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REVIEW OF SUPERCRITICAL FLUID
EXTRACTION OF ORGANIC
CONTAMINANTS IN SEDIMENTS

H.B. Lee and D.R. Gere

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Review of Supercritical Fluid Extraction of Organic Contaminants in Sediments

by

Hing-Blu Lee¹ and Dennis R. Gere²

¹Aquatic Ecosystem Protection Branch
National Water Research Institute
Environment Canada
Burlington, Ontario, Canada L7R 4A6

²Hewlett-Packard Company
Little Falls Site
2850 Centerville Road
Wilmington, Delaware, USA 19808

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MANAGEMENT PERSPECTIVE

Supercritical fluid extraction (SFE) is the most promising technique for the preconcentration of organic contaminants in sediments without the use of solvents. Some of these methods have already reached the status of proposed or draft methods for solid wastes and are being evaluated by the USEPA as a replacement for conventional extraction methods. This article describes the basic principles and hardware involved in SFE. An up-to-date literature review on the applications of SFE to the determination of organic priority substances in aquatic sediments is also given.

SOMMAIRE À L'INTENTION DE LA DIRECTION

L'extraction par fluide supercritique (EFS) est la technique la plus prometteuse de préconcentration des contaminants organiques contenus dans des sédiments, qui ne fasse pas appel à des solvants. Certaines méthodes applicables aux déchets solides sont déjà rendues à l'état de projet ou au stade des essais. L'EPA des É.-U. a commencé d'évaluer si elles peuvent se substituer aux méthodes classiques d'extraction. Dans cet article, nous décrivons les grands principes de cette technique et l'appareillage requis. En outre, nous avons procédé à un dépouillement à jour de la littérature relative à l'application de l'EFS à la détermination des substances organiques d'intérêt prioritaire dans les sédiments aqueux.

ABSTRACT

This manuscript reviews the applications of supercritical fluid extraction (SFE) to the determination of organic priority substances in the aquatic environment. The basic principles of SFE are explained and the design of a generic SFE instrument is discussed. Examples of SFE in the extraction of the major classes of priority substances, including polychlorinated biphenyls, polynuclear aromatic hydrocarbons, total petroleum hydrocarbons, insecticides and herbicides, phenols, chlorinated dibenzo-*p*-dioxins and furans, resin acids, and organotins, are described. Over 100 recent references in this topic are cited.

RÉSUMÉ

Ce manuscrit examine l'application de l'extraction par fluide supercritique (EFS) à la détermination des substances organiques d'intérêt prioritaire dans les milieux aqueux. Les grands principes de l'EFS sont donnés et la conception d'un appareil-type d'EFS est étudiée. Nous décrivons des applications de l'EFS à l'extraction des grandes classes de substances d'intérêt prioritaire, notamment les biphényles polychlorés, les hydrocarbures aromatiques polycycliques, les hydrocarbures du pétrole totaux, les insecticides et les herbicides, les phénols, les dibenzo-*p*-dioxines et furanes chlorés, les acides résiniques et les organo-étains. Nous avons réuni plus de cent références sur le sujet.

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I. Introduction

What is supercritical fluid extraction (SFE)? It is an extraction technique in which the extracting "liquid" is a supercritical fluid. The sample is usually a solid or semi-solid and in environmental applications, it can be sludge, mud, soil, sediment or biological tissue. Even liquids may be extracted by SFE if the liquids are first passed through a solid phase extraction (SPE) material such as an Empore filter to sorb the analytes of interest onto a solid bed with the solvent (not of analytical interest) passing on through the solid bed to waste. The solid phase material containing the analytes of interest is then placed in the SFE extraction vessel for the last stage of sample preparation. Examples of this will be discussed in a later section of this chapter.

SFE appears to the neophyte to be a complicated technology. We would like to dispel some of the perceptions that lead to this concern while showing examples that already exist of robust yet simple and efficient SFE methods for environmental samples.

One of the major concerns in environmental protection is the need to reduce, in the analytical laboratory, the usage of organic solvents that are restricted by the *Montreal Protocol*. This international treaty addresses the reduction of use of chemicals containing halogens such as chloro-fluoro hydrocarbons and other halocarbons which cause ozone depletion in the atmosphere (Hileman, 1993; Zurer, 1993). Many of these solvents are commonly used in environmental sample preparation. SFE uses primarily supercritical CO₂ as the extraction fluid and thus can substantially reduce the solvent usage and disposal as expected by the Montreal Protocol.

Another challenge in today's laboratory is the expected need to improve productivity. This consideration involves the idea that the SFE may be considered as a *stand-alone* operation. That is, an operator can place weighed samples in the device, walk away and come back when the sample is extracted. The analytes are in an appropriate solution for direct introduction (i.e., injection) into an analytical device. It is expected that there will be continued improvements and developments which will allow enhanced automation.

There are substantially reduced costs derived from use of SFE vs. traditional extraction in the areas of solvent purchase costs, solvent disposal costs, and reduced labor charges. By switching to SFE, it also significantly reduces the human intervention involved in classical manual extraction techniques such as Soxhlet and liquid solid extractions. The elimination of potential human error further reduces labor costs and improves the overall data quality in today's environmental analysis laboratory.

SFE has good potential for selective extraction. It is therefore very useful as a sample cleanup technique prior to an analytical determination such as gas chromatography. David et al. (1992, 1993), described SFE studies where lipid-free fractions of polychlorinated biphenyls (PCBs) were extracted from sea gull eggs. Independent extraction and analysis of the lipid fraction of the eggs indicated a 35 % by weight fat content, while after the selective SFE extraction with judicious choice of density/temperature conditions at each fractionation step, the fat or lipid content was less than 0.1%. These studies provided the seminal information later used to develop a robust method of extracting PCBs from environmental samples which may contain significant amounts of lipids.

It is appropriate to briefly discuss the topic of overall sample size for SFE. Most SFE methods in environmental analysis have been developed for general sample sizes of 1 to 5 g. The smaller sample size of SFE methods requires serious consideration of the time-honored statistical sampling protocols (Diehl, 1974). If the material to be analyzed is homogenous, subsampling is no problem. Any portion of the mass may be taken as the sample for the analysis. If the sample is inhomogenous, however, the problem is not so simple, for a small portion taken at one point may not at all represent the composition of the total mass. Obviously, the problem is more difficult if the particles are large, and if they vary greatly in composition from piece to piece. Under such conditions, the sample first taken, the so-called *gross sample*, is quite large and this large preliminary sample is subjected to a careful process of alternate crushing and dividing until a suitable amount of material of much smaller particle size remains.

II. Principles of Supercritical Fluids

In practice, there are many and varied definitions of the supercritical fluid state. Some discussions suggest that supercritical fluid is a fourth state of matter. That is simply not true, and leads to some confusion because a supercritical fluid may have properties of more than one of the common three states of matter, i.e. solid, liquid, and gas. It may be somewhat easier to sort this out by reference to some simple phase diagrams for the appreciation of the physical-chemical significance of a supercritical system. Figure 1 is a phase diagram for water in which pressure is plotted against temperature. The actual form of the diagram roughly looks like a forked branch of a tree. For the sake of qualitative discussion, the X-axis is neither linear nor logarithmic. Some literary freedom has been taken in drawing this diagram for the sake of simplification of the introductory remarks. A typical physical chemistry text will provide more accuracy for the advanced reader, if desired.

There are depicted the three physical states of matter (zones from left to right), solid, liquid and gas. A fourth zone but not a fourth state of matter at the far right is called the supercritical fluid region. The solid lines dividing the individual zones are the boundaries between the solid-liquid, solid-gas, and liquid-gas phases. The dotted line that sets off the supercritical fluid zone separates liquids from supercritical fluids and gases from supercritical fluids. This suggests that a supercritical fluid is neither a gas nor a liquid, but, in fact, supercritical fluids possess some characteristics of both gases and liquids. There are also three *points* in this diagram that merit some discussion. The first of these is the point that is the juncture of the solid-gas, the solid-liquid, and the liquid-gas lines. This is known as the *triple point* and is the one set of invariant conditions in which solid, liquid and gaseous states can coexist. For water, this point is at 0°C and 0.06 bar pressure. It is also commonly known as the freezing-melting point of water. Another invariant point on the diagram is the *critical point*. For water, this is at 374 °C and 232 bar. A third point, T_b , is commonly known as the *boiling point* and is located at 100°C and 1.0 bar in Figure 1. The boiling point is a dependent-variable which can be any point upon the line dividing liquid and gas phases, thus not a true constant such as the triple

point and the critical point.

In terms of importance or priority, the second point of consideration is the *critical temperature*. This invariant point, unique to each chemical, is defined by the temperature only. The critical pressure value appears to have a lesser or secondary significance since it is merely the vapor pressure for the chemical that exists at the critical temperature. The critical (or supercritical) fluid region exists at *all* pressures, at or above the critical temperature for a pure substance. At or above this critical temperature, there exists only one phase, completely independent of the pressure. That is, no matter how high (or how low) you cause the pressure to be, the one phase will not condense to a liquid.

This becomes somewhat awkward when you consider that there is no formal distinction between a *liquid* and a *gas*. When two fluid phases of a pure substance coexist we may call the denser the liquid and the less dense phase the gas. When there is only one fluid phase, any distinction is arbitrary. Nevertheless, the properties of a dilute gas (such as low density, high compressibility, and positive temperature coefficient of viscosity) are very different from those of a liquid at temperatures well below the critical temperature (high density, low compressibility, and negative temperature coefficient of viscosity).

An intriguing way of defining a critical (or supercritical) fluid is the consideration of kinetic energy and the potential energy of a simple closed system. The kinetic energy is a measure of the molecular motion activity or a manifestation of the degree of *heat* within a system. A higher kinetic energy implies a higher temperature and thus more motion of a given set of molecules within this closed system. Imagine a small cube in space containing one mole of a pure substance, 18 g of water or 44 g of CO₂, with the molecules vibrating, rolling, moving in three dimensions. The potential energy is the *intermolecular glue* holding similar molecules of a pure substance together in a *condensed phase* such as a liquid. In Figure 1, visualize a point on the graph positioned on the X-axis at -100°C and on the Y-axis at 100 bar. As one moves from left to right, traveling along an imaginary line parallel to the X-axis, the kinetic energy (the temperature) increases while the potential energy, which is intrinsic to the type and number of atoms

making up the molecules, stays at a constant value.

Approaching the solid-liquid line in Figure 1, the increase in kinetic energy now exceeds the potential energy. This represents enough energy to exceed the bonding strength of the three dimensional physical connections, i.e. the transition from a solid to the less condensed liquid state. The kinetic energy continues to increase as our imaginary progression across the graph in Figure 1 moves over the liquid-gas line boundary. At that junction or line, sufficient kinetic energy is available in the system, to allow molecules free 3-dimensional travel over significantly longer distances (increased mean free path - often 100 to 1000 times the molecular diameter). This internal energy allows gases, as compared to liquids, at a constant pressure, significantly improved transport properties such as lower viscosity, and higher diffusivity.

If two molecules of the same type collide in the gas phase, the collision is described as an *inelastic* collision. As it happens, the probability is that the molecules will stick together for a short, but finite period of time. This phenomenon has a negative impact upon the transport properties such as viscosity and diffusivity.

Continuing the imaginary trip from left to right, we next encounter the gas-supercritical region border. This transition is much more subtle than the previous transitions as denoted by a dotted line in Figure 1, rather than a solid line. It is instructive to remember that this border is the point at which the enthalpy of vaporization goes to a zero value or disappears from consideration. Thus, *right at, and beyond* the dotted, transition line, there is no further energy needed to take a mole of pure compound from one "state" (gas) to the next "region" (supercritical fluid).

What then is the difference? The difference is that, in the supercritical region, molecules have the long mean free paths that they experienced in the gas phase *and* now if one molecule collides with another similar molecule, the collision is described as an *elastic* collision. The molecules collide, and then they bounce off each other without a finite sticking-together. This is another way of saying that at the critical temperature, the

kinetic energy is equal and equivalent to the potential energy. Because this is independent of the pressure, the supercritical region goes from the bottom of the graph (the X-axis) all the way to an infinitely high pressure with no distinction at the pressure corresponding to the Y-axis position of the critical temperature. The only thing that is happening as we would move up in this diagram in the supercritical region is that the density would increase with the pressure.

Consider what is more favorable in the supercritical region as the system conditions are kept under constant pressure but at ever-increasing temperature. The density continues to decrease. The transport properties of viscosity and diffusion or diffusivity have become more favorable in the sense that the individual molecules of the same kind have less *drag* or retardation of their velocity as they pass close to each other or actually collide. These two properties have very positive effects upon extraction.

In extraction, more favorable diffusion implies a more efficient penetration of matrices with the supercritical fluid and thus a more favorable mass transfer, shorter extraction times as compared, for example, with liquid-solid Soxhlet-type extraction. More favorable viscosity implies the ability to use relatively high volume (mass or molar) flow rates while retaining small volume capillary tubing. Further, this low viscosity means that the fluid dynamics in the packed sample matrix or extraction thimble zone will also not contribute significantly to overall pressure gradient from the pump through all of the apparatus to the restrictor-nozzle zone. This allows a well-controlled set of parameters for the extraction, such as flow rate of the fluid, density, pressure, diffusion and repeatability of the method.

A. Supercritical fluid extraction hardware and the flowing fluid process

The SFE hardware used today in analytical laboratories, whether it is home built or one of the commercially available systems, is virtually all derived from equipment, drawings and patents of chemical engineering. The analytical equipment is usually just scaled down. This transformation is actually, in some cases, more difficult than it might appear at first

consideration. This is especially true for the expansion nozzle (restrictor) needed to interface with the analytical SFE equipment.

The equipment or hardware begins with the source of CO₂. In analytical SFE, we use liquid CO₂ of the highest purity (>99.9999%) that is contained in metal, usually aluminum, cylinders under relatively high pressure. The pressure in a given cylinder is the actual vapor pressure at ambient temperature. Liquid CO₂ has a vapor pressure of approximately 58 bar at 21°C. The triple point is low in temperature (-57°C), but high in pressure (5.1 bar).

A typical cylinder contains ca. 27 kg of CO₂. When it is full, the upper 1/3 of the cylinder volume is occupied by the gas phase and the lower 2/3 by the liquid phase. This phase ratio changes continually as the liquid is drawn out from the bottom of the cylinder by a dip-tube (siphon-tube or an eductor-tube) which comes down from the top on-off valve and extends down below the original liquid-gas interface. If the tank can be drawn down to the bottom of the dip-tube, the gas occupies 4/5 of the volume and the liquid remaining occupies only 1/5 of the volume. The dip-tube usually stops short of the bottom of the cylinder in order to avoid drawing-up into the tubing any particulate matter which may be at the bottom of the cylinder. When the liquid level drops below the open bottom end of the dip-tube, no more CO₂ can be drawn into the SFE apparatus.

The combination of remaining gaseous CO₂ and a small pool of liquid CO₂ below the bottom of the dip-tube usually make up ca. 4.6 kg of CO₂ that are left in the tank at the end of use. The actual fraction or weight of CO₂ left is a function of the actual dip-tube installed by the gas manufacturer. This can vary widely and the reader is warned to check this carefully with the CO₂ supplier.

The substantial vapor pressure in the cylinder under ambient conditions is sufficient to feed enough liquid CO₂ for a normal reciprocating pump. Older design pumps, such as those large syringe pumps, require an additional pressure charge to the tank (usually with helium) to artificially increase the vapor pressure to as much as 170 bar. Although this

works in principle, there are many drawbacks such as an inability to facilitate low density extractions which favor selective extraction of volatile fractions (aroma constituents). Thus, this type of pump is no longer incorporated in the construction of new equipment.

Pumps with pressure measuring transducers provide an indication of the actual pressure, or in more sophisticated equipment, provide a feedback signal for pressure-temperature-density control. After the pump, the CO_2 , still in the liquid phase, passes through small diameter tubing until it approaches the extraction thimble. At this point or near to it, the temperature is adjusted to the choice desired for the supercritical extraction. That is, the CO_2 finally is adjusted to conditions (temperature-pressure-density) of the supercritical state. This is indicated as a *pre-heat zone* in Figure 2.

As the CO_2 passes through the pre-heat zone and into the extraction thimble, the CO_2 becomes a supercritical fluid. The exact conditions are set by the temperature and pressure. The flow rate of the CO_2 does not affect the nature of the phase.

After passing through the necessary capillary tubing, the CO_2 , now containing any analytes or solutes that could possibly be dissolved from the matrix in the sample thimble, moves on to the *restrictor*.

The restrictor or nozzle serves one important function and several secondary functions. The restrictor is the throttle point or the narrowing of the passage way for the moving fluid. It is the most restricted flow region in the entire flow path. The pump is the source of pressure as well as the flowrate-determining device. The pump needs a control point downstream to limit the passage of molecules per unit time. This restriction then holds back the previously unlimited flow of molecules to a definite, pre-determined level. Ideally, the restrictor serves to restrict the flow until the density of the fluid required for extraction is achieved.

In a simple, home-built, apparatus, the restrictor often is a length of small diameter capillary tubing, for instance, a 15 cm length of 10 micrometer internal diameter tubing placed at the end of the apparatus pointing into or within a sample collection thimble.

This is one example of a so-called *fixed restrictor*. A fixed restrictor has a finite length and diameter. For a given volumetric (mass or molar) flow-rate, it produces a pressure measurable some place between the pump and the final outlet point into the ambient. If the flow-rate varies by itself, or is deliberately varied by the experimenter, the pressure adjusts proportionately, as the restriction itself is fixed and constant.

The finite length of tubing has a distributed resistance, meaning that the resistance is additive from the front to the end of the capillary. As a result, the pressure drops continuously, but not necessarily linearly, from the operating extraction pressure of perhaps several hundred bar at the beginning of the restrictor down to one bar (ambient pressure) at the end of the restrictor. This decrease in pressure yields a decrease in density which always leads to diminished solubility of analytes.

At the terminal end of the restrictor, the goal is the complete removal of solubility power of the flowing CO₂ with precipitation of the solutes. However, in the case of such a fixed restrictor with distributed resistance, the loss of solubility power will be gradual and continual throughout the length of capillary tubing. Thus, it is likely that precipitation will begin *prematurely* within the restrictor itself. If the concentration of solute is low and the resulting precipitate is formed in very small particle size, it may physically be blown through the open space in the restrictor and into the collection zone. More likely, however, it will adhere to the inner walls of the tubing and further restrict flow with an increase in pressure locally. In the worst case, the tubing closes itself completely to further flow and it causes a catastrophic system overpressure and cessation of extraction.

This situation is further compounded by the accompanying *Joule-Thomson* cooling effect, owing to the significant expansion of the CO₂ from a highly dense fluid, perhaps at several hundred bar pressure, down to a non-dense gas at ambient pressure. This cooling can produce a temperature gradient over a very short distance of several hundred °C. The cooling of the narrow opening of the tubing encourages freezing of high concentration bulk solutes such as water or lipids, for example. Localized heating of the capillary tube can help minimize this effect, but the actual temperature setting is problematic. If the

tubing is fused silica, it often breaks under these conditions of stress. Stainless steel capillary is somewhat more tolerant, but most people chose to dry their sample to avoid this. That avoids the problem if water is the cause of freezing. If lipids or oils are causing the problem, it can be even more difficult.

This situation and other considerations such as the distributed resistance across a finite distance of capillary tubing lead to the design and use of fixed restrictors of many varieties. Conceptually this is easy: one simply takes a small piece of capillary fused silica tubing, and with a small flame, the end of the tubing is drawn down to a very small diameter. In practice, this can be difficult to control. The first question might be, what diameter would one desire. The second question might be how to obtain a given size opening at the terminus of the tubing. If the first two questions could be answered, a third question might be, how do I precisely and accurately repeat the process whenever needed. The answers to all of these three questions are difficult for the average practitioner to obtain.

The first question brings up the observation that a fixed restrictor provides a specific pressure for a defined flow rate. As the flow rate and the pressure are dependent variables, an increase or decrease in flow means a corresponding linear change in pressure. If this is combined in an environment where the resistance changes as a solute flux passes, then the flow-pressure domain is uncontrolled, unpredictable and very difficult to reproduce between any two fixed restrictors.

Flow, pressure (density), temperature, and time must be controlled precisely in order to yield the same amount or mass of supercritical fluid needed to partition a given amount of analyte from a unit amount of matrix. Quoting extraction efficiency or percent recovery under such uncontrolled conditions is thus an empirical matter where coincidence is random or indiscriminate.

There are many variations on fixed restrictors including a carefully defined fritted zone at the end of a capillary tube. Most of these have led to an unending number of

comments such as “the biggest hurdle in SFE is limited restrictor availability and technology” at SFE conferences. For more discussion on fixed restrictors, especially for supercritical fluid chromatography (SFC), the reader is referred to the work by Greibrokk et al. (1987, 1993).

Gere et al. (1982) described a variable back-pressure regulator as a post-column restrictor for SFC, although this was by no means the first of such devices to be made from off-the-shelf apparatus. For at least 20 years, SFE and SFC have been practiced successfully, under certain favorable combinations of experimental parameters, with back-pressure regulators at the terminus of the apparatus. These favorable circumstances usually involve larger (than analytical scale) SFE. Larger scale work with larger flow pumps, flow rates and appropriately-sized ancillary hardware can tolerate rather large void labyrinth volumes in the zone of expansion from the high pressure fluid to ambient fluid. If this large poorly-swept volume can be tolerated, back-pressure regulators have a fine characteristic that they can decouple flow and pressure. Thus, one gains independent control over two very important parameters involved in the integrity of SFE.

These large scale devices were not adequate for small scale volumes needed for analytical SFE with trace concentrations of analytes. Thus it took some additional years of development before miniaturized, automated back-pressure regulator restrictors were commercially available.

Finally, in Figure 2, we shall focus our attention on the zone just beyond the restrictor where the expanding CO_2 and precipitating analytes impinge upon a solid surface or a retaining liquid. The zone which we discussed above in detail can be defined as the expansion zone, whereas the zone we will now discuss is defined as the collection zone. Collectively, as seen in Figure 2, these two zones make up the *reconstitution zone*.

Simplistically, the collection zone can be made up of an empty thimble such as a test tube or small vial with the exit of the restrictor placed into this zone, perhaps vertically with the end of the restrictor zone close to but not touching the bottom or the walls of the

thimble. Usually in simple, home-built apparatus, the thimble or vial is glass. Thus the bottom or the walls of the thimble are hopefully the impinging surfaces or areas. To a first approximation, a solute would be expected to merely precipitate out of solution as the expanding CO_2 changes to a low density gas. Then the precipitating solutes would hypothetically drop to the bottom of the thimble and a clean pure phase separation (gas-solid) takes place. Reality is often quite different and much adjustment needs to take place in this zone in order to achieve something close to 100 % collection of the solute in concentration ranges from parts per billion (e.g. PCBs in sediment) up to 50 % (total fat in a chocolate candy). Several physical-chemical parameters cause these deviations from ideality. They include, but are not limited to, volatility of the solute, degree of co-precipitation of solid CO_2 (followed almost immediately with uncontrolled sublimation of the solid), aerosol formation, surface tension, occlusion in solid CO_2 , rebound from impinging surface, and many other interacting phenomena.

Beyond simple empty thimbles, a time-honored approach has been to bubble the expanding CO_2 into another liquid. Although an improvement, it still suffers from many of the other above complications and a few new ones such as volatility and aerosol formation between the solutes and the chosen trapping liquid.

Most recently, some types of commercial equipment have included temperature controlled solid trapping zones and also a liquid-reconstitution dispensing pump. This appears to have the maximum flexibility and potential for full recovery over the widest range of analytes. For example, the use of a non-polar solid, PoraPak Q, at perhaps -10°C can even trap volatile compounds such as pentane, benzene or toluene quantitatively. Although it may be possible to accomplish the same collection-reconstitution with liquid trapping, it is more problematic to choose optimal liquids. For instance, an alcohol may indeed provide near optimal trapping for many organics but may be very inappropriate for introduction into a GC capillary column. This then would lead to an evaporative solvent exchange to the proper solvent for the GC, but the evaporation step introduces several new difficulties. Fortunately, if one has the apparatus for sub-ambient, as well as ambient and above ambient, solid trapping, it is easy to convert to liquid trapping with

very minor changes, if needed.

B. Advantages of supercritical fluid extraction method

SFE works very much like conventional liquid extraction, but with these important differences: a) the extraction is usually carried out above the critical temperature of the fluid (this is not always necessary if the extraction pressure is above the critical pressure). and b) the solvent power of carbon dioxide fluid depends upon density (a manifestation of temperature and pressure).

Traditional liquid extraction uses an assortment of solvents to extract different analytes. Hydrocarbon solvents such as hexane and isooctane are good for extracting non-polar analytes. Benzene and toluene work for aromatic compounds. Methanol and others are useful for polar analytes. No single solvent is good for all possible samples.

The solvent power of a supercritical fluid increases as its density increases. Thus a single supercritical fluid may extract a variety of components depending on the pressure and temperature applied to the system. It is possible to fractionate by extracting the sample sequentially at two or more different densities.

Supercritical fluids are attractive candidates for sample extraction because they provide an unusual combination of properties: a) gas-like properties allow them to penetrate a sample much more easily than liquid solvents can, b) liquid-like properties allow them to dissolve analytes from the sample matrix, leaving behind unwanted interference such as salts and inorganic compounds, and c) variable solvent power allows a single supercritical fluid to substitute for a variety of conventional solvents.

C. Practical candidate fluids for supercritical fluid extraction

Many fluids have been used over the past few years for SFE. Table 1 lists the critical temperature and pressure for some of them.

Both the chemistry and the mechanics of a supercritical fluid system depend on temperature and pressure. Excessively high pressure or temperature requirements could make the apparatus too expensive to be practical. Commercial equipment economics follow severe price/volume curves. In today's laboratory, safety in the work-place regulations places further constraints on the choices of fluids.

Hydrocarbons are tempting, but the flammability and explosion hazards cause one to pause before using them for widespread applications.

Ammonia is very unpleasant to work with. A fume hood or other venting precautions are needed to keep it out of the laboratory atmosphere. Ammonia is very toxic and is actually a weak reducing agent.

Nitrous oxide has been used and cited in several early publications. It is polar and has reasonable values of critical temperature and pressure. However, there are several recent citations of violent explosive reactions between nitrous oxide, an oxidizing agent, and organic compounds such as ethanol (Sievers and Hansen, 1991) or oils and lipids (Raynie, 1993). For this reason, great caution should be used before this fluid is considered. Common opinion now considers nitrous oxide not suitable for a general purpose SFE fluid.

Water is included in the table and is also a tempting choice. Although home-built equipment has been used for experiments cited in the literature repeatedly over the past 20 years, engineering, safety, materials of construction, and ultimately the cost of robust commercial equipment have precluded wide-spread application of supercritical water.

Perhaps this will change with time, but the economics currently do not point in a positive direction.

In summary, CO₂ is still the practical choice because of several coincidental properties. The critical temperature is near ambient and easily reached and controlled. The critical pressure is reasonably reached and controlled by slightly modified HPLC pumps. Carbon dioxide is non-flammable, non-toxic, odorless and chemically inert. It is also widely available at a reasonable price in a variety of purity levels. It also does not present any unusual or expensive disposal problems.

In the near future, attention will be given to the so-called *alternate refrigerants*. They will soon be widely available in price and purity comparable to CO₂. They are already screened for their potential acceptance with the "Montreal Protocol" requirements. A limited number of studies indicate several candidates may be shortly available.

III. Applications of supercritical fluid extraction in environmental analysis

In the following sections, a brief review on the applications of SFE in the determination of organic contaminants in environmental samples is given. It should be noted that, a comprehensive review of this topic is beyond the scope of this article and the reader is referred to several other excellent reviews on similar subjects that have been published in the past few years (King, 1989; Hawthorne, 1990; Pipkin, 1990; Knipe et al., 1992; Camel et al., 1993; Hawthorne et al., 1993a; Janda et al., 1993; Kane et al., 1993; Chesler et al., 1994; Gere et al., 1994 a and b; Gere et al., in press). Emphasis, in this article, is given on the extraction conditions for the various organics in aquatic sediments and related samples. Since there are no standardized SFE methods available for these samples, a recommended procedure for the extraction of a class of compounds is given at the end of each section if most or all of the following conditions are met: (1) A detailed description of the method performance, i.e. precision, accuracy and method detection limit, etc., has been generated by one or more laboratories. (2) The procedure produces satisfactory and reproducible recoveries when it is applied to standard or

certified reference materials (SRMs/CRMs). (3) If SRMs are not available, the SFE recoveries should be similar to the Soxhlet results generated on some naturally contaminated samples. (4) The entire method has either been validated by an interlaboratory study or by two or more independent laboratories.

A. Polychlorinated biphenyls (PCBs) and chlorobenzenes

One of the first SFE procedures for the removal of trace organics such as PCBs from solid samples was reported by Schantz and Chesler (1986). In their work, extraction of PCBs from a sediment sample was described. Extraction was carried out at 40°C with a CO₂ density of 0.93 g/mL (345 bar) for 4 hr. The recovery of Aroclor 1254 in that sample was quantitative as it was similar to the Soxhlet value. No information for the recovery of individual PCB congeners was given. Later, quantitative recoveries of total PCBs from sediments have also been reported by other investigators in shorter extraction times using CO₂ modified by methanol or at higher extraction temperatures. For example, up to 100% recovery of total PCBs was achieved (Onuska and Terry, 1989a), in less than 10 minutes, from a certified sediment reference material (EC-1) developed by Environment Canada (Lee and Chau, 1987b). In that work, optimal results were obtained by extraction with 2% methanol modified CO₂ at 203 bar and 40°C.

The presence of modifiers such as methanol or toluene was shown to improve the recovery of spiked PCBs from soils by 10 to 15% (Liu et al., 1991). Extractions were done at 40 or 50°C with CO₂ at 0.73 or 0.75 g/mL for 60 min. In another report, optimal results for six PCB congeners from spiked soil samples were obtained by a 10 minute static extraction followed by a 20 minute dynamic extraction using CO₂ at 50°C and 196 bar (van der Velde et al., 1992).

The efficiencies of supercritical chlorodifluoromethane (Freon-22), N₂O and CO₂ for the extraction of PCBs from a river sediment (NIST SRM 1939) were compared (Hawthorne et al., 1992). Extractions were performed for 40 min at either 405 bar and 50°C (for CO₂ and N₂O) or at 111 bar and 100°C (for Freon-22) so that the densities of the fluids were

ca. 0.93 g/mL in all cases. Under such conditions, both CO₂ or N₂O generated an average recovery of 62% (vs. the certified values) for the nine PCB congeners. In contrast, average PCB recoveries of 90% or higher were obtained by extractions with Freon-22 and 5% methanol modified CO₂ (at 70°C and 405 bar).

Using certified reference materials from USEPA and NIST, the effects of temperature and pressure on the SFE efficiencies of PCBs were studied (Hawthorne et al., 1993). Experiments were carried out at with pure CO₂ at 50° and 200°C and pressures at 152, 355 and 658 bar. In that work, PCBs were more effectively extracted at any of the above pressures when the extraction was carried out at the higher temperature. The recoveries of 12 PCB congeners from a river sediment (SRM 1939) ranged from 67 to 163% of the certified values obtained by Soxhlet extraction. The same authors later reported the role of modifiers for the SFE of PCBs in SRM 1939 (Langenfeld et al., 1994). This river sediment was extracted at 80°C and 405 bar for 15 min (5-min static and 10-min dynamic) and a flow rate of 1 mL/min. Under such conditions, they found that the modifier identity was more important than its concentration for increasing extraction efficiencies. Modifiers such as methanol, acetic acid and aniline were more effective than dichloromethane (DCM), toluene, hexane, and acetonitrile in the enhancement of PCB recovery.

The extraction of PCBs from a sewage sludge was successfully attempted by using pure CO₂ at 355 bar and 80°C (Porter et al., 1992). A static extraction of 15 min and a dynamic extraction of 45 min with a gas flow rate of 300 ± 30 mL/min were performed. The SFE and Soxhlet recoveries of four PCB congeners (PCBs 101, 138, 153, and 180) were identical. Another method for the extraction of PCBs in sulfur-containing sediments under supercritical conditions was described by Bøwadt and Johansson (1994). This procedure involved a 20-minute static extraction with pure CO₂ at a density of 0.75 g/mL (218 atm) at 60°C followed by a 40-minute dynamic extraction at the same density and temperature and a flow rate of 1 mL/min. Sulfur was conveniently removed during the extraction by mixing the sample with activated copper powder. The extracted PCBs were adsorbed on a Florisil trap and were eluted by n-heptane at the end of the extraction.

The optimization of supercritical CO₂ extraction for PCBs in sediment CRMs EC-1 was studied (Lee and Peart, 1994). The extracts were analyzed by GC/MS for PCB homologs from the tri- to the octa- chlorobiphenyls. Extractions were carried out at 40, 60, 80, 100, and 120°C and 343 bar with unmodified CO₂ for 21 minutes (1-minute static and 20-minute dynamic extractions). While the recovery of PCBs increases with increasing extraction temperature, there was a much bigger dependence of PCB recovery on temperature for the higher (e.g. hepta- and octa- chlorobiphenyls) homologs than the lower ones (e.g. tri- and tetra- chlorobiphenyls). Since the overall contribution to total PCBs by the hepta- and octa- chlorobiphenyls was small, there was practically no observable difference in total PCB concentrations for the 80, 100, and 120°C extractions.

The efficiency of several solid-phase traps in the SFE of PCBs from sewage sludge samples was evaluated (Bøwadt et al., 1994). The traps were filled with ca. 1 cc of stainless-steel beads, ODS, silica gel, and Florisil. Extractions were carried out at 60°C and a fluid density of 0.75 g/mL for 30 min with pure CO₂ as well as CO₂ modified with 2 or 5% methanol as well as 2% ethanol. They found that, if heptane was used as a trap eluent, only the ODS and Florisil traps were able to provide a PCB extract clean enough for direct GC/ECD analysis. These two sorbents were also suitable for the trapping of PCBs even if 5% methanol modified CO₂ was used for extraction, provided that the trap was maintained at 65°C (boiling point of methanol). A comparison of SFE and Soxhlet extraction was conducted as a part of the certification of PCB congeners in an industrial soil (BCR CRM 481) (Bøwadt et al., 1995).

Although they were much less studied in comparison to PCBs, chlorobenzenes are another class of USEPA priority pollutants that can be extracted simultaneously by the same procedure. The Soxhlet and SFE recoveries of several native chlorobenzenes, hexachloro-1,3-butadiene, and octachlorostyrene from a lake sediment sample were compared (Lee and Peart, 1994). After addition of 500 µL of water, the sample (1 g) was extracted by CO₂ at 100°C and 343 bar for 21 min (1 min static and 20 min dynamic) at a flow rate of 2 mL/min. While the results for octachlorostyrene obtained by the two techniques were quite similar, the SFE recovery of chlorobenzenes and hexachloro-1,3-butadiene

were 10 to 50% higher than the Soxhlet results. Lower evaporative losses of these volatile compounds by the SFE technique were presumably the cause of the discrepancy in recoveries.

Recommended extraction procedure for PCBs in solid matrices (abstracted from the USEPA Draft Method 3562 for Solid Wastes)

1. Weigh out 1.0 to 5.0 g of the dry and homogenized sample into a weighing dish. Mix the sample with 2 g of activated copper powder (electrolytic grade).
2. If necessary, spike the mixture with 150 μL of a surrogate (e.g. hexabromobenzene, 1,2,3,4-tetrachloronaphthalene, or octachloronaphthalene, etc. at 10 mg/mL).
3. Transfer the sample quantitatively to the extraction vessel on top of a 2 cm layer of Celite or anhydrous sodium sulfate. Place another 2 cm layer of Celite at the top of the sample. Fill the void volume, if any, of the extraction vessel with an inert, porous material such as pre-cleaned Pyrex glass wool, Celite, etc.

4. Extraction conditions:

CO ₂ pressure (bar):	305
CO ₂ density (g/mL):	0.75
Extraction fluid composition:	unmodified CO ₂
Extraction chamber temperature (°C):	80
Static extraction time (min):	10
Dynamic extraction time (min):	40
Extraction fluid flow rate (mL/min):	2.5

5. Extract collection conditions:

Sorbent trap packing material:	Florisil
Trap temperature (°C):	15-20
Nozzle temperature (°C):	45-55 (variable restrictor)

6. Elution of the extract from the sorbent trap:

Rinse solvent:	<i>n</i> -heptane
Rinse volume (mL):	3.2 (in two rinses)
Rinse solvent flow rate (mL/min):	1

Trap temperature (°C): 38

Nozzle temperature (°C): 30

7. After each sample, the trap is cleaned and regenerated by rinsing it with 4.0 mL of a 1:1 (v/v) mixture of DCM and acetone followed by 3.0 mL of n-heptane.
8. The combined n-heptane extract is evaporated and adjusted to 1.0 mL for GC/ECD analysis. Further cleanup is normally not necessary.

Discussion:

1. This method has been validated by three independent laboratories using sediment, soil and sludge standard reference materials developed by Environment Canada, National Institute for Standards and Testing (NIST), and BCR European Union. Precision and accuracy data for the following 12 most commonly found PCB congeners (IUPAC numbers 28, 52, 101, 105, 118, 128, 138, 149, 153, 156, 170, and 180) from trichloro- to heptachloro- biphenyls were obtained from replicate extractions. The mean % recovery for all congeners varied from 87% to 105% and the mean relative standard deviation from 3.1% to 4.9%.

2. Based on a 1 g sample and a 1 mL final volume, the method detection limits (MDL) for PCB congeners with GC-ECD analysis are on the order of 6.6 µg/kg.

B. Polynuclear aromatic hydrocarbons (PAHs)

Hawthorne and Miller demonstrated that SFE could be used for the rapid and quantitative recovery of several PAHs from solid samples such as diesel exhaust particulate (NIST SRM 1650) and from spiked Tenax-GC sorbent traps (1986). Extractions were carried out at 304 bar for either 90 min (at 45°C with carbon dioxide) or 30 min (at 65°C with 5% methanol modified CO₂). Partial fractionation of *n*-alkanes from PAHs in SRM 1650 was achieved by varying the pressure, i.e. the solvating power, of the supercritical fluid. While over 84% of the aliphatic hydrocarbons were readily extracted at 76 bar, the majority of PAHs were only extracted when the pressure was raised to 304 bar.

Meanwhile, a quantitative SFE procedure for five PAHs in an urban dust standard reference material (SRM 1649) was reported (Schantz and Chesler 1986). Using supercritical CO₂ at 345 bar and a density of 0.93 g/mL, the extraction was carried out at room temperature for 4 hr. While the SFE recoveries of fluoranthene, benzo[a]anthracene and benzo[a]pyrene were in good agreement with the certified values, those for indeno[123cd]pyrene and benzo[ghi]perylene were 30 and 18%, respectively, higher than the certified values.

Determination of PAHs in solid matrices by on-line SFE-capillary GC methods was described by various authors, including Wright et al. (1987), Hawthorne et al. (1987a, 1989), and Levy et al. (1989). SFE of PAHs from environmental solids such as urban dust, fly ash, and river sediment, using ethane, CO₂, N₂O, and methanol modified CO₂ and N₂O, was also described (Hawthorne and Miller, 1987b). A 60-min extraction with supercritical N₂O modified by 5% methanol was found to give quantitative results for the five PAHs in SRM 1649. Presumably due to its higher dipole moment, Freon-22 was also shown to yield high extraction efficiency for PAHs in solids (Hawthorne et al., 1992a).

Because of the undesirable properties of supercritical N₂O, most workers focused on the use of CO₂ as the extractant for PAHs. However, incomplete recovery of some native PAHs from soil or sediment, particularly those with a molecular mass of 252 and higher, was observed under some extraction conditions. The effects of temperature and pressure on the SFE recoveries of PAHs using unmodified CO₂ as the extractant were studied (Langenfeld et al., 1993). At 50°C, raising the extraction pressure (from 355 to 658 bar) had no effect on the extraction efficiencies from the SRM 1649 and a highly contaminated soil (USEPA certified). Higher PAH recoveries were observed at 200°C for both samples, however, higher pressure has a more dramatic effect on the PAH recovery from the air particulate sample than the soil sample. It should be noted that the best recoveries for benzo[ghi]perylene and indeno[123cd]pyrene in SRM 1649 from a 40-min extraction were 60 and 45%, respectively. Levy et al. also reported that raising the extraction pressure and temperature increased the SFE recovery of PAHs from naturally contaminated soil

and sediment samples using unmodified CO₂ (1993). These authors found that, for quantitative recovery of PAHs with a molecular weight 228 or higher, higher extraction pressure (456 vs. 355 or 253 bar) was needed for the soil and higher temperature (150 vs. 100°C or lower) was needed for the sediments.

The effects of solvent modifier, extraction temperature and number of consecutive extractions on the recoveries of PAHs from a certified reference material EC-1 were evaluated (Lee and Chau, 1987a; Lee et al., 1993b). Although spiking 500 µL of water, methanol, or DCM to 1 g of sediment improved the recovery of all PAHs, the effect was much greater for those PAHs of molecular mass 228 or higher. Higher extraction temperature also had a positive effect on the extraction efficiencies of all PAHs as the recoveries increased progressively from 60 to 120°C. With a static addition of modifier, a single extraction would produce low recovery (<65%) for PAHs with five or more rings (molecular mass 252 or higher). This situation was remedied by two more consecutive extractions of the same sample at 120°C and 338 bar with the addition of fresh modifier for each extraction or by the continuous introduction of modifier by means of a second pump.

The benefits of using modified CO₂ to extract PAHs from sediments and soils were also reported by other workers. Using pure CO₂ (in a single-step extraction) and 10% methanol modified CO₂ (in a multi-step extraction), SFE of PAHs from a few soil standard reference materials, including HS-3 (National Science and Engineering Research Council of Canada) was reported (Lopez-Avila et al., 1990). The recoveries for most PAHs in HS-3 were lower than 50% (four were even lower than 20%) if pure CO₂ was used. The presence of methanol improved the recoveries considerably as only four of the 16 PAHs were less than 50% recovered. The extraction of PAHs at ng/g level from a marine sediment (NIST SRM 1941) and a mussel tissue (NIST SRM 1974) was described (Porter et al., 1992). The extraction was performed by using 10% DCM modified CO₂ at 507 bar, 125°C and a flow rate of 600 ± 50 mL/min for 40 min. The SFE recoveries ranged from 87 to 148% (for the 11 PAHs in SRM 1941) and from 84 to 126% (for the 9 PAHs in SRM 1974) of the corresponding certified values. Quantitative recovery of

spiked PAHs in soils was achieved by the addition of DCM (400 $\mu\text{L/g}$ sample) as a static modifier (Dankers et al., 1993). The extractions were carried out with carbon dioxide of 0.76 g/mL density and a temperature of 90°C.

The role of various organic modifiers for the supercritical CO_2 extraction of PAHs in reference materials was examined (Langenfeld et al., 1994). Their results indicated that low molecular weight PAHs were best extracted with modifiers such as aniline, acetic acid, acetonitrile, methanol/toluene, hexane, and diethylamine. In contrast, modifiers capable of dipole-induced dipole interactions and π - π interactions such as toluene, diethylamine and DCM were the best modifiers for the SFE of high molecular weight PAHs. The relative extraction rates of spiked versus native PAHs from environmental samples using SFE were compared (Burford et al., 1993). In this detailed extraction kinetics study, samples such as petroleum waste sludge, urban air particulates (NIST SRM 1649), and railroad bed soil were sequentially extracted with pure supercritical CO_2 and 10% methanol modified CO_2 at 60°C and 405 bar. Regardless of the spiking method, the extraction rates for most of the spiked deuterated PAHs were up to 10-fold higher than those of the same native PAHs. In most cases, a 30-min extraction with pure CO_2 recovered over 90% of the spiked deuterated PAHs, yet ca. 25 to 80% of the native PAHs were extracted. These results clearly demonstrate that the extraction conditions established from spiked recovery alone may not be valid for the quantitative extraction of incurred organics in aged environmental samples.

Using 8% (mol) modified CO_2 at 392 bar and an extraction temperature of 80°C, results similar to or better than Soxhlet extraction for the 16 USEPA PAHs from a real world loam soil sample were obtained (Reindl and Höfler, 1994). Quantitative recovery of 1-nitropyrene from a diesel exhaust particulate standard reference material (NIST SRM 1650) as well as the extraction of some nitro-PAHs from bus soot by SFE procedures were demonstrated (Paschke et al., 1992). The highest results were obtained by extractions with Freon-22 or 10% toluene modified CO_2 at 100°C and 405 bar for 45 min at a flow rate of 0.3 mL/min. The SFE recoveries for the PAHs in SRM 1650 using the above two extracting fluids were much higher than those reported by NIST based on

Soxhlet extraction.

An unique example for the extraction of PAHs from environmental solids with sub- and supercritical water was described (Hawthorne et al., 1994). Water has a critical temperature of 374°C and a critical pressure of 221 bar. Extraction of the native PAHs from a soil sample by water was attempted at 50, 120, 200, 250, 300, and 400°C and various pressures. Since the solubilities of hydrocarbons in water are low due to its high polarity, the recoveries of PAHs were very low at 50 and 120°C. However, the dielectric constant for water drops drastically at higher temperatures and under moderate pressure. Hence, quantitative recoveries of all PAHs were obtained by a 15 min extraction at 250°C and 50 bar using subcritical water.

Recommended procedure for the extraction of PAHs in solid samples (abstracted from the USEPA Proposed Method 3561 for Solid Wastes):

1. Determine the sample's moisture content from an aliquot of the homogenized sample.
2. Prepare the extraction thimble as described earlier for PCBs (steps 1 to 3) and replace the surrogate standard by a 10 mg/mL solution of m-quaterphenyl in a 1:1 acetonitrile/THF mixture.
3. For subsequent HPLC analysis, extract the sample with the following three-step procedure:

	Extraction 1	Extraction 2	Extraction 3
Extraction conditions:			
CO ₂ pressure (bar):	120	338	338
CO ₂ density (g/mL):	0.30	0.63	0.63
Extraction fluid composition:	CO ₂	CO ₂ /MeOH/H ₂ O 95/1/4 (v/v/v)	CO ₂
Extraction chamber temp. (°C):	80	120	120
Static extraction time (min):	10	10	5
Dynamic extraction time (min):	10	30	10
Extraction fluid flow rate (mL/min):	2.0	4.0	4.0

Extract collection condition:

Sorbent trap material:	ODS	ODS	ODS
Trap temperature (°C):	-5	80	80
Nozzle temperature (°C):	80	80	80
Reconstitution of extract:			
Rinse solvent:	THF/CH ₃ CN	none	THF/CH ₃ CN
	1/1 (v/v)		1/1 (v/v)
Rinse volume (mL):	0.8	NA	0.8
Rinse solvent flow rate (mL/min):	1.0	NA	1.0
Trap temperature (°C):	60	NA	80
Nozzle temperature (°C):	45	NA	45

4. For subsequent GC analysis, substitute the extraction fluid with CO₂/MeOH/DCM (95/1/4, v/v/v) and the rinse solvent with a mixture of 3:1 (v/v) DCM and isooctane.
5. Combine the extracts from extractions 1 and 3 and readjust the volume to 1.0 mL for HPLC (USEPA Method 8310) or GC/MS (USEPA Method 8270) analysis.

Discussion:

1. This SFE method eliminated the use of hundreds of millilitres of organic solvent in the extraction of PAHs from solids. The cleaner SFE extract required no column or gel permeation cleanup before LC or GC analysis; it thereby further reduced the amount of organic solvent used per sample.
2. Activated copper was incorporated with the sample in order to eliminate the coextracted sulfur which could cause plugging of the restrictor or inline filter and the stoppage of extraction.
3. To improve the extraction recovery of native PAHs from sediment samples, three consecutive extractions were performed for each sample. The first extraction was carried out at a lower temperature (80°C) with carbon dioxide at a low density (0.30 g/mL) to remove the lower molecular weight hydrocarbons. The rest of the PAHs including the

high molecular weight hydrocarbons in the sample were extracted at a higher temperature (120°C) and carbon dioxide density (0.63 g/mL) in the presence of a methanol/water mixture as a solvent modifier. The third extraction with pure CO₂ rid the system of modifiers and readied it for the subsequent extraction.

4. This procedure was validated with sediment reference materials certified for PAHs. In general, the SFE and Soxhlet results were comparable. However, the SFE recoveries for naphthalene and methylated naphthalenes were ca. 150 and 125%, respectively of the Soxhlet values. Higher SFE recoveries in these cases were presumably due to much lower evaporative loss of these volatile compounds since the SFE procedure required very little or no solvent evaporation.

5. Method 8310 is an HPLC method for PAHs with either UV/Vis or fluorescence detection with lower limits of detection between 0.010 and 1.00 mg/kg. Method 8270 is a GC/MS method with a detection limit of 0.70 mg/kg.

C. Total recoverable petroleum hydrocarbons (TPHs)

Over the last few years, application of SFE to the analysis of TPHs from soil and solid wastes has received significant attention. The extraction of hydrocarbons up to C₃₅ with supercritical CO₂ has been reported (Monin et al., 1991). Emery et al. (1992) studied the SFE recovery of diesel fuel adsorbed on montmorillonite, kaolinite and illite clay samples. These samples were extracted for 20 min with CO₂ (density 0.8 g/mL) either at 45 or 80°C. Quantitative (>95%) recoveries of *n*-C₁₄ to *n*-C₂₂ alkanes were obtained at the lower temperature and a flow rate of 1 mL/min from the illite and kaolinite clays either spiked or coated with the hydrocarbon mixture. In contrast, quantitative recovery was not achieved for many of the hydrocarbons even at the higher extraction temperature and a flow rate of 2 mL/min from the calcium montmorillonite clay coated with hydrocarbons. The presence of water in the sample also reduced the extraction efficiency.

An off-line SFE-IR method for the determination of hydrocarbons in soils was described (Lopez-Avila et al., 1992). The extraction was performed at 344 bar and 80°C using supercritical CO₂ for 30 minutes. The extracted hydrocarbons were collected in 3 mL of tetrachloroethene, which was found to be a better solvent than Freon-113 for the collection of hydrocarbons containing 30 or more carbons. Side-by-side comparison of SFE and Soxhlet extraction (with Freon-113) showed that both methods produced equivalent results. Using spiked and naturally contaminated samples of hydrocarbon level from 1,450 to 32,600 µg/g, the SFE method accuracy and precision ranged from 80 to 104% recovery and from 4 to 20% RSD, respectively. This SFE procedure was further evaluated in the field and in the laboratory, and the results were compared with those obtained by Soxhlet extraction (Hawthorne et al., 1993b). For those gasoline-, diesel-, motor-oil-, and crude-oil- contaminated soil samples tested, the field extracted and the laboratory extracted samples by the SFE technique produced virtually identical results, and they were within 20% of the Soxhlet data.

A method for the determination of hydrocarbons in soils fortified with diesel fuels using subcritical CO₂ extraction and offline SFC analysis with a flame ionization detector was described (Brooks and Uden, 1993). Aliquots (1 to 2 g) of the sample were extracted for 10 min at 294 bar and ambient temperature (23 to 25°C) and the extracts were collected in 10 mL of DCM. Extraction efficiency was >90% at a spiking level of 30 µg/g regardless of the organic content of the soil and even after an aging period of 5 days. Selective extraction of hydrocarbons from C₁₂ to C₂₂ in contaminated soils was achieved by extraction with subcritical water at 50 bar and 250°C (Hawthorne et al., 1994). Under such conditions, the heavier hydrocarbons (C₂₄ and higher) were largely unextracted.

An offline, coupled SFE and GC method for the automated analysis of petroleum hydrocarbons in soil was developed (Wylie et al., 1994). Soil samples spiked with the NIST SRM 1642b (sulfur in distillate fuel oil) were extracted by CO₂ at 80°C and 339 bar at a flow rate of 3 mL/min for 30 min. The hydrocarbons were adsorbed on an ODS trap that was cooled to -10°C during extraction for maximum recovery (102%). The trap was then eluted with 1.5 mL of isooctane into a vial which was transported from the

extractor to the GC autosampler by a robotic arm of the latter. To save time, the sample extract was subsequently analyzed by GC-FID while a second sample was being extracted.

Recommended procedure for the extraction of TPHs from solid samples (abstracted from the USEPA Proposed Method 3560 for Solid Wastes):

1. Determine the sample's moisture content from an aliquot of the homogenized sample.
2. Weigh 3 g of sample into a precleaned aluminum dish. A drying agent (e.g., anhydrous magnesium sulfate or diatomaceous earth) may be added to sample that contains water in excess of 20%.
3. Transfer the weighed sample to an extraction vessel that has a volume slightly larger than the sample. Use two plugs of silanized glass wool to hold the sample and fill the void volume. Alternatively, drying agent or clean sand can be used to fill the void volume.
4. Extract the sample with pure CO₂ at 344 bar and a temperature of 80°C for 30 min in the dynamic mode. Alternatively, extract the sample with CO₂ at a pressure greater than or equal to 344 bar at 150°C for 25 min and a gas flow of 3500 to 4000 mL/min. In the latter case, the use of drying agent is not necessary.
5. Collect the extract in 3 mL of tetrachloroethylene. If a sorbent trap is used, set the trap temperature at -10°C during extraction and 60°C during rinsing. Rinse the trap with 1.5 mL of iso-octane or tetrachloroethylene.
6. For samples known to contain elemental sulfur, use copper filings to remove the coextracted sulfur. The extract is ready for analysis by USEPA Method 8015, Non-halogenated Volatile Organics by Gas Chromatography, or Method 8440, Total Recoverable Hydrocarbons by Infrared Spectrophotometry.

Discussion:

1. This SFE method for total recoverable petroleum hydrocarbons from soils, sediments, fly ash, and other solid wastes, published in December 1992, is the first USEPA SFE method to reach the draft status.

2. Based on a 3 g sample, a final extract volume of 3 mL and analysis with infrared detection, the method detection limit is 10 $\mu\text{g/g}$.
3. According to one estimate, a complete conversion from the Freon extraction method to the EPA Draft Method 3560 would eliminate the use of 30,000 litres of liquid Freon 113 per year in the United States (Lopez-Avila et al., 1992).

D. Insecticides and herbicides

Extraction conditions for organochlorine insecticides from spiked soil and sand using supercritical CO_2 were evaluated (Lopez-Avila et al., 1990). With the exception of methoxychlor, the SFE recovery for all insecticides from spiked sand was quantitative (>75%) regardless of the extraction temperature (50, 60 or 70°C) and pressure (152 or 253 bar). However, due to matrix effects, the recoveries for some insecticides were low when they were spiked onto dry soil samples. SFE of organochlorine insecticides from spiked soil samples was attempted (van der Velde et al., 1992). The test compounds included in this work were hexachlorobenzene, the BHC isomers, heptachlor epoxide, dieldrin, DDD, as well as *o,p*- and *p,p*- DDTs. The use of CO_2 at 50°C and 196 bar, 10 min static followed by 20 min dynamic extraction with collection in iso-octane were found to be the optimal extraction conditions. At a spiking level from 1 to 10 ng/g, the recoveries of organochlorines from peat soil ranged from 84 to 108%. The SFE extracts were suitable for GC/ECD analysis without further cleanup.

Improved SFE efficiency for the organochlorinated pesticides from spiked soils was observed when a polar modifier, especially DMSO, was added to CO_2 (Liu et al., 1991). The extraction efficiency of SFE for six organochlorines and six organophosphates from soils was compared with sonication and Soxhlet extraction (Snyder et al., 1992). SFE was carried out with 3% methanol modified CO_2 at 355 bar and 50°C. The overall mean recoveries of all 12 pesticides for the sonication, Soxhlet, and SFE methods were 95, 93, and 92%, respectively. However, with an overall RSD of 2.9%, the SFE results were the most precise. Comparable SFE and sonication results were obtained from soils with

incurred organochlorines at ng/g levels using this extraction method. Later, these authors also found that, while pesticide recoveries increased with CO₂ density, temperature over a range from 40 to 120°C had little effect on the extraction (Snyder et al., 1993). In fact, dichlorvos and endrin aldehyde showed a drop in recoveries at elevated temperatures due to thermal breakdown of these compounds.

A SFE method for the extraction of spiked and incurred pesticides from fatty and nonfatty food was also reported (Hopper and King, 1991). The sample was first mixed with a pelletized diatomaceous earth (Hydromatrix) as an enhancer prior to extraction. SFE was carried out at 80°C and 676 bar with a total flow of 100 L gaseous CO₂. Recoveries in excess of 85% for over 30 organochlorine and organophosphorus pesticides at incurred levels ranging from 0.005 to 2 µg/g were reported. The efficiency of supercritical CO₂ for the extraction of organochlorine, organophosphorus, and organonitrogen pesticides from spiked grain matrices was investigated by King et al. (1993). SFE was performed between 40 and 80°C with pressures from 135 to 676 bar. In most cases, pesticide recoveries exceeding 80% were observed over the above temperature and pressure ranges.

A procedure for the SFE of herbicides 2,4-dichlorophenoxyacetic acid (2,4-D) and dicamba using *in situ* chemical derivatization was developed (Hawthorne et al., 1992). Quantitative recovery of the two herbicides from naturally contaminated agricultural soil at the low µg/g level was obtained by CO₂ extraction at 80°C and 405 bar in the presence of trimethylphenylammonium hydroxide in methanol as a methylating agent. However, three sequential derivatization/SFE steps, i.e. 15-min static followed by 15-min dynamic extractions, were required to achieve quantitative recovery of the two native herbicides from soil. It should be noted that the BF₃/methanol complex could also be used for the *in situ* SFE/methylation of 2,4-D but not dicamba since the reagent does not methylate benzoic acids.

Various procedures for the extraction of seven chlorophenoxy acid herbicides from soil were investigated (Lopez-Avila et al., 1993). SFE with CO₂ at 405 bar and 80°C without any derivatizing agent failed to recover 2,4-D from spiked sand and topsoil at low µg/g

levels. Among the many reagents tested, the combination involving tetrabutylammonium hydroxide/methyl iodide (TBA/MI) as methylating agents was most effective and it was applicable to the qualitative determination of chlorophenoxy acid herbicides in soil spiked at 50 and 250 $\mu\text{g/g}$ levels. The extraction was carried out at 405 bar and 80°C for 15 min static, followed by 15 min dynamic, at a flow rate of 1.5 mL/min and in the presence of 0.5 mL of 25% TBA in methanol and 0.5 mL of MI. The herbicides were converted, *in situ*, into their methyl esters during the extraction. Another example for the extraction of 2,4-D from a spiked Hoypus sandy loam soil using CO_2 was also reported (Rochette et al., 1993). No 2,4-D was recovered at 86 bar and 80°C using pure CO_2 . Improved SFE recoveries of the herbicide were obtained by using a solvent modifier (methanol), an ion-pairing reagent (*m*-trifluoromethylphenyl trimethylammonium hydroxide), an ionic displacement reagent (0.2 M calcium chloride in methanol) and by *in situ* silylation (with a 2:1 mixture of hexamethyldisilazane and trimethylchlorosilane) as well as methylation (with BF_3 /methanol) of the herbicide. Recovery of 2,4-D from the sandy loam sample was as high as 90% by the ionic displacement and the *in situ* methylation procedures.

Extraction of 47 organophosphorus (OP) pesticides spiked onto an inert matrix such as sand with pure and methanol modified CO_2 have been reported (Lopez-Avila et al., 1990). SFE conditions were optimized for the isolation of eight OP pesticides from soil by Wuchner et al. (1993). Quantitative recoveries of OPs from an aged (7 to 9 days), slurry-spiked soil (4 $\mu\text{g/g}$) were achieved by an extraction with 3 to 5 mL of CO_2 pre-mixed with methanol (2% m/m) at 50°C and 250 bar. Alternatively, similar results were also obtained by a static addition of 35 μL of methanol to the soil followed by the extraction with 3 to 5 mL of pure CO_2 .

The feasibility of an online SFE/SFC for the determination of sulfometuron methyl (Oust), a sulfonylurea herbicide, from agricultural products, has been demonstrated (McNally and Wheeler, 1988). SFE was carried out with 2% methanol modified CO_2 at 40°C and 223 bar and a flow rate of 6 mL/min. Later, the same authors reported the SFE/SFC of diuron and linuron from spiked soil and grain samples (Wheeler and McNally, 1989). In order to achieve extraction recoveries of 95% or better for both compounds, the samples were

extracted, under static conditions, at 120°C with CO₂ of densities 0.6 or 0.7 g/mL. The addition of 200 to 300 µL of methanol (for diuron) or ethanol (for linuron) to 1 g of soil or wheat was required in order to obtain these high recoveries. Extractions of sulfometuron methyl (Oust) and chlorsulfuron (Glean) by supercritical CO₂ and trifluoromethane have also been reported (Howard et al., 1993). Quantitative recoveries of the above two herbicides were obtained from spiked Celite samples with 2% methanol modified CO₂. The extraction was performed at 50°C and 350 bar for 7 min (2 min static and 5 min dynamic) with a flow rate of 2 mL/min. The extracts were collected on a stainless-steel bead trap and were subsequently eluted by acetonitrile. While a 30% increase in extraction efficiency for chlorsulfuron and sulfometuron methyl was experienced when trifluoromethane was used as the solvent instead of pure CO₂, quantitative recoveries of the two herbicides from spiked Celite samples were only obtained by the use of 2% methanol modified CO₂.

Factors affecting the SFE efficiency for the herbicide fluometuron and its metabolites from spiked and field soil samples were evaluated (Locke, 1993). The best recoveries were obtained if the extractions were carried out at 50°C with CO₂ of a density of 0.80 g/mL and a flow rate of 3 mL/min in the presence of water as a static modifier for 24 min (6 min static and 18 min dynamic). Under such optimal conditions, the SFE results of the herbicide were similar to those with a conventional Soxhlet extraction using methanol. The extraction of incurred pirimicarb from topsoil was shown to be ineffective with neat supercritical CO₂, N₂O or CHClF₂ (Alzaga et al., 1995). The addition of methanol modifier to CO₂ only led to a small increase in recovery. Quantitative (Soxhlet equivalent) recovery of pirimicarb in soil at ng/g levels was obtained by SFE at 100°C and 294 bar using 10% methanol in N₂O or 5% pyridine or triethylamine in CO₂ as the extracting fluid.

A comparison of SFE and liquid-liquid extraction for the isolation of eight selected pesticides stored in freeze-dried water samples was reported by Alzaga et al. (1994). These pesticides included triazine herbicides, organophosphorus and other pesticides. Water samples (150 L) spiked with these pesticides were freeze-dried and homogenized.

Aliquots of the freeze-dried samples were then extracted with 30 mL of CO₂ at 50°C and 196 bar and by hexane and DCM. Recoveries of the pesticides by the SFE method were consistently better than those obtained by solvent extraction.

The successful SFE of *s*-triazine herbicides such as atrazine, simazine, cyanazine, propazine, and terbutylazine at µg/g levels from spiked sediments was reported (Janda et al., 1989). Recoveries of >90% for all triazines were obtained by adding 20 µL of methanol directly to the sample (0.5 g) prior to the extraction with 18 mL of CO₂ at 48°C and 230 bar. The extract was collected in 1 mL of methanol. The extraction of *s*-triazine and phenylurea herbicides from spiked sediment by supercritical CO₂ was also described (Robertson and Lester, 1994). The highest recovery for *s*-triazines was obtained by a 30 min dynamic extraction with 20% acetone modified CO₂ at 486 bar and 150°C with a flow rate of 2 mL/min. For the more labile phenylureas, an extraction temperature of 60°C was used.

Recommended procedure for the extraction of organochlorine insecticides (abstracted from the USEPA Draft Method 3562 for Solid Wastes):

1. Follow steps 1 to 3 for the SFE of PCBs in solids described earlier.

2. Extract the sample using the following conditions:

CO ₂ pressure (bar):	299
CO ₂ density (g/mL):	0.87
Extraction chamber temperature (°C):	50
Extraction fluid composition:	unmodified CO ₂
Static extraction time (min):	20
Dynamic extraction time (min):	30
Extraction fluid flow rate (mL/min):	1.0

3. Extract collection condition:

Sorbent trap packing material:	ODS
Trap temperature (°C):	20
Nozzle temperature (°C):	50

4. Reconstitution conditions for the collected extracts:

Rinse solvent:	<i>n</i> -hexane
Rinse volume (mL):	1.3
Rinse solvent flow rate (mL/min):	2
Trap temperature (°C):	50
Nozzle temperature (°C):	30

Discussion:

1. This procedure will also co-extract, quantitatively or semi-quantitatively, PCBs, chlorobenzenes and other chlorinated pesticides contained in the same samples. Further cleanup of the extract may be required to eliminate possible interference in the final GC-ECD analysis.

2. The following 14 pesticides have been tested in the development of this procedure: aldrin, β -, γ -, and δ -BHC, α -chlordane, *p,p'*- DDE, DDD, and DDT, dieldrin, endosulfan II, endrin, endrin aldehyde, heptachlor, and heptachlor epoxide. The mean % recoveries of these pesticides in three different soils and two different spiking levels (5 and 250 $\mu\text{g/kg}$) varied from 74 to 108%. The mean relative standard variation and MDL for these pesticides varied from 4.0 to 7.4 % and from 0.6 to 1.3 $\mu\text{g/kg}$, respectively.

E. Phenols

The extraction of pentachlorophenol (PCP) from a soil reference material SRS 103-100 using 10% methanol modified CO_2 was reported by Lopez-Avila et al. (1990). The recovery of PCP using this multi-step extraction was 46% of its certified value. Meanwhile, two other reports described the successful SFE of chlorophenols from spiked soil samples. In all of the above cases, the extracts were either analyzed by GC/MS as free phenols or by GC after an offline derivatization into the acetyl derivatives (Janda and Sandra, 1990; Richards and Campbell, 1991). SFE of free chlorophenols from spiked soils (Liu et al., 1991) and wood chips (Kapila et al., 1992) was also attempted. The

highest recovery of these phenols was obtained when the extraction was carried out at 50°C and 172 bar with methanol modified CO₂.

Although not quantitative, the direct methylation of phenol and some methylphenols in a small volume (1 mL) of coal gasification wastewater using 20% TMPA was demonstrated (Hawthorne et al., 1992b). SFE was carried out with CO₂ at 80°C and 405 bar for 30 min (15 min static and 15 min dynamic). For wood soot leachates (50 mL), the samples were first acidified and filtered through Empore C₁₈ disks. The methyl and methoxy phenols adsorbed on the disks were then methylated and extracted as described above. If a mixture of TMPA and 2,2,2-trifluoroethanol was used, these authors were able to convert phenol into its trifluoroethyl ether derivative (Hawthorne et al., 1992b).

A quantitative, *in situ* SFE and acetylation procedure was developed for the determination of native PCP and other chlorophenols in soil (Lee et al., 1992). Phenols were extracted from soil and acetylated during a static extraction with CO₂ at 365 bar and 80°C in the presence of acetic anhydride and triethylamine. Quantitative recovery of the di-, tri-, tetra-, and penta- chlorophenols was obtained by a 10-min extraction (5-min static and a 5-min dynamic) from soil samples fortified to 0.5 and 5 µg/g. In comparison, this SFE method and the steam distillation procedure produced very similar results for 2,3,5-trichlorophenol, the tetrachlorophenols and PCP in a reference soil sample SRS 103-100. The same technique, with minor modifications, can also be applied to a wide variety of phenols. For example, chlorinated phenolics such as guaiacols, catechols, vanillins, and syringols in sediments collected downstream of chlorine-bleaching pulp mills were extracted and acetylated by this procedure (Lee et al., 1993a). For optimal results, the extraction was carried out with CO₂ and acetic anhydride at 365 bar and 110°C in the presence of triethylamine. Presumably due to incomplete derivatization in the static extraction step, lower extraction temperatures produced much lower yields of the acetyl derivatives, particularly for the guaiacols. Recoveries of these phenolics at spiking levels of 500 and 50 ng/g ranged from 84 to 100%. A method for the determination of 4-nonylphenol, an environmental estrogen that was linked to the feminization of male fish, in sewage treatment plant sludge and aquatic sediment was developed by the application

of this SFE/*in situ* acetylation procedure (Lee and Peart, 1995a). This alkylphenol is a bio-refractory metabolite of nonylphenol ethoxylates, a major class of non-ionic surfactant used in Canada.

Recommended procedure for the extraction and acetylation of chlorinated phenolics

1. Cut a few circles of filter paper of the same diameter of the extraction thimble. Place one circle at the bottom of the thimble and then seal it with a cap.
2. Weigh 200 mg of Celite and then 1 g (range 0.1 to 2 g) of the homogenized and dry sediment/soil sample into the thimble. If needed, spike a surrogate solution containing a suitable phenol (e.g., a bromophenol or an alkyl phenol, depending on the parameters of interest) to the sample.
3. Add 30 μ L of triethylamine to the sample and then cover it with another 200 mg of Celite.
4. Add 30 (for chlorophenols) or 120 (other phenols) μ L of acetic anhydride to the top Celite layer. Place a glass rod or other inert, porous material to fill the void volume and seal the other end of the thimble with a cap.

5. Extraction condition:

CO ₂ pressure (bar):	365
CO ₂ density (g/mL):	0.71
Extraction temperature (°C):	110
Static extraction time (min):	10
Dynamic extraction time (min):	5

6. Extract collection conditions:

Sorbent trap material:	ODS
Trap temperature (°C):	15
Nozzle temperature (°C):	45

7. Elution of extract from the trap:

Rinse solvent:	DCM
Rinse volume (mL):	1.0 x 2
Rinse solvent flow rate (mL/min):	2.0

Trap temperature (°C): 38

Nozzle temperature (°C): 38

8. Partition the combined organic extracts with 3 mL of 1 % K_2CO_3 solution to remove the coextracted acetic acid and anhydride. Exchange solvent into isooctane and adjust the final volume of the organic extract to 1 mL for GC/ECD or GC/MS analysis.

Discussion:

1. This procedure is highly time efficient since it combines extraction and derivatization in the same process. Typically, the SFE requires 45 min or less compared to hours of either Soxhlet extraction or steam distillation. The extraction method only consumes a few millilitres of solvent as well as microlitres of the derivatization reagents.

2. The acetyl derivatives of phenols produce abundant and characteristic ions that are readily detected by GC/MS. Those derivatives for phenols with two or more chlorine atoms per molecule also have high electron capture detector sensitivity.

3. The present method has been validated by the Ontario Ministry of the Environment and Energy and is being used as one of the routine methods for the determination of chlorophenols in sediments.

4. Based on a 1g sample and a final volume of 1 mL, the MDL of this method with GC-ECD detection is 10 $\mu\text{g/kg}$.

5. The same procedure has also been successfully applied to the determination of methylphenols, methylchlorophenols, and nitrophenols in sediments and solid wastes (Gere and Lee, unpublished results, 1995).

F. Resin and fatty acids

A SFE method for the determination of phospholipid fatty acids in whole lyophilized E.

coli cells was developed (Hawthorne et al., 1992b). The extraction was carried out with CO₂ at 405 bar and 100°C for 30 min (15 min static and 15 min dynamic). Methylation of the fatty acids by trimethylphenylammonium hydroxide (either 1.5 or 15% in methanol) occurred during the static extraction stage.

A SFE method for the determination of native resin and fatty acids from river sediments collected at pulp and paper mill locations was also developed (Lee and Peart, 1992). Without any modifier, none of the resin acids and only a small amount of palmitic acid could be recovered by CO₂ at 80°C and 365 bar in a 15 min extraction (5 min static and 10 min dynamic). Static addition of 300 µL of methanol to 500 mg of sediment improved the recovery of all acids, however, acetic acid or formic acid was an even better modifier. With a 1:1 mixture of methanol and formic acid, the best modifier found for these acids, the recovery was over 85% (vs. Soxhlet) for all compounds. It should be noted that the SFE recovery for palustric acid was 267% of the Soxhlet result. In addition, neoabietic acid, a compound that was never recovered by the Soxhlet procedure (Lee and Peart, 1991), could also be extracted by the SFE technique. Presumably, thermal decomposition of these two labile resin acids in the Soxhlet procedure was the major cause for the different results.

G. Polychlorinated dibenzo-*p*-dioxins and furans

The SFE of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) from spiked sediment was reported (Onuska and Terry, 1989b). At a spiking level of 200 µg/kg, the recovery of 2,3,7,8-TCDD was almost 100%. The extraction was carried out at 40°C and 314 bar for 30 min with supercritical CO₂ modified with 2% methanol. Their results also indicated that nitrous oxide and 2% methanol modified nitrous oxide also extracted 2,3,7,8-TCDD efficiently while pure CO₂ and sulfur hexafluoride produced recoveries of ca. 50%. Alexandrous and Pawliszyn (1989) investigated the SFE of native polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in a municipal incinerator fly ash using CO₂, 10% benzene modified CO₂ and N₂O. In contrast to the results reported in the previous study for spiked sediment, no significant amounts of dioxins were extracted

by pure CO₂ or even 10% methanol modified CO₂ at 405 bar for 2 hr from the fly ash sample. In contrast, the SFE recoveries of the dioxins and furan were quantitative in 2 hr (compared to a 20-hr Soxhlet extraction) when 10% benzene modified CO₂ or pure nitrous oxide was used. Another approach to achieve high recoveries for these toxins was to destroy the fly ash matrix by exposing it to 1 N HCl.

In two other publications by Onuska and Terry (1991, 1992), the highest recoveries of PCDDs from fly ash were obtained by using 2% methanol modified N₂O at 405 bar and 45°C on a hydrochloric or formic acid treated sample. The SFE of PCDDs and PCDFs from naturally contaminated soil samples was also described (von Holst et al., 1992). After addition of 200 µL of methanol to 5 g of soil, the sample was extracted at 80°C with CO₂ of densities 0.25 and 0.8 g/mL for 18 or 25 min. The recoveries of 2,3,7,8-TCDD and TCDF at ng/kg levels were similar to, or better than, those obtained by Soxhlet extraction.

A 3-step, extraction and cleanup procedure for the fractionation of fly ash SFE extracts containing PCBs, chlorobenzenes, PCDDs and PCDFs was described (Alexandrous et al., 1992a). The municipal fly ash (1 g) was extracted as previously described (Alexandrous and Pawliszyn, 1989) with nitrous oxide for 60 min at 414 bar. The SFE extract, after concentrating to 100 µL and spiking onto Florisil, was cleaned by a 15-min CO₂ extraction at 207 bar which removed over 75% of the chlorobenzenes and PCBs. The PCDDs and PCDFs were then back extracted from Florisil by N₂O at 414 bar for 90 min. All extractions were done at 40°C. Another similar SFE and cleanup procedure optimized for the GC/MS determination of PCDDs and PCDFs in fly ash and pulp samples was also described (Alexandrous et al., 1992b).

H. Organotins

SFE of six tetraalkyltin and seven organotin compounds from spiked topsoil samples with CO₂ or CO₂ modified with 5% methanol was investigated by Liu et al. (1993). Tetraalkyltin species were readily extracted (90 to 110% recovery) with pure CO₂ at 101

bar and a temperature of 40°C. For the ionic organotins, more drastic conditions using modified CO₂ at 456 bar and 80°C for 40 min (static) and 20 min (dynamic) extractions at a flow rate of 1.5 mL/min were needed. Moreover, the addition of sodium diethyldithiocarbamate (NaDDC) as a complexing agent to improve the solubility of tin complexes in the supercritical fluid is required to improve the recovery to 70% or above. For the SFE extracts of ionic organotins, an offline Grignard reaction was performed prior to GC/AED analysis.

Later, a SFE procedure for the determination of tributyltin in sediment was described (Dachs et al., 1994). Optimum recovery of tributyltin (82%) was obtained by a 30-min extraction at 343 bar and 60°C using 20% (v/v) methanol doped with HCl in CO₂. This procedure was applied to the extraction of tributyltin in two CRMs certified for organotins, namely, PACS-1 obtained from the National Research Council of Canada and CRM-462 obtained from the Community Bureau of Reference (BCR). The uncorrected recovery for tributyltin by this procedure was 69.4% from PACS-1 and ca. 75% from CRM-462. In another publication, a SFE procedure with an *in situ* derivatization step for the determination of butyl- and phenyl- tin compounds in sediment was developed (Cai et al., 1994). Derivatization was carried out under CO₂ at 355 bar and 40°C during the 10-min static extraction in the presence of hexylmagnesium bromide. Extraction of the hexyl derivatives was completed with 10 mL of CO₂ at the same temperature and pressure and at a flow rate of 1 to 1.5 mL/min. The recoveries of dibutyltin and tributyltin from PACS-1 were 38 and 78%, respectively, and those from CRM-462 were 63 and 91%, respectively. Monobutyltin was not recovered by this method.

More recently, an off-line complexation/SFE and GC/AED procedure for the determination of organotin species in soils and sediments was reported (Liu et al., 1994). Instead of solid NaDDC, a DCM solution of diethylammonium diethyldithiocarbamate (DEA-DDC) was added to the sample and used as a complexing agent for the ionic tin compounds. DEA-DDC was preferred since it is more soluble than NaDDC in supercritical CO₂. The organotins were extracted by 5% methanol modified CO₂ at 456 bar at 60°C for 50 min (20 min static and 30 min dynamic) with a flow rate of 1.5

mL/min. The recoveries of mono-, di-, and tri- butyltin in PACS-1 obtained by this procedure were 9, 95, and 108%, respectively.

Recoveries of 85 and 79% for tributyl- and dibutyl- tin, respectively, from PACS-1 were also reported by using supercritical CO₂ modified with 10% methanol (Chau et al., 1995). Optimal results were obtained by mixing 0.5 g of PACS-1 with 0.1 g of NaDDC, a 70°C extraction temperature, and a 30-min extraction with CO₂ pressures at 253 bar (2 min), 355 bar (2 min), and 507 bar (26 min). Although the SFE recovery for monobutyltin from spiked sediment was only 62%, it was the highest recovery so far reported by the SFE technique.

A method for the determination of alkyltins and alkylleads in solids by Freon-22 extraction under supercritical and subcritical conditions followed by micellar electrokinetic capillary chromatography was described (Li and Li, 1995). Much higher recoveries of trimethyllead, triethyllead, and tributyltin halides from spiked soil samples were obtained with subcritical Freon-22 at 50°C than supercritical Freon-22 at 100°C, both at an extraction pressure of 245 bar. However, the addition of NaDDC to the sample as a complexing agent was required in order to improve the recoveries of the trimethyltin and trimethyllead halides from <60% to >89%.

IV. Auxiliary techniques in supercritical fluid extraction

A. Sulfur removal

Sulfur and sulfur compounds are present in nearly all bottom sediment and soil samples. Due to the non-polar nature of elemental sulfur, it is readily extracted by organic solvents and is coeluted with other non-polar and less polar analytes such as PCBs and organochlorines in column cleanup procedures. Because of its response to electron capture detectors which are routinely used for the final analysis of many environmental samples containing polychlorinated analytes, an extra sulfur removal procedure is required. The more commonly used reagents to eliminate sulfur interference are metallic

mercury, activated copper powder, activated Raney nickel, and tetrabutylammonium sulfite.

In supercritical fluid extractions, the presence of a large amount of sulfur in the sample also causes problems such as the plugging of restrictors or inline filters, both of which would eventually stop the flow of CO_2 . A technique for using granular copper to remove elemental sulfur in SFE extracts of soils was described (Pyle and Setty, 1991). It was found that a 2 g copper scavenger column placed after the extraction chamber was successfully applied to the extraction of the NIST SRM 1941 which contains ca. 25% sulfur by weight. No interruption in flow was experienced during the extraction. Sulfur removal in the SFE of sludge and SRM 1941 was also achieved by placing 2 g of copper granules (10-40 mesh) at the outlet end of the extraction cell (Porter et al., 1992). No evidence of restrictor plugging by sulfur was observed during those extractions. Another approach reported for sulfur removal under SFE conditions involved mixing the sediment (2 g) with prerinsed copper powder (1.5 g, electrolytic grade) (Bøwadt and Johansson, 1994). This method works well for the extraction of PCBs in sediments with sulfur contents from 0.8 to 2.5%. In this case, copper powder was activated by rinsing it sequentially with deionized water, acetone, and hexane. The residual solvent was evaporated on a Rotovap and the copper was stored under argon.

B. Lipid removal

A supercritical fluid cleanup technique for the separation of organochlorine insecticides from fats has been developed by France et al. (1991). The lipid matrices examined in this study were either chicken fat with incurred residues or commercial lard spiked with the insecticides at low $\mu\text{g/g}$ levels. The separation was performed at 40°C and a pressure from 190 to 270 bar using a modified supercritical fluid chromatograph equipped with a stainless steel column (7 cm x 4.6 mm i.d.) packed either with 5% deactivated neutral alumina (1.4 g) or silica gel (0.5 g). The mobile phase was either CO_2 (alumina column) or 2% methanol modified CO_2 (silica gel column). It was noted that the amount of methanol in CO_2 was critical when the silica gel column was used. While the addition

of methanol was necessary to improve the recoveries of endrin and dieldrin, large amounts of lipids would be coeluted if 3% of methanol in CO₂ was used. The precision and accuracy of the SFE cleanup method for lindane, heptachlor, heptachlor epoxide, dieldrin, endrin, and *o,p'*-DDT compared favorably with those obtained by the conventional column cleanup method.

Based on a similar concept, a quantitative SFE method for the determination of PCBs in fish with high (ca. 30% by weight) lipid content was developed (Lee et al., 1995b). Fish tissues mixed with granular anhydrous sodium sulfate were extracted in the presence of activated basic alumina at 100°C and 345 bar with pure CO₂. The incorporation of alumina in the extraction thimble successfully reduced the amount of lipid in the extract to 2% or less, thereby eliminating the need of the time-consuming and solvent-consuming gel permeation cleanup. If necessary, the remaining lipid could be easily removed by a drop of concentrated sulfuric acid. This procedure was also applicable to the simultaneous determination of organochlorine insecticides such as hexachlorobenzene, *p,p'*-DDE and mirex in fish tissues.

C. *In situ* derivatization

The most widely used supercritical fluid, CO₂, is a non-polar solvent because of its lack of a dipole moment. As a result, polar organics have relatively low solubility in CO₂, leading to the less than quantitative SFE recovery of such compounds relative to Soxhlet extractions using polar solvents. In many cases, this problem can be alleviated by the addition of a modifier to CO₂ to increase the polarity of the extracting fluid, or by switching to a more polar supercritical fluid such as N₂O. Another popular approach is the so called *in situ* derivatization/SFE technique. It involves the conversion of a polar, active group (usually an active hydrogen) into a less polar functional group which is more readily extracted. Because of its lower polarity, the derivative is also more amenable to column cleanup if necessary. This technique is also very time efficient since the derivatization is done *in situ* during the static extraction stage. With a judicious choice of reagents, derivatives that are more sensitively and selectively detected by electron-

capture and mass spectrometric detectors than their parent compounds can be formed.

Hill et al. demonstrated the feasibility of simultaneous derivatization and extraction of polar compounds with supercritical CO₂ as a rapid alternative to solvent extraction followed by derivatization (1991). After an initial SFE with CO₂ at 304 bar and 60°C on a marine sediment, additional reactive analytes were extracted in a second SFE in the presence of a mixture of hexamethyldisilane and trimethylchlorosilane.

In order for the *in situ* derivatization to be successfully incorporated into the extraction scheme, conditions for the two procedures must be compatible with each other. For example, the temperature for extraction and derivatization should be similar and the reagents and derivatives must be stable under SFE conditions. Thus, if a modifier is used for the extraction, it must not react with the derivatizing agent. Examples for the application of *in situ* derivatization technique in the determination of organic contaminants in environmental samples are summarized in Table 2.

D. Supercritical fluid extraction of organics in water samples via solid phase extraction

Despite the numerous application of SFE of organic contaminants from solid matrices, there have been few examples reported for water samples. Using a setup similar to the conventional purge-and-trap system for semivolatile analytes, direct aqueous extraction of phenols, phosphonates, caffeine, and triprolidine with CO₂ have been demonstrated (Hedrick and Taylor, 1990, 1992). Since their approach was limited to small sample sizes (3 mL), it was not applicable to trace analysis in environmental samples. The major difficulties of direct SFE of water samples as cited by these authors were the mechanical mobility of the matrix as well as the relatively high solubility of water in CO₂. More recently, another example for the direct SFE of organochlorines in aqueous samples was given by Barnabas et al. (1994a). In addition to less than quantitative recoveries and long extraction time, this method was again limited by a small sample size (45 mL) and thus could not be applied to trace analysis.

SFE of liquid samples is more conveniently done in a two-step process: enrichment of the organics with a solid phase adsorbent followed by the SFE of the adsorbent. The indirect SFE of sulfometuron methyl and chlorsulfuron in water (0.1 or 1 L) was reported (Howard and Taylor, 1992). Water samples were first filtered through Empore C₁₈ disks and the adsorbed urea herbicides were extracted from the disks with 2% methanol modified CO₂ at 350 bar and 50°C. Total extraction time was 26 min (2 min static and 24 min dynamic at a flow rate of 2 mL/min). Recoveries of the analytes at spiking levels of 50 and 500 µg/L were over 90% using a stainless steel trap. The SFE of phenols from an acidified wood soot leachate (50 mL) adsorbed on an Empore disk has been described earlier (Hawthorne et al., 1992).

The application of combined solid phase extraction using disks or cartridges made of a bonded C₁₈ phase and SFE to extract semivolatile and nonvolatile organic compounds from water was demonstrated (Tang et al., 1993). The samples consisted of a selected group of PAHs, PCBs, organochlorine insecticides, and phthalate esters spiked into particulate-free, reagent grade water. The adsorbed organics on the cartridge or disk were then extracted by 30 mL of CO₂ at 304 bar and 60°C. The SFE recoveries were similar to those obtained by cartridge extraction followed by solvent elution. However, they also observed that, for large sample sizes, the disks were more efficient than the cartridges in terms of total analysis time and recovery of the organics. In a related study, Ho and Tang (1992) optimized the SFE conditions for environmental pollutants such as PAHs and organochlorinated insecticides from spiked C₁₈ solid phase extraction cartridges. Most of the above pollutants were quantitatively recovered by CO₂ at ≥40°C and 355 or 405 bar for an extraction time of 20 to 35 min. For those analytes that were not extracted efficiently with pure CO₂, the addition of 300 to 500 µL of methanol to the cartridge greatly improved the recoveries. Examples for the extraction of organochlorines and herbicides (Barnabas et al., 1994a and b) as well as PAHs (Messer and Taylor, 1995) in water using solid phase extraction disks prior to SFE were also documented.

Figure Legends

Figure 1. Phase diagram of water.

Figure 2. Generic SFE hardware.

Table Legends

Table 1. Candidates for SFE fluids.

Table 2. Examples of *in situ* derivatization of contaminants in soils and aquatic sediments under SFE conditions.

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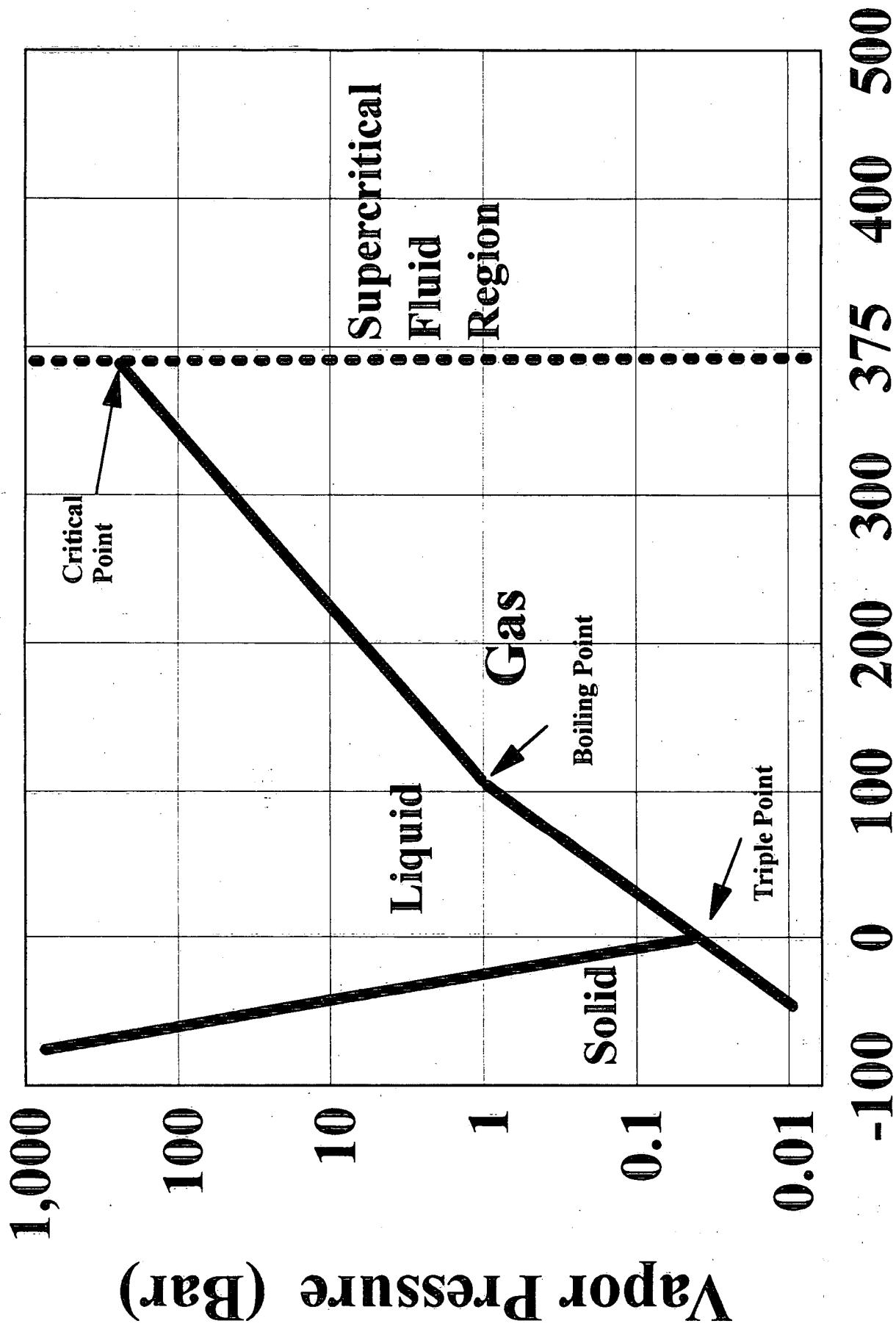
Table 1. Candidates for SFE fluids.

Fluid	Critical Temperature, ° C	Critical Pressure, bar
Ethylene	9.3	50.4
Carbon Dioxide	31.1	73.8
Ethane	32.3	48.8
Nitrous Oxide	36.5	72.7
Propylene	91.9	46.2
Propane	96.7	42.5
Ammonia	132.5	112.8
Hexane	234.2	30.3
Water	374.2	220.5

Table 2. Examples of *in situ* derivatization of contaminants in soils and aquatic sediments under SFE conditions.

Analytes	Reagents	Derivatives	Recoveries (%)	Reference
Acids, resin and fatty	PFBBr/TEA	PFB esters	35 - 45 (native resin acids)	Lee and Peart, 1992a
Herbicides, 2,4-D, dicamba	TMPA	methyl esters	116 - 137 (native herbicides)	Hawthorne et al., 1992b
Herbicides, 2,4-D	HMDS/TMCS	silyl ester	31 (spiked sandy loam)	Rochette et al., 1993
Herbicides, 2,4-D	BF ₃ /methanol	methyl ester	90 (spiked sandy loam)	Rochette et al., 1993
Herbicides, phenoxy acid	TMPA	methyl esters	13 - 96 (spiked sand)	Lopez-Avila et al., 1993
Herbicides, phenoxy acid	TBA/methyl iodide	methyl esters	69 - 141 (spiked clay)	Lopez-Avila et al., 1993
Herbicides, phenoxy acid	PFBBr/TEA	PFB esters	24 - 83 (spiked topsoil)	Lopez-Avila et al., 1993
Phenols, chloro-	acetic anhydride/TEA	acetates	99 (native PCP in soil)	Lee et al., 1992b
Phenols, catechols/guaiacols	acetic anhydride/TEA	acetates	87 - 98 (spiked sediment)	Lee et al., 1993a
Phenol, alkyl-	acetic anhydride/TEA	acetates	96 - 98 (spiked sediment)	Lee and Peart, 1995a
Organotin, tri-/dibutyltin	hexylmagnesium bromide	hexyl derivatives	78 (native TBT in PACS-1)	Cai et al., 1994

Legend: PFBBr=pentafluorobenzyl bromide, TEA=triethylamine, TMPA=trimethylphenylammonium hydroxide, HMDS=hexamethyldisilazane, TMCS=trimethylchlorosilane, TBA=tetrabutylammonium hydroxide
PCP=pentachlorophenol, TBT=tributyltin chloride



Temperature degrees Centigrade

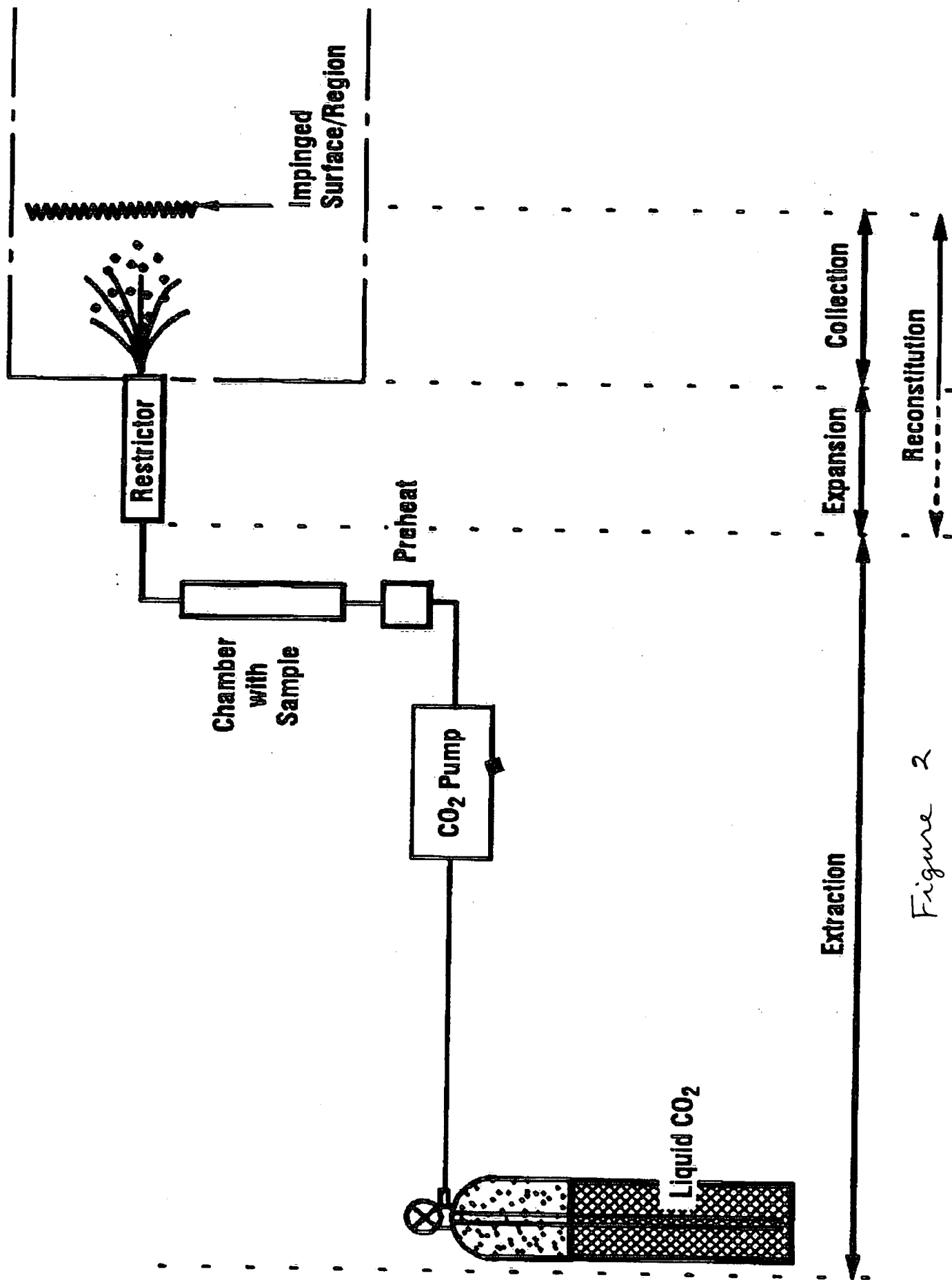
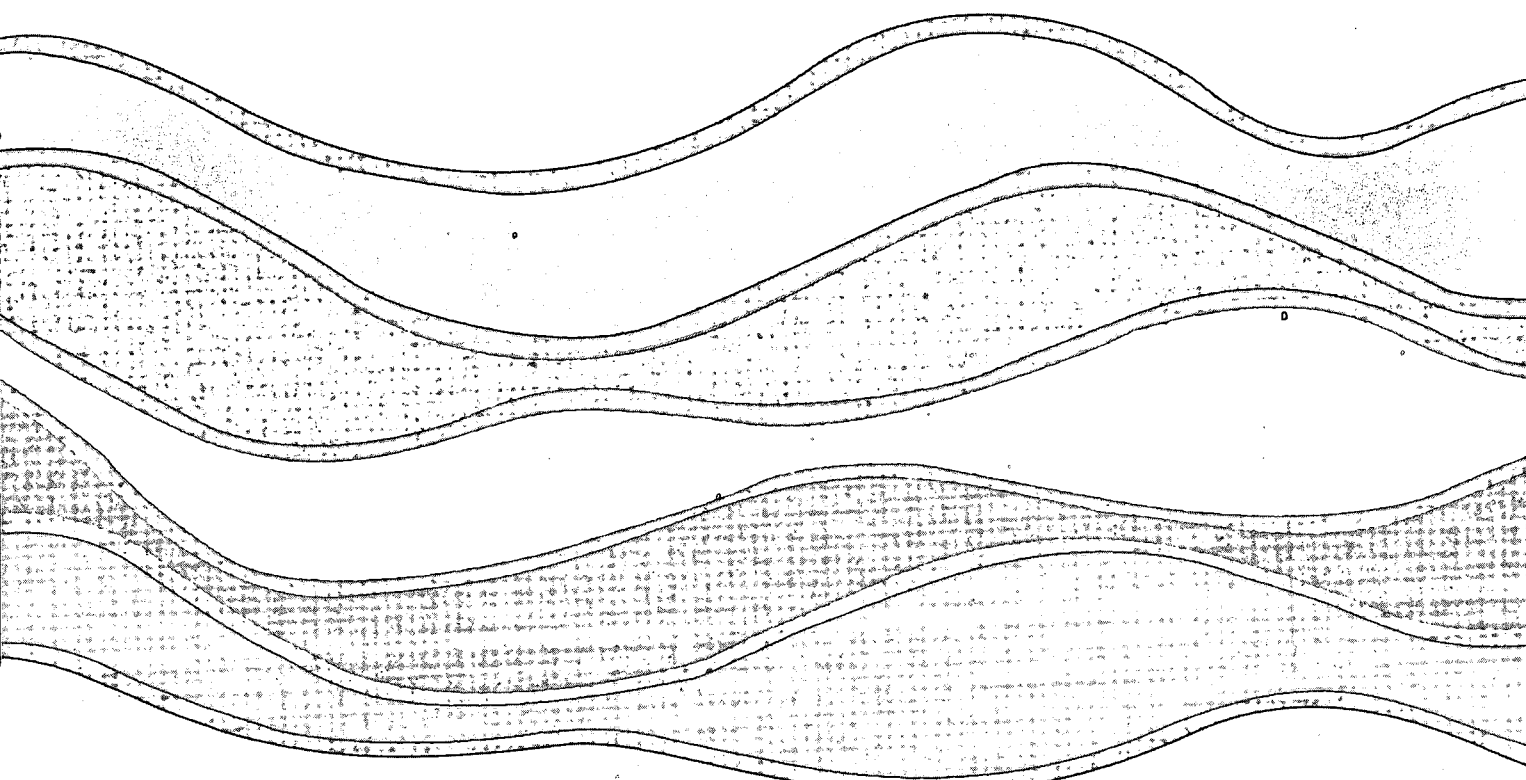


Figure 2

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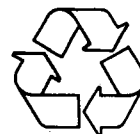


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