Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2011, **21**, 270–271
Mendeleev Communications

Subcritical water for the desorption of 2-chlorophenol in on-line solid-phase extraction–HPLC analysis

Mikhail A. Statkus,* Alexandra S. Sokhranyaeva, Grigory I. Tsysin and Yury A. Zolotov

Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. Fax: +7 495 939 4675; e-mail: mstatkus@gmail.com

DOI: 10.1016/j.mencom.2011.09.013

The on-line solid-phase extraction and HPLC analysis for the determination of 2-chlorophenol is based on analyte desorption with subcritical water, the subsequent effluent cooling and analyte focusing at the beginning of a chromatographic column.

Reversed-phase HPLC (RPLC) analysis is often coupled on-line with solid-phase extraction (SPE). The increase in sensitivity is complicated by so-called peak broadening, which reduces RPLC separation efficiency.[1,2] Subcritical water (SW), *i.e.*, water heated to 100–300 °C under pressure sufficient to keep it liquid, can be used as an eluent to perform RPLC separation (SW-RPLC).[3–5] Its elution strength at 200–250 °C is comparable to that of pure acetonitrile.[6] SW is rarely used for SPE,[7–10] especially, for the on-line coupling of SPE and HPLC.

Chlorophenols are priority environmental pollutants. We used 2-chlorophenol (CP) for the optimization of SPE and SW desorption conditions. We optimized[11] conditions for the quantitative SPE of eleven phenols from US EPA list (including CP) on a Strata-X sorbent (chemically modified polystyrene–divinylbenzene).†

CP was extracted from a 10 ml aqueous sample on an SPE column packed with Strata-X. After SPE extraction, the oven was heated to 150–200 °C and water was pumped through the SPE column at a constant flow rate. The effluent was collected in 0.5–1.5 ml fractions, which were analyzed by RPLC.

Temperature is the most important parameter governing the desorption of analytes with SW. Phenols were separated[12] by SW-RPLC at 100–200 °C, and we studied the desorption of CP in this temperature range. The SPE column was conditioned with 5 ml of acetonitrile and 5 ml of deionized water. Then, 10 ml of an aqueous solution of CP was passed through the column at 1 ml min^{-1}. After that, the water flow was stopped and the oven was heated for 10 min; next, desorption was performed at a water flow rate of 0.5 ml min^{-1} (Figure 1). Desorption was not observed below 150 °C. A minimum analyte peak width was obtained at 200 °C (the peak widths at half-height and at baseline were 1 and 2.5 ml, respectively). Off-line desorption was also performed with pure acetonitrile at ambient temperature (Figure 1). The peaks obtained with water at 200 °C and with acetonitrile are similar in width, although the volume corresponding to a peak maximum for acetonitrile desorption is 0.5 ml smaller than that for SW desorption. A further increase in the temperature can result in the decomposition of either the analyte or the SPE packing; thus, the on-line experiments were performed at 200 °C.

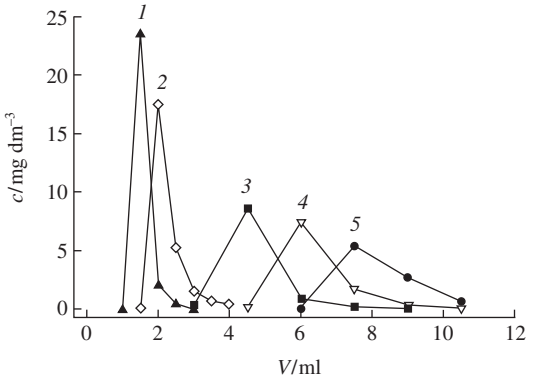

Figure 1 Off-line desorption of CP from a Strata-X SPE column performed (*1*) with acetonitrile at room temperature, with subcritical water at (*2*) 200, (*3*) 175, (*4*) 160 and (*5*) 150 °C. CP was extracted from 10 ml of an aqueous solution (1.3 mg dm^{-3}).

Figure 1 shows that the volume corresponding to peak maxima almost linearly increases with decreasing SW temperature. This fact is in good agreement with published data,[6] which were obtained in a range from 50 to 180 °C.

The on-line desorption was performed with SW; the effluent was cooled down to room temperature and passed through a RPLC column. A 5 ml effluent portion was allowed to pass through the RPLC column; next, the rest of the effluent was discarded to waste and the RPLC separation with an acetonitrile–water gradient at room temperature was started.

Figure 2 represents the resulting chromatograms. CP was focused at the beginning of the RPLC column as a narrow peak (half-width of 8.1±0.2 s), which is similar to the peak obtained with the direct injection of 20 μl of an acetonitrile solution (half-width of 9.1±0.3 s).

The on-line SPE–RPLC analysis is based on the simultaneous SPE elution and RPLC separation with the same mobile phase. A similar experiment was performed: CP was desorbed from the SPE column with the same gradient program used for RPLC

† The device for on-line SPE-HPLC was assembled in-house from commercially available HPLC equipment (for schematic diagram, see Online Supplementary Materials). It consisted of three Stayer-2 HPLC pumps, an MS-16 gradient mixer, two automatic injectors, and a UVV-104 UV-visible detector. All HPLC equipment was from Aquilon, Russia. The device for SW desorption was also assembled in-house. A forced convection oven from an LKhM-80 gas chromatograph (Khromatograf, Russia) was equipped with a 1.8 kW heating element. Heating was controlled by a TRM-10 electronic thermostat (Oven, Russia). A P-455 pressure restrictor (Upchurch Scientific, USA) was used to prevent water from boiling. RPLC separation was carried out on a Luna 5 μm C18 column (4.6 mm i.d.; 150 mm in length) purchased from Phenomenex (USA). SPE was carried out on a stainless steel HPLC precolumn (3 mm i.d.; 40 mm in length) packed in-house with a Strata-X polymeric sorbent (Phenomenex, USA). The gradient profile for RPLC separation was 100% water at 0 min, then to 30% acetonitrile for 1 min, then from 30 to 60% acetonitrile for 10 min, then from 60 to 100% acetonitrile for 5 min. Afterwards, the mobile phase composition was returned to initial conditions for 4 min. Detection wavelength was 275 nm.

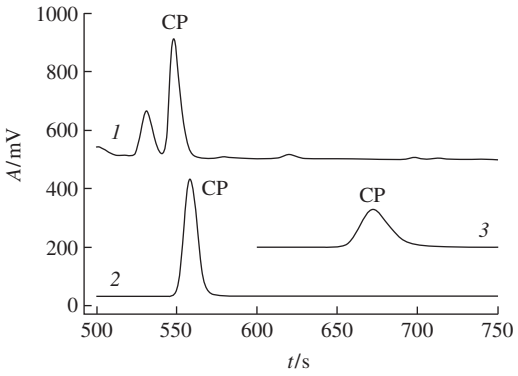

Figure 2 (*1*) On-line coupling of SPE and RPLC *via* SW desorption at 200 °C, (*2*) direct injection RPLC analysis of 20 μl of acetonitrile solution of CP, (*3*) on-line coupling of SPE and RPLC *via* acetonitrile gradient desorption. 1.3 μg CP was dissolved in 20 μl of acetonitrile for direct injection (c = 65 mg dm^{-3}) or in 10 ml of water for SPE (c = 0.13 mg dm^{-3}).

analysis. The peak half-width was 20.6±0.5 s, and the retention time significantly increased (up to 20%) (see Figure 2, curve *3*).

However, we faced significant SPE column bleeding when on-line desorption was performed with SW at 200 °C. A blank on-line SPE–RPLC run was carried out with the SPE of 10 ml of a deionized water sample and SW desorption. A large number of extraneous peaks were present in blank chromatograms, thus complicating the identification of the CP peak. Fortunately, we have not observed any significant decrease in recovery or gradual back-pressure rise during 20–30 successive on-line SPE–HPLC runs. The column bleeding complicates the development of the technique aimed at the simultaneous RPLC determination of EPA phenols.

Thus, the proposed procedure increases the effectiveness of the on-line coupling of SPE and HPLC. It is based on the desorption of analytes with SW, the subsequent effluent cooling and analyte focusing at the beginning of the RPLC column. Conditions for the SW desorption of 2-chlorophenol from Strata X sorbent were chosen.

This study was supported by the President of the Russian Federation (grant no. NSh-4836.2010.3), the Russian Foundation for Basic Research (grant no. 09-03-00301-a), and the Ministry of Education and Science of the Russian Federation (grant no. 14.740.11.0365).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2011.09.013.

References

1 E. R. Brouwer, S. Kofman and U. A. T. Brinkman, *J. Chromatogr. A*, 1995, **703**, 167.
2 R. Wissiack, E. Rosenberg and M. Grasserbauer, *J. Chromatogr. A*, 2000, **896**, 159.
3 K. Hartonen and M.-L. Riekkola, *TrAC, Trends Anal. Chem.*, 2008, **27**, 1.
4 Y. Yang, *J. Sep. Sci.*, 2007, **30**, 1131.
5 B. Yan, J. Zhao, J. S. Brown, J. Blackwell and P. W. Carr, *Anal. Chem.*, 2000, **72**, 1253.
6 T. M. Pawlowski and C. F. Poole, *Anal. Commun.*, 1999, **36**, 71.
7 L. J. Lamm and Y. Yang, *Anal. Chem*., 2003, **75**, 2237.
8 J. R. Bone and R. M. Smith, *Anal. Commun.*, 1999, **36**, 375.
9 R. Tajuddin and R. Smith, *J. Chromatogr. A*, 2005, **1084**, 194.
10 R. Tajuddin and R. M. Smith, *Analyst*, 2002, **127**, 883.
11 A. S. Sokhranyaeva, M. A. Statkus, G. I. Tsizin and Yu. A. Zolotov, *Zh. Anal. Khim.*, 2010, **65**, 1181 [*J. Anal. Chem.* (*Engl. Transl.*), 2010, **65**, 1155].
12 T. Yarita, R. Nakajima and M. Shibukawa, *Anal. Sci.*, 2003, **19**, 269.

Received: 17th March 2011; Com. 11/3698