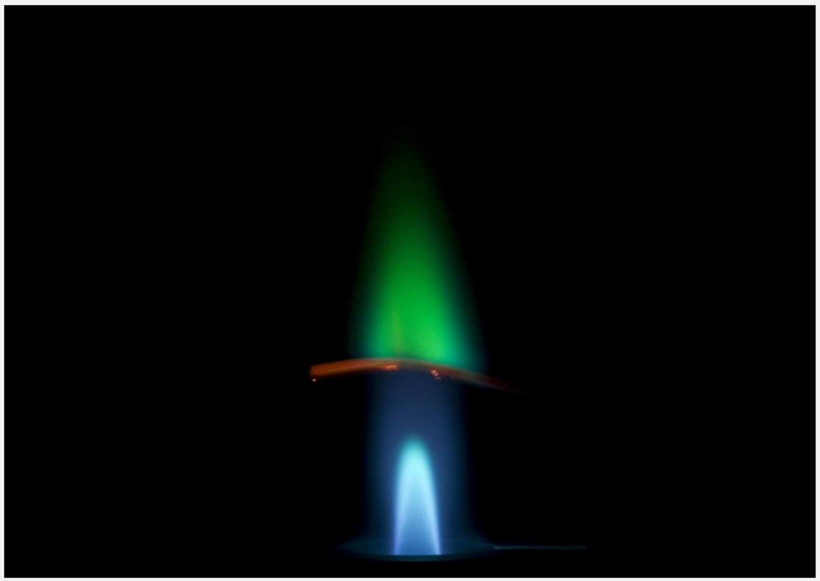
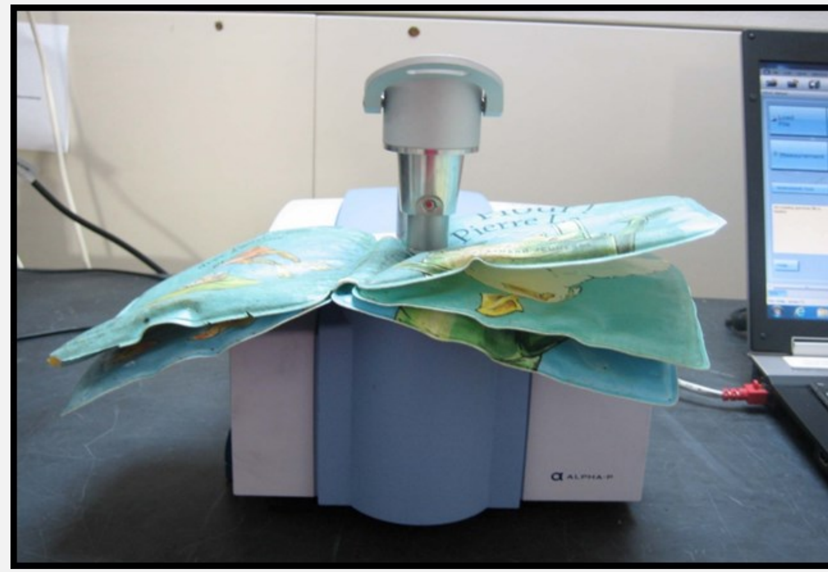
Identification of Plastics-workshop

22nd November 2017, National Museum of Denmark





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First commercial availability of plastics

Date	Plastics type	Uses	Comments
1862	SEMI-SYNTHETICS Cellulose nitrate	synthetic ivory, tortoiseshell, film base	Highly inflammable
1894	Cellulose acetate	Doping for aircraft wings, 'safety' film, synthetic textiles	Rayon, Celanese, Tricel
1902	Casein-formaldehyde	Buttons, hot-stamped products	Erenoid, Galalith, Ameroid Could not be moulded. No longer used widely
1909	SYNTHETICS Phenol-formaldehyde	Radio cases, cables, insulators, heared hair rollers, fine boxes, photo	Bakelite, Catalin 'The material of 1000 uses' Only made in dark colours
1926	Urea and thiourea- formaldehyde	kitchenware	Available in pale colours
1924	Melamine-formaldehyde	Formica laminated surfaces	Scratch resistant and hard
1935	Polyvinyl chloride (PVC)	Cable insulation, Barbie dolls, toys	Replaced rubber in WWII. Needs lots of additives
1937	Polymethyl methacrylate	Aircraft windows, glazing, lighting	Plexiglas, Perspex
1938	Polystyrene	Heat insulation, plastic cups	Flamingo foam
1939	Nylon	Parachutes, synthetic silk, clothing	Very tough, withstands hot water
1942	Polyethylene	Tupperware	melts at 130°C
1947	Epoxy	Adhesives, sculptures	Yellows quickly
1950	Polyester	Textiles, cola bottles,	PET
1956	Polypropylene	car bumpers, bottle crates	stiffer than polyethylene
1967	Polycarbonate	CDs, greenhouse roofs	tough

What is a plastic?

- What is a plastic?

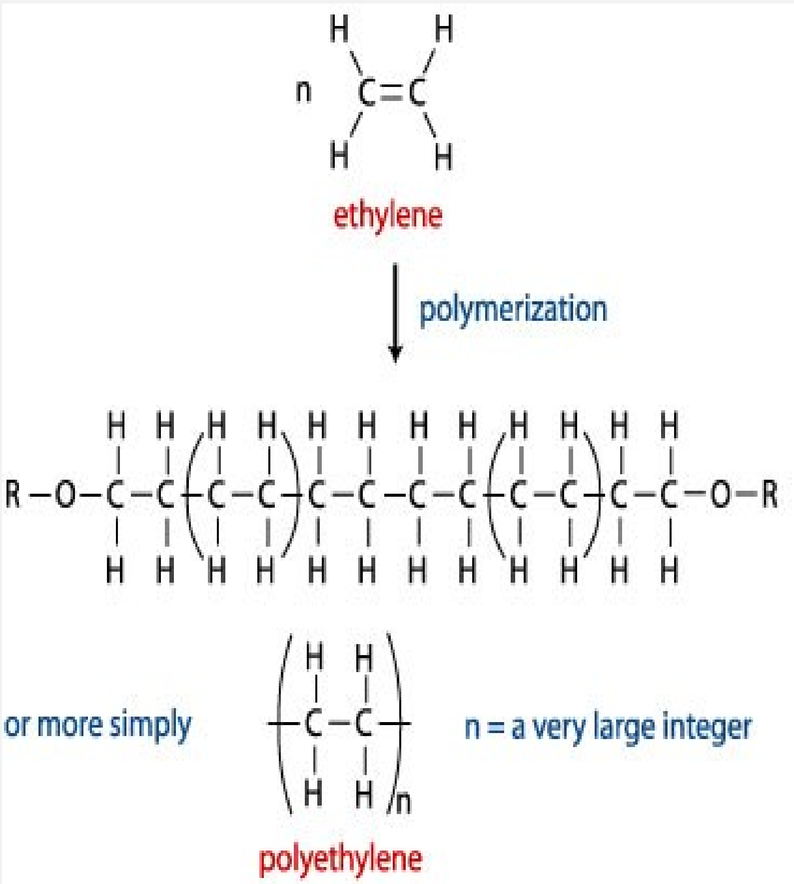
  POLYMER + additives +colour

- What is a polymer?

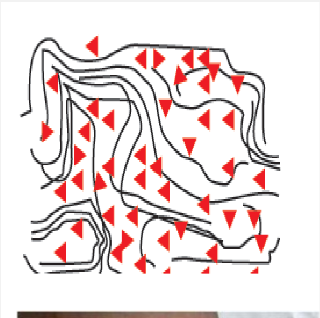
  Large molecule built from small, repeated, chemical units (MONOMERS). From 1000-10,000 monomers comprise a polymer.

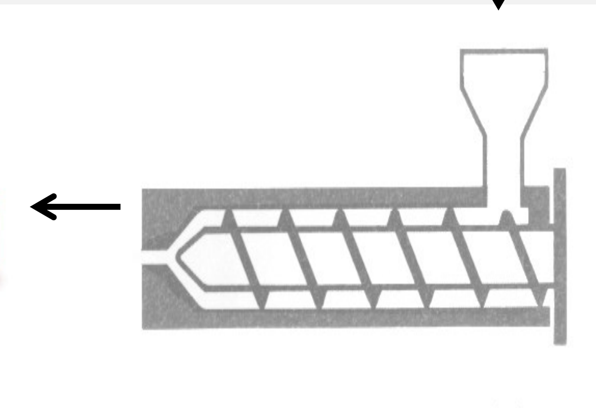
High molecular weight=hard, stiff, high melting point

Low molecular weight=soft, flexible, low melting point

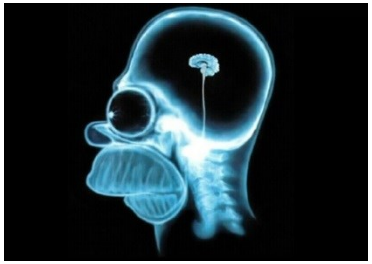


plasticizers
antiageing
additives,
lubricants
colour





Analytical techniques for plastics

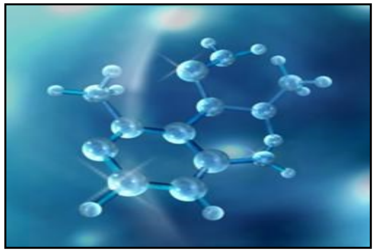


non-instrumental techniques –non -& destructive

•appearance

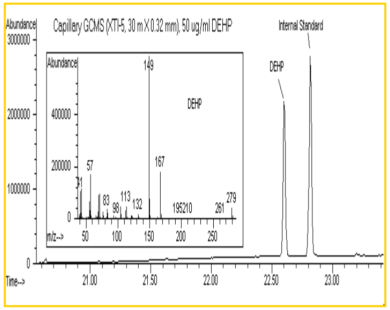
•physical and thermal properties- density, burning

• chemical properties- pH, spot tests



vibrational spectroscopy –semi destructive

•Fourier Transform Infrared (FTIR) spectroscopy



separation techniques-destructive

•gas- chromatography-mass spectrometry

Identification of plastics using non-destructive techniques

- **Date of manufacture** –if earlier than 1909 is not synthetic, more likely cellulose nitrate or acetate
- **Appearance and feel-**

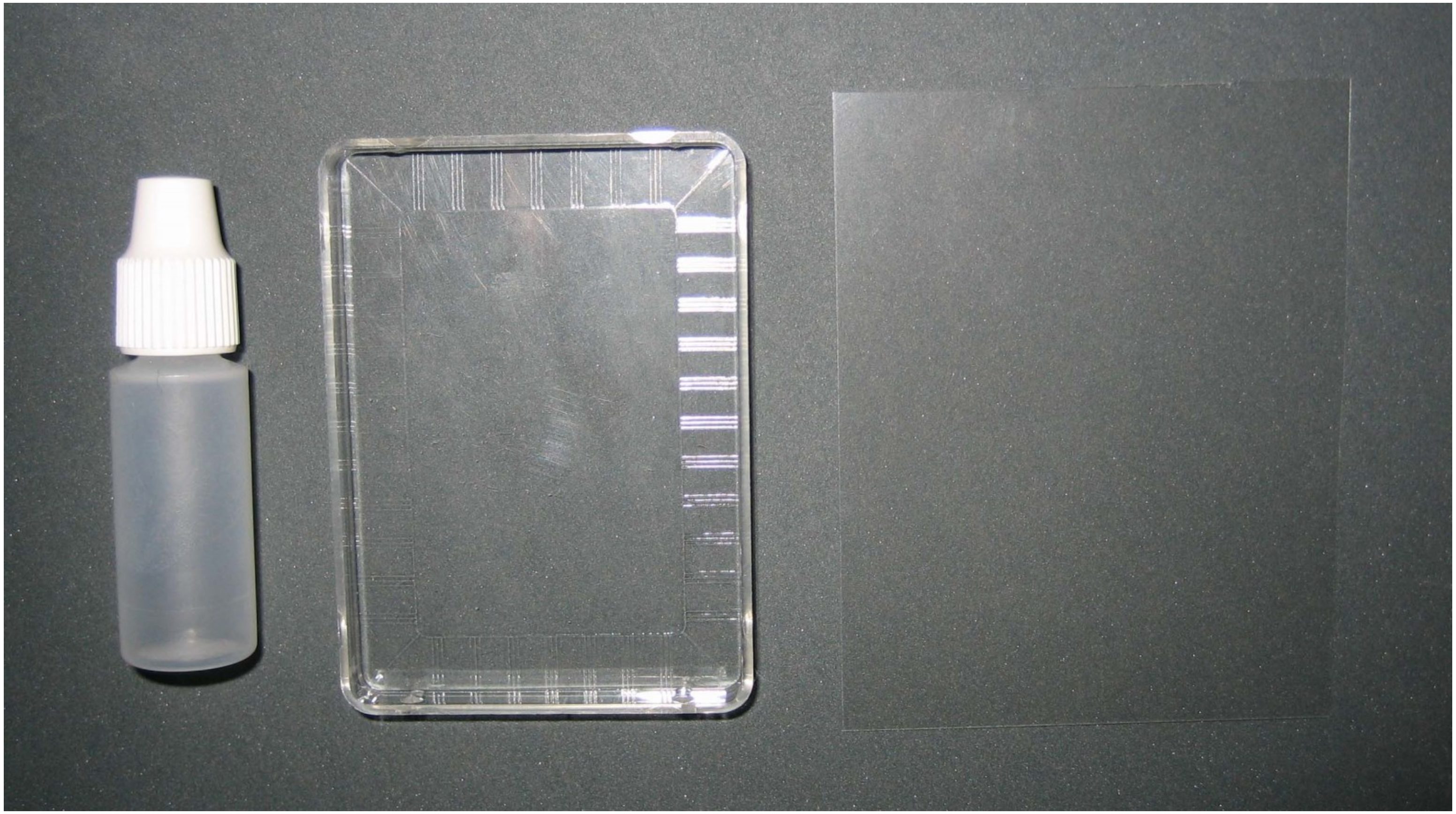
  recycling mark?
  transparency/cloudiness/opacity/colour/filler?

  hardness/flexibility-beware that it changes with time
- **Smell** –vinegar=cellulose acetate, phthalate 'plasticy' =PVC
- **Sound** when tapped-polystyrene sounds like metal

Appearance of plastics

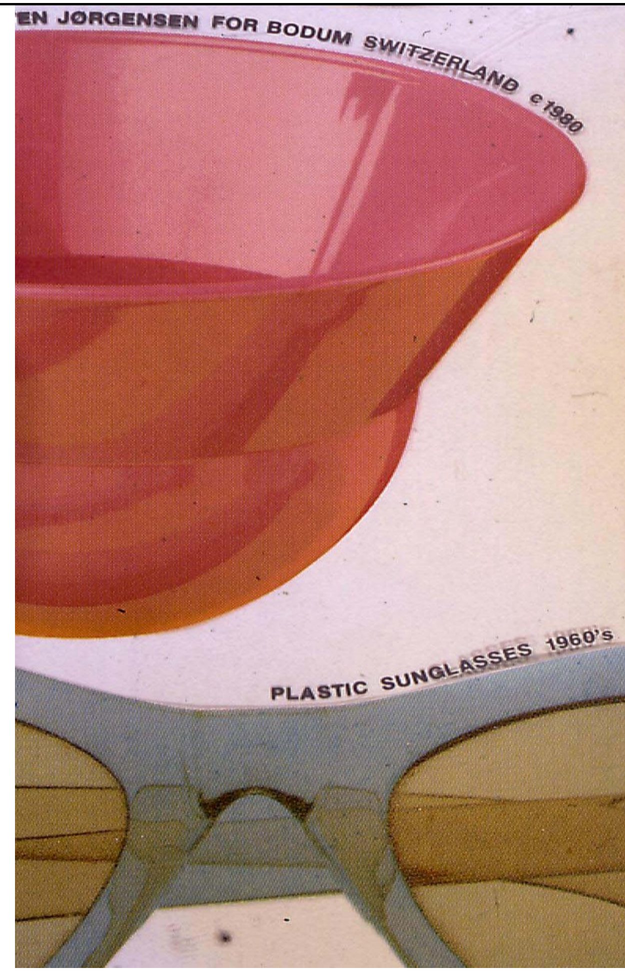
transparent as sheet	**opaque/ cloudy**	**filled**
cellulose nitrate	bakelite	bakelite
cellulose acetate	formaldehyde plastics	
PVC	polyethylene	
PMMA	polypropylene	
polystyrene		
polyester		
polycarbonate		

Optical clarity helps identification polyethylene- polystyrene- polyester



Deterioration of PVC polymer

PVC poster

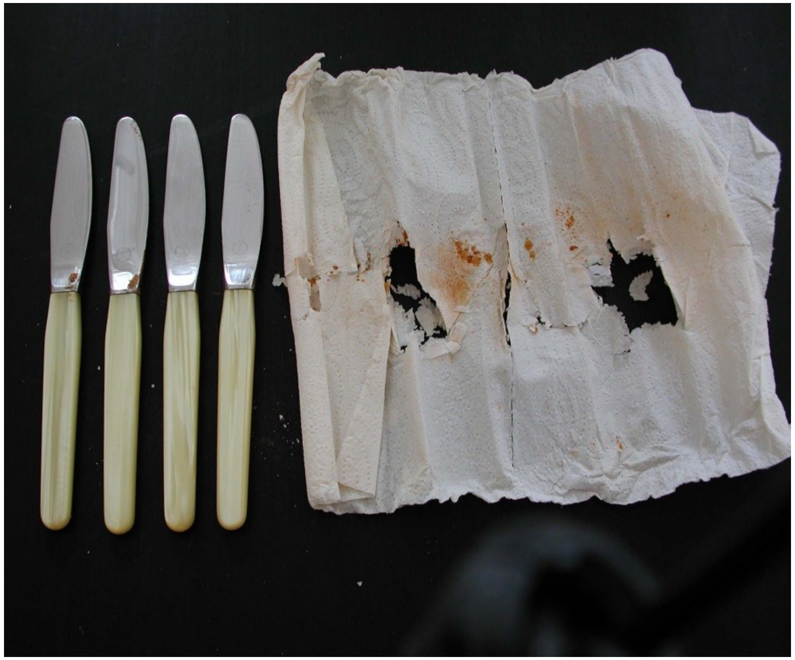


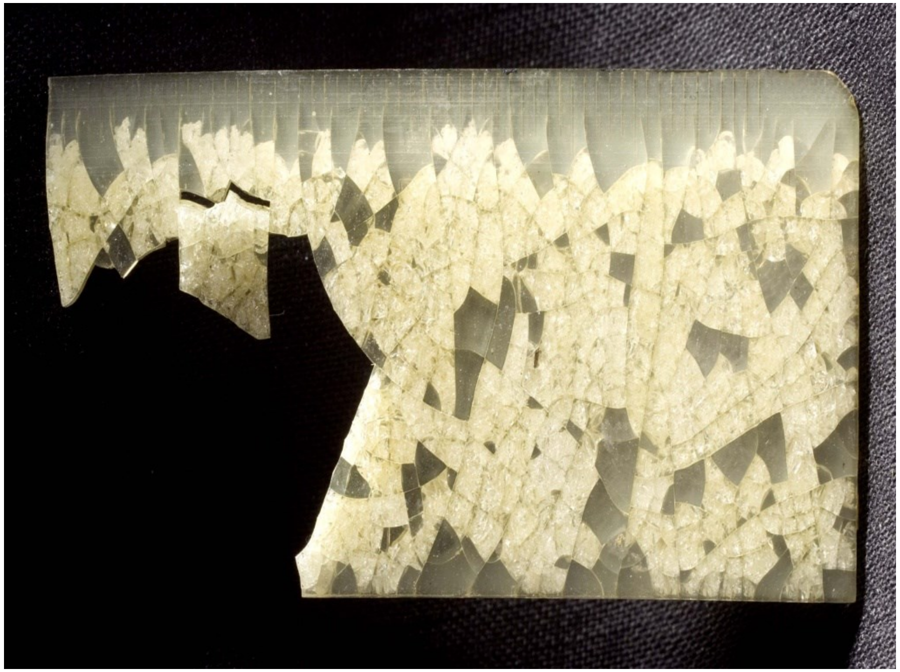
yellowed section

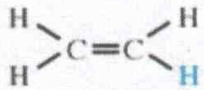
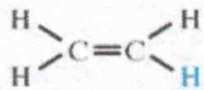
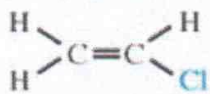
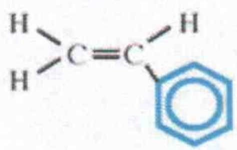
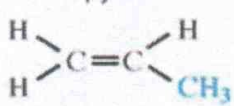
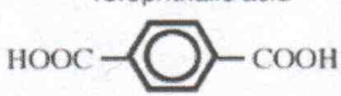
Degradation symptoms as identification tool

degrading ***cellulose acetate*** produces acetic acid which has burned tissue

degrading *cellulose nitrate* crazes from inside





Polymer	Monomer	Properties of Polymer	Uses of Polymer
Polyethylene (LDPE) 4 LDPE	Ethylene 	Opaque, soft, flexible, impermeable to water vapor, unreactive toward acids and bases, absorbs oils and softens, melts at 100°–120°C, does not become brittle until −100°C, oxidizes on exposure to sunlight, subject to cracking if stressed in presence of many polar compounds	Plastic bags, toys, electrical insulation
Polyethylene (HDPE) 2 HDPE	Ethylene 	Similar to LDPE, more opaque, denser, mechanically tougher, more crystalline and rigid	Milk and water jugs, gasoline tanks, cups
Polyvinyl chloride 3 V	Vinyl chloride 	Rigid, thermoplastic, impervious to oils and most organic materials, transparent, high impact strength	Plumbing pipe, garden hoses, "bubble" package wrap
Polystyrene 6 PS	Styrene 	Glassy, sparkling clarity, rigid, brittle, easily fabricated, upper temperature use 90°C, soluble in many organic materials	Styrofoam insulation, inexpensive furniture, drinking glasses
Polypropylene 5 PP	Propylene 	Opaque, high melting point (160°–170°C), high tensile strength and rigidity, lowest density commercial plastic, impermeable to liquids and gases, smooth surface with high luster	Battery cases, indoor-outdoor carpeting, bottle caps, auto trin
Polyethylene terephthalate 1 PETE	Ethylene glycol $HOCH_2CH_2OH$ Terephthalic acid 	Transparent, high impact strength, impervious to acid and atmospheric gases, not subject to stretching, most costly of the six	Clothing, soft-drink bottles, audio- and videotapes, film backing

Identification of plastics-simple tests

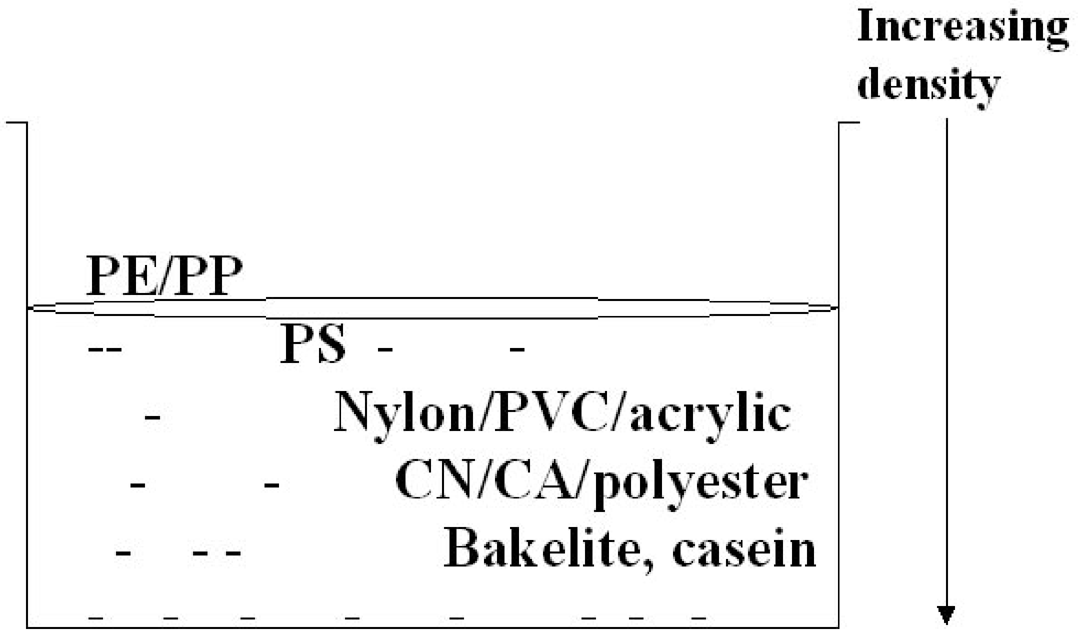
- **Hardness-thumbnail test. Marked or not?**
- Heat –melting in boiling water/smell/pH of vapour
- **Density test-look at floatation (means lower density) of plastics in water (density = 1), saturated sodium chloride (1.2), magnesium chloride (1.34), calcium chloride (1.45)**
- Beilstein test to identify chlorine eg PVC
- **Diphenylamine spot test for cellulose nitrate (CN) –drop solution onto plastic, becomes dark blue if CN present**

Plastics that can be marked with a thumbnail

- polyethylene (PE)
- polypropylene (PP)
- plasticised PVC
- polyurethane

Density/specific gravity-measured by flotation of plastics in water

Density Table	
Substance	**Density (g/mL)**
Water	1.00
(1) PETE	1.38-1.39
(2) HDPE	0.95-0.96
(3) PVC	1.16-1.35
(4) LDPE	0.92-0.94
(5) PP	0.90-0.91
(6) PS	1.05-1.07



Odours from heated plastics

- Casein
- Cellulose acetate
- Cellulose nitrate
- Melamine or urea formaldehyde
- Nylon
- PMMA
- Polyethylene
- Polyester
- Polystyrene
- Polyurethane foam

- burnt milk
- vinegar
- camphor (moth balls)
- fish
- burnt hair
- sweet
- wax, paraffin
- raspberry jam
- natural gas
- acrid, stinging

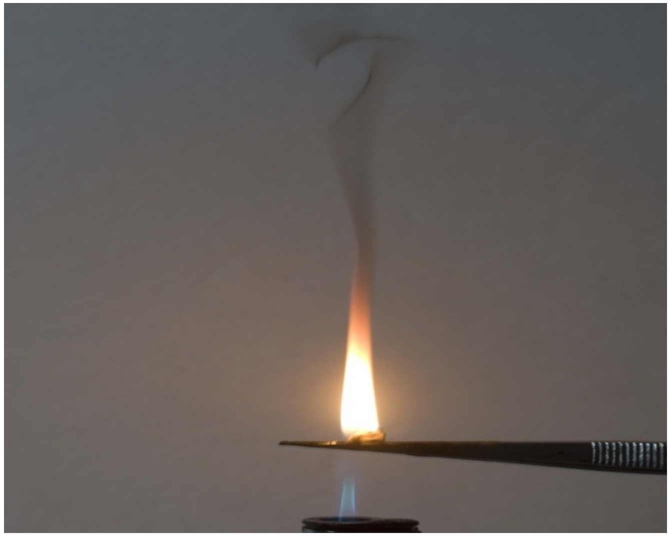
Burning tests as identification tool

cellulose nitrate sparks

cellulose acetate

polyethylene drips

polystyrene is sooty



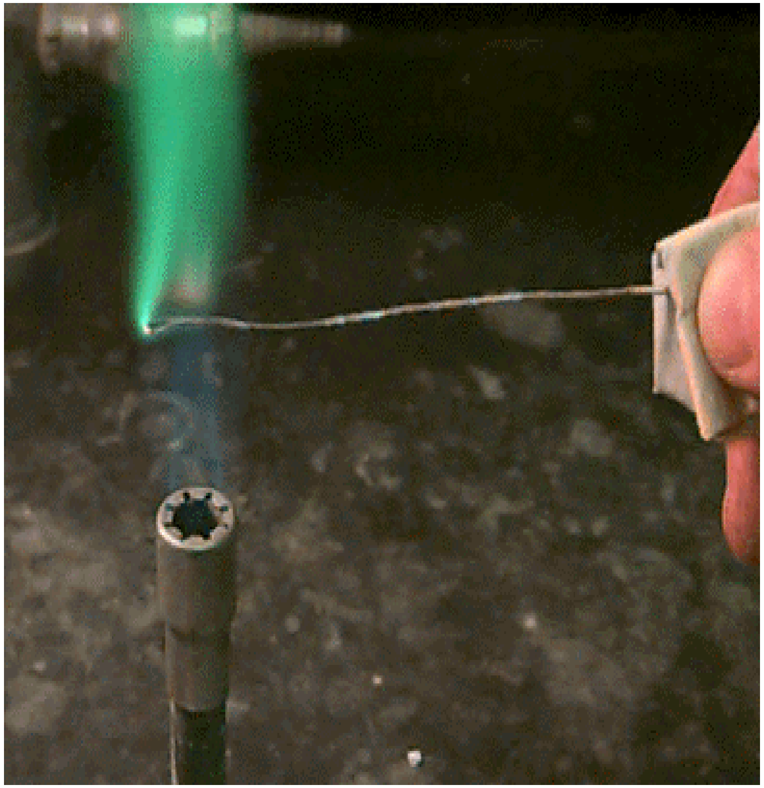
pH of vapours from heated plastics

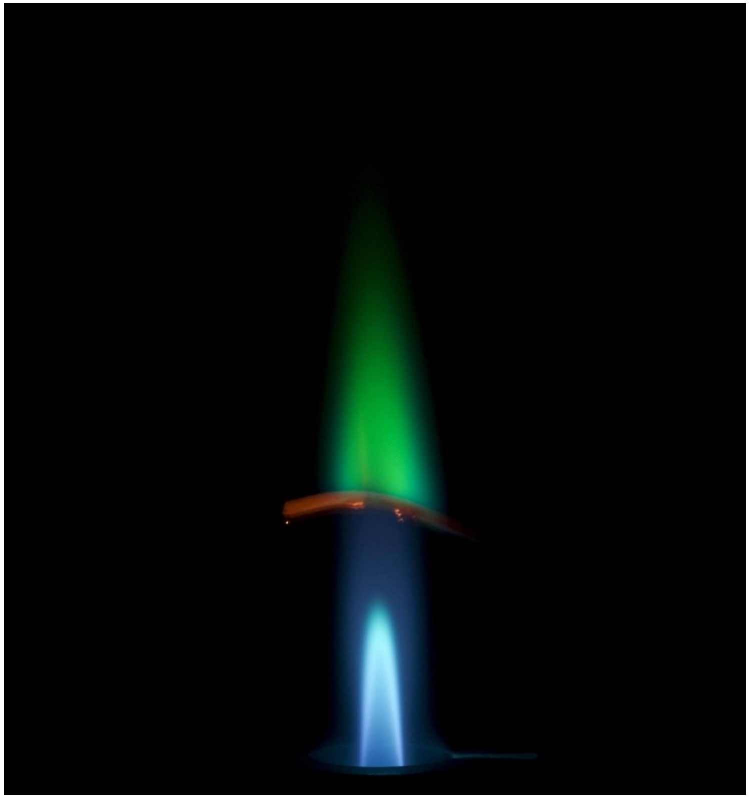
Acid (pH 1-4)	Neutral (pH 5-7)	Alkaline (pH 8+)
cellulose acetate	polyethylene	nylon
cellulose nitrate	polystyrene	phenol-formaldehyde
polyester	PMMA	Urea/thiourea/ melamine-formaldehyde
polyurethane	polycarbonate	
PVC	silicones	
	epoxies	

Beilstein test to detect PVC

$Cu (s) + O_2 (g) \rightarrow CuO (s)$

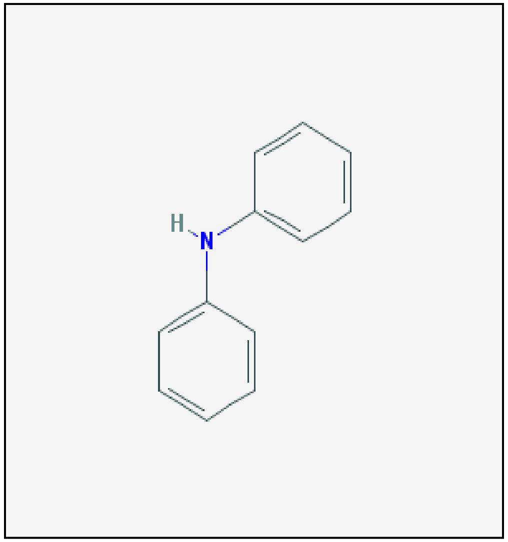
$CuO + 2\ R\text{-}Cl \rightarrow CuCl_2 + 2\ R\text{-}O\text{-}?$

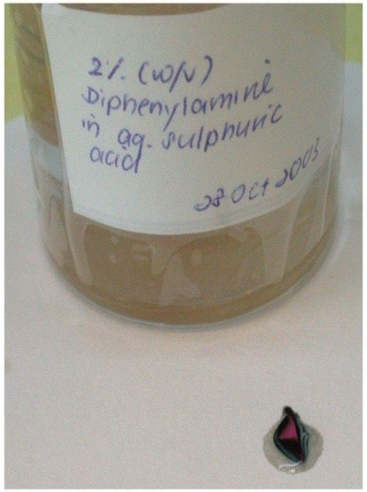




diphenylamine test for cellulose nitrate

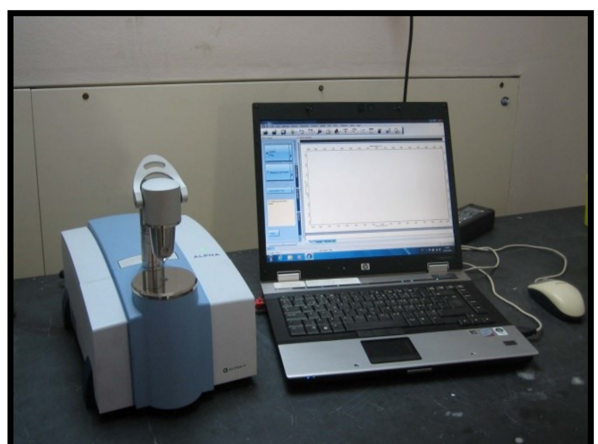
Diphenylamine in conc. sulphuric acid detects the presence of the nitrate ion. Nitrogen oxide ions are formed from cellulose nitrate by reacting with sulphuric acid. Colourless diphenylamine is oxidized, giving a **blue** coloration.





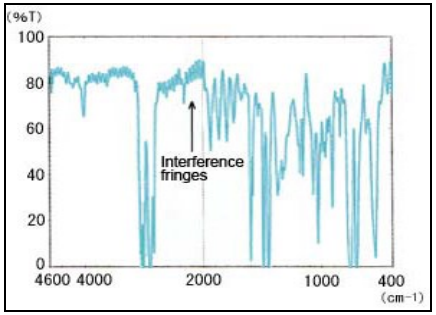
Principles of FTIR spectroscopy

- radiation in the mid infrared region (4000-400cm^{-1}) causes especially covalent bonds to vibrate at specific frequencies or wavelengths
- detector determines energy absorbed at each wavelength
- position, shape and intensity of peaks in the resulting spectrum reflect molecular structure



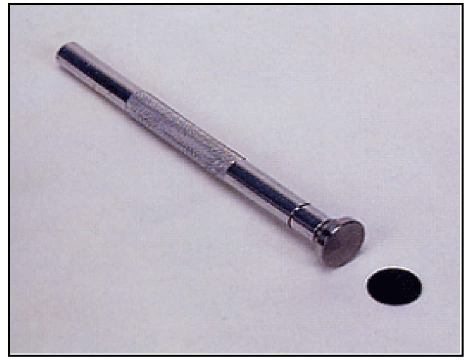
Presenting samples to FTIR spectrometer

- transmission-unprepared plastic

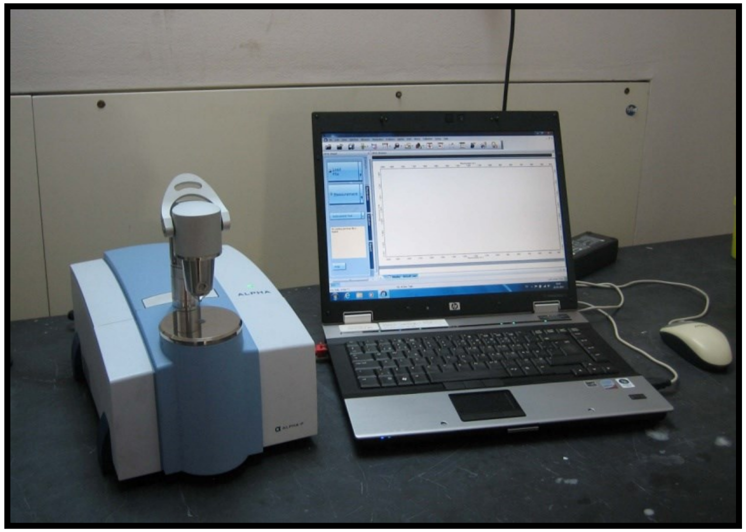


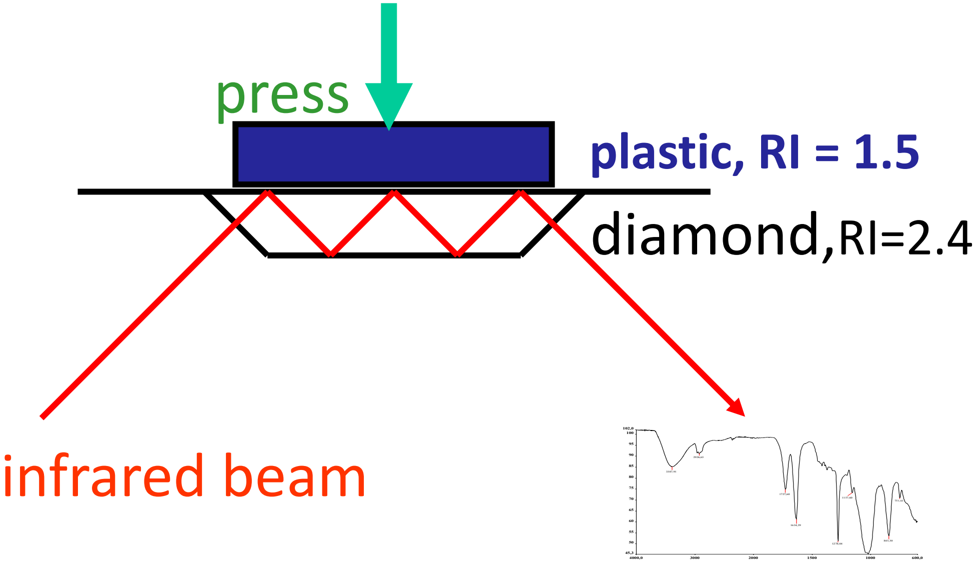
- transmission – dissolved or crushed into KBr pellet

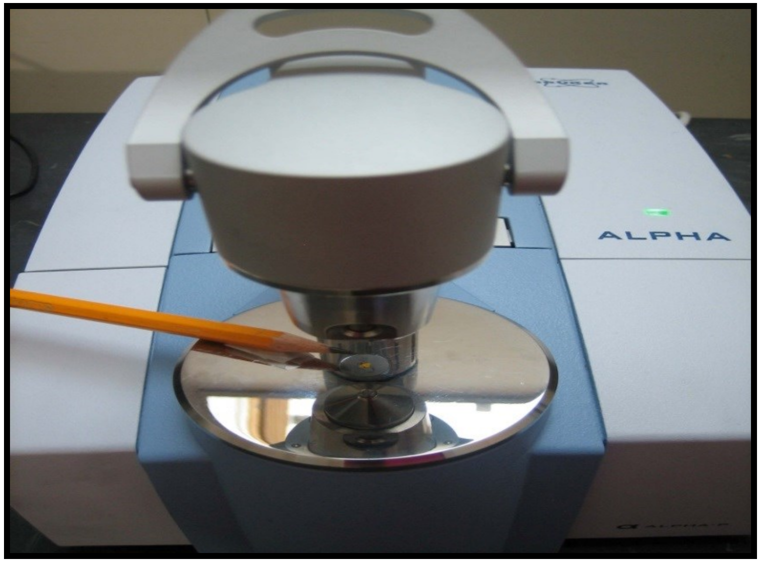
- reflectance – surface abraded with SiC paper. IR beam bounces off surface



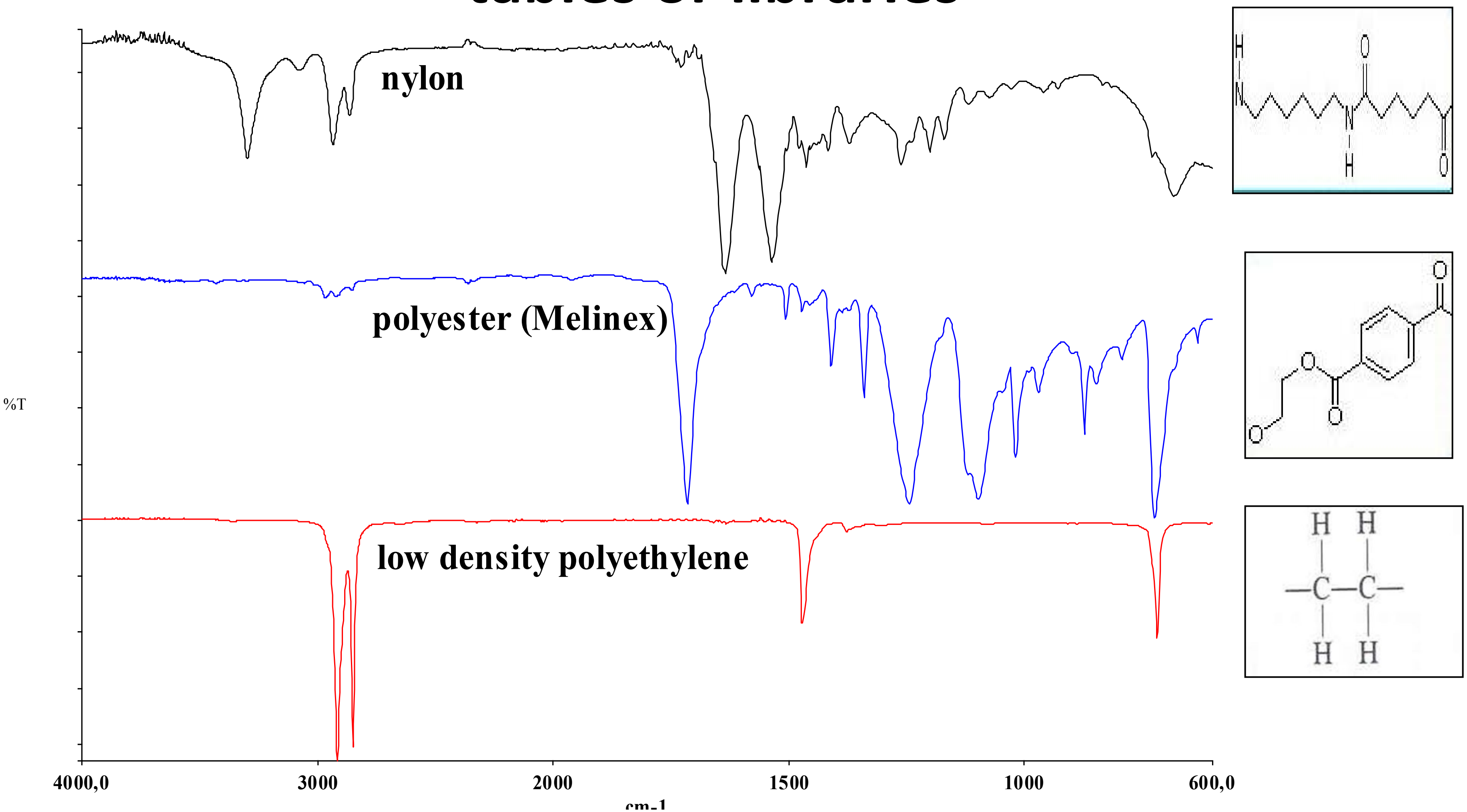
Attenuated Total Reflection (ATR) – FTIR spectroscopy

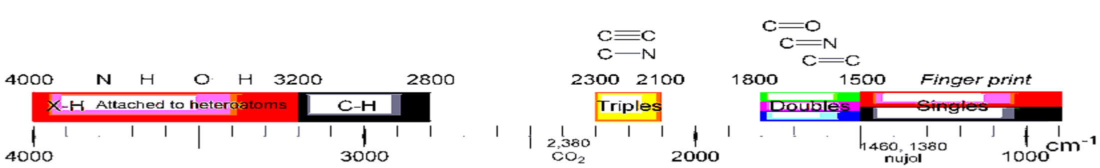




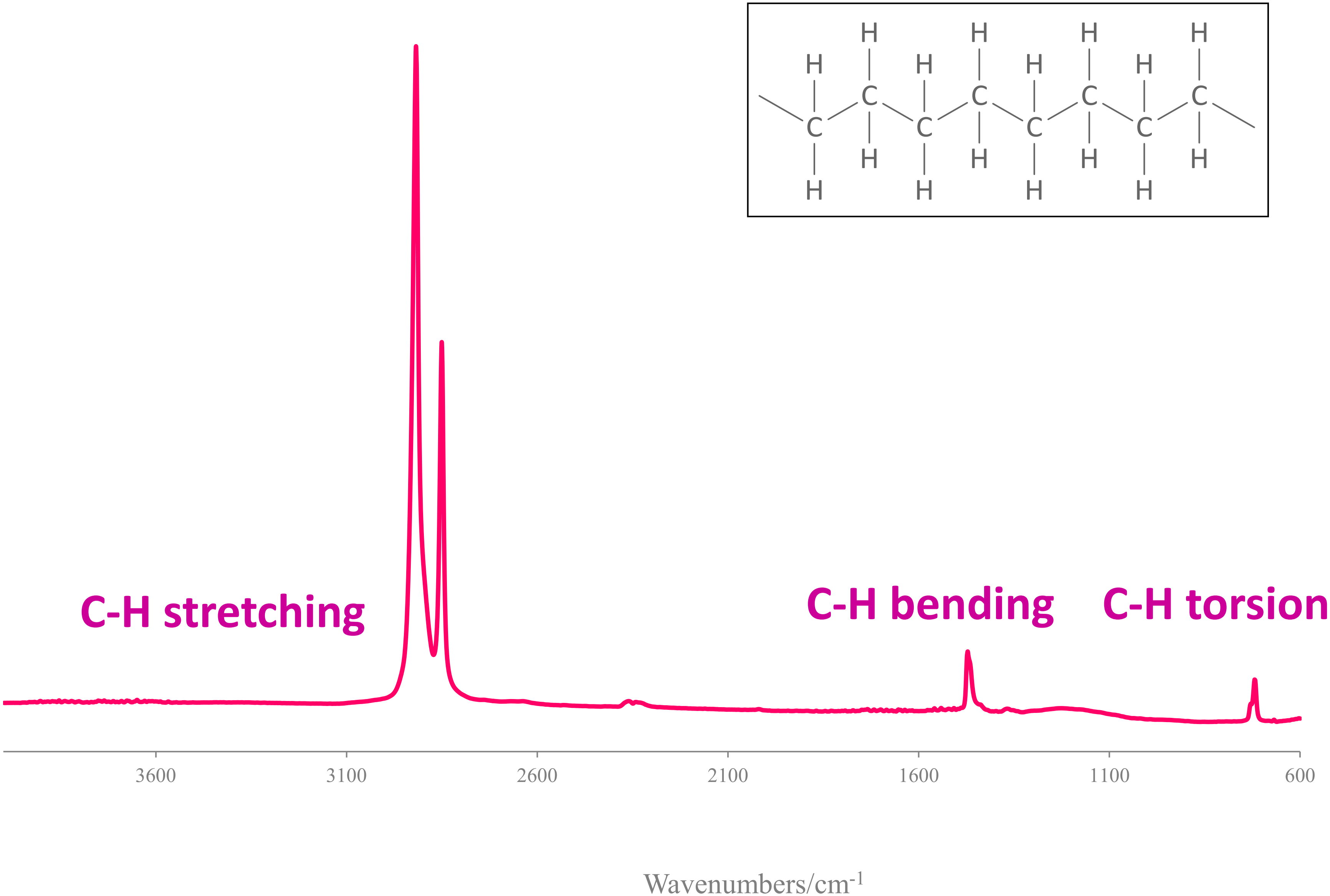


Interpreting ATR-FTIR spectra-assignment tables or libraries

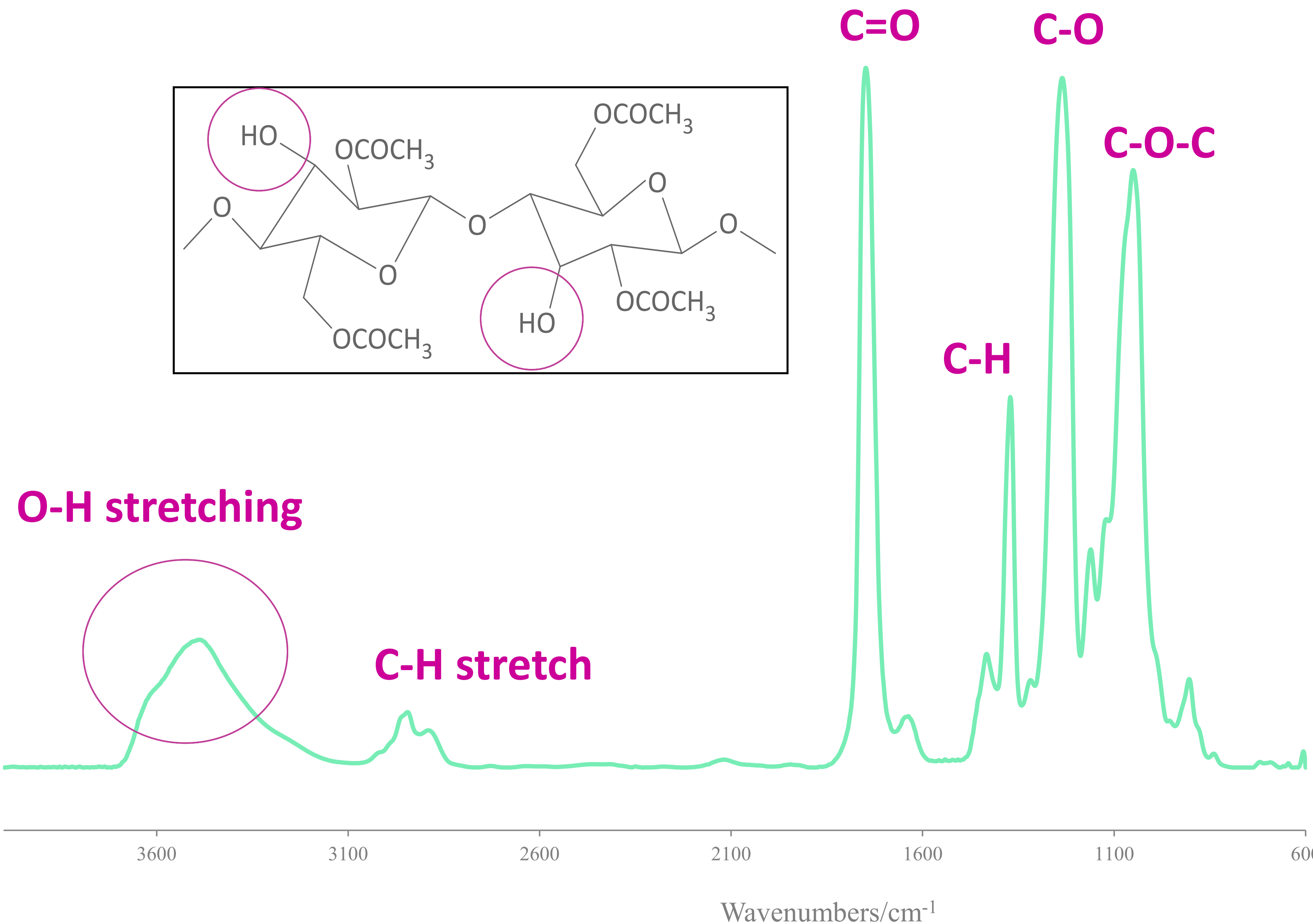




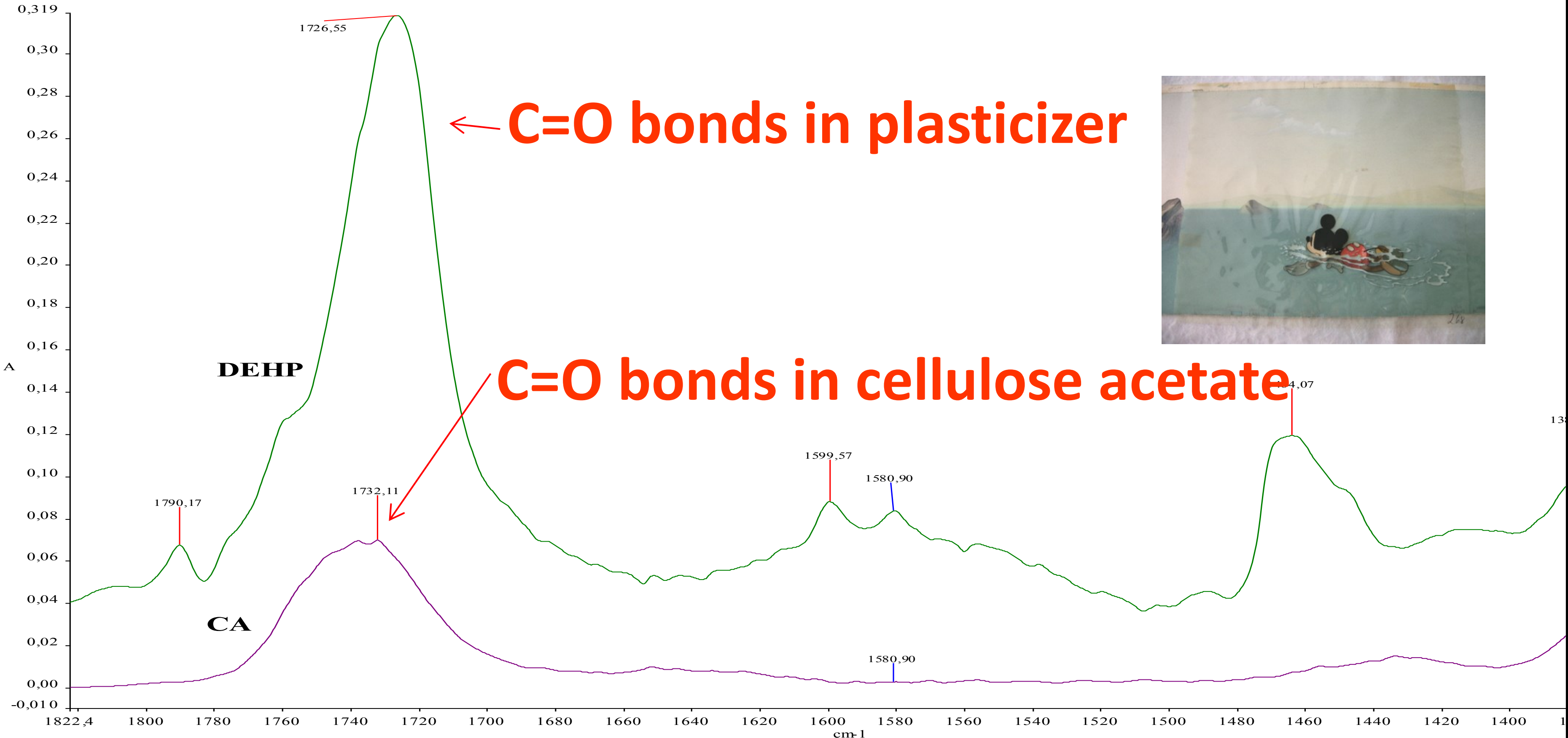
FTIR spectrum of polyethylene in absorbance units



FTIR spectrum of cellulose acetate in **absorbance** units



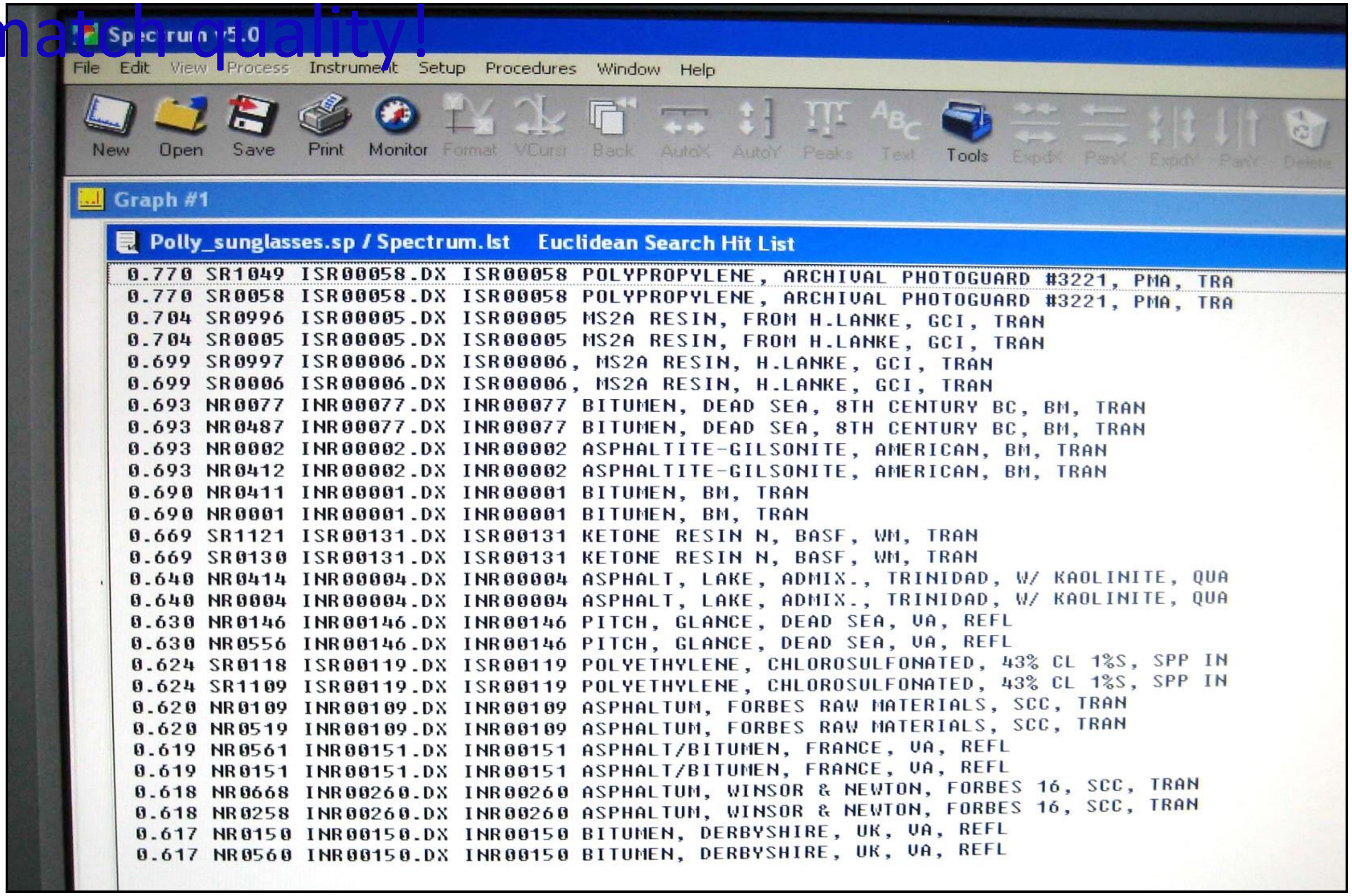
Warning-FTIR spectra reflect ALL IR active materials in sample and may overlap!



Sue Mossman's paper 'Testing treatments to slow down the degradation of cellulose acetate' in Plastics-Looking at the Future and Learning from the past, V&A, 2007

Electronic spectroscopy library eg Infrared Users Group (IRUG)

warning- different accessories will influence match quality!



Conclusions

polymers in plastics can be identified using simple, destructive tests – but not definitively

FTIR spectroscopy can identify both polymers and additives and be either non- or semi-destructive

identification tools include absorbance tables, spectral databases or (optimal) own references

FTIR is less sensitive to low levels of degradation and should be combined with other instrumental techniques