Analytical extractions with water at elevated temperatures and pressures

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Water can be used effectively as solvent in pressurized hot water extraction (PHWE) because the physico-chemical properties of water are readily altered through changes in temperature and pressure. Temperature is the main parameter affecting extraction, but time and flow rate are also essential in solubility-limited extractions. PHWE has been applied to a variety of analytical extractions (e.g., organic pollutants, pesticides, flavors, fragrances, and metals). PHWE has often shown similar or better extraction recoveries and efficiencies than many conventional methods (e.g., Soxhlet, accelerated solvent extraction and supercritical fluid extraction). PHWE systems can easily be coupled to chromatographic separation (e.g., LC or GC).

Keywords: Extraction; Flavor; Fragrance; Isolation; Metal; On-line coupling; Organic pollutant; Pressurized hot water; Sub-critical water

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1. Introduction

Pollution of the environment is a source of increasing concern. Modern technology, if properly applied, offers one way to reduce the stress on the environment. Finding techniques and processes that at the same time are effective, economical, safe, environmentally friendly and practical is of critical importance. Recycling of materials and chemicals within processes is desirable as part of this. On the laboratory scale, new knowledge and advanced techniques are making it possible to replace traditional analytical methods relying on hazardous organic solvents with approaches that reduce or eliminate the need for organic chemicals. Beyond the environmental issues, improving the efficiency and the reliability of techniques and reducing total analysis times are important in their own right.

In addition to the most common supercritical fluids (e.g., carbon dioxide), water is interesting for use as medium and reagent in chemical reactions and isolation and purification processes. Its benefits are that it is non-toxic, non-flammable, cheap and easily available. At room temperature, water is too polar a solvent for many organic compounds, but, at elevated temperatures, it becomes less polar, making it an interesting and environmentally friendly alternative to organic solvents. Because many compounds are degraded above the critical temperature of water (374°C), analytical applications usually take advantage of lower temperatures, where the useful physicochemical properties of water still exist to an adequate degree. Pressurized hot water extraction (PHWE) of a wide variety of compounds from different matrices can be efficient at temperatures considerably below the critical temperature of water.

The purpose of this review is to present information on applications in the area of analytical chemistry relevant to PHWE. Other review-type articles have recently been published in this area:

- Smith [1] and Ramos et al. [2] gave general overviews of extractions with superheated water;
- Ong et al. [3] described the applicability of PHWE to the analysis of bioactive marker compounds in botanicals and medicinal plant materials; and,
- Herrero et al. [4] included water as extraction medium in their review of sub-critical and supercritical fluid extraction (SFE) of functional ingredients from different natural sources.

References related to the applications in the area of PHWE of natural sources and quoted in these two last publications [3,4] are not included in the present review. The reader is also referred to the new, comprehensive review of Weingärtner and

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Franck [5], which focuses on the properties and the use of supercritical water as a solvent.

2. Properties of water affecting extractions

The critical temperature (T_c) of water (H_2O) is 374.1°C and the critical pressure (P_c) is 221 bar. Pressurized hot water (PHW) (the terms sub-critical water, near-critical water and superheated water are also applied) is typically used in extractions at temperatures above 100°C but below 374.1°C. These conditions are often sufficient to produce the physicochemical properties of interest. Pressure is usually high enough to keep the water in liquid state. However, the term PHW may also be applied to the vapor phase, where sufficient pressure (ca. 5–10 bar) is applied to provide transportation.

The dissolving power of supercritical water (SCW) is high, and solubility can be tuned through changes in temperature and pressure [6–9]. Also, PHW offers this advantage on a smaller scale. In the vicinity of the critical point, density is a strong function of pressure (Fig. 1). The relative permittivity (e_r) of water at room temperature is high (ca. 78.5), but it decreases with increasing temperature, making organic non-polar compounds more soluble in water (Fig. 1) [10–15]. The mass-transfer properties of PHW are enhanced because diffusion coefficients of solutes are higher in PHW than in water at STP [16–18]. The reduced viscosity and the surface tension of PHW also allow more favorable mass-transfer properties than in water at STP.

Hydrogen bonding of water is strong at STP, and, in general, the hydrogen bonding in water becomes weaker with increasing temperature and decreasing density. This contributes to the properties of PHW. Under supercritical conditions, hydrogen bonding is noticeably weakened but not completely absent [19–26].

The reactivity of PHW greatly depends on pressure and temperature. High temperatures may have negative effects on extraction and isolation processes because thermally-labile compounds may be degraded, the amount of co-extracted compounds (other than

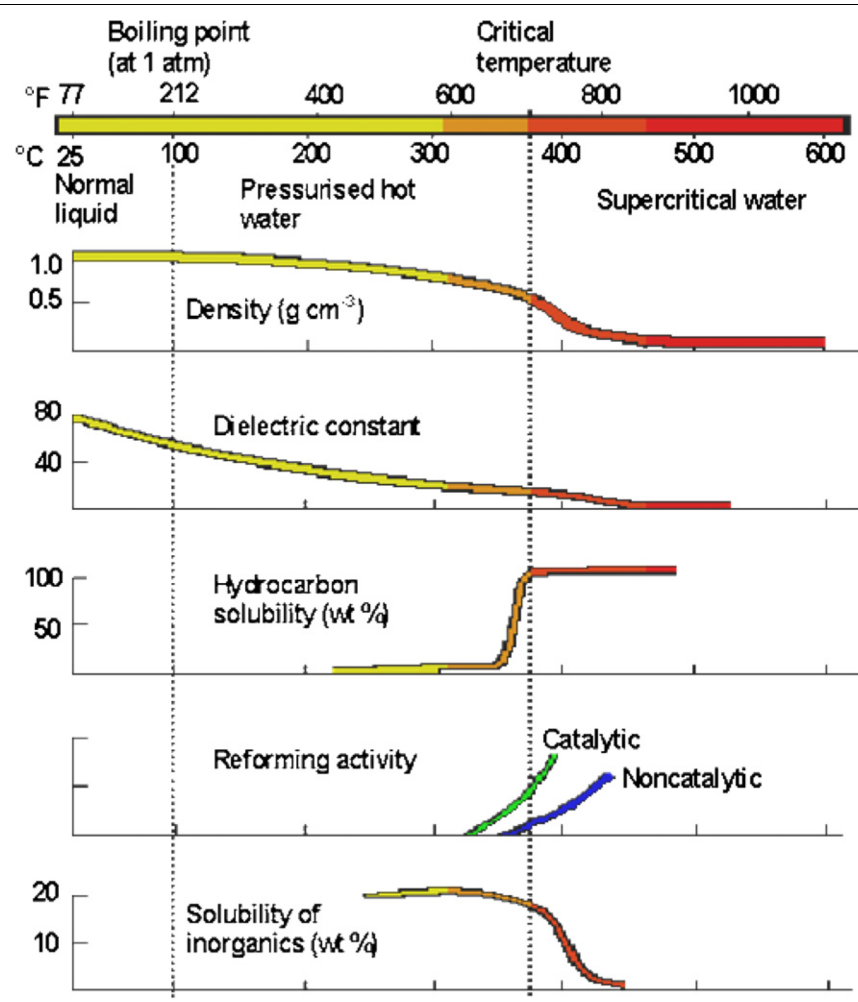

Figure 1. Some properties of water in the pressure range 21.8–30 MPa [27].