Application Note No. 057

The Analysis of High Molecular Weight Polymer Additives Using the Large Volume AT-Column Concentrating Technique

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Introduction

The analysis of high molecular weight compounds by GC is often very difficult. There are many opportunities for sample loss, particularly on transfer of the sample from the injector to the column, caused by incomplete transfer and/or adsorption of the target analytes by charred components on the walls of the liner, hence RSDs are often very high. The AT-Column concentrating technique is presented as a method of analysing these high molecular weight compounds with low RSDs and good recoveries. The sample studied contained polymer additives in DCM with molecular weights of over 1200.

The fraction eluting from an LC or GPC is often very large in comparison to the volume that is possible to inject into a GC, therefore on coupling them a large concentration factor is lost. Using a speed-controlled injection with the AT-Column concentration technique it is possible to inject the majority, if not all of the fraction. In this case it was planned to analyse the additives in a GPC fraction by injecting a volume of 500 µL.

AT-Column Concentration

The AT-Column concentration technique enables the injection of large volumes without the use of packing materials. This prevents the loss of high molecular weight compounds in the liner, as the special AT-Column liner may be heated to the Optic maximum temperature of 600 °C.

The large volume of injected sample is held in the liner by equilibration of the carrier gas entering the top of the liner with the solvent vapour pressure caused by a small amount of solvent entering the pre-column just above it's corrected boiling point. Solvent is vented through a small hole in the side of liner, concentrating the target analytes towards the head of the column, where they are transferred in the liquid state with a small volume of solvent. See Technical Note No 19 for further details about this technique.

Instrumentation & Conditions

- ATAS Optic 2-200 programmable injector
- ATAS Focus Autosampling Robot
- Agilent HP5890 GC with FID

Optic Conditions

Liner:	AT-Column
Mode:	Large Volume
Initial temperature:	43 °C
Vent time:	Auto
Ramp rate:	1 °C/s
Final tmperature:	475 °C
Split open time:	0 mins
Purge pressure:	3.6 psi
Transfer pressure:	20 psi
Transfer time:	1 min
Initial pressure:	9 psi
Final pressure:	35 psi
Solvent threshold:	15

GC conditions:

Column: DB5-HT, 15 m x 0.32 mm i.d. x 0.1 µm film
Pre-column: J&W deactivated prosteel, 2 m x 0.53 mm i.d.
Initial Temperature: 56 °C hold 3 mins
Ramp 1: 20 °C/min to 300 °C hold 0 mins
Ramp 2: 35 °C/min to 400 °C hold 7 mins
FID Temperature: 400 °C

Focus Parameters:
Injection volume: 500 µL
Fill speed: 50 µL/s
Injection speed: 1 µL/s

Chromatograms

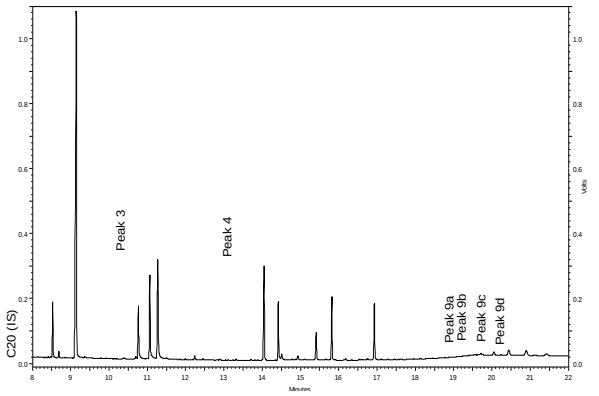

Figure 1: *500 µL injection 100 ppb polymer additives*

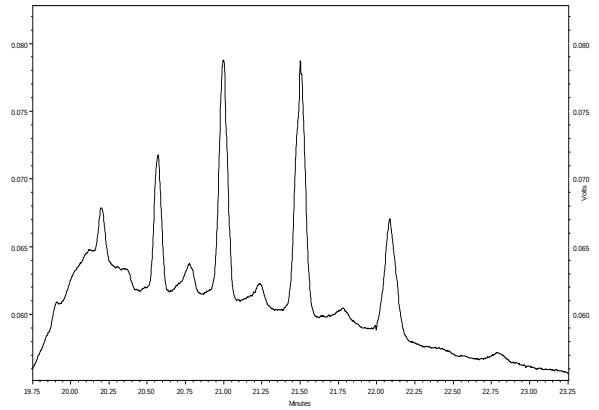

Figure 2*: Close-up of the high molecular weight peaks*

Relative Standard Deviations

Peak	3	4	9a	9b	9c	9(a+b+c)
1	535918	467272	30861	51733	61879	144473
2	539799	442368	27053	50634	61636	139323
3	552289	432008	26637	50561	61000	138198
4		451010	26666	53226	61785	141677
5	635149	481358	27131	56050	63848	147029
6	588275	454805	25432	52020	58465	135917
7	622443	486696	27148	56696	64710	148554
8		456649	24918	49825	55526	130269
9	635978	516415	18716	60865	70686	159367
10	635900	502055	28175	54745	61090	144010
%RSD	**3.43**	**2.06**	**7.18**	**3.69**	**5.71**	**4.44**

Table 1*: Peak areas and RSDs of 10 injections of 500 µL of 100 ppb polymer additives internally standardised to eicosane.*

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Recoveries

Peak	3	4	9a	9b	9c	9d
Average Peak Area	644052	469064	271847	53636	62063	31005
Splitless Injection	615385	694276	33292	63719	70815	31152
% Recovery	1.05	0.68	0.82	0.84	0.88	1.00

***Table 2**: Recoveries, comparing the average peak areas of the 10 AT-Column concentration injections to a splitless injection, not standardised.*

Conclusions

Using the large volume AT-Column concentration technique for the analysis of high molecular weight polymer additives gives low RSDs and good recoveries, therefore is suitable for this application. This technique is also a good interface for the injection of very large speed-controlled injections.

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