LOW TEMPERATURE PYROLYSIS OF POLYMERS

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ABSTRACT: When you take a pyrolysis temperature of about 450°C you get as main products the additives, monomers and oligomers of the polymer which you had pyrolised. In a second step you pyrolisis the same sample at 800°C, were you get nearly the same pyrogram as if you had pyrolised it only at 800°C.

For the identification of the gotten products in the pyrogram by low temperature pyrolysis we pyrolised additives for polyolefines from Ciba Geigy and additives for all kind of coatings and polymers from Byk.

In the common MS-libraries the spectra of the additives are not included. So we build up our own library with about 100 entries.
With this method you get an excellent discrimination power by the analysis of polymers and coatings.

KEY WORDS: Pyrolysis; Additives; Coatings; Polymers.

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INTRODUCTION

The plastics and coatings are composed of binding agent, filling material, pigments and additives. In the cases of clearcoats and transparent plastics only of binding agents and additives.

In the meantime we have very good methods to analyse and differentiate the binding agents, filling material and pigments. But about additives we cannot say anything. Additives are very important and without additive none of the plastics or coatings would work. For the different materials and kind of production you need different additives. So the analytic of additive components would be a powerful instrument of differentiation.

Shimadzu did together with VW Wolfsburg a study of the additives used in their coatings and plastics. They used Pyrolisis/GC/MSD and built up an MS-library, which you can only get from Shimadzu if you buy their Pyrolisis-GC/MSD system. They used a pyrolisis temperature of 550°C.

So we did our own experiments in this field.

CONDITIONS

For pyrolisis we used a Pyrola system. The analysis of the samples was realised at different temperatures. We put the samples on the platinum filament and put 1 µl 3% tetramethylammoniumhydroxid to it. Then we waited 3-5 minutes, before we put the filament into the Pyrola system and started to pyrolisis.

We used 450°C as pyrolisis temperature and afterwards we pyrolised the same sample at 800°C. In addition the samples were pyrolised only at 800°C. As GC/MSD system we used from HP the GC 5980 and MSD 5971.

Following GC/MSD conditions were used:

- Column: 30 m ZB 35, ID 0.25 mm, film thickness 0.25 µm.
- Temperature program: 2 min at 40°C, with 15°C/min to 190°C, then with 4°C/min to 215°C, then with 20°C/min to 340°C and hold this temperature for 6 min.
- Pressure program: 1.5 bar for 1 min, then with 4 bar/min to 0.6 bar, then with 0.042 bar/min to 1 bar, then with 0.13 bar/min to 1.8 bar (end pressure).

RESULTS

The concentration of single additives is about 0.1% to 1%.

First you must see what happened at different temperatures with your pyrolised material. Normally we use for pyrolising temperature about 700–800°C. At this temperature you get many small fragments of the polymer matrix, so you can very well differentiate. But the additives built at this temperature many fragment so you have no change to find them in the big polymermatrix.

At 550°C you get bigger fragments of the polymermatrix, but the amount of fragments often is sufficient for identification and differentiation. Even from the additives you get lesser fragments, so that this temperature is ok for several additives.

At 450°C the temperature is to small to get a sufficient amount of small fragments from the polymermatrix but you also get only few fragments from the additives and this is what you want. In the most cases the additives built at this temperature the main peaks of the pyrogram.

To find the best pyrolisis temperature different temperatures (800°C, 600°C, 550°C, 500°C and 450°C) measured some additives. I will show this with the example of Irganox 1076 (Figure 1). You can see that at 450°C mainly two peaks appear, while at higher temperatures much more peaks appear.

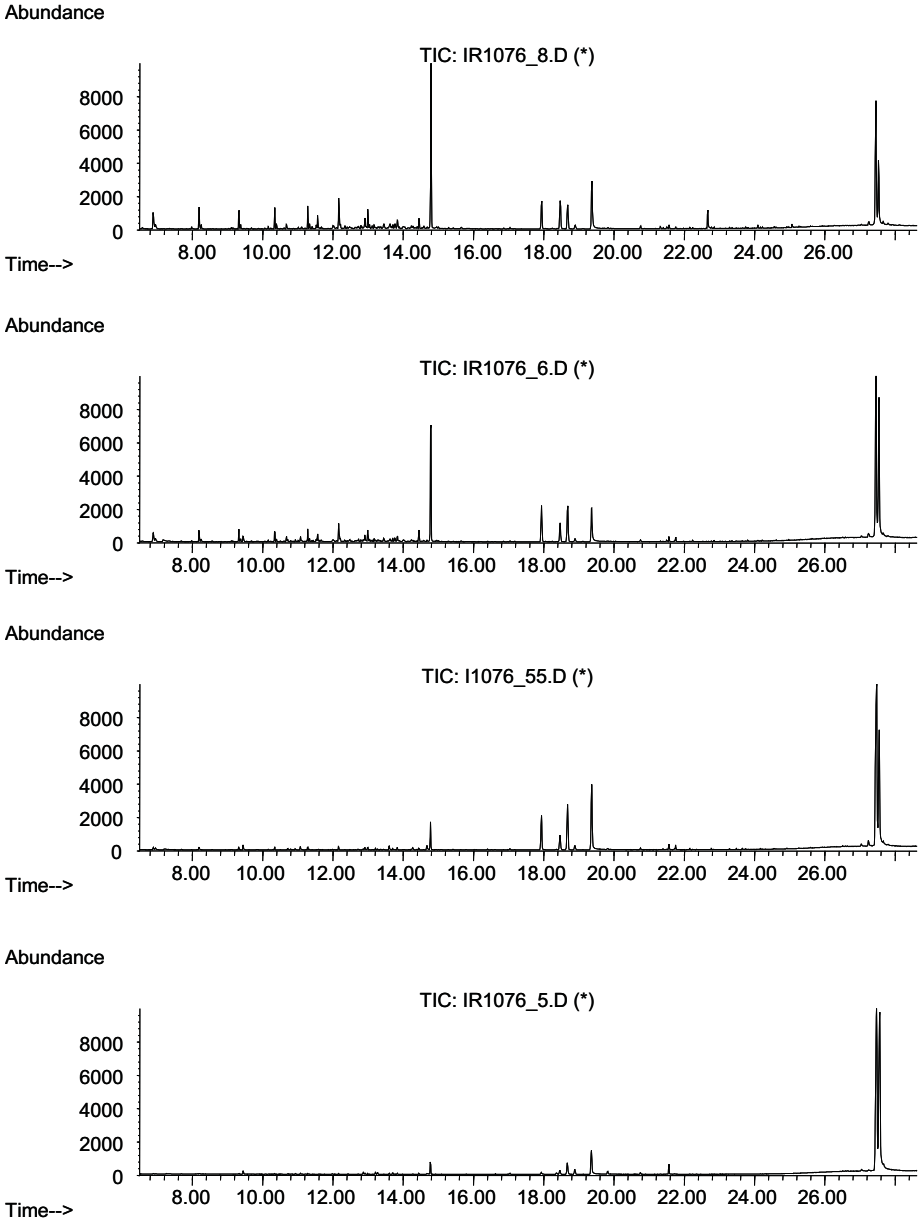

Fig. 1. Pyrolysis of Irganox 1076 (Ciba/Geigy) at different temperatures.

At time we have about 50 additives from the companies Ciba Geigy and Byk Chemie, which all were pyrolised (Figure 2 and 3). Since 3 additives (this were silicon compounds) all could be pyrolised very well. In some cases

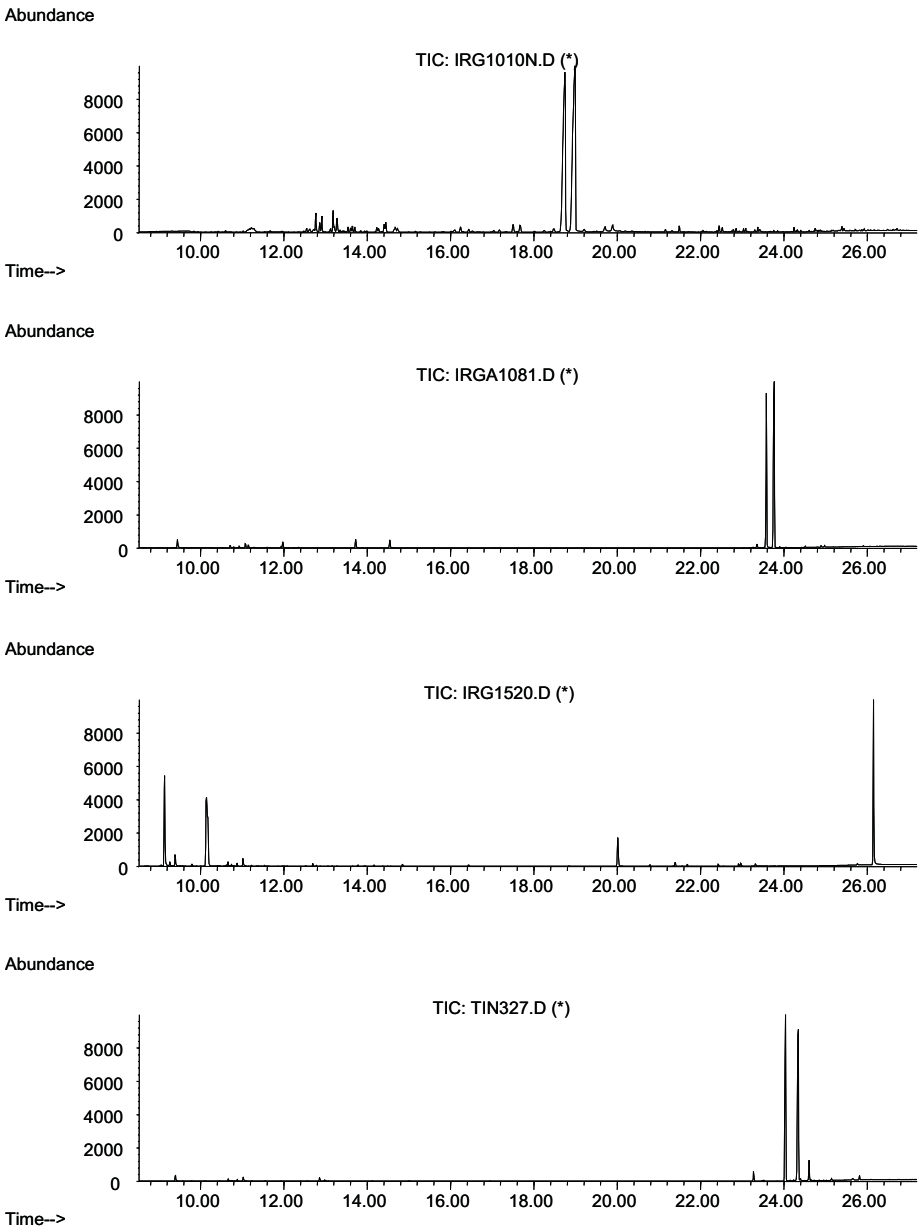

Fig. 2. Pyrolysis of Polyolefine additives (Ciba/Geigy).

the retention times of different additives are the same, but the MS spectra were closely different (Figure 4 and 5).

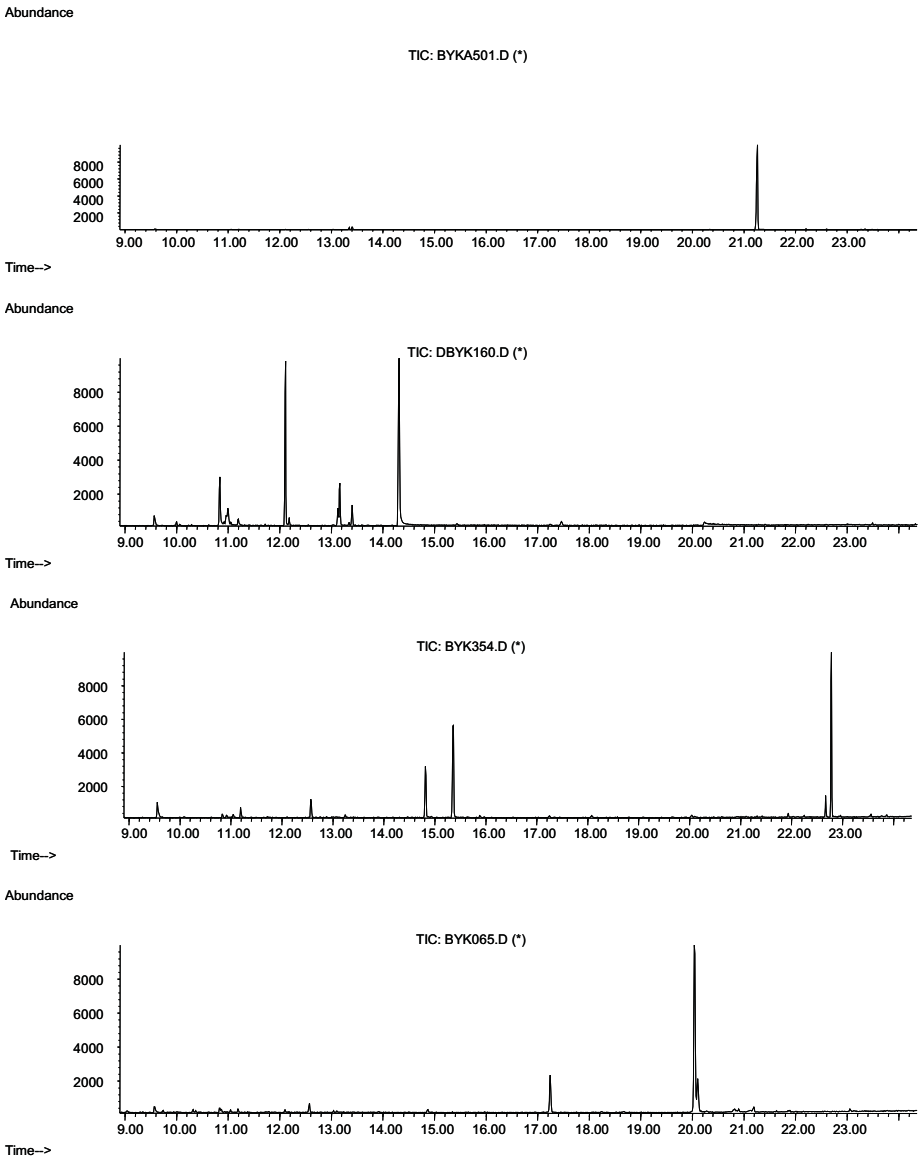

Fig. 3. Additives for polymers and coatings (Byk-Chemie).

The MS-spectra of the fragments which were built from the additives during pyrolisis you cannot find in the normally libraries like Wiley or Nist. So you must create an own library. The MS-spectra of the main components were put into an MS library with which you can identify these additives in coating/plastic samples.

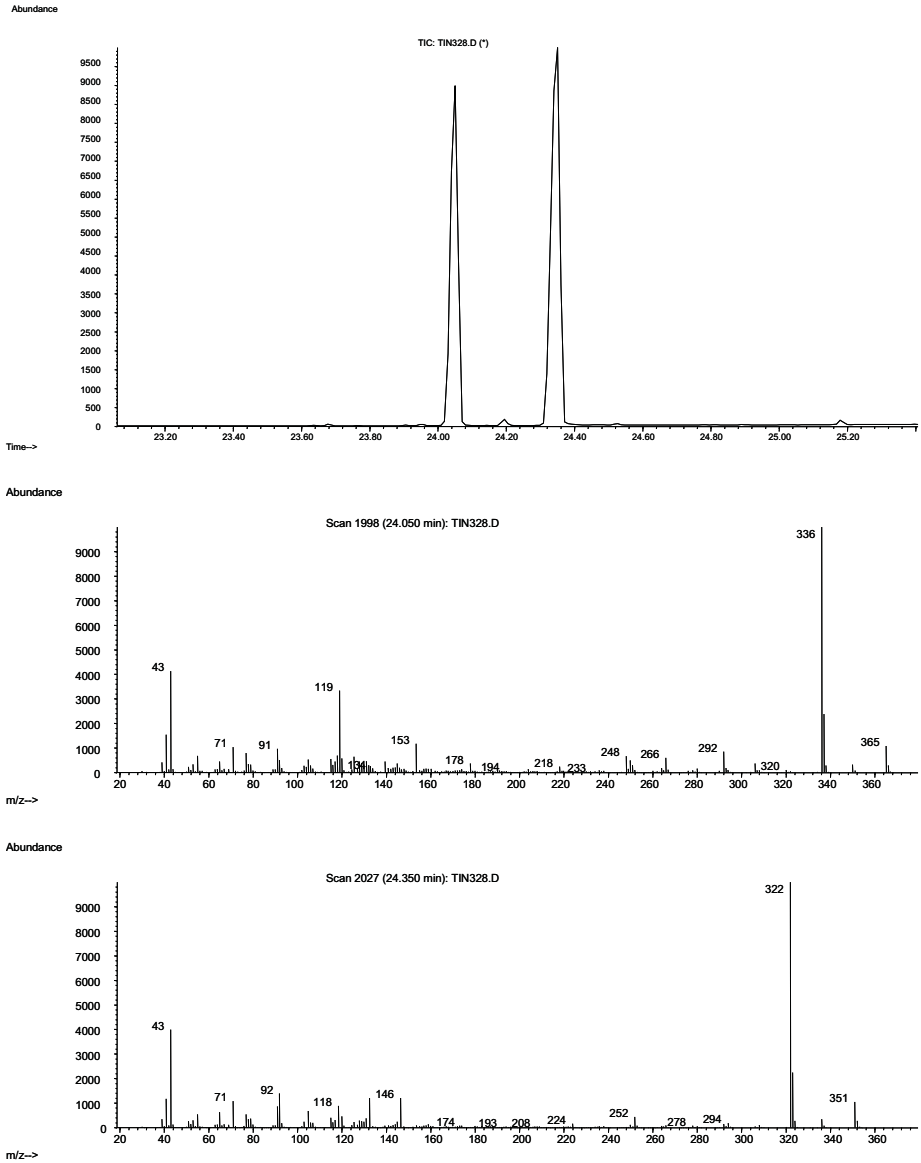

Fig. 4. MS-spectra of Tinuvin 238 (Ciba-Geigy).

From the additives we have got detailed information about chemical structure, characteristic values, support, comment concentration, mode of operation and properties.

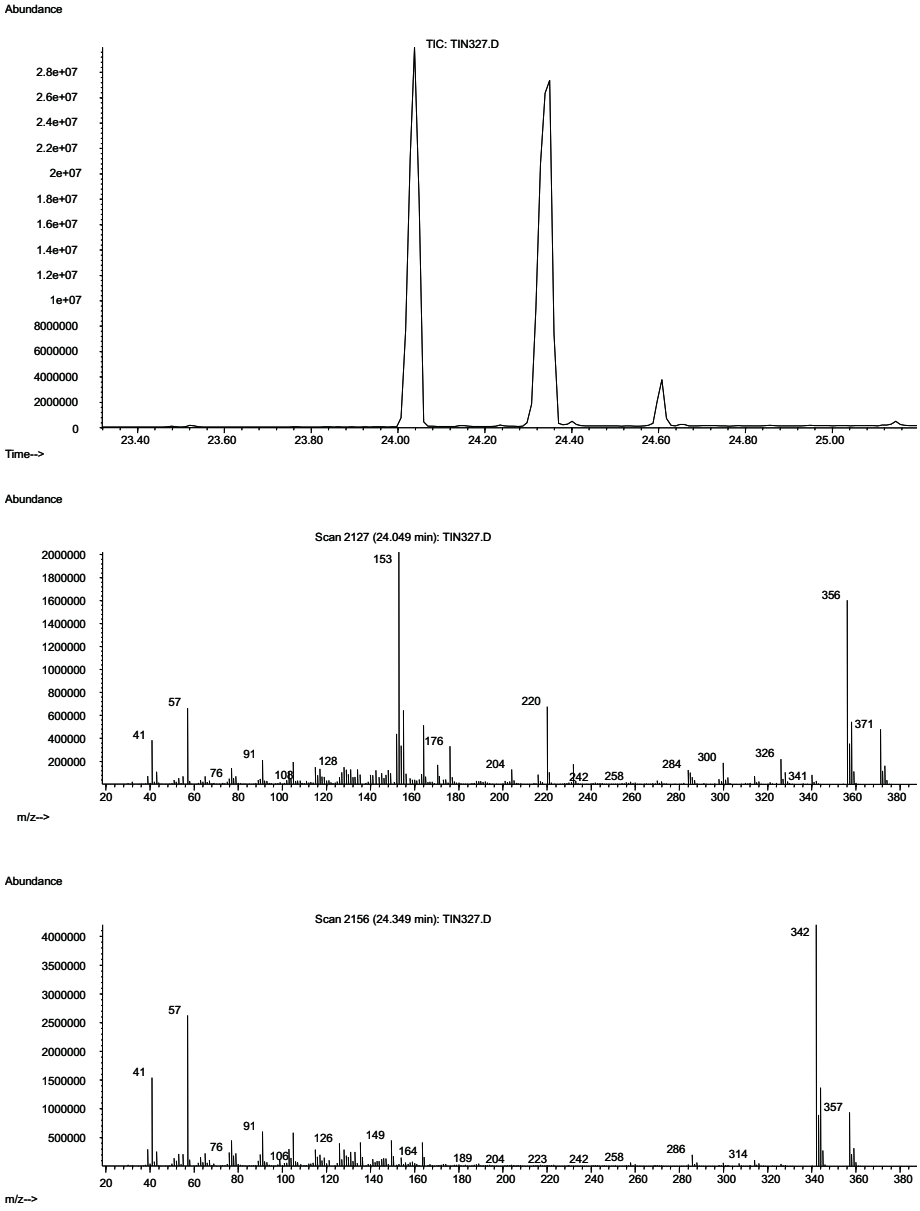

Fig. 5. MS-spectra of Tinuvin 237 (Ciba-Geigy).

When you pyrolise polypropylene at 800°C, you often can see only small differences in the programmes of different polypropylenes, so that it is often very hard to estimate whether the samples agree or not. When you pyrolise

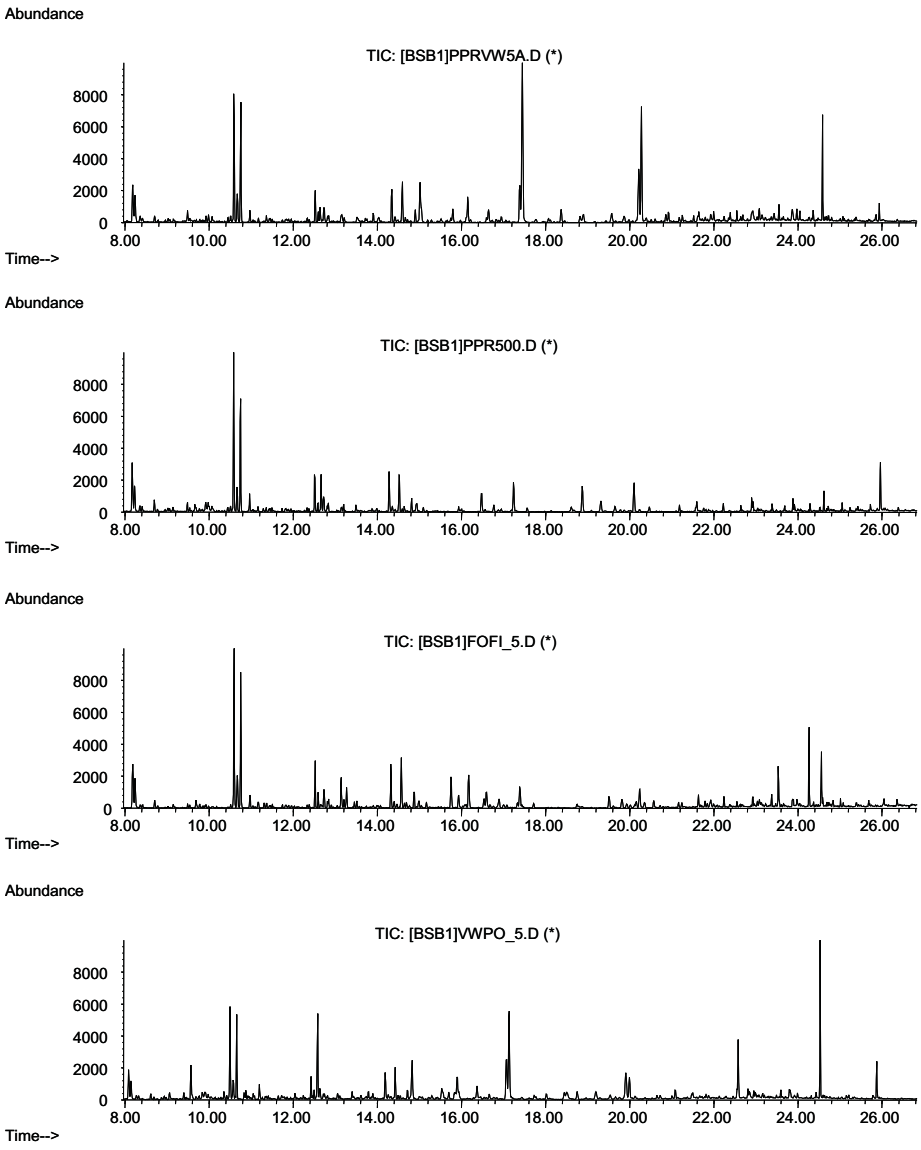

Fig. 6. Pyrolysis of Polypropylene at 450°C.

polypropylene at 450°C, you can see, that from the polymer only small parts are pyrolised, the main sample doesn't react (Figure 6). The plasticiser and additives you can see clear in the pyrograms and they were mainly different. Parts of the additives can be identified with the MS additive library at time (Figure 7 and 8).

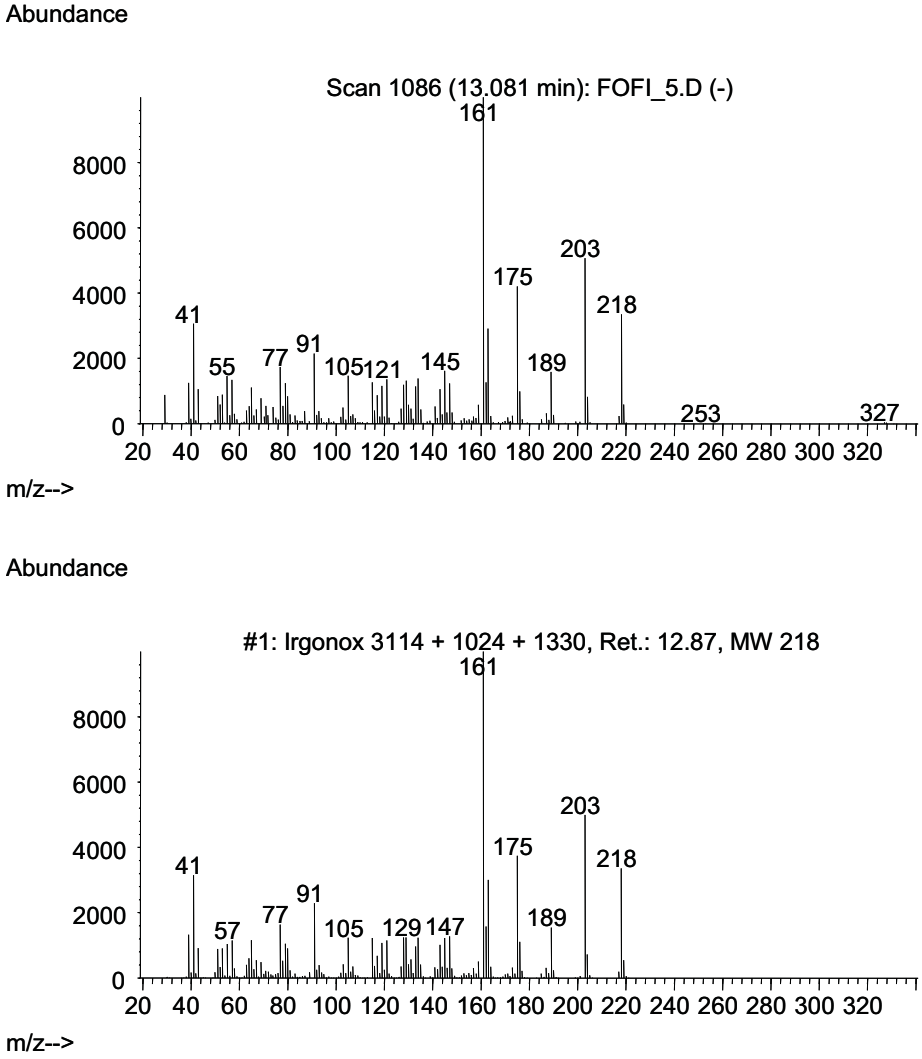

Fig. 7. MS-spectra comparison with the additive library.

Figure 9 shows the same 4 polypropylenes of different cars as shown in Figure 6, which at the first step were pyrolised at 450°C and afterwards a second time at 800°C. Now you can see no characteristic differences.

In Figure 10 in comparison the same polypropylene is shown pyrolised at 450°C and then at 800°C and direct pyrolised at 800°C. You can see that they built nearly the same pyrograms.

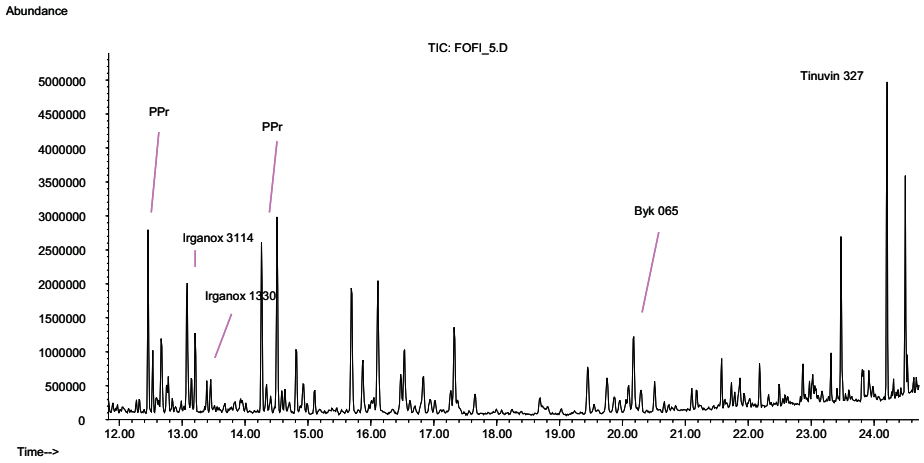

Fig. 8. Additives in polypropylene.

Clearcoats of the same IR type (for example KCN) show in there IR spectra no or only very small differences (Figure 11). If you pyrolise them at 800°C you can often see strong differences and built up several subgroups. The pyrograms of the same subgroup show no or only very small differences (Figure 12). You can get much more differences if you pyrolise the same samples at 450°C (Figure 13).

Figure 14 shows, that you can identify some of the additives with our MS additive library. The result of one peak is shown in Figure 15.

Even basecoats pyrolised at 450°C (Figure 16) show a very good differentiation. The identification of some additives is shown in Figure 17.

SUMMARY

By variation of the pyrolysis temperature was found, that at 450°C the most of the analysed additives decompose only into a few compounds and only small parts of the most polymers did decompose.

The additive then was pyrolised at 450°C and the MS spectra of the main compounds put into an MS library. With this library it is possible to identify additives in paintings/polymers.

The investigation of polypropylene, clearcoats and basecoats, which were pyrolised at 450°C, that mainly, the additives were shown in the pyrograms. If you pyrolisis sample in two steps first at 450°C, then at 800°C in the most

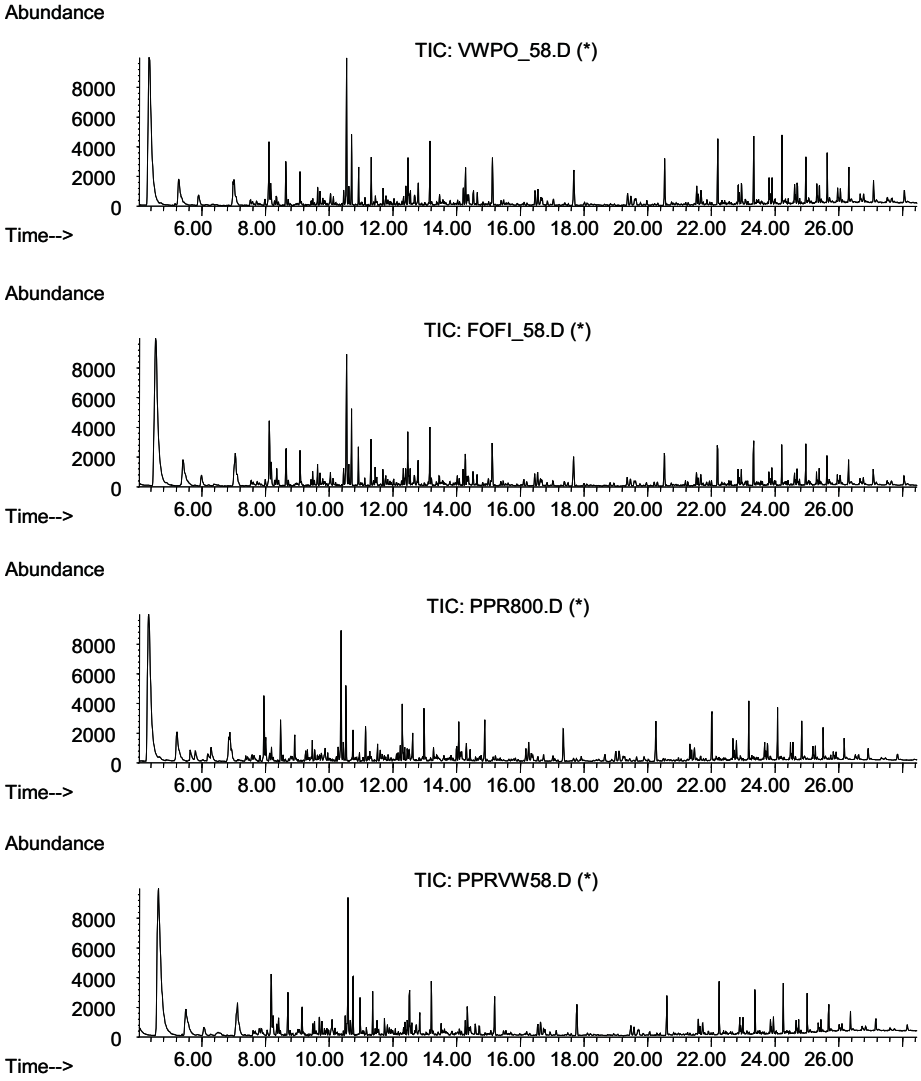

Fig. 9. Pyrolysis of Polypropylene at 450°C/800°C.

cases you get in the second step the same pyrogram as you pyrolisis directly in one step at 800°C.

With this method it is possible to get much more information about the composition of paintings/polymers and you get a much better differentiation.

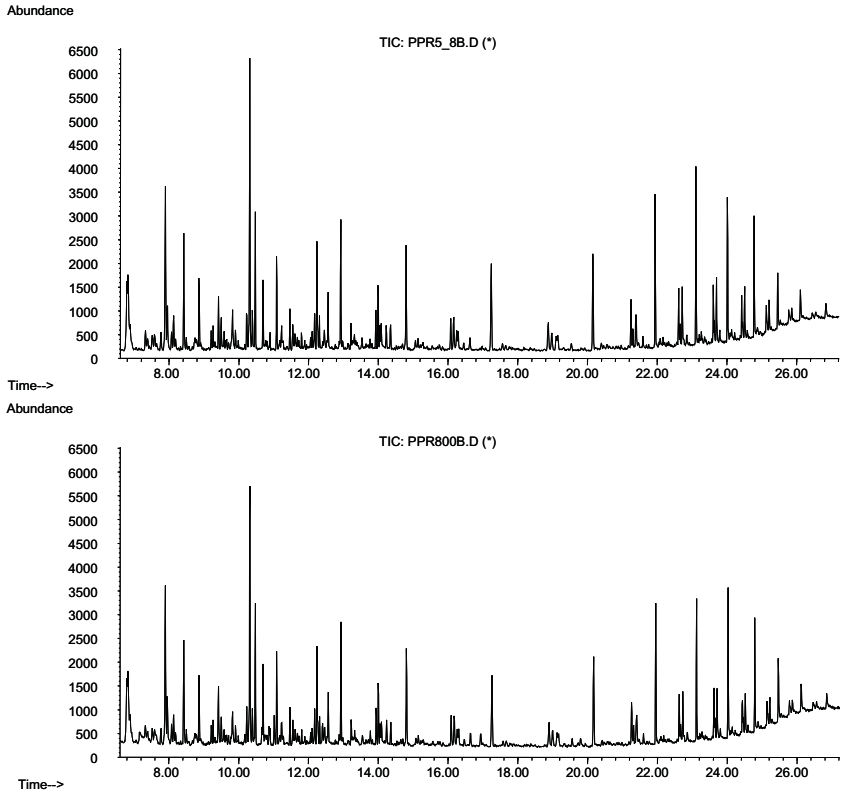

Fig. 10. Pyrolysis of polypropylene at 450°C/800°C and 800°C.

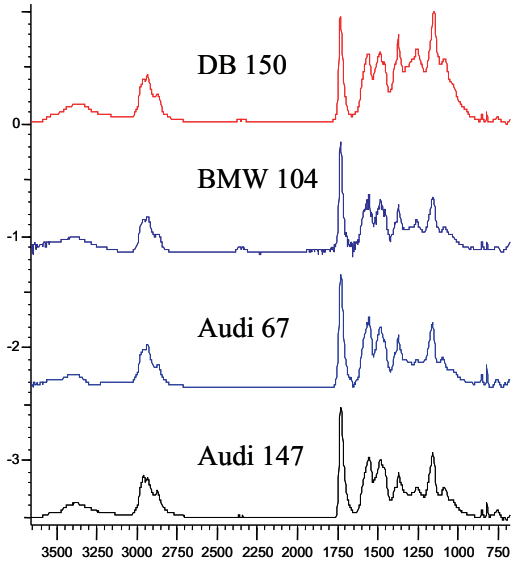

Fig. 11. FTIR-spectra of Clearcoats (KCN).

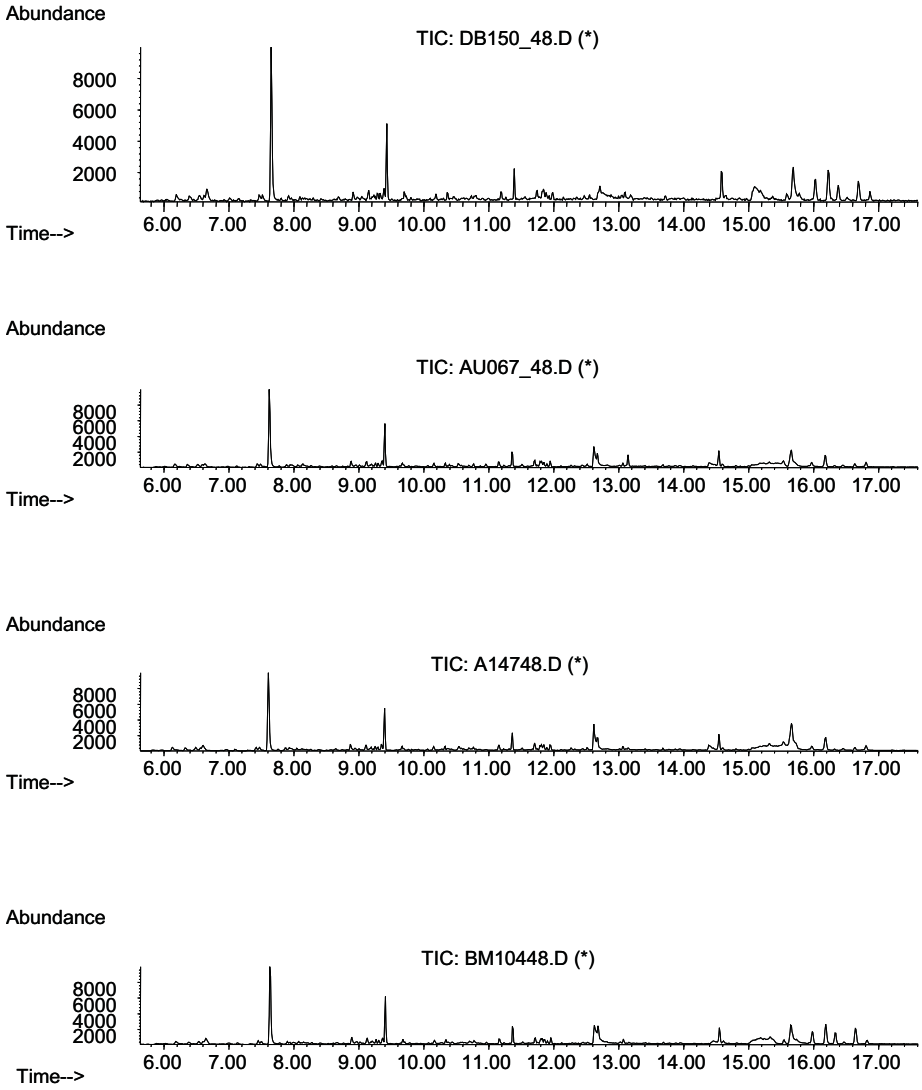

Fig. 12. Clearcoats (IR-type KCN) pyrolised at 800°C.

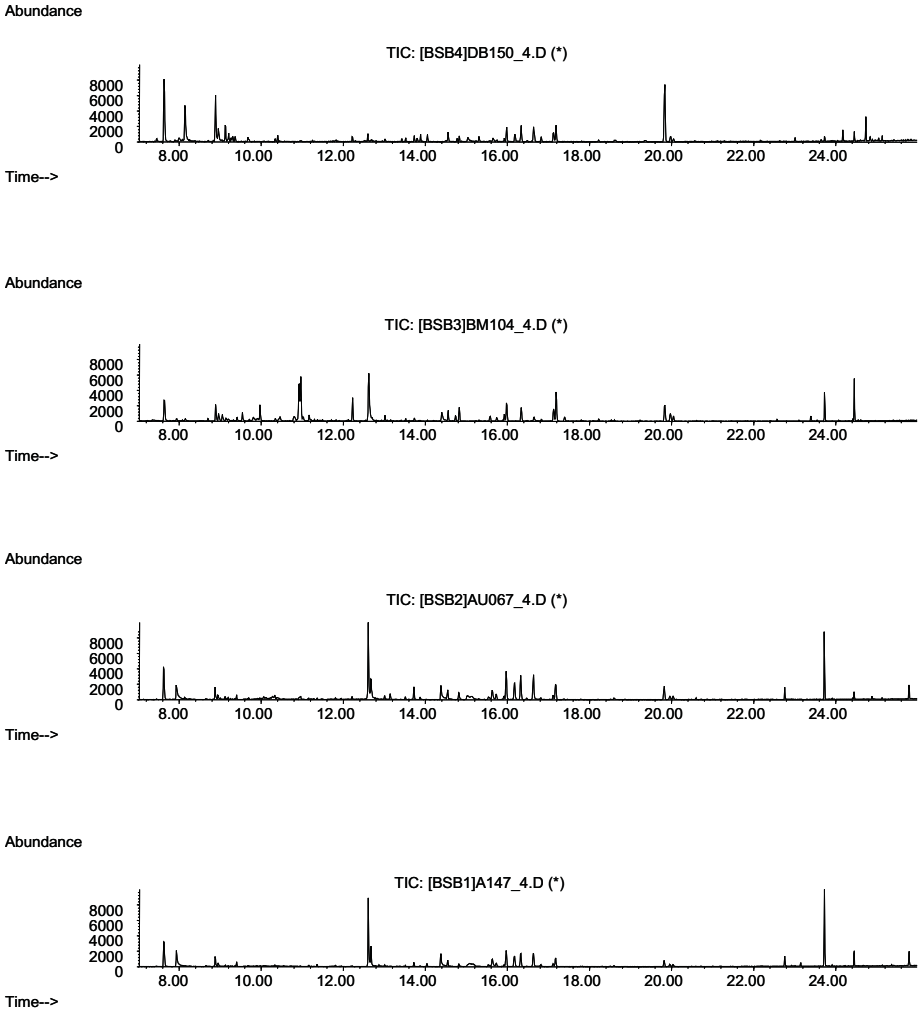

Fig. 13. Clearcoats (IR-Type KCN) pyrolised at 450°C.

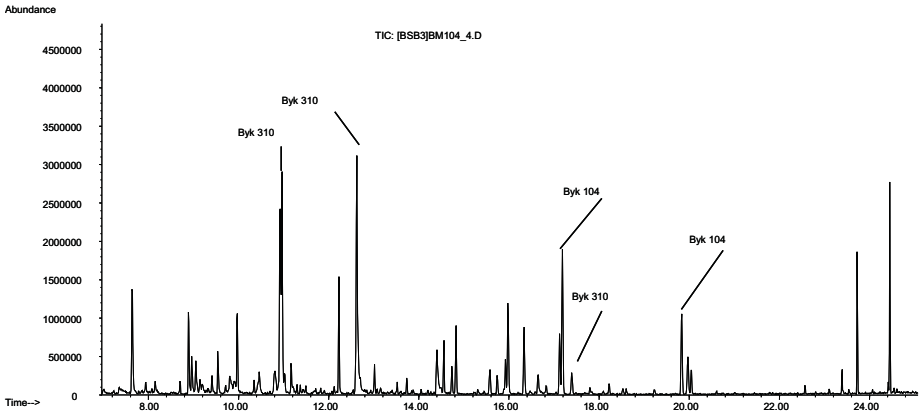

Fig. 14. Additives in Clearcoats (KCN) BMW.

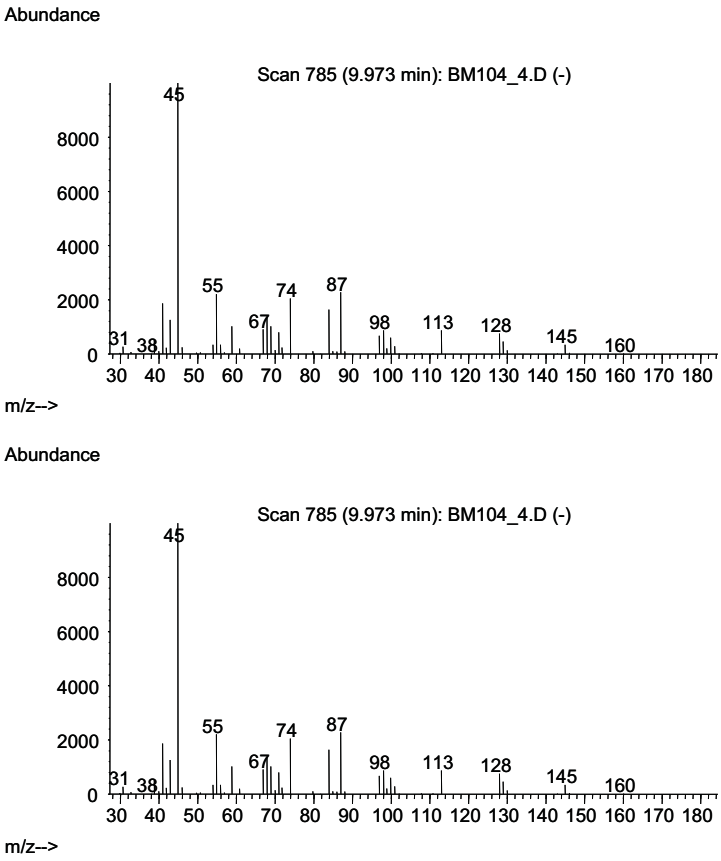

Fig. 15. MS-spectra comparison with the additive library.

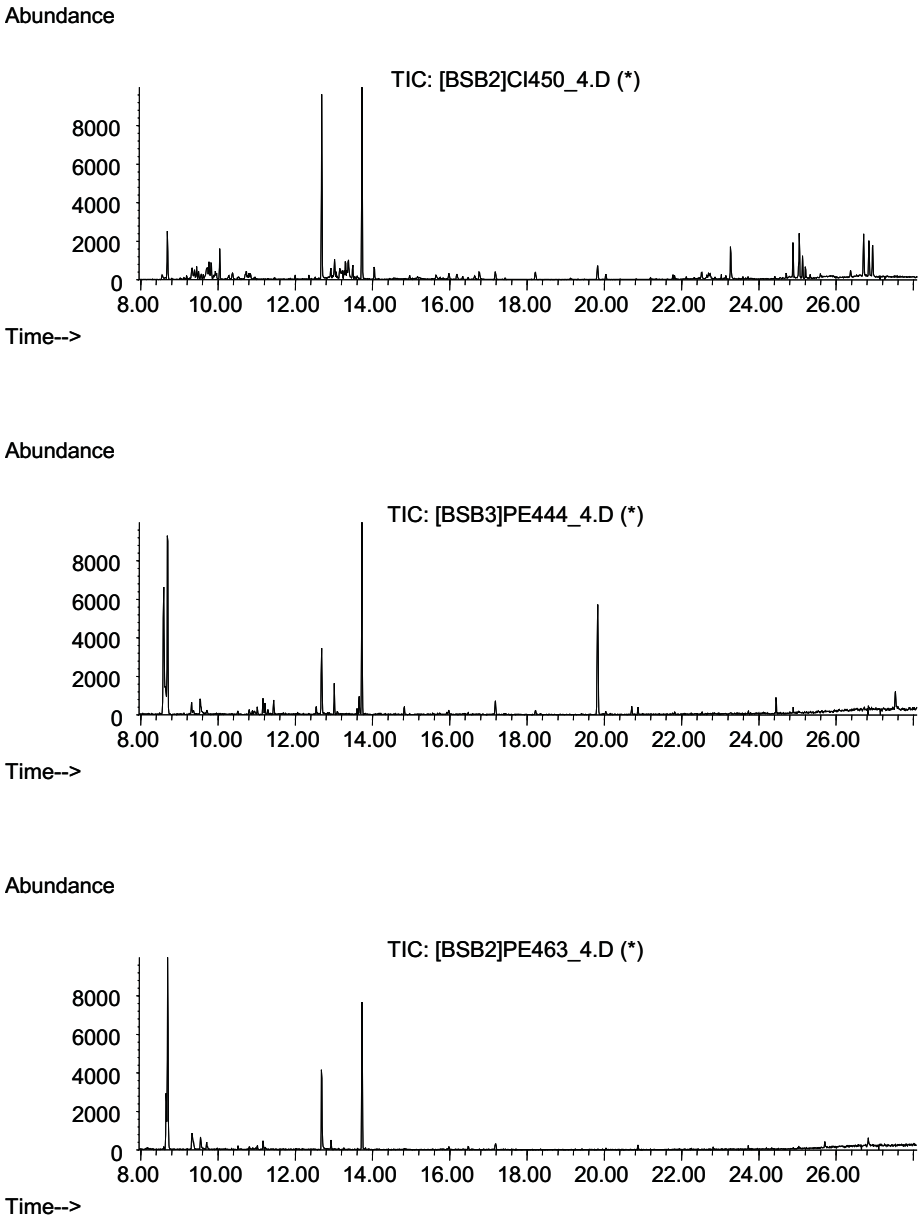

Fig. 16. Basecoats pyrolised at 450°C.

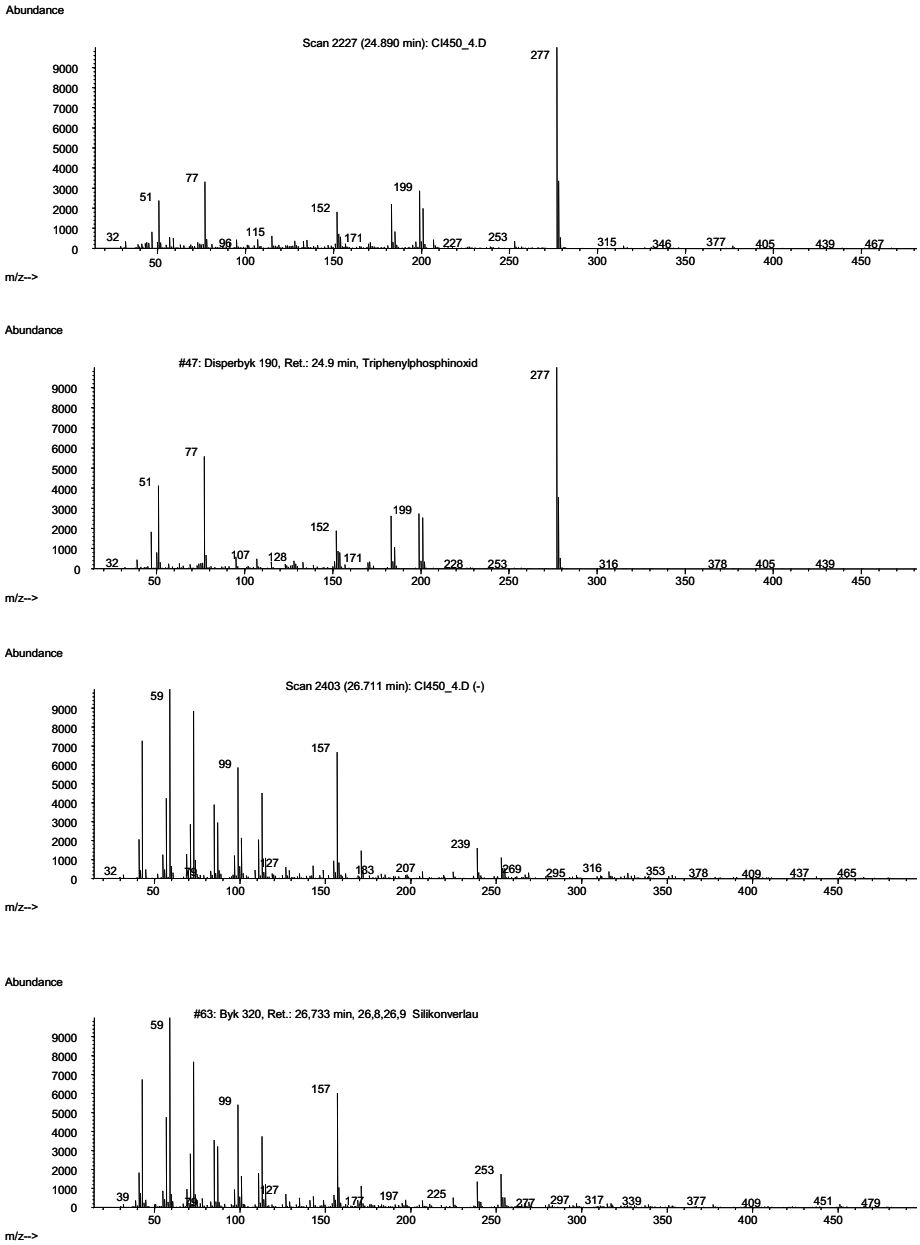

Fig. 17. MS-spectra comparison with additive library.