

Evaluation of Accelerated Solvent Extraction of deuterated Benzo(a)pyrene and Dibenzo(a,i)pyrene from Diesel Standard Reference Material 2975

C. BERGVALL, L. ELFVER and R. WESTERHOLM

Department of Analytical Chemistry, Arrhenius Laboratory,
Stockholm University SE-106 91 Stockholm Sweden.

AIM

The aim of the present study was to evaluate the extraction recoveries of deuterated benzo(a)pyrene (B(a)P-d12) and dibenzo(a,i)pyrene (DB(a,i)P-d14) added to the standard reference material (SRM) 2975 diesel particulate matter using accelerated solvent extraction.

INTRODUCTION

One group of compounds with high mutagenic and carcinogenic properties found in ambient air particles and diesel particulate matter are polycyclic aromatic hydrocarbons (PAH) [1]. In recent years attention has been focused on PAH with high molecular weights due to reports of high carcinogenic potency among this group of compounds [1]. In particular the dibenzopyrene isomers dibenzo(a,l)pyrene, dibenzo(a,e)pyrene, dibenzo(a,i)pyrene and dibenzo(a,h)pyrene (molecular weight 302) have been shown to be very potent carcinogens. These compounds are classified by The US Department of Health and Human Services as potential carcinogens to humans [2] and by International Agency for Research on Cancer (IARC) as probably (group 2A) and possibly (group 2B) carcinogenic to human beings [3]. They have also been appointed high toxic equivalency factors (TEF) in various studies indicating a higher carcinogenicity than benzo(a)pyrene [1]. The potentially high carcinogenic potency of high molecular weight PAH demands accurate analytical methods to determine the concentrations of these compounds in our environment.

However, analysis of high molecular weight PAH in diesel particulate matter have shown that extraction of these compounds from the diesel particles are more difficult than from ambient air particles when using common extraction methods such as ultrasonically assisted extraction [4-7], supercritical fluid extraction [8] and Soxhlet extraction [5-7]. High extraction recoveries are important considering that small amounts of particulate material often are obtained when collecting ambient air particles or exhaust particles emitted from vehicles. Furthermore, incomplete extraction could produce inaccurate results when quantifying with the isotope dilution technique due to different extraction yields of the analytes and internal surrogate standards. Accelerated solvent extraction (ASE) is a extraction technique introduced in 1996 by Richter et al. [9]. Solid or semisolid samples are extracted in closed cells using liquid solvents at elevated temperatures (50-200 °C) and pressures (500-3000 psi). Extracting with solvents at high temperature and pressure enhance their extraction ability. This is probably due to improved solubility and mass transfer and to disruption of surface equilibria [9]. The usage of ASE in environmental analysis of different compounds, including PAH, has recently been reviewed by Schantz [10]. In another report by Schantz et al. [7] PAH was extracted from various standard reference materials (SRMs) and comparable results between ASE and Soxhlet extraction for urban air particulate matter (SRM 1649a) was found. However, ASE showed greater extraction efficiencies for the diesel SRMs 2975 and 1650. In a more recent study Baldassari and co-workers investigated the extraction recoveries of several deuterated PAH added to SRM 1650 and another diesel particulate material using ASE with different solvents, pressures, temperatures, static extraction times and number of extraction cycles [6]. The authors reported higher concentrations than Schantz et al. [7] for SRM 1650. This finding was attributed to the more extreme extraction conditions used by Baldassari et al. [6]. However, in spite of the drastic extraction conditions used, complete extraction of the deuterated PAH from the diesel particulate matter was not achieved.

METHODS

The extractions of 5 mg of diesel SRM 2975 were performed using an ASE 200 instrument (Dionex, USA). The samples were placed in 5 ml extraction cells and solutions of B(a)P-d12 and DB(a,i)P-d14 were added to the particulate matter. After evaporation of the solvent the caps were tightened and the cells placed in the instrument. The extraction times, e.i. static times, tested were 5, 10 and 20 minutes. Other extraction parameters were: oven temperature 200°C, 2000 psi, 3 minutes preheat time, 9 minutes heat time and three extraction cycles. The solvent used for the extractions was toluene. The eluate from each extraction cycle was collected in a separate 60 ml collection vial yielding three fractions from each cell. Two cells were extracted for each extraction time. The extracts were then cleaned up using silica solid phase extraction (SPE) cartridges. Deuterated coronene was added to the SPE eluate as a volumetric internal surrogate standard for calculation of the recovery of B(a)P-d12 and DB(a,i)P-d14. The samples were then analyzed using online hyphenated LC/GC/MS according to [4].

RESULTS

From Figure 1 it is apparent that the major part of the analytes is extracted during the first extraction cycle and that the recoveries for both compounds, considering the standard deviations, does not improve with extraction time. It should be noted that the recoveries displayed in Figure 1 are in fact method recoveries, i.e. the extraction recovery plus the recovery of the clean up method, since the volumetric internal standard was added just before analysis on the LC/GC/MS system. The results for B(a)P-d12 are in fair agreement with those obtained by Baldassari and co-workers [6]. The authors used accelerated solvent extraction at similar operating conditions as in this study for the extraction of deuterated PAH from a diesel particulate material sampled from a heavy-duty diesel engine. The sum of the recoveries of the three extraction cycles when using 5 min extraction time are close to the determined recoveries of only the SPE step indicating that three 5 min extraction cycles with toluene at 200 °C and 2000 psi is enough for almost complete extraction of the deuterated PAH used. However, it was noticed that the peak areas of the deuterated internal surrogate standards in the sequential fractions were decreasing more than the non labeled analytes indicating that the deuterated internal surrogate standards added to the material are more easily extracted than the analytes.

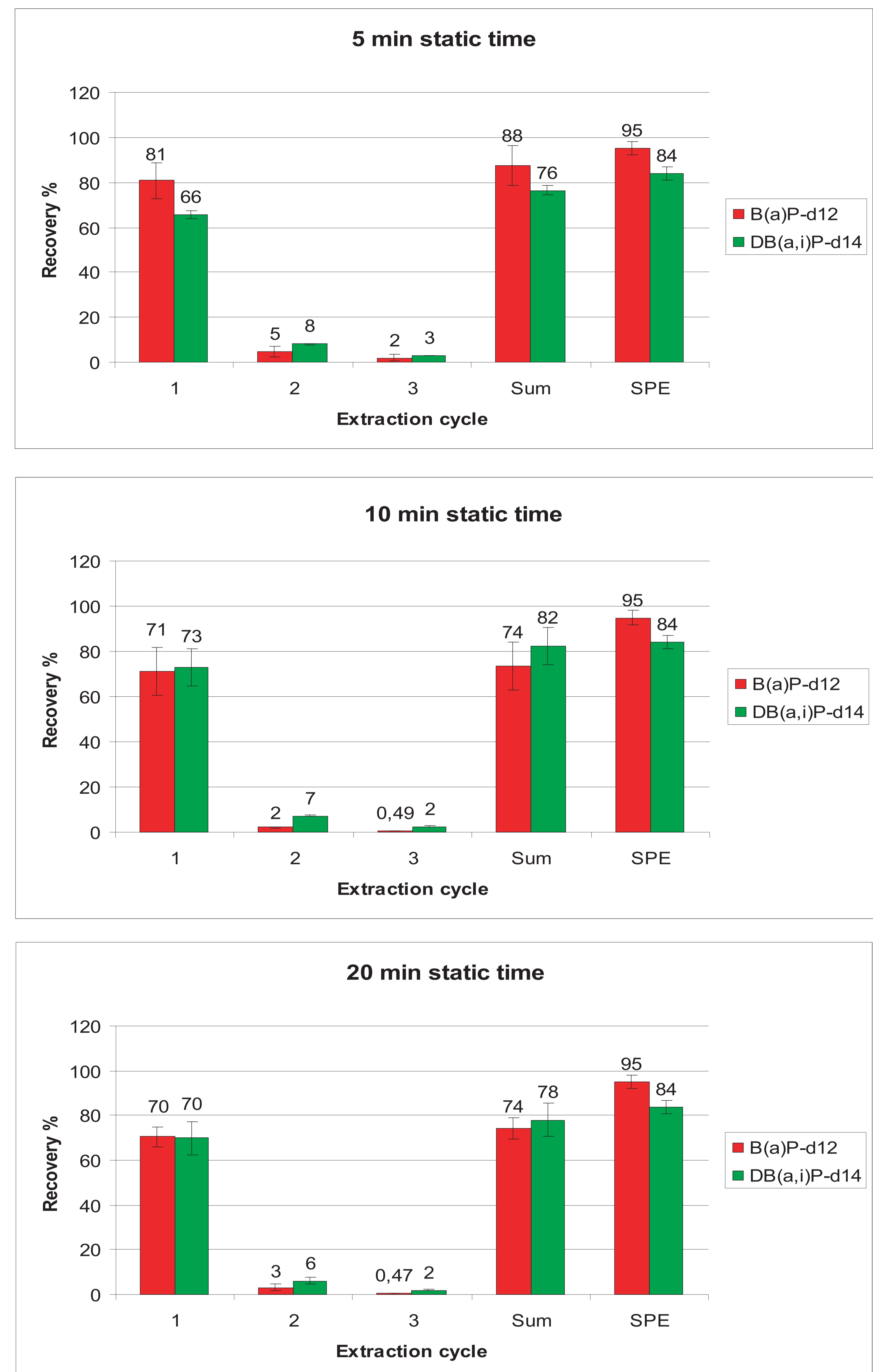
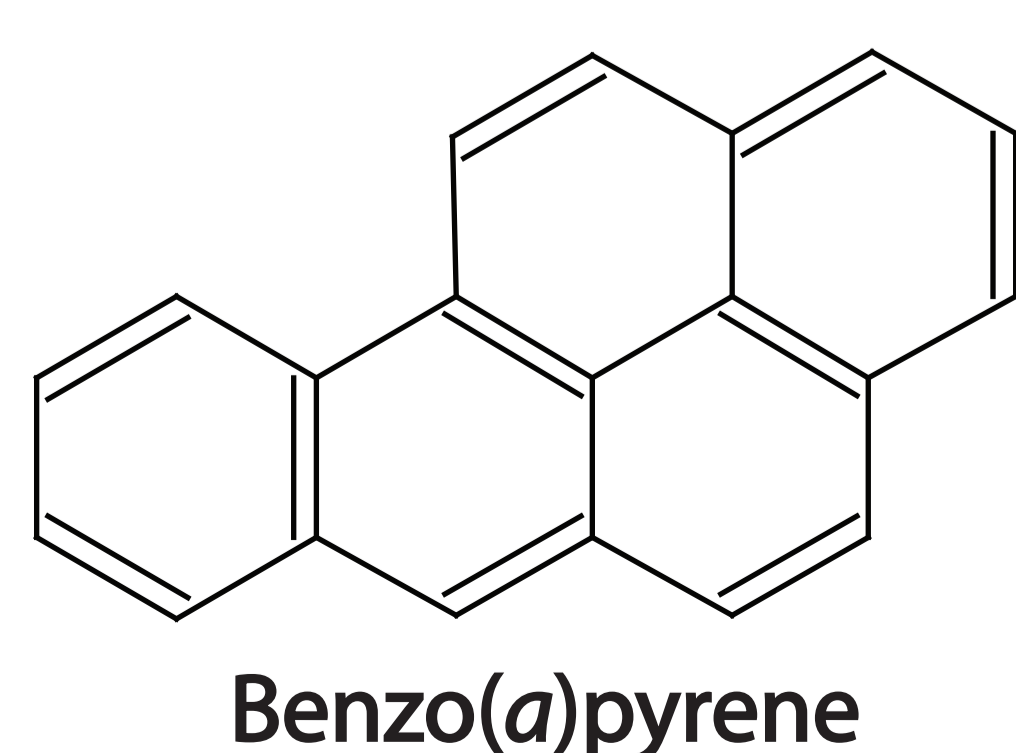
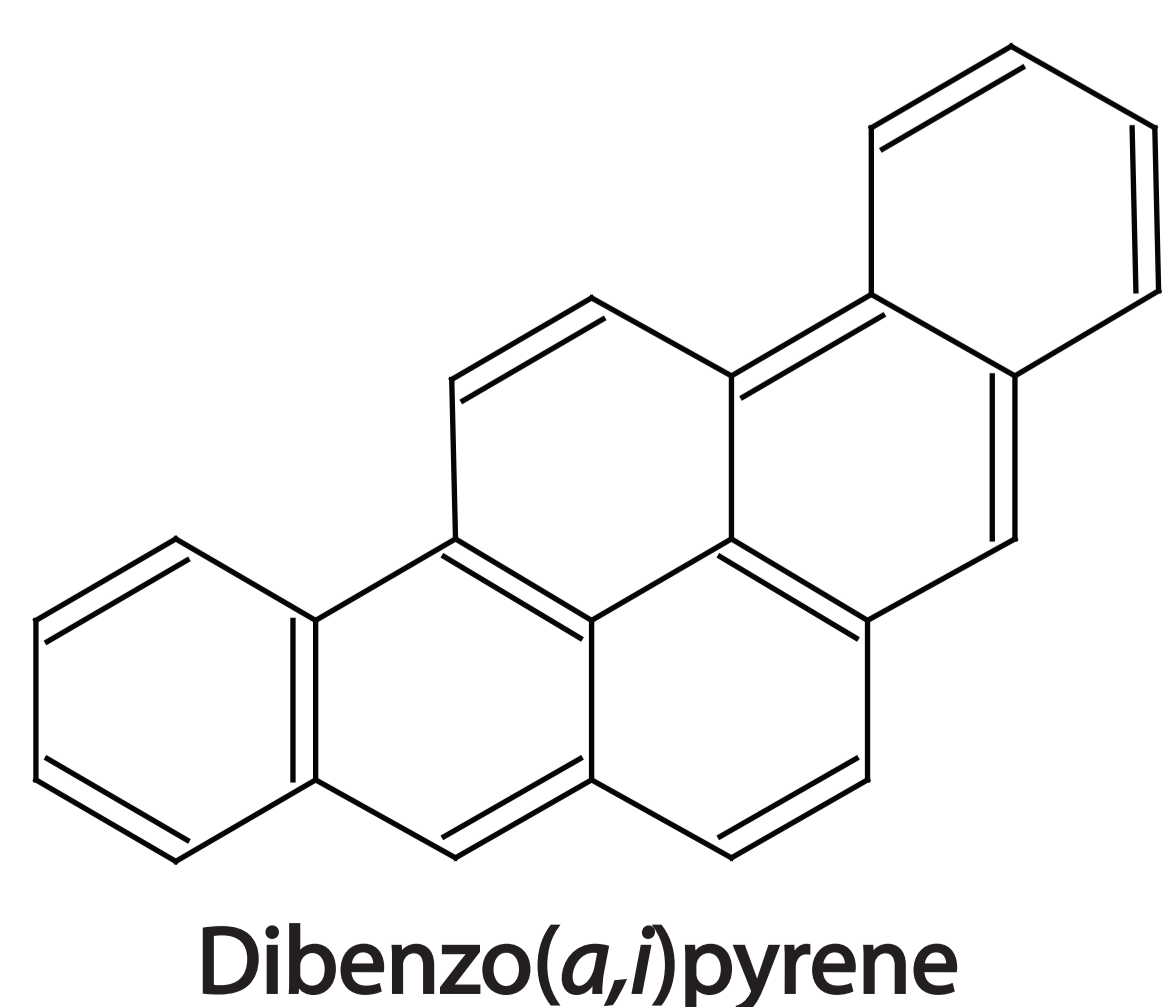


Figure 1 Mean (n=2) method recoveries (%) of deuterated benzo(a)pyrene and dibenzo(a,i)pyrene from SRM 2975 Diesel Particulate Matter in three sequential extraction cycles using the extraction times 5, 10 and 20 minutes. Sum corresponds to the sum of the recoveries from the three extraction cycles. SPE is the recovery from only the SPE clean up step.

CONCLUSIONS

- The major part of the analytes is extracted during the first 5 min extraction cycle.
- No improvement in extraction recovery when extracting for 10 and 20 min.
- Three 5 min extraction cycles using toluene at 200 °C and 2000 psi is enough for quantitative extraction of the deuterated PAH used.
- It was noticed that the added deuterated PAH standards are more easily extracted compared to the non labeled analytes from the diesel particulate matter.

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REFERENCES

1. Boström C-E., Gerde P., Hanberg A., Jernström B., Johansson C., Kyrklund T., Rannug A., Törnqvist M., Victorin K. and Westerholm R. *Environ Health Perspect* 2002, 110(3), 451-488
2. US Department of Health and Human Services. Polycyclic Aromatic Hydrocarbons: 15 Listings; Ninth Report on Carcinogens, 2001. Available at: <http://ehp.niehs.nih.gov/roc/ninth/rahc/pahs.pdf>
3. Straif K., Baan R., Grosse Y., Secretan B., El Ghissassi F. and Coglianò V. *Lancet Oncol* 2005, 6, 931-932
4. Bergvall C. and Westerholm R. *Anal Bioanal Chem* 2006, 384(2), 438-447
5. Christensen A., Östman C. and Westerholm R. *Anal Bioanal Chem* 2005, 381, 1206-1216
6. Turrio-Baldassarri L., Battistelli C. and Iamiceli A. *Anal Bioanal Chem* 2003, 375, 589-595
7. Schantz M., Nichols J. and Wise S. *Anal Chem* 1997, 69, 4210-4219
8. Wise S., Poster D., Kucklick J., Keller J., VanderPol S., Sander L. and Schantz M. *Anal Bioanal Chem* 2006, 386, 1153-1190
9. Richter B., Jones B., Ezzell J. and Porter N. *Anal Chem* 1996, 68, 1033-1039
10. Schantz M. *Anal Bioanal Chem* 2006, 386, 1043-1047