Review

Direct supercritical fluid extraction of water-based matrices

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Abstract

A short review on direct supercritical fluid extraction (SFE) of organic compounds from aqueous samples is presented. The SFE methodology of water samples is conceptually different from that of solid matrices, and a relatively small number of papers on this subject has been published. As the most promising appears continual SFE of water samples with pure CO_2.

Keywords: Supercritical fluid extraction; Water analysis; Reviews

Contents

1. Introduction

Supercritical fluid extraction (SFE) has proved to be a method for sample preparation with very good perspectives. The advantages of SFE over conventional liquid extraction methods follow from the properties of a supercritical fluid, which at moderate densities possesses sufficient solvation power, lower viscosity, and higher solute diffusivity. All parameters can be simply controlled by varying pressure (density) and temperature. Because of enhanced mass transfer in the supercritical fluids, the sample preparation is

much faster and more selective. The separation of solute from the supercritical effluent is usually performed by decompression to atmospheric pressure at room temperature because SFE solvents are usually gaseous at ambient conditions (CO_2, N_2O, etc.).

However, analytical SFE applications are so far focused mainly on solids. The experimental setup of the apparatus for SFE of contaminants from solids is conceptually simple and straightforward. To obtain quantitative analyte recovery in a limited time under given conditions of pressure and temperature of the supercritical fluid and at a specified volume flow-rate through a matrix, optimization and quantitation of sever-

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al steps are required. These include sufficient analyte solubility in a supercritical fluid, successful analyte displacement on the matrix surface by a supercritical fluid, and its sufficiently fast transport from matrix particles to the expanding supercritical fluid. The analyte transport from the extraction vessel and its quantitative trapping from the expanding stream of supercritical effluent also must be quantitated.

SFE of aqueous (or commonly liquid) samples can be performed, as that of solid, in static or dynamic mode. The process resembles liquid–liquid extraction and a decisive parameter is the analyte distribution coefficient between supercritical fluid and aqueous (liquid) phase. From the point of view of analyte transport from the extraction vessel, the dynamic mode is preferred, because of possible precipitation of analytes during pressure decrease in static mode.

As supercritical CO_2 is mostly used at densities of 0.4–0.8 g/ml, the dynamic extraction is based on movement of supercritical fluid drops through a bulk of aqueous sample upward or liquid drops downward in the extraction vessel. From the kinetic point of view, analyte diffusivities in water and supercritical CO_2 and efficiency of phase exchange are decisive for quantitative extraction recoveries, accessible under given values of analyte distribution coefficients. The specific surface area of the supercritical fluid bubbles plays of course an important role [1]. In case of kinetic limitations, the extraction rate may be e.g. independent of the flow-rate of the supercritical fluid.

The analyte distribution coefficient is defined as the ratio of the analyte molar fractions, $K = y/x$, in the supercritical (y) and the aqueous (x) phase. For a rough estimation of the K value, the molar fractions can be replaced by the solubilities of the analyte in the phases (solubilities of compounds in supercritical carbon dioxide are given e.g. in [2]). There also exist equilibrium data for SFE from water of alcohols, acetone, polycyclic aromatic hydrocarbons, volatile aromatics, chlorinated hydrocarbons, phenols ([3–5] and references cited therein) and other polar [6] and non-polar [7] compounds.

Supercritical carbon dioxide is mostly used as the extracting fluid. It behaves as a non-polar

solvent. The SFE of water samples with CO_2 will thus be a suitable method for analysis of non-polar analytes. For example, the K value for benzene is four orders of magnitude higher than that for phenol [7]. In an early paper on direct SFE of water samples by Ehntholt et al. [8] is, on the basis of experimental results, written: "In general, compounds that were volatile and/or not highly soluble in water were readily extracted under conditions used. Compounds of higher solubility did not show evidence of extraction." From this point of view, the SFE of water samples in the simple and mostly used setup for SFE of solids can hardly be competitive with the classical and established liquid–liquid extraction, because the same effect can be achieved by simpler means. It is not a problem to separate non-polar compounds from water using liquid–liquid extraction, solid-phase extraction, solid-phase microextraction [9], microwave extraction [10], etc. Modification of the carbon dioxide polarity by addition of a polar organic solvent like at SFE of solids need not be helpful because the polar modifiers (e.g. methanol) can be readily dissolved in the aqueous phase. The use of more-polar supercritical fluids like ammonia and/or nitrous oxide for the purpose of SFE of organics from water is questionable.

There are further problems associated with the SFE of contaminants from water. The solubility of water in supercritical carbon dioxide is several grams per liter [11] (depending on temperature and pressure). Linear restrictors, which are mostly used in SFE, suffer from plugging by ice formation during supercritical fluid expansion. Moreover, at the SFE on-line mode a fluid may introduce water into the final analytical system, which is usually undesirable. Although it has been recently shown [12] that the stream of a supercritical fluid can be dried by means of various solid sorbents without losses of analytes, the presence of water in the effluent stream after extraction may be a weak point of the method.

2. Applications

Only papers dealing with direct SFE of aqueous-based matrices are reviewed. Indirect

SFE (solid-phase extraction followed by SFE of analytes from the sorbent or disk) is not discussed. These methods have been used e.g. for analysis of polychlorinated benzenes [13], pesticides and phthalate esters [14], organochlorine pesticides and herbicides [15], phenols [16], poly-aromatic hydrocarbons [17], explosives (dinitro- and trinitrotoluenes) [18], polychlorinated bi-phenyls [19], non-ionic surfactants [20] and other compounds in water. It is interesting that direct SFE for concentration of organic compounds from water at ppb levels was tested already in 1983 [21].

The majority of works described in the papers uses for direct SFE of aqueous matrices usually one of two setups: either the bulk volume of liquid is extracted with supercritical fluid or a small volume of water is loaded onto a cartridge packed with a suitable inert grained material. The latter arrangement has the advantage that the equipment for the SFE is similar to that for common SFE of solids. A disadvantage is the small sample volume available and the detection limit may not be sufficient for some applications.

In the work by Koski et al. [22] an on-line SFE–supercritical fluid chromatography (SFC) analysis of prostaglandins in aqueous solutions is described. A small amount (100 μl) of the solution was loaded into an extraction chamber packed with ODS or XAD-2 adsorbent material. SFE was performed using carbon dioxide (density 0.8 g/ml) at 35–50°C. The extracted solutes were focused in the solute trap. After finishing the SFE, a ten-port valve was switched to another position and the content of the trap was analyzed by SFC with flame ionization detection (FID). Minimum detectable quantities were 9–60 ng according to the type of the prostaglandin.

Hawthorne et al. [23] extracted directly phenolic compounds from waste water in a 3.5-ml cell into which 1 g of clean sand and 1 ml of waste water was placed together with derivatizing agent (trimethylphenylammonium hydroxide). After 15 min of derivatization in the closed cell (400 atm, 80°C) the phenolic methylesters were extracted from the water phase during 15 min by means of dynamic SFE.

Hedrick and Taylor [24] described an apparatus in which supercritical carbon dioxide is recirculated through the water sample. After reaching an equilibrium, a sample of the super-critical fluid is transferred by means of a valve system into the supercritical fluid chromatograph. Diisopropyl-phosphonate was analyzed using this 'closed-loop stripping' system in the concentration range of 0.834–834 mg/l (volume of water sample 8 ml). Further work of the same authors [25] showed that also other polar organic compounds, like triprolidin, pseudoephedrin and phenol, are extractable by SFE. However, SFE of organic bases from water was not successful [6] due to the fact that the pH of water during extraction decreased to 3.5 (water is saturated by supercritical carbon dioxide). Organic bases protonation increases their solubilities in water and decreases those in supercritical carbon dioxide.

When off-line SFE was used for removing of organics from water in the above works, super-critical fluid enters into the extraction cell at its bottom and a restrictor is placed at its top to prevent water breakthrough into the restrictor (see Fig. 1). A similar design of the extraction cell was used also by Ong et al. [27].

An interesting approach to the SFE of water samples was chosen by Thiebaut et al. [28]. Water sample and supercritical carbon dioxide were pumped into an extraction coil (1.3 m × 0.5 mm I.D. stainless-steel capillary). The mixture of carbon dioxide and water was then separated in a phase separator by means of a hydrophobic membrane. Only supercritical carbon dioxide with dissolved solutes is able to migrate through the membrane. The supercritical phase was then analyzed by SFC with UV detection. Sampling of the supercritical phase was done by means of a valve with a loop (200 μl). Two materials of the membrane in the phase separator were able to withstand high pressures: PVDF $(-CH_2-CF_2-)_n$ and Delrin $(-CH_2-O-)_n$. Phenol and 4-chlorophenol were used as solutes for testing of the method.

Croft et al. [29] extracted chlorophenoxyacetic acids from aqueous solution by supercritical carbon dioxide containing methyl iodide in the presence of tetrahexylammonium hydrogen sulfate. The test analytes (2,4-dichlorophenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid)
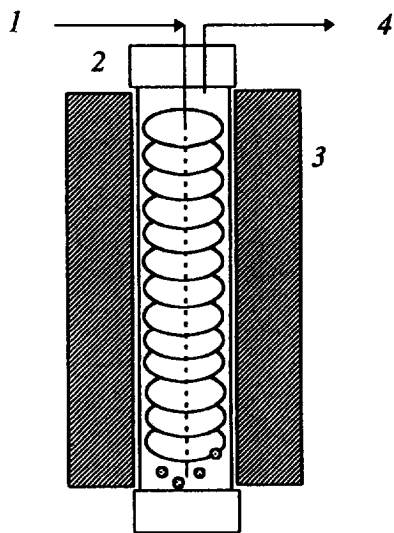
Fig. 1. Design of the extraction cell for SFE of organics from aqueous solutions used in authors' lab [26]: 1 = carbon dioxide inlet; 2 = extraction cartridge containing aluminium coil (to enhance retention of carbon dioxide in the cell; volume of the cell 30.1 ml); 3 = termostatted jacket; 4 = carbon dioxide outlet (fused-silica capillary restrictor inserted into a collection device).

were only extracted as their methyl esters when methyl iodide was present in the extraction solvent. The aqueous samples for the methylation and SFE were prepared in the inert porous matrix, which was packed into the SFE vessel (volume 10 ml). Conversion to the derivatives from 1 mg/l aqueous solution was complete in 30 min, with recoveries of 89% for 2,4-dichlorophenoxyacetic acid and 104% for 2,4,5-trichlorophenoxyacetic acid, respectively. The SFE was performed mostly at 90°C and 200 bar.

Barnabas et al. [30] extracted organochlorine pesticides from a water sample by supercritical carbon dioxide. They investigated the influence of the flow-rate of carbon dioxide and the ionic strength of the aqueous sample on recovery of analytes (lindane, aldrin, dieldrin). The volume of the water sample was 45 ml and the flow-rate of supercritical fluid varied from 0.7 to 1.5 ml/min. Extraction time was up to 2 h. It was found that the flow-rate of carbon dioxide had little effect on the analyte recoveries from water, indicating that the process is kinetically limited

by diffusion through the matrix. The recoveries of the analytes were also not affected by salt addition to the matrix.

Shimoda et al. [1] compared gaseous, liquid and supercritical carbon dioxide extraction for removing of flavor compounds from liquid foods. Alcohols, aldehydes and esters were used as model compounds (concentration 50 mg/l). The SFE was performed using a 120-ml vessel, the applied pressure ranged from 6.0 to 25 MPa and the temperature from 20 to 50°C. Extraction time was 40 min and flow-rate of carbon dioxide was maintained at 4.0 g/min. SFE showed to be highly effective in comparison with gaseous or liquid extraction. More than 95% of volatile compounds consisting of 6 to 12 carbon atoms were removed from the aqueous solution by SFE at 20 MPa and 35°C.

It is also possible to extract from water solution inorganic metal cations in the form of their chelates, as suggested by Laintz et al. [31]; free metal ions are not extractable by SFE. Laintz and Tachikawa [32] used for the SFE of lanthanides trivalent ions from 6 mol/l nitric acid + 3 mol/l lithium nitrate aqueous solution carbon dioxide with tributyl phosphate. Tributyl phosphate served as both polarity modifier of carbon dioxide and chelating agent. The best recoveries of lanthanides were achieved using 30% of tributyl phosphate in carbon dioxide with addition of thenoyltrifluoroacetone as a second extractant. Extraction were made for 15 min in a static mode and the solution was then subjected to a dynamic extraction for 30 min (350 atm and 60°C). Near quantitative recoveries were obtained for Sm^{3+}, Eu^{3+}, Gd^{3+} and Dy^{3+}. Recovery of La^{3+}, Ce^{3+}, Yb^{3+} and Lu^{3+} was lower. The worst recovery was achieved for La^{3+} (61.2%).

Some metals (Zn, Cd and Pb) are extractable from water solution as dialkyldithiocarbamate ion pairs [33]. SFE was performed for 20 min in a static mode (volume of aqueous sample 3 ml). Supercritical carbon dioxide was saturated with complexing agent (tetrabutylammonium dibutyldithiocarbamate). After in situ complexation under static conditions the product complexes were then purged from the extraction

vessel by a dynamic SFE. Recoveries of the metals for concentrations of 12–20 μg/ml were above 94% within 15 min dynamic extraction. Acidification of aqueous matrix prior to extraction resulted in recoveries greater than 95% within ten min of the SFE.

Kane et al. [34] tested direct SFE of non-ionic surfactants (alcohol phenol ethoxylates) from an aqueous matrix. Extraction cell had an internal volume 50 ml. Extraction pressure was 220 atm, temperature 45°C (density of carbon dioxide 0.84 g/ml) and flow-rate of the fluid 1 ml/min. Better results were obtained using 10 mm frit for introducing supercritical carbon dioxide into the extraction cell in comparison with simple introduction of the extracting fluid by means of 1/16 I.D. tubing. However, recovery of the non-ionic surfactant was only 60% within 120 min extraction time, even when using the frit in the inlet of the carbon dioxide.

3. Conclusion

It is apparent that in comparison with a huge number of papers in scientific literature dealing with SFE of solid samples, there is only a limited number of works devoted to the direct SFE of aqueous samples. The reasons were given already in the Introduction of this short review paper.

Authors of this paper would like to express their disbelief that direct SFE of aqueous samples has a chance to become a routine method using such relatively simple experimental apparatuses which are employed commonly for SFE of solids. However, promising way would be development of an SFE instrumentation, which will be able to utilize entirely one of supercritical fluid advantages: it is usually gas at ambient conditions (together with a certain selectivity it is also a principal advantage of the work cited above in this paper). This feature could be very useful for dynamic devices, where great volume of water is continuously pumped together with supercritical fluid into the extraction cell. In a well designed collection device will be then possible to obtain the water contaminants in a very concentrated form, which would lead to great concentration factors and good detection limits of the analysis.

References

[1] M. Shimoda, H. Ishikawa, T. Kawano and Y. Osajima, J. Food Sci., 59 (1994) 231.
[2] K.D. Bartle, A.A. Clifford, S.A. Jafar and G.F. Shilstone, J. Phys. Chem. Ref. Data, 20 (1991) 713.
[3] D. Ghonasgi, S. Gupta, K.M. Dooley and F.C. Knopf, AICHE J., 37 (1991) 944.
[4] S.-D. Yeo and A. Akgerman, AICHE J., 36 (1990) 1743.
[5] S. Sengupta, S. Gupta, K.M. Dooley and F.C. Knopf, J. Supercrit. Fluids, 7 (1994) 201.
[6] J.L. Hedrick and L.T. Taylor, J. High Resolut. Chromatogr., 15 (1992) 151.
[7] S. Gupta, D. Ghonasgi, K.M. Dooley and F.C. Knopf, J. Supercrit. Fluids, 4 (1991) 181.
[8] D.J. Ehntholt, C. Eppig and K.E. Thrun, in I.H. Suffet and M. Malaiyandi (Editors), Advances in Chemistry Series No. 214, Organic Pollutants in Water: Sampling, Analysis and Toxicity Testing, American Chemical Society, 1987, p. 483.
[9] D. Louch, S. Motlagh and J. Pawlyszin, Anal. Chem., 64 (1992) 1187.
[10] F.I. Onuska and K.A. Terry, in P. Sandra and G. Devos (Editors), Sixteenth International Symposium on Capillary Chromatography, Vol. 1, Hüthig, Heidelberg 1994, p. 830.
[11] M.S. Kuk and C.J. Montagna, in M.E. Paulitis, J.M. Penninger, R.D. Gray and K.P. Davidson (Editors), Chemical Engineering at Supercritical Fluid Conditions, Ann Arbor Science Publishers, Ann Arbor, MI, 1983, p. 101.
[12] M.D. Burford, S.B. Hawthorne and D.J. Miller, J. Chromatogr., 657 (1993) 413.
[13] J.B. Pawliszyn and N. Alexandrou, Water Pollut. Res. J. Can., 24 (1989) 207.
[14] J.L. Ezzell and B.E. Richter, J. Microcol. Sep., 4 (1992) 319.
[15] I.J. Barnabas, J.R. Dean, S.M. Hitchen and S.P. Owen, J. Chromatogr. Sci., 32 (1994) 547.
[16] P.H.-T. Tang and J.S. Ho, J. High Resolut. Chromatogr., 17 (1994) 509.
[17] S.B. Hawthorne and D.J. Miller, J. Chromatogr. Sci., 24 (1986) 258.
[18] G.C. Slack, H.M. McNair, S.B. Hawthorne and D.J. Miller, J. High Resolut. Chromatogr., 16 (1993) 473.
[19] P.H. Tang, J.S. Ho and J.W. Eichelberger, J. Assoc. Off. Anal. Chem., 76 (1993) 72.
[20] M. Kane, J.R. Dean, S.M. Hitchen, C.J. Dowle and R.L. Tranter, Anal. Proc., 30 (1993) 399.
[21] D.J. Ehntholt, K. Thrun, C. Eppig and P. Ringand, Int. J. Environ. Anal. Chem., 13 (1983) 219.

[22] I.J. Koski, B.A. Jansson, K.E. Markides and M.L. Lee, J. Pharmacol. Biomed. Anal., 9 (1991) 281.

[23] S.B. Hawthorne, D.J. Miller, D.E. Nivens and D.C. White, Anal. Chem., 64 (1992) 405.

[24] J. Hedrick and L.T. Taylor, Anal. Chem., 61 (1989) 1986.

[25] J.L. Hedrick and L.T. Taylor, J. High Resolut. Chromatogr., 13 (1990) 312.

[26] V. Janda, J. Fanta, J. Vejrosta and K.D. Bartle, The 3rd European Symposium on Analytical Supercritical Fluid Chromatography and Extraction, Uppsala, Sweden, September 6–8, 1995.

[27] C.P. Ong, H.M. Ong, S.M.Y. Li and H.K. Lee, J. Microcol. Sep., 2 (1990) 69.

[28] D. Thiebaut, J.-P. Chervet, R.W. Vannoort, G.J. De Jong, U.A.Th. Brinkman and R.W. Frei, J. Chromatogr., 477 (1989) 151.

[29] M.Y. Croft, E.J. Murby and R.J. Wells, Anal. Chem., 66 (1994) 4459.

[30] I.J. Barnabas, J.R. Dean, S.M. Hitchen and S.P. Owen, J. Chromatogr., 665 (1994) 307.

[31] K.E. Laintz, C.M. Wai, C.R. Yonker and R.D. Smith, Anal. Chem., 64 (1992) 2875.

[32] K.E. Laintz and E. Tachikawa, Anal. Chem., 66 (1994) 2190.

[33] J. Wang and W.D. Marshall, Anal. Chem., 66 (1994) 1658.

[34] M. Kane, J.R. Dean, S.M. Hitchen, C.J. Dowle and R.L. Tranter, Analyst, 120 (1995) 355.