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Application of Velocity-Selective Freeze-Displacement to the Separation and Characterization of Particulate Matter in Air Pollution Samples

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June, 1975

Abstract

A new method for separating and characterizing solid particulate matter in air pollution samples is described. The method utilizes the phenomenon of velocity-selective freeze-displacement of particulate matter during controlled solidification of organic liquids to selectively separate particles by differences in their interfacial physical properties. The theoretical basis of this phenomenon is discussed with respect to factors enhancing the efficiency of particle separation by this technique. A new analytical characterization method, freeze-displacement zone chromatography, is described. Experimental data for the freeze displacement of mineral particles are examined and conditions determined for optimum separation by freeze-displacement zone chromatography.

Introduction

The increasing public concern for environmental pollution has led to intensive research on pollution monitoring and characterization methods. Problems associated with particulate pollutants in atmosphere are many. Procedures for the identification of specific compounds contributing to air pollution are largely tedious and expensive. The development of new, inexpensive and operationally simple methods for identifying the chemical composition and physical state in which air pollutants occur is of paramount importance, as these properties relate to particulate toxicity, retention within the lung, visability and to the modification of weather through cloud nucleation.[1-3]

Much current research has been applied to the determination and analysis of particle size of air-borne particulate matter in air pollution samples.[4] The measurement of the distribution of chemically disparate components in air pollution samples has received relatively little attention because of the complexity of the problem.

In this paper, an analytical technique for separating solid particulate matter on the basis of surface properties is presented. The method utilizes the phenomenon of velocity-selective freeze pushing of partiuclate matter by a solid-liquid interface during controlled solidification. The method of zone chromatographic freezing utilized in this analytical technique is described and tested experimentally. The method is applied to determine the freeze-displacement and degree of particulate separation of mineral particles.

Sources of Particulate Pollutants

The sampling of particulate matter from air pollution sources is based primarily on filtration methods which detect solid particles by capture on porous filters. The size range of the particles depends on the porosity of the filter. The mass of particles collected is easily measured by a number of techniques, but the phase identification, chemical composition and size distribution of the particles require complex laboratory methods usually involving expensive and complicated equipment. Thus, a need exists for relatively simple separation techniques which are sensitive to the chemical and physical properties of a heterogeneous particulate sample. From Table I, which summarizes the major pollutant sources of particulate matter, it can be appreciated that such separation techniques must be applicable to a wide range of particulate materials.

A principle function of air pollution control technology is the monitoring and collection of particulate matter from particulate pollution sources. Sampling methods may be divided into two functional groups: (i) those which capture and collect the sample in sufficient bulk for convenient transport to the analytical laboratory, and (ii) those instruments which during collection bring about an initial separation or classification which simplifies subsequent analytical evaluation. The analytical technique described in this paper falls into the second group, in that separation of particles is based on surface properties rather than on size, but the method can be extended to cover both functions. In addition, alternately, samples collected

Table I

Major Pollutant Sources of Particulate Matter

Chemical Process Industries

- Carbon black
- Charcoal
- Explosives (TNT and nitrocellulose)
- Paint and varnish manufacturing
- Plastics manufacturing
- Printing ink manufacturing
- Sodium carbonate

Food and Agricultural Industries

- Alfalfa dehydration
- Coffee roasting
- Cotton grinding
- Feed and grain processing
- Fertilizer processing and distribution
- Meat smokehouse operation
- Starch manufacturing
- Sugar cane processing

Metallurgical Industries

- Primary metals
  - Aluminum ore reduction
  - Coke manufacturing
  - Copper and lead smelling
  - Ferrous alloy production
  - Iron and steel milling
  - Zinc refining
- Secondary metals
  - Aluminum processing
  - Bronze, brass, lead, and magnesium smelting
  - Ferrous alloy processing

Table I (continued)

Steel and cast iron foundary operation

Zinc processing

Mineral Products Industries

Asphalt roofing

Asphalt and concrete preparation

Brick, ceramics, and clay products manufacture

Calcium carbide processing

Cement making

Clay, and fly ash sintering

Coal cleaning

Fiberglass manufacture

Glass and frit manufacture

Gypsum and lime manufacture

Mineral wool manufacture

Phosphate rock preparation

Refractory casting

Rock, gravel and sand quarrying

Petrochemical Industries

Petrochemical manufacture

Petroleum refining

Power Industries

Steam electric power stations

Waste Disposal Industries

Municipal incinerators

Wood Industries

Fibreboard manufacture

Forest products manufacture

Paperboard manufacture

Saw mill operation

by a method from the first group can be subjected to the freeze-displacement separation process.

Theory of Freeze-Displacement of Particles

The phenomenon of the displacement of solid particles in a liquid by the motion of a solid-liquid interface has been known for some time.[5,6] From experimental studies[6] it is known that a critical maximum freezing velocity exists for sustaining this effect, for each type of particulate matter suspended in the solidifying host liquid. At freezing rates below the critical freezing velocity, the particles are rejected by the solid-liquid interface and retained in the liquid phase. At velocities above the critical velocity, the particles are partially trapped in the solid, with the entrapment probability increasing with the freezing rate.

The distribution of particle density between the solid and liquid phases in the vicinity of solid-liquid interface depends on the interfacial properties of the suspended particulate matter relative to the suspension medium, as well as on the freezing rate. At a constant freezing rate of an appropriate, low-melting inorganic or organic host medium, the fraction of suspended particles displaced by the freezing interface can be shown from theoretical grounds to be different for different particulate materials. Therefore, the freezing conditions and the host phase can be chosen to produce a difference in separation factors for particulate materials with different surface properties. There is thus a theoretical basis for

a novel separation device for use in separating and characterizing particulate mixtures: suspending them in an appropriate host medium and directionally freezing this medium at a rate where different particulate materials have different entrapment probabilities. In order to determine the separation factors achievable by this method, it is important to review the theoretical bases for the displacement of particles by a solidifying interface.

The particle freeze-displacement process is attributable to the surface tension and electrostatic forces exerted by the crystal interface on the particle during crystallization. When a particle is in intimate contact with the crystal surface, an amount of work is required to separate the particle from the solid-liquid interface of the solidifying fluid and to produce the increased solid-liquid and particle-liquid interfacial areas, while the original particle-solid interfacial area decreases.

If the interfacial energy between solid and particle, σ_{sp}, is greater than the sum of the solid-liquid interfacial energy, $\sigma_{s\ell}$, and the particle-liquid interfacial energy, $\sigma_{p\ell}$, i.e., $\sigma_{sp} > \sigma_{s\ell} + \sigma_{p\ell}$, then the crystal will displace the particle into the liquid by interfacial tension forces. On the other hand, when $\sigma_{sp} < \sigma_{s\ell} + \sigma_{p\ell}$ the particle simply adheres to the crystal, and continued freezing entraps the particle. The magnitudes of interfacial energies therefore provide a basis for predicting whether or not it is possible for the growing crystal to push the external particle.

A theory developed by Uhlmann, Chalmers and Jackson[5] for assessing the force exerted by a crystallizing interface on a solid particle is based on an assumption of short-range particle-interface repulsion due to the differences in interfacial energies. This effect is combined under dynamic conditions with the force required to drive liquid into the contact region between the crystal and the particle adjacent to the solid-liquid interface. The relation between these processes is assumed to be a function of particle surface roughness. However, this theory predicts no difference in the particle-pushing force exerted by different the solid-liquid interface on different types of particles as long as their sizes are the same.

Bolling and Cisse[7,8] combined fluid-flow, viscous drag and diffusion effects to modify the basic theory. They also considered the effect of solid-liquid interfacial curvature produced by the interaction between the particle and the interface, to derive theoretical relations for the critical velocity. When the basic theory was treated in more detail to include the effects of particle roughness, gravity and thermal conductivities, their experimental results were found to support very well the modified theory. However, the assumption that there is preferential wetting of some types of particles by the solid interface is still obscure. It is believed that in order to understand and predict the discriminatory pushing of the particles, all the forces acting on the particles by the solid-liquid interface, such as surface energies, viscous drag,

electrostatic forces and external forces have to be taken into consideration.

The critical velocity for particle trapping by the freezing interface can be calculated by equating the liquid-phase diffusion force, produced by liquid flow into the contact region, to the gradient in differential interfacial energy with respect to the distance of particle separation from the interface. For an atomically smooth particle and a planar freezing interface, the critical velocity is then

$$V_c \cong \frac{3LV_a aD}{kTR^2} . \qquad (1)$$

This theoretical expression is somewhat unsatisfactory, however, because anomalously high diffusion coefficients are needed to give satisfactory experimental agreement with the theory. If the interface is assumed to be indented in the vicinity of the particle, then the interfacial area of contact is increased, as is the force gradient, and agreement of theory and experiment is improved. Also, if the particle is atomically rough, the channel width for diffusion is increased, also leading to improved agreement.

It is possible that electrostatic forces between the host liquid-solid interface and the suspended particulate phase are more significant than the crystallization force. The electrical double layer force is well known in such selective separation processes as foam fractionation and floatation. It is also possible to introduce

an electrostatic force by passing a current along the direction of freezing to induce an electrophoretic effect which could aid in selective separation by the freeze displacement process.

Particulate Distribution Coefficients for Freeze-Pushing

A particulate distribution coefficient for suspended particles of solid phase i , k_i^* , can be defined as the ratio of the particulate concentration in the solidified solid to that in the liquid phases near the solid-liquid interface, during solidification of an appropriate, low-melting host liquid. If all the particles of a given solid phase are displaced by the interface, then the particulate distribution coefficient is equal to zero, whereas if all are entrapped, the particulate distribution coefficient is equal to unity. The particulate distribution coefficient is freezing-velocity dependent and fundamentally different from the chemical distribution coefficient which describes the ratio of solubilities in the solid and liquid phases. This means for defining the distribution coefficient for particulate freeze-pushing is exceptionally useful in the assessment of the efficiency of a given particle separation process using particulate freeze-pushing.

Particle Separation by Zone Chromatography

Because the freeze-displacement phenomenon is very sensitive to the properties of the interface between the particulate matter and the liquid or solid phase of the separation medium, the physical

distribution coefficients has a specific value for a given particulate material and separation medium. This fact suggests a chromatographic method for applying the freeze-displacement phenomenon to particulate separation. In this method of separation, the particulate pollution sample should be initially concentrated at the freezing interface. Since those particles with small distribution coefficients tend to be pushed farther by the freezing interface before entrapment in the solid, the different materials can be identified from the average distance those particles are displaced by directional freezing.

If there is a finite difference between physical distribution coefficients for different types of particles, then velocity-dependent freezing can bring about separation of component particles. The efficiency of separation will depend on factors such as particulate concentration, the particle interfacial properties and the interactions among the particles in the liquid medium. In the following development the host medium is assumed an organic compound, and all particle entrapment processes are assumed to contribute to the particulate distribution coefficient.

Consider an infinite column of solid extending in the x-direction from $x = -\infty$ to $x = +\infty$. The differential equation determining the distribution of solute in the solid after nth pass of a solidifying interface is

$$\left(\frac{\ell}{k^*}\right)\left(\frac{dc_n(x)}{dx}\right) + c_n(x) = c_{n-1}(x + \ell) \qquad (2)$$

where k^* is the particulate distribution coefficient and ℓ is the liquid zone length. Using the assumption that the initial distribution of particle is a delta function centered at $x = \ell$, Reiss and Helfand[9] have solved this equation by using Fourier Transforms and obtained,

$$\frac{c_n(x)}{k^* c_i} = \frac{1}{m!}\left[k^*\left(\frac{x}{\ell} + m\right)\right]^m \exp\left[-k^*\left(\frac{x}{\ell} + m\right)\right] . \qquad (3)$$

Equation 3 is a modified Poisson distribution function.

An approximate criterion for the zone-chromatographic separation of two components by zone melting has been developed by Pfann.[10] This criterion can be extended to freeze-displacement zone chromatography by introducing the particulate distribution coefficient. If the two phases have particulate distribution coefficients k_1^* and k_2^*, respectively, then the number of zone passes required for resolution of two particulate phases is given by

$$n = [m + 1] \qquad (4)$$

where

$$m = \left[\frac{1 + \sqrt{k_2^*/k_1^*}}{1 - \sqrt{k_2^*/k_1^*}}\right]^2 .$$

Thus, the number of zone-passes required to bring about a given degree of separation depends only on the ratio of distribution coefficient.

The estimation of the length of column required to separate two types of particles is given by

$$L^* = m\left(\frac{k_2^* - k_1^*}{k_2^* k_1^*}\right)\ell \ , \tag{5}$$

where ℓ is the zone length. The time required for a given separation can be expressed as

$$t^* = \frac{L^* + (n - 1)\ \ell d}{V} \ , \tag{6}$$

where V is the freezing velocity and d is a separation constant. These equations can be used to deduce the conditions required for particle separation by freeze-displacement zone chromatography.

Comparison with Experimental Data

There is limited experimental data in the literature on the basis of which the critical velocity for the freeze-displacement process and the particle distribution coefficient for freeze-displacement can be determined. Corte[6] investigated the effect of the freezing velocity and the particle size dependence on particle displacement by an ice-water interface, for particles of calcite, rutile, shale and quartz in the size range of 149 to 590 μm. The fraction of particles retained in the liquid phase by displacement of the freezing interface was measured at different freezing rates in the vertical direction. In this study the freezing rates were

in the range from 10^{-5} to 10^{-4} cm/sec in order to prevent decomposition of the water-ice interface.

The data on the particle fraction pushed by the freezing interface moving at a given velocity can be converted to data on distribution coefficients for freeze-displacement, k^*, by normalizing particle concentrations in the solid with respect to the concentration of particles at the freezing interface. The reduced data is shown as a function of freezing rate in Fig. 1. This figure shows that the distribution coefficients are significantly different for the four minerals studied, for freezing rates within a relatively wide range of values. Those materials which exhibit a small physical distribution coefficient tend to be pushed farther by the freezing interface before trapping within the solid.

Utilizing the particle distribution coefficients determined for calcite, rutile, slate and quartz, it is now possible to apply the results shown above for zone chromatographic separation to determine the number of zone passes required for effective phase separation at a given freezing velocity. The results of the application of the zone chromatographic separation technique to the separation of the minerals shown in Fig. 1 was explored at different freezing velocities and zone passes. The results are shown in Figs. 2, 3 and 4 for freezing velocities of 5×10^{-5}, 8×10^{-5} and 1.2×10^{-4} cm/sec, respectively. Less than twenty zone passes are required to resolve the separation of the different minerals at the lowest velocity, while a larger number of zone passes is required at

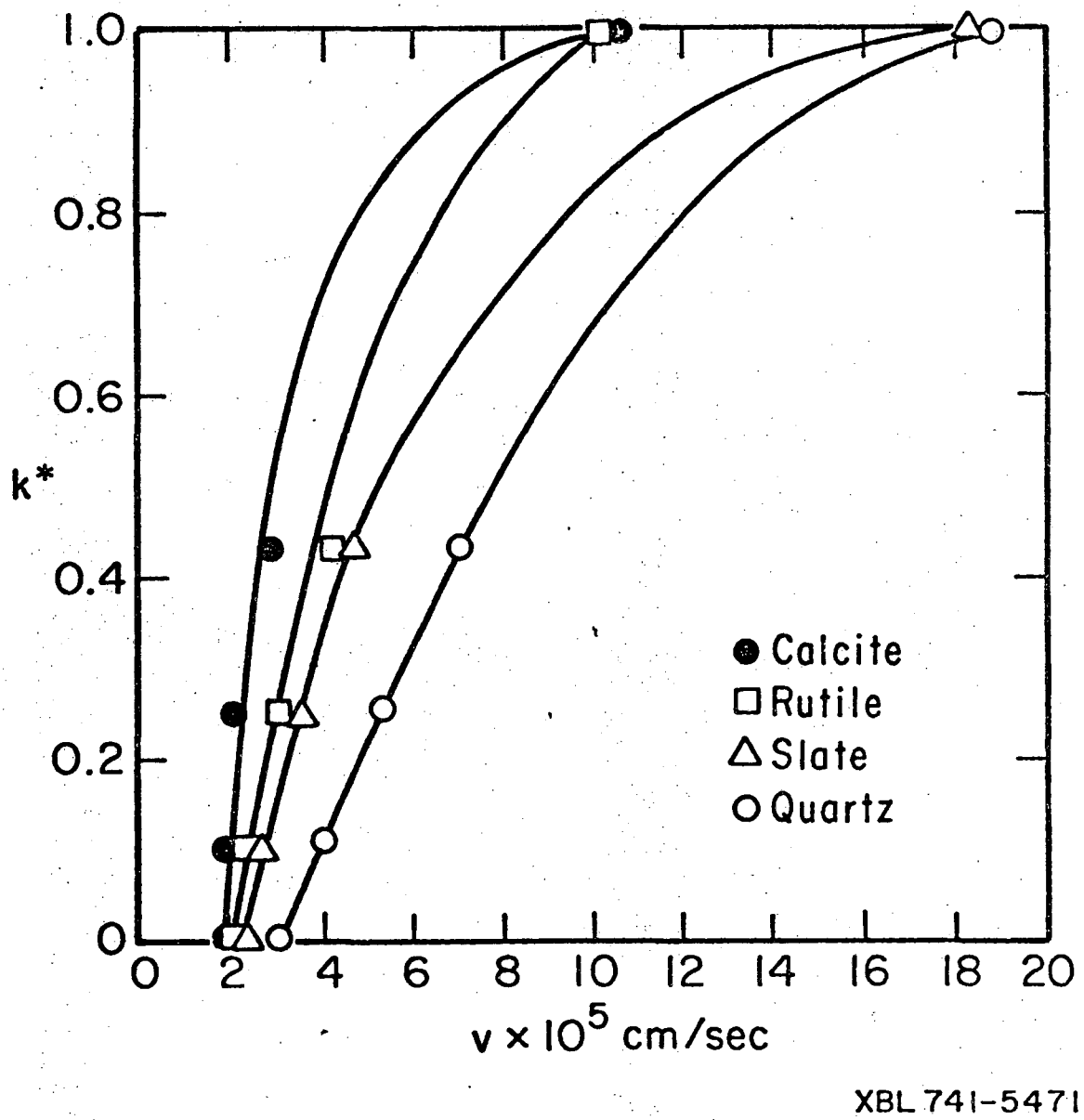
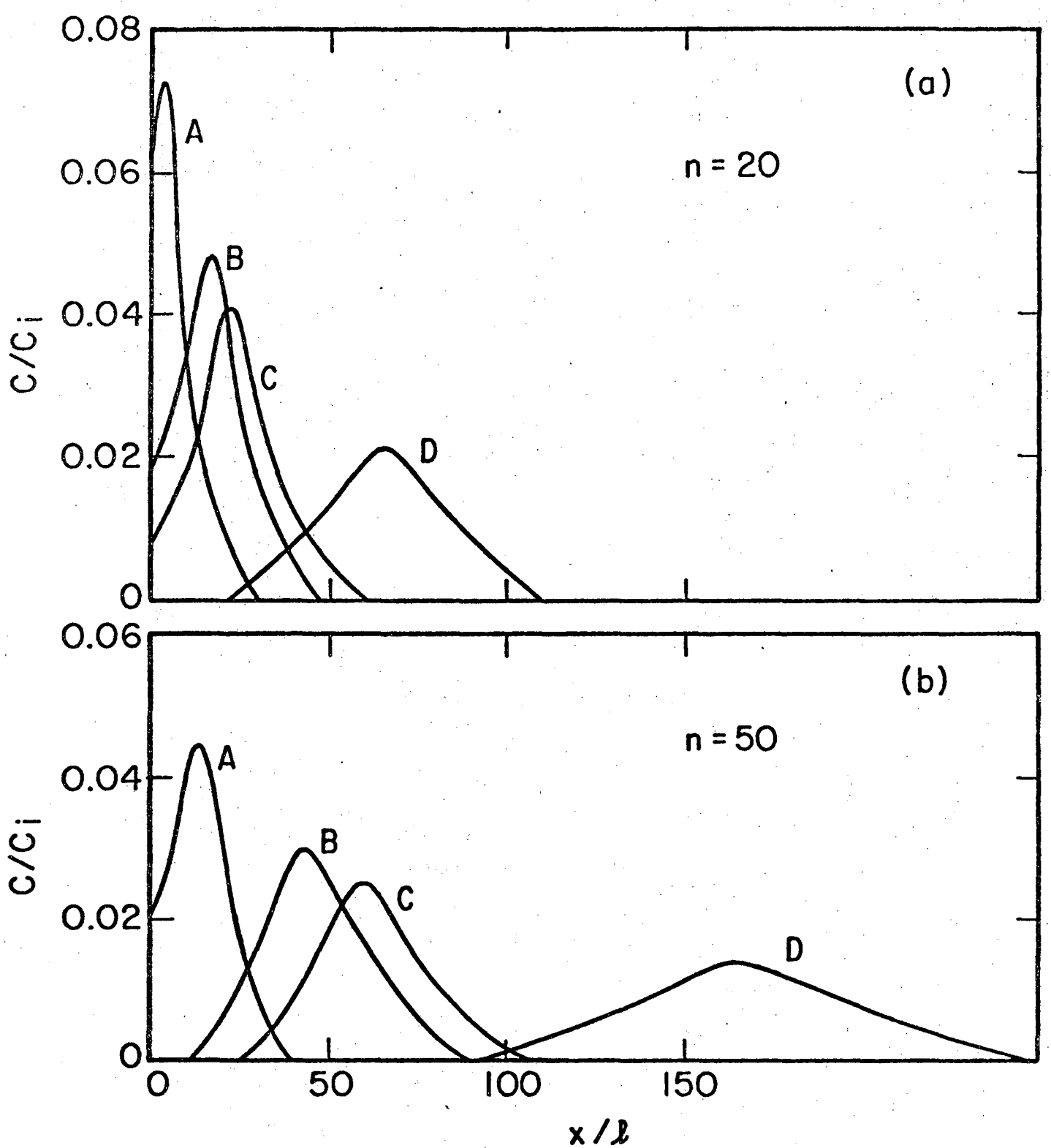


Figure 1. Variation of the particulate distribution coefficient on the freezing velocity of water for powdered calcite, rutile, slate and quartz.



XBL 741-5473

Figure 2. Zone chromatographic separation of (A) calcite with $k^* = 0.79$, (B) rutile with $k^* = 0.53$, (C) slate with $k^* = 0.45$ and (D) quartz with $k^* = 0.23$, at 5×10^{-5} cm/sec. The number of zone passes is (a) 20, and (b) 50.

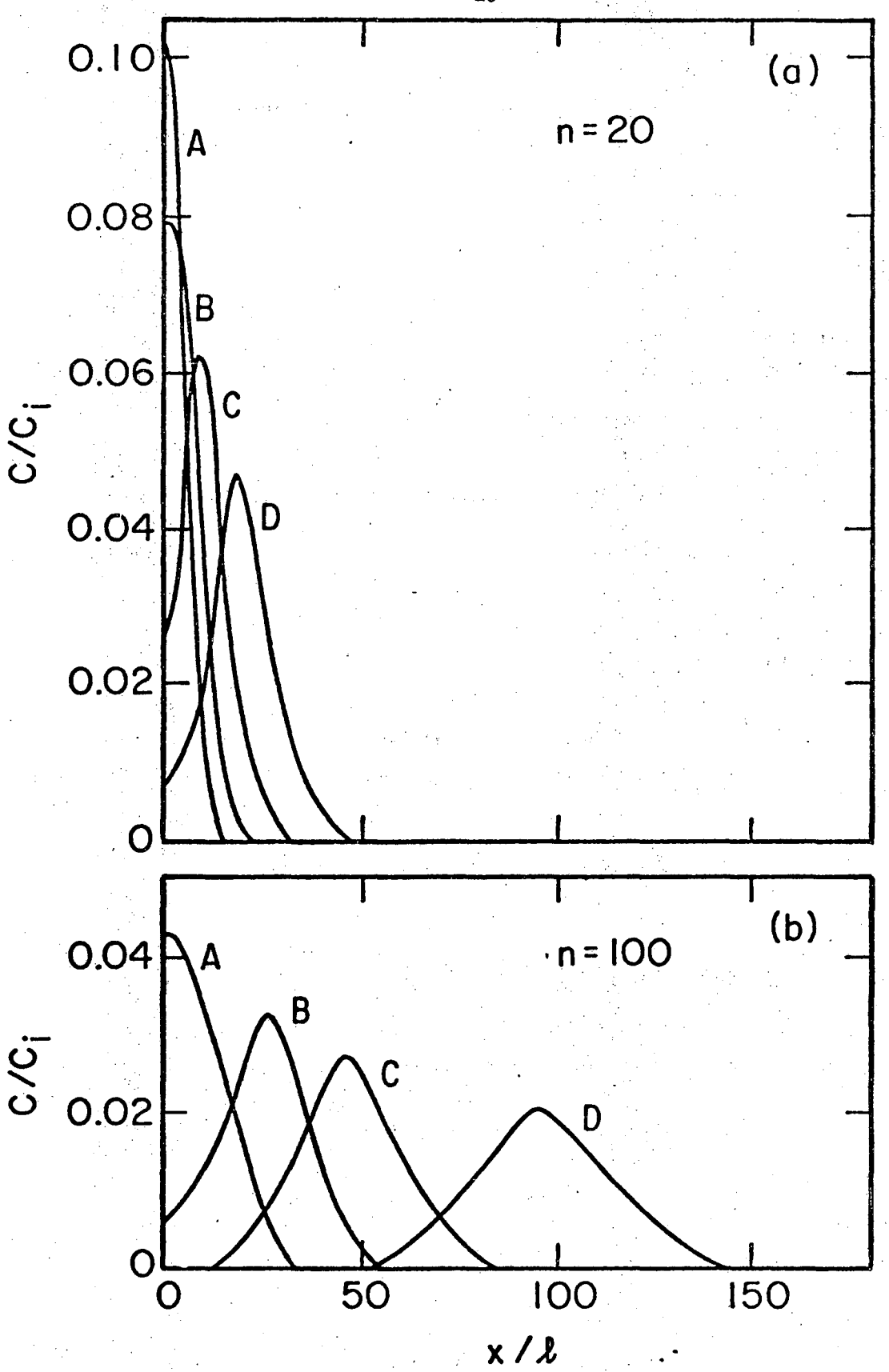


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Figure 3. Zone chromatographic separation of (A) calcite with $k^* = 0.93$, (B) rutile with $k^* = 0.81$, (C) slate with $k^* = 0.68$ and (D) quartz with $k^* = 0.51$, at 8×10^{-5} cm/sec. The number of zone passes is (a) 20, and (b) 100.

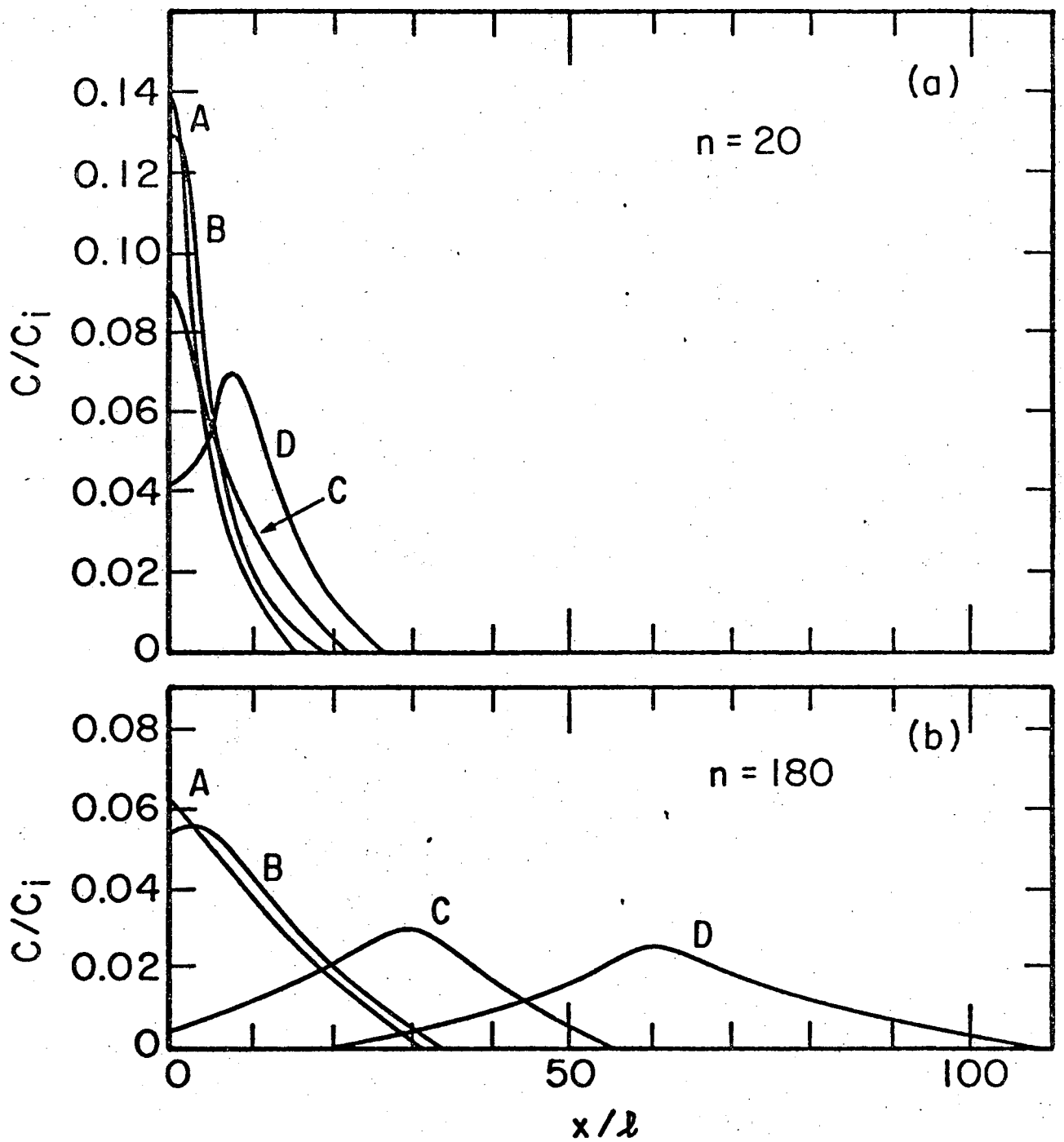

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Figure 4. Zone chromatographic separation of (A) calcite with $k^* = 1.0$, (B) rutile with $k^* = 0.98$, (C) slate with $k^* = 0.86$, and (D) quartz with $k^* = 0.75$, at 1.2×10^{-4} cm/sec. The number of zone passes is (a) 20, and (b) 180.

the higher velocities. These results show that a minimum separation time is required at a freezing velocity of 8×10^{-5} cm/sec . At this freezing velocity the distribution coefficients for the different components have the most widely separated values.

To further test freeze-displacement zone chromatography as a characterization method, several particulate minerals were studied using thymol as a host material. In one series of experiments, graphite powder having a chemical purity of >99.99% and a particle size distribution ranging from 0.3 to 10 μm was mixed in liquid thymol (melting point, 49.5°C) to form a 20wt% mixture. This sample was solidified at the end of a cylindrical pyrex tube, of length 45 cm and 1 cm internal diameter, containing solid, purified thymol. This experimental arrangement is shown in Fig. 5. The tube was then subjected to freeze-displacement zone chromatography at different freezing rates. For a freezing velocity of 1.0×10^{-4} cm/sec , the graphite powder was displaced a distance of 35 cm after seven zone passes. A small dependence of the freeze-displacement distance on particle size was found, with smaller particles tending to be displaced through larger distances.

In another series of experiments, freeze-displacement zone-chromatographic separation of a mixture of powders was studied. For example, a mixture of iron oxide and graphite powders was found to be easily separated by a limited number of zone passes into clearly defined colored bands along the column. The red iron oxide was concentrated in a band near the source end of the column, while the graphite powder

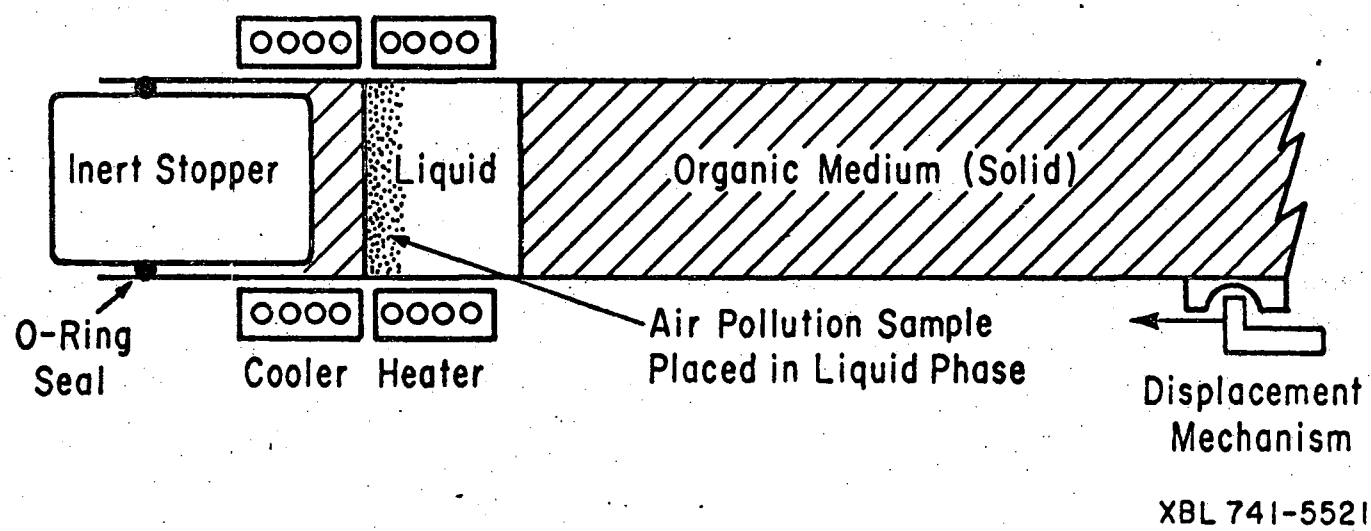

Figure 5. Schematic of apparatus for zone chromatographic separation by freeze-pushing.

was concentrated in a band further from the source end. The experimental method was very effective in separating dissimilar particulate materials.

Air-Borne Particle Sampling

Air-borne particle sampling methods compatable with the freeze-displacement zone chromatographic process were examined for application to air pollution monitoring.

Methods for the classification of particulate matter and the determination of particle size distributions have been adequately reviewed by Silverman, et al.[4] The sampling of air-borne particles in the size range near 1 μm can be achieved by a variety of methods: filtration, electrostatic deposition, condensation, precipitation and impingement. Many of these methods have limitations as to capital or maintenance cost, and leave the collected material in a state which does not permit direct use in the freeze-displacement apparatus.

A modification of the filtration method was found to yield the highest compatability with the freeze-displacement zone chromatographic method. Using vapor-liquid contacting methods, such as sparging the air through the host liquid held at a temperature above the melting point, air-borne particles could be collected to produce a suspension in the host liquid. This liquid could then be solidified for transport to the freeze-displacement apparatus.

Potential Contributions to Atmospheric Chemistry

The critical velocity and the particulate distribution coefficience for the freeze-displacement process are highly sensitive to the properties of the interface between the particulate solid and the host material which is to be directionally solidified. The interfacial properties of a given particulate material are expected to be influenced by the chemical components found in polluted air which can chemisorb on the surfaces of air-borne particulate solids. The surface concentration and type of chemisorbed component would thus change the critical velocity for freeze-displacement and also the displacement length under conditions of zone-chromatographic freezing. Consequently, the zone-chromatographic freezing process is potentially useful as a characterization technique in the study of atmospheric chemistry.

The presence of chemisorbed species on particulates can cause shifts in the freeze-displacement distance produced by n zone passes at a fixed freezing velocity. Since a particular chemisorbed species will produce a specified displacement distance, specific species can be identified from the shifts in displacement distances they produce relative to a chemisorption free particulate phase. For the success of this characterization, it is necessary that particle size effects be absent and that the contributions of specific chemisorbed species to changes in interfacial properties be non-interacting. Also, it is necessary that the host material is sufficiently inert that the chemisorbed species do not dissolve in them.

It is important to point out the fact that the characterization of a specific particulate material or of a chemisorbed species on a particulate material does not lead to a unique identification of the particulate phase or the chemisorbed species. Rather, the freeze-displacement properties of a given particulate material provides a measure of shifts in interfacial tension and other properties of the particulate - host liquid - solid interface. Thus, the zone-chromatographic freezing process is primarily useful as a practical, inexpensive method of primary characterization, rather than as a definitive, quantitative analytical technique. Nevertheless, the particulate fractions separated into distinct bands by the zone-chromatographic freezing process could be separated by filtration and drying, then further characterized by other analytical methods.

Discussion

The particle freeze-pushing phenomenon is effective in separating particulate components. To carry out analytical characterization by this method, the particulate matter in air pollution samples is first scrubbed by an organic medium and subsequently subjected to freeze-displacement zone chromatography, with the suspended particles initially concentrated at one end of a column of pure organic solid. This method requires a low melting host liquid which freezes with a planar interface, and which is chemically inert with respect to the particulate phase. For a given air pollution sample, an appropriate, low melting liquid must be found which will affect separation of the components by freeze-displacement.

The degree of efficiency of displacement by freeze-pushing depends on the particule distribution coefficients and on the operation conditions. Since the freezing interface is the displacement force which affects the separation, many molten zones could be required to achieve a given spatial separation. It is expedient to design the zone chromatographic apparatus so that molten zones move simultaneously, thereby reducing the time required for the separation process.

The displacement length produced by freeze-displacement at a specific freezing velocity can be utilized to characterize different particulate materials in air pollution samples provided that the distribution coefficient is known or measured. Because zone chromatography tends to separate the sample into bands of materials with distinct distribution coefficients, the displacement distance L^* can be easily standardized for identifiable particulate materials.

Particle distribution coefficients were found to be easily determined experimentally. Also, the zone chromotograph theory can qualitatively and semi-quantatively predict the particle separation on the basis of measured distribution coefficients. This analytical method should be very useful in sampling and characterizing air-borne particulate matter in air pollution sample. Additional fundamental research is needed, however, for better understanding of the discrimination of the freeze-displacement process to particle sizes below 1 μm , and for the determination of the sensitivity of the method to important particulate air pollutants in actual fixed-source

or ambient-air concentrations. Additional work is also needed for implementing equipment for the sampling and rapid analytical determination of particulate components in air pollution samples so as to provide direct, analytical benefits to air pollution monitoring.

Acknowledgment

The financial assistance of the U.S. Atomic Energy Commission is gratefully acknowledged.

List of Symbols

a molecular diameter of the liquid phase, cm

c particle concentration, cm^{-3}

c_n particle concentration after n passes, cm^{-3}

D self diffusion coefficient of the liquid phase, cm^2/sec

d zone chromatographic separation constant

k Boltzmann constant

k^* physical distribution coefficient

ℓ liquid zone length, cm

L latent heat of fusion, $ergs/cm^3$

L^* length of column required for separation, cm

m separation constant

R particle radius

t^* separation time

V freezing velocity, cm/sec

V_c initial freezing velocity, cm/sec

V_a atomic volume of the liquid phase, cm^3

x distance along the freezing direction, cm

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