provide heating/cooling. Filtration of the particles at high pressures also requires special equipment.

In summary, both RESS crystallization and SAS crystallization appear to be promising methods for generating supersaturation and therefore represent alternatives to conventional crystallization. Such alternatives may prove attractive in applications such as polymer and pharmaceutical processing, or in particle design for drug delivery. It is possible to obtain a variety of morphologies and particle sizes in these processes by proper choice of conditions and expansion devices. However, *a priori* design of supercritical crystallization processes is not yet possible because the interaction between phase equilibria, expansion paths, and crystallization kinetics in these processes is not yet well understood.

See also: **II/Crystallization:** Control of Crystallizers and Dynamic Behaviour; Polymorphism.

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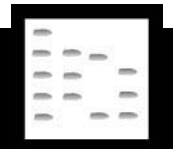
SUPERCRITICAL FLUID EXTRACTION–SUPERCRITICAL FLUID CHROMATOGRAPHY



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Introduction

The transfer of extracted analytes to a chromatography column can be either offline or online. In offline analysis, the extracted analytes are collected and then an aliquot is manually transferred to the chromatography system. Online analysis is where the extracted analytes are automatically transferred to the analytical column. The intrinsic problems with offline collection are that sample loss and contamination are possible, the process is difficult to automate and the sample must be diluted with solvent to allow transfer, resulting in higher detection limits. Coupling extraction and chromatography minimizes many of these problems. Supercritical fluid extraction (SFE) and supercritical fluid chromatography (SFC) are ideally suited for coupling together as the most frequently used solvent, carbon dioxide (CO_2), is the same for both techniques. In the case where pure CO_2 is used, the extracted analytes can be deposited at the start of the analytical column simply by reducing the pressure, and chromatography started by increasing the pressure again. Capillary SFC (cSFC) benefits particularly from online methods. The columns are small and easily overloaded, particularly with injection solvent. For example, a 1-μL injection occupies 0.5 m of a 50-μm i.d. column. Larger injections can easily cause band broadening and peak splitting. The limitation of injection size increases the detection limit. A logical method of solving the intrinsic problems of offline collection and cSFC is to link them online.

Samples for which SFE–SFC is Applicable

The main alternatives to SFC are GC and HPLC. Online coupling of SFE and HPLC is difficult, as the presence of gaseous CO_2 is incompatible with HPLC

analysis. If the analytes are thermally stable and volatile GC is the best separation technique to use. Many flavour and fragrance compounds in complex food samples should therefore be analysed by SFE–GC. The same is true of polychlorinated biphenyls (PCBs), pesticides and polyaromatic hydrocarbons (PAHs) in environmental samples.

When the sample contains thermally labile or reactive compounds, SFE–SFC is recommended. The procedure is excellent for thermally unstable polymer additives in commercial plastics or for fatty acids and triglycerides in food, etc. which cannot be analysed by GC very easily without derivatization. Natural products such as those containing terpene compounds or hops which contain highly reactive bitter compounds such as humulone and lupulone must also be analysed by SFC or HPLC as rearrangement can easily occur at elevated temperatures. Speciation studies on organotins, an important environmental pollutant, are difficult using GC or HPLC as derivatizations are required to increase volatility or provide a chromophore. Other application areas specific to SFC include the analysis of explosives and certain steroids, vitamins and other drug residues in biological samples. SFE–SFC finds important applications in environmental science. The analysis of pollutants in matrices such as soil and sediments, and extraction of sorbents on which pollutants in air or water have been selectively adsorbed have been analysed with this technique.

Capillary and Packed Column SFC

There are two broad categories of SFC, capillary and packed column. Capillary SFC was developed from capillary GC, and packed column SFC is more akin to HPLC. There are advantages to each. cSFC uses open tubular capillaries with bonded stationary phases. Compounds with differing solubilities in CO_2 are eluted using pressure programming, where the pressure, and hence density and solvent strength of the mobile phase is increased during the separation. This is the equivalent of temperature programming in GC. Use of modifiers is rare, partly due to difficulties of mixing at very low flow rates and partly because the 'universal' FID cannot be used with modifiers present. Open tubular capillaries offer little resistance to the flow of the fluid and columns can be long. A major problem with capillary SFC is the low sample capacity. The capillary columns are easily overloaded and very small injections are required, reducing sensitivity. Packed column SFC uses columns packed with HPLC packing materials. Small particles offer a high resistance to the fluid flow, and hence there is a pressure drop across the column. This results in a reverse density gradient along the column, in which the fluid has the lowest solvent strength at the elution end of the column. This gradient is working against any pressure gradient appl ied, and can lead to precipitation of solutes. Elution in packed column SFC is now often controlled by addition of a modifier such as methanol rather than pressure programming. Use of modifiers means that the FID cannot be used, and detection for packed column SFC is more usually by UV absorbance detectors. However, modifiers allow more polar stationary phases to be used, which have much greater interaction with polar molecules. When CO_2 alone is used, the stationary phase must also be nonpolar, otherwise the solvent strength is not sufficient to elute polar compounds. The analyte interacts only poorly with both stationary and mobile phases, resulting in poor peak shape. The poor results with polar compounds on packed SFC columns has also been attributed to polar active sites (residual silanols) present on the silica. These are thought to be better shielded in coated capillaries. The solvent strength of modified CO_2 can be varied from similar to pentane for pure CO_2 to similar to acetonitrile with addition of 40% methanol.

The different natures of capillary and packed column SFC also lead to differences in instrumentation. The flow rates in cSFC are very low, and pressure is usually controlled by restrictors. These can be linear capillaries whose diameter and length can be adjusted to provide the required pressure. Adjustable, heated needle valves have also been used. The problem with whichever system is used is that the restrictor is a passive device, limiting mass flow at the pressure set by the pumps. Blockages can occur, and the flow rate is not well controlled. Flow rates in packed column SFC are much higher, which allows the use of manual or automatic back pressure regulators, which control the pressure independently of flow rate. Pressure, flow rate and solvent composition can, therefore, be much better controlled in packed column SFC. In reality, packed column and capillary SFC are very different techniques, with different areas of application.

SFE–SFC Interface

The analytes extracted during the SFE step can be introduced onto the analytical column in two main ways. The SFE extract can be passed through a sample loop and an aliquot directed to the SFC column, or the analytes can be trapped after the SFE and introduced onto the column in one go.

Aliquot Sampling

The simplest of interface for SFE–SFC is by aliquot sampling. A part of the extract is sampled by passing

it through an injection loop of the SFC system. A closed- or an open-loop system may be used. Closed-loop static SFE–cSFC involves the sample being sealed in an extraction cell for a period of static extraction. The extraction cell is connected to the sample loop of an injection valve. The analytes diffuse to the loop, and after equilibrium is reached the valve is actuated and an aliquot is injected into the SFC column.

The major advantage of this procedure is that small aliquots of the extract can be taken for consecutive analysis with virtually no difference in the extraction profile. However, a major disadvantage is that the solute containing extraction fluid has to reach equilibrium and diffuse out of the cell and into the injection valve before sampling is made. This can take many hours before complete equilibrium is attained. Recirculating pumps could be used to reach equilibrium in a shorter time, but these can easily become contaminated.

The system can be sampled more rapidly by allowing a portion of the extraction solution to pass through the loop to atmosphere, to flush the loop with fresh solution. A low-flow restrictor is connected to a valve inline after the injector, as shown in **Figure 1**. Static extraction can be carried out with the high-pressure valve closed. Opening this valve to the restrictor allows dynamic extract and filling of the sample loop. Actuation of the rotary valve passes the contents of the loop to the analytical column, and either static or dynamic extraction can be continued. This is known as open-loop SFE, and with this configuration one also has the opportunity of passing the sample through a detector (UV or FID). At periodic intervals aliquots of the extract can be injected into the SFC column for analysis.

Aliquot sampling diverts only a small portion of the extract to the SFC column, and is therefore not suitable for quantitative SFC analysis. SFE–SFC with aliquot sampling is a good technique for basic qualitative investigation and for measuring fundamental parameters such as partition coefficients of solutes in supercritical fluids. However, it is limited in that it is not usually suited to quantitative or trace analysis where analytes in the whole extract must be accumulated prior to chromatographic analysis.

Trapping of Analytes

In contrast to static extraction with aliquot sampling, dynamic SFE–SFC operates principally by continuously exposing the analytes to a fresh stream of supercritical fluid. Extracted components are accumulated from this stream in a trap of some kind. Only after extraction is complete are the trapped analytes transferred to the SFC column for analysis. The major advantages of dynamic SFE–SFC are that it is much more rapid than static SFE–SFC and that trace analysis can be performed. The whole of the extracted material is passed to the SFC column, therefore the sensitivity is much greater than for offline analysis. **Figure 2** shows a schematic of a simple online SFE–SFC system. A high-pressure syringe pump supplies the extraction cell with fluid. The outlet of the cell is connected to a capillary flow restrictor which is connected to an accumulating trapping system. During extraction the depressurized gas from the restrictor passes through the trap and is then vented to the atmosphere through valve 1. The extracted analytes

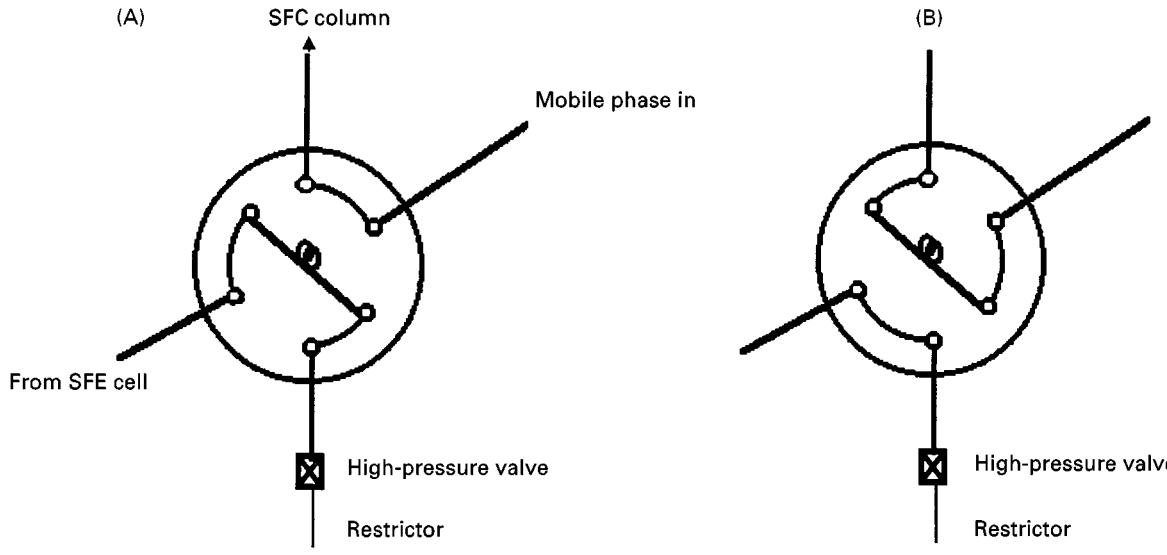

Figure 1 Schematic of open-loop aliquot sampling system (A) Filling loop, dynamic extraction mode. (B) Injecting to column.

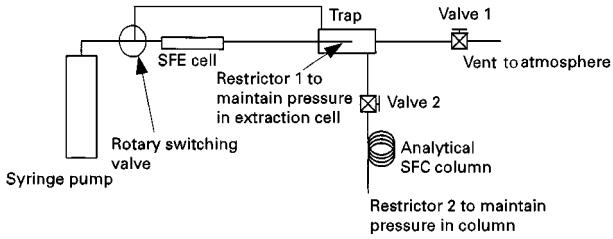

Figure 2 Schematic of SFE–SFC system.

are concentrated within the trap. After extraction is completed, valve 1 closes and valve 2 opens, switching the CO_2 onto the SFC column. The rotary valve switches the flow to the trap to avoid the cell and associated restrictor. This raises the pressure within the trap and the CO_2 becomes a supercritical fluid and capable of dissolving the trapped analytes and carrying them to the column.

If uncoated fused silica tubing is used to connect the trap to the analytical column (the retention gap), the analytes will, in theory, be unretained during the transfer. The pressure of CO_2 needed to effect the transfer need only be enough to provide some solubility of the analytes. Once they reach the stationary phase film of the SFC column they become concentrated as a narrow band, as the relatively low density solvent is not strong enough to elute the compounds from the stationary phase. After trapping is complete, the chromatography can be initiated using a pressure programme. If such phase ratio focusing occurs successfully, then good chromatographic efficiency is observed during the separation. If this process works well, the length and internal diameter of the retention gap do not significantly affect the resolution.

Other more complicated systems have been reported using on–off and multiport switching valves to allow continuous extraction or to permit the extraction cell to be vented during simultaneous chromatographic analysis. The 'plumbing' of such a system can be constructed to any specific requirement.

Since analytical SFE is most often performed with fluids that decompress to gases at ambient conditions (such as CO_2, 1 mL min^{-1} of which produces a gas flow of approximately 500 mL min^{-1}), the success of trapping depends on the success of recovering the analytes from the expanded gas. Fast flow rates tend to elute volatile analytes from the trap, thus, for quantitative results, recovery of extracted components should be performed at lower flow rates. The problem of loss of volatile analytes is often not severe in SFE–SFC, as these are likely to be analysed by SFE–GC. Therefore SFE–SFC traps generally need be more concerned with trapping less volatile materials.

Trapping procedures

There are several methods of trapping extracted components from dynamic SFE in preparation for online SFC analysis. The requirements are to efficiently trap all the material from the gas or low-pressure stream from the extractor, and then to release all the components when the flow is switched to the analytical column. Two methods are used for this:

- cryogenic trapping; and
- trapping on an adsorbent stationary phase; the stationary phase can be either on particles packed into the trap, or coated onto a fused silica capillary.

Cryogenic trapping

Trapping on uncoated fused silica retention gaps A length of uncoated fused silica capillary can be cooled by expanding CO_2. Solutes passing through the capillary in the depressurized gas stream from the SFE will be trapped in the cooled section. The cooling can then be switched off, and the section pressurized with CO_2 to redissolve the analytes. **Figure 3** shows an arrangement for a cryogenically cooled fused silica trap. In this arrangement the expanded mobile phase from the extraction cell is released from a different outlet than the incoming CO_2 for the SFC. This minimizes contamination of the system from previous analyses. The extracted analytes are in contact only with deactivated fused silica after leaving the extraction cell, which reduces loss of polar analytes by adsorption on metal surfaces.

The flow rate of the expanding extraction fluid and the temperature at which analytes are trapped markedly affect the recoveries obtained when uncoated fused silica tubing is used. In many systems, linear extraction restrictors are used, since they provide the correct flow rate range for online coupling with capillary SFC. They also tend not to plug as quickly as other restrictors when used for SFE. The length and internal diameter of the capillary restrictor tubing

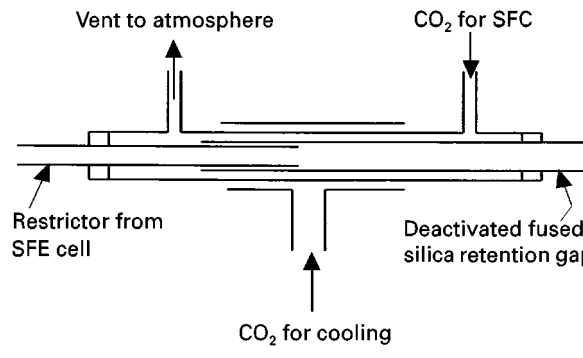

Figure 3 Cryogenically cooled trap.

and the pressure at which the extraction is performed should therefore be considered to obtain suitable flow rates.

Restrictors with internal diameters greater than 30 μm result in higher extraction efficiencies, but lower recoveries and significant band broadening of more volatile components. However, restrictors with internal diameters less than 15 μm do not allow sufficient flow for efficient extractions over a short period of time, but yield good chromtographic peak shapes. As a rough guide, the gaseous flow rates from 15-cm lengths of 15-, 20-, 25- and 30-μm restrictors at a pump pressure of 300 atm are, approximately, 80, 150, 240 and 300 mL min^{-1}, respectively. A good compromise therefore is to use a restrictor with a flow rate of 100–200 mL min^{-1}. Lengths of capillary tubing of 20 or 25 μm i.d. are suitable for most needs.

The trapping efficiency is also strongly dependent on the trapping temperature. The higher the temperature, the more volatile components will be lost from the trap. Cooling in the region of $-40°C$ to $-60°C$ will allow trapping of C_{10} hydrocarbons with reasonable efficiency. The trap should only be cooled to a sufficient temperature to trap the analytes of interest, as too low a cryofocusing temperature may result in restrictor plugging, or components, such as water, freezing in the restrictor. This reduces the rate of extraction and makes it difficult to reproduce analyses. An alternative arrangement for trapping volatile substances is to keep the restrictor hot and deposit the analytes in the transfer line held in a cryogenically cooled oven as shown in **Figure 4**.

The use of micropacked columns has also been reported. In this case the restrictor can be vented onto the head of the analytical column. The cooling of the expanding gas cools the column and the analytes are deposited on the packing at the start of the column.

Trapping on coated fused silica retaining pre-columns An alternative to the cryotrapping method is the use of a coated fused-silica retaining pre-column for concentrating extracted solutes. Compared to uncoated fused silica, coated columns such as GC columns are much more effective at trapping. The key is to trap effectively, but allow the mobile phase to elute the trapped materials during the pressure programme. It is likely that a column coated with a similar material to the analytical column will be effective. The phase thickness on the column is also important, thicker phases having a greater trapping power. This method allows the trapping at room temperature using widely available bonded-phase GC columns.

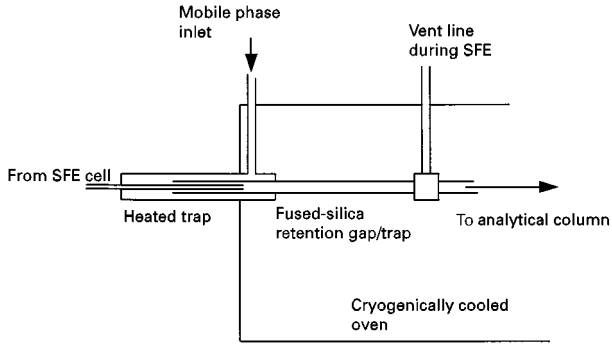

Figure 4 Arrangement for keeping restrictor hot and trapping in cryogenically cooled oven.

Trapping on sorbent traps Sorbents may also be used as an effective method of trapping. This entails the use of short traps (usually 2 cm in length) packed with organic sorbents such as Tenax-GC, Carbotrap or with HPLC packing materials. Bonded silica and polymeric stationary phases designed for solid-phase extraction (SPE) are available with a wide variety of functionality, and would make ideal packing material for this application. These materials will effectively trap the analytes from the low-pressure gas stream, and can then be desorbed by high-pressure supercritical CO_2. The considerations are similar to those when using coated silica columns. It is important when using such a system that breakthrough of the analytes from the sorbent does not occur and also that the desorption behaviour is suitable for online chromatographic analysis. Desorption is performed by increasing the trap temperature or by using the supercritical fluid to desorb the sample. The process is effectively the same as SPE, with supercritical CO_2 as the desorbing solvent. The stationary phase should be selected to have a strong enough affinity to trap the analytes from the gas stream, but to be desorbed by supercritical CO_2. Supercritical CO_2 is essentially non-polar, and it is unlikely that polar compounds could be eluted from polar stationary phases. It is not always possible to elute all the trapped analytes with CO_2, and supercritical nitrous oxide has been found to be more effective than supercritical carbon dioxide in removing solutes from adsorbents. However, the oxidizing nature of this material has resulted in explosions, and is not recommended. It is therefore more important to select the most appropriate stationary phase which will trap the analytes, and then be desorbed by the mobile phase.

Use of Modifiers and Solvent Venting

Although CO_2 is a versatile extraction solvent, sometimes modifiers are needed to solvate particular analytes or overcome analyte–matrix interactions.

This presents a problem in SFE–SFC. With cryogenically cooled traps, the modifier will be trapped and block the restrictor, or flood the column when the flow is switched to the analytical column. If the modifier becomes liquid after depressurization, it will dissolve the analytes and elute them from coated traps. Coated capillaries can be used to trap the analytes, provided the modifier is present at a sufficiently low concentration to remain as a vapour in the CO_2 gas stream. Therefore the upper limit for the modifier addition is that at which CO_2 is saturated at atmospheric pressure and the trapping temperature. For methanol the maximum addition at 25°C is 14%. It is important that the pressure in the trap does not rise, as this may cause the modifier to liquefy. Wide-bore coated capillaries may be needed for the trap to reduce back pressure, and a second, narrow-bore column will catch any breakthrough from the wide-bore trap. A short gas purge will remove any residual modifier, and the analytes can then be transferred to the analytical column dissolved by supercritical CO_2. It may be necessary to introduce a refocusing trap, which will focus the analytes from the supercritical CO_2, as the trap volumes may be quite large, which would otherwise lead to band broadening.

Apart from use of modifiers, other situations occur when large amounts of solvent are trapped with the analyte. Co-extraction of low-molecular-weight solvents or reactants along with the desired analytes is one example. Provided the co-extractant is sufficiently volatile and the analyte involatile, then the unwanted material can be removed from the intermediate trap by gas purge. The analytes can then be transferred to the analytical column with supercritical CO_2.

SFE as a Sample-Introduction Technique

As stated previously, one of the problems of cSFC is sample introduction without flooding the column with solvent. Aqueous samples are a problem for capillary and packed-column SFC, as water is only slightly soluble in CO_2. SFE can be used as a solventless sample introduction technique to avoid this problem. One method to achieve this is to inject the sample onto a pre-column fitted with a restrictor. The solvent will flood the column for some distance. The solvent can be removed by gas purging, leaving the less volatile analytes behind. The entire pre-column is then pressurized with supercritical CO_2 to dissolve the analytes and carry them to the analytical column. In effect, the pre-column is acting as an SFE cell. Samples dissolved in aqueous media can be concentrated and transferred to packed or capillary columns while maintaining high efficiency. The use of solid sorbents has proved very useful in sample introduction to SFC. The dissolved analytes are injected onto a sorbent, the solvent can then be removed by evaporation and the analytes transferred to the analytical column using SFE–SFC. The whole process has been called SPE–SFE–SFC. This method is particularly applicable to biological samples where the analyte has no chromophore. These are often thermally labile, and therefore analysis by GC or HPLC is problematical. Direct sample introduction to SFC is also a problem due to the aqueous nature of the samples. Use of an intermediate trap and solvent purging to remove the water and introduce the analytes to the SFC column allows much larger samples to be introduced, improving sensitivity by a factor of 100 or more. In environmental analysis, samples of several hundred millilitres can be passed through a solid-phase extraction cartridge to concentrate impurities. The cartridge can then be eluted with CO_2 to the analytical column. This system could also be used as an HPLC–SFC interface.

Optimization of Conditions for SFE–cSFC

A number of parameters must be optimized for successful analysis by coupled SFE–cSFC. Principal among these are the conditions for quantitative extraction. This should begin with a determination of the supercritical fluid extractability of the analyte(s) from the non-sorptive matrices (filter paper, etc.) to assess the appropriate solvent, density and temperature conditions. Trial runs on spiked samples then allow investigations of matrix–solute interactions; if necessary these may be overcome by a period of static extraction. The kinetics of extraction must then be determined in order to define the required extraction time.

Factors affecting the efficiency of intermediate trapping must then be addressed. The nature of the analyte is crucial, while the possible presence of co-extracted, interfering compounds demands either selectivity during extraction, or the trapping on an adsorbent from which selective desorption into the SFC column is possible. The sample size must be carefully chosen so that the capacity of the SFC column is not exceeded, and the extracting supercritical solvent must be of sufficient purity to avoid introduction of extraneous material into the column. Finally, the conditions for efficient SFC analysis must be optimized, preferably offline. Correct choice of column, temperature and pressure/density programme are vital. Compromises may be inevitable if the extracted analytes have a range of polarities.

Conclusion

Coupled SFE–SFC has shown itself to be a very useful technique for those samples for which it is applicable. The ability to transfer all the extract to the analytical column without manipulation increases sensitivity, reduces contamination and sample handling. The overloading of capillary columns is avoided. Now that methods for using modifiers in the extraction solvent and SFE sample injection methods have been developed, there is every likelihood that SFE–SFC will become a more widely used technique.

See also: **II/Chromatography: Supercritical Fluid:** Fourier Transform Infrared Spectrometry Detection; Historical Development; Instrumentation; Large-Scale Supercritical Fluid Chromatography; Theory of Supercritical Fluid Chromatography.

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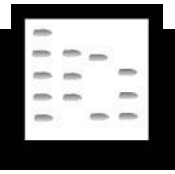
SUPERHEATED WATER MOBILE PHASES: LIQUID CHROMATOGRAPHY



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At room temperature, water on its own is an unattractive solvent in liquid chromatography. In reversed-phase chromatography, water is a weak eluent and is often regarded as an inert component of the mobile phase. It is mainly used to dilute a stronger organic component and thus control the overall eluent strength. In contrast, in normal-phase chromatography, water is a powerful eluent and interacts strongly with the stationary phase, often deactivating it. Even trace amounts in a nonpolar eluent (or even in a sample) will markedly alter the retention properties of a silica surface. In separation methods aqueous eluents are used primarily for ion exchange chromatography or for the size exclusion separation of biological molecules.

However, this represents the situation at room temperature and atmospheric pressure. When liquid water is heated under pressure, its dielectric constant, viscosity and surface tension all decrease. These changes in the properties of water are well known but have largely remained the province of the physical chemist and chemical engineer. They have been widely studied because of the importance of water as a heat transfer agent and they play their part in the design and construction of steam power generation plant and in related areas. Above 374°C under a pressure of 221 bar, a single supercritical phase is obtained. Although these conditions seem extreme for the laboratory, they occur in nature in the ocean depths at the spreading points in the earth's crust where water issues from fumeroles at 350–400°C and 250 bar.

In recent years organic chemists have been attracted by the possibility of using superheated or supercritical water to achieve clean solvent-free conditions and to generate novel reaction conditions which are not available at room temperature. It has also been employed as a solvent for the high temperature oxidation for waste remediation or for the destruction of hazardous materials such as nerve gases and explosives as an alternative to high temperature incineration. In inorganic chemistry, supercritical water has been used as a solvent to enable high temperature reactions to be carried out without the inconvenience of using molten salts.

However, the analytical chemist has made little use of water under pressure, although the potential of supercritical water as a fluid solvent for chromatography was recognized by Lovelock in 1958. Some work has exploited steam as a mobile phase in gas chromatography, but the condensed phase has largely been ignored. Although liquid chromatographers have used elevated temperatures to improve separations or efficiencies, in almost every case the composition of the organic–aqueous eluent was kept