

Parameters affecting the accelerated solvent extraction of polymeric samples

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Parameters Affecting the Accelerated Solvent Extraction of Polymeric Samples

Xianwen Lou, Hans-Gerd Janssen,* and Carel A. Cramers

Laboratory of Instrumental Analysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Accelerated solvent extraction (ASE) is applied for the extraction of monomers and oligomers from polymeric samples. Two polymers, nylon-6 and poly(1,4-butylene terephthalate), are selected as the model samples. The kinetics of mass transfer in ASE of polymeric samples are discussed. The effects of various experimental parameters, such as temperature, pressure, static time, flow rate, etc., on the ASE extraction efficiency are investigated systematically. Furthermore, some general guidelines for the optimization in ASE extraction of polymeric samples are given. The extraction temperature and the type of solvent used are found to be the most important parameters affecting the ASE extraction efficiency of polymeric samples.

Most of the samples that have to be analyzed by chromatography are too complex, too dilute, or, in their original state, incompatible with the chromatographic system. For these samples, direct injection cannot be used and sample pretreatment prior to injection of the sample into the chromatography system is required. Sample preparation methods generally used by analytical chemists nowadays are both time and solvent consuming. According to a recent survey, two-thirds of the analysis time in chromatographic analyses is devoted to sample preparation. Moreover, this step accounts for at least one-third of the error generated by the analytical method.¹ The importance of sample preparation in analytical chemistry, therefore, cannot be overemphasized. The improvement of sample preparation methods or the development of new methods will reduce the analysis time and allow the analyst to produce more precise results.

For solid samples, the most widely used extraction method is Soxhlet extraction. In the last few years, various new sample preparation techniques, such as microwave-assisted extraction (MAE),^{2,3} sonication extraction,^{4,5} supercritical fluid extraction (SFE)^{6–8} and accelerated solvent extraction (ASE)⁹ have been developed as alternatives to the Soxhlet procedure. Compared

to Soxhlet extraction, each of the new techniques reduces the amount of solvent required and/or shortens the sample preparation time. The time- and solvent-consuming nature of Soxhlet extraction is generally imputed to the slow diffusion of the analytes from the sample matrix into the extraction fluid and/or to the slow desorption of the components from the sample matrix. By the introduction of microwave or sonication, by using supercritical fluids, or by extracting the components at elevated temperatures, the rates of diffusion and desorption can be increased significantly. Among the new sample preparation methods, ASE is the method introduced most recently. Only very few reports on ASE have been published so far.^{9,10} One of the general conclusions of these reports is that method development in ASE is relatively straightforward. The number of experimental parameters that have to be optimized is reduced, and at least for the extraction of the environmental samples studied, no matrix dependency of recoveries was observed. Additionally, the solvents used for conventional Soxhlet extraction can also be used for ASE.

In ASE, a solid sample is packed into the extraction cell and is then extracted with a suitable solvent at elevated temperature and pressure conditions. Richter et al.⁹ investigated the ASE extraction of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls, and total petroleum hydrocarbons from environmental samples and found that the extraction temperature, pressure, and volume of solvent used are important parameters affecting the extraction efficiency in ASE. In their experiments, the samples were first extracted statically. After the static period, fresh solvent was introduced to flush the cell and the lines. Liquid remained in the cell and the tubing was purged with pressurized nitrogen gas. In the extraction of these environmental samples, ASE gave recoveries comparable to or better than those obtained with Soxhlet and other conventional techniques. So far, no reports on ASE of polymeric samples have been published.

In this contribution, the ASE extraction of monomers and oligomers from polymeric samples is studied. A simple experimental setup is proposed which allows ASE extraction to be performed in the static mode, the dynamic mode, or as a combination of these two modes. Two polymeric materials, nylon-6 and poly(1,4-butylene terephthalate) (PBT), are selected as the model samples. The mechanisms of ASE extraction of polymeric samples are discussed. The effects of various experimental parameters, such as temperature, pressure, flow rate, static time, and type and volume of solvent used are investigated systematically. Furthermore, guidelines for the optimization of ASE extractions of polymeric samples are given.

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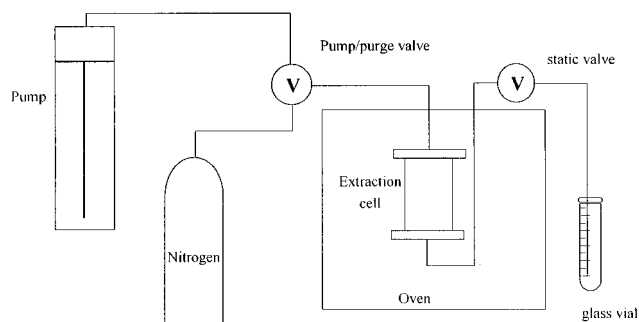


Figure 1. Schematic illustration of the ASE system.

EXPERIMENTAL SECTION

A home-built ASE system was used. Figure 1 shows a schematic diagram of this system. Apart from being suited for ASE, the system could also be used for SFE. A modified Varian 8500 syringe pump (Varian Associates, Sunnyvale, CA) was used to deliver the extraction solvent. The pump was equipped with a safety rupture disk and was operated in the pressure-controlled mode. A 3 mL stainless steel cell (Suprex, Pittsburgh, PA) was used as the extraction cell, unless stated otherwise. The extraction cell was fitted with hand-tight connectors (Suprex) for easy installation. Stainless steel frits ($3\ \mu\text{m}$) were located at either end of the extraction cell. Fused-silica capillaries with different internal diameters and lengths were used as the restrictors to maintain the pressure inside the extraction cell during dynamic extraction. In the extraction of PBT at extraction temperatures higher than $110\ ^\circ\text{C}$, the restrictor was heated to prevent restrictor blockage. Both the purge/pump valve and the static/dynamic valve were six-way valves (CH6214, Vici AG, Schenkon, Switzerland). The extracted material was collected by directly inserting the restrictor outlet into a glass vial ($18\ \text{cm} \times 1.2\ \text{cm}$ i.d.). After collection, the extraction solvent was evaporated under a gentle flow of nitrogen, and the extracted material was redissolved in a suitable amount of chloroform.

The polymeric samples used in this study, nylon-6 (glass transition temperature, $T_g = 62.5\ ^\circ\text{C}$) and PBT ($T_g = 66\ ^\circ\text{C}$), were purchased from Aldrich (Milwaukee, WI). The polymers were ground by milling under liquid nitrogen before extraction. The highest extraction temperature tested for both polymers was $170\ ^\circ\text{C}$. At higher temperatures, the restrictor or the static/dynamic valve often blocked due to partial melting of the polymers. Soxhlet extractions and SFE extractions were performed to provide frames of reference. The details of the Soxhlet and SFE extraction of the polymers were reported previously.¹¹ Extraction efficiencies for ASE were calculated relative to the Soxhlet data.

The extracted components were analyzed using a gas chromatograph equipped with an on-column injector and a flame ionization detector (FID) (GC 8000 series, Carlo Erba, Milan, Italy). A Carbowax column ($25\ \text{m} \times 0.32\ \text{mm}$ i.d., $1.2\ \mu\text{m}$ film thickness) purchased from Chrompack (Middelburg, The Netherlands) was used for the analysis of the extracts from nylon-6. The initial temperature for the analyses was $50\ ^\circ\text{C}$. Temperature was then programmed to $250\ ^\circ\text{C}$ at $20\ ^\circ\text{C}/\text{min}$. For the analysis of the PBT extracts, an HT SimDist-CB column ($10\ \text{m} \times 0.53\ \text{mm}$ i.d., $0.17\ \mu\text{m}$ film thickness) from Chrompack was used. The initial temperature for the gas chromatographic separation was

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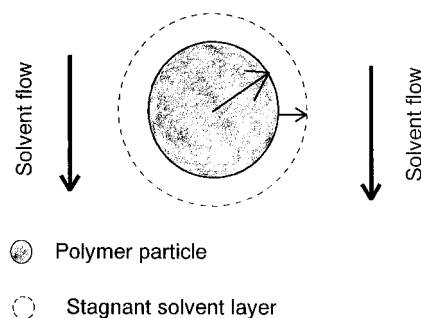


Figure 2. Schematic presentation of the three subsequent steps in the ASE extraction process.

$50\ ^\circ\text{C}$. Temperature was then programmed to $400\ ^\circ\text{C}$ at $20\ ^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

The first challenge in ASE method development is the selection of a suitable extraction solvent. For environmental samples, the selection of the solvent is relatively straightforward. For this type of samples, it was found that ASE can be performed with the same solvent as that employed in conventional extraction methods (such as Soxhlet).⁹ However, in the ASE extraction of polymeric samples, a different situation might occur. The solvents used for Soxhlet extraction of polymers are normally good swelling agents for the polymer to be extracted. Use of these solvents can be troublesome in ASE, because the polymers may (partially) dissolve in the solvents at the high extraction temperatures used. Moreover, the connecting tubing in the ASE system can be blocked by polymer molecules dissolved in the hot solvent. In this article, therefore, hexane, which is a poor swelling solvent for both nylon-6 and PBT, is chosen as the extraction solvent. Despite the poor swelling capability of hexane, with this solvent at high temperatures, excellent ASE extraction recoveries can be obtained in a short time as will be demonstrated later in this article. In the following sections, the kinetics of mass transfer in the ASE extraction process are discussed. The various operational parameters, such as temperature, pressure, static time, and flow rate, on ASE extraction recovery are investigated systematically with the ultimate aim of improving the understanding of the processes occurring during ASE extraction of polymeric samples.

Kinetics of Mass Transfer in ASE of Polymeric Samples.

The extraction process in ASE can be modeled as three subsequent steps. First, the solutes must diffuse from the core of the polymeric particles to the surface. Next, they should be transferred from the surface into the extraction fluid. Finally, the solutes are eluted out of the extraction cell. A schematic representation of these subsequent steps is depicted in Figure 2. The ASE extraction rate is limited by the slowest of these three steps. Extensive investigations on mass transfer in polymer particles have already been conducted by chemical engineers¹² and, more recently, by chromatographers.^{13–15} In previous work,¹⁵ we used the two-film kinetic model to qualitatively describe the

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extraction mechanism in SFE. In this section, the kinetic model is used to predict the effects of experimental parameters on the ASE extraction efficiency of polymeric samples.

In ASE, mass transfer from the core of the polymer particles to the surface and from the surface through the layer of stagnant solvent outside the polymer particles into the extractant is controlled by molecular diffusion. The respective diffusion coefficients are determined by parameters such as properties and structures of the polymer and the solutes, extraction temperature, and type of extraction solvent. Diffusion both in the polymer and through the layer of stagnant solvent around the polymer particles can be increased by raising the extraction temperature. Evidently, the time required for mass transfer from the core of the polymer particles to the surface will also be shorter if the size of the polymer particles is reduced. After being transferred into the extractant, the components are eluted out of the extraction cell by the flow of solvent. This elution process closely resembles a chromatographic separation. A solute is distributed between the extractant (the mobile phase) and the surface of the polymer particles (the stationary phase). Elution is faster if the solubility (the solute concentration at saturation) of the component in the extraction solvent is increased, if the interaction between the solute and the polymer surface is reduced, or if higher solvent flow rates are used. Temperature is a very effective parameter for increasing the extraction rate of the components. Elevated temperatures will increase the solubility of the solutes in the extractant¹⁶ and reduce their interaction with the polymer surface. Moreover, as already discussed above, the use of higher temperatures also enhances diffusion inside the polymer and through the stagnant solvent layer around the polymer particles. From the discussion presented above, it is evident that the kinetics of mass transfer in all the three steps governing the ASE process can be improved by operating at higher temperatures. A certain pressure is required to keep the extractant in the liquid state at temperatures above its normal boiling point.

An alternative approach to enhance molecular diffusion and transport of the extracted solutes out of the extraction cell in ASE is to use organic solvents that are both good swelling agents for the polymer and good solvents for the analytes. Diffusion is faster in the swollen polymer particles. Good solubility characteristics, on the other hand, result in rapid "elution" out of the extraction cell. Unfortunately, however, in ASE the positive effects of these solvents cannot be fully exploited because at the elevated extraction temperatures used the polymer can dissolve in the solvents. In this situation, plugging of the system tubing, valves, or restrictor easily occurs.

Although SFE and ASE are different in many respects, the mechanisms of extraction in these two techniques are very much similar. It was reported that in SFE the effects of solvent flow rate on the extraction efficiency can be used to identify which step controls the SFE extraction rate.^{15,17} A similar approach can also be adopted in ASE to determine whether the extraction is limited by diffusion inside the polymer, by transfer from the polymer surface to the flowing extraction fluid, or by the solubility in the extractant. The main difference between ASE and SFE lies in the diffusion coefficients and viscosities of the extraction fluids used. In SFE, mass transfer from the polymer surface to the

supercritical fluid extractant is very fast because of the high diffusivity in supercritical fluids. Moreover, the layer of stagnant supercritical fluid around the particle is very thin. Therefore, the rate-limiting step in SFE is either diffusion in the polymer particles or solubility in the supercritical fluid. Which step actually controls the extraction kinetics can be identified by monitoring the extraction yields at different temperatures or different flow rates.¹⁵ Compared to SFE, a slightly more complicated situation prevails in ASE. In ASE, mass transfer from the surface of the polymer particles through the layer of stagnant solvent around the particles into the extraction solvent is much slower because of the lower solute diffusivity in the extraction solvent and the relatively thick layer of stagnant solvent around the particles. In the ASE extraction of polymeric samples, the rate-limiting step hence can be diffusion inside the polymer particles, transfer from the surface into the extractant, or solubility in the extractant. If the extraction rates are controlled by solubility, larger solvent flow rates will yield higher extraction recoveries. In contrast, if the extraction rates are controlled by diffusion inside the polymer particles and/or transfer through the layer of stagnant extractant around the polymer particles, the solvent flow rate will show little or no influence on the extraction recovery unless unpractically high flow rates are used to reduce the thickness of the stagnant layer.

Effects of Temperature in ASE. An important operational difference between ASE and Soxhlet extraction is the extraction temperature. In ASE, extraction temperatures well above the normal boiling point of the solvent are used. Contrarily, in Soxhlet extraction, the extraction temperature is limited by the boiling point of the solvent used. At elevated temperatures, diffusion of the components from the inside of the polymer particles to their surface is enhanced. Moreover, transfer from the surface of the particles into the extraction solvent will be faster. In addition to these, the solubility of the components in the extraction fluid will be improved when working at increased temperatures. Hence, the extraction rate at elevated extraction temperatures will be significantly higher. In order to investigate the effects of temperature on the extraction rates of polymers under ASE conditions, nylon-6 and PBT were extracted with hexane at different temperatures at a pressure of 200 bar. In these extractions, a static time of 20 min and a dynamic time of 30 min were used. The results are illustrated in Figure 3. From this figure it can clearly be seen that the effect of temperature in ASE is relatively straightforward. The extraction recoveries for both polymers increase significantly when the extraction temperature was raised from 50 to 170 °C. In this figure, the extraction recoveries obtained in SFE with pure carbon dioxide are also shown. Later in this article, a brief comparison of ASE and SFE will be given.

Effects of Pressure. In ASE, a certain minimum pressure is required to maintain the extraction solvent in the liquid state at a temperature above the atmospheric boiling point. It was reported by Richter et al. that pressure had no effect on the ASE recoveries in the extraction of PAHs from dry soil samples.⁹ Also in our experiments, no difference in extraction yields was observed when pressure was varied in the range from 100 to 300 bar.

Effects of Static Time, Solvent Flow Rate, and Air Inside the Extraction Cell. ASE can be performed in the static mode, the dynamic mode, or as a combination of these two modes. In static ASE, the sample is extracted with a solvent at elevated temperature and pressure conditions without any outflow of solvent. When the extraction has reached equilibrium, the

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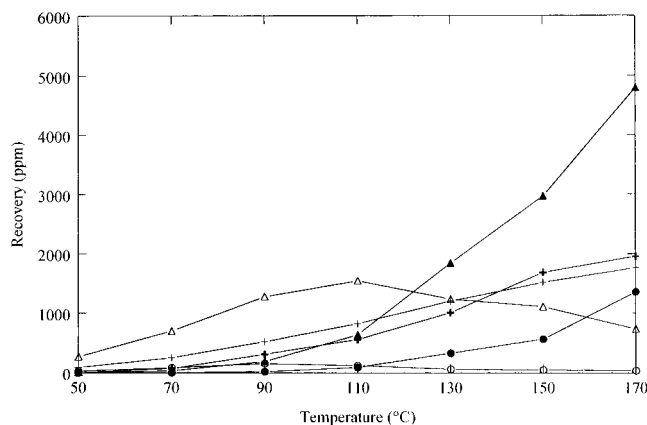


Figure 3. Effects of temperature on extraction recoveries in ASE and in SFE. Extraction conditions: ASE with hexane at 200 bar, restrictor 1.5 m \times 50 μ m i.d. fused-silica capillary; SFE with pure carbon dioxide at 300 bar, restrictor 70 cm \times 50 μ m i.d. fused-silica capillary. Extraction time: static 20 min and dynamic 30 min. SFE of (+) caprolactam from nylon-6, (Δ) the dimer from PBT, and (\circ) the trimer from PBT. ASE of (boldface +) caprolactam from nylon-6, (\blacktriangle) the dimer from PBT, and (\bullet) the trimer from PBT.

Table 1. Effects of Static Time on ASE Extraction Recovery^a

static time (min)	analyte/polymer ^{b,c}		
	caprolactam/nylon-6 (ppm)	dimer/PBT (ppm)	trimer/PBT (ppm)
10	878.7 (6.5)	1978.0 (3.0)	387.7 (4.7)
20	1135.2 (5.6)	2425.2 (4.7)	496.1 (5.8)
40	1124.0 (0.5)	2333.8 (1.2)	534.3 (1.6)

^a Extraction solvent, hexane; temperature, 150 °C; pressure, 200 bar; dynamic time, 10 min; restrictor, 1.5 m \times 50 μ m i.d. fused-silica capillary. ^b Extracted amounts relative to the mass of polymer weighed into the extraction cell. ^c Values in parentheses are relative standard deviations based on three repeated extractions.

analytes are collected by rapidly flushing the extraction cell with solvent and an inert gas. In dynamic ASE, the extraction solvent is continuously flowing through the extraction cell. Some type of a flow restrictor is used to maintain the pressure inside the extraction cell at a desired value. An advantage of dynamic ASE is that the solvent is continuously refreshed during the extraction. Evidently this technique requires a larger volume of solvent than static ASE and is, therefore, less suited for trace analysis. Static ASE, on the other hand, may lead to incomplete extraction because of the limited volume of solvent used. In our experiments, a combination of static and dynamic extraction was used. In this regard the practice of ASE is very much similar to standard practice in SFE. After a certain period of static extraction, the samples were further extracted in the dynamic mode. The effects of static time on ASE extraction recoveries are listed in Table 1. In these experiments, a dynamic time of 10 min was used. From Table 1 it can be seen that the extraction recoveries for both polymers increase considerably when the static time was increased from 10 to 20 min. Opposedly, on increasing the static time from 20 to 40 min, no further improvement of extraction recoveries was observed. Most likely, after 20 min of static extraction an equilibrium state has been established. Therefore, in the following experiments, a static time of 20 min was used.

Table 2. Effects of Solvent Flow Rate on ASE Extraction Recovery^a

flow rate ^b (mL/min)	analyte/polymer ^{c,d}		
	caprolactam/nylon-6 (ppm)	dimer/PBT (ppm)	trimer/PBT (ppm)
2.0	1195.1 (1.8)	2517.0 (1.1)	510.2 (3.1)
0.9	1134.6 (4.1)	2485.5 (2.0)	509.6 (2.9)
0.4	1135.2 (5.6)	2425.2 (4.7)	496.1 (5.8)

^a Extraction solvent, hexane; temperature, 150 °C; pressure, 200 bar; dynamic time, 10 min. ^b Approximate values obtained by adjusting the length of the fused-silica restriction capillaries of 50 μ m i.d.; lengths, 43, 74, and 150 cm, respectively. ^c Extracted amounts relative to the mass of polymer weighed into the extraction cell. ^d Values in parentheses are relative standard deviations based on three repeated extractions.

After static extraction, the polymeric samples were extracted dynamically. In order to investigate the effects of the extractant flow rate on ASE efficiency, fused-silica capillary restrictors (50 μ m i.d.) with different lengths were used to adjust the flow rate while pressure was kept constant. Table 2 lists the effects of the extractant flow rate on the ASE extraction recoveries at 150 °C and 200 bar. No changes in extraction yields were observed when the flow rate was changed from \sim 0.4 to \sim 2 mL/min. Flow rates lower than 0.4 mL/min were not tested. Similar results were also observed at other extraction conditions tested. Apparently, under the experimental conditions used, the ASE extraction rate was not controlled by solubility of the components. This conclusion is further supported by a separate series of independent experiments where no differences in extraction recoveries were observed whether the extraction cell was either fully or only partly packed with the polymeric samples. When lower (relative) extraction recoveries are obtained for a fully packed cell, this is an indication that solubility in the fluid is the limiting parameter for extraction.¹⁷

In all experiments described above, the static/dynamic valve was opened prior to starting the extraction. This allows the air inside the extraction cell to be eliminated by the extraction solvent. After the removal of the air, the static/dynamic valve was closed and the oven was heated. Slightly lower extraction recoveries were observed for both nylon-6 and PBT if the air inside the system was not eliminated prior to extraction. Most likely, residual air can block direct contact between the solvent and the sample matrix. Therefore, it is recommended that air inside the system be eliminated before the oven temperature is raised. This is particularly important for samples that are susceptible to reactions with air at elevated temperatures.

Optimization in ASE of Polymeric Samples. Optimization is, perhaps, the area of the greatest concern in ASE method development. In this section, some general guidelines for the optimization of ASE extractions of polymeric samples will be given. Because ASE is still in its early stage of development, the discussion here can only be general.

Sample Size. The sample size is one of the parameters that should be considered before an ASE extraction is performed. Evidently, the sample size should be large enough to ensure sample homogeneity and to obtain sufficient sensitivity for trace analysis. However, larger samples require large amounts of solvent for quantitative extraction and may more easily block the

system or its restrictor. Normally, a small sample size is preferred provided that the requirements for sample homogeneity and sensitivity are satisfied.

Particle Size. The influence of particle size on ASE extraction yields depends on which parameter controls the extraction efficiency. It is obvious that if the ASE extraction rate is limited by diffusion of the analytes in the polymer particles, the extraction rate can be greatly increased by decreasing the particle size. Therefore, polymers should generally be ground or cut into small particles prior to extraction.

Extractant. The selection of a suitable extraction solvent is probably the most difficult step in method development in ASE. The solvents used in conventional Soxhlet extraction may not be suited for ASE because the polymeric materials may dissolve or swell to too large an extent at the higher temperatures used in ASE. In the selection of the extraction solvent, the following two demands should be fulfilled: (a) The polymer should not be soluble in the solvent selected at the ASE temperatures used. (b) The analytes of interest must have a good solubility in the solvent under ASE conditions. As almost no data on the solubility of polymers or solutes in high temperature solvents are available, solvent selection in ASE is still largely empirical.

Temperature. As discussed above, temperature is the most important parameter affecting the kinetics of mass transfer in ASE. The ASE extraction rates can be increased significantly at higher temperatures. Evidently, however, the extraction temperature should not be above the melting point of the polymer that is to be extracted. Unfortunately, again no information of melting points of polymers under ASE conditions is available. Care should also be taken not to exceed the temperature values where either the polymer or the analytes start to degrade. Information on the allowable temperature is only scarcely available. The optimal extraction temperature depends on the polymer, the extraction solvent, and the target analytes and, thus, can only be determined experimentally.

Pressure. In ASE, a certain minimum pressure is required to maintain the extraction solvent in the liquid state. Fortunately, these pressures need not to be excessive. For example, 20 atm is sufficient to keep hexane (atmospheric bp 68.7 °C) in the liquid state at 209 °C. The minimum pressure required can be estimated from simple equations as described by Hass and Newton.¹⁸ These authors also listed boiling points of many organic solvents at various pressures greater than 1 atm. In our experiments, pressure was found to have no influence on the ASE extraction efficiency for the polymeric samples studied. This implies that the selection of extraction pressure is fairly easy. Pressures well above the values required to keep the extraction solvent from boiling should be used.

Static/Dynamic Extraction. In the process of ASE extraction, the analytes are extracted from the inside of the polymer particles into the extraction solvent. Dynamic ASE might be expected to yield faster extractions by continuously providing fresh extraction solvent to the sample, but this technique requires more solvent than static ASE, particularly when large samples are extracted. Therefore, a combination of static and dynamic extraction will often be the best choice in practice.

Table 3. Comparison of Extraction Recoveries between ASE and Soxhlet Extraction

	analyte/polymer ^d		
	caprolactam/nylon-6 (ppm)	dimer/PBT (ppm)	trimer/PBT (ppm)
ASE ^a	1956.1	4795.5	1358.5
Soxhlet ^b	158.7	137.4	2.6
Soxhlet ^c	1827.8	4886.0	2039.0

^a Extraction conditions: hexane, 170 °C and 200 bar; static time, 20 min; dynamic time, 30 min; restrictor, 1.5 m × 50 μm i.d. fused-silica capillary. ^b Soxhlet extraction, hexane, 40 h. ^c Soxhlet extraction, 30 h, methanol for nylon-6 and chloroform for PBT. ^d Extracted amounts relative to the mass of polymer weighed into the extraction cell.

Flow Rate. The effect of flow rate on ASE extraction rates can be used to determine whether the extraction is limited by analyte solubility in the extractant, diffusion in the polymer particles, and/or transfer from the polymer surface to the extractant. If the extraction recoveries do not change when the flow rate is increased, the extraction is not solubility limited. The rate-limiting step is diffusion inside the polymer particles and/or transfer from the polymer surface into the extractant. The extraction rate now can be enhanced by raising the extraction temperature. The use of very low flow rates is not recommended because it may easily lead to blockage of the restrictor. From a practical view of point, the initial solvent flow rate can be selected at ~0.5 mL/min.

Advantages of ASE over Other Sample Preparation Methods. In addition to the reduced solvent consumption, shorter extraction time required, and ease of method development, another important advantage of ASE over Soxhlet extraction is the wide range of possible extraction solvents. In ASE, the samples are extracted at temperatures well above the boiling point of the extractant used. The kinetics of mass transfer can be greatly improved at elevated temperatures. Therefore, it is very well possible that a poor extraction solvent in a Soxhlet extraction can be a good solvent in ASE at high temperatures. As demonstrated in Table 3, hexane, which is a poor extraction solvent in the Soxhlet extraction of nylon-6 and PBT, yields excellent extraction recoveries in ASE. The extraction recoveries of caprolactam from nylon-6 and the dimer from PBT in 50 min (20 min static and 30 min dynamic) are comparable with those found after extensive Soxhlet extraction with methanol and chloroform. For the extraction of the large trimer molecule from PBT, the extraction recovery at an extraction duration of 50 min is still lower than that of Soxhlet extraction with chloroform. To obtain higher extraction recoveries for the trimer, a longer extraction time is required.

In Soxhlet extractions, considerable amounts of precipitate were observed in the extracts when methanol and chloroform were used as the extraction solvent for nylon-6 and PBT, respectively. Moreover, the quality of the GC columns used notably deteriorated after a few injections of these extracts, probably because large molecules that could not be eluted out the GC column were coextracted with the target analytes and injected into the GC system. In contrast to this, the extracts of ASE with hexane as the extractant are much cleaner. No precipitation of the extracts and deterioration of the GC columns were observed with ASE using hexane as the extractant. From this it is clear that, due to the flexibility in the selection of the

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extraction solvent in ASE, some additional selectivity can be introduced by using different solvents.

It is interesting to compare the extraction recoveries of SFE and ASE at identical extraction temperatures (Figure 3). Hexane is the organic solvent having polarity properties most similar to supercritical carbon dioxide. It can be seen from Figure 3 that at high extraction temperatures the extraction recoveries for both nylon-6 and PBT obtained in ASE are considerably higher than those obtained in SFE. This is especially the case for the relatively large molecules (dimer and trimer from PBT). The extraction recoveries in ASE of caprolactam from nylon-6, and the dimer and trimer from PBT at 170 °C, the highest temperature tested, are approximately 1.1, 6.5, and 37.6 times higher, respectively, than those obtained in SFE. From the discussion above it can be concluded that, in the extraction of polymeric samples, ASE is more effective than SFE with pure carbon dioxide, particularly in the extraction of components having a poor solubility in supercritical carbon dioxide and/or when high extraction temperatures are necessary to increase diffusion of the analytes in the polymer particles. Nevertheless, SFE has its unique advantages such as adjustable selectivity by tuning the extraction conditions, ease of on-line combination with other analytical techniques, etc.

CONCLUSIONS

Accelerated solvent extraction is a promising technique for sample preparation. In the process of ASE extraction of polymeric

samples, three subsequent steps can be identified, i.e., diffusion of the components from the core of the polymer particles to their surface, transfer of the components from the surface into the extraction fluid, and elution of the components out of the extraction cell. The kinetics of mass transfer in these three subsequent steps are improved significantly at higher temperatures. ASE gives recoveries comparable to those obtained with Soxhlet extraction. Method development in ASE is relatively straightforward because less parameters affect the extraction efficiency. Besides the selection of the extraction solvent, temperature is the most important parameter to be optimized. The range of solvents applicable in ASE is much wider than that in Soxhlet extraction. This is because a poor solvent for Soxhlet extractions can be a good solvent in ASE due to the higher extraction temperatures used. Some additional selectivity can be introduced in ASE by careful selection of the extraction solvent and the temperature.

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