Optimization of an analysis method for the determination of N-nitrosamines in rubber

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Introduction

CTC is developing a method to analyze N-nitrosamines in rubbers and elastomeric materials. These compounds are dangerous for the environment and humans because of their carcinogenic properties. Therefore, it is important to identify and quantify them. This article will focus on 12 components to be analyzed by gas chromatography-mass spectrometry.

Materials

Five grams of polymer are extracted with thirty milliliters of methanol with an ultrasonic device at room temperature during thirty minutes. An optional clean-up step based on a C18 SPE cartridge could be conducted before the analysis.

The N-nitrosamines are analyzed by GC-MS/MS (Agilent 7000 and 7890A GC System). The mass spectrometer uses an Electronic Impact source and has a triple quadrupole. The carrier gas used was Helium with a flow rate of 1.0mL/min.
The mass spectrometer will operate in MRM mode.

The analytical standard is provided by Sigma-Aldrich and consists of one mixture with the 12 components at 2000 mg/l in methanol.

Experimental procedures

In order to create the MRM transitions for each compound, several runs in full scan mode were performed in order to:

- Find the right oven gradient
- Determine the retention time of each target compound
- Have a full spectrum of the target compound for choosing the precursor ion

After several test, the right gradient starts with 40°C for 4 minutes then a slope of 10°C/min until it reaches 255°C which lasts 4 minutes. The chromatogram can be seen in the figure 1. Firstly, the splitless mode for the injector was used with a temperature of 250°C but the pulsed splitless mode showed that it was better for the resolution. The reduction of the injection temperature to 200°C prevented the degradation of two compounds: the N-nitroso N-methylaniline (1) and the N-nitroso N-ethylaniline.
Nevertheless, some decomposition was still there (2). Thus, some compounds are thermolabile.
After that, the Product Ion Mode was used for determining the produced ions. For each compound, the precursor ion is broken with different collision energy and the produced ions are recorded. Two transitions were chosen for each target/compound.
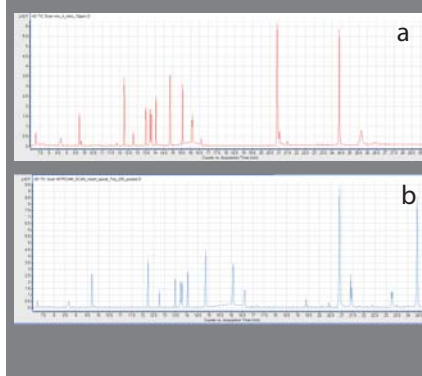Example of transition for the N-nitroso morpholine:

116 -> 86 with a collision energy of 5 eV.
116 -> 56 with a collision energy of 10 eV.

Figure 1: Comparison of two chromatograms of N-nitrosamines in full scan mode.
a. In splitless mode – b In pulsed splitless mode

Conclusion

This method could be used to identify and quantify the N-nitrosamines. The only problem is the decomposition of the N-nitrodiphenylamine in diphenylamine[3]. Maybe a solution for this problem is to test the analysis of these compounds in HPLC-MS-MS

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