols by introducing different quantities of seed particles into the growth medium. Alternatively, with a large and variable monomer reservoir particles can grow until the monomer is exhausted. This procedure is used in emulsion polymerisation to produce variable sized latices which are used as size calibration materials. The other physical control techniques such as aerosols and microemulsions can also produce different size particles by control of the size of the growth volume.

The application of chemical control methods to produce particles of different sizes has been limited. Several studies of alkoxide hydrolyses have given different particles sizes depending on the concentration ratio of the reactants (refs. 26 & 27). Understanding the kinetics and mechanisms of the complex dynamics of particle formation and growth is necessary before particles of particular sizes can readily be prepared.

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