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MECHANICAL TECHNIQUES: PARTICLE SIZE SEPARATION

A. I. A. Salama, Natural Resources Canada, Devon, Alberta, Canada

Introduction

Particles of many kinds and various sizes have played an important role in man's interaction with his physical environment. They abound in the soil and earth below; they are also present in water, air, chemical products, and many other sources. If particles were spherical or cubical, it would be easy to characterize them. Unfortunately, most of the particles present in our environment are of irregular size and shape. Therefore, it is desirable to try to develop methodologies and techniques to characterize particles of irregular size and shape, and this is the main objective of particle size analysis. Moreover, particle size analysis is important in studying particle behaviour in a medium as in many analytical sciences and industrial applications.

Particle size analysis in physical, chemical, and biological processes involves many concepts and techniques; however, this article focuses on the methods of particle size analysis utilizing mechanical techniques.

This article will first introduce some basic principles used in particle size analysis. This will be followed by a summary of the applicable particle size ranges for the different methods and the size ranges of most common particles found in industrial, chemical, environmental, and clinical applications. The most common mechanical techniques and methods used in particle size analysis will be briefly presented.

Particle Properties

Particle size analysis plays an important role in many analytical sciences and industrial applications. To assist in developing useful methodologies and techniques it is essential to identify the main factors that control the behaviour of particles in a medium. Such factors include particle density, shape, size, size distribution, concentration, and surface characteristics, and the carrier medium dynamics (**Figure 1**). This article focuses on particle size analysis using mechanical techniques in relation to clinical, industrial, and environmental applications: therefore, the particles under consideration could be solid or liquid and the medium could be liquid or gas. In aerosol systems the medium is gas (air).

Density

Particles originating from a solid will have the same density as that of the parent material. However, if the material undergoes hydration or surface oxidization or if it agglomerates in clusters, its specific gravity will change. The particle density plays an important role in the separation of solids as in centrifugal and gravitational sedimentation, for example.

Particle Shape

Shape factors The method of formation influences the resultant particle shape. In comminution, attrition or disintegration, the generated particle resembles the parent material. On the other hand, if the method of formation is condensation from vapour, the smallest unitary particle may be spherical or cubical. In many cases condensation is followed immediately by solidi-

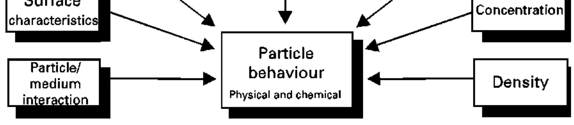

Figure 1 Main factors affecting particle behaviour in a medium.

fication and formation of chain-like aggregate (e.g. iron oxide fumes, carbon black).

Based on experimental data it has been found that for a collection of groups of particles having an average diameter D_{pi} for group i, the total surface area can be expressed as:

$$A_p = \alpha_s(\textstyle\sum n_i D_{pi}^2) \quad [1]$$

where α_s is defined as the surface shape factor. The total volume can be expressed as:

$$V_p = \alpha_v(\textstyle\sum n_i D_{pi}^3) \quad [2]$$

where α_v is defined as the volume shape factor. The surface and volume shape factors may be related to a combined shape factor k_p as:

$$k_p = \frac{\alpha_s}{\alpha_v} \quad [3]$$

In the case of spherical or cubical particles it can be shown that the shape factor is 6. For irregular particles, values vary from 6 to 10. Some other relationships can be obtained by using eqns [1]–[3]:

$$A_v = \frac{A_p}{V_p} = \frac{k_p}{D_p^*} \quad [4]$$

$$D_p^* = \frac{\sum n_i D_{pi}^3}{\sum n_i D_{pi}^2} \quad [5]$$

$$A_m = \frac{k_p}{\rho_p D_p^*} \quad [6]$$

where A_v = specific surface area (surface area per unit volume): D_p^* = specific surface diameter: A_m = surface area per unit mass: ρ_p = density of the particle material. The surface and volume information are used in estimating the equivalent spherical particle diameter which is used in studying particle behaviour in a medium.

Fractal geometry Mandelbrot introduced the basic concepts and theories of a new type of geometry called fractal geometry, in order to describe rugged structures. The main idea put forward by Mandelbrot is that the boundary of a rugged system can be described in its embedding space by a fractal dimension which describes its space filling effect. In the case of a fractal surface the estimate of surface area (A_λ) tends to increase without limit as the step size (resolution) λ of an elemental square decreases. This can be expressed as:

$$A_\lambda = k_a \lambda^{-(\delta-2)} \quad [7]$$

where k_a is a constant and the fractal dimension δ is greater than 2. Hence a plot of $\ln(A_\lambda)$ versus $\ln(\lambda)$ will have a slope of $[-(\delta-2)]$, where 'ln' designates a natural logarithm.

Kaye applied fractal geometry in his studies of the profiles of carbon black agglomerates. In subsequent studies he demonstrated the usefulness of fractal geometry in studying boundary and mass fractal dimensions of aerosol systems, fractal structures of fine particle systems, fragmentation, description of porous bodies and gas adsorption.

Surface Characteristics and Interfacial Phenomena

The surface characteristics of small particles include surface area, rate of evaporation and condensation, electrostatic charge, adsorption, adhesion and light scatter. In certain circumstances, changes in the environment of a particle during sampling and particle size analysis may change its size or state of aggregation or its surface characteristics. Such changes must be considered in the selection of a suitable sampling device or method for particle size analysis.

Surface area One of the important characteristics of small particles is the rapid increase in exposed surface area per unit mass as size decreases, which leads to increased chemical reaction rate. Fine powders of organic and inorganic oxidable materials (such as coal, iron, flour, sugar, and starch) burn vigorously or explode violently when in the form of an aerosol. Moreover, an increase in surface area increases the toxicity of some granular materials.

Evaporation and condensation Evaporation and condensation are diffusion mass transfer processes which proceed at rates proportional to the surface area exposed. The temperature and partial pressure in the vicinity of the surface control the time required for small particles (e.g. water) to evaporate into still air. The evaporation time is given by:

$$\tau = \frac{RT}{8M}\frac{\rho_p D_p^2}{D\Delta_p} \quad [8]$$

where τ = evaporation time (s); ρ_p = density of particle material (kg m^{-3}); D_p = particle diameter (m); D = diffusion coefficient of vapour from particle (m^2 s^{-1}); Δ_p = difference between the particle pressure at the particle surface and in the surrounding fluid (N m^{-2}); R = gas constant (8.3144 J mol^{-1} K^{-1}); T = absolute temperature (K); M = molecular weight of evaporating particulate material. Finer particles can act as centres for

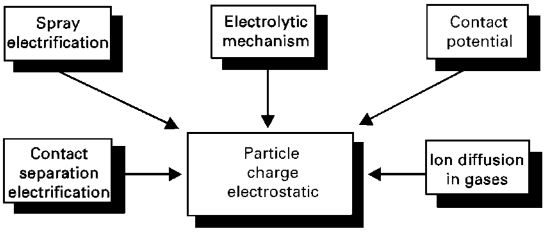

Figure 2 Mechanisms producing natural charge on particles.

condensation of moisture, leading to an increase in their size.

Electrostatic charge Electrostatic charge represents an excess or deficiency of electrons on the particle surface. This charge may be assumed to reside on the particle surface in an absorbed gas or moisture film. Mechanisms which produce natural charge on particle surfaces are shown in **Figure 2**. The electrostatic charge generated on a particle is proportional to the particle surface area, which is the principle used in the design of electrostatic classifiers and precipitators. Furthermore, the presence of electrostatic charge on particle surfaces controls the behaviour of particles in an electric field (see II/PARTICLE SIZE SEPARATION/Electrostatic Precipitation).

Scattering properties Scattering of radiation arises from inhomogeneities, such as dispersed dust or water drops, in the fluid medium. Scattering is often accompanied by absorption, and both scattering and absorption remove energy from the incident beams. The quantitative response of the intensity of transmitted and/or scattered beams can be used to characterize the size of a particle.

Kinetic Behaviour of Particles

The equivalent spherical particle diameter of an aggregate of irregularly-shaped particles can be determined by studying the inertial motion of particles in a medium. Such inertial motion can be found in many applications such as pulmonary deposition, design of industrial ventilation, particle collectors, and electrostatic precipitation. The various processes that affect particle motion in a field are shown in **Figure 3**.

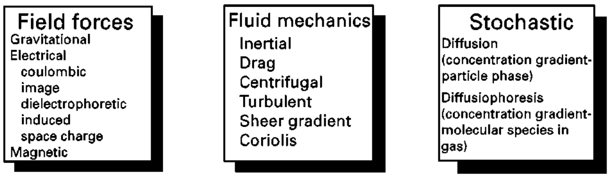

Figure 3 Processes affecting particle motion in a medium.

Medium Resistance

For a small spherical particle moving in a medium at low velocities (i.e. laminar flow), the drag (medium resistance) force acting on the particle is given by Stokes' Law as:

$$F_R = 3\pi\mu_m D_p V_{pm} = C_D \frac{\rho_m A V_{pm}^2}{2} \qquad [9]$$

where F_R = medium resistance (N); D_p = particle diameter (m); ρ_m = medium density (kg m^{-3}); μ_m = medium viscosity (kg m^{-1} s^{-1}); V_{pm} = relative velocity between particle and medium (m s^{-1}); A = projected area of particle normal to its motion (m^2).

It is useful to relate the magnitudes of the inertial and viscous forces in the form of a dimensionless Reynolds' Number as:

$$Re_p = \frac{\rho_m D_p V_{pm}}{\mu_m} \qquad [10]$$

The relationship between the drag coefficient C_D and the Reynolds' Number can be found in any fluid mechanics textbook. However, for spheres with $Re_p < 1, C_D = 24/Re_p$.

In finite containers a particle experiences an increase in the drag force due to two effects. First the fluid streamlines around the particle impinge on the container walls and are reflected back causing increased drag on the particle. The second effect occurs because the fluid is stationary at a finite distance from the particle, and there is a distortion of the flow pattern which reacts back on the particle. Taking into consideration these two effects, the drag force may be modified as:

$$F_R = 3\pi\mu_m D_p V_{pm}\left(1 + \frac{kD_p}{L}\right) \qquad [11]$$

where L represents the distance from centre of particle to the container walls and k = 0.563 for a single wall or container bottom and k = 2.104 for a cylindrical container.

Particle Motion

Particle motion in a gravitational/drag field The linear motion of a particle in a direction X relative to time t and under the influence of the drag, gravitational, and buoyancy forces is governed by:

$$\frac{\pi}{6}\rho_p D_p^3\left(\frac{\mathrm{d}^2X}{\mathrm{d}t^2}\right) = \frac{\pi}{6}(\rho_p - \rho_m)D_p^3 g - 3\pi\mu_m D_p \frac{\mathrm{d}X}{\mathrm{d}t} \qquad [12]$$

where g denotes gravitational acceleration. If the particle starts from zero velocity it will accelerate until it reaches a terminal velocity given by:

$$\left(\frac{\mathrm{d}X}{\mathrm{d}t}\right)_{t\to\infty} = V_{gt} = \left[\frac{D_p^2(\rho_p - \rho_m)}{18\mu_m}\right]\cdot g \qquad [13]$$

from which the particle diameter can be expressed as:

$$D_p = \left[\frac{18\mu_m}{(\rho_p - \rho_m)g}\cdot V_{gt}\right]^{1/2} \qquad [14]$$

Note that eqns [12] to [14] are applicable for $Re_p < 1$.

For a particle settling in air, it is usual to neglect the buoyancy correction, since ρ_p is of the order of unity, the air density is of the order of $10^{-3}\,\mathrm{g\,cm^{-3}}$, and viscosity of ambient air is $1.8\times10^{-5}\,\mathrm{kg\,m^{-1}\,s^{-1}}$. Equation [13] reduces to:

$$V_{gt} = 3.03\times10^4\,\rho_p D_p^2 \qquad [15]$$

where V_{gt}, ρ_p, and D_p are expressed in $\mathrm{m\,s^{-1}}$, $\mathrm{kg\,m^{-3}}$, and m, respectively.

Particles with diameters less than or close to the mean free path of the fluid molecules begin to slip between molecules and settle at a higher velocity than that predicted by eqn [13] for settling velocity. Cunningham considered this so-called slip effect and introduced a correction term to the terminal settling velocity as:

$$V_{gtc} = C_c V_{gt} \qquad [16]$$

$$C_c = \left(1 + \frac{2\alpha\lambda}{D_p}\right) \qquad [17]$$

where C_c denotes the Cunningham slip correction factor, λ is the mean free path of medium molecules, and α is a constant of approximately one.

Particle motion in a rotational (centrifugal) field In a centrifugal field the radial motion of a particle at a distance R from the centre of rotation is governed by:

$$\frac{\pi}{6}\rho_p D_p^3\left(\frac{\mathrm{d}^2R}{\mathrm{d}t^2}\right) = \frac{\pi}{6}(\rho_p - \rho_m)D_p^3\omega^2 R - 3\pi\mu_m D_p\frac{\mathrm{d}R}{\mathrm{d}t} \qquad [18]$$

where ω is the angular velocity of the particle. Assuming that the particle movement outward is resisted by viscous drag, Stokes' law provides a reasonable approximation for the drag. Therefore, the terminal radial velocity at equilibrium is given by:

$$\left(\frac{\mathrm{d}R}{\mathrm{d}t}\right)_{t\to\infty} = V_{rt} = \left[\frac{D_p^2(\rho_p - \rho_m)}{18\mu_m}\right]\cdot\omega^2 R \qquad [19]$$

which is equivalent to eqn [13].

To evaluate the performance of a centrifugal separation process, a separation factor '*SF*', defined as the ratio of centrifugal acceleration to gravitational acceleration:

$$SF \text{ or } g\text{-force} = \frac{\omega^2 R}{g} \qquad [20]$$

is used. For dust-collecting cyclones (particles $> 100\,\mu\mathrm{m}$), $SF = 200$, while conventional centrifuges used in precipitation of submicron particles and large molecules in liquid suspension have $SF = 5000$. See II/PARTICLE SIZE SEPARATION/Hydrocyclones for Particle Size Separation.

Particle motion in an electrostatic field When particles larger than 1 μm are passed through a corona discharge as the result of bombardment charging, they acquire charges from electrons and adsorbed gas ions proportional to the surface area of the particle. The saturation charge acquired is given by:

$$Q_{pb} = ne = \pi\varepsilon_0\varepsilon_1\kappa D_p^2 E \qquad [21]$$

$$\kappa = \frac{3\varepsilon_2}{\varepsilon_2 + 2\varepsilon_1} \qquad [22]$$

where Q_{pb} = saturation bombardment charge acquired (C); n = number of electron charges acquired; e = electron charge (1.6022×10^{-19} C); ε_0 = permittivity of vacuum ($8.8542\times10^{-12}\,\mathrm{F\,m^{-1}}$); ε_1 = relative permittivity of medium (gas); ε_2 = relative permittivity of particle material; E = external electric field strength ($\mathrm{V\,m^{-1}}$). For particles less than 0.2 μm, diffusion charging predominates and the charges acquired at time t are given approximately by:

$$Q_{pb} = ne = \frac{D_p kT}{2e}\ln\left(1 + \frac{\pi D_p V_i N_0 e^2}{2kT}t\right) \qquad [23]$$

where Q_{pd} = diffusion charge acquired (C); k = Boltzmann constant ($1.3807\times10^{-23}\,\mathrm{J\,K^{-1}}$); T = absolute temperature (K); N_0 = ion density (ions $\mathrm{m^{-3}}$); V_i = ion velocity (root mean square, $\mathrm{m\,s^{-1}}$). Based on the acquired charge on the particle and assuming that air resistance is approximated by Stokes' Law, the particle terminal velocity in an electric field is given by:

$$V_{et} = C_c\left(\frac{EQ_p}{3\pi\mu_m D_p}\right) \qquad [24]$$

where C_c = Cunningham slip correction factor; μ_m = medium (gas) viscosity; Q_p = acquired (bombardment or diffusion) charge on the particle.

Particle motion in a thermal gradient field It has been observed that particles in suspension move from hotter to colder regions. Later it has been shown that in a thermal gradient field and at atmospheric pressure, the thermal force acting on a particle is given by:

$$F_t = (-9\pi)\left(\frac{D_p}{2}\right)\left(\frac{\mu_m^2}{\rho_m T}\right)\left(2+\frac{\kappa_p}{\kappa_m}\right)^{-1}\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right) \qquad [25]$$

where κ_p = thermal conductivity of the particle material ($\mathrm{J\,m^{-1}\,s^{-1}\,K^{-1}}$); κ_m = thermal conductivity of the air ($\mathrm{J\,m^{-1}\,s^{-1}\,K^{-1}}$); T = absolute temperature (K); $\mathrm{d}T/\mathrm{d}x$ = temperature gradient in the air ($\mathrm{K\,m^{-1}}$). The negative sign in the equation indicates that the force is in the direction of negative thermal gradient. By setting the thermal force equal to the resistive force of the medium, the terminal velocity of a particle is given as:

$$V_{tt} = (-1.5)\left(\frac{C_c\mu_m}{\rho_m T}\right)\left(2+\frac{\kappa_p}{\kappa_m}\right)^{-1}\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right) \qquad [26]$$

The particle velocity and the flow velocity and geometrical configuration are used in the design of thermal precipitators.

Common Methods of Particle Size Analysis and Particle Size Ranges

To assist in covering the scope of the different techniques used in particle size analysis, an attempt was made to survey the current literature on particle size analysis techniques. The results of this investigation are summarized in **Figure 4**. It should be emphasized that this summary is not exhaustive. There are other sophisticated techniques which are outside the scope of this article. Of more importance is the identification of the size ranges of most common particles found in industrial, environmental, chemical and clinical applications (**Figure 5**). From an industrial point of view, the different types of gas particulate collecting equipment are summarized in **Figure 6**. Some basic definitions of particle size ranges of gas and atmospheric dispersoids and soil are included in **Figure 7**.

Mechanical Techniques for Particle Size Analysis

Based on the information given in Figures 4–7, it can be seen that the most common mechanical techniques for particle size analysis relevant to analytical sciences and industrial applications are: sieving, sedimentation (gravitational or centrifugal), elutriation, electrostatic precipitation, thermal precipitation, hydrodynamic chromatography and impaction. Each technique will be briefly presented; the details of each technique can be found in the references listed in the bibliography.

Sieving

Sieving is an obvious and most widely used technique for particle size analysis. The particles are classified based on their size, independent of any other particle characteristics such as density and surface properties.

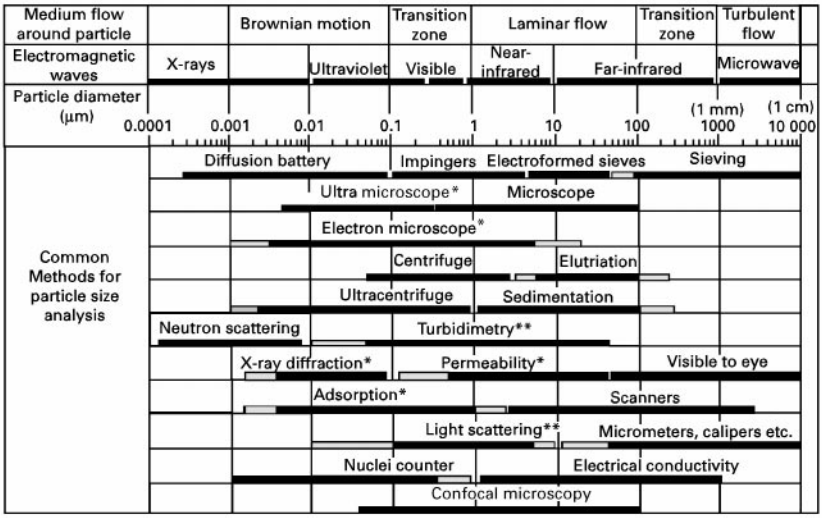

Figure 4 Common methods of particle size analysis. *Average particle diameter but not size distribution. **Size distribution may be obtained by special calibration.

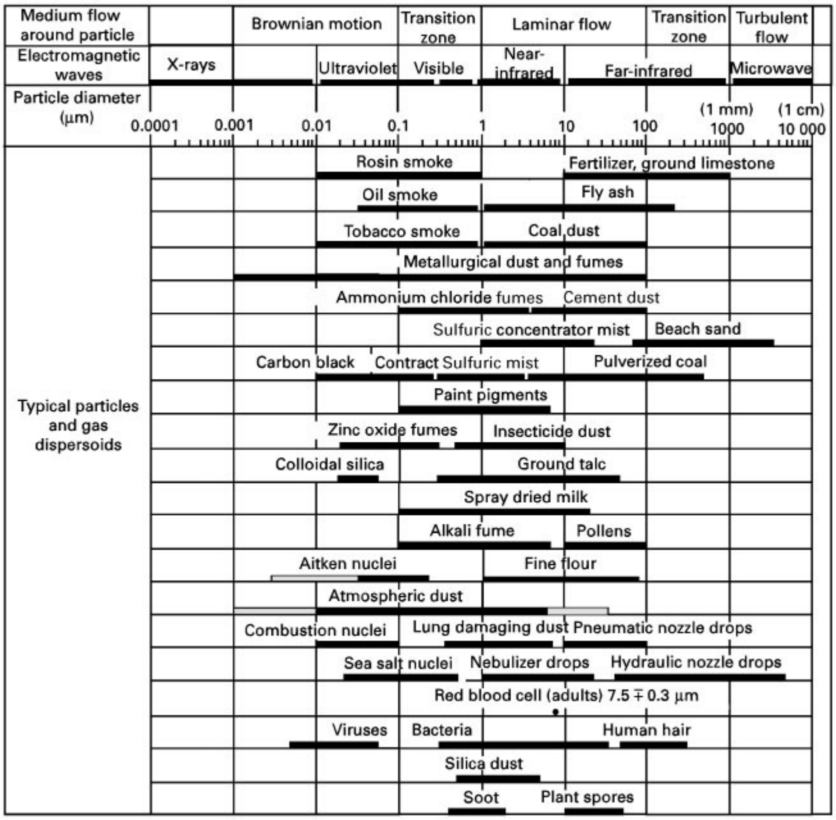

Figure 5 Typical particles and gas dispersoids.

Micromesh sieves are used to classify particles of size range 5–20 μm, while particles of size range 20–125 μm are classified in the standard woven wire sieves. Coarse particles (> 125 μm) are classified in punched plate sieves. Punched plate sieves are commonly used in industrial applications where the openings are circular or rectangular; the sieves can take different configurations.

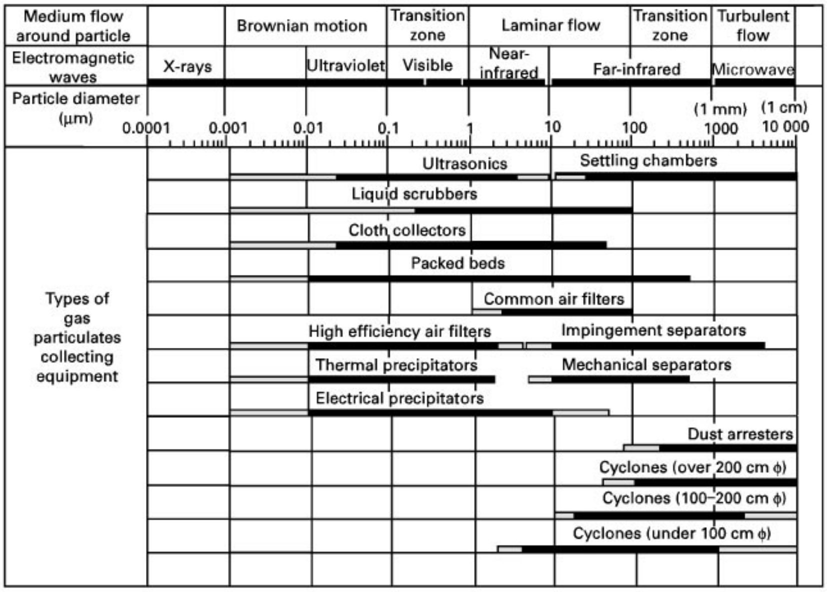

Figure 6 Different types of gas particulates collecting equipment (ϕ, diameter).

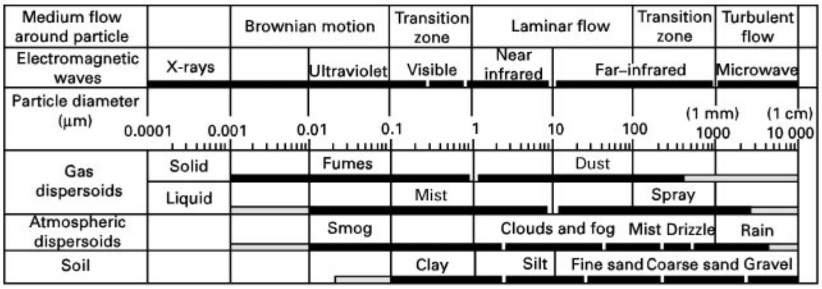

Figure 7 Some size range definitions.

The sieving test is conducted using up to 11 sieves stacked with progressively larger aperture openings towards the top, and placing the powder on the top sieve. A closed pan (receiver) is placed at the bottom. There are several schemes for shaking the sieves by mechanical or ultrasonic means. The residues in each sieve are recorded and expressed in percentage as cumulative values against the nominal sieve aperture values.

The common methods for fine sieving are machine, wet, hand and air-jet sieving. Wet-sieving is recommended for material originally suspended in a liquid and is necessary for powders which form aggregates when dry-sieved. In such tests the stack of sieves is filled with liquid and the sample is fed to the top sieve. Sieving is accomplished by rinsing, vibration, reciprocating action, vacuum, ultrasonication or a combination of these.

Table 1 presents the different international sieve standards and the corresponding sieve types. There are several sieve aperture progression ratios commonly available depending on the different international standards. In the USA, a progression ratio of $2^{1/2}$ is used. This ratio corresponds to successive particle groups of 2 : 1 particle surface ratio. The progression rate of $2^{1/3}$ ($10^{0.1}$) which has been adopted by the French corresponds to successive particle groups of 2 : 1 particle volume ratio. The progression ratios of $10^{0.1}$ and $10^{0.05}$ are recommended for narrow size distributions.

Table 1 International sieve standards

Country	*Standard*	*Sieve type*
Great Britain	BS 410	Woven wire
USA	ASTM E11	Woven wire
	ASTM E161-607	Micromesh (electroformed)
Germany	DIN 4188	Woven wire
	DIN 4187	Perforated plate
France	AFNOR NFX 11-501	Woven wire
International	ISO R565 1972(E)	Woven wire Perforated plate

The probability of a particle passing through sieve apertures depends on the particles size distribution, the number of particles on the sieve (sieve loading), the method of sieve shaking, the dimension and shape of the particle, and the ratio of open area of sieve to total area. In addition, the sieving operation can be affected by the friability and cohesiveness of the powder.

Sedimentation

Sedimentation of fine powders in a suspension is an important tool in the determination of particle size distribution. **Table 2** presents a classification of the methods and techniques used in sedimentation (gravitational or centrifugal). To conduct particle size analysis using sedimentation, the suspension can be prepared using the line start (two-layer) or the homogeneous suspension techniques. In the two-layer technique, the powder is introduced at the top of a column of clear liquid. In the homogeneous suspension technique, the powder is uniformly dispersed in the liquid. As the particles start to settle the change in solids concentration at a particular fixed height with time or the sedimentation time rate is measured. The solids concentration or density measurements is used in the incremental methods, while the settling rate measurement is used in the cumulative methods. Incremental methods may be divided as fixed time and fixed depth methods, the latter being more popular, although a combination is sometimes used.

A powder is made up of three types of particles: primary particles, aggregates and agglomerates. The

Table 2 Sedimentation methods and techniques

Incremental methods	*Cumulative methods*
Solids concentration variation	*Sedimentation rate*
Line start	Line start
Homogeneous suspension	Homogeneous suspension
Suspension density variation	
List start	
Homogeneous suspension	

primary particles are crystalline or organic structures bound together by molecular bonding, while the aggregates are primary particles tightly bound together at their point of contact by atomic or molecular bonding. The force required to break these bonds is considerable. In case of agglomerates, the primary particles are loosely bound together with weak van der Waals forces. It is often necessary to disperse the powder in a liquid prior to analysis. Dispersion is affected by the use of wetting agents which break down the agglomerates to their constituent parts. This process is facilitated by mechanical or ultrasonic agitation.

Gravitational sedimentation In gravitational sedimentation there are four main techniques: volume sample, mass sample, manometry and sedimentation vessel-wall pressure sensing as shown schematically in **Figure** 8.

Incremental methods Based on the results of motion of a particle in a gravitational/drag field, it can be shown that the solids concentration of settling suspension at depth h can be related to the cumulative undersize mass distribution as:

$$\frac{C(h,t)}{C(h,0)} = \frac{\int_{D_{\min}}^{D_t} f(D)\,\mathrm{d}D}{\int_{D_{\min}}^{D_{\max}} f(D)\,\mathrm{d}D} = \Psi \qquad [27]$$

$$D_t = \left[\frac{18\mu_m}{(\rho_p - \rho_m)g}\cdot\frac{h}{t}\right]^{1/2} \qquad [28]$$

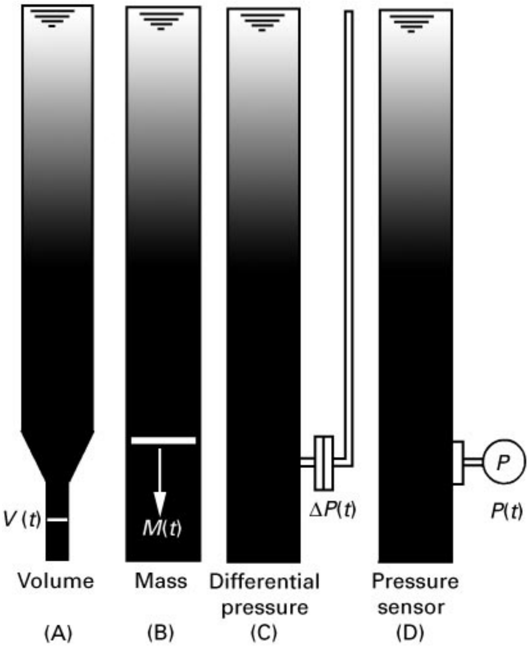

Figure 8 Main gravitational sedimentation techniques.

where $\mathrm{d}m(D) = f(D)\mathrm{d}D$ represents the mass fraction having particle size between D and $D + \mathrm{d}D$. In eqns [27] and [28], it is assumed that the volume of particles (powder) in suspension is very small compared with the total volume of suspension. By plotting 100Ψ against the free-falling particle diameter D_t the resulting curve shows the cumulative undersize percentage curve by mass.

Similarly, it can be shown that:

$$\frac{C(h,t)}{C(h,0)} = \frac{\phi(h,t) - \rho_m}{\phi(h,0) - \rho_m} = \Phi \qquad [29]$$

where $\phi(h,0)$ and $\phi(h,t)$ are the suspension density at a height h at $t = 0$ and $t = t$, respectively. By plotting 100Φ against D_t, the resulting curve shows the cumulative undersize percentage size curve.

The pipette method In this method, the changes in concentration occurring within a settling suspension are determined by drawing off definite volumes at a set of discrete intervals of time by means of a pipette. The solids concentration in the suspension is required to be between 0.2 and 1.0 vol%. If the concentration exceeds 1% the hindered settling adversely affects the results of the analysis. Initially the powder is made into a paste; this is followed by slow addition of the dispersing liquid, using a spatula plus mixing, to form a slurry. Further dispersion may be carried out in an ultrasonic bath. The suspension is washed into a sedimentation vessel. The analysis starts with violent agitation of the vessel avoiding the use of a stirrer. It is recommended that the container be continually inverted by hand for 1 min. Since initially the particles are not at rest, it is advisable to wait 1 min before withdrawing samples. The use of a time scale progression of 2 : 1 which produces a $2^{1/2}$ particle size progression is recommended. The collected samples are prepared to determine the solids concentration for particle size cumulative mass determination.

Hydrometers and divers The variation in density of settling suspension may be monitored with hydrometers, a method used widely in the cement industry. The method starts with a fully dispersed suspension and the densities at known depths are recorded as the solid phase settles out. The hydrometer technique is useful for quality control but not as an absolute method.

Divers are an extension of the hydrometer technique. They act as miniature hydrometers where each diver is calibrated to a particular density. Several divers of different densities are added to the fully dispersed suspension and each will settle at a height where its density is equal to the suspension around it.

Sealed in each diver is a copper ring which enables an external search coil to monitor and determine the location of the diver using high-frequency alternating current.

The specific gravity balance The specific gravity balance may be used to monitor the change within a settling suspension. Such a balance comprises two bobs, one in clear fluid and the other in the suspension being studied. The bobs are connected to the two arms of a beam balance. The depth of immersion of the bobs is adjustable. The change in buoyancy is counterbalanced by means of solenoids which are connected to a pen recorder. From the trace of the pen recorder, the particle size distribution can be calculated.

Cumulative methods Cumulative methods have an advantage over incremental methods in that the amount of sample required is small (about 0.5 g), which reduces the interaction between particles. This is a useful feature when only a small quantity of powder is available or when dealing with toxic materials.

Line start method In this case the size distribution may be directly determined by plotting the fractional weight settled against the free-falling diameter of particles. Special care needs to be exercised to eliminate the streaming problem, especially when the suspension at the top has higher density than the liquid.

Homogeneous suspension method Let us consider a powder with a mass distribution such that $\mathrm{d}M = f(D)\mathrm{d}D$, where $\mathrm{d}M$ represents the fractional mass of particles having a diameter between D and $D + \mathrm{d}D$. Let us assume that the powder is completely dispersed in a liquid, and consider a suspension chamber of height h. It can be reasoned that mass per cent P which has settled out at time t is made up of two parts:

(1) all the particles with a free-falling speed greater than that of D_t as given by Stokes' Law or some related law, where D_t is the size of particle which has a velocity of fall h/t:

(2) particles smaller than D_t which started off at some intermediate position in the chamber. The falling velocity of one of these smaller particles is v, the fraction of particles of this size that have fallen out at time t is (vt/h).

This mechanism can be represented mathematically as:

$$P = \int_{D_t}^{D_{\max}} f(D)\,\mathrm{d}D + \int_{D_{\min}}^{D_t} \frac{vt}{h} f(D)\,\mathrm{d}D \qquad [30]$$

which after some manipulation can be rewritten as:

$$P = M + t\frac{\mathrm{d}P}{\mathrm{d}t} \qquad [31]$$

eqn [31] may be written in a different form as:

$$M = P - \frac{\mathrm{d}P}{\mathrm{d}\ln(t)} \qquad [32]$$

Both eqns [31] and [32] can be used to determine M. The most obvious way is to tabulate t and P, and hence derive $\mathrm{d}P$, $\mathrm{d}t$, and finally M (cumulative percentage oversize) versus D_t. Equation [32] is recommended in cases of wide size distribution.

Centrifugal sedimentation Gravitational sedimentation for particle size analysis has limited flexibility. Firstly, the only means of varying the particle velocity is by selecting a medium with different density or viscosity. Secondly, gravitational sedimentation cannot handle particles smaller than 5 μm. Thirdly, most sedimentation devices suffer from the effects of convection, diffusion and Brownian motion. These difficulties can be reduced by speeding up the settling process by centrifuging the suspension. Furthermore, by the use of a centrifugal field, a substantially lower size limit and reduced analysis time can be achieved. As with gravitational methods the data may be cumulative or incremental and the sample may be homogeneous or two-layer.

Calculations of size distribution from centrifugal data are more difficult than calculations from gravitational data, since particle velocities increase as they move away from the axis of rotation (i.e. the particle velocity depends on its radial position). One way to overcome this difficulty is to use a relatively small settling radial zone at a far distance from the centre of rotation (i.e. the centrifugal force acting on all particles is approximately the same). Another solution is to use the line start technique. The most common techniques used in centrifugal sedimentation are schematically presented in **Figure 9** where S and D designate source and detector, respectively.

Line start method Rewriting eqn [19] as:

$$V_{rt} = \frac{\mathrm{d}R}{\mathrm{d}t} = \left[\frac{D_t^2(\rho_p - \rho_m)}{18\mu_m}\right]\cdot\omega^2 R \qquad [33]$$

together with separation of variables and integration of eqn [33], yields:

$$D_t = \left[\frac{18\mu_m}{(\rho_p - \rho_m)\omega^2 t}\cdot\ln\left(\frac{R}{S}\right)\right]^{1/2} \qquad [34]$$

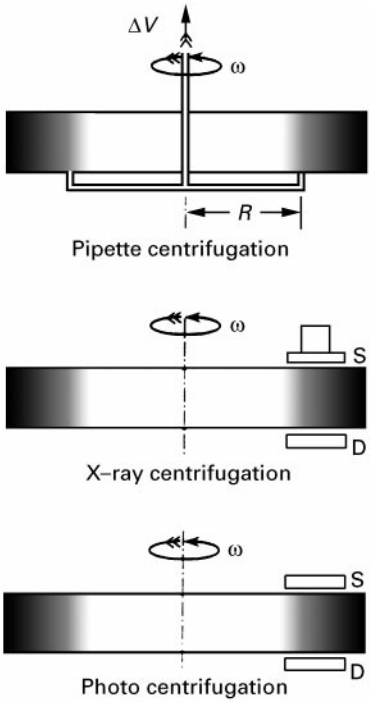

Figure 9 Main centrifugal sedimentation techniques.

where t is the time for a particle of size D_t to settle from the surface of the fill (at distance S from the centre of rotation) to a radial distance R. Hence, at time t, all particles at R will be of size D_t. Monitoring the per cent solids or density of the suspension at specified intervals of time will produce the particle size distribution which can be represented using cumulative values at different values of D_t.

Homogeneous suspension method Equation [34] still applies: however, at time t, all particles of size greater than D_t will have settled out radially to a distance R. Conversion of the sedimentation curve into a cumulative curve is not as simple in this case as for that of gravitational sedimentation. Difficulties involved in evaluating the sedimentation curve may be overcome in the case of a centrifugal field by assuming a constant centrifugal field, i.e. for $(R - S)$ interval is small enough to allow the approximation:

$$\ln\left(\frac{R}{S}\right) \approx \frac{(R-S)}{R} \qquad [35]$$

when the value $(R - S)$ is one twentieth of R, the cumulative curve can be obtained directly by the pipette technique with an error of 1%.

Elutriation

In fluid classification, the effects of different forces on the movement of suspended particles control the separation of dispersed particles. As discussed in the kinetic behaviour of particles, the field forces are gravitation, as with elutriators, or centrifugal or Coriolis force in classifiers. The medium is usually water or air. In general all fluid classifiers can be divided into two classes, counterflow equilibrium (elutriation) and inverse flow separation. The elutriation is presented briefly below.

In the elutriation technique, the field and the drag forces act in opposite directions and particles leave the separation zone in one of two directions, depending on their size. Particles of a certain size stay in equilibrium in the separation zone. The grading is carried out in a series of vessels (cylindro-conical form) of successively increasing diameter. Hence, the fluid velocity decreases in each stage, the coarse particles being retained in the smallest vessel and the relatively finer particles in the following vessels. For air elutriation, the analysis is considered complete if the rate of change of weight in residues is less than 0.2% of the initial weight in half an hour, and for water elutriation the analysis ends when there is no sign of further classification.

Using Stokes' Law, the particle size retained in an intermediate vessel can be predicted approximately as

$$D_p = \left[\frac{18\mu_m}{(\rho_p - \rho_m)g} \cdot V_{\max}\right]^{1/2} \qquad [36]$$

$$V_{\max} = 2V = 2\frac{Q}{A} \qquad [37]$$

where Q = volumetric flow rate, A = vessel cross-sectional area at the equilibrium zone. In eqn [37] it is assumed that the flow profile in the vessel is parabolic. It is clear that elutriation is only suitable for rough dispersions. With small particles, sedimentation may be speeded up by using a centrifuge. This technique is utilized when classifying aerosols using a stream of air which flows in the direction opposite to the centrifugal force.

Electrostatic Precipitation

The electrostatic precipitator consists of an ionizing cathode at high potential surrounded by a collecting anode; typically, these anodes consist of concentric cylinders, the inner one often being a single wire. The gas suspension passes between the cylinders, picks up the charge, and travels to the anode where the charge is deposited. The transfer of electrons from one anode to the other constitutes an electric current. The magnitude of this current is proportional to the number of particles deposited. Particle sizes can be determined by varying the flow rate or applied potential.

Classification in an electrostatic field by differences in charge is related explicitly to particle size. This type of instrument has been used for collecting aerosol bacteria. The instrument consists of a glass cylinder with a central electrode. The inner surface of the cylindrical glass is coated with a suitable material to act as the other electrode and to collect samples. The principal advantages of this type of instrument are high collection efficiency over a wide size range, low resistance and high flow-rate capacity.

Thermal Precipitation

Particles in a thermal gradient medium move in the direction of negative gradient, i.e. from hotter to colder regions. Based on this principle, the instrument typically consists of two parallel round microscopic plates and a heated wire in between as shown in **Figure 10**. The sample is drawn between the plates and the particles deposit on the glass plates and are collected for further analysis.

Normally a sample flow of 1–2 $\mathrm{cm}^3\,\mathrm{s}^{-1}$ is recommended and the collection efficiency is high for particles smaller than 5 μm. The collecting device may be modified so that the sample is collected directly on an electron microscope grid. Modifications of the basic design include means of centering the wire in position, substitution of the wire by a ribbon to give more uniform deposits, and using inlet elutriators to exclude coarse particles. The practical application of thermal precipitation in gas cleaning plants has only rarely been attempted.

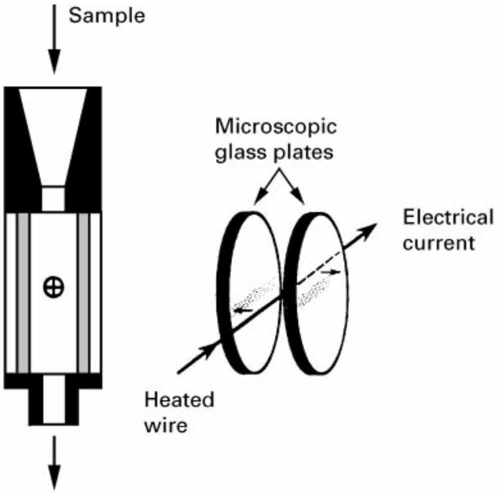

Figure 10 Thermal precipitation.

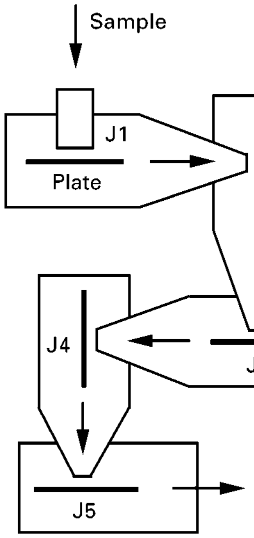

Figure 11 Cascade impactor.

Impaction

Impactor Inertial impaction devices cause an air sample to be drawn into a round or rectangular nozzle where the gas velocity is substantially increased. The jet from the nozzle is discharged against an adjacent flat surface, causing the air to diverge sharply. Particles in the air have more inertia than the air, and tend to continue forward as the air passes off to the sides, causing some of the particles to impact onto the surface. To prevent the particles from re-entrainment, a viscous material such as silicone fluid (or substrate) is used to coat the plate. The efficiency of impaction may be defined in terms of the dimensionless impaction factor as:

$$I = \left(\frac{C_c \rho_p D_{pa}^2 V_j}{18 \mu_m D_j}\right)^{1/2} \qquad [38]$$

where D_{pa} = particle aerodynamic diameter: D_j = jet diameter or width: V_j = average air velocity at the jet outlet.

Classification of a particle cloud into discrete sizes using cascade impaction may be interpreted as measuring aerodynamic (equivalent spherical particle) diameter. Several impaction stages (cascade impactor) are used in the classification of a polydisperse cloud (see **Figure 11**). The stages are arranged to permit jet velocity to increase with each succeeding stage (by successive reduction in jet diameter or width), and to therefore cause particles of progressively smaller sizes to be impacted. In effect, the cascade impactor classifies particles according to their aerodynamic size. The aerodynamic diameter can be expressed in terms of Stokes' diameter as:

$$D_{pa} = D_{\mathrm{Stokes}} \rho_p^{1/2} \quad [39]$$

where D_{Stokes} is the measured diameter. The aerodynamic size is important because it controls the motion of a particle in an air stream. Therefore, it is significant for studies concerning lung inhalation, spray effectiveness, and gaseous cleaning devices. A special duty impactor (five-stage cascade impactor) has been developed for sampling and grading acid mists in the size range 0.3–3 μm.

Impinger Another sampling instrument, referred to as an impinger, also utilizes inertial impaction: however, deposition occurs at the bottom of a liquid-containing vessel. The downward-directed air-jet displaces the liquid and uncovers the bottom of the vessel. The particles that impinge against the wet surface are subsequently washed off by the liquid. The undeposited particles may be caught as air bubbles rise through the liquid. The particles are usually examined in the liquid suspension. Water is the most commonly used liquid.

Hydrodynamic Chromatography

Size information about colloidally suspended particles (0.01–1 μm) can be obtained by employing hydrodynamic chromatography (HDC). A medium (an aqueous solution) is pumped through a column packed with impermeable spheres. A pulse of colloidal suspension (0.2 cm^3) containing about 0.01 wt% polymer is injected into the flowing stream of the column entrance. The mobile phase from the column effluent is passed through a suitable detection system, such as a flow through spectrophotometer of the type used in liquid chromatography, and the detector response of the colloid is determined as a function of elution time. An extra step is needed to determine the concentration of solids in the eluted solution.

It has been observed that the larger particles elute faster than the small ones. It has also been found that the smaller the packing diameter the better the separation. Other factors which affect the rate of transportation through the bed are the size of bed particles, the ionic strength, and flow velocities, as well as the particle size of eluting particles.

In general, HDC has been successfully applied to the size characterization of a number of polymer lattices. The method is applicable to the size separation of particles between 0.02 and 1 μm, if they are rigid. Moreover, it is expected that HDC has wide applicability to sub-μm particles such as in lattices, carbon black, colloidal silica, paint, and photographic pigments, dyes, food colours, natural and artificial blood, and metallic fumes.

Another extension of HDC is to replace the packed bed with a long capillary. Capillary particle chromatography (CPC) requires 30 kPa pressure and has a separating range of 0.2–200 μm. In such techniques the particle transit time is a logarithmic function of particle size.

Liquid Particle Size Measurement Techniques

In the areas of combustion and chemical processes and in the pharmaceutical and agriculture industries, measurement of droplet size and velocity distributions is important. In one respect the measurement of droplets is easier than that of solid particles because droplets are usually spherical and smooth. In another respect the measurement of droplets is more difficult because they are not easy to collect and stabilize, and they may be volatile. Thus, an *in situ* measurement is usually preferable. The applications commonly used can be grouped as spray diagnostics (using ensemble scattering techniques and optical single-particle analysis) and spray measurement.

Acknowledgement

This work was supported in part by the Federal Panel on Energy Research and Development (PERD).

See also: **II / Chromatography:** Hydrodynamic Chromatography. **Flotation:** Cyclones for Oil/Water Separations; Historical Development; Oil and Water Separation. **Particle Size Separation:** Electrostatic Precipitation; Field Flow Fractionation: Thermal; Hydrocyclones for Particle Size Separations; Sieving/Screening.

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MEDICINAL HERB COMPOUNDS: HIGH-SPEED COUNTERCURRENT CHROMATOGRAPHY

T. Zhang, Beijing Institute of New Technology Application, Beijing, China

Introduction

Medicinal herbs are an important source of natural products for medicine. They include various chemical components ranging from fat-soluble to water-soluble compounds. The isolation of the biologically active components is the starting point of further research in chemistry and pharmacology as well as in the utilization of these compounds.

Traditional Chinese medicine is an extremely rich source of the experience acquired over a long period of time. In order to make greater use of traditional Chinese medicine, modern scientific methods are used to find the bioactive compounds in the traditional drugs and to use them as leading compounds for new drug design. New drugs developed in this way include anisodamine and the antimalarial agent Qinghaosu (artemisine).

For separating and purifying bioactive compounds from medicinal herbs, modern chromatographic techniques, such as gas chromatography, high performance liquid chromatography, thin-layer chromatography and electrophoresis have significantly raised the technical level and have shortened the time required for research projects.

High speed countercurrent chromatography (HSCCC) has been recognized as an effective means for separation and purification of a wide variety of bioactive components. It is a liquid–liquid partition chromatography system based on a coil planet centrifuge system without the use of any solid support. This technique has developed rapidly during the past decade. It has been demonstrated to have preparative capabilities and unique properties for fractionating a variety of natural products and medicinal herbs.

Here some applications of the separation of bioactive compounds, such as alkaloids and flavonoids, in medicinal herbs by HSCCC are described.

Separations of Alkaloids

Separations of Alkaloids Extracted from *Stephania tetrandra* S. Moore

Dried roots of *Stephania tetrandra* S. Moor (Menispermaceas) or Fenfangji in Chinese is a traditional Chinese drug used for rheumatism and arthritis. The total active alkaloid content in the natural products is 2.3%. Three major alkaloids have been identified as tetrandrine (I, 1%), fangchinoline (II, 0.5%) and cyclanoline (III, 0.2%). I and II are inseparable by conventional methods, while III is well separated from the other two. As illustrated in **Figure 1**, I and II are both bisbenzylisoquinoline alkaloids, whereas III is a water-soluble quaternary protoberberine-type alkaloid.

A sample solution was prepared as a mixture of I and II with purified III to obtain a 10 : 5 : 2 weight ratio to simulate their composition in the natural drug. 3 mg of this sample was dissolved in 0.5 mL of the upper stationary phase of the selected solvent system. The solvent system was composed of n-hexane/ethyl acetate/methanol/water at two different volume ratios of 3 : 7 : 5 : 5 in the first experiment and 1 : 1 : 1 : 1 in the second. In both cases the lower phase was used as the mobile phase at a flow rate of 60 mL h^{-1} in the normal elution mode. The apparatus used in these experiments was a Pharma-Tech Model CCC-2000 analytical countercurrent