



## Review

# The many faces of packed column supercritical fluid chromatography – A critical review



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## ARTICLE INFO

## Article history:

Received 2 August 2014

Received in revised form

15 December 2014

Accepted 30 December 2014

Available online 10 January 2015

## Keywords:

Carbon dioxide

Elution strength

Fluid properties

Retention mechanisms

Subcritical fluid chromatography

Supercritical fluid chromatography

## ABSTRACT

Packed column sub- and supercritical fluid chromatography (SFC) is a versatile separation method: on the one hand the number of parameters acting on the quality of a separation is very large, and the effects of these parameters can be complex (and not always fully understood). But on another hand, due to numerous advantageous properties of CO<sub>2</sub>-based mobile phases, method development is a fast task. This paper is a review of the main features of SFC, focusing essentially on achiral separations. However, several fundamental aspects discussed here are also relevant to chiral SFC separations. This is not intended to be an extensive review, as the way to practice SFC has somewhat evolved with time. We rather wished to provide an expert opinion on the characteristics of the method, pointing at the sources of difficulty and displaying the wide possibilities that it offers. A large number of selected applications concerning several different areas are also presented.

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## 1. Introduction

In this young 21st century, on a global scale, carbon dioxide is an object of fantasy and worry. Its concentration in the earth atmosphere increases continuously and may be the cause, alongside other factors, of global warming. Thus it may seem paradoxical that carbon dioxide in chemistry could be considered a green solvent. Because relativity applies to human judgment as well as the laws that rule the universe, this positive aspect of carbon dioxide is revealed when comparing it to other solvents classically used in chemistry (aromatics, alkanes, chlorinated solvents).

In analytical chemistry, and separation science in particular, the quest for methods with low consumption of solvents, or environmentally friendly solvents has gone through a number of stages. We will exclude from this discussion the aqueous methods applying to ionic species, as ion-exchange chromatography and capillary electrophoresis (CE) are intrinsically “greener” than other chromatographic methods, because they employ water, and no solvent could be greener than water. CE has the extra advantage of employing extremely small quantities of solvent per analysis.

The definition of a green solvent given by Capello [1] takes account of health, safety and biodegradability, while also respecting the environment (avoiding ozone depletion and producing less emission to air) and involving renewable resources. To evoke the greenness of a solvent, one should also take account of the production and possible recycling processes and their energy costs [2].

For column chromatography, recent years have seen a tendency to reduce column dimensions. The decrease in column length is favored by the concomitant decrease in stationary phase particle diameter that allows a high efficiency to be maintained. As a consequence of column internal diameter decrease, proportional flow rate reduction is causing a reduced consumption of solvents. This all resulted in the creation of ultra-high performance liquid chromatography (UHPLC), that necessitated special pumping systems that could achieve 1000 bars and highly resistant silica supports to stand up to such high pressures. However, a complete assessment of the greenness of UHPLC should not be limited to reduced solvent consumption but should also take account of the energy

costs associated with the manufacture, maintenance and usage of the instrument and columns.

Other possible ways, which seemed appealing some years ago, are attracting less attention today, such as high-temperature liquid chromatography (HTLC). This method was attractive in many ways, because it promised the use of pure water as a mobile phase. Indeed, while water is a weak solvent in reversed-phase liquid chromatography at room temperature, when heated to high temperature (100–200 °C) its polarity is getting closer to that of organic solvents. As a result, high-temperature water has a higher elution strength and can elute compounds with low polarity that would have only limited aqueous solubility at room temperature. Unfortunately, the technical constraints, imposed by the need to heat and cool down the fluid, the limited number of available stationary phases capable of withstanding high temperatures [3] and the question of stability and solubility of the analytes have so far restricted the progress of HTLC to the academic laboratories.

However, other proposals have taken the long way to go from the university lab benches to the industry. The case for superficially porous particles is emblematic: in 1969, Jack Kirkland demonstrated a high speed HPLC separation with so-called “controlled surface porosity support” of 40 μm diameter in less than 30 s [4]. It took more than 20 years to find a commercial version available with the marketing of 7 μm Poroshell particles [5] and another 20 years to find them used routinely with sub-3 μm particle size. The progress of supercritical fluid chromatography, as will be further discussed below, has been similarly slow. Thus who may draw a conclusion on the future of HTLC?

If high temperature is not desirable, the possible solvents applying for the title of “green solvents” and possibly useful for chromatography are not numerous. Indeed, a good solvent for column chromatography should also have a limited viscosity to favor high diffusion coefficients and possible high flow rates, and an appropriate polarity allowing for the elution. For instance, glycerol that is produced in large quantities as a by-product of the transesterification of triglycerides of vegetable oils [6], or its derivatives like solketal [7] are very polar and viscous, two qualities that make them unfit for HPLC at usual temperatures.

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