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Optimization of Capillary SFC-MS for the Determination of Additives in Polymers

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Polymer additives analysis

Summary

A standard direct introduction capillary interface is used for the SFC-MS analysis of polymer additives. The system is optimized with respect to the position of the restrictor, probe tip temperature, and ion source temperature. EI-like charge-exchange spectra are obtained. CI using ammonia as the reagent gas is used for the quantitative analysis of a real world sample.

The experimental capillary SFC-MS spectra obtained show a good similarity with those recorded using the direct insertion probe. The influence of the experimental conditions on the mass spectra obtained is evaluated statistically.

1 Introduction

Polymer additives can be analyzed by means of size exclusion chromatography (SEC), liquid chromatography (LC), or gas chromatography (GC). LC and SEC have less resolution compared to capillary methods [1–4]. Moreover, detection in LC is generally cumbersome. Additionally most LC-MS techniques lack the possibility of producing electron impact-like spectra [5,6]. Due to the high molecular weight of the additives, capillary GC is difficult to apply [7,8].

The determination of polymer additives using capillary supercritical fluid chromatography (cSFC) [9–11] and cSFC coupled with mass spectrometry (cSFC-MS) is more advantageous [12,13]. Several authors have reported on the use of cSFC-MS. An important step in the coupling of cSFC with MS is the interface [14–16]. Although different approaches of interfacing are described in literature, none of these publications contain a truly quantitative optimization of a direct interface for cSFC-MS. Moreover, some of the interfaces described in literature still lack sensitivity and are prone to problems with plugging of the flow restrictor [15].

In this work several instrumental parameters of the direct interface are optimized in terms of sensitivity, signal-to-noise ratio and quality of mass spectral data. The applicability of the optimized system will be demonstrated by the quantitative determination of additives in industrial samples of polymeric materials. As MS is used as a technique for structural elucidation, EI-like charge exchange spectra are produced and compared to electron impact spectra obtained using direct insertion probe sample introduction.

2 Experimental

2.1 SFC Instrumentation

The supercritical chromatograph used in the experimental work, was an SFC 3000 instrument (Carlo Erba Instruments, Milan, Italy). This system consisted of an SFC 300 syringe pump and an SFC 3000 chromatographic oven, both controlled by the SFC 3000 software package running on a PC-AT.

The chromatographic column was a 10 m × 50 μm i.d. SB-Biphenyl-30 with a film thickness of 0.25 μm (Lee Scientific, Dionex, Salt Lake City, UT, USA). Flow restriction was accomplished using a polished integral tapered restrictor [17]. Injection was performed in the timed-split mode using a Valco 3N14W internal loop valve, with a 0.6 μl sample loop (Vici, Schenkon, Switzerland). The temperature of the oven was held at 120°C and the temperature of the injection valve at 30°C. The pressure upon injection was 150 bar. After an initial hold of 5 minutes, pressure was programmed to 350 bar at a rate of 10 bar/min.

2.2 Mass Spectrometer

The mass spectrometer was a Finnigan-MAT TSQ-70 triple stage quadrupole mass spectrometer (Finnigan-MAT, San Jose, CA, USA). The instrument was operated with the first and second quadrupole in the rf-only mode while the third quadrupole was used as the mass filter. The analyzer manifold temperature was held at 70 °C. The filament electron current was held at 200 μA. The electron multiplier was operated at 2000 V, the conversion dynode at -15 kV and the electrometer gain at 10⁻⁷ A/V. For both the positive ion CI and EI spectra, the electron energy was set at 70 eV. The mass filter was scanned from 100 to 1200 amu in 2 seconds.

2.3 SFC-MS Interface

A standard Finnigan-MAT direct fluid introduction capillary SFC-MS interface was used. The transfer line of the interface was held at the temperature of the chromatographic oven (120 °C). The temperature of the SFC probe tip was varied between 240 and 320 °C. The position of the flow restrictor was varied between +5 and -5 mm relative to the end of the heated SFC probe tip. (A negative value represents a position inside the heated probe tip.)

2.4 Materials

A standard solution of 8 polymer additives (Oleamide, Irganox 1076, Irganox 1520, Irgafos 168, Cyasorb 531, Tinuvin 770, Tinuvin 144, and DSTDP) at a concentration of approximately 2.3 g/l in chloroform was used for the optimization experiments. All analysis were performed in triplicate. Carbon dioxide with a purity of 99.996% was obtained from Hoekloos (Amsterdam, the Netherlands). Ammonia CI spectra were obtained using gaseous ammonia (Hoekloos).

3 Results and Discussion

The combination of a separation technique with mass spectrometry forms a very powerful tool for the analysis of unknown samples. In many respects SFC is an intermediate technique between gas chromatography and liquid chromatography. This intermediate position is nicely reflected in the ease with which SFC is combined with mass spectrometry. In contrast to the situation in LC, where fairly complicated interfaces are required to couple the technique to MS, the properties of SFC mobile phases and the low flow rates in open-tubular SFC allow direct interfacing with MS. An important difference with GC-MS interfacing is that in SFC-MS the flow restrictor must be heated in order to prevent solute precipitation.

In this contribution the influence of the SFC probe tip temperature, the position of the flow restrictor relative to the heated probe tip and the source temperature on the MS results is investigated. The peak height, noise level and signal to noise ratio as well as the peak shape and the quality of the mass spectral data obtained are used to evaluate the performance of the coupled capillary SFC-MS system. The experimental mass spectra are compared with spectra generated using a direct insertion probe.

3.1 Influence of the Restrictor Position

In GC-MS, the end of the capillary column is inserted directly into the ion source. This simple method of interfacing cannot be used for coupling supercritical fluid chromatography with mass spectrometry. In SFC-MS a pressure restrictor has to be used, which has to be heated to prevent plugging by solute precipitation. In this work a polished integral restrictor was used. The length of this restrictor was approximately 1 mm.

Three different positions of the flow restrictor are examined: -5 mm, -1 mm, and 5 mm relative to the end of the heated probe tip (where -5 mm means that the restrictor is retracted 5 mm relative to the end of the heated probe tip). Direct heating of the restrictor will of course only be obtained if the flow restrictor is withdrawn to a position inside the heated probe tip region. For these experiments the probe tip temperature was set at 320 °C. In **Figure 1** the influence of the position of the restrictor on the peak height (S) and the signal to noise ratio (S/N) is shown for Irganox 1076.

From the data given in Figure 1 it can be concluded that the signal level increases as a function of the relative restrictor position. Maximum sensitivity is obtained if the restrictor is placed outside the heated region, close to the ion source (+5 mm). However, in this case, the noise level increases more than proportionally. Hence, the signal to noise ratio decreases substantially. A maximum signal to noise ratio is observed at a relative restrictor position of -1 mm. The trend described above is observed for all test components except Irgafos 168. For that particular component, no clear conclusions can be drawn because of the high standard deviation of the measurements.

For practical use of the SFC-MS interface, not only the S/N ratio is important, but also the chromatographic performance in terms of

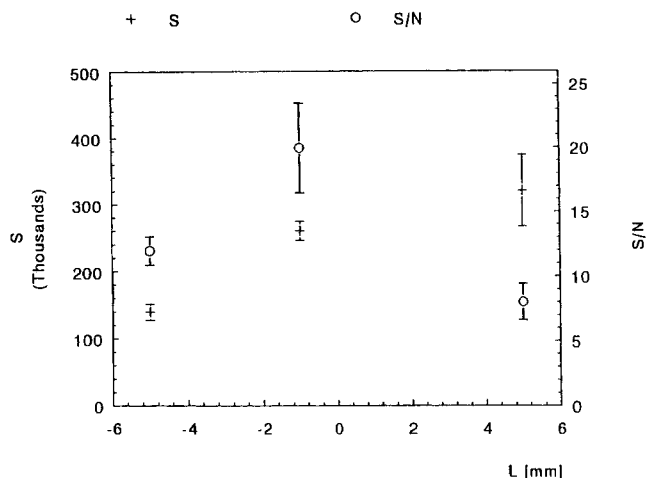


Figure 1
Peak height and signal to noise ratio for Irganox 1076 as a function of the position of the restrictor relative to the end of the heated SFC probe tip. The vertical bars represent plus/minus one standard deviation.

peak shape should be considered. For this parameter the best results are obtained if the restrictor is placed inside the heated region. At a position outside the SFC probe tip, a high and unstable background level is obtained. This is most likely due to clustering of carbon dioxide molecules. In the mass spectrum of the background noise, strong $n \times 44$ peaks ($n = 1, 2, 3, \dots$) can be observed, up to even $m/z = 484$ ($11 \times \text{CO}_2$). These mass peaks are virtually absent if the restrictor position is maintained within the heated zone.

3.2 Influence of the Probe Tip Temperature

The influence of the temperature of the SFC probe tip on the performance of the interface has been investigated for two different restrictor positions. First the flow restrictor was positioned inside the heated region ($L = -5$ mm). As the restrictor in this case is completely surrounded by the heated probe tip, both the restrictor and the expanding CO_2 are heated effectively. In **Figure 2** the influence of the tip temperature on S and S/N is given for Tinuvin 770.

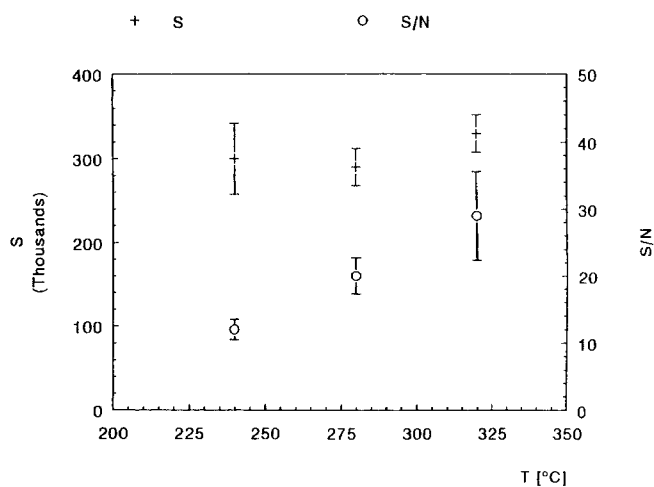


Figure 2
Signal and signal to noise ratio as a function of the probe tip temperature at a relative restrictor position of -5 mm (test component: Tinuvin 770). The vertical bars represent plus/minus one standard deviation.

From Figure 2 it can be concluded that the tip temperature under these conditions has no significant influence on the peak height of Tinuvin 770. Because the noise level decreases at higher temperatures, the *S/N* level increases with increasing probe tip temperature. Similar experiments with other components revealed slightly different trends. For example for Irganox 1076, a decrease of the peak height with increasing temperature was found. For this component the signal to noise level was found to be independent of temperature as also the noise decreased at higher temperatures.

In a second series of experiments, the flow restrictor is positioned slightly outside the heated region ($L = +3$ mm). Under these conditions no significant influence of the temperature neither on the peak height nor on the signal to noise ratio was found. Apparently, neither *S* nor *S/N* were affected by the probe tip temperature.

The explanation for the observed trends is rather straightforward. Rapid heat exchange is obtained only if the restrictor is placed within the heated region of the SFC probe tip. Under these conditions heat transfer to the restrictor effectively compensates for cooling caused by the expansion of the supercritical fluid in the restrictor. Carbon dioxide clusters, which are formed during the expansion process, will be broken up effectively. The rapid heat exchange also favors mass transfer of low volatile components to the ion source.

3.3 Influence of the Ion Source Temperature

In order to investigate the influence of the ion source temperature, peak heights and signal to noise ratios were measured at two different source temperatures. In these experiments the restrictor was placed 5 mm outside the SFC probe tip. At a source temperature of 190 °C a very high background and ill-shaped tailing peaks were obtained. This was caused by clustering of CO₂ molecules as has been discussed before. When increasing the source temperature to 250 °C, a dramatic reduction of the background level was observed. Moreover, the peak shapes improved significantly. In particular this was the case for DSTDP, the most retained component in the test sample.

The best results, from a chromatographic point of view, are obtained with a relative peak distance of -1 mm and a probe tip temperature of about 320 °C. In Figure 3 a representative chromatogram of the separation of the test solution is shown at the optimal conditions identified in the present study. Under these conditions the detection

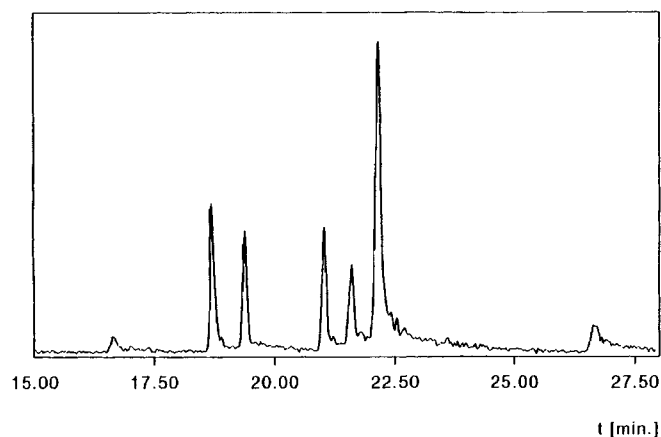


Figure 3
Reconstructed ion current chromatogram of polymer additives test sample ($L = -1$ mm, $T_{tip} = 320$ °C).

limit is estimated to be approximately 0.05 g/l in the full scan mode. Chemical ionization conditions improve the sensitivity more than 10 times.

3.4 Comparison of Mass Spectra

Due to the high carbon dioxide pressure in the ion source, no true EI spectra can be generated in SFC-MS. Fortunately, however, EI-like charge exchange spectra can be obtained. Hence, chemical structure determination is possible in SFC-MS.

To evaluate the applicability of cSFC-MS for the identification of polymer additives, a comparison was made of experimental spectra and mass spectral data obtained with the direct insertion probe. A direct comparison of experimental spectra with library spectra was not possible due to the limited availability of library data for polymer additives. The mass spectra obtained in the SFC-MS experiments show a good similarity with spectra generated using the direct insertion probe. In Figure 4 the SFC-MS spectrum and the probe spectrum of Cyasorb 531 are compared. In the comparison of SFC-MS and direct insertion probe spectra, in general, two trends were observed. Firstly, the abundance of the molecular ion peak is generally lower in the SFC-MS spectrum. Secondly, the SFC-MS spectra exhibit an increased abundance of ions in the low mass range (100–200 amu). Apparently a stronger fragmentation occurs under SFC conditions.

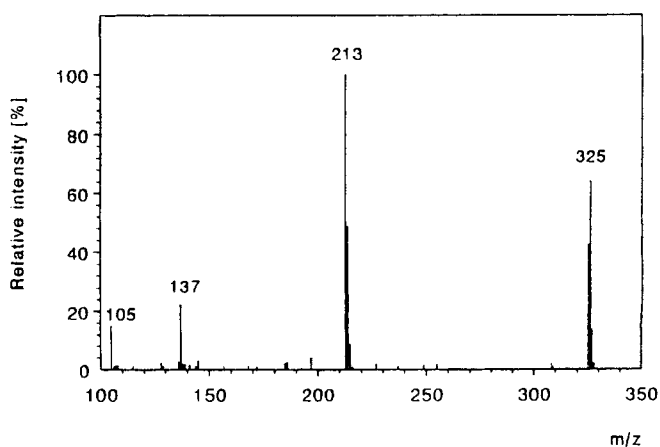
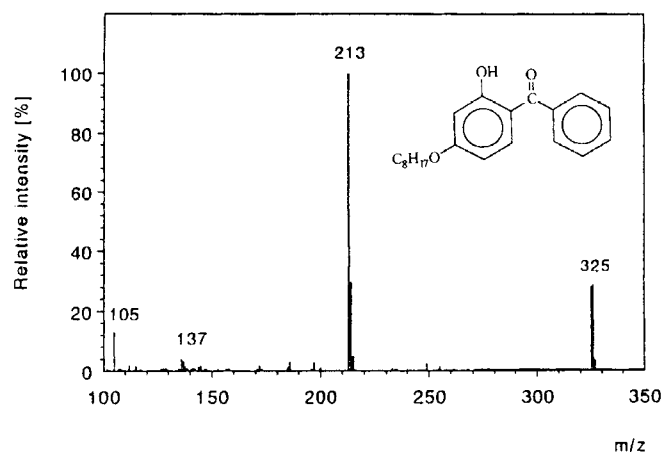


Figure 4
SFC-MS spectrum (top, conditions: $L = -5$ mm, $T_{tip} = 320$ °C) and direct insertion probe spectrum (bottom) of Cyasorb 531.

Table 1
Mean relative abundance of four masses in the SFC-MS spectrum of Cyasorb 531 as a function of experimental conditions.
The values between brackets give the relative standard deviations of the experimental data.

<i>m/z</i>	<i>L</i> = -5 mm <i>T</i> _t = 320 °C <i>T</i> _s = 190 °C	<i>L</i> = -5 mm <i>T</i> _t = 280 °C <i>T</i> _s = 190 °C	<i>L</i> = -5 mm <i>T</i> _t = 240 °C <i>T</i> _s = 190 °C	<i>L</i> = -1 mm <i>T</i> _t = 320 °C <i>T</i> _s = 190 °C	<i>L</i> = +5 mm <i>T</i> _t = 320 °C <i>T</i> _s = 190 °C	<i>L</i> = +5 mm <i>T</i> _t = 320 °C <i>T</i> _s = 250 °C
105	19 (± 2)	18 (± 3)	17 (± 1)	20 (± 1)	16 (± 4)	21 (± 10)
137	17 (± 1)	16 (± 2)	17 (± 1)	17 (± 2)	16 (± 4)	17 (± 2)
213	100 (± 2)	100 (± 14)	100 (± 2)	100 (± 5)	100 (± 8)	100 (± 2)
325	44 (± 3)	39 (± 10)	50 (± 1)	40 (± 3)	35 (± 4)	39 (± 5)

In order to investigate the influence of the restrictor position, the probe tip temperature and the source temperature on the quality of the spectra, the spectral data of a number of selected compounds has been evaluated statistically. No significant trends in the spectra could be observed. Although, for some compounds, a lower abundance of the molecular ion was obtained at increased source temperatures. A similar trend is frequently also observed in GC-MS. In **Table 1** the mean relative abundances of four ions in the spectrum of Cyasorb 531 are shown as a function of the experimental conditions. From the values in this table it can be seen that the variations in experimental conditions have no significant effect on the MS spectra obtained. From this in turn, it can be concluded that in the process of optimizing a system for capillary SFC-MS only the sensitivity and the chromatographic integrity of the system have to be considered.

3.5 Practical Application

To test the applicability of the SFC-MS system for real world samples, a supercritical fluid extract of a polyethylene sample has been analyzed under ammonia chemical ionization conditions. The ion source pressure was approximately 5200 mTorr. The samples contained the additives Irgafos 168, Irgafos 168 phosphate and Irganox 1076. For quantification of the peaks, the internal standard method has been used. Tinuvin 770 was used as the internal standard. The quadrupole mass filter was scanned from 400 to 700 amu in 1 s. Calibration curves were made with standard solutions at concentrations of 0.05, 0.1, 0.5, and 2.5 g/l. The concentration of the individual components in the extract was calculated by integration of the reconstructed ion current chromatogram of one or two intense mass peaks (**Figure 5**). The relative deviation between two analyses of one extract is approximately 8% for the sum of Irgafos

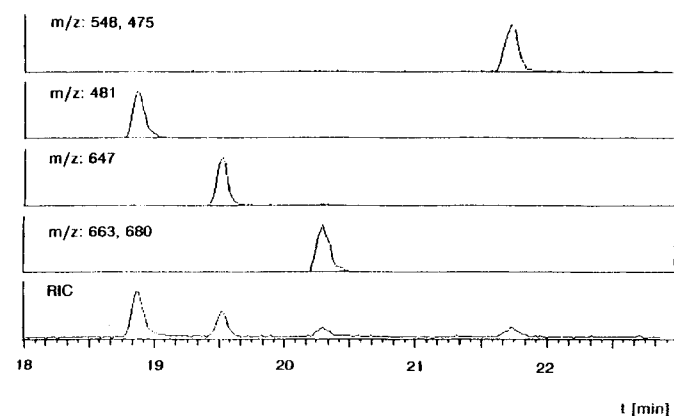


Figure 5
Total ion current chromatogram and selected reconstructed ion current chromatograms of the separation of a polyethylene extract.

168 and Irgafos 168 phosphate and 13% for Irganox 1076. The relative deviation between two extracts was better than 12% for the sum of Irgafos 168 and Irgafos 168 phosphate and better than 8% for Irganox 1076.

4 Conclusions

Experimental conditions as for example probe tip temperature, relative position of the restrictor and source temperature were found to have a significant influence on the sensitivity and the chromatographic performance of the combined capillary SFC-MS system. Optimum sensitivity and good chromatographic results were obtained when the restrictor was positioned close to the end of the SFC probe heater. The optimum temperature was found to be 320 °C. Non-optimized conditions result in both a poor sensitivity and a loss of chromatographic resolution.

The SFC-MS spectra were found to be independent of the experimental conditions and showed a good similarity to direct insertion probe spectra.

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