Application Note No. 007

LARGE VOLUME OIL IN WATER

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Introduction.

The determination of mineral oils in water is of major importance in the environmental analysis. Mineral oils are present in water as well as in soil. In areas near gasoline stations, for example, the soil is often very contaminated with mineral oils.
Concern for the environment is getting more and more important. Natural processes are being disrupted so that the quality of life is being threatened. Modern laboratories get more and more requests for the determinations of organic pollutants in water.
The required detection limits seem to get lower and lower. Large volume injection can aid to meet these requirements.

Large Volume Injection.

The analysis of mineral oils is often a very difficult one. The required detection limits are often very low and the sample matrices very dirty.
Pre-treatment of the samples is a must. A solvent evaporation step is inevitable for a plane injection into the GC. A major disadvantage of this technique is for example the loss of volatiles if the step is carried out to fast. As a consequent it takes a lot of time.
Large volume injection is the solution for the above problem. In doing large volume injection detection limits will decrease and also sample pre-treatment time.

There are two ways to do a large volume injection, the on column technique or the PTV (programmable temperature vaporiser) technique. The difficulty of oil samples is the high level of contamination. This means that by using the on-column technique all of the contaminants are transferred to the retention gap. The retention gap must be very well
Deactivated and after a limited amount of samples it must be replaced. In contrary to the PTV injection where replacing the liner is necessary after a much larger amount of samples. Replacing the liner is not a difficult task and about fifteen times cheaper then a retention gap. This makes the on-column method a much less robust one to automate.

PTV Large volume injection.

The method mostly used is called the solvent split injection. Here the sample is injected with the split exit open and at an injector temperature below the solvent boiling point. After elimination of the solvent the analytes (*down to C8*) retained in the liner are transferred to the analytical column in the splitless mode. The liner has to be partially filled with a packing, to prevent the liquid sample from being pushed to the base of the injector which results in losses via the split exit or in flooding of the column inlet.
The maximum volume of liquid that can be held within the injector depends mainly on the dimensions of the liner and the amount of packing material. Sample volumes

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exceeding the maximum volume have to be introduced in several steps or in a speed-controlled manner.
The OPTIC 2 liner has a large inner diameter which means it is possible to do **rapid at once injections of 135µl.** Using speed programmed injection, larger volumes may be injected by controlling the rate of sample introduction.

OPTIC 2 Large volume mode.

The OPTIC 2 is the *most versatile injector* for gas chromatography. It will bring unrivalled sample introduction and offers you the ability to analyse samples in ways that are better, quicker and more cost effective.
It has its own *electronic pressure control* (EPC) and is thus independent of any GC. Some of the capabilities are: *hot split, cold split, hot splitless, cold splitless, thermal desorption mode, pyrolyse, multi-ramping and off course large volume mode.*
Each mode has its own specific settings. The advantage of the large volume mode is the possibility to use the *solvent monitoring*. This simplifies the optimisation. Also the use of a vent exit next to the split exit gives a great advantage. After the injection the solvent venting occurs with a high vent flow. During the analyses however, the split flow should not be too high. The OPTIC 2 gives this possibility to do this with two parallel flow exits, one split flow exit and one vent exit. So the large liner, the ability to control all injector parameters, the solvent monitoring and the double split exit makes the OPTIC 2 the ideal injector for large volume injections.

Experimental.

The analysis is done on a HP6890 GC with an OPTIC 2 injector. The liner contained a packing material of uncoated supelcoport which is available by ATAS B.V. The column used is Ultra-1 of 25 m, 0.32mm I.D. and a film thickness of 0.17 µm. The oven temperature was kept low at 35°C for 2 minutes and the ramp rate was 15°C/min. to 350°C until end of analyses. In the OPTIC 2 a method for large volume was used. The pressures were kept constant in all modes. The initial temperature was 30°C with an automatic solvent vent time measured by the solvent monitoring mode. After the vent time the injector was heated by 4°C/sec. to 335°C (maximum of supelcoport). The split open time was 2 min.

Results.

An Alkane sample of 1 µl was injected in the splitless mode. After determining the solvent threshold value the same sample was diluted 50 times and 50µl injected in the large volume mode. The areas of the Alkanes of the two different chromatograms were compared and no significant discrimination was observed

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The chromatogram of the 50µl injection is given in figure 1.

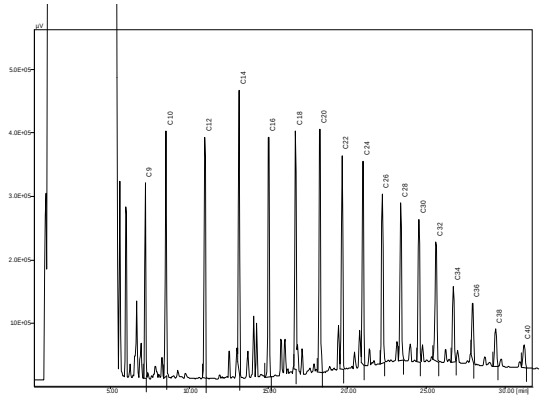

Fig. 1: 50µl injection of n-Alkane mixture.

n-C	1	2	3	4	5	RSD %
9	722909	712104	634461	732133	734767	5.9
10	857423	875856	823772	894015	908643	3.7
12	1229052	1242988	1243087	1261478	1273618	1.4
14	1391526	1437816	1488763	1480736	1493501	2.9
16	1293672	1323466	1302202	1357804	1338697	2.0
18	1279188	1328430	1337045	1408701	1350281	3.4
20	1480291	1579177	1499219	1490166	1590377	3.4
22	1420455	1442664	1379816	1500058	1446246	3.0
24	1321238	1341971	1276633	1426911	1339092	4.0
26	1143513	1198926	1150022	1262549	1212508	4.1
28	1277376	1166814	1137718	1182417	1184044	4.4
30	1090085	1092479	1078506	1144947	1107799	2.3
32	956415	951395	943715	1004994	1006885	3.2
34	606676	618282	612125	651996	615576	2.9
36	542316	576089	578103	626176	622744	5.4
38	348464	359325	351079	384283	373309	4.2
40	241275	247726	243687	255480	249260	2.2

Table 1: Reproducibility of 5 standard injections

The reproducibility is given in table 1. The injections were all done by hand.
In between the standards real oil samples are analysed. The oil sample is taken of soil near a gasoline station. The soil was extracted with hexane and injected into the system.

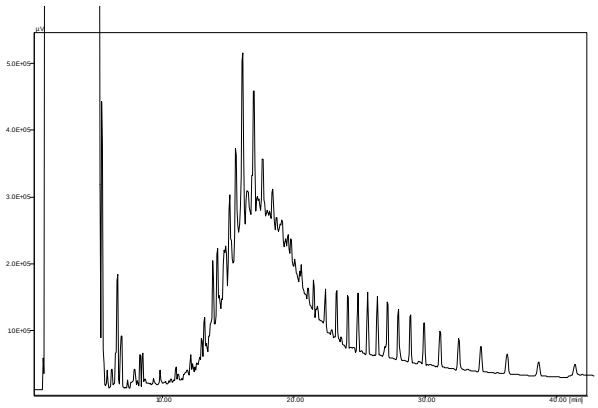

Figure 2 shows the chromatogram.

Fig 2: 50µl injection of oil sample.

Conclusion.

Oil samples can be measured with Large Volume Injection to improve detection limits, and reduces sample pre-treatment time.

The **OPTIC 2** injector is with its unique features like solvent monitoring, large volume **at-once injection** capability (**135 µl**) and EPC ***the*** injector for doing large volume injections.
The system does not require speed-controlled injection, but is nevertheless easily automated with all commercially available auto samplers.

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