Analysis of Polymers, Additives and Contaminates in Medical Devices using Pyrolysis-GCMS

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Abstract

Polymers and additives are used in a variety of subcutaneous and intravascular medical devices, such as sutures and drug delivery systems. These devices typically can be classified as being either absorbable or non-absorbable by the human body.

Natural materials, such as silk and catgut, are largely being replaced by synthetic materials. So, the reliability of these devices relies on the quality and proper application of these synthetic compounds. But regardless of their composition, the materials used are foreign to human tissue and will elicit a foreign body reaction to a greater or lesser degree.

This poster will show the analysis of several types of implanted medical devices from different manufacturers using pyrolysis-GCMS. Traditionally, pyrolysis has been used as a technique to identify polymers, which will be shown. But in addition, one or more "pre-pyrolysis" steps will be programmed first so that we can analyze for residual monomers, solvents, additives and contaminates, if present. Undesired contaminates or the incorrect quantity of an additive can often lead to product failure or worse.

Experimental

Pyrolyzer

Samples were pyrolyzed using a resistively heated coil filament pyrolyzer (Pyroprobe 5200). The samples were placed into a quartz tube and held in place using plugs of quartz wool.

Interface Temperature: 325°C
Py Filament Temperature: 150, 350, or 700°C for 15 sec. (noted in figures)
Pyrolysis Gas: Helium
Valve Oven: 325°C
Transfer Line: 325°C

GC-MS

Injection port: 325°C
Carrier: Helium, 1ml/min
Column: 30m x 0.25 mm 5% phenyl methyl silicone
Split: 75:1

Oven:	Detector:
Initial: 40°C 2 minutes	Type: Quadrupole
Ramp: 10°C/min	Scan: 35-550 AMU
Final: 300°C 5 minutes	Ion Mode: EI+

Results & Discussion`

Several samples were analyzed including an absorbable suture and drain tubes. Multiple step runs at increasing temperatures were programmed for each so that we could analyze for additives, monomers and any contaminants before pyrolyzing the remaining polymers. In addition to using a NIST library, a polymer library developed by CDS was used in helping to identify the polymers.

Penrose Drain Tube

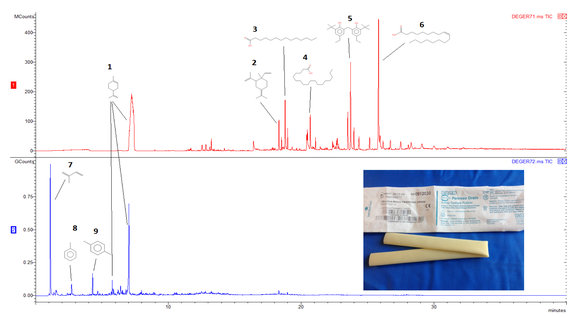

Figure 1: Penrose Drain Tube, 300°C (Top) & 700°C (bottom).

1. **Limonene**
2. **Cyclohexane, 1-ethenyl-1-methyl-2-(1-methylethenyl)-4-(1-methylethylidene)-**
3. **Tetradecanoic acid**
4. **Octadecanoic acid**
5. **Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4- ethyl (antioxidant 425)**
6. **9-Octadecenamide, (Z); (Oleamide)**
7. **Isoprene**
8. **Toluene**
9. **p-Xylene**

The first sample (figure 1) is a Penrose Drain Tube, which is typically placed in a wound to prevent the build-up of fluids. The sample was heated to two temperatures; 300C and then 700C .

At 300C we see several compounds thermally extracted including limonene (1), which is the dimer of latex rubber and also the trimer (2). So at 300C, we can see a slight degradation of the polymer but it mostly is still intact. There are a series of fatty acids (3 & 4) that probably are mold-release compounds on the surface of the airway tube left over from its manufacture. Two additives detected include an antioxidant (5) and another, Oleamide (6), which is sometimes used as a lubricant.

When the remaining sample is pyrolzyed to 700C, the pyrogram is typical for polyisoprene and it fully breaks down to the monomer (isoprene marked as 7) and the dimmer (limonene, marked as 1). The small peaks for toluene and benzene are common residuals seen when latex rubber (mainly polyisoprene) is pyrolyzed.

Airway Tube

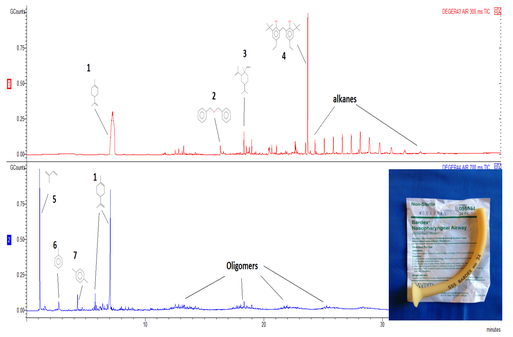

Figure 2: Airway Tube, 300C (Top) & 700C (Bottom)

1. **Limonene**
2. **Dibenzylamine**
3. **Cyclohexane, 1-ethenyl-1-methyl-2-(1-methylethenyl)-4-(1-methylethylidene)-**
4. **Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-ethyl (antioxidant 425)**
5. **Isoprene**
6. **.. Toluene**
7. **p-Xylene**

In figure 2 we have a Nasopharyngeal Airway Tube. The tube is designed to be inserted into the nasal passageway to secure an open airway. This tube was also pyrolyzed at 300C and 700C. We can see several residual oligomers from latex rubber, limonene (1) and the trimmer (3) in the run at 300C. Also shown are several additives including an antioxidant (4) and a series of alkanes that may have been added for lubrication.

Another compound identified is Dibenzylamine (2) which is sometimes added as an accelerator during the rubber manufacturing process. Although Dibenzylamine is a known eye and skin irritant, residual levels appear to be very low and should not have any adverse effect for the patient.

In the second run at 700C, the latex rubber fully breaks down giving us mostly isoprene (5), limonene (1) and traces of several higher oligomers,

Coated Suture

A named brand suture, Vicryl Plus (Figure 3) was analyzed using three programmed steps; 150C, 300C and 700C. This suture is sold as an absorbable type which breaks down in the body by hydrolysis in 60-90 days. In the first run we see Triclosan (1), which is added as an antibacterial agent. At 300C, we still see some residual Triclosan and another peak for Octadecanoic acid (2). Some sutures are coated to ease the threading process and often the coating is Magnesium Stearate. In this case, it is believed that the Octadecanic acid (or stearic acid) is a pyrolysis product of the Magnesium Stearate coating.

Coated Suture continued

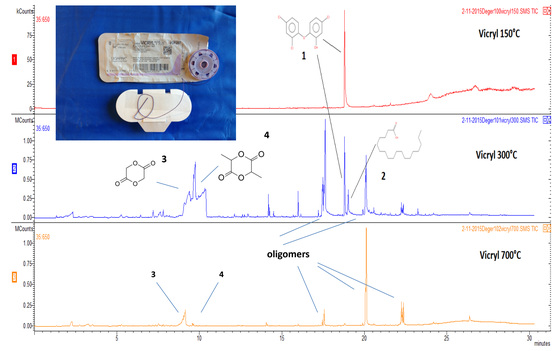

Figure 3: Coated Suture 150C (Top), 300C (Middle) & 700C (Bottom)

1. **Triclosan**
2. **Octadecanoic acid (stearic acid)**
3. **Glycolide**
4. **Lactide**

Finally, we come to the polymer. Vicryl is marketed as a copolymer of 90% glycolide and 10% L-lactide. We can see from peaks 3 and 4 that the polymer begins to degrade even at 300C, although the peaks are poorly resolved. We have the monomer produced for each of the polymers as the primary pyrolysis break down products. Several oligomers of each are also produced, although they have a poor quality match with the NIST library. A standard run on each of these polymers showed a similar break down based on retention times. The CDS polymer library , based upon the averaged mass spectra of the complete run, also verified the match.

Summary

Pyrolysis-GC/MS can take on the role of several analytical techniques allowing the user to determine the total make up of a polymeric sample, including contaminates, additives and the polymer itself. And as an added benefit, running samples at a minimum of 3 temperatures makes the data easier to interpret since there are fewer peaks in each run. This will also help confirm that all the peaks in the final pyrolysis run (typically around 700C) are fragments from pyrolysis of the polymers, not from additives. There are many cases where a polymer fragment can also be the same as an additive, so a multiple step run will easily clear this up.