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GC-MS GCMS-QP™ 2020 NX

Application News

Pyrolysis/Thermal Desorption -GC/MS for Deterioration Markers of Chemical Products

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User Benefits

- Scan data can be deconvoluted and annotated with NIST and Shimadzu libraries on AnalyzerPro XD .
- Multivariate analysis and machine learning can be performed on eMSTAT Solution by loading the annotated scan data from AnalyzerPro XD.

Introduction

In modern life, many people are exposed to synthetic polymer products. Among them, polymer products for medical devices such as artificial joints and cardiac pacemakers are important items to support the life of users. However, due to long-term use and environmental effects, synthetic polymer products can deteriorate, and this deterioration is difficult to determine by color, shape, etc., thus requiring accurate objective measurements.

For example, if the material of a synthetic polymer product deteriorates, the synthetic polymer product may release harmful chemicals. These substances can have adverse effects on the human body and can have adverse health effects. In addition, by investigating the mechanism and cause of deterioration in detail, you can find countermeasures and improvement measures to improve the durability and life of the product. This will make your product more competitive in the market.

A gas chromatograph mass spectrometer is useful for objectively assessing the degree of deterioration of chemical products such as synthetic polymer products.

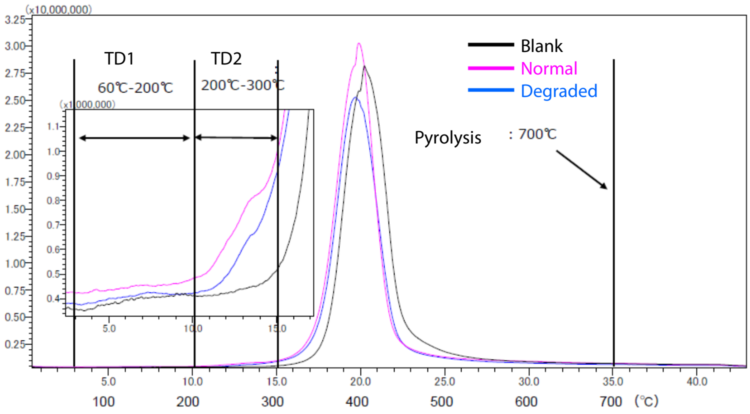
In this report, we performed deconvolution and annotation using the GCMS-QP2020 NX equipped with a pyrolyser EGA/PY-3030D (Frontier Labs, Inc.), and AnalyzerPro XD, which eliminates the cumbersome task of identifying all peaks by conventional visual inspection (Fig. 1). The annotation results were imported into eMSTAT Solution™ for PLS-DA analysis to create a list of differentiating compounds. We introduce an appropriate and efficient GC/MS measurement and analysis workflow to help you manufacture and develop safe synthetic polymer products.

Fig. 1 GCMS-QP™2020 NX with EGA/PY-3030D

Experimental

Normal (n=4) and degraded (n=4) chemically synthesized polymer products were used for analysis. The correlation between the heating temperature and the generated gas was confirmed for each sample by the EGA-MS method (Fig. 2). From the thermogram results, the heating conditions of the pyrolysis-GC/MS method (Py-GC/MS method) and the thermal desorption-GC/MS method (TD-GC/MS method) were determined, and the separation analysis of the generated gas was carried out by the double shot method combined with both methods. For each sample, a cryofocus (cooling trap) was used in the TD-GC/MS method to prevent loss of analysis of low boiling point components.

The chromatograms obtained for each sample were loaded into AnalyzerPro XD and annotated using NIST20 and the Polymer Additive Library 16S. This improved the number of detection peaks and reduced labor-hours compared with the conventional visual method (Fig. 3 on the next page).



determined heating conditions

Low temp. thermal desorption (TD1)
60 ˚C to 200 ˚C

Mid temp. thermal desorption (TD2)
200 ˚C to 300 ˚C

Pyrolysis (PY)
700 ˚C

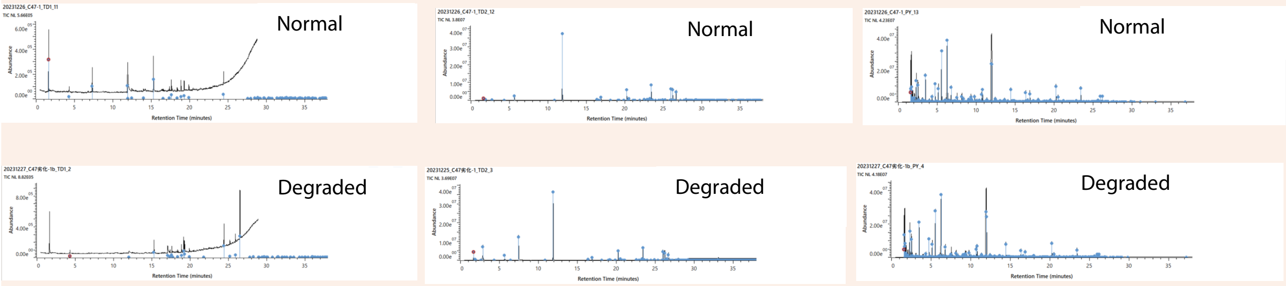
Fig. 2 EGA/MS thermogram

AnalyzerPro XD **SpectralWorks**

New Workflow

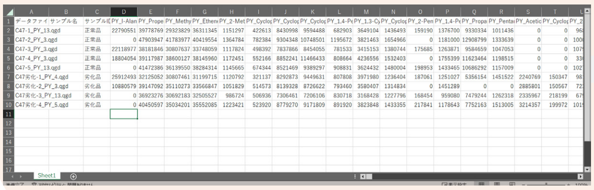
Automatically deconvolve and annotate in AnalyzerPro XD, and analyze differences in eMSTAT Solution

Thermal Desorption at Low Temperatures TD1 Thermal Desorption at Medium Temperatures TD2 Pyrolysis at high temperature



Deconvolved and annotated in AnalyzerPro XD

Integrate in CSV, save in txt file and load into eMSTAT Solution



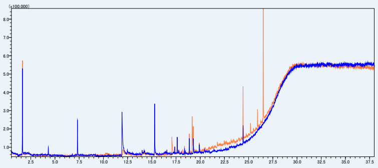
eMSTAT Solution

This software is recommended for those who have samples that are not separated by PCA, those who want to search for marker compounds between two or more groups of samples, and those who want to identify unknown samples.

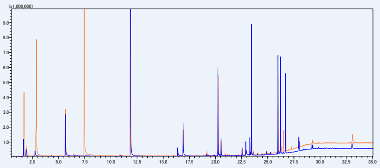
Conventional workflow

Visually check for chromatogram peaks

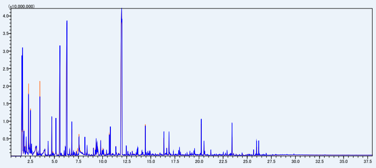
Thermal Desorption at Low Temperatures TD1 (ca. 100 peaks)



Thermal Desorption at Medium Temperatures TD1 (ca. 200 peaks)



Pyrolysis at high temperature (ca. 300 peaks)

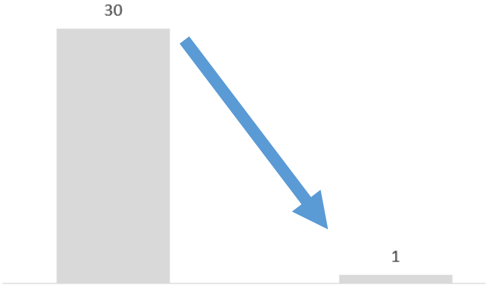


[Drawbacks]

1. It takes long labor-hours
2. Small peaks are easily overlooked
3. It is easy to understand when there is no detection at all, but it is difficult to determine subtle differences in the area values of commonly detected compounds between product groups.

Creating a list of compounds with differences

Work that takes 30 hours in the conventional workflow was completed in 1 hour.



Number of detected peaks ANALYZERPRO® XD

Deconvolution improved the number of detected peaks from 600 peaks in 1 sample to nearly 900 peaks.

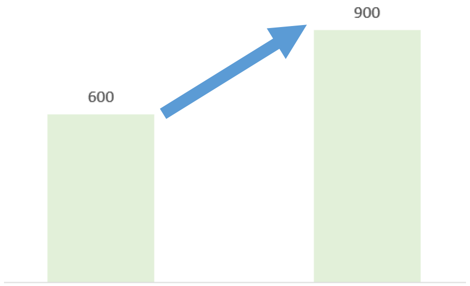


Fig. 3 Comparison of the workflow between the conventional method and this paper

■ Results

Analyzed normal (n=4) and degraded (n=4) chemically synthesized polymer products and deconvolved them with AnalyzerPro XD. Approximately 3700 peaks were detected. After the annotation was carried out by NIST20 and the Polymer Additive Library 16S, the difference between normal and degraded products was analyzed by t-test and PLS-DA in eMSTAT Solution (Fig. 4).

A t-test p value was calculated, and 125 of the 3700 components had a p value of 0.05 or less (statistically significant difference). The 125 components consisted of 1 compound detected by low-temperature thermal desorption, 28 by moderate-temperature thermal desorption, and 96 by high-temperature pyrolysis. The higher the temperature, the more specific components were detected.

For example, the compound X, which is a pyrolytic product of polymers, was found to be specifically high in degraded products, while the compound Y was specifically low in degraded products (the compound names were hidden here on purpose as they were both quite characteristic of the materials used as the samples).

eMSTAT Solution allows you to sort compounds by p-value, making it easy to create a list of compounds with differences.

We also divided the samples into two groups by PLS and created a regression model for discriminating unknown samples by SVM (Fig. 5). Only those with p-values less than or equal to 0.2 were used in the regression model, rather than all 3700 compounds.

When an unknown sample (a normal product) was loaded into the regression model, it was correctly identified as a “normal product ” with a score of 100. From this, it was found that this unknown sample was either a normal product, or a deteriorated product that was improved to be equivalent to the normal product.

Chemical product categories are constantly changing, and new categories may appear. Therefore, by regularly checking the number of clusters with PLS or PCA and performing random quality assessment tests in batches using machine learning, rapid and accurate assessments are possible.

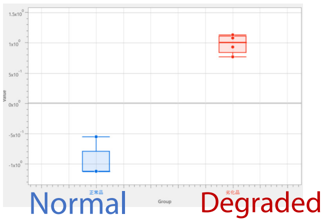
■ Summary

Normal (n=4) and degraded (n=4) chemically synthesized polymer products were measured with a GCMS-QP2020 NX equipped with a pyrolyzer EGA/PY-3030D. Scan data were deconvolved using AnalyzerPro XD, annotated using NIST20 and the Polymer Additive Library 16S, and then subjected to differential analysis using PLS and t-test in eMSTAT Solution.

We also created a regression model using machine learning SVM. When an unknown sample (actually a normal product) was loaded into the regression model, it was correctly identified as “normal ” with a score of 100. Machine learning can be used to learn data features and patterns to predict the characteristics of unknown chemical products, which can be used for product development and improvement.

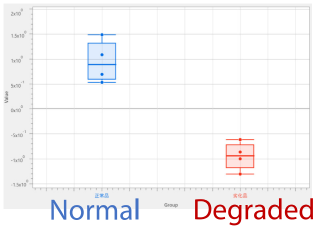
An example of compounds specifically detected at high levels in degraded products

Compound X P-value 0.0001

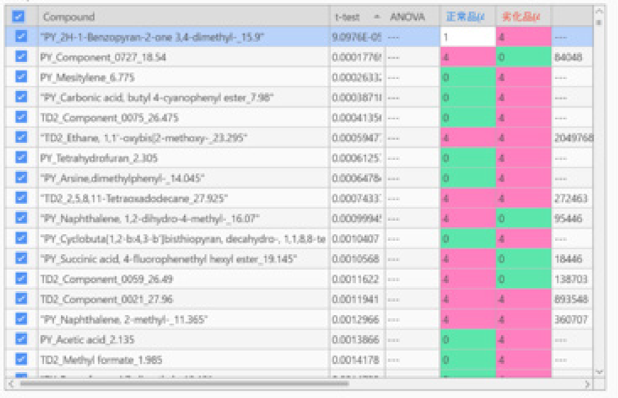


An example of compounds specifically detected at low levels in degraded products

Compound Y P-value 0.0006

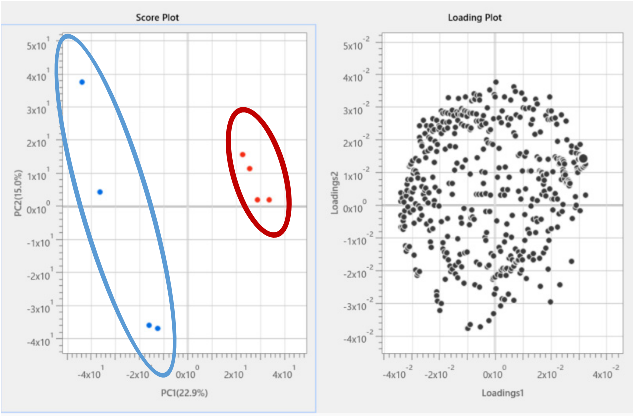


List of compounds with statistically significant differences between normal and degraded products



☑	Compound	t-test	ANOVA	正常品(	劣化品(	
☑	"PY_2H-1-Benzopyran-2-one 3,4-dimethyl-_15.9"	9.0976E-0	---	1	4	---
☑	PY_Component_0727_18.54	0.0001776	---	4	0	84048
☑	PY_Mesitylene_6.775	0.000263	---	0	4	---
☑	"PY_Carbonic acid, butyl 4-cyanophenyl ester_7.98"	0.0003871	---	0	4	---
☑	TD2_Component_0075_26.475	0.0004135	---	0	4	---
☑	"TD2_Ethane, 1,1'-oxybis[2-methoxy-_23.295"	0.0005947	---	4	4	2049768
☑	PY_Tetrahydrofuran_2.305	0.0006125	---	0	4	---
☑	"PY_Arsine,dimethylphenyl-_14.045"	0.0006478	---	0	4	---
☑	"TD2_2,5,8,11-Tetraoxadodecane_27.925"	0.0007433	---	4	4	272463
☑	"PY_Naphthalene, 1,2-dihydro-4-methyl-_16.07"	0.0009994	---	4	0	95446
☑	"PY_Cyclobuta[1,2-b:4,3-b']bisthiopyran, decahydro-, 1,1,8,8-te	0.0010407	---	0	4	---
☑	"PY_Succinic acid, 4-fluorophenethyl hexyl ester_19.145"	0.0010568	---	4	0	18446
☑	TD2_Component_0059_26.49	0.0011622	---	4	0	138703
☑	TD2_Component_0021_27.96	0.0011941	---	4	4	893548
☑	"PY_Naphthalene, 2-methyl-_11.365"	0.0012966	---	4	4	360707
☑	PY_Acetic acid_2.135	0.0013866	---	0	4	---
☑	TD2_Methyl formate_1.985	0.0014178	---	0	4	---

Example of Separation of Normal and Degraded Products by PLS



Low Temp.
1 compound

Mid Temp.
28 compounds

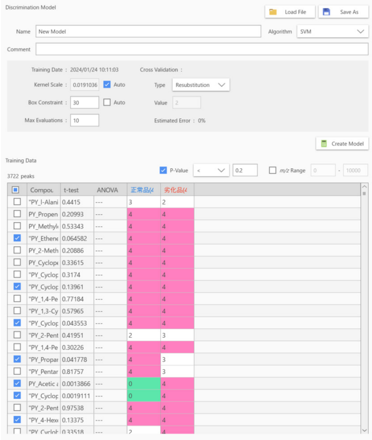
High Temp.
96 compounds

125
compounds

Breakdown of 125 components with statistically significant differences between normal and degraded products

Fig. 4 T-test with eMSTAT Solution (top), list of compounds with differences (bottom left), PLS (bottom right)

SVM regression model was developed for compounds with P value less than 0.2.



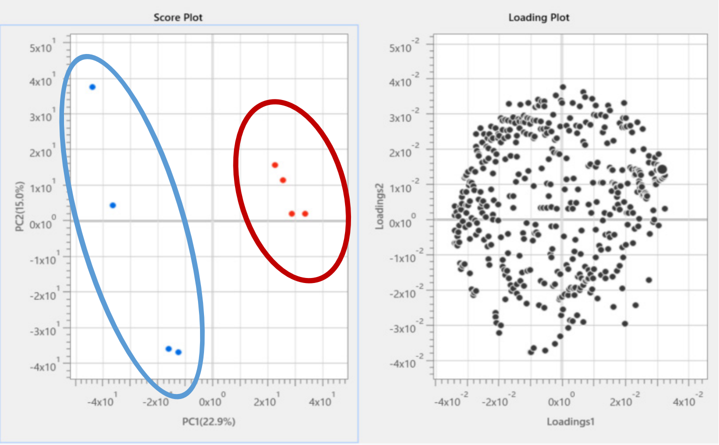
Name: New Model
Algorithm: SVM
Comment:

Training Date : 2024/01/24 10:11:03
Kernel Scale : 0.0191036 ☑ Auto
Box Constraint : 30 ☐ Auto
Max Evaluations : 10

Cross Validation :
Type: Resubstitution
Value: 2
Estimated Error : 0%

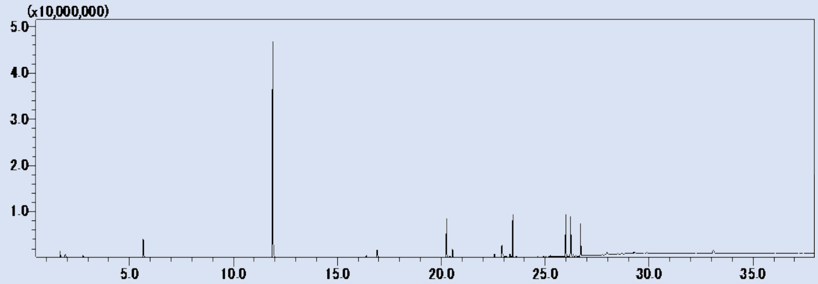
Training Data
3722 peaks
☑ P-Value < 0.2 ☐ m/z Range 0 - 10000

☐	Compou	t-test	ANOVA	正常品(4	劣化品(4
☐	"PY_l-Alani	0.4415	---	3	2
☐	PY_Propen	0.20993	---	4	4
☐	PY_Methyl	0.53343	---	4	4
☑	"PY_Ethene	0.064582	---	4	4
☐	PY_2-Meth	0.20886	---	4	4
☐	PY_Cyclope	0.33615	---	4	4
☐	"PY_Cyclop	0.3174	---	4	4
☑	"PY_Cyclop	0.13961	---	4	4
☐	"PY_1,4-Pe	0.77184	---	4	4
☐	"PY_1,3-Cy	0.57965	---	4	4
☑	"PY_Cyclop	0.043553	---	4	4
☐	"PY_2-Pent	0.41951	---	2	3
☐	"PY_1,4-Pe	0.30226	---	4	4
☑	"PY_Propar	0.041778	---	4	3
☐	"PY_Pentar	0.81757	---	4	3
☑	PY_Acetic a	0.0013866	---	0	4
☑	"PY_Cyclop	0.0019111	---	0	4
☐	"PY_2-Pent	0.97538	---	4	4
☑	"PY_4-Hex	0.13375	---	4	4
☐	"PY_Cyclob	0.33518	---	2	4

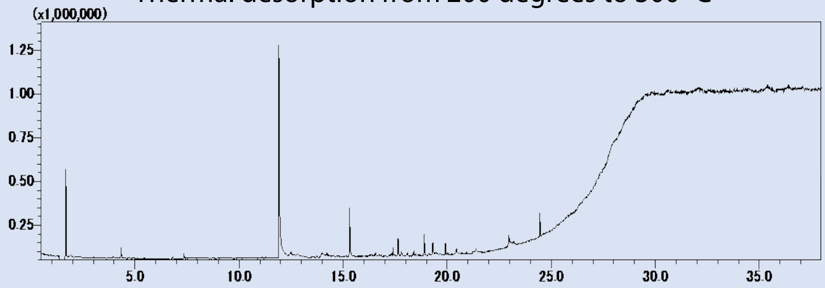


Chromatogram of an unknown sample

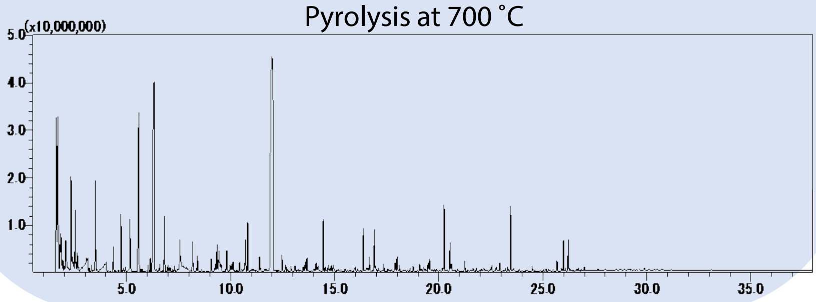
Thermal desorption from 60 degrees to 200 ˚C



Thermal desorption from 200 degrees to 300 ˚C



Pyrolysis at 700 ˚C



Unknown sample (actually normal) is considered normal

☐
Unknown new material
Normal
100

41472386
36139550
38284314
1145665
674344
8521469

Fig. 5 Determination of the origin of an unknown meat sample by SVM Regression Model

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