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Trace Analysis of PAHs in Soil and Groundwater

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Sample Preparation for Trace Analysis of PAHs in Soil and Groundwater Using Syncore Analyst

The Syncore® Analyst is scrutinized for sample preparation in the determination of polycyclic aromatic hydrocarbons according to ISO 17025. The parallel evaporator excels in sample throughput, reliability and convenience. Within an evaluation period of six months labor costs have been reduced by a factor of six.

Introduction

BECEWA is an independent contract laboratory specialized in the analysis of soil, solid waste, ground-, drinking- and wastewater. Although its clients are private organizations, the results of the analyses are mostly used to comply with legal regulations. Thus the laboratory operates in accordance with the ISO 17025 protocol[1].

Polycyclic aromatic hydrocarbons (PAHs) are organic polluants derived from the incomplete combustion of organic materials such as gasoline, wood or coal. Since their solubility decreases with increasing molecular weight they tend to accumulate in the environment and in organisms causing genetic mutations and cancer.
The determination of PAHs in water, soil and solid waste typically includes an extraction step with subsequent concentration, followed by analysis with gas chromatography (GC) and mass spectrometry (MS).
The conventional procedure for the concentration of the extraction samples includes a rotary evaporator for concentration to approximately 10 ml followed by further evaporation under a stream of nitrogen or air.
Volatile PAHs thereby tend to evaporate during the final stage of the evaporation process, whereas heavier components stick to the glass vessel, both lowering the recovery rates of the concentration step. In addition, this procedure requires frequent and cumbersome sample handling, which is very time-consuming.

Hence, the Syncore Analyst® is evaluated in terms of efficiency, *i.e.* high recovery rates, accuracy, covenience and speed.

Fig.1: Syncore Analyst R-12 for parallel evaporation of 12 samples to a pre-defined residual volume of 1 ml.

Experimental

Solid samples are doped with deuterated internal standards (Reke) to determine the reliability of the analytical procedure. PAHs are extracted in two stages: Step 1 includes a conventional Soxhlet extraction with a 1:1 mixture of hexane and acetone (Biosolve, suprasolve quality). In step 2 the solvent is switched to pure hexane. The two extracts are combined and concentrated to a volume of approximately 1 ml. In the conventional method a Buchi Rotavapor® R-124 is used. Parallel concentration is performed with the Buchi Syncore® Analyst with a 12 position rack, vacuum system and recirculating chiller (see Fig. 1).
A selection of 16 different PAHs (EPA 16) are analyzed by GC/MS (Agilent 6890 series with 5973 series MSD, column: Restek RTX 5 MS, 60 m, 0.25 mm, 0.25 µm film) in *n*-nonane (ACROS, p.a. quality).

Results and Discussion

Evaluation of the recovery rates with internal standards

In order to evaluate the reliability of the Analyst, a series of 10 standard solutions (1 µg/ml in *n*-nonane) are diluted to 100 ml in *n*-hexane and concentrated to a volume of 1 ml. The recovery rates of the different deuterated internal standards are then compared to the conventional method.

Table 1 shows that the Syncore® Analyst provides significantly (up to 27%) higher recovery rates for both the lower and higher boiling components. Furthermore, the accuracy of the method is markedly better, illustrated by the lower standard deviation compared to the results of the Rotavapor® set-up.
The reason for this unexpected finding lies in the entirely different shape of the sample vessel. For small volumes the surface to volume ratio for the rotary evaporator is much higher compared to the Analyst vessel. In addition, the Analyst's design principle with a cooled appendix prevents evaporation of volatile compounds when it comes to small volumes.

[1] ISO 17025 describes the general requirements for the competence of testing and calibration laboratories. The analytical methods are provided by Vito, the Flemish reference laboratory, and are largely based on ISO, EPA or other internationally recognized standard methods.

ecovery rates of evaporation step

Deuterated PAH	Rotavapor® R-124 recovery [%]	Syncore® Analyst recovery [%]
Naphthalene-d6	60.6 ± 18.0	82.7 ± 8.3
Acenaphthene-d10	67.9 ± 13.1	88.0 ± 6.4
Phenanthrene-d10	68.3 ± 12.9	89.4 ± 5.4
Chrysene-d12	71.1 ± 14.6	97.7 ± 10.2
Perylene-d12	73.8 ± 20.6	104.1 ± 10.2

Table 1:
Comparison of the recovery rates (in %) of the conventional evaporation method (Rotavapor®) with the parallel evaporator Syncore® Analyst (third row) reveals a markedly higher yield and better accuracy. Evaporation settings of the Rotavapor®: rotational speed 65 rpm, water bath temp. 50°C, cooling water temp. 8°C, vacuum 280 mbar. Evaporation settings of the Analyst: rotational speed 170 rpm, rack temp. 45°C, cooling water temp. 10°C, vacuum 280 mbar

Reproduction of certified values (Hamilton Harbour Sediment EC-1) with Analyst

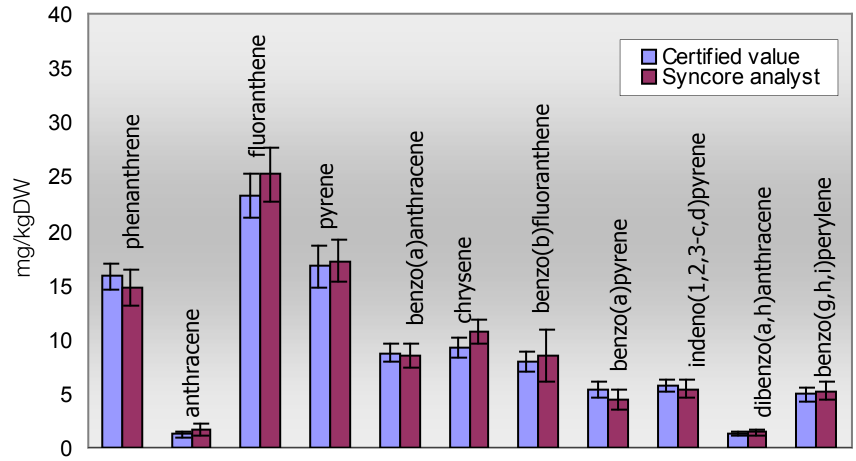

Figure 2: Analysis of reference soil with the Analyst and comparison with the theoretical value (left).

Recovery rates of internal standards of entire analysis process

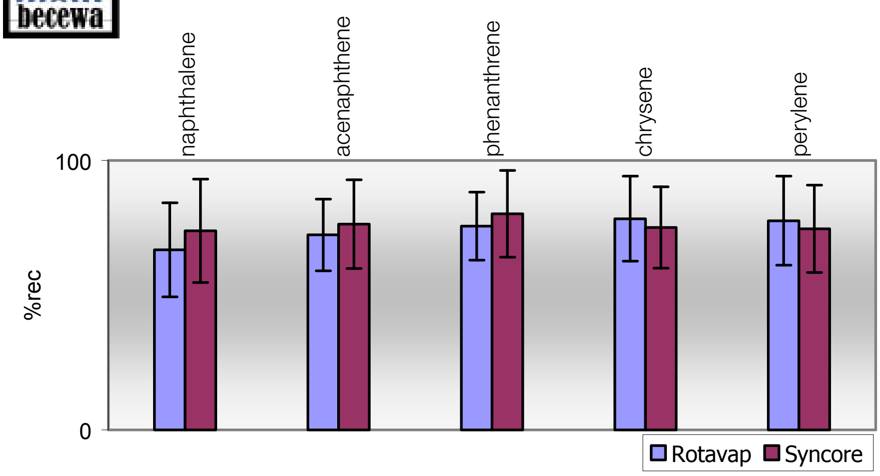

Figure 3: Long-term evaluation of recovery rates of internal standards over a period of six months.

best@buchi 42/2006

Long-term evaluation

Since these preliminary tests conducted on standard solutions demonstrated the reliability of the method in terms of recovery and reproducibility, the system has quickly been introduced in the production laboratory. For a period of six months the Analyst has been used on a daily basis and has proved its ruggedness. In each series of 12 samples, a blank and a certified reference material were included as a laboratory control sample (LCS) and the analytical data were accumulated in a Shewhart chart. The system settings were optimized to ensure a sufficient recovery of the more volatile species. The tendency of the higher molecular weight components to stick on the glass vessels was compensated using the Flushback module. The conventional method requires an extra rinsing step with *n*-hexane to achieve a similar effect.

The results for the reference soil are shown in ***Fig. 2***, including the confidence interval of the Shewhart chart and the uncertainty of the reference values. These data show that the results obtained for the reference material correspond well with the theoretical values, confirming the reliability of the method under production-like conditions.

Fig. 3 depicts a comparison of recovery rates of internal standards in a long-term evaluation with the conventional method, *i.e.* rotary evaporator and nitrogen stream, compared with the parallel method using the Syncore® Analyst.
The values show no statistically significant change using either method. Consequently, the reproducibility of the results is confirmed using the Analyst. Deviation from 100% recovery is rather due to losses in the extraction step and GC injection than to evaporation, since evaporation tests with internal standards showed significantly higher recoveries (see Tab. 1).

However, there is a significant gain in time using the parallel method with the Analyst (vide infra).

Test runs with solvent blanks after the evaporation of particularly heavy contaminated extracts show that there is no cross-contamination between consecutive runs.

Conclusion

Recovery rates in the evaporation of extraction samples have been recorded over a period of six months in a production environment using the parallel evaporator Syncore® Analyst yielding the following results:

- A comparison of a rotary evaporator with the Syncore® Analyst in evaporation of internal standards revealed up to 27% higher yields for the Analyst.
- Moreover, results obtained by the laborious conventional method have been reliably reproduced with the parallel method in a long-term evaluation of six months.
- Lastly, for a commercial laboratory the amount of time spent in manipulation of samples and extracts plays an important role in the total cost of the analysis. With the Syncore® Analyst a series of twelve samples are concentrated in the time spent for two samples with the conventional method, thus reducing the cost of manual labor six-fold.

Acknowledgement

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[i] Shewhart charts are presently widely used to monitor the stability of analytical processes in chemistry laboratories. They are also known as “Levey-Jennings” charts.

[ii] The Flushback module is an optional accessory for the Syncore® Analyst, which partly condenses the vapor at the top of the vessel, thus gently rinsing the glass wall.

[iii] Results for benzo(k)fluoranthene were omitted since the in-lab method does not discriminate between benzo(j)- and benzo(k)fluoranthene.

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