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Analysis of magnetic nanoparticles using quadrupole magnetic field-flow fractionation

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Abstract

The new technique of quadrupole magnetic field-flow fractionation is described. It is a separation and characterization technique for particulate magnetic materials. Components of a sample are eluted from the separation channel at times dependent on the strength of their interaction with the magnetic field. A quadrupole electromagnet allows a programmed reduction of field strength during analysis of polydisperse samples.

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Field-flow fractionation (FFF) is a separation and characterization technique conceived by Giddings in 1966 [1]. It is an elution technique similar to chromatography in which different components of a sample mixture elute from the system at different times. As in liquid chromatography, a flow of carrier fluid is provided by a pump (commonly, a high performance liquid chromatography (HPLC) pump), the sample is introduced to this stream using an HPLC sample valve, and a

detector (such as a UV-visible HPLC spectrophotometer) downstream of the separation device is used to detect the elution of sample components. Whereas chromatography exploits differences in partition between the mobile phase and a stationary phase to separate sample components as they are carried along a column, FFF separation is achieved within the mobile phase alone. In fact, there is no stationary phase present. Rather than the packed or open tubular column of HPLC, the separation device takes the form of a thin, ribbonlike channel, across the thickness of which a uniform, or close to uniform, field is applied. Due to viscous drag, the fluid velocity profile

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across the channel thickness is parabolic, or nearparabolic, with the highest fluid velocity near the channel center and zero velocity at the walls. For a channel cross section of high aspect ratio, and parallel channel walls, the fluid velocity profile may be assumed constant across the channel breadth with small perturbations at the edges due to the drag of the side-walls. The field acts to drive susceptible sample components toward one of the walls (the so-called accumulation wall), and therefore into relatively slowly moving fluid. For particles smaller than about a micron in diameter, the resulting increase of concentration close to the wall is opposed by diffusion. The result is a steady state where the concentration of each sample component decays exponentially away from the wall. Particles that interact strongly with the field form thin zones adjacent to the wall, and are confined to the very slow moving fluid close to the wall. Particles that interact less strongly with the field form more diffuse concentration profiles, and they may sample faster fluid streamlines in addition to those close to the wall. The outcome is that particles that interact less strongly with the field are carried to the channel outlet more quickly than those that interact more strongly. Particles therefore elute in the order of increasing strength of interaction with the field. Furthermore, the time of elution may yield quantitative information on the strength of interaction of the particles with the field.

The nature of the applied field determines the sample property that is characterized. For example, a gravitational or centrifugal field retains particles in the channel according to their buoyant mass, $V_p\Delta\rho$, where V_p is the particle volume and $\Delta \rho$ is the density difference between the particles and the carrier fluid. An electrical field separates particles according to their electrical charge. Fieldflow fractionation has developed into a versatile family of techniques that exploits a variety of field types to characterize different particle properties [2,3]. There have been previous attempts to implement magnetic FFF, with varying degrees of success. These will be discussed briefly below. The advantages of the quadrupole magnetic FFF system that is under development in our laboratory will then be described.

In 1980, Vickrey and Garcia-Ramirez [4] attempted to demonstrate magnetic FFF by coiling a 304 cm Teflon tube of 0.15 cm internal diameter against the windings of a 400 Gauss (0.04 T) electromagnet. The coiled tube lay close to the plane of one end of the iron core. No retention of the Ni-BSA complex sample was observed, which is not surprising given the far from ideal tubular channel geometry [3], the low field strength, and the channel position in a region of low field gradient.

Schunk, Gorse, and Burke [5,6] reported in 1984 the use of a parallel plate channel with a magnetic field provided by an electromagnet. The channel was made of 0.5 in (1.27 cm) and 0.125 in (0.32 cm) thick glass plates separated by a 250 µm spacer. The thinner wall was placed in contact with one end of the iron core of the magnet to maximize field strength and field gradient in the channel. A maximum field strength of about 275 Gauss (0.0275 T) and field gradient of about 21 Gauss/ mm (2.1 T/m) were obtainable, with less than 1% variation in field strength along the length of the channel. They were able to separate singlet from doublet 0.8 µm rod shaped iron oxide particles used in the recording industry (i.e., fairly large, high susceptibility particles).

Semenov and Kuznetzov [7], in 1986, proposed the use of a ferromagnetic wire at the axis of a tubular channel placed perpendicular to a magnetic field that magnetized both the wire and the particles to be separated. They presented calculations that suggested retention of both paramagnetic and diamagnetic particles was possible in such a system. The coaxial channel geometry is also far from ideal. The force on retained particles would rapidly increase as the wire is approached, which would tend to induce particle capture. Also, the small surface of the wire would have to serve as the accumulation wall, which would make the system highly susceptible to overloading. In the same year, Semenov [8] proposed a parallel plate channel in which the field would be provided by the induced magnetization of parallel ferromagnetic wires arrayed uniformly in the surface of one of the walls. The wires were to lie in the direction of flow and the field was to be applied across the channel breadth, perpendicular to the wires and

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