

FT-IR & FT-IR Microscope Spectrometer



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1. FT-IR 기본이론
2. Sampling Method
3. FT-IR & Microscope 소개
4. 미세플라스틱 분석 방법
5. 각 플라스틱 별 Spectrum 차이

Connects

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FT-IR 기본이론

What is the FT-IR?

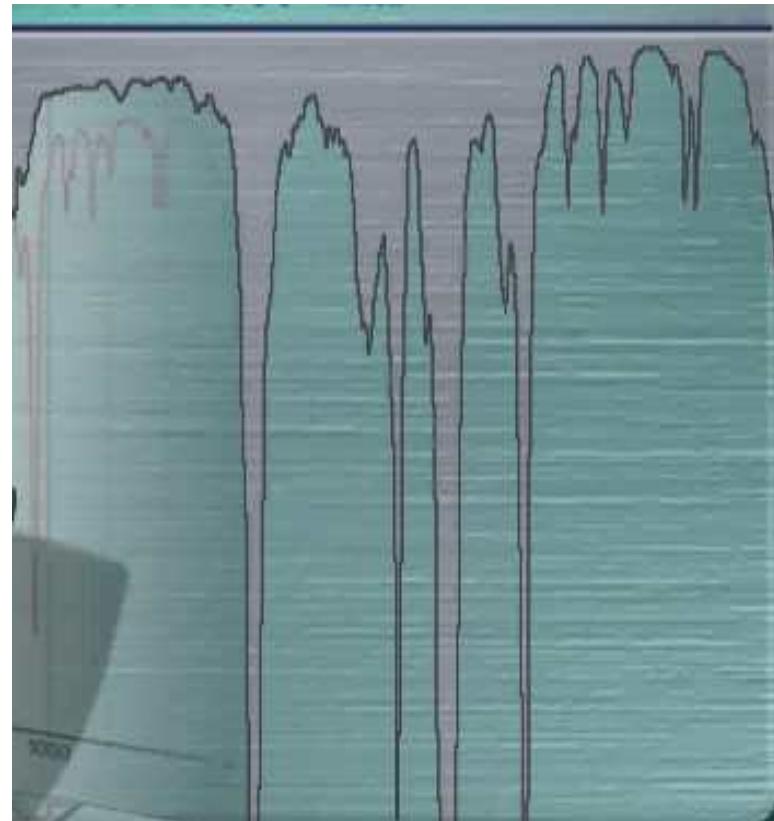
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FT-IR Spectrometer

: Fourier Transform Infrared
Spectrometer

Use of FT-IR

- Qualitative Analysis
- Quantitative Analysis
- Kinetics



Fourier Transform이란

FT는 Fourier-transform의 준말이다.

Fourier는 France의 수학자였고 transform이란 수학에서 함수를 특정한 domain에서 다른 domain으로 변형시키는 작업을 의미한다.

특히 Fourier transform이란 다음과 같은 형식으로 한 개의 함수를 변형시키는 것을 말한다.

$$f(x) = \int_{-\infty}^{\infty} g(y) e^{-2\pi i \omega y} dy$$

What is the FT?

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- FT-IR, Mass, Raman, NMR



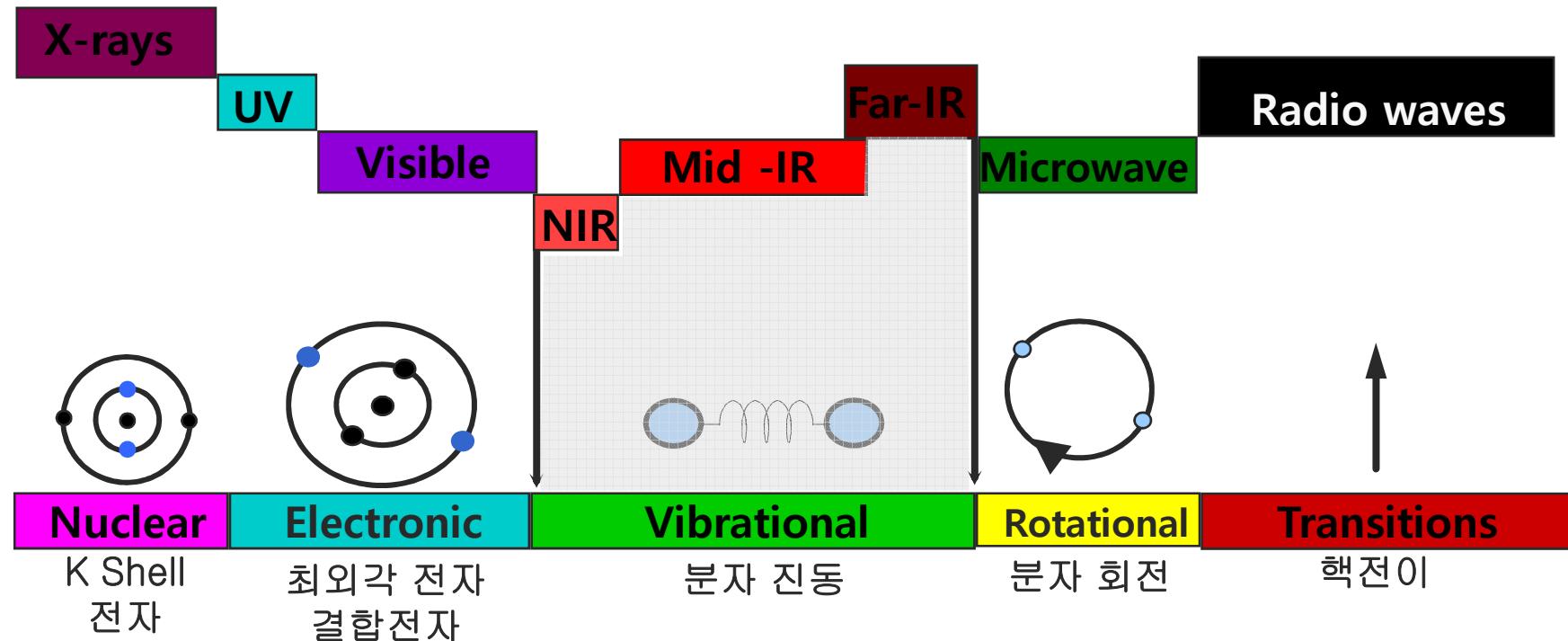
- FT-UV or FT-X-ray ??



The Unit of Radiation (Wavenumber)

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Electromagnetic Spectrum



The Unit of Radiation (Wavenumber)

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Wavenumber	12800	4000	400	10 cm^{-1}
Wavelength	0.78	2.5	25	1000 μm

$$c = \nu \lambda$$

$$\nu(\text{Hz}) = c(\text{ms}^{-1}) / \lambda(\text{m})$$

$$\nu \times c = \nu = c / \lambda \text{ 이므로}$$

$$\nu(\text{cm}^{-1}) = 1 / \lambda$$

c=The Speed of Light

ν =Frequency

λ =Wavelength

$$\text{Ex) } 1 / 2.5 \mu\text{m}$$

$$= 0.4 \mu\text{m}^{-1}$$

$$= 4000 \text{ cm}^{-1}$$

$$\text{Ex) } 1 / 25 \mu\text{m}$$

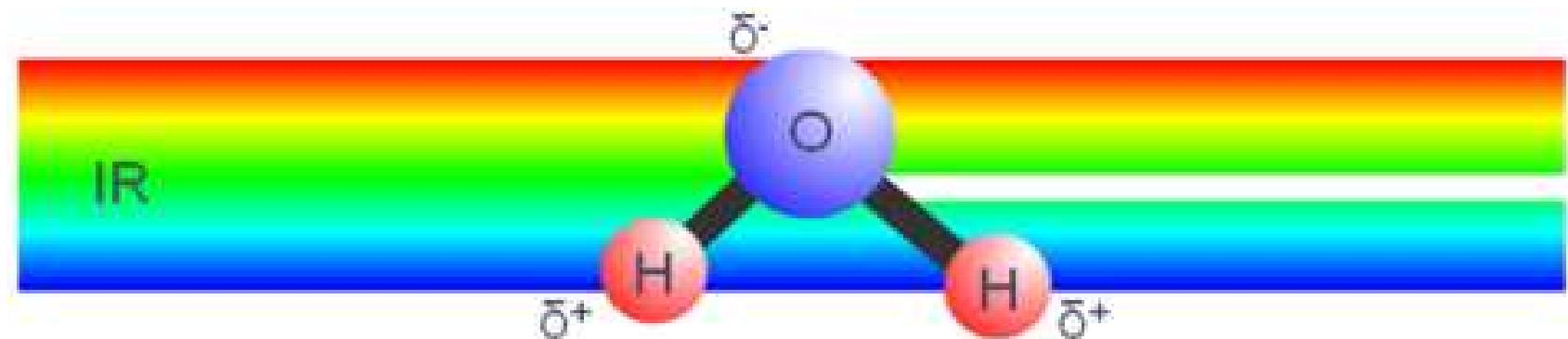
$$= 0.04 \mu\text{m}^{-1}$$

$$= 400 \text{ cm}^{-1}$$

What is the FT-IR?

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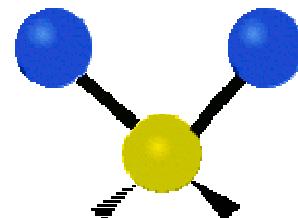
고유한 **진동 운동**을 하는 분자에 연속적으로 변화하는 IR(Infrared Radiation)을 조사하고 흡수된 파장을 스펙트럼으로 나타내어 분석하는 장비



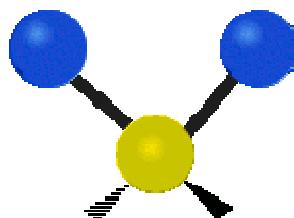
Molecular vibration

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- 신축(stretching) 운동

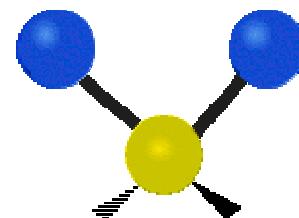


대칭 신축 운동

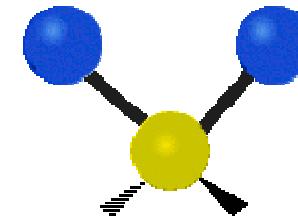


비대칭 신축 운동

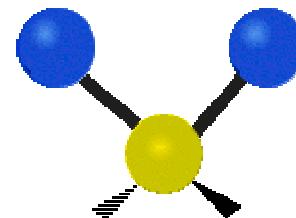
- 굽힘(bending) 운동



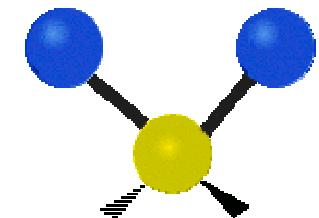
Scissoring 운동



Rocking 운동

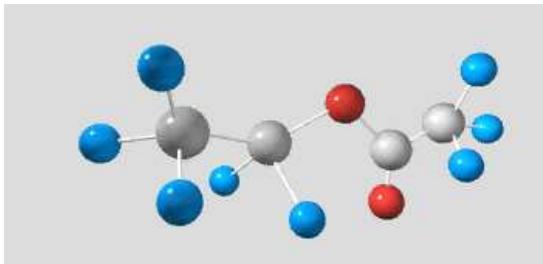


Wagging 운동

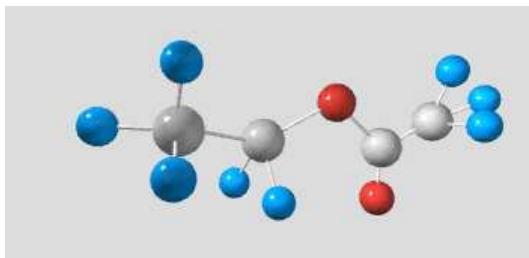


Twisting 운동

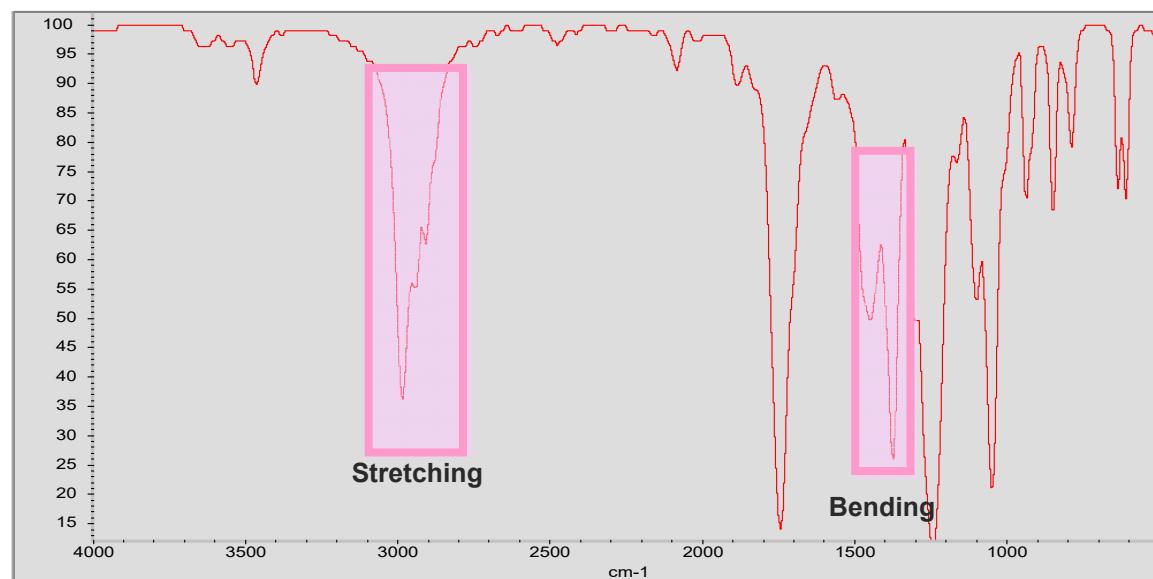
Ethyl Acetate ($\text{CH}_3\text{COOC}_2\text{H}_5$)



Stretching



Bending



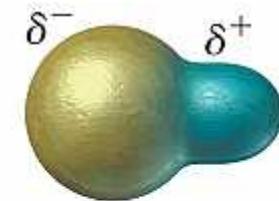
Absorbances of the Methylene (CH_2)

- Stretching : $2800 \sim 2900\text{cm}^{-1}$
- Bending : 1470cm^{-1}



**Pure (nonpolar)
covalent bond:**
electrons shared
equally

- IR Inactive
- No Dipole Moment

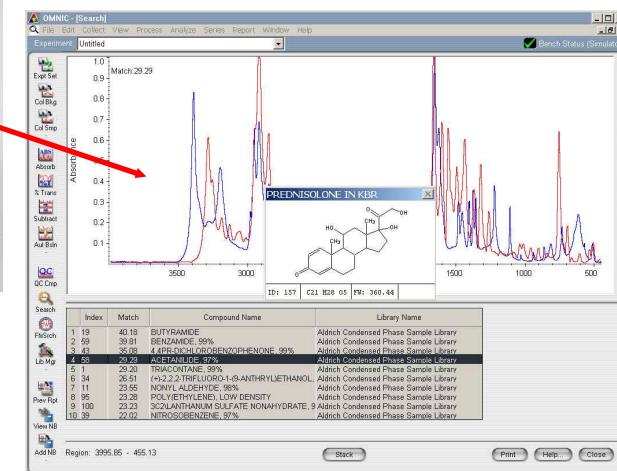


Polar covalent bond:
electrons shared
unequally

- IR Active
- Dipole moment change

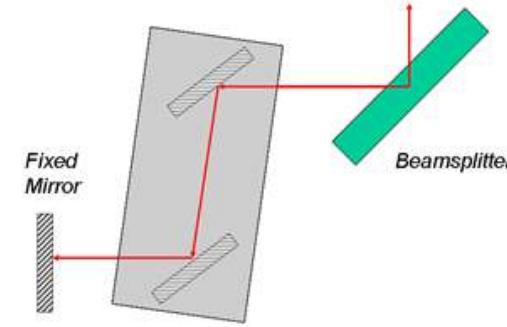
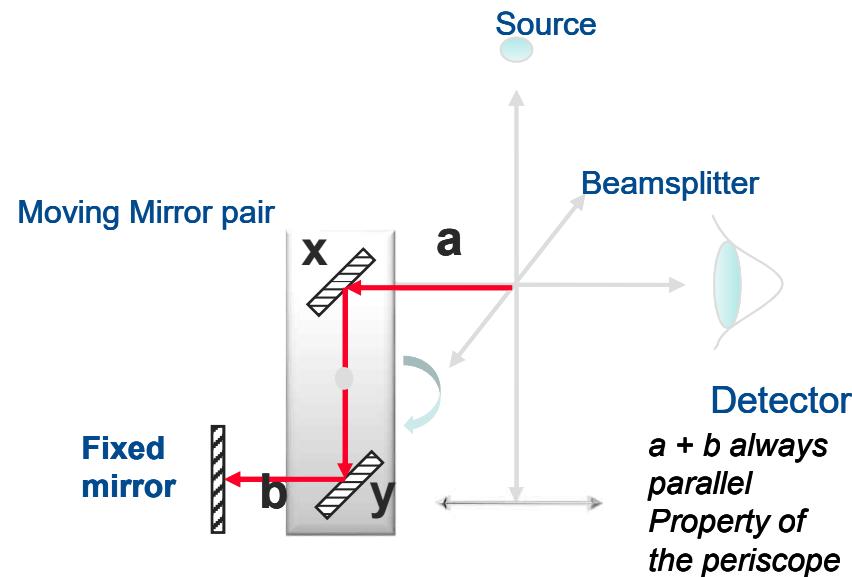
What is the FT-IR?

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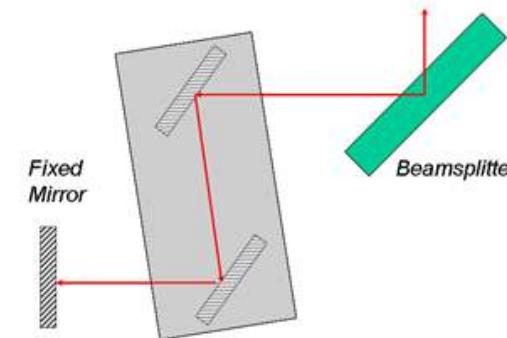


Dynascan™ Interferometer

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< 짧은 경로 >

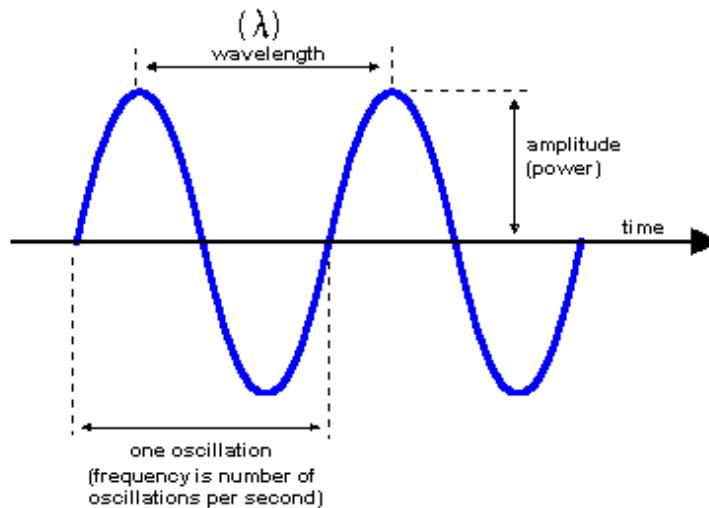


< 긴 경로 >

- Tilt & shear에 의한 오류 발생 제거
- 1/4 만 구동시켜도 동일한 Resolution을 만들 수 있어 안정도가 높음

Wavelength

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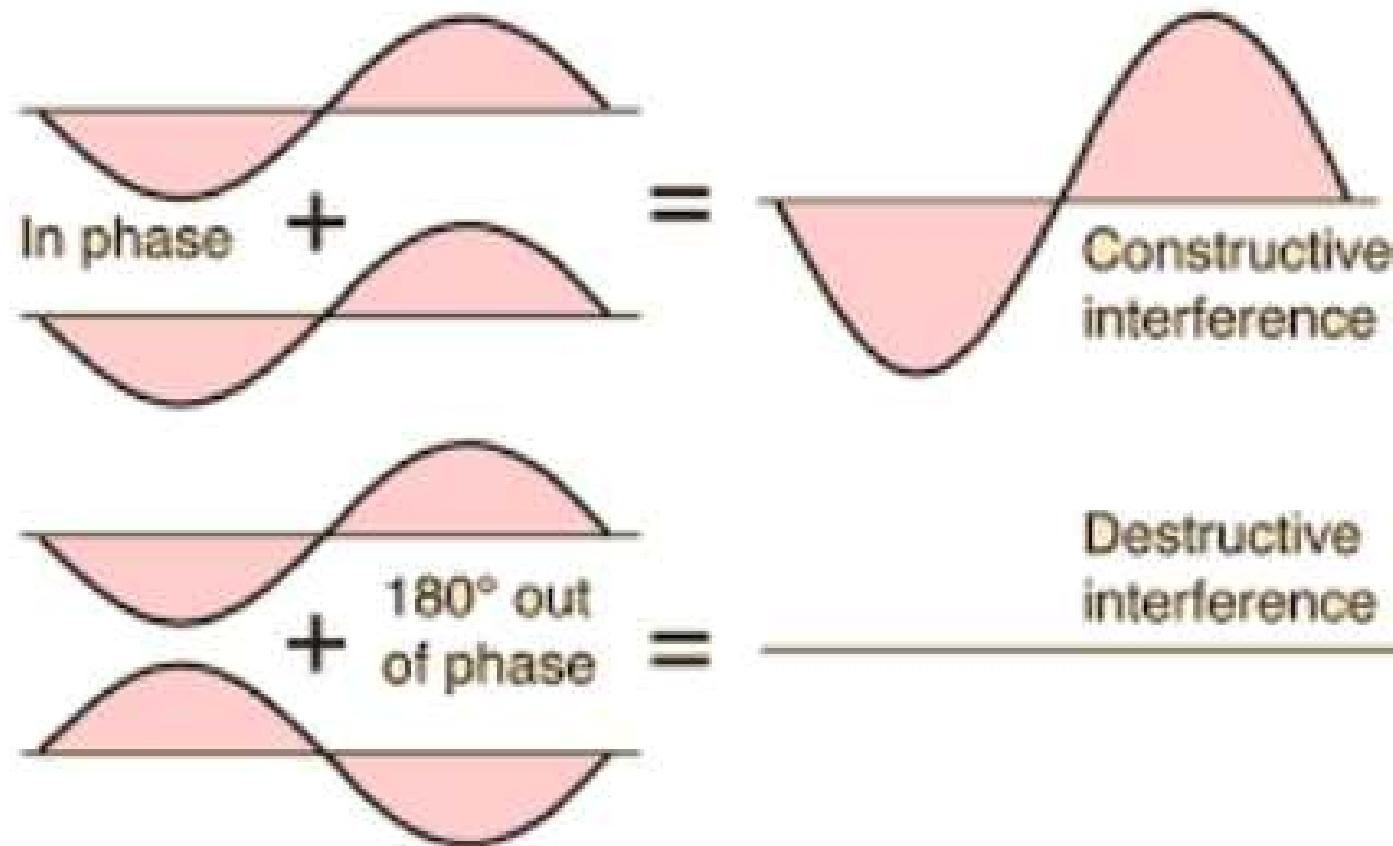
$$\tilde{\nu} = \frac{1}{\lambda} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

조화 진동하는 물체의 고유 진동수

- ☞ $\tilde{\nu}$ = frequency in cm^{-1}
- ☞ μ = reduce mass- m_1xm_2/m_1+m_2
; mass of atoms in gram
- ☞ K = 진동하는 계에 작용하는 결합력
즉 force constant in dyne/cm
- ☞ c = velocity of light=3x10¹⁰cm/sec
 - * m_1, m_2 는 진동하는 결합의 양 끝에 달려있는 원자 혹은 원자단의 질량

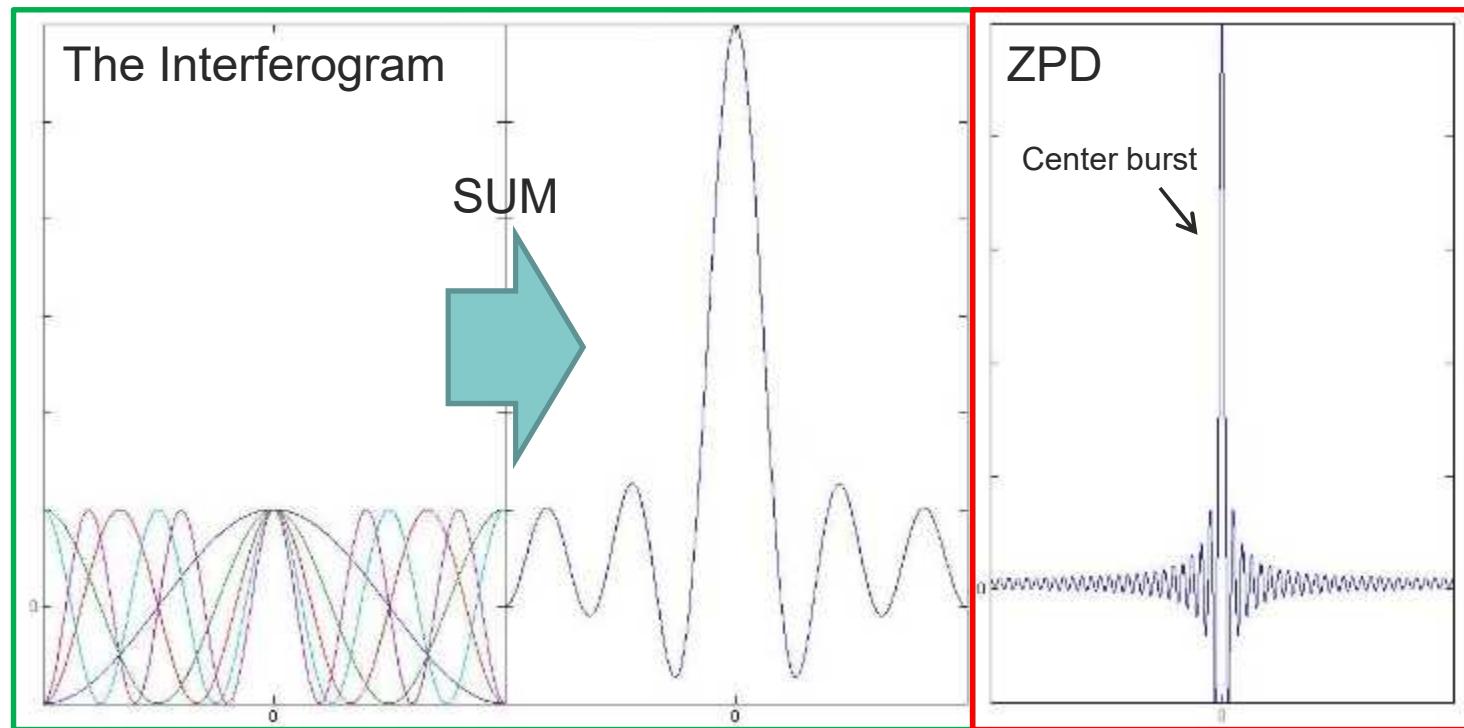
Interference

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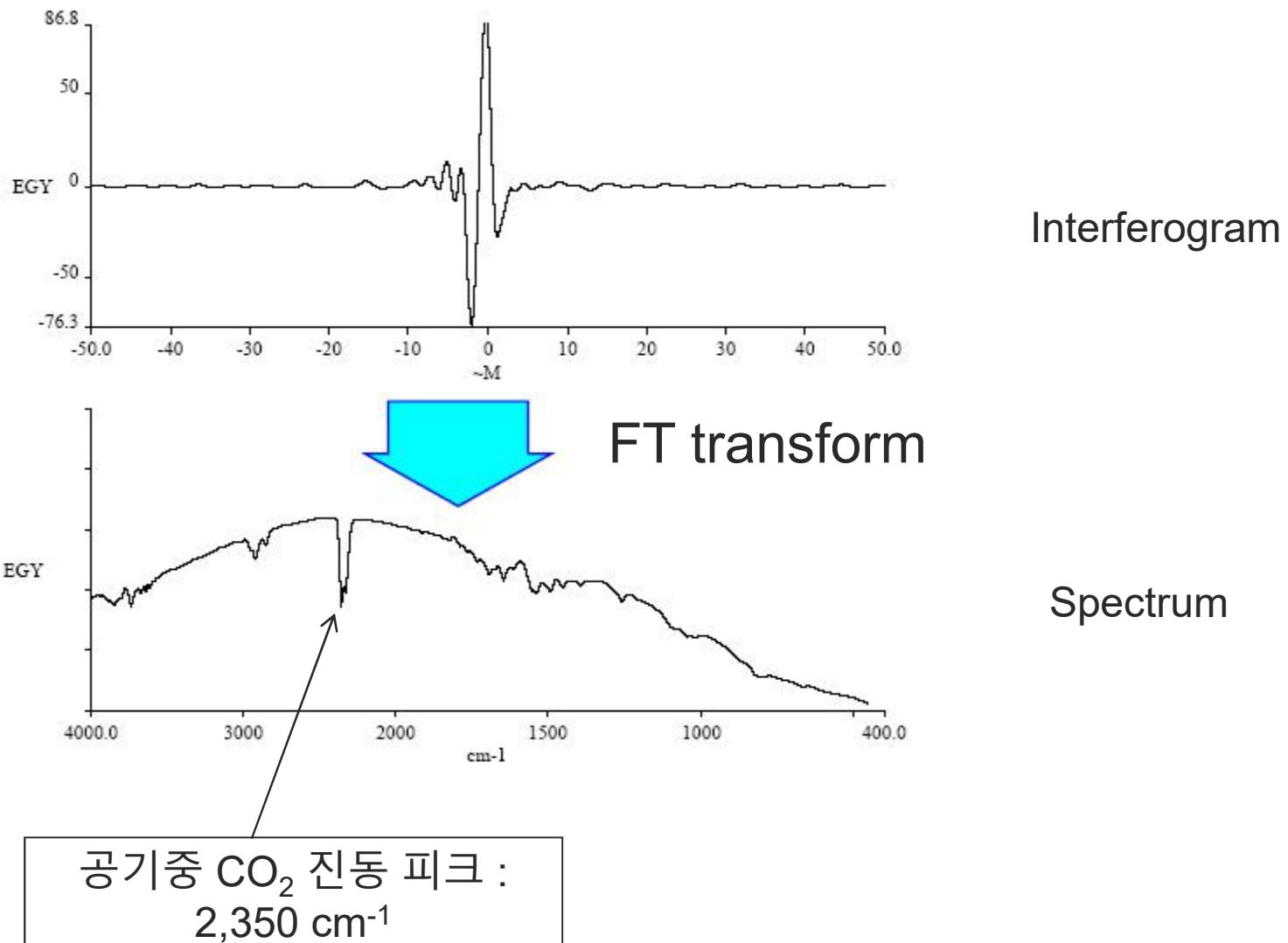
Interferogram

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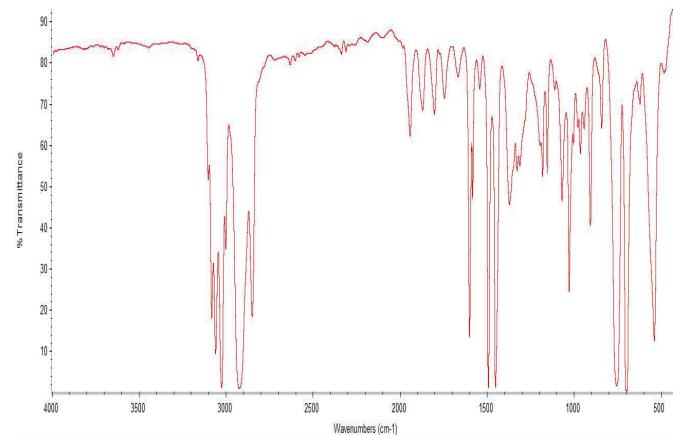
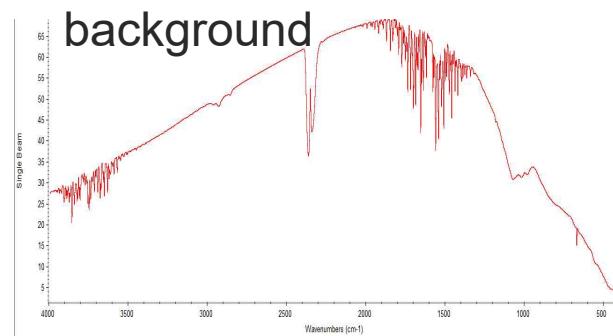
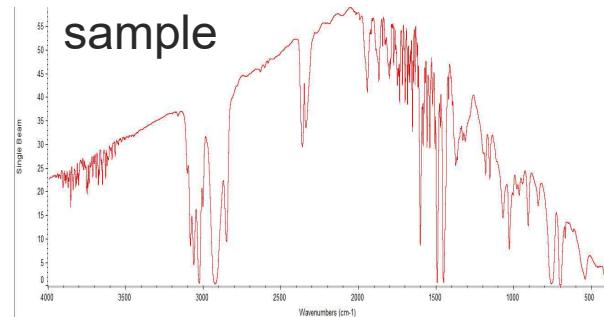
Theory of FT-IR spectroscopy

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Transmittance

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$$E_{\text{sample}}/E_{\text{background}} * 100\% = \% \text{Transmittance}$$

FT-IR의 장점

- 높은 S/N ratio
- Frequency의 정확도
- Accumulation of scans
: S/N ratio는 대략 $(N)^{1/2}$ 만큼 높아진다 (N은 scan 수).
- Fast scan
- 기기의 내구성

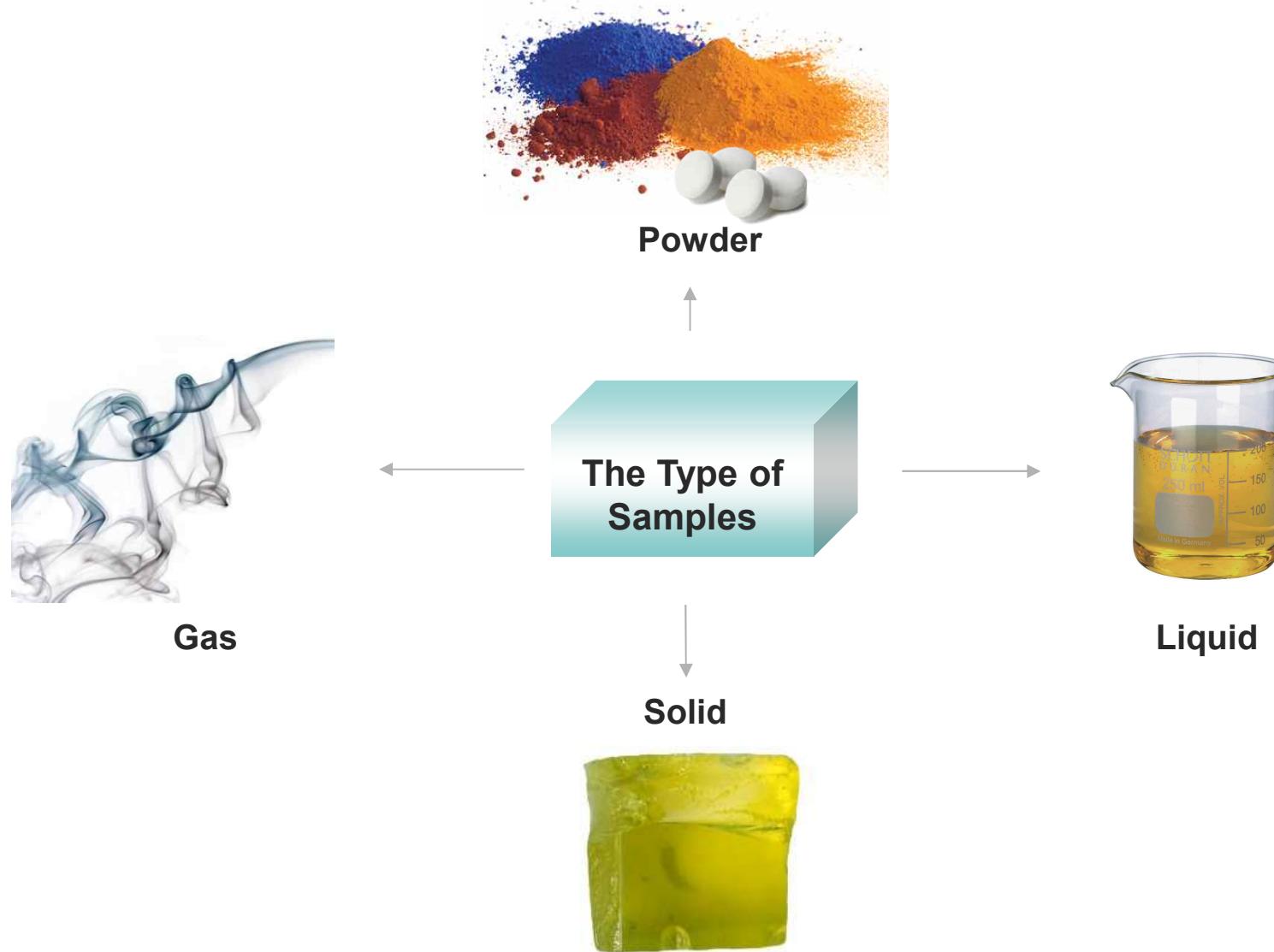
Contexts

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Sampling Method

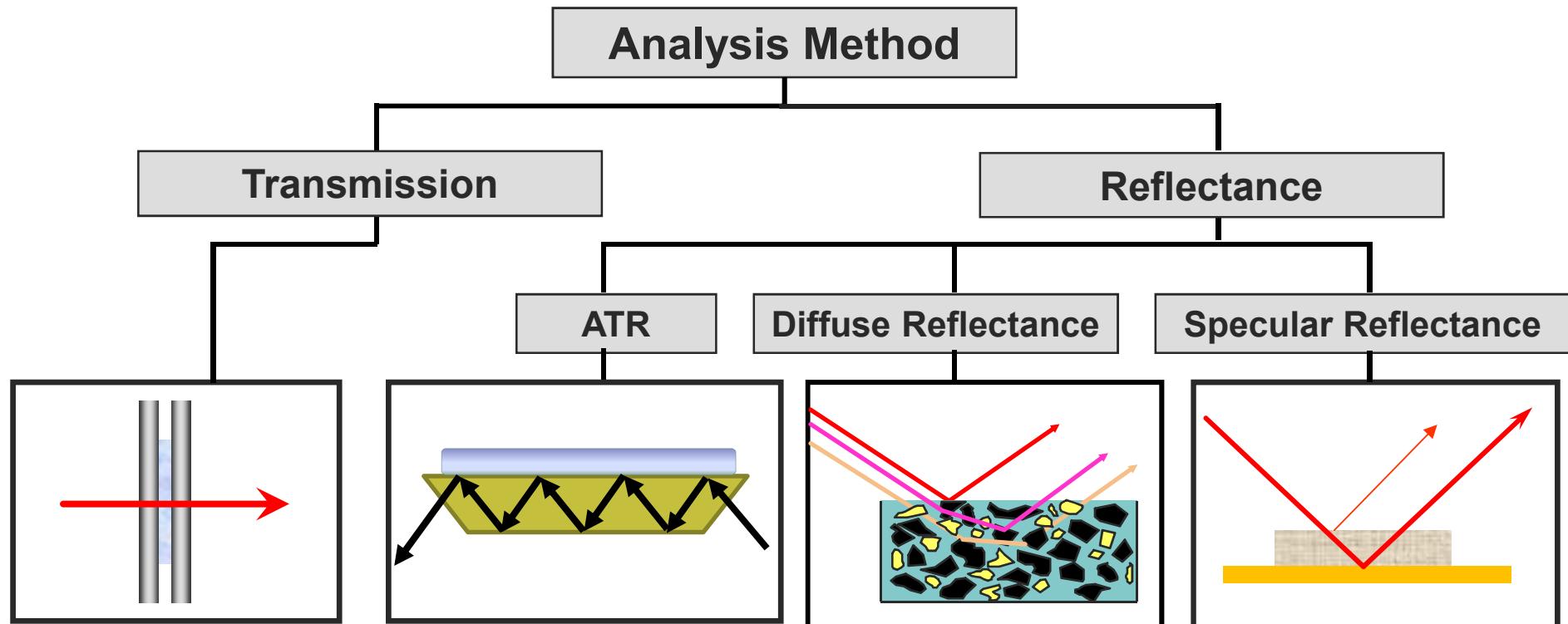
The Type of Samples

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Sampling Techniques

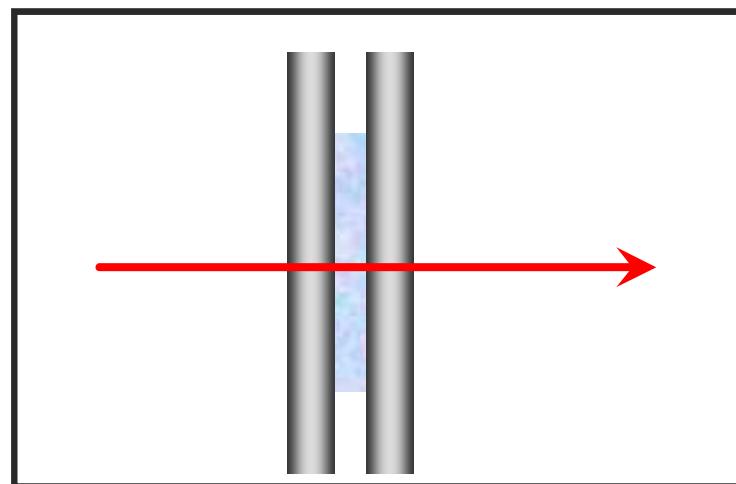
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Sampling Techniques (Transmission)

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- Unique Features
 - Highest quality and representative spectral data, consistent with a wide range of digital libraries
 - Easy pathlength (sensitivity) control
 - Supports experiments under varying temperature and pressure
- Suitable for
 - Transmission measurements of solids, gels, pastes, liquids and gases
 - Qualitative and quantitative applications
 - Automated (high throughput) analysis of solid samples



Sampling Accessories – Transmission (Powder)

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Solid Sampling Kit – Transmission

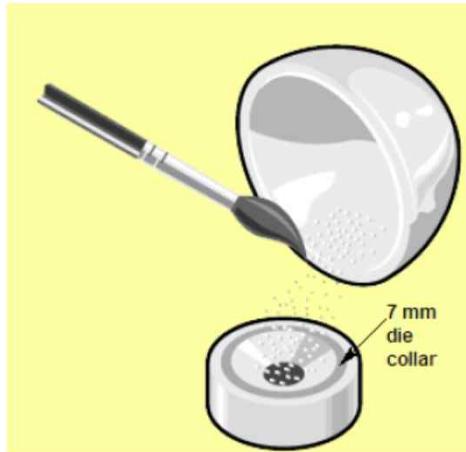
- Hydraulic Press & Die Kit (13mm)
or Hand-Press & Die Kit (7mm)
- Agate Mortar & Pestle
- Magnetic film Holder
- KBr Powder 100g



Sampling Accessories – Transmission (Powder)

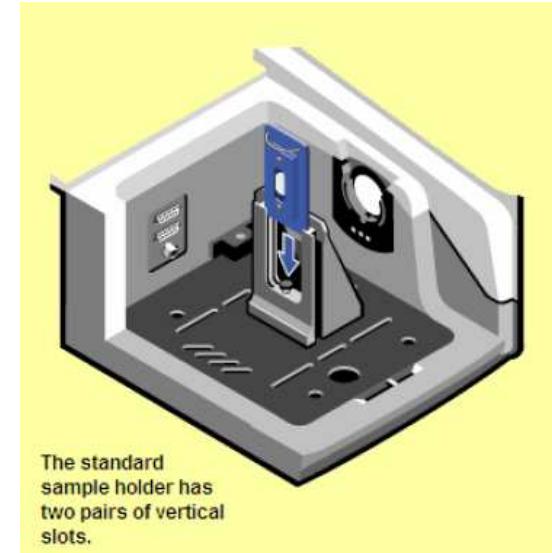
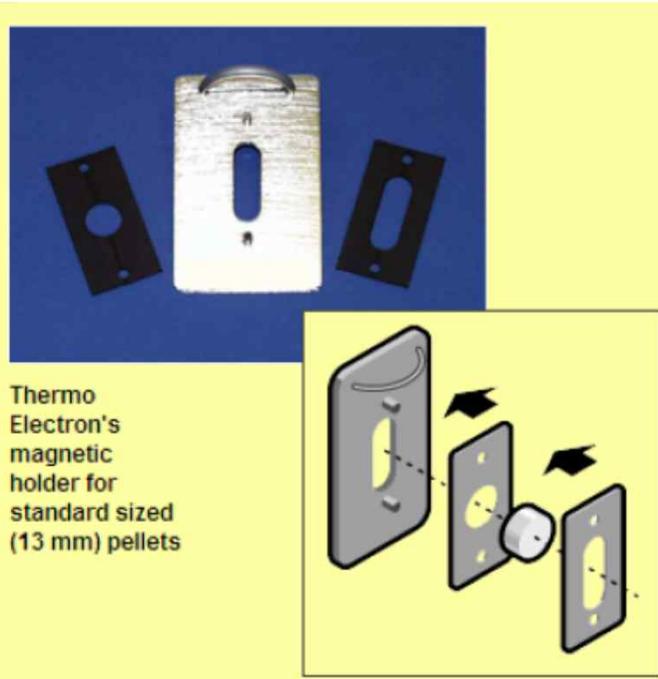
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1. Transmission by KBr Pellet : Powder, Drugs



▲ Filling the Press

▼ Mounting a Pellet Sample



▲ Installation a pellet card

Sampling Accessories – Transmission

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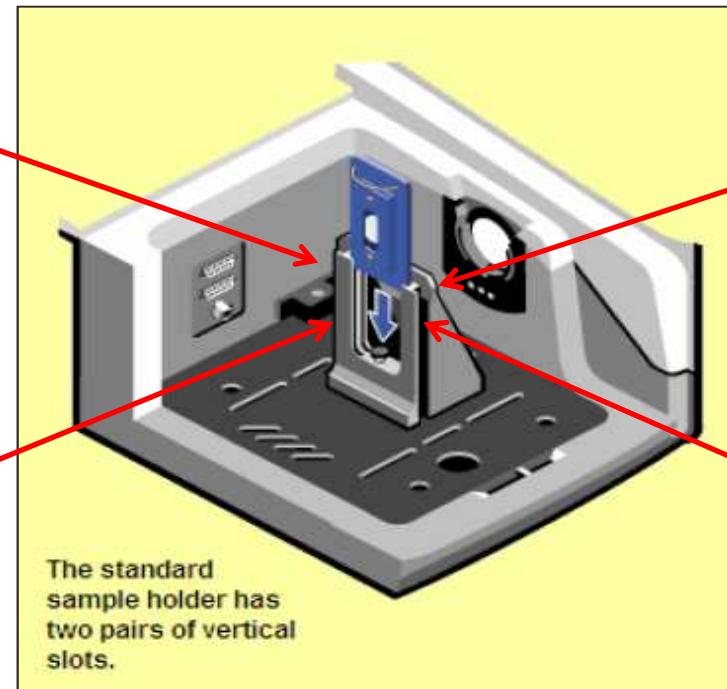
2. Transmission by Film Holder : Films, Coatings, Paints



Magnetic Film / Pellet Holder



Sampling Card



The standard
sample holder has
two pairs of vertical
slots.



Dual Pellet Holder



Single Pellet Holder

3. Transmission by Rubber Sample : Not Available

Sampling Accessories – Transmission (Film Maker)

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- Fast, efficient means of making thin films for transmission spectroscopy
- Temperature range – ambient to 300 °C
- Standard stainless steel spacer set (15, 25, 50, 100, 250 and 500 microns all with 25 mm ID) included with accessory
- Integral design for easy insertion and removal of heated platens into the hydraulic press
- Included insulating disks to minimize heat loss during film pressing
- Standard cooling chamber included with accessory

Sampling Accessories – Transmission (Liquid)

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Liquid Sampling Kit

- Presslok Holder
- KBr 25x4mm Window
- KRS-5 25x4mm Window



Press-On Demountable Cell



Demountable Liquid Cells for Versatile Pathlength



Sealed Liquid Cell – Fixed Pathlength

Sampling Accessories – Transmission (Liquid)

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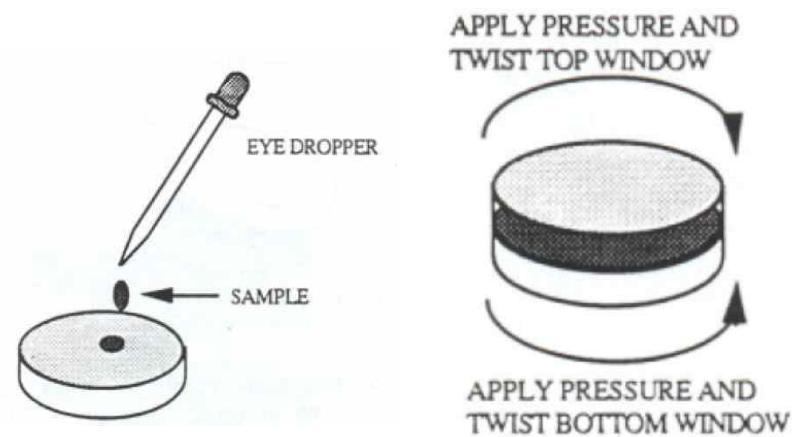
Step 1. Choice the window material.(ex : KBr or KRS-5)



Step 2. Place a small amount of sample onto the window using the eye dropper or spatula.

Step 3. Once enough sample is deposited on the window, place the other infrared window on top of the sample.

Step 4. Twist the windows together in opposite directions to get rid of air bubbles and to decrease the pathlength.



Step 5. Mount the sample windows

Step 6. Install the sample holder
and collect the sample spectrum

Sampling Accessories – Transmission (Liquid)

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Pearl® Liquids Analyser

The easiest to use FTIR liquid sampling system available



- 기존 투과 셀보다 신속하고 정확한 측정 가능
- Pearl 만의 특수한 wedge cell을 채용하여 기존 투과셀의 fringe 현상을 완벽하게 제거
- ZnSe, CaF₂ 윈도우 호환 및 Pathlength 옵션
- (50mm, 100mm, 200mm, 500mm, 1000mm)
- 점성이 있는 샘플도 완벽 클리닝 가능

Sampling Accessories – Transmission (Gas)

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* High Concentration Gas
(1000ppm ~ 100%)



Short – path Gas cell



* Low Concentration Gas
(ppb ~ 3%)



2.4M Gas Cell

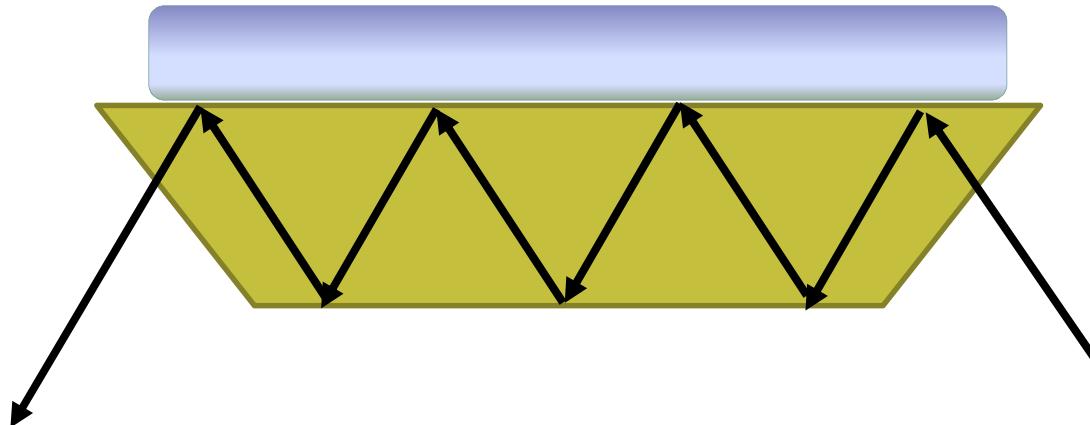


Long-path Gas cell

Sampling Techniques (ATR)

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- High Efficiency
 - No sample preparation
 - Easy cleaning
 - Short sampling time
 - Versatile
- Suitable for analyzing
 - Solids, liquids, pastes, gels and powders
- Quantitative and Qualitative analysis of samples

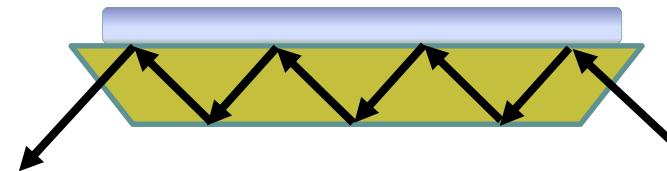


Sampling Accessories - ATR

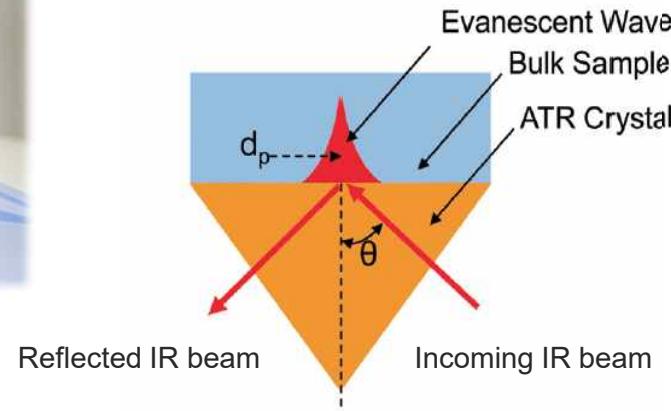
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ATR Accessories

- Main Frame
- Crystal
(ZnSe, Diamond, Ge, Si)
- High Pressure Clamp



Multi-bounce ATR



Single-bounce ATR



Single Bounce

vs.

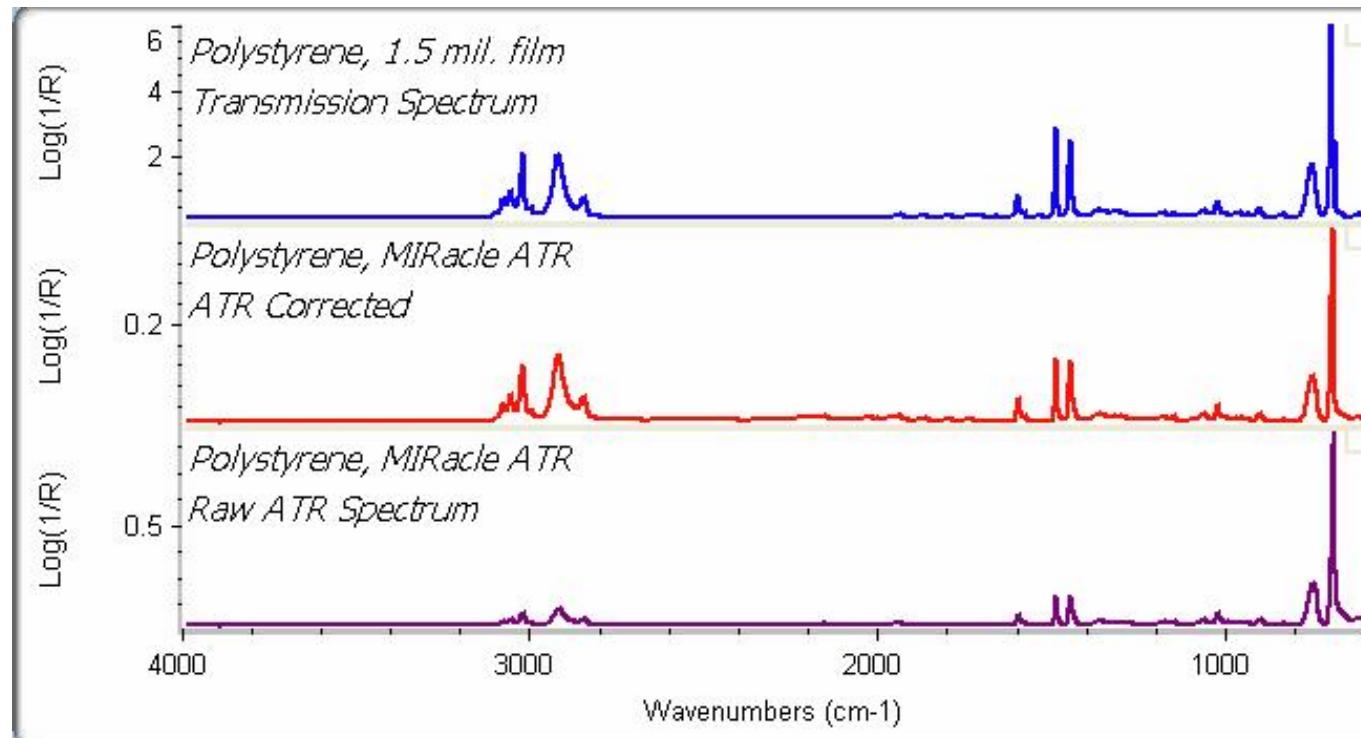
Multi-bounce

- Small sampling area
 - Use for strong absorbers
 - Black rubber, neat solvents
 - Solid or liquid samples
 - Powders, droplets, flakes
-
- Broad sampling area
 - larger contact with the sample
 - Use for weak absorbers or dilute solutions

ATR(Attenuated Total Reflectance)

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● Transmission VS ATR



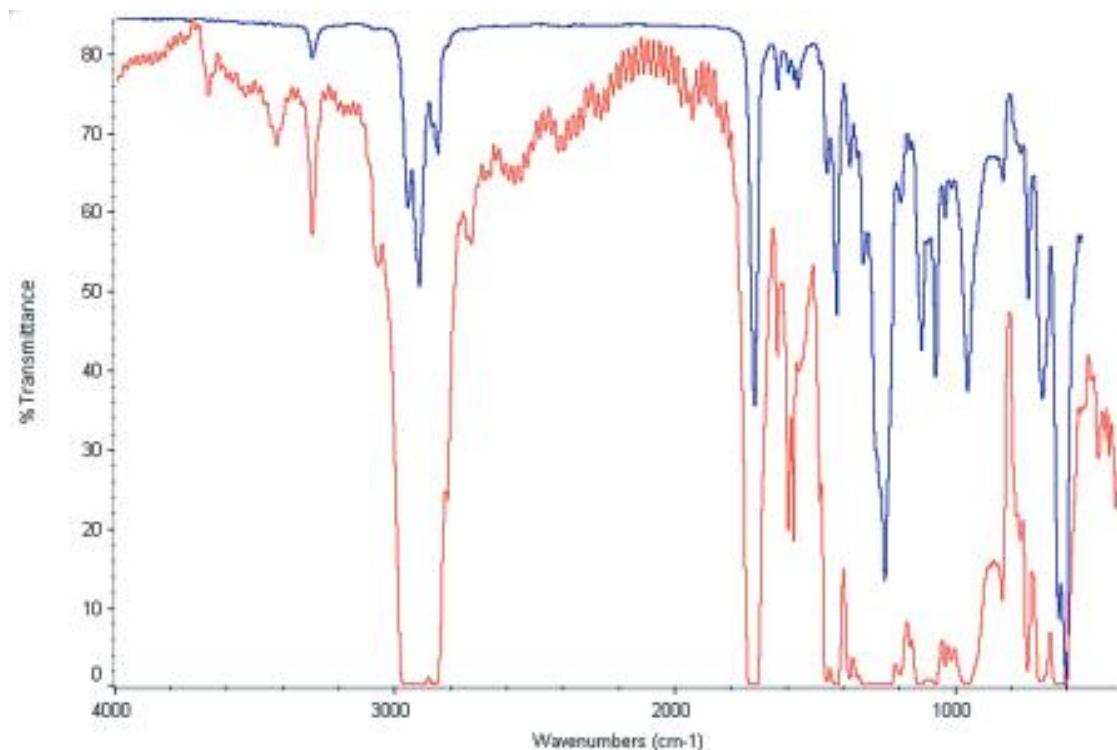
- 1) Polystyrene collected by transmission
- 2) After ATR correction
- 3) Polystyrene collected by ATR.



ATR(Attenuated Total Reflectance)

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● Benefits of ATR vs. Transmission for FT-IR Analysis(1)



- Sample
150 micron thick polymer film
(PVC Based Polymer)

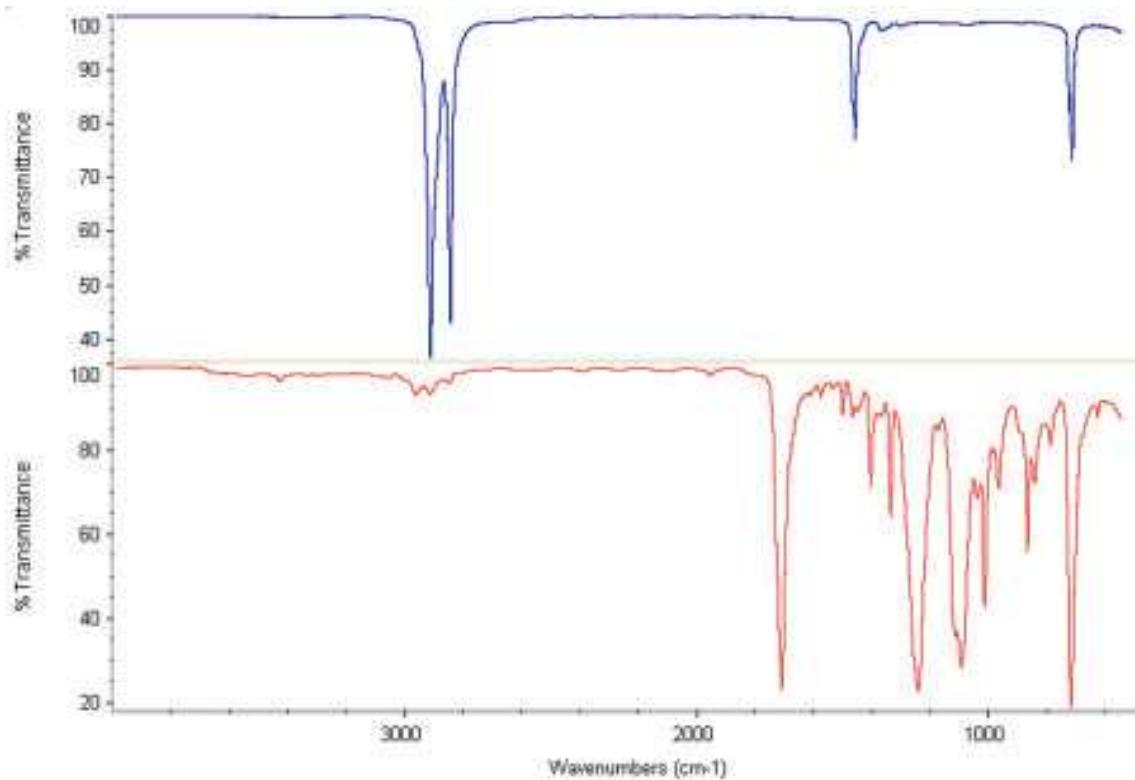
Blue Spectrum – Collected by ATR
Red Spectrum – Collected by Transmission



ATR(Attenuated Total Reflectance)

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● Benefits of ATR vs. Transmission for FT-IR Analysis(2)



- Sample Electronics Storage Bag

Blue Spectrum – Inner layer of Sample (polyethylene)
Red Spectrum – Outer layer of Sample (Polyethylene terephthalate)



Sampling Accessories - ATR

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Material	ATR Spectral Range (cm ⁻¹)	Refractive Index	Depth of Penetration (μ) (at 45° & 1000 cm ⁻¹)	Uses
Germanium	5,500 - 675	4	 0.66	Good for most samples, especially strong absorbing samples, such as dark polymers
Silicon	8,900 - 1,500 & 360-120	3.4	 0.85	Resistant to basic solutions
AMTIR	11,000 - 725	2.5	 1.77	Very resistant to acidic solutions
ZnSe	15,000 - 650	2.4	 2.01	General use
Diamond	25,000 - 100	2.4	 2.01	Good for most samples. Extremely caustic or hard samples

Contexts

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FT-IR & Microscope 소개

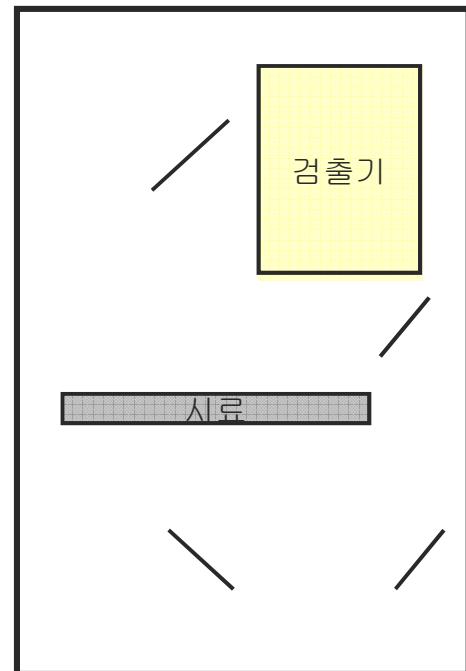
미소샘플 측정

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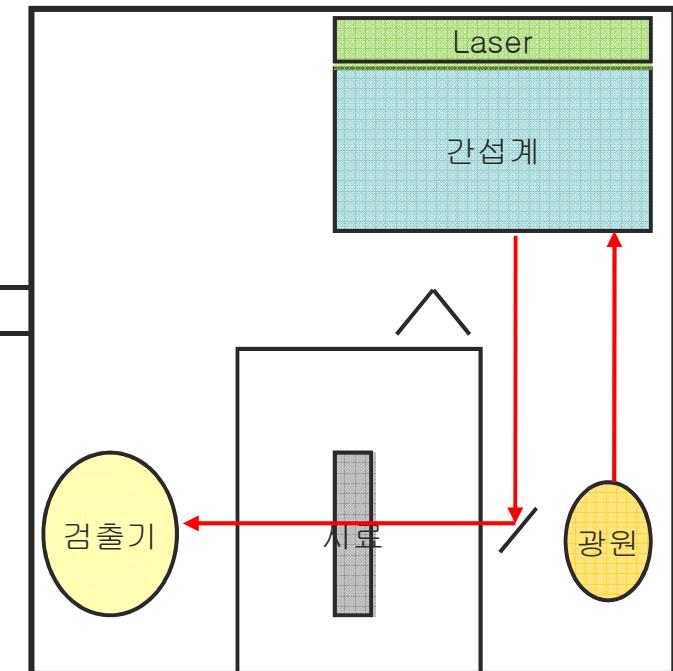
- FT-IR에서 샘플의 사이즈가 um단위일 경우 정확히 내가 원하는 샘플만을 측정하기는 거의 불가능합니다.
- 하지만 FT-IR & Microscope를 사용하면 전처리 없이 또는 최소한의 전처리를 통해 최소 1.56um 사이즈의 샘플을 측정하는 것이 가능합니다.
- 또한 유저 라이브러리 구축이 가능하기 때문에 추후 방대한 양의 D/B를 구축할 수 있습니다.
- 이러한 이점 때문에 미소샘플에서 유기물 분석은 FT-IR Microscope를 필수장비로 사용하고 있으며 무기물 분석은 SEM(EDS)을 사용합니다.

Main Bench 측정 시 IR Beam 경로

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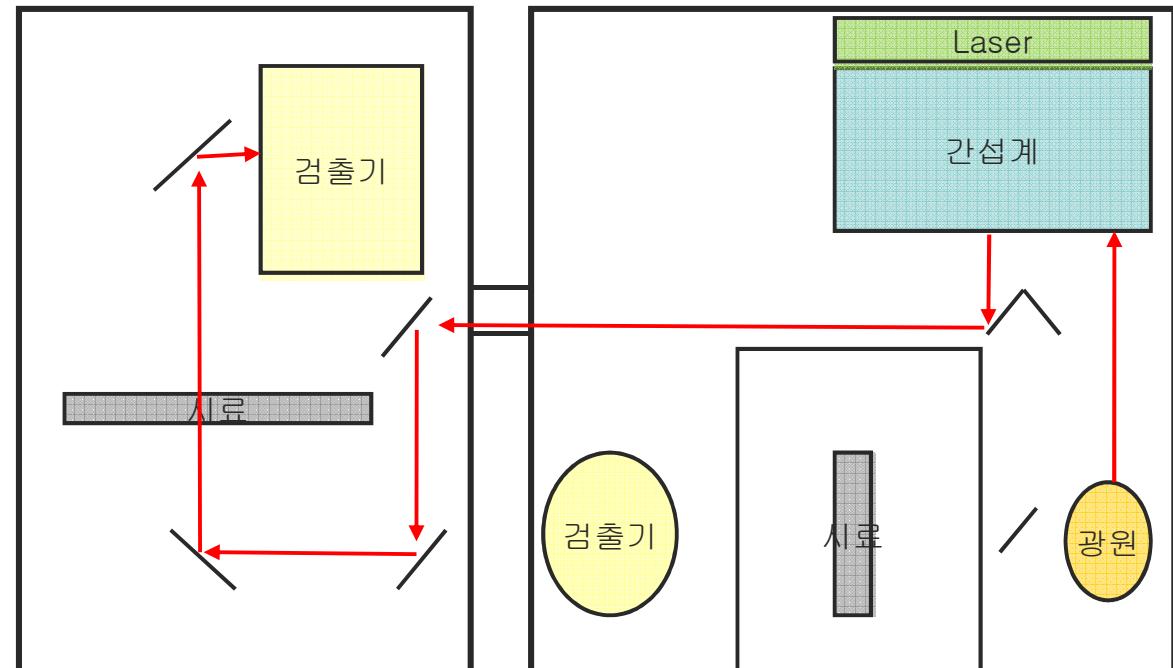
Microscope



FT-IR Main Bench

Microscope 측정 시 IR Beam 경로

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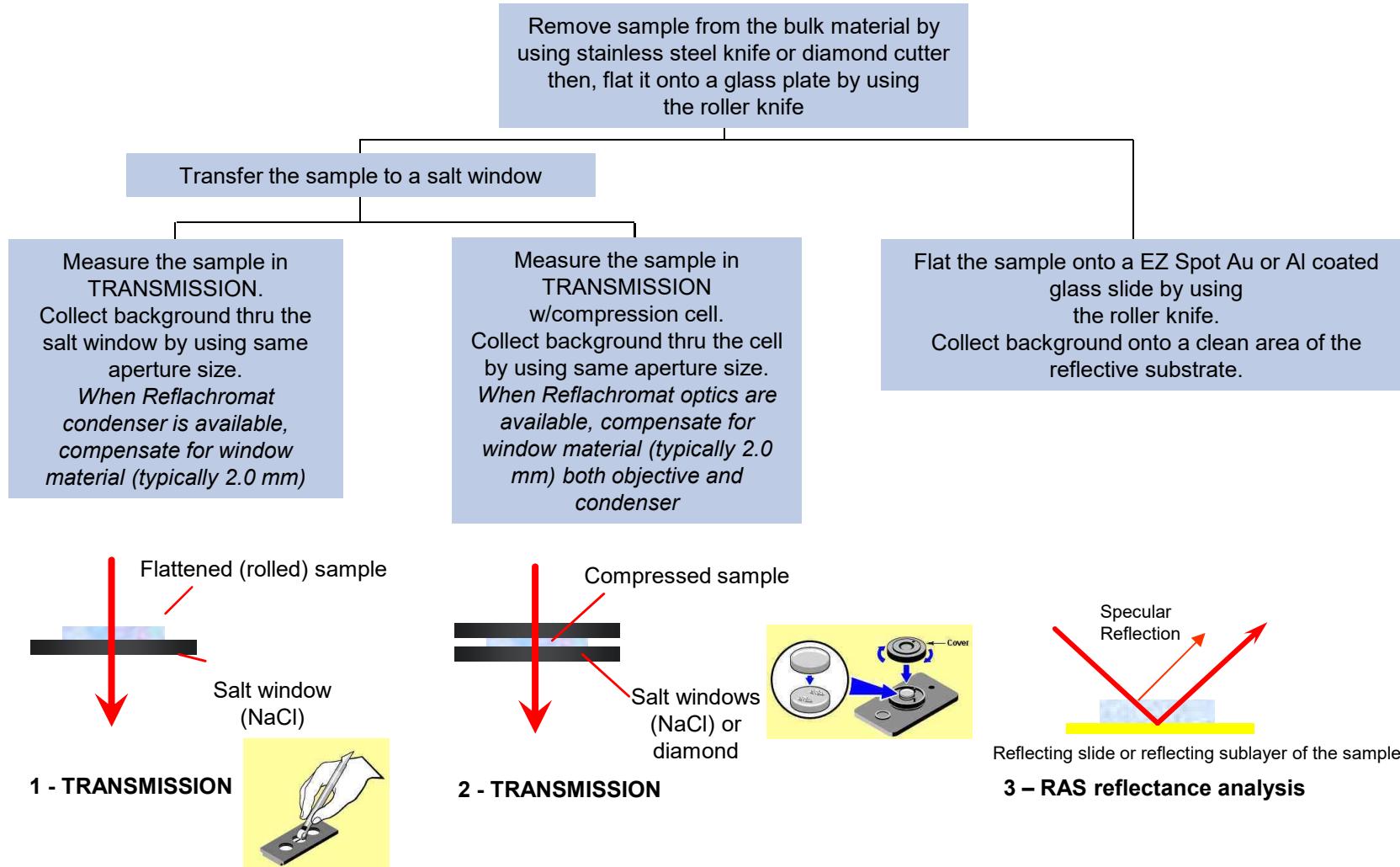
Microscope

FT-IR Main Bench

Factor #1 - Sample Preparation

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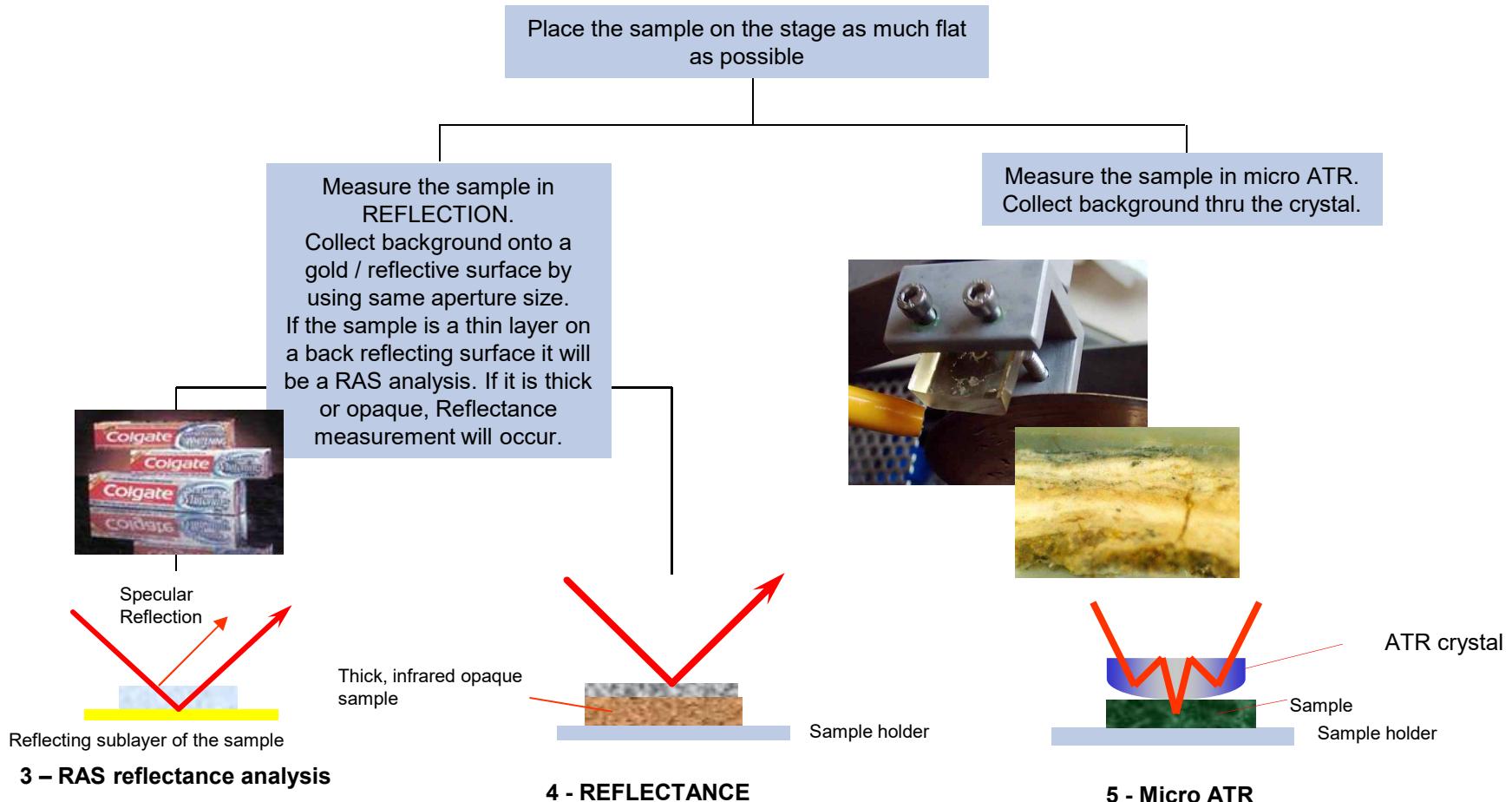
Sample can be removed from its bulk / media



Factor #1 - Sample Preparation

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Sample can not be removed from its bulk / media



PerkinElmer FT-IR Spectrometer Family

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SPOTLIGHT 150i



SPOTLIGHT 200i

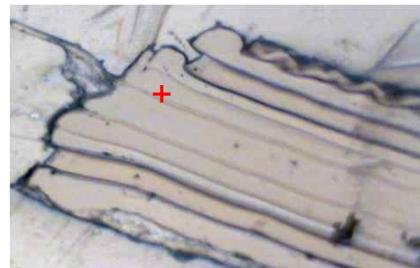


SPOTLIGHT 400

Mapping Mode

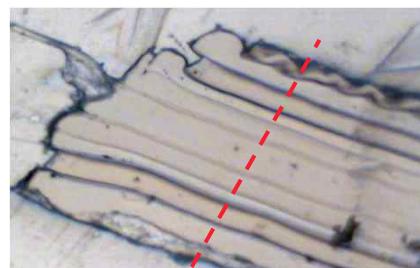
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1. Point Mapping



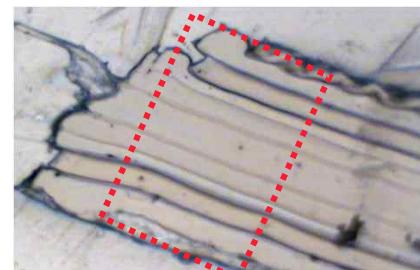
Spotlight150i

2. Line & Area Mapping



Spotlight200i

3. Imaging

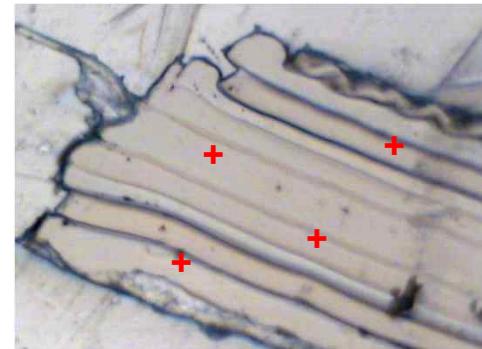


Spotlight400

SPOTLIGHT 150i

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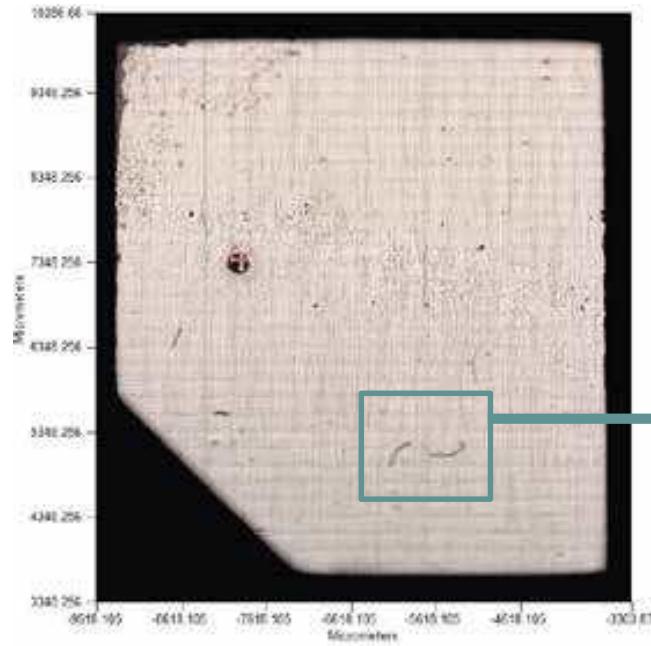
- Discrete Points
 - The stage moves to each specified location
 - Only spectra from those locations are collected



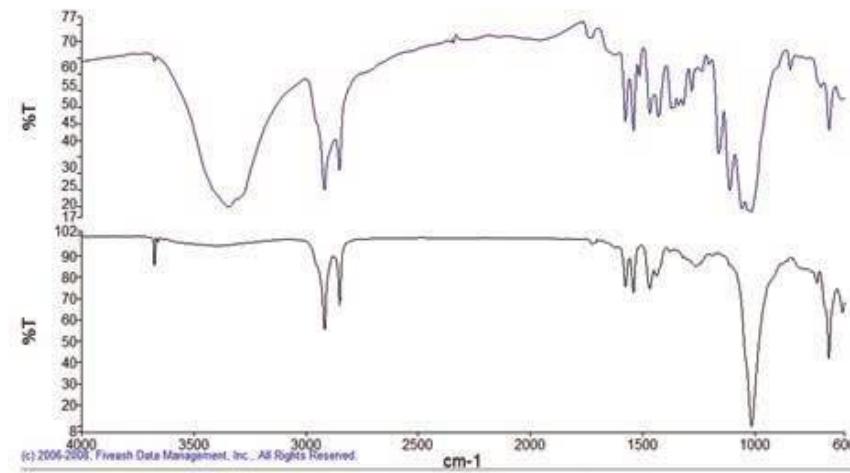
SPOTLIGHT 150i

Detection and Identification of Contaminations

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The Visible Image Survey



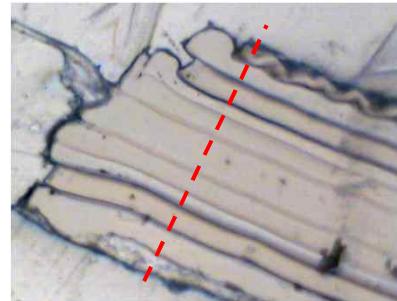
Spectra of two contaminant fibers

SPOTLIGHT 200i

scinco

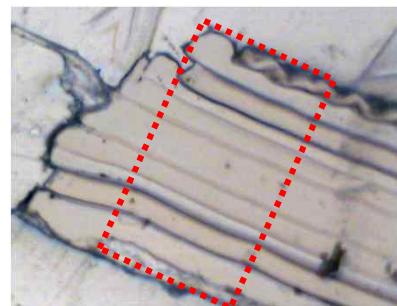
- Line Maps

- The stage moves along a line dragged across the sample
- Number of spectra depends on line length and step size



- Area Maps

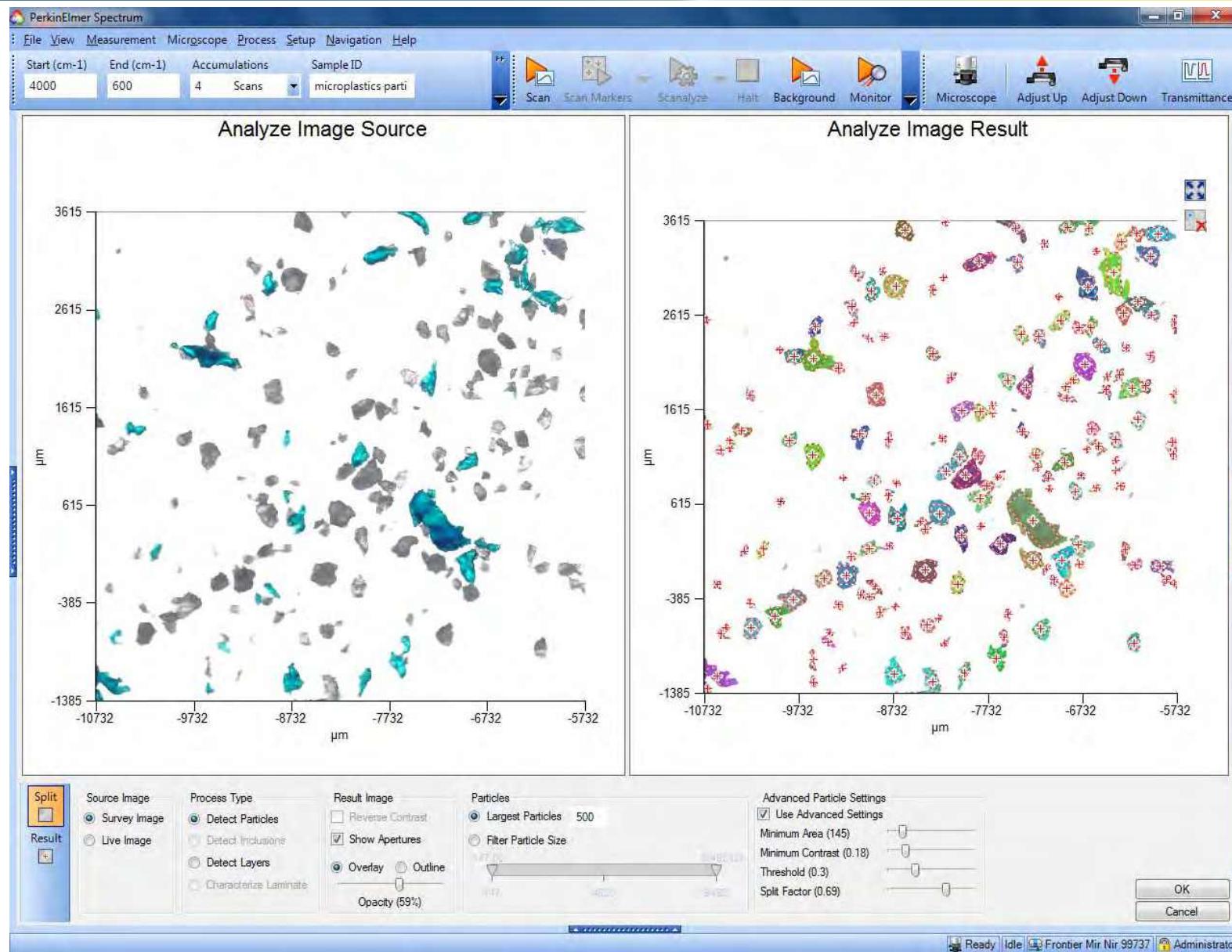
- The stage moves until a complete area of the sample is completed
- Spectra within the whole area are collected



SPOTLIGHT 200i

Detection and Identification of Microplastic

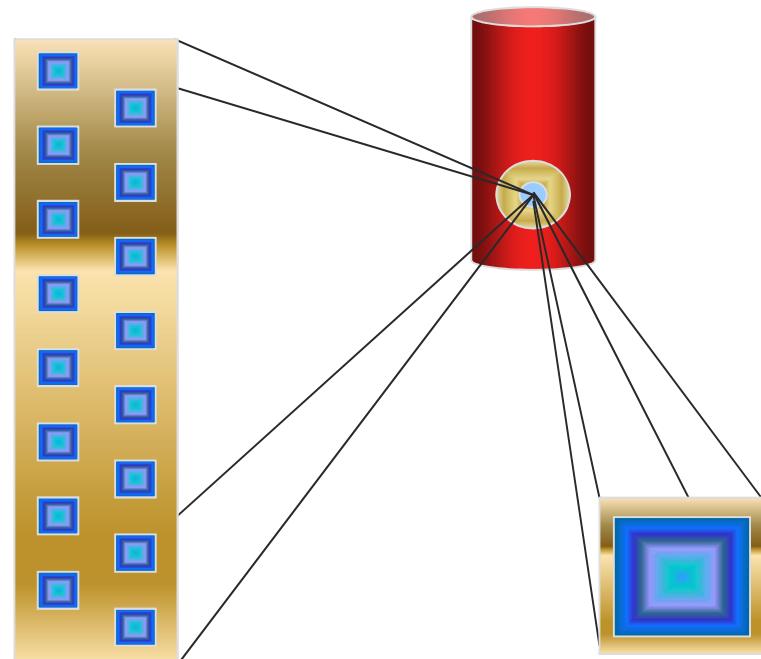
scinco



SPOTLIGHT 400

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Two-in-One Duet™ 검출기
• 다른 검출소자의 동시탑재



Line Array 검출소자
30µm의 16소자가 직렬로
나열된 **검출소자**

100µm의 단소자



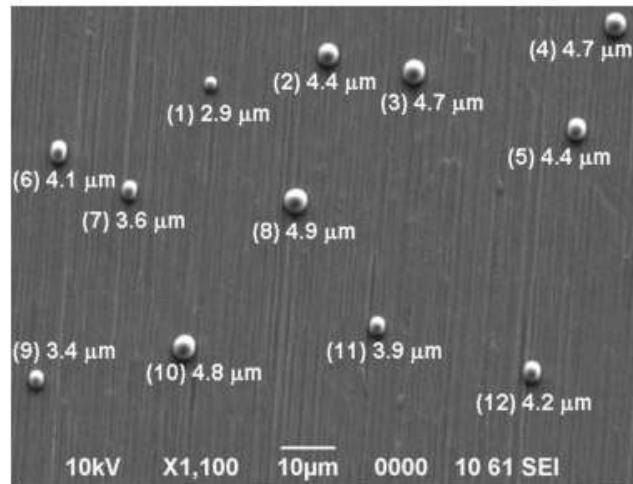
ATR imaging accessory



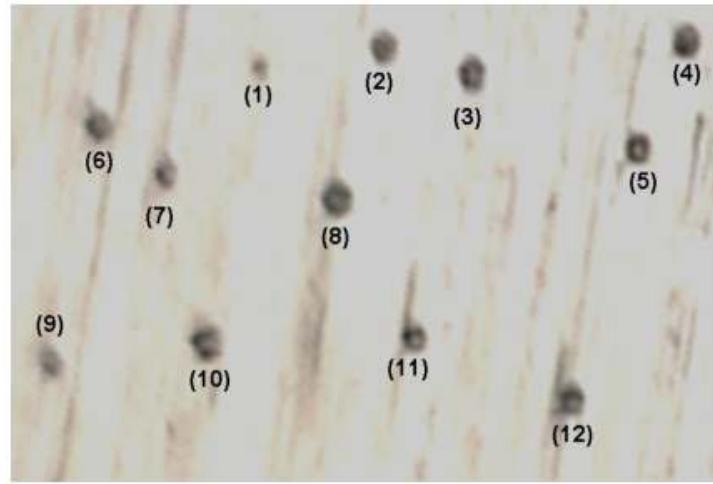
SPOTLIGHT 400

Single Particle Analysis

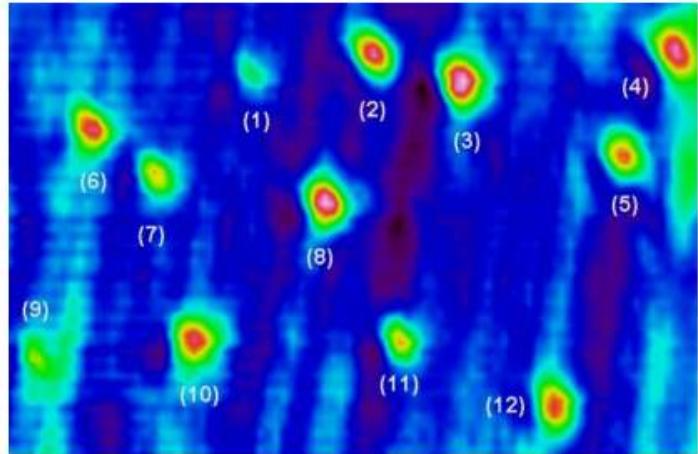
scinco



(SEI of ascorbic acid aerosol particles)



(optical image of the same particles)



(ATR-FT-IR image of the same particles – based on transmission signal at 1032 cm⁻¹)

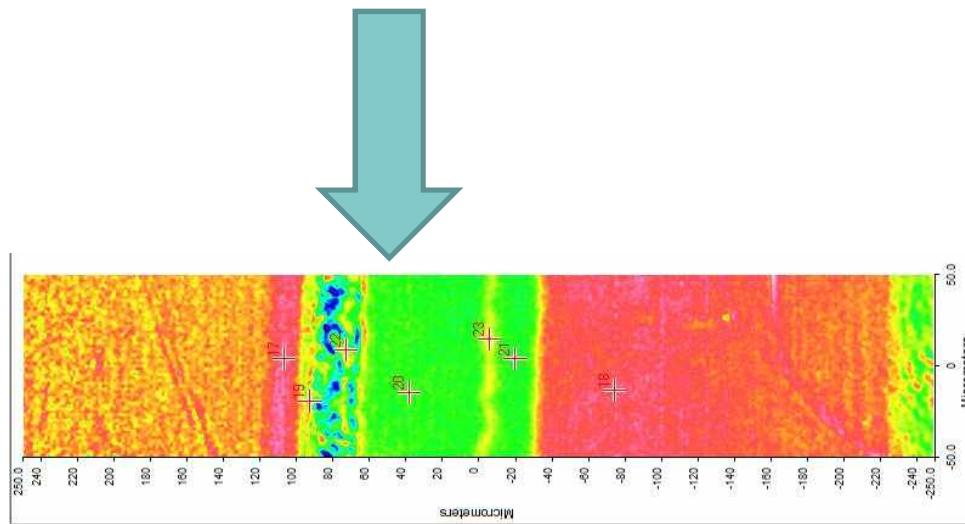
Anal. Chem.
2009, vol 81, p6695~6707
Chul-Un Ro, Inha Univ.

ATR Imaging of multilayer food packaging

scinco



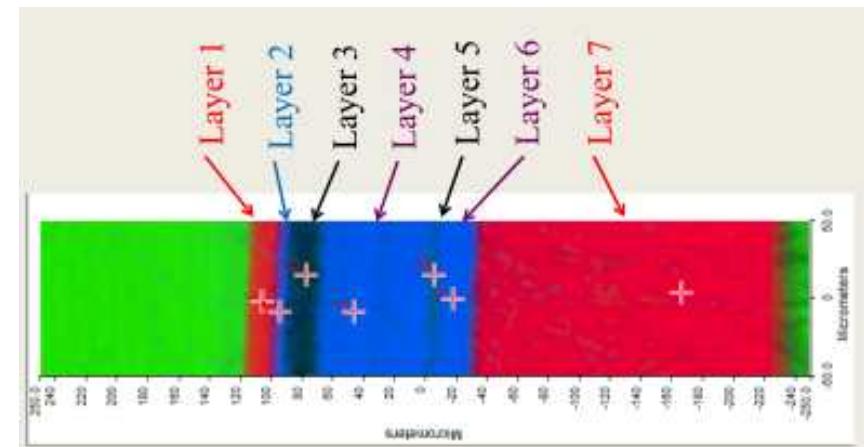
(Visable Image of Sample)



(Abs. data)

Sample Name	Search Score
layer 1 – PET	0.981077
layer 2- PET	0.897881
layer 3- Foil	0.679307
layer 4- HDPE	0.975834
layer 5- EVOH	0.945797
layer 6- HDPE	0.974802
layer 7- PET	0.98173

(Result Table)

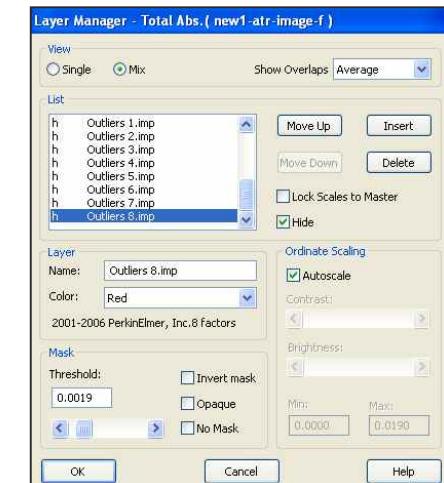
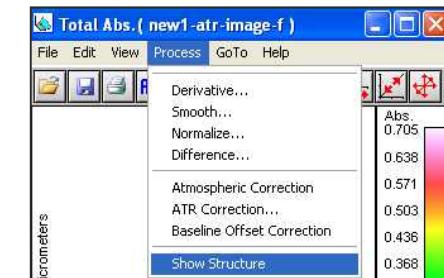
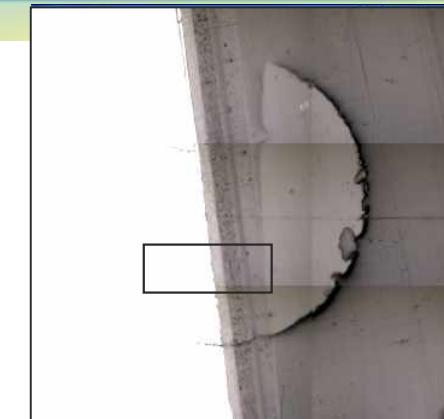
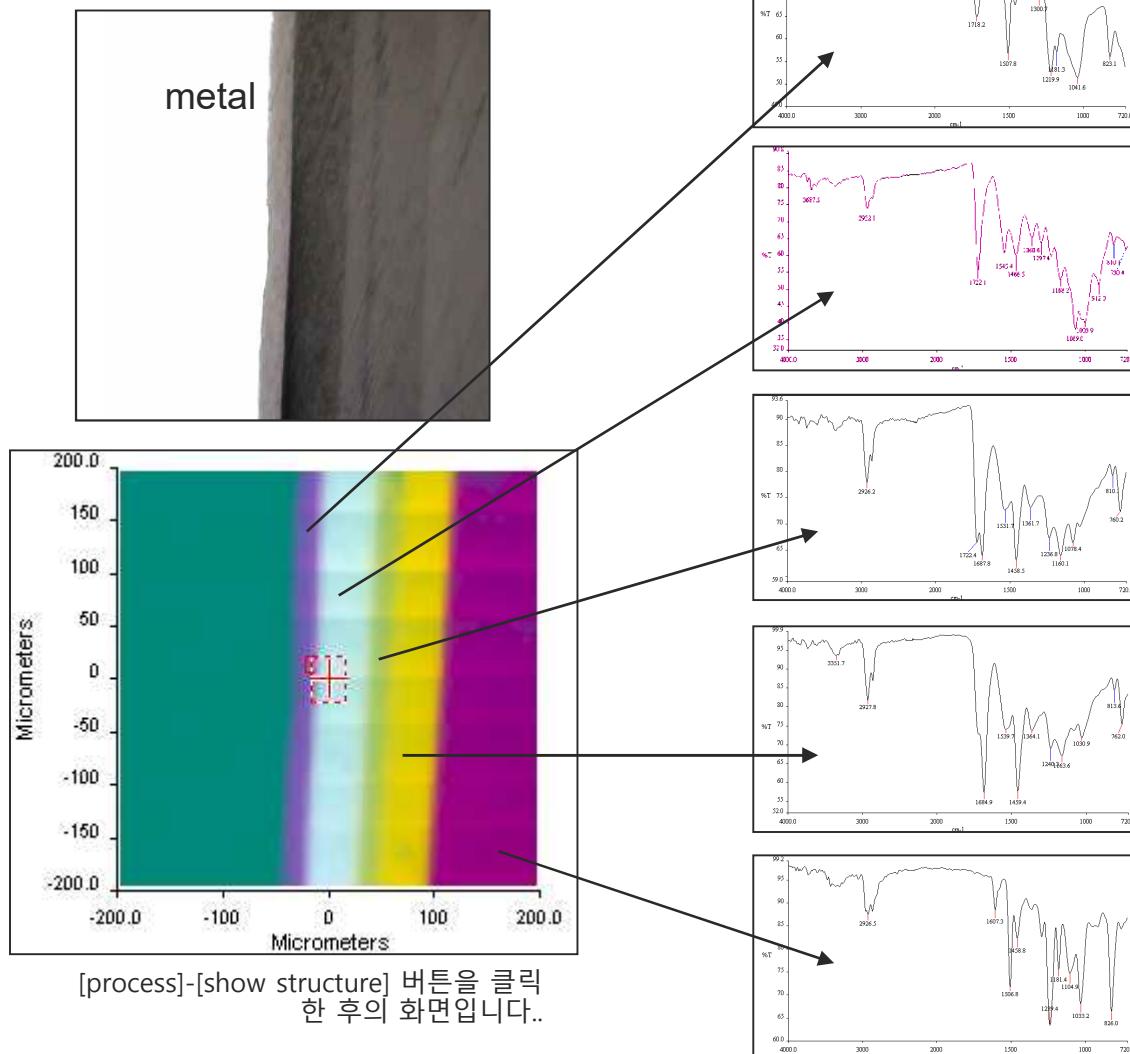


(Chemical Imaging)

SPOTLIGHT 400 : 1.56 um

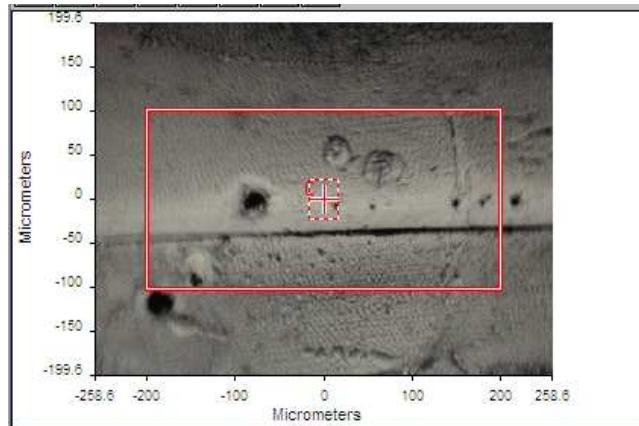
scinco

ATR imaging accessory를 사용하여
측정하기 전의 visible image 입니다.

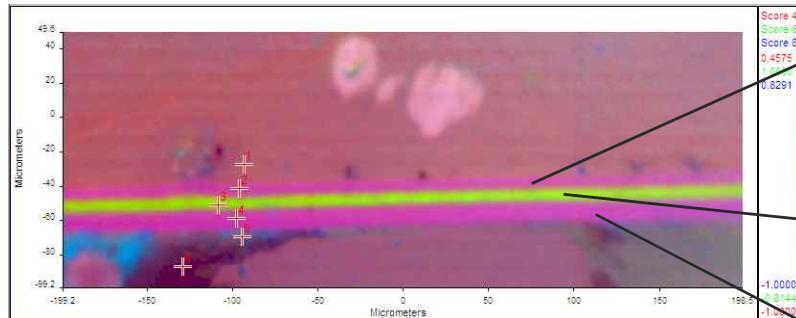


Multilayer analysis 1 (1.56 um)

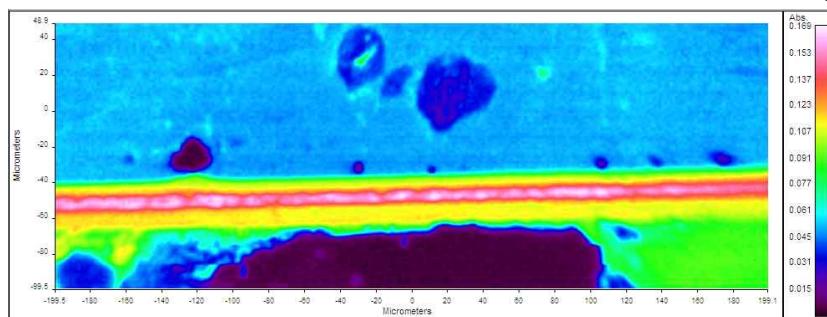
scinco



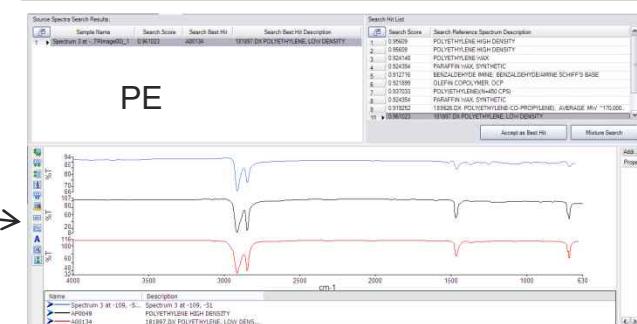
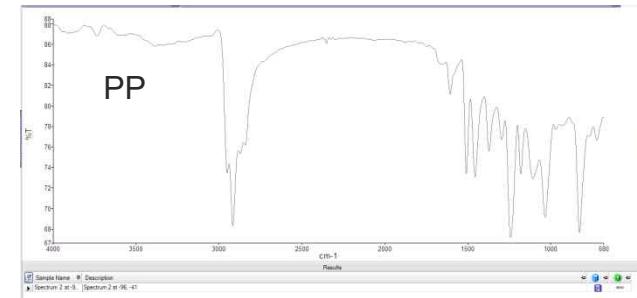
ATR imaging accessory를 사용하여 측정하기 전의 visible image 입니다.



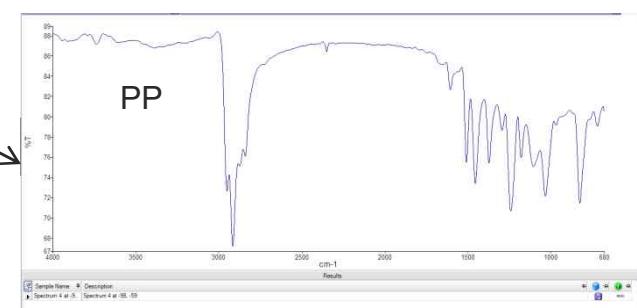
Show structure 아이콘을 클릭하면 비슷한 스펙트럼을 가진 영역을 같은 색깔로 표시해줍니다.



2915 cm-1 extraction



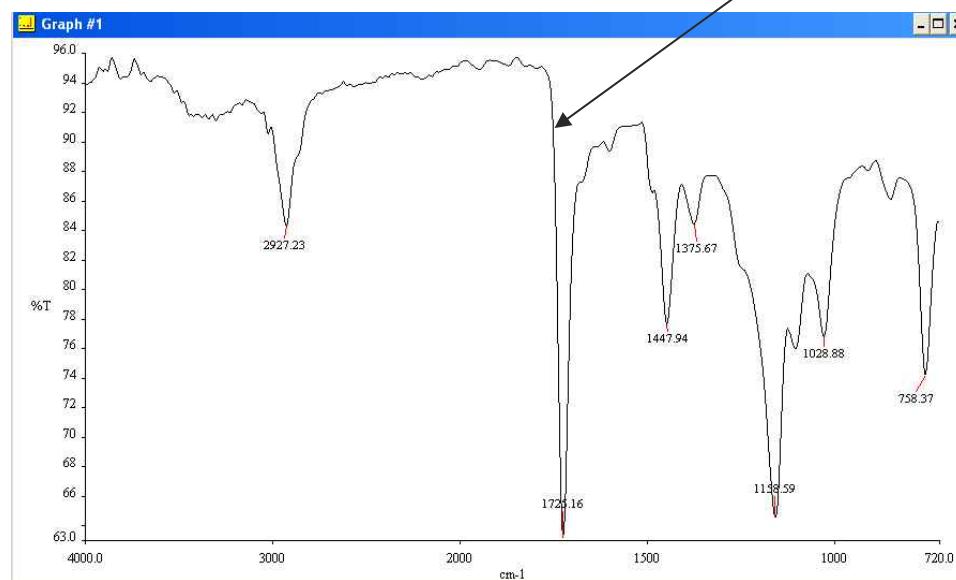
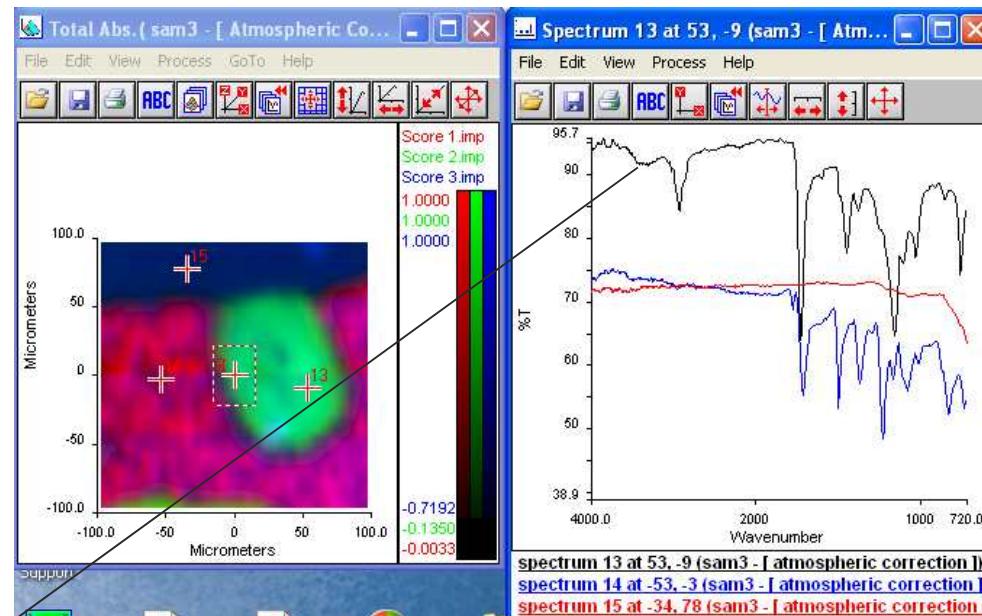
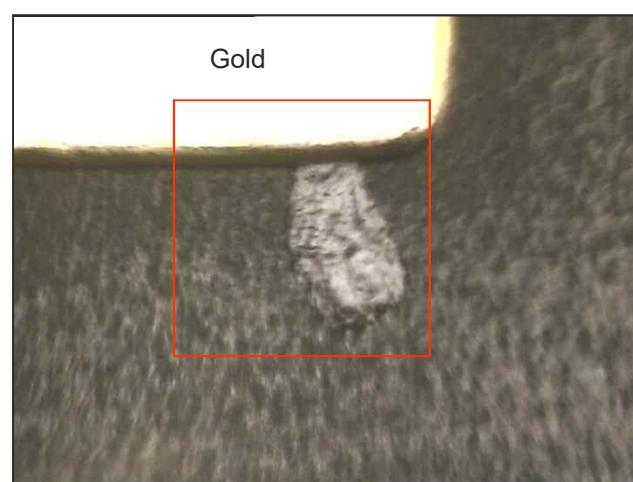
PP



PP

Contaminant analysis I : impurity on PCB board

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sam3-atr.sp / Spectrum.1st Euclidean Search Hit List	
0.995	SE0193 TEXIGEL 13-097 PACIFIC SCOTT BADER ACRYLIC, STYRENATED ACRYLIC, STYRENATED
0.934	SE0098 UCAR Vehicle 443 Polymer - Acrylic Union Carbide
0.924	SE1895 UCAR 4510 UNION CARBIDE STYRENATED ACRYLIC, CARBOXYL AND HYDROXYL FUNCTIONAL. ACRYLIC, STYRENATED
0.922	SE0034 JONCRYL 95 JOHNSON ACRYLIC, COLLOID DISP ACRYLIC
0.915	SE0022 Acryloid AT-70 Polymer - Acrylic Rohm and Haas
0.915	SE1884 RHOPLEX AC-25 ROHN & HAAS ACRYLIC EMULSION ACRYLIC
0.914	SE1927 NACRYLIC X-4483 NATIONAL STARCH ACRYLIC ACRYLIC
0.914	SE1841 HYCAR 2600X84 GOODRICH RESIN ACRYLIC EMULSION. SELF CROSSLINKING ACRYLIC
0.913	SE1864 SYNTHEMUL 97-735 REICHHOLD RESIN. MODIFIED CARBOXYLATED ACRYLIC ACRYLIC
0.913	SE1664 ROBOND L-12 ROHM & HAAS ACRYLIC POLYMER (AQUEOUS) *
0.913	SE0024 Acryloid AT-85 Polymer - Acrylic Rohm and Haas
0.912	SE0160 Poly(ethyl acrylate:styrene) Film 0-00-0
0.911	SE0152 Poly(ethyl acrylate:styrene:acrylamide) Film//Osi 0-00-0
0.911	SE0017 POLY(ETHYLACRYLATE:ST:ACRYLAMIDE)
0.910	SE1758 RHOPLEX LC-40 ROHM & HAAS ACRYLIC ACRYLIC
0.909	SE0075 Rhoplex AC-234 Polymer - Acrylic Rohm and Haas
0.908	SE0044 Acryloid QR-916 Polymer - Acrylic Rohm and Haas
0.908	SE1737 RHOPLEX B-600 ROHM & HAAS ACRYLIC EMULSION ACRYLIC
0.908	SE1843 HYCAR 2600X288 GOODRICH RESIN ACRYLIC EMULSION ACRYLIC
0.906	SE1883 RHOPLEX AC-234 ROHM & HAAS ACRYLIC ACRYLIC

Double-click on compound name for overlay comparison

미세플라스틱 분석 방법

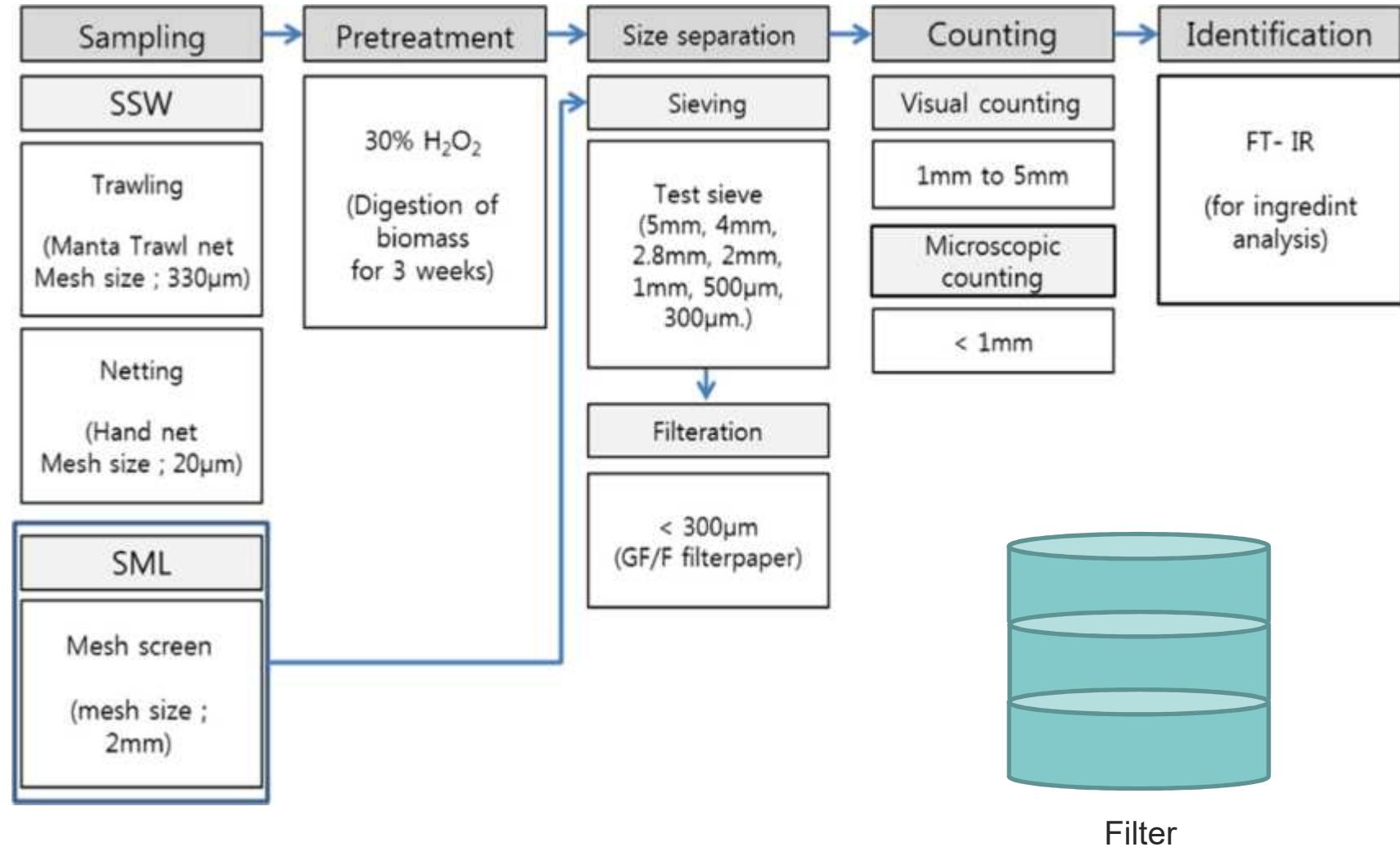
물 속 미세 플라스틱

scinco

- 2017년 9월 환경부 수돗물 속 미세플라스틱 함유실태 조사 공고
- 조사대상 정수, 상수원수(미세플라스틱 분리 작업 필요)
- 정수처리 공정별 미세플라스틱 제거 효율 파악
- 미세플라스틱 < 5mm
- Ex) 7억개의 미세플라스틱이 바다로 유입
- 미세플라스틱 인체 유해성 파악 필요

미세 플라스틱 분석 개요

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미세 플라스틱 분석 개요

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- 샘플 채취
- 전처리(30~50% H₂O₂ 용액 이용)
- 크기별 분류 (100~300um, 300um~1mm, 1~5mm)
- 유리섬유여과지 여과
- 실체현미경 관찰
- FT-IR 이용 미세플라스틱 판명 및 정성 분석

미세플라스틱 관찰

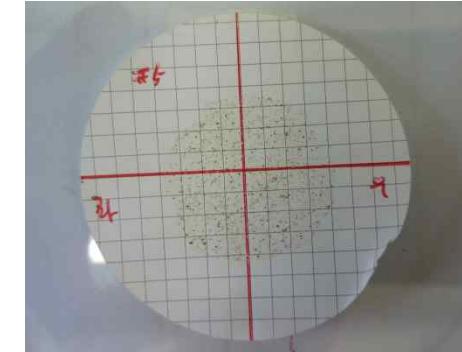
scinco



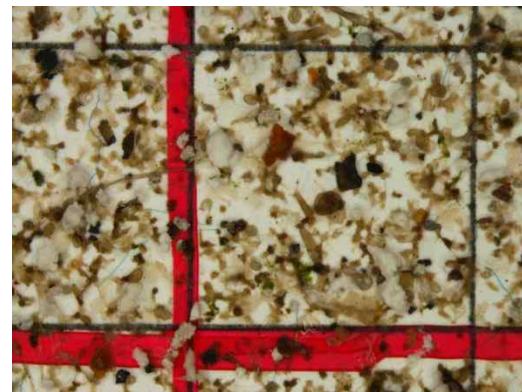
1 ~ 5mm



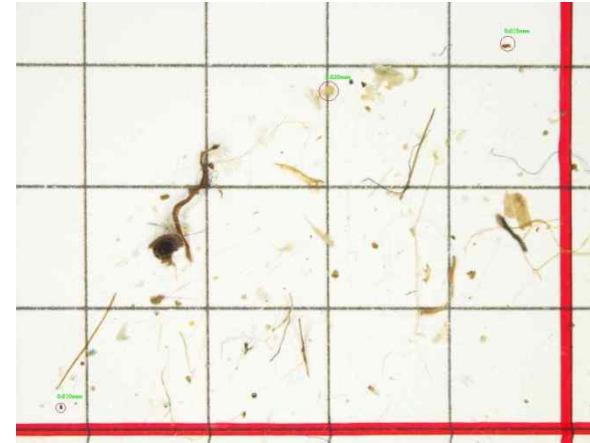
300um ~ 1mm



100 ~ 300um



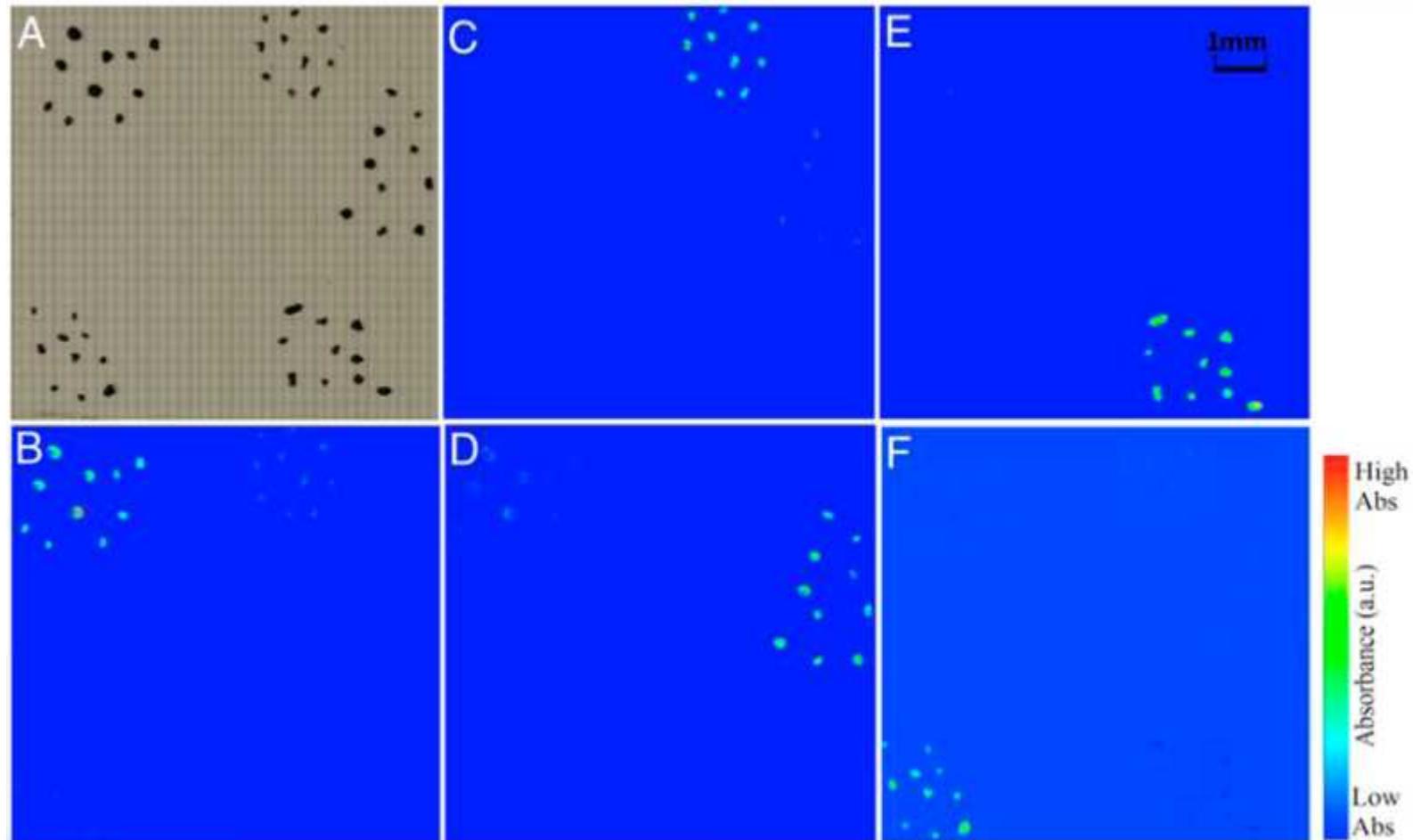
300um ~ 1mm by stereoscope



100um ~ 300um by stereoscope

미세플라스틱 검증 by FT-IR

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Color images of microplastics in known positions on a glass slide achieved using a PerkinElmer micro-FT-IR spectrometer with a imaging detector. Each map displays a particular polymer type

A: Visible image; B: PP; C: PVC; D: Nylon; E: PS; F: PE

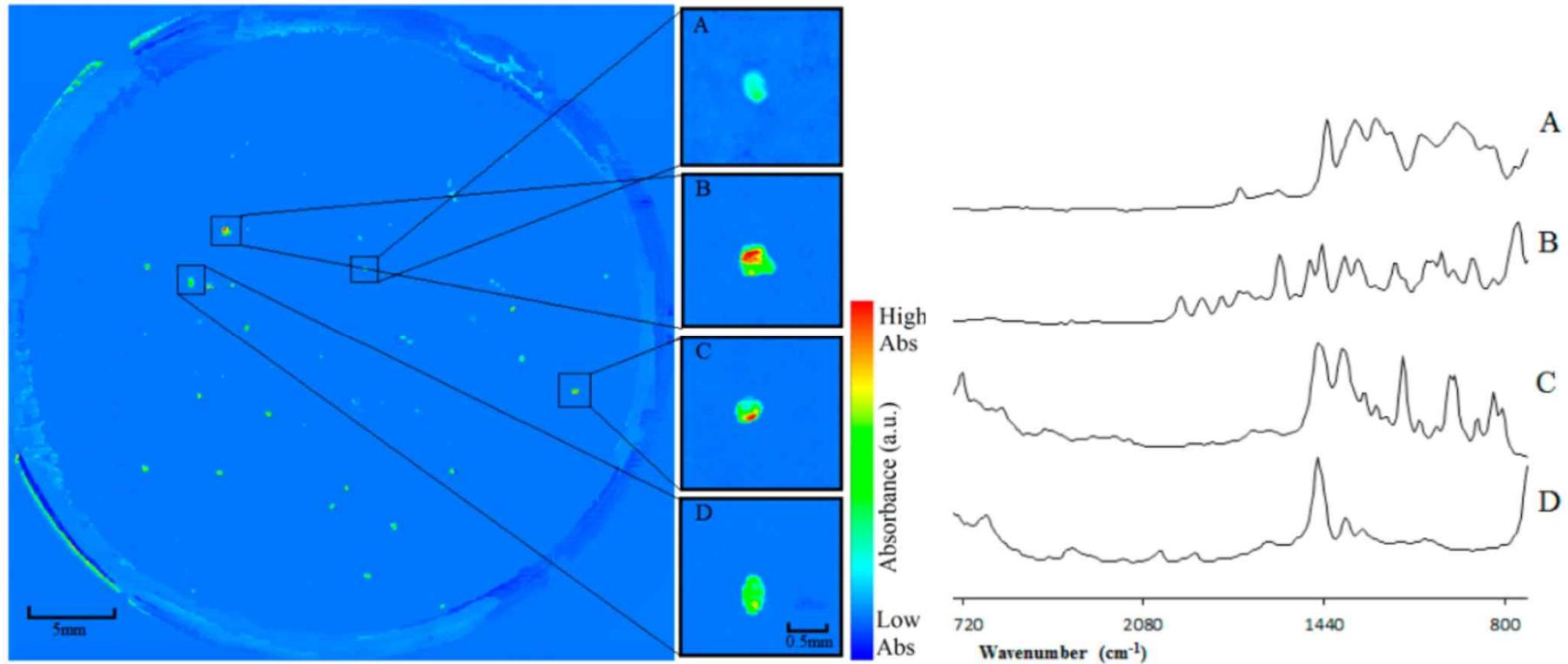
Polymer Absorbance Bond

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Polymer	Wavenumber(cm-1)	Vibration mode
PP	2,700~2,950 / 1,460 / 1,375	C-H stretch / C-H3 bend
PVC	2,800 / 2,900 / 1,460	C-H stretch / C-H2 bend
PS	2,900 / 2,850 / 1,600 / 1,025	C-H stretch / C-O stretch
PE	2,750 / 2,900 / 1,470	C-H stretch / C-H2 bend
Nylon	3,300 / 2,950~2,800 / 1,650	O-H / C-H stretch / C-O stretch

Microplastic Spectrum

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Four fragments of each polymer type have been selected and magnified. FT-IR spectra of selected and magnified microplastic fragments; these spectra are typical of plastic fragments mapped using these parameters .
A: PVC; B: PS; C: PP; D: PE.

Micro Product

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Product	Spatial Resolution
IR Microscope	>10um
Imaging Microscope	>3um
Raman Spectrometer	>1um
PTIR	>0.5um

각 플라스틱 별
Spectrum 차이

Spectrum of Plastic

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- Polyethylene terephthalate (PET)
- Polyethylene (PE)
- Polyvinyl chloride (PVC)
- Polypropylene (PP)
- Polystyrene (PS)
- Nylon
- Polymethyl methacrylate (PMMA)

Table 1. Polymer Identification Codes (PIC)

	Acronym	Full Name	Example of Uses
 PETE	PET	Polyethylene Terephthalate	Fizzy drink bottles and frozen ready meal packages.
 HDPE	HDPE	High-Density Polyethylene	Milk and washing-up liquid bottles.
 V	PVC	Polyvinyl Chloride	Food trays, cling film, bottles for squash, mineral water and shampoo.
 LDPE	LDPE	Low Density Polyethylene	Carrier bags and bin liners.
 PP	PP	Polypropylene	Margarine tubs, microwavable meal trays.
 PS	PS	Polystyrene	Yogurt pots, foam meat or fish trays, hamburger boxes and egg cartons, vending cups, plastic cutlery, protective packaging for electronic goods and toys.
 OTHER	Other	Any other plastics that do not fall into any of the above categories.	Melamine, often used in plastic plates and cups.

Spectrum of Plastic

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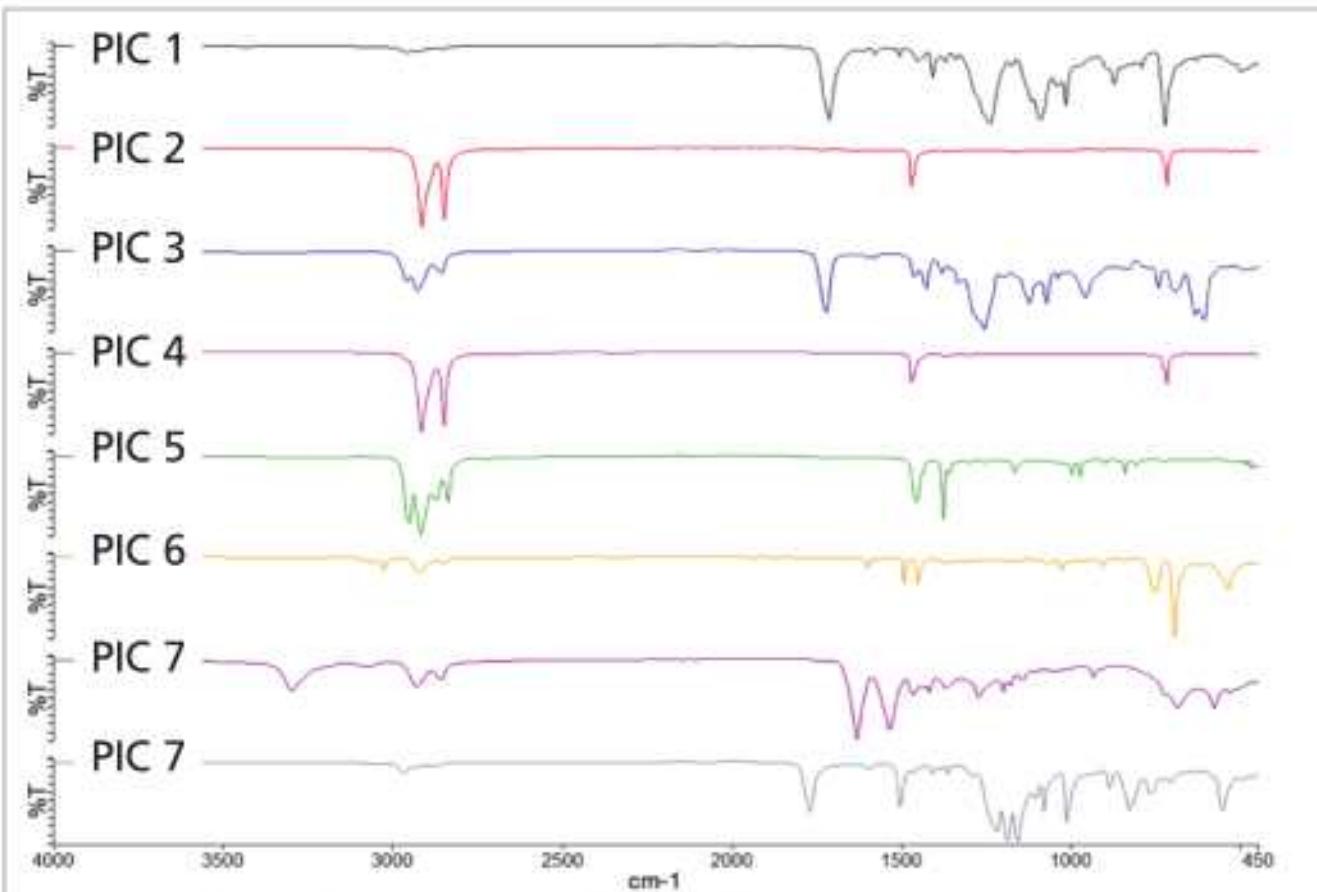


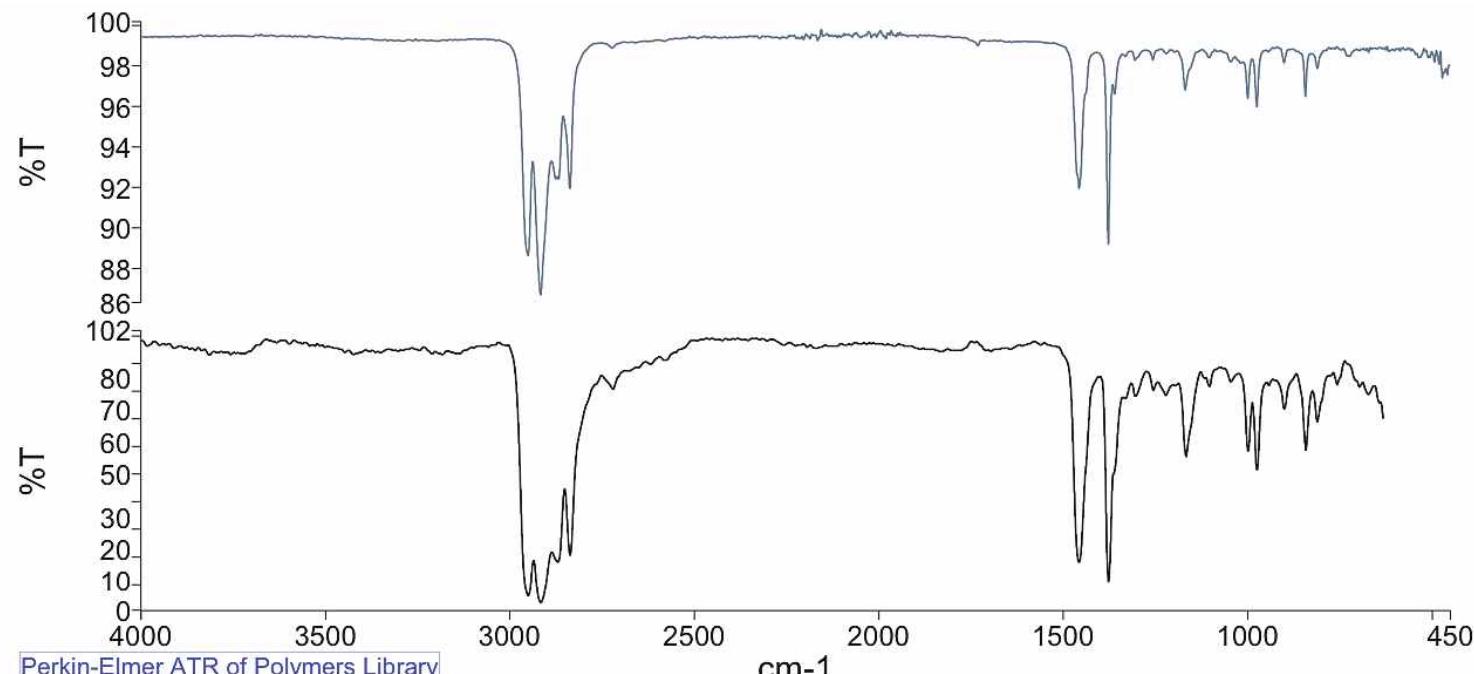
Figure 2. Mid-infrared spectra from the different PIC categories.

Table 1. Polymer Identification Codes (PIC)

	Acronym	Full Name	Example of Uses
PETE	PET	Polyethylene Terephthalate	Fizzy drink bottles and frozen ready meal packages.
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OTHER	Other	Any other plastics that do not fall into any of the above categories.	Melamine, often used in plastic plates and cups.

Spectrum of Plastic

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Perkin-Elmer ATR of Polymers Library

Name	Description
PP PIC 5	Polymers for recycling 023 25 April 2014
AP0065	POLYPROPYLENE, ISOTACTIC

Sample Name	Description	Search Score	Search Best Hit	Search Best Hit Description
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PP PIC 5	Polymers for recycling 023 25 April 2014	0.970074	AP0065	POLYPROPYLENE, ISOTACTIC
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Spectrum of Plastic

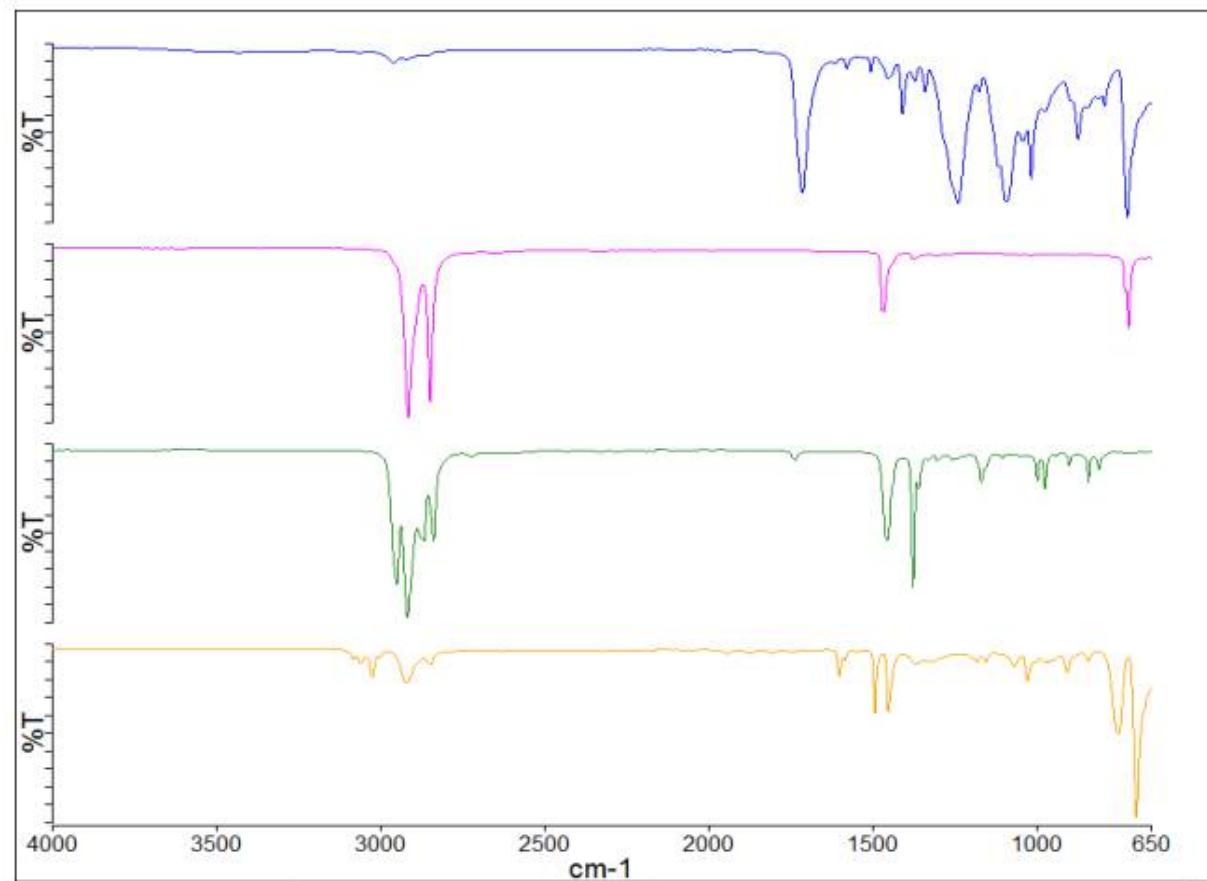
scinco

Search Score 0.977896
Poly(ethylene terephthalate)

Search Score 0.991831
Polyethylene, low density

Search Score 0.991771
Polypropylene

Search Score 0.99229
Polystyrene



ATR spectra of larger (>1mm) plastic fragments Identified as PET, polyethylene, polypropylene and polystyrene

The End

The Scinco logo is located in the top right corner. It consists of the word "scinco" in a lowercase, sans-serif font. The letter "s" is blue, while the rest of the letters are white, set against a blue background. A decorative wavy line made of small blue dots runs behind the text.

감사합니다!!

www.scinco.com

sc01best@scinco.com