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APPLICATION OF VELOCITY-SELECTIVE FREEZE-PUSHING TO THE SEPARATION AND CHARACTERIZATION OF AIR-BORNE SOLID PARTICULATE MATTER IN AIR POLLUTION SAMPLES

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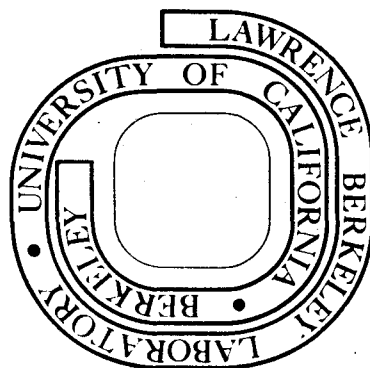Particulate Matter in Air Pollution Samples

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December, 1973

Abstract

A new method for sampling and characterizing air-borne solid
particulate matter in air pollution samples is described. The method
utilizes the phenomenon of velocity-selective freeze-pushing 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 the separation factor, k^*.
An analytical sampling and characterization apparatus is described
for particulate matter separation. Experimental results of the
separation of graphite and hematite particles with thymol using zone
chromatographic separation is described.

Introduction

The increasing public concern for environmental pollution has led to intensive research on pollution monitoring and control. 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 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 particulate matter by a solid-liquid interface during controlled solidification. The method of zone chromatography utilized by this analytical technique is described and tested experimentally. The method is applied to the freeze-pushing properties and separation of iron oxide from graphite 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. Alternately, samples collected by a method from the first group can be subjected to the breeze-pushing separation process.

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

Velocity-Selective Freeze Pushing

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 freezing velocity exists for this effect, for each type of particulate matter. 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 entrappment probability increasing with 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. Since the distribution of particles between phases is different for a given freezing rate in organic media, there is a theoretical bases for separating particulate mixtures in an appropriate organic medium by freezing this medium at a rate where different particulate materials have different entrappment probabilities, or different liquid-solid distribution coefficients.

The particle distribution coefficients can be defined as the ratio of the particle concentration in the solid to that in the liquid phases near the solid-liquid interface during solidification. If all the particle materials are all pushed by the interface, the distribution coefficient is equal to zero, whereas if all are entrapped,

the 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.

Theory of Freeze Pushing

The phenomenon of particle pushing, by a freezing interface is

attributable to the force exerted by the crystal 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 crystal and produce 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 between solid-liquid interfacial energy,

σ_{sl} , and between particle-liquid interfacial energy, σ_{pl} , i.e.,

$\sigma_{sp} > \sigma_{sl} + \sigma_{pl}$, then the crystal will displace the particle into

the liquid by freezing. On the other hand, when $\sigma_{sp} < \sigma_{sl} + \sigma_{pl}$

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, Chalmer and Jackson[5] is based

on the assumption of short-range particle-interface repulsion due

to the difference of interfacial energies. This effect is combined

with diffusion of the melt into the contact region between the crystal

and particle. The relation between these processes is assumed to be a function of particle surface roughness. However, their theory predict no difference in the pushing force for different types of particles as long as their sizes are the same.

Bolling and Cisse[7,8] combined fluid-flow, viscous drag and differsion effects to modify the basic theory. They also considered the indentation of the interface shape formed 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, electricstatic 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 particle separation from the interface. For an atomically smooth particle and a planar freezing interface, the critical velocity is

$$V_c \cong \frac{3LV_e aD}{kTR^2} \, . \tag{1}$$

This theoretical expression is somewhat unsatisfactory, however, because anomalously high diffusion coefficients are needed for comparison with theory. If the interface is assumed to be indented in the viscinity 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.
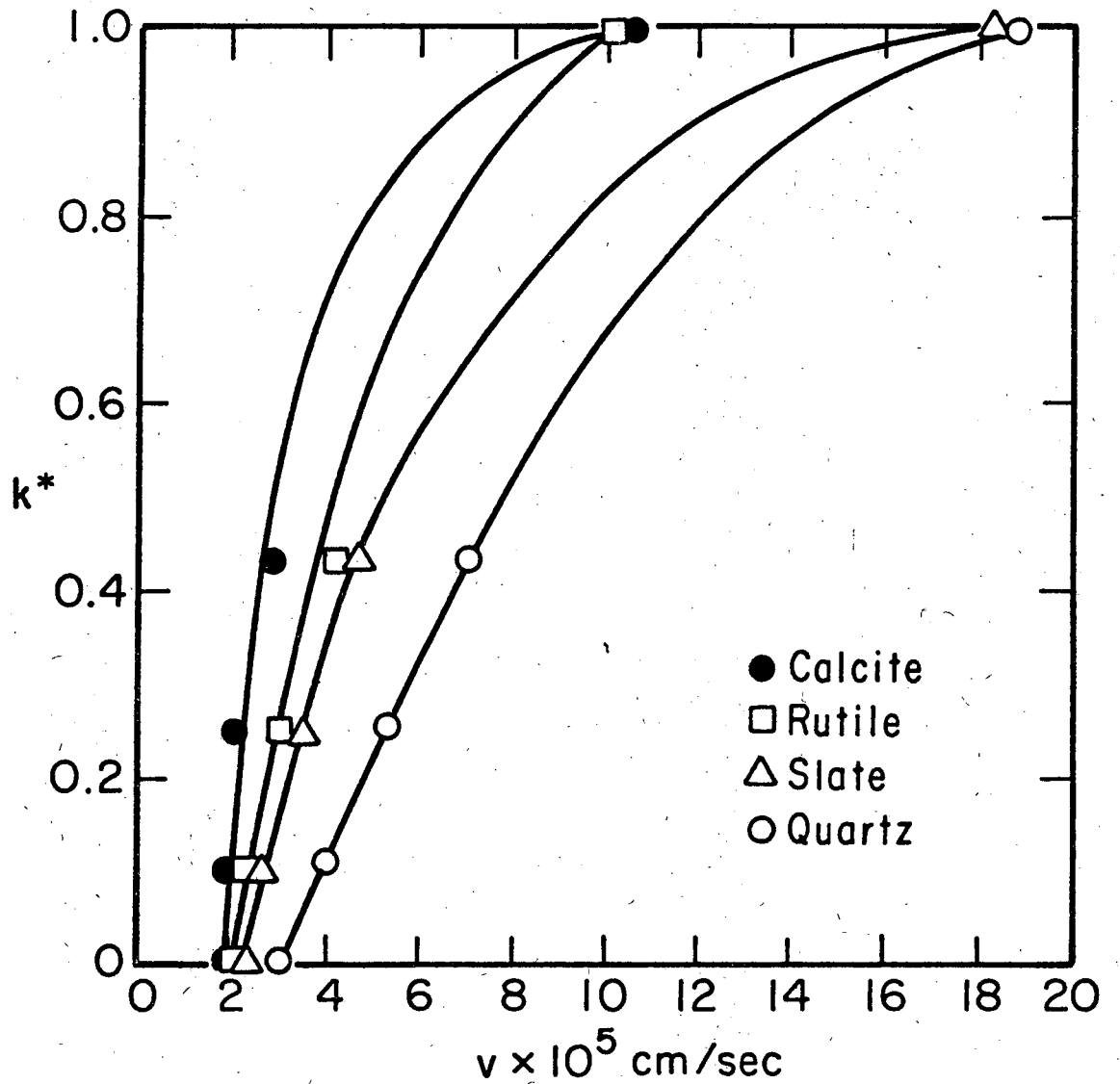
Distribution Coefficients for Freeze-Pushing

There is limited experimental data in the literature on the physical distribution coefficient for freeze-pushing. Corte[6] investigated the freezing velocity, and particle size dependence, of 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 because of the large particle size range studied.

The data on particle fraction pushed at a given velocity can be converted to data on distribution coefficients for freeze-pushing k^* by normalizing with respect to the density of coverage of 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 a constant
freezing rate within a relatively wide range. Those materials which
exhibit a small physical distribution coefficient tend to be pushed
farther by the freezing interface before trapping within the solid.

Because the freeze-pushing 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 several alternative
methods for applying the freeze-pushing phenomenon to particulate
separation. Since those particles with small distribution coefficients
tend to be pushed farther before trapping in the solid, the different
materials can be identified from the average distance those particles
are displaced by directional freezing. In this mode of separation, the
particulate pollution sample should be initially concentrated at
the freezing interface, as in zone chromatography. The wide range
of freezing velocity over which the distribution coefficient is
velocity-dependent suggests a second separation made in which the
freezing rate is programmed to rise with time. In this mode, the
particle matter is again identified by the length of displacement
of a band of the material along the sample. This latter mode is
capable of identifying a broader range of materials with widely different
initial velocities. Particle separation by constant-velocity freezing
is easier experimentally, however, and a convenient constant freezing-
velocity process, that of zone chromatography is explored in the
following section.

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Figure 1. Dependence of the physical distribution coefficient
for particle freeze pushing on freezing velocity
for calcite, rutile, slate and quartz.

Particle Separation by Zone Chromatography

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. Here the liquid medium will be assumed an organic compound.

Consider a 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

$$\left(\frac{\ell}{k^*}\right)\left(\frac{dC_n(x)}{dx}\right) + C_n(x) = C_{n-1}(x + \ell) \ . \qquad (2)$$

On the assumption that the initial distribution of particle is a delta (δ) function centered at $x = \ell$, Reiss and Helf[9] solved this equation by using Fouier Transformations and obtained,

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

Equation 3 is a modified Poisson distribution function.

Pfann[10] has defined the approximate criterion for zone chromatographic δ separation and gave the number of zone-passes of the freezing interface required as

$$\dot{n} = m + 1 = \left[\frac{1 + \sqrt{k^*_2/k^*_1}}{1 - \sqrt{k^*_2/k^*_1}}\right]^2 + 1 \; , \tag{4}$$

where k^*_i is the physical distribution coefficients for component i .
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

$$L^* = m\left(\frac{k^*_2 - k^*_1}{k^*_2 k^*_1}\right)\ell \; . \tag{5}$$

The time required for a given separation is expressed by

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

These equations can be used to deduce the zone chromatographic
conditions required for particle separation.

The application of zone chromatographic technique to the
separation of the minerals of Fig. 1 is 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} 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 the higher velocities. The
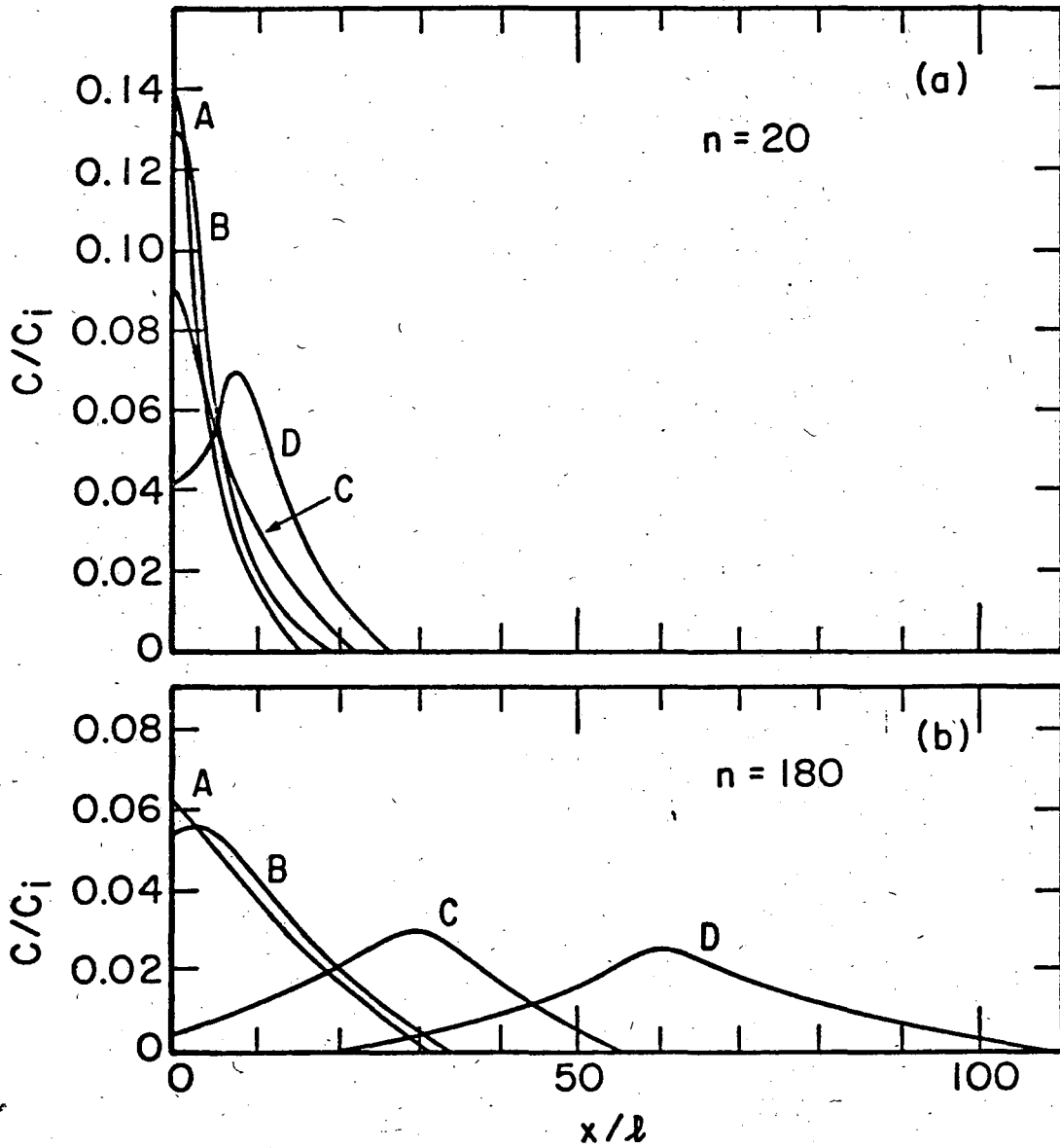time required to bring about an average separation of particulate
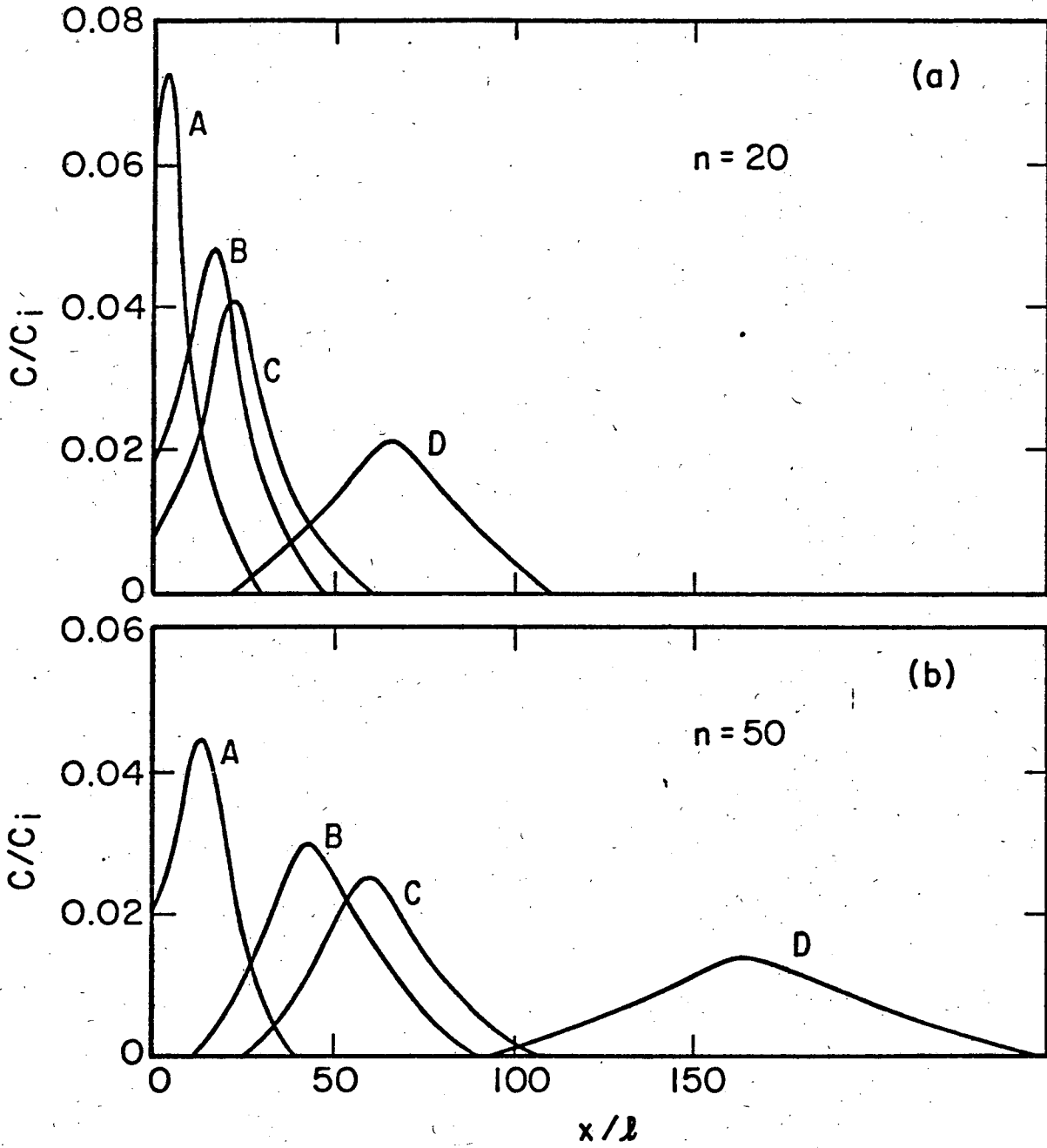
Figure 2. Zone chromatographic separation of
(A) calcite with $k^* = 0.79$, (B) rutile with $k^* = 0.53$,
(C) slate with $k^* = 0.45$ and (D) quartz with $k^* = 0.23$,
at 5×10^{-5} cm/sec.
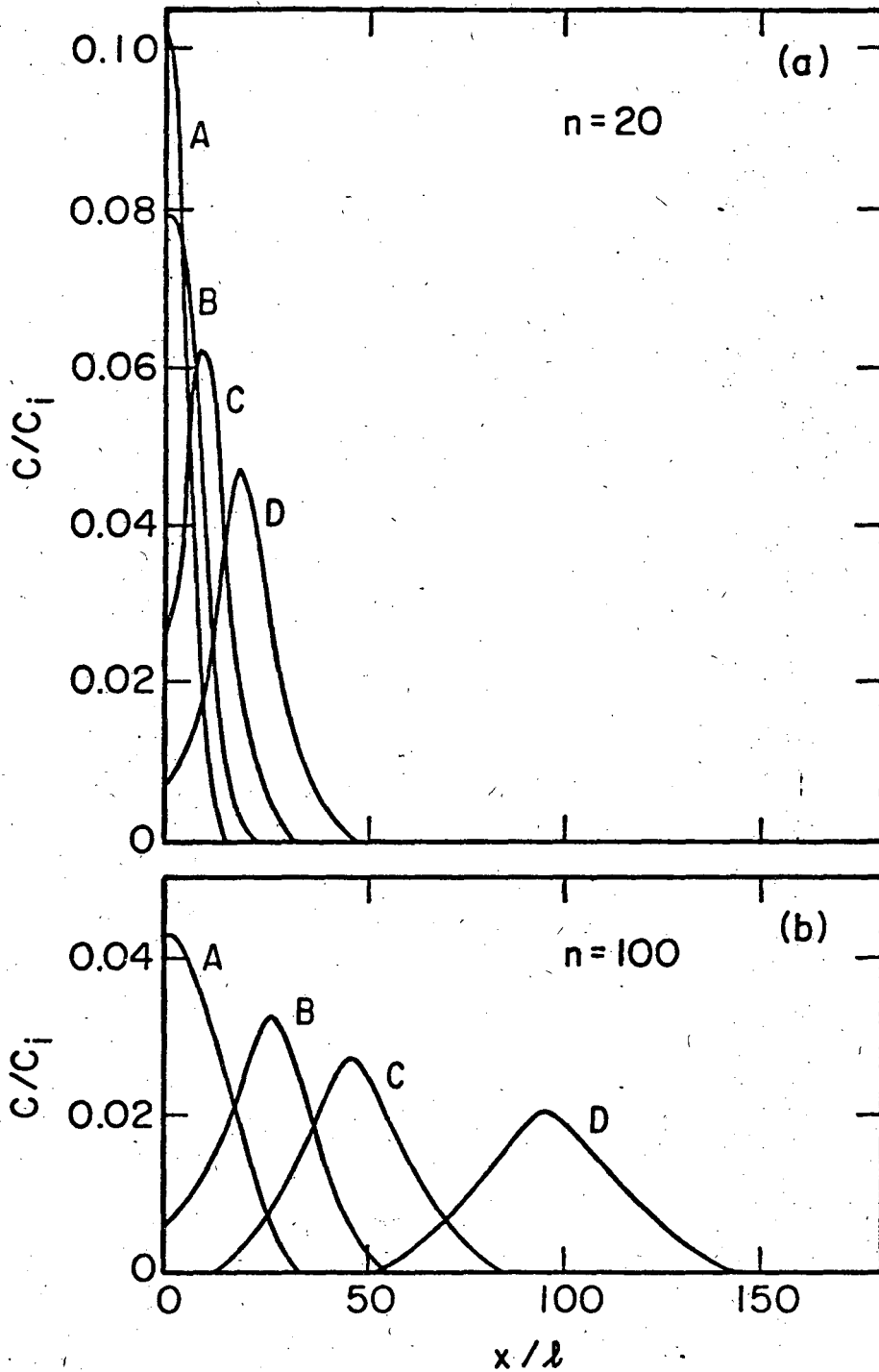
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Figure 3. Zone chromatographic separation of
(A) calcite with $k^* = 0.93$, (B) rutile with $k^* = 0.81$,
(C) slate with $k^* = 0.68$ and (D) quartz with $k^* = 0.51$,
at 8×10^{-5} cm/sec.

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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.

matter peaks by zone chromatography is shown in Fig. 5. The figure shows that a minimum separation time is required at 8×10^{-5} cm/sec. At this freezing velocity the distribution coefficients for the different components have the most widely separated values.

Experimental Studies

The displacement length produced by freeze pushing 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. For a given air pollution sample, an appropriate, low melting liquid must be found which will affect separation of the components by freeze pushing. In the following, a method is described for determining the freezing velocity-dependence of the distribution coefficient.
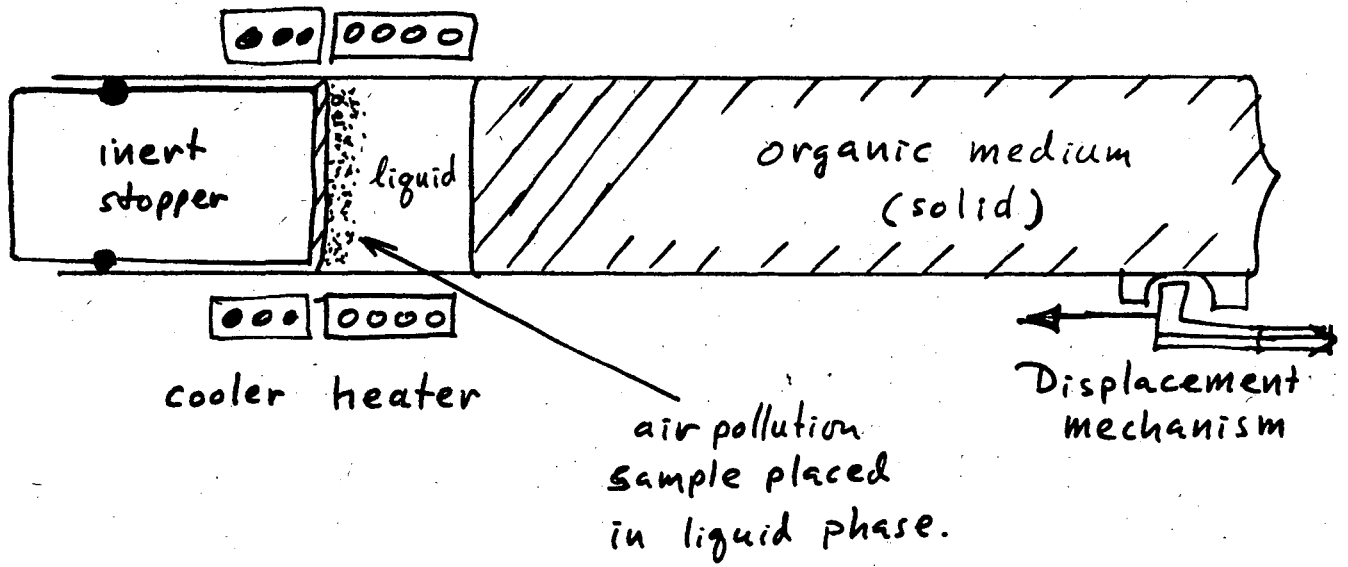
Apparatus

The apparatus required for particle separation is shown schematically in Fig. 6. The charge column is a long cylinderical glass tube. A organic substance of fairly low melting point is placed into the tube and solidified. A small zone of the organic is melted and particles are then placed in this zone. This charged column is placed horizontally and rotated about its own axis to distribute heat from a ring heater which maintains a narrow liquid zone of length ℓ .
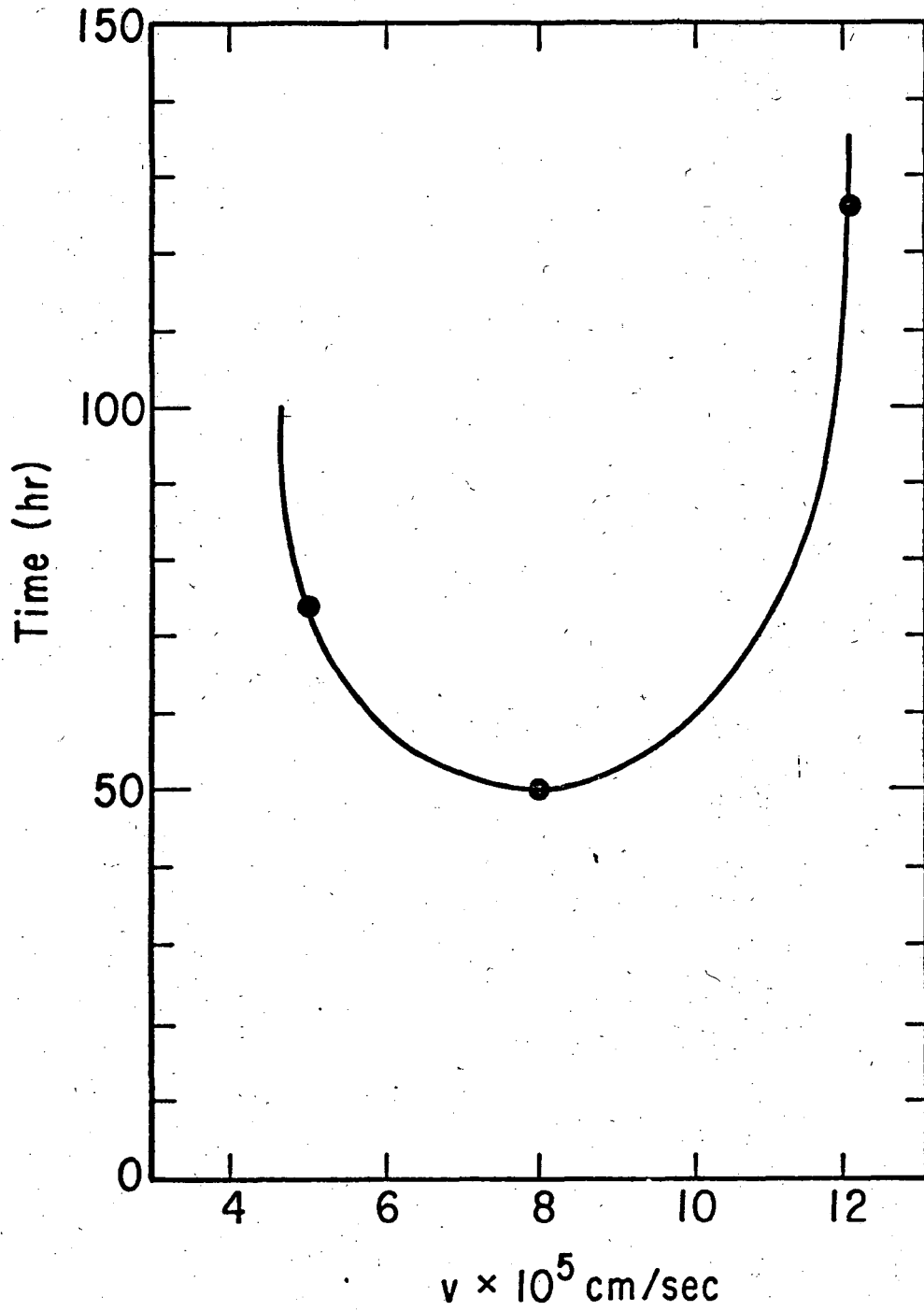
Figure 5. Dependence of the zone chromatography time versus freezing velocity to bring about an average particulate peak separation of 0.5 cm.

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Figure 6. Schematic of apparatus for zone chromatographic separation by freeze-pushing.

Materials

The freezing velocity dependence of the physical distribution coefficient in air pollution samples was studied with ferric oxide and graphite powders and thymol used as the separation medium. A mixture of 1 gm each of ferric oxide (Fe_2O_3) and graphite powders were mixed with pure, liquid thymol (melting point, 49.5°C) to form a 20 weight % mixture. This sample was then placed into the end of a cylindrical pyrex tube, of length 45 cm and interior diameter of 1 cm, and solidified. The remainder of the tube was then filled with pure thymol, and the upper tube end closed. A Fisher Zone Refiner, type 5-712-100 was used to carry out zone chromatographic separation. The molten zone was heated by a circular wire heater adjacent to an air cooling unit which maintained a planar solid-liquid interface during zone displacement.

Although Fe_2O_3 and graphite powders both have densities much higher than that of thymol, the zone chromatographic separation displaced the graphite particles a distance of 35 cm by seven zone passes. The resulting sample showed colored bands along the column: red Fe_2O_3 near the source end, and black graphite near the top of the column. The two types of powders were very effectively separated by this process.

Determination of k^*

The distribution coefficients for both ferric oxide and graphite powders in thymol were measured by carrying out zone chromatographic separation for each component separately at different velocities. After

a single zone pass the sample was sectioned, and the powder was

recovered from each section by vaporizing the organic. The weights

of powder in different sections was then fitted to the zone

chromatographic distribution function valid for one zone pass. The

results showed that the optimum freezing velocity for separation

to be 1.0×10^{-4} cm/sec for which,

$$k^*_{Fe_2O_3} = 0.81$$

$$k^*_c = 0.25 .$$

(7)

The large difference in these coefficients explains the relative

ease of complete separation by a limited number of zone passes.

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

zone melting as described above with the solved particles initially

concentrated at one end of a column of pure organic solid. Particles

are pushed selectively by the solid-liquid interface as the molten

zone moves along the column. The degree of efficiency of displacement

by freeze-pushing depends on the particle distribution coefficients

and on the operation conditions. Since the freezing interface is the

only effective surface to affect the separation, many molten zones

may be required, and several can be incorporated to move simultaneously.

A spectrum of particulate bands are then obtained, each displaced a
distance dependent on interfacial properties with respect to the
organic phase. The bands of particles then can be separated by
mechanical means for subsequent chemical analysis. The factors that
affect the particle pushing are the physical properties of the
suspended particles and organic medium such as interfacial energies,
thermal conductivity, particle size and shape, viscosity electrostatic
forces, and surface morphology.

Particles distribution coefficients are shown to be easily
determined experimentally. The zone chromotograph theory can
qualitatively and semi-quantative 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 the discriminatory
pushing of particles by solid-liquid interfaces and for implementing
equipment design for sampling and rapid analytical determination of
particulate components in air pollution samples.

Acknowledgment

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_e atomic volume of the liquid phase, cm^3

x distance along the freezing direction,   cm

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