Extraction of PAHs in soil

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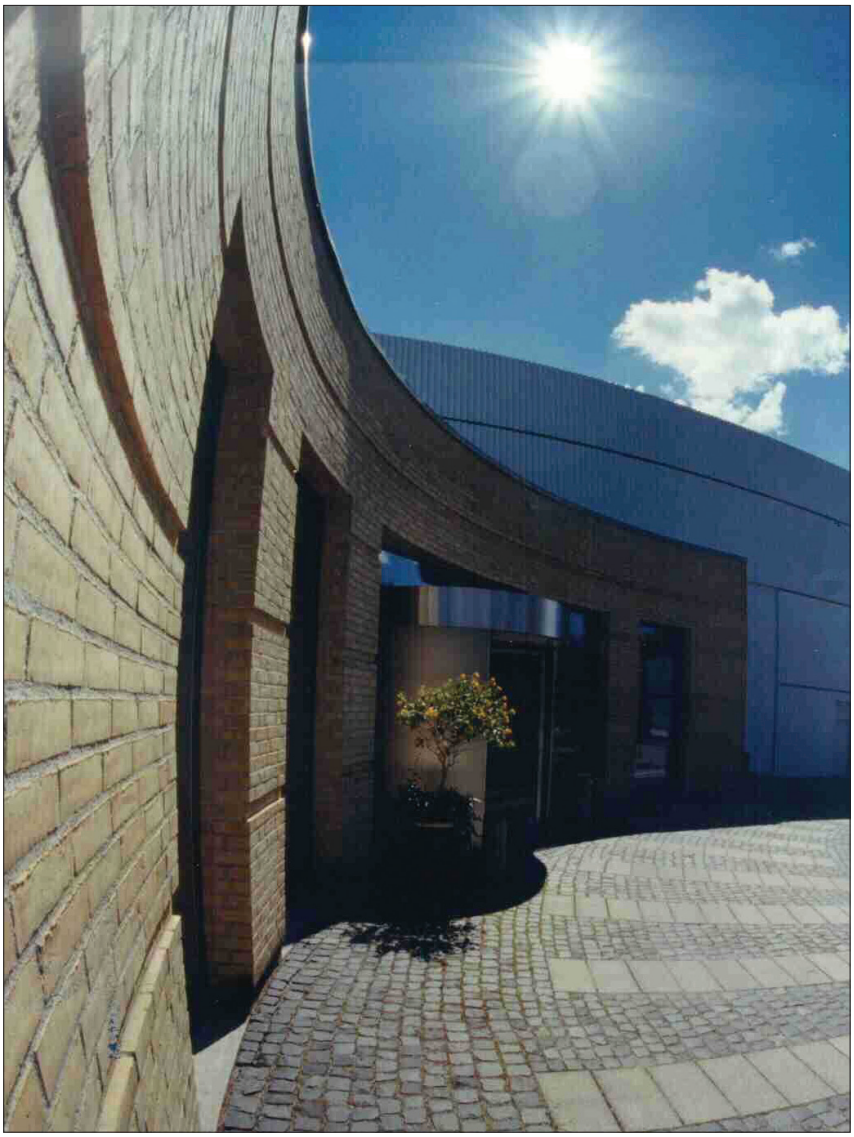


The Danish institute for water research, DHI, has 460 employees. Its head office is in Hørsholm north of Copenhagen, and it has subsidiaries and branches in a number of countries. DHI offers expert knowledge in the fields of ecology and environmental chemistry, water resources, hydraulic structures, hydrodynamics and related areas. DHI's laboratory is a reference laboratory for the Danish Environmental Protection Agency, undertaking assignments for development of analytical methods and offering proficiency tests for water quality analysis for metals, nutrients, organic matter etc, as well as certified reference materials.

DHI WATER & ENVIRONMENT

Recently the Danish Environmental Protection Agency assigned DHI Water & Environment the task of developing a quick, automated and environmentally safe method of determining PAHs in soil. As a result, Soxtec™ is now one of the systems recommended for extraction of PAHs in soil.

PAHs

Polycyclic Aromatic Hydrocarbons (PAHs) are a group of organic compounds with structures consisting of 2-7 aromatic rings. These compounds are found in soil after it has been contaminated, especially by tar; on the sites of former gasworks; and sometimes where oil spills have occurred. The reason for measuring PAHs is that they are very slow to degrade, that they can cause cancer in humans and that they are toxic to other organisms living in the soil. They are difficult to extract, since they are bound to the soil, and the longer they have been present the more difficult they are to extract.

Danish legislation currently calls for measurement of 7 different PAH compounds, while environmental legislation in the USA calls for measurement of 16 compounds (Table 1).

Development of method for determination

Up until now the various methods used have been based on Soxhlet or simple extraction by shaking. These methods

PAH compounds	US EPA	Danish EPA
Naphthalene	X	
Acenaphthylene	X	
Acenaphthene	X	
Fluorene	X	
Phenanthrene	X	
Anthracene	X	
Fluoranthene	X	XX
Pyrene	X	
Benz(a)anthracene	X	
Chrysene	X	
Benzo(b+j+k)fluoranthene	XX	XXX
Benzo(a)pyrene	X	X
Indeno(1,2,3-cd)pyrene	X	X
Dibenzo(a,h)anthracene	X	X
Benzo(g,h,i)perylene	X	

Table 1. The Danish EPA requires analysis for 7 PAH compounds and the US EPA for 16 PAH compounds.

Parameter	Soxtec™
Amount of sample	10 g
Solvent	cyclohexane:acetone (1:1)
Amount of solvent per sample	50 ml (temp. on hot-plate 160°C)
Extraction time	2 h Boiling 1 h Rinsing 1 h
Evaporation	Until 10 ml is left
After extraction, the sample is carefully evaporated, under nitrogen gas until 5 ml remains. The extract is quantitatively transferred to a 10 ml measuring cylinder. Cyclohexane is filled up to the mark. 1 ml is then transferred to a GC vial. An isotope labelled standard of known concentration might also be added before injection into the GC-MS, to compensate for injection uncertainty.	

Table 3. Application summary – Soxtec extraction as sample preparation for determination of PAH in soil.

are time-consuming, may expose personnel to solvents that constitute environmental and health hazards, and are labour-intensive. For these reasons the Danish Environmental Protection Agency was keen to promote development of a new method.

The study carried out at DHI was in three parts:

– Development of a reliable extraction method
– Evaluation of a quantification method
– Development of two reference materials

This article deals mainly with the work done on development of a reliable extraction method.

What was called for was a simple and reliable method for extraction of PAHs in soil. The aim was to shorten extraction time and avoid the use of environmentally hazardous solvents such as toluene and dichloromethane. The properties, quantity and exposure of the solvent to be used were also to be taken into account. The method was to be automated and not to be time-consuming.

The following goals were set:

– The method was to be capable of measuring a detection limit on 1/10 of soil quality criteria, i.e. 0,1 mg/kg DM for single PAH compounds.
– The method was to be capable of measuring a minimum of 7 PAHs, but if possible was to be capable of measuring the 16 PAHs required

PAH compounds	Low level				High level			
	Soxhlet		Soxtec™		Soxhlet		Soxtec™	
	Mean* mg/kg DM▲	%RSD△	Mean* mg/kg DM▲	%RSD△	Mean* mg/kg DM▲	%RSD△	Mean* mg/kg DM▲	%RSD△
Naphthalene	0,23	18	0,11	2,2	0,62	4,3	0,48	6,2
Acenaphthylene	0,16	10	0,18	9,8	0,72	16	0,96	6,7
Acenaphthene	0,03	1,8	0,03	1,	0,16	7,4	0,19	3,7
Fluorene	0,07	13	0,08	4,1	0,37	8,7	0,50	3,0
Phenanthrene	0,91	10	0,81	1,3	6,2	3,0	6,3	0,9
Anthracene	0,18	16	0,17	2,4	0,97	5,0	1,1	0,7
Fluoranthene	1,4	5,6	1,5	2,4	10,6	1,5	13,0	0,4
Pyrene	1,1	1,6	1,1	4,0	8,4	0,5	10,3	0,9
Benz(a)anthracene	0,53	2,3	0,57	2,7	3,6	6,9	3,9	0,8
Chrysene/triphenylene	0,66	4,9	0,67	3,4	3,5	5,0	4,0	1,8
Benzo(b+j+k)fluoranthene	1,4	5,8	1,4	1,9	7,2	3,6	8,6	0,3
Benzo(a)pyrene	0,54	9,8	0,57	2,1	3,6	1,7	4,1	2,0
Indeno(1,2,3-cd)pyrene	0,63	8,1	0,63	1,7	3,5	1,3	3,6	1,0
Dibenzo(a,h)anthracene	0,14	6,5	0,12	3,3	0,70	12	0,68	4,3
Benzo(g,h,i)perylene	0,63	3,6	0,57	0,6	3,5	2,9	3,6	0,9
SUM 16 PAH (US EPA)	8,6	1,9	8,6	1,2	54	1,2	61	0,62
SUM 7 PAH (Danish EPA)	4,1	1,3	4,3	1,9	26	2,0	30	0,48

Table 2. Soxtec™ results on individual PAH compounds in comparison to the reference method Soxhlet.
**Each result is a mean value from triplicates. ▲ Dry matter, △ Relative standard deviation*

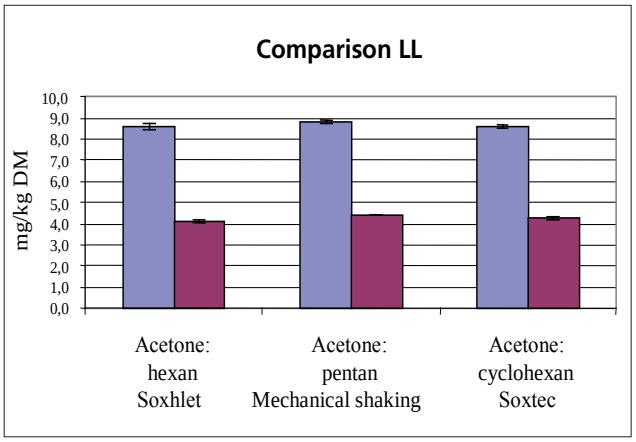


Figure 1. Soxhlet (reference method), Mechanical shaking method and Soxtec results on a low level (LL) PAH in soil. The blue columns are the sum of 16 PAHs and the purple columns the sum of 7 PAHs.

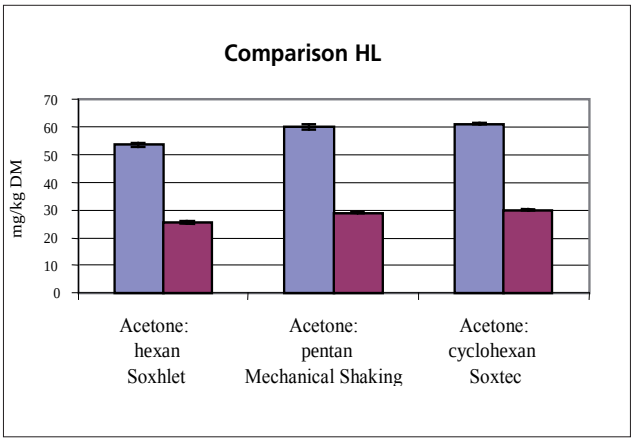


Figure 2. Soxhlet, Mechanical shaking method and Soxtec™ results on a high level (HL) PAH in soil.

by environmental legislation in the USA.
- Reproducibility was to be better than ± 10%.
- Maximum analysis time per sample was to be 1 h, but if possible analysis time was to be 30 min per sample.

The study

The study was carried out using two reference samples from naturally contaminated sites and therefore containing 'natural' PAHs. The samples were of sandy and clayey soil, with low and high PAH levels respectively. At least two 'blank' samples and one soil sample with known (added) PAH level were included in each batch for the purpose of quality control.

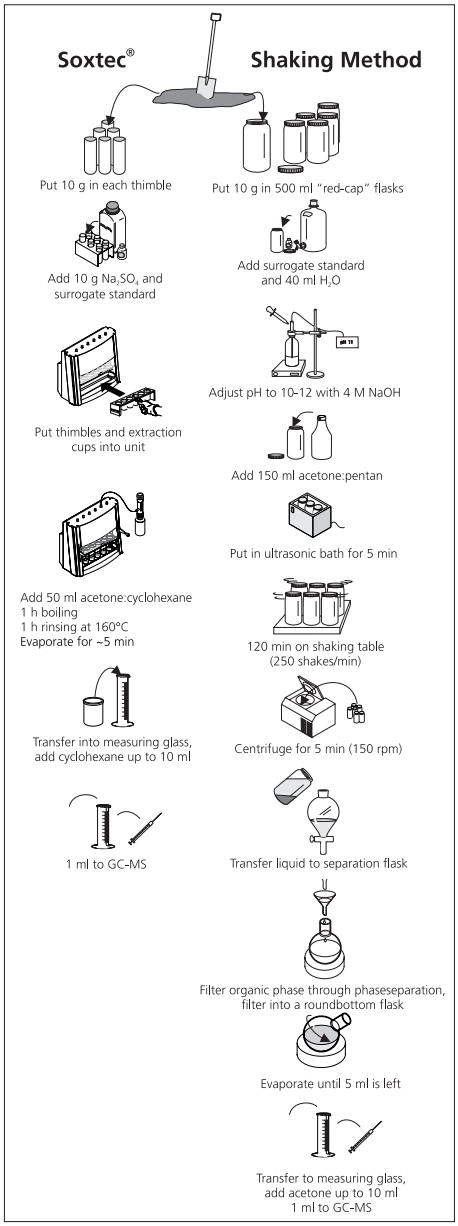
Besides simple extraction and Soxhlet the study also included Soxtec, accelerated solvent extraction (ASE), microwave extraction (MAE) and supercritical fluid extraction (SFE).

The methods were evaluated using various solvents and solvent mixtures, with a view to achieving high extraction efficiency, good precision and low background level. The reference method for comparison purposes was 16 h Soxhlet extraction.

Table 2 indicates Soxhlet and Soxtec results for individual PAH compounds at low and high levels respectively. Evaluation of the Soxtec Avanti for extraction of PAHs in soil resulted in the parameters in Table 3 being recommended.

Conclusions

- Mechanical shaking is the method in most common use at the present time, as most labor- atories are able to run it without having to make major investments.
- Soxtec is one of the three altern- ative, equivalent methods re- commended, and produced proven, comparable results (Figures 1 and 2).
- The detection limit is lower than 0,01 mg/kg DM, the criterion to be met if the limit is to be controlled for single PAH compounds.
- The study has resulted in the development of a measuring method that is simple, reliable and fast, based on GC-MS single ion monitoring and the use of isotope labelled internal standards.
- The methods have been validated against two certified reference materials from the Canadian National Research Council, with satisfactory results.
- Two reference materials for extraction of PAH in soil have been produced for subsequent use in an interlaboratory method study. Content is 0,2-13 mg/kg DM (high level, clayey soil) and 0,03-1,6 mg/kg DM (low level, sandy soil).



The Soxtec™ 2050

– The complete method including extraction method, measurement method and quality control procedures has been described, and the description distributed to Danish environmental laboratories as a recommended procedure.

GC-MS equipment required

The equipment required consists of a gas chromatography system with temperature adjustment, capillary column and splitless injection.

A mass spectrometer with SIM (single ion monitoring) capability, and a PC for collection and storage of all data acquired during analysis is also required.

Soxtec™ – a sound choice

At the left is a comparison of Soxtec and the manual shaking method.

Reference

Development of methods for analysis polycyclic aromatic hydrocarbons (PAHs) in soil/Udvikling af analysemetode til bestemmelse af polycycliske aromatiske hydrocarboner (PAH'er) I jord, Report in Danish to the Danish Environmental Protection Agency, download from www.mst.dk.

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