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Separation of inorganic nanopowders using the concentration gradient method

Summary — In the present paper a modified method to separate inorganic nanopowders using the concentration gradient method has been presented. Extraction of individual fractions as a non-destructive method has been discussed. The technique in question allows obtaining a grain size that varies from several micrometers down to several nanometers using simple devices and within a short time.
Keywords: nanopowders, separation methods, ficoll.

ROZDZIELANIE NANOPROSZKÓW NIEORGANICZNYCH Z ZASTOSOWANIEM METODY GRADIENTU STĘŻEŃ

Streszczenie — Artykuł przedstawia technikę rozdzielania nanoproszków nieorganicznych za pomocą zmodyfikowanej metody gradientu stężeń na przykładzie boranu glinowo-itrowego. Opisana metoda separacji jest metodą nieniszczącą. Pozwala w krótkim czasie oraz za pomocą prostych urządzeń laboratoryjnych uzyskać frakcje nanocząstek o rozmiarach od kilkunastu mikrometrów do kilku nanometrów.
Słowa kluczowe: nanoproszki, metody rozdzielania, fikol.

INTRODUCTION

Inorganic material of compact structure has been obtained using the sol-gel method. The substance was ground to powder in an agate mortar. This method allows obtaining a grain size from 10 μm down to 50 nm, depending on the kind of polymer precursor applied in the reaction. Polymers are basic components that are of crucial importance to the nanopowder grain size [1].

They include such dicarboxylic acids as: citric acid, tartaric acid, edetic acid, salicylic acid and such diols as: ethylene glycol, mannitol and sorbitol. Unfortunately, this method allows obtaining powder with diverse grain sizes. Therefore, the obtaining of a nanofraction is complicated and requires separation of fractions.

Two of the oldest separation methods are concentration gradient and density gradient method. In 1957 Meselson, Stahl and Vinograd introduced and developed in subsequent years a new separation technique, which was first used for analysis of biopolymers [2—4]. Since then, the described separation method has become widely known and important in microbiology research [5]. These laboratory techniques are used to separate mixtures into appropriate fractions by using a preparative ultraseparator. The primary role of the density gradient is the stabilization of sedimentary strips to prevent their diffusion [6]. Aqueous solution containing particles to be separated is poured on the top of the solution with the density gradient and subsequently centrifuged. Particles move to the part of the separating solution whose density is identical to the particle's density.

Thus it is possible to use the two kinds of gradients. The choice of an approach depends on individual requirements. The stroke technique helps obtain different densities or concentrations of solutions layers (Fig. 1a). The separation of fractions can be performed until the density or concentration of separated particles is the same as that of gradient solution is obtained. A linear gradient where concentration evolving linearly from the meniscus to the bottom of the test-tube can also be reached (Fig. 1b). Hence, as biological particles exhibit small difference in molecular weights, the density gradient method seems to be more useful than concentration gradient.

In the described density gradient method specific solutions called gradiols are used. Their density should be the same as that of the molecules to be separated. A homogenate of the separated molecules should be applied on the gradiol area in a very careful way in order not to mix the fractionated molecules with the gradient solution. The choice of a solution depends on the type of separating materials. Consequently, individual solutions have to be chosen for each kind of fractionated molecules. The case of biological molecules is more complex since

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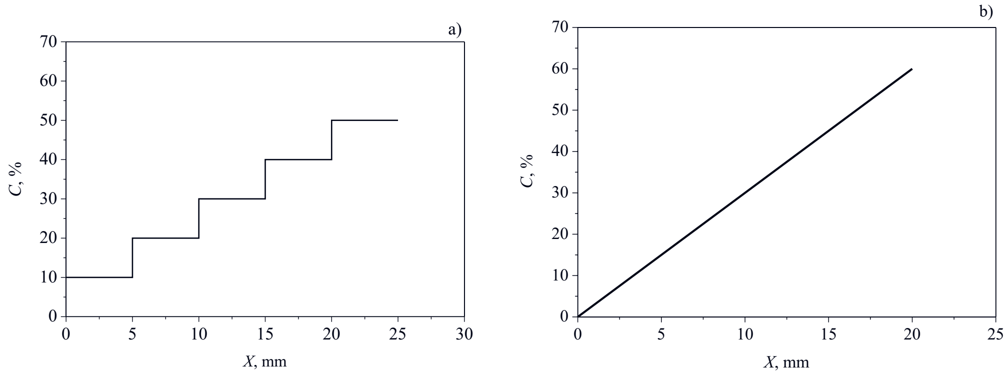


Fig. 1. Graphics of: a) stroke gradient, b) linear gradient angle; C — concentration of gradiol, X — distance from the meniscus in the tube

they have to meet numerous conditions. For example a gradient solution has to be non-toxic and cannot dissolve separated molecules. These problems are not so important for inorganic separated nanopowders because these are characterized by higher immunity to melting and are not used in medicine as biological molecules. Gradiols such as sucrose (1.32 g/cm^3), cesium chloride (1.98 g/cm^3), cesium formate (2.1 g/cm^3) and cesium nitrate (2 g/cm^3), sodium chloride (2.17 g/cm^3) are most often used for biological biopolymers.

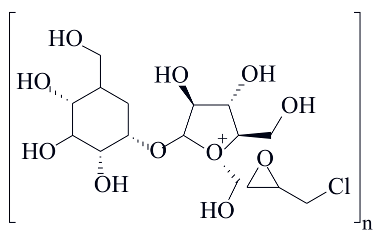
Moreover, ready to use gradiols having particular densities are applied in medical procedures, especially in hospital analytical laboratories. These gradiols are characterized by low densities from 1 to 2 g/cm^3 only. Unfortunately, for inorganic powders much higher densities of gradiols used as separation solution are necessary. Commercially available compounds used for making gradiol solutions are insufficient.

In this study, we further prove that the modified gradient concentration technique can be used in separation of nanoparticles. Consequently, the gradient method for inorganic nanopowders has had to be modified.

EXPERIMENTAL

Materials and methods

Suspensions of yttrium aluminum borates (YAB) nanopowders (prepared in our laboratory) in hexane for separation with a density of 3.7 g/cm^3 and dispersion molecules from 50 nm to 10 μm were prepared. A beaker containing the suspension was placed in ultrasound for 5 hours in order to reduce particle agglomeration.



(I)

Synthetic polysaccharide in Ficoll PM400 form [formula (I), Sigma Aldrich Chemie GmbH, Germany] was used to separate the nanopowder. Preliminary fractionation was made using polymeric membranes PTFE syringe (Millipore, Carrigtwohill, Co. Cork, Ireland) with 1, 0.6 and 0.45 μm pores diameter because of considerable price of Ficoll. The beaker with nanopowder solution was placed in ultrasound after the separation of every successive fraction for one hour. Subsequently, different fractions of YAB powder were obtained respectively for: 1, 0.6 and 0.45 μm grain size. It is vital that all of the steps should be performed very slowly.

The next step was to prepare a Ficoll solution in deionized water using mechanical or magnetic stirrer. Two concentration given by weight ratios 20:1 and 10:1 were prepared. In this way two fractions of nanopowders were obtained in the form of two distinctive white stripes.

In this case gradiol became a milky mixture. That mixture was put away to degas for one hour. Solution of gradiol became transparent and pale yellowish. The time of degassing the mixture should be not too long because of fast polymer crosslinking that may occur. Therefore, gradiol should be used fresh and kept in a refrigerator.

Gradiol in higher concentration was placed in a centrifuge tube. In the next stage, the lower concentration gradiol was applied on the higher gradiol concentration area. This activity should be performed very carefully in order not to mix the two gradiol concentrations.

YAB nanoparticles in physiological salt were suspended and put on the gradiols area in the tube. The tube was placed in the centrifuge. Our study showed that the optimal time for borates nanopowder is 6 min at speed 1500 rpm. Visible white stripes of nanofractions, characteristic for these parameters were obtained. The tube was placed in a position perpendicular to the axis of the rotor upon spinning. Thus the particles fell down in the direction conformant to increasing concentration gradient.

Two characteristic white stripes of nanoparticles are discernible in the tube. These stripes were extracted using a disposable pipette and suspended in physiological salt. Those samples were drained off, rinsed in distilled water and dried at room temperature.

A scanning electron microscope (SEM) images were used to measure the size of the separated particles.

Purity investigation of YAB powders before and after separation were made by X-ray diffraction (XRD) using Brucker D8 Discover with CuKα radiation at the wave length λ = 0.15406 nm. Powder diffractograms were taken in the angle range from 15° to 60° using the step size of 0.003°/s and step time of 74.8 s.

RESULTS AND DISCUSSION

SEM images of two fractions of particles obtained by separation with the concentration gradient method and particles before separation are shown in Figure 2. In the first fraction we found particles with size about 50 nm and in the second about 100 nm.

Figure 2c shows the distribution of nanoparticles size before separation. The optimal centrifugation conditions for YAB was used: *i.e.* time 6 min and speed 1500 rpm. The characteristic strips of nanofractions did not appear during centrifugation time over or below 6 min and centrifugation speed over 1500 rpm. It has been concluded that optimal time and rotation speed in a centrifuge depend on density of separation materials. Standard acceleration applied for biological materials is much higher than for inorganic materials, the former having lower density.

Nanoparticles of YAB were neither destroyed nor contaminated during the separation in Ficoll. It was proved in our research by analysis of XRD diffraction as it is shown in Figure 3. Spectrum recorded for nanocrystalline of YAB before separation is identical with nanocrystalline of YAB after gradient separation.

Conventional powder material separation methods (with the use of engineering measuring equipment including: separators, screeners and classifiers) can only yield a grain size not smaller than micrometer-range [7].

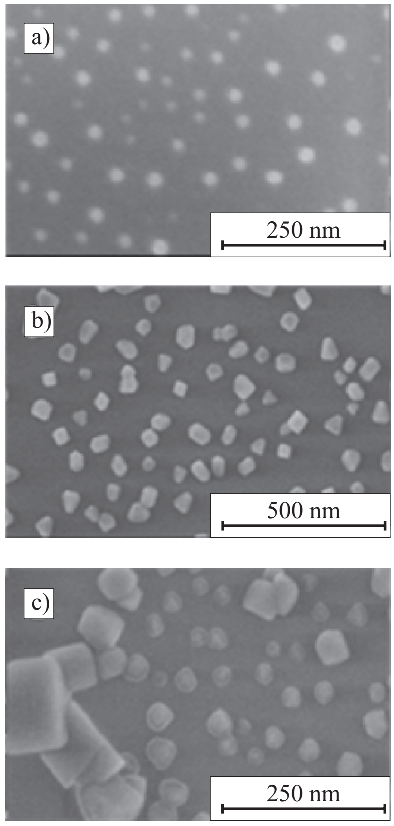


Fig. 2. SEM images of YAB nanoparticles obtained as a first fraction — 50 nm (a) after separation, second fraction — 100 nm (b) and before separation process (c)

Selection methods for appropriate separation are depicted in Figure 4. The application of a method depends on the grain size of separation molecules. The presented methods permit obtaining a grain size of 10^{-3} m. A possible way to obtain smaller grains could be that used in microbiology, that allows separating proteins and viruses

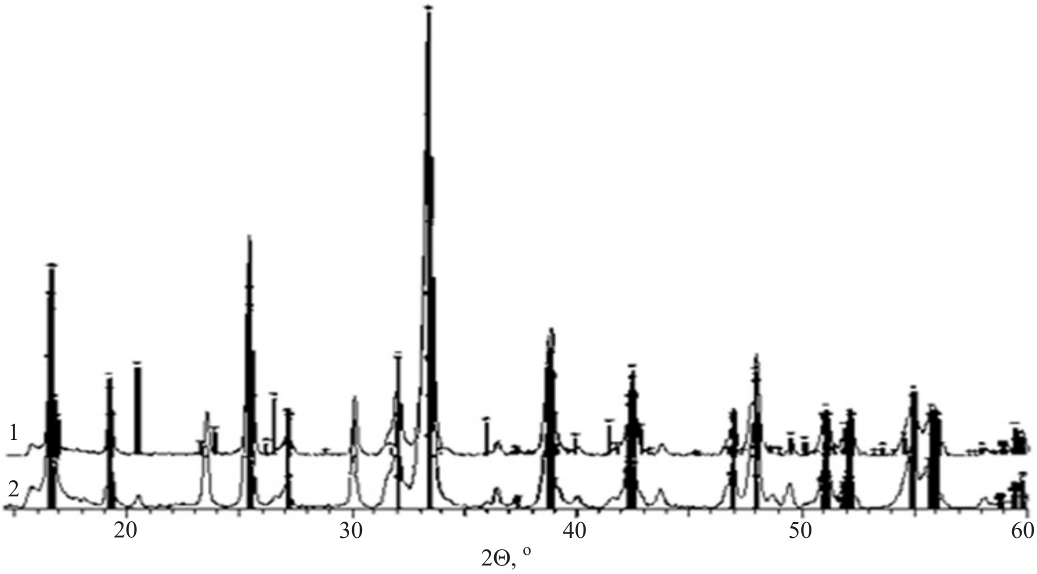


Fig. 3. X-ray diffraction of patterns of YAB nanopowders before (1) and after separation (2)

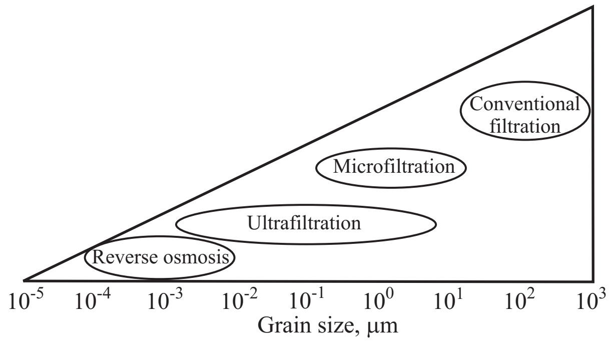


Fig. 4. Methods of filtration of particles depending on grain size

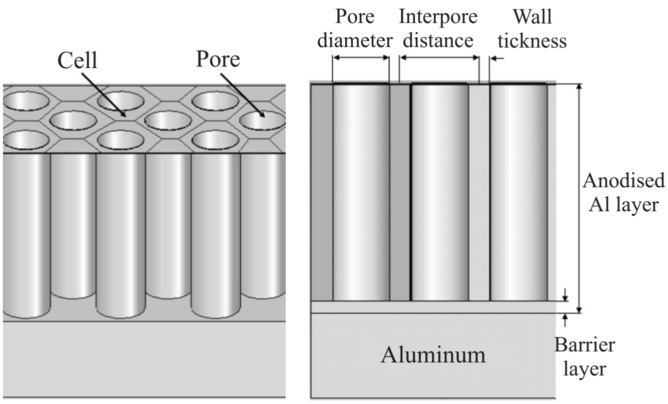


Fig. 5. Anodized aluminum structure

sized from 10^{-8} down to 10^{-10} m. One of the possibilities is to use polymer filters. Unfortunately, this kind of separation technique allows obtaining of grains not smaller than 200 nm in diameter.

Some authors [8] provide information on highly-organized aluminum filter structures presented in Figure 5. These structures are packed densely and have a nanopore diameter less than 100 nm. However, they require an appropriate pressure. Besides, they tend to immediately block up and dispersion of grain sizes is large.

YAB nanoparticles were separated using concentration gradient method. Ficoll, which was used to obtain concentration gradient, appears to be a universal material. This polymer can be used for most inorganic nanopowder compounds.

Unfortunately, the size of the fractioned nanoparticles has to be measured by particular other standard methods, such as: X-ray technique, layer diffraction in the air stream, aerodynamic aerosol analyzer method or analyzing SEM photos.

The separation gradient technique described has important advantages as a non-destructive method. It also permitted separating quite small quantities of fractionated molecules. The amount of the obtained nanoparticles fractions depends on the amount of the prepared concentration and on the density gradients applied. Furthermore, it is fairly easy in manual handling, is not time-consuming and does not require the use of any specialist devices.

The concentration gradient method seems to be convenient and economical in separation procedures. Any quantity of fractions can be obtained according to what is needed.

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