



# **Determination of mineral oil in compost**

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## ABSTRACT

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Determination of mineral oil in compost is considerably influenced by the presence of natural organic matter. Part of the organic matter is co-extracted and has to be removed with a clean-up. This is possible if enough clean-up material is used and reliable results can be obtained. Gas chromatography provides qualitative information and demonstrates that the mineral oil in the raw products contains easily biodegradable components. Mineral oil concentrations in composted materials are shown to be much lower.

Keywords: Mineral oil, compost, clean-up, determination

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## Summary

In order to determine the mineral oil content of compost and the raw materials used for compost, it is necessary to extract the mineral oil using a solvent. Unfortunately, a considerable amount of more polar organic compounds are co-extracted and these compounds have to be removed from the extract by a clean-up process before analysis. This report describes the clean-up of the extract to achieve reliable results. The method is based on a principle used in ISO standards for the determination of mineral oil in environmental matrices.

It has been shown that the determination of mineral oil in compost is considerably influenced by the presence of natural organic matter, which may lead to an overestimation of the mineral oil content. It is possible to remove the co-extracted organic matter with a clean-up. Providing that enough clean-up material is used, reliable results can then be obtained.

The method has been used for the analysis of different compost products originating from the waste treatment company VAM in Wijster, NL. Gas chromatography also gives qualitative information and demonstrates that the mineral oil in the raw products contains easily biodegradable components. They are degraded during composting and mineral oil concentrations in composted materials have been shown to be much lower.

# 1 Introduction

Mineral oil is one of the most important of all environmental contaminants. This is mainly due to the widespread use of mineral oil products for energy supply and as lubricants. It is, however, not a single product. It originates from crude oil which, in turn, is used to produce several products with different properties. The highly volatile gasoline and kerosene are mineral oil products, as are lubricants and asphalt. For environmental purposes, all these products are measured as the parameter 'mineral oil'.

Waste, and products made from waste, often contain mineral oil products. The re-use of these products is limited by their mineral oil content. The waste treatment company VAM, in Wijster, NL, manufactures products from waste. One of these products is made from the organically wet fraction (OWF). This product, when analysed, has a mineral oil content that is too high. However, it is known that mineral oil determination is extremely sensitive to disturbance by naturally occurring components. These components are extracted together with the mineral oil. Especially in matter with a high organic content such as compost fractions, this could lead to overestimating the mineral oil content.

This report discusses mineral oil determination in OWF materials. The different methods used to determine the mineral oil content are evaluated. Results following the removal of the contaminating organic matter and the influence of organic matter on the measured mineral oil content are presented.

## 2 Analytical methods for the measurement mineral oil content

### 2.1 Extraction

Mineral oil in soil and compost can be present as free oil, oil adsorbed to the solid matrix and oil present in small soil pores. For isolation, it is important to dissolve the oil in a solvent, and also to break up the soil aggregates to allow the solvent to reach the mineral oil. There are two main extraction procedures.

- Continuous extraction using Soxhlet. The sample is continuously extracted with fresh non-polar solvent, which makes the method suitable if dissolving in the solvent is the main process for isolation.
- Agitation procedures: To allow intensive contact between extractant and individual soil particles, it is important for the procedure to be able to break up soil aggregates, and in this case acetone in combination with mechanical agitation is suitable. After break up, a non-polar solvent is added to dissolve the mineral oil. Instead of agitation, it is also possible to supply energy either by using an ultrasonic bath or by raising the temperature.

Results of the two procedures are comparable for most samples. Differences occur if either dissolving of the mineral oil or breaking up of the soil particles is the main process during extraction.

### 2.2 Clean-up and detection

Mineral oil is not a single component but a mixture of hydrocarbons. All these components are non-polar. It is possible to isolate these oil components from environmental matrices (water and soil) by using a non-polar solvent. Initially, mineral oil analysis was done in water. Because the solubility of mineral oil in water is rather low, an extremely sensitive instrument had to be used. In the seventies, when the method was first developed, infra-red spectroscopy (IR) was found to fulfil these pre-conditions. The solvent used should not contain hydrocarbons because infra-red measures the total amount of hydrocarbons. At first, carbon tetrachloride (CCL<sub>4</sub>) was used but because of its toxicity it was later replaced by Freon (1,1,2-trichloro-1,2,2-trifluoro-ethane, C<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub>). There is no solvent that can extract mineral oil selectively.

Naturally occurring organic compounds were always co-extracted. These compounds are more polar and should be removed before analysis. Clean-up procedures using aluminium oxide, florisil and silica are able to remove these contaminants. For the research described in this report, we used florisil. Different standards prescribe different amounts of florisil and also different amounts of solvents. It is known that the effectiveness of florisil not only depends on the total amount used but also on the ratio solvent/florisil.

When, in the eighties, soil analysis became much more important, analyses were started using the method developed for water. One example is the use of DIN 38409. This method was developed for water, waste water and sludge. Inter-laboratory

research has shown that using this method good results can be obtained for sandy soils and clay soils. In organically rich soils especially, such as peat, it was found that the clean-up procedure was critical and co-extracted organic matter could often explain a high mineral oil concentration. Because of the high content of naturally occurring organic matter such as terpenes and ethereal oils from plants (Gottschal, 1999), these problems are also to be expected with compost and especially with the raw material used for compost.

In soil, concentrations are not limited by solubility; pure mineral oil can be present, which may give high concentrations, thus allowing analysis using gas chromatography (GC). One of the advantages of GC is that it provides qualitative information, making it possible to distinguish the different types of mineral oil. Even though many of the co-extracted compounds could not pass through the GC column, clean-up was still necessary.

For several years, both the IR and the GC method were used. In an ISO method (ISO/TR 11046) extraction with Freon was prescribed followed by measurements using either IR or GC. The results were usually comparable, but not always. This is due to the difference in measurement principles. IR measures all CH<sub>2</sub> and CH<sub>3</sub> groups, even when they are not part of the mineral oil. GC measures all compounds leaving the column between the n-alkanes with 10 and 40 C atoms. Neither method is selective for hydrocarbons only and this non-selectivity is responsible for differences in results with difficult samples.

Several countries now forbid the use of Freon. In the ISO working group responsible for the standard for mineral oil, no alternative solvent has been found suitable for both a GC and an IR method. There are several solvents suitable for GC measurements. Fortunately, GC has become much more sensitive in the last ten years. It is now possible to measure low concentrations. This has led to the use of GC for all environmental matrices. The ISO method for soil will be GC, and it is also recommended even for water (SINTEF, 1999). A new draft is already being prepared for an ISO method (ISO 9377-4).



### 3 Materials and Methods

Compost and especially OWF materials are very heterogeneous. The materials were thoroughly mixed by hand and a representative sample of 500 g taken. Fresh OWF material and the end-product after composting (LACO, biowaste compost) was prepared according to ISO-14507 (cryogenic grinding) to obtain a homogeneous material from which it is possible to take a representative sample for chemical analysis. These prepared samples are extracted for isolation of the mineral oil. Two extraction methods are used, Soxhlet extraction with petroleum ether (PE) and agitation with acetone/PE.

- Soxhlet: 15 g of sample was extracted in Soxhlet equipment during a 3.5 hour period using 350 ml PE (boiling range 40 to 60 °C).
- Agitation: 200 ml of acetone was added to 20 g of sample in a 500 ml conical flask. The mixture was agitated for 10 minutes. 100 ml PE was added and the mixture agitated for a further 10 minutes. After settling, the supernatant was decanted into a 1 litre separation funnel and the acetone removed with two portions of 400 ml water. The remaining extract was dried over anhydrous sodium sulphate.

To test the clean-up, the PE from more extractions were combined and divided into portions of 75 ml. Different amounts of florisil were added. To obtain some indication of the amount of co-extracted organic matter, absorbance at 330 nm was measured. After concentration of the extract to about 10 ml using Kuderna Danish equipment, and further concentration under a flow of nitrogen to 1 ml, mineral oil was measured using GC. (On-column injection, Column Fused silica 10 m x 0.32 mm ID coating SimDist DF = 91, FID detection.) Mineral oil was expressed as the total concentration, but also as fractions in the ranges C10-C18, C18-C25 and C25-C40. The presence of volatile compounds (<C10) and heavy compounds (>C40) was observed qualitatively.

After establishing the necessity of the clean-up procedure, the mineral oil concentration in several compost fractions was measured.

For comparison, the same pre-treated samples as used for testing the clean-up procedure were sent to Dr. H. Marx at his laboratory in Germany for the IRS analysis according to DIN 38409 H18 (Soxhlet extraction with Freon and clean-up with Al<sub>2</sub>O<sub>3</sub>). The total amount of lipophylic compounds was measured according to DIN 38409 H17 (mass measurement).

## 4 Results

### 4.1 The clean-up

The extraction liquids obtained from OWF (Organically Wet Fraction) and LACO (biowaste compost) after using Soxhlet and agitation were divided into portions of 75 ml. Different amounts of florisol (0; 5; 10; 15; 20 and 40 g) were added. Absorbance of the samples were measured at 330 nm and are presented in Table 1.

*Table 1. Influence of florisol on the absorbance at 330 nm of the extraction liquid (florisol in g/75ml, absorbance no dimension)*

	Amount of florisol	Acetone/PE	Soxhlet
OWF	0	0.626	0.487
	5	0.092	0.120
	10	0.059	0.065
	15	0.048	0.071
	20	0.037	0.027
	40	0.024	0.033
LACO	0	0.310	0.206
	5	0.069	0.090
	10	0.028	0.080
	15	0.018	0.028
	20	0.016	0.023
	40	0.014	0.023

Table 1 shows that the amount of co-extracted organic matter is about twice as high in OWF. Most of the organic matter is removed by the first 5 g of florisol, but at least 15 g of florisol are required to reach a background value. Using the agitation procedure with acetone/PE, more contaminants are extracted. This is to be expected because acetone is more polar. After clean-up with florisol both extraction procedures give comparable results.

In the same extract, mineral oil content was measured. The results of the total mineral oil content, as well as the different fractions, are given in Table 2. The total mineral oil content is also shown in Figure 1.

Table 2. The influence of florisil on mineral oil and fractions of mineral oil in ONF and LACO

	sample	Florisil (g)=	Total mg/kg d.m.	C10-C18 mg/kg d.m.	C18-C25 mg/kg d.m.	C25-C40 mg/kg d.m.	
Soxhlet	OWF	0	32135	540	13912	17683	
		5	10842	113	2325	8404	
		10	9913	93	1812	8008	
		15	7004	82	1334	5588	
		20	6277	74	1148	5055	
		40	7120	44	1313	5762	
		Laco	0	967	31	253	683
	5		618	25	176	417	
	10		544	18	136	390	
	15		682	48	180	454	
	20		444	31	106	308	
	40		704	36	184	483	
	Agitation		OWF	0	35240	412	23451
		5		9546	173	2229	7144
10		7693		119	1466	6107	
15		5191		60	909	4222	
20		7023		95	1290	5638	
40		6776		103	1388	5284	
Laco		0		1482	46	299	1136
		5	523	23	144	356	
		10	531	18	141	372	
		15	368	8	102	259	
		20	403	17	111	275	
		40	539	29	149	362	

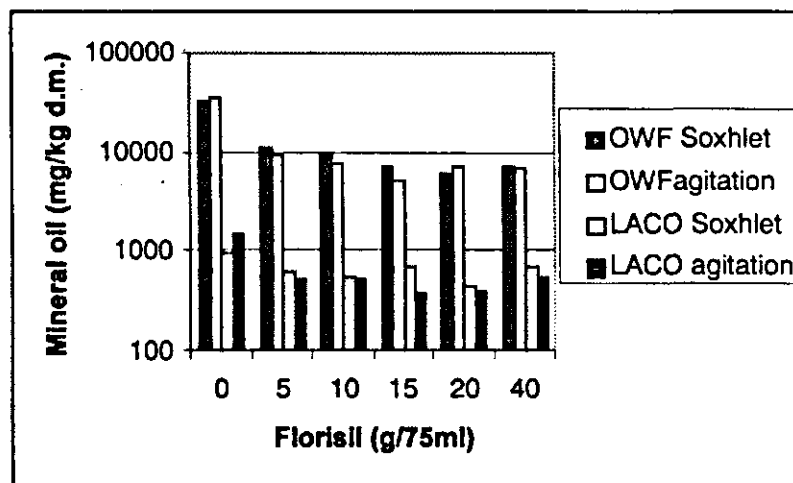
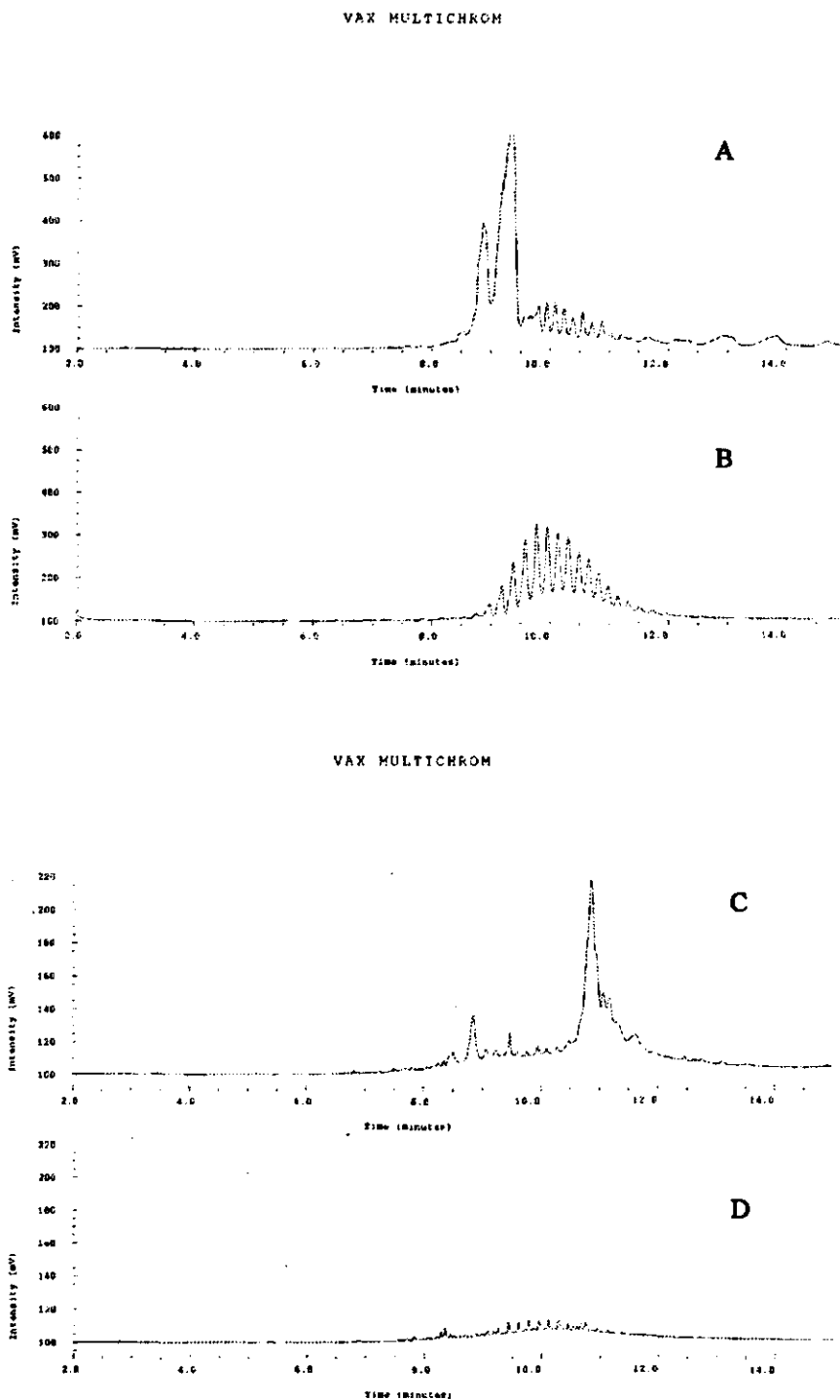


Fig 1 The influence of florisil on the mineral oil content in OWF and LACO

To obtain a stable mineral oil content, at least 15 g of florisil is required for 75 ml of extraction liquid (20 g/100 ml). This is double the amount used for routine analysis of mineral oil in the Netherlands. In the past, this amount was even lower (5 g/100 ml). Research on the validation of the Dutch standard has shown that higher amounts were necessary, especially for the analysis of soils with a high organic matter content. Research on the biodegradation of Polycyclic Aromatic Hydrocarbons (PAHs) and mineral oil in a mixture of polluted soil and compost from mushroom farms, carried out by van den Toorn et al., 1997, has shown that at least 15 g/100 ml florisil was required for clean-up.

The necessity for clean-up is also visible on the chromatogram. Without clean-up, the co-extracted organic matter influences the shape of the chromatogram, even the separation of individual peaks. The contaminants are not identified, but they will contain carboxylic groups. After clean-up, the chromatogram is recognised as representing a mineral oil. In the OWF sample even individual n-alkanes are visible (Figure 2). They are not present in the LACO sample because they are the most easily biodegradable compounds in mineral oil. The mineral oil in both samples is not very volatile. Most compounds contain more than 20 C atoms. In both samples, but especially in the OWF sample, high boiling compounds (>C40) are present. These compounds are not included in the mineral oil content.



**Figure 2. Influence of the clean up on the chromatogram**

- |          |   |                       |  |
|----------|---|-----------------------|--|
| <b>A</b> | = | <b>OWF agitation</b>  | <b>Without clean-up</b>                  |
| <b>B</b> | = | <b>OWF agitation</b>  | <b>Clean-up with florisil (15g/75ml)</b> |
| <b>C</b> | = | <b>LACO agitation</b> | <b>Without clean-up</b>                  |
| <b>D</b> | = | <b>LACO agitation</b> | <b>Clean-up with florisil (15g/75ml)</b> |

After clean-up, the results of the Soxhlet and agitation procedure are comparable. Both methods give mineral oil concentrations (C10 to C40) in OWF and LACO of approximately 6000 and 500 mg/kg d.m. respectively. If only the hydrocarbons up to C25 are of interest, mineral oil concentrations are approximately 1400 and 200 mg/kg d.m. respectively. In detail there is a small difference. Soxhlet extracts slightly more of the heavy oil compounds. The Soxhlet chromatogram of OWF shows more peaks above C40 (Figure 3).

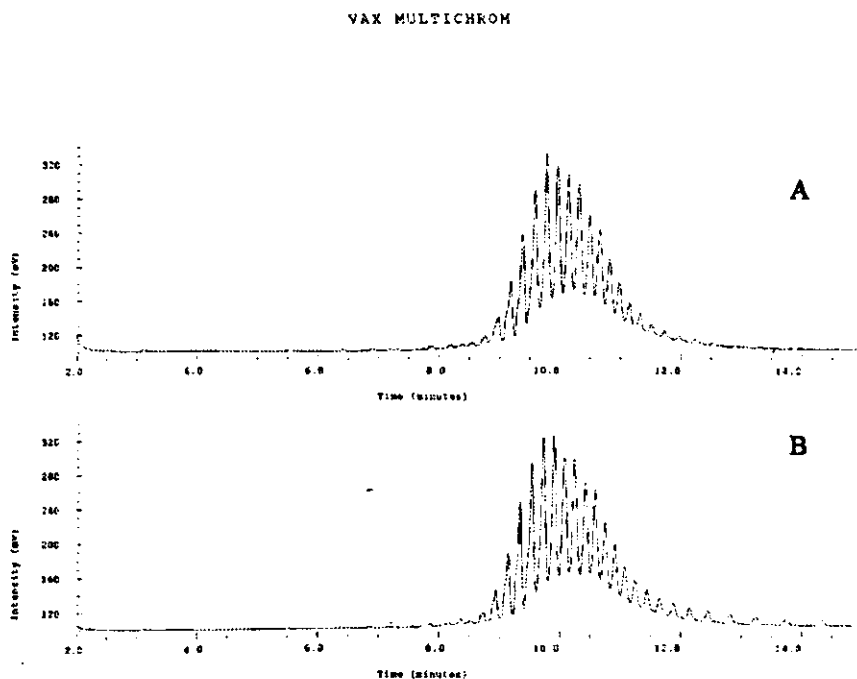


Figure 3. Chromatogram of OWF after agitation extraction (A) and Soxhlet extraction (B). Both after clean-up with Florisil (15g/75ml)

The same two samples were analysed in the laboratory of Dr. H. Marx GmbH using an infrared spectroscopy method based on DIN 38409 (Kohler, 1999). The results are given in Table 3. The standard clean-up with Al<sub>2</sub>O<sub>3</sub> was tested using an extra clean-up with florisil (a column with 8 g of florisil).

Table 3. Lipophylic compounds and mineral oil in OWF and LACO (mg/kg d.m.) measured according DIN 38409 (Kohler, 1999)

Measured compounds	Clean-up	OWF	LACO
Lipophylic substances (mass)	-	179.000	940
Extracted compounds (IR)	-	52.200	836
Mineral oil (IR)	Al <sub>2</sub> O <sub>3</sub>	16.600	171
Mineral oil (IR)	Al <sub>2</sub> O <sub>3</sub> + florisil	16.200	176

Table 3 shows that the clean-up using the method described in DIN 38409 was sufficient. The extra clean-up with florisil did not give a lower mineral oil concentration. The IR results of the LACO sample, before and after clean-up, are comparable with the GC results. The amount of lipophylic compounds is of the same

magnitude as the amount measured with IR before clean-up. The amount of fats will be low.

Results of the OWF sample are more complex. Eighteen per cent of the sample consists of lipophylic compounds (mineral oil, fats and oils). Before clean-up, the IRS method gives a higher mineral oil concentration compared with the GC method (52 000 compared with 32 000 mg/kg d.m.). Using GC, only the extracted compounds that pass the chromatographic column are measured. IR measures all the compounds in the extract. The solvent used, PE for GC and Freon for IR, also affects the results. After clean-up, the IR result is much higher than the GC result (16 600 compared with 6000 mg/kg d.m.). This can be explained by the high boiling compounds (>C40). They are not measured with GC, but are visible on the chromatogram. The amount is probably even higher than indicated, because not all extracted high boiling compounds will pass the analytical column. As already mentioned, these non-volatile compounds are measured with IR. Because GC gives well recognisable chromatograms after clean-up, it can be concluded that IRS overestimates mineral oil concentration in OWF and is therefore only an alternative method for measuring mineral oil in cleaner waste end-products such as LACO.

#### 4.2 Mineral oil in different VAM-products

Because the results of the agitation procedure were comparable with the Soxhlet procedure, agitation, which is the standard method for mineral oil determination in the Netherlands, was used for analysis of the different VAM products. They were achieved from an experiment at the VAM in Wijster. Lab scale composting bins were filled with fresh OWF on June 2, 1999. The material was composted and mixed four times (treatment 1-4). Mini 1 and 2 are two parallel investigations (duplo). Compared with the standard, double the amount of florisol was used to remove the co-extracted organic matter (15 g/75 ml). The results are presented in Table 4. This table also contains results from other compost and soil materials

Table 4. Mineral oil and fractions of mineral oil in different VAM products (mg/kg d.m)

	C10-25	C10-40	C10-18	C18-25	C25-40
OWF fresh 2/6	969	5191	60	909	4222
mini 1 treatment 1 7/6	221	1084	26	195	868
mini 2 treatment 1 7/6	330	1793	99	231	1466
mini 1 treatment 2 10/6	174	947	30	144	777
mini 2 treatment 2 10/6	367	2471	94	273	2117
mini 1 treatment 3 14/6	148	1179	16	132	1035
mini 2 treatment 3 14/6	163	1520	19	145	1359
mini 1 treatment 4 17/6	189	1147	8	180	962
mini 2 treatment 4 17/6	303	1479	13	290	1180
mini 1 end	185	1448	36	149	1267
mini 2 end	85	545	7	77	462
LACO	109	368	8	102	259
Gft compost (<150)	435	1987	58	377	1558
Peat	20	94	4	16	73
Sand from demolltion waste	77	248	13	64	172

At the first treatment at 7/6 n-alkanes were still visible. At 14/6 they have almost disappeared. The values measured in peat and sand are close to the detection limit of the method. The product in which the mineral oil was measured is extremely heterogeneous. The variation in mineral oil content is probably caused by the heterogeneity.

### 4.3 Polycyclic Aromatic Hydrocarbons in OWF and LACO

Polycyclic Aromatic Hydrocarbons (PAHs) were measured in OWF and LACO. The concentrations were close to the reference value used in the Netherlands (table 5)

Table 5. PAHs in OWF and LACO (mg/kg d.m.)

PAH	OWF	LACO
Naphthalene	0.09	0.05
Acenaphthene	1.53	0.60
Fluorene	0.09	0.04
Phenanthrene	0.70	0.10
Anthracene	0.10	0.02
Fluoranthene	0.51	0.43
Pyrene	0.46	0.31
Benz(a)anthracene	0.22	0.18
Chrysene	0.33	0.22
Benzo(b)fluoranthene	0.19	0.19
Benzo(k)fluoranthene	0.09	0.08
Benzo(a)pyrene	0.20	0.14
Dibenz(ah)anthracene	0.03	0.02
Bezo(ghi)perylene	0.20	0.12
Indeno(1,2,3-cd)pyrene	0.13	0.14
10 of VROM <sup>1</sup>	2.58	1.47
16 of EPA	4.89	2.63

<sup>1</sup> National list in the Netherlands



## 5 Conclusions

To determine the mineral oil content in waste and compost, mineral oil was isolated from the matrix using extraction. With extraction, large amounts of other polar organic matter are co-extracted. This material must be removed before analysis. This is possible using florisil. However, larger quantities are needed than the amounts prescribed in standards for measuring the mineral oil content in soil. If an adequate amount of florisil is used the results of Soxhlet extraction and an agitation procedure with acetone/PE are comparable. Most of the mineral oil components in OWF are high boiling compounds (>C25). IRS overestimates the mineral oil concentration in OWF but is an alternative method for measuring the mineral oil content in cleaner end-products of waste such as LACO.

N-alkanes, normally present in 'fresh' mineral oil, are still present in OWF. These compounds are easily biodegradable, and composting this material will reduce the apparent mineral oil content. This was shown in samples from a composting experiment at VAM. The amount of mineral oil in composted products was much lower. The amount of PAHs in the measured samples was low.

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