

Progetto Alfa-pinene



Consiglio Nazionale delle Ricerche



NIR & WOOD – SOUNDS GOOD! #2

Pollutants detection on wood waste using FT-IR-ATR

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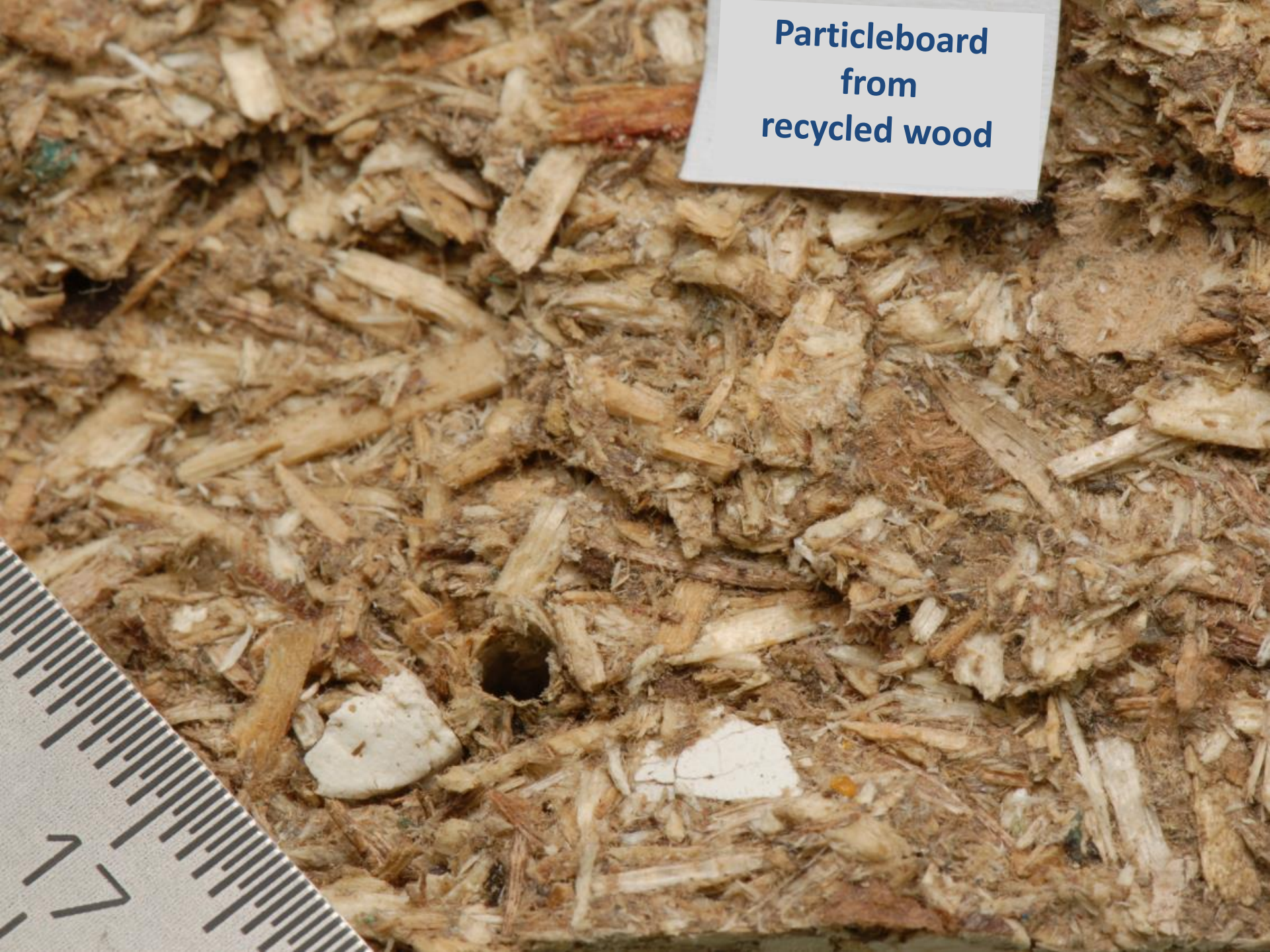
Italian wood recycling system



**Particleboard
from
virgin wood**



Particleboard
from
recycled wood



Why?

- To sort the polluted from non-polluted wood;
- To discard from the recycling cycle wooden materials contaminated with heavy metals;
- To avoid the continuous re-cycling of hazardous pollutants in particleboards (or particleboard production combusted dusts);
- To exploit the non contaminated wood as biomass;
- To test an analysis method cheaper and faster than the ICP-OES (and other spectrometers) or traditional wet chemistry.

Sampling: brand new wood products: solid wood, panels...



Sampling: polluted and non polluted wood from recycling facilities







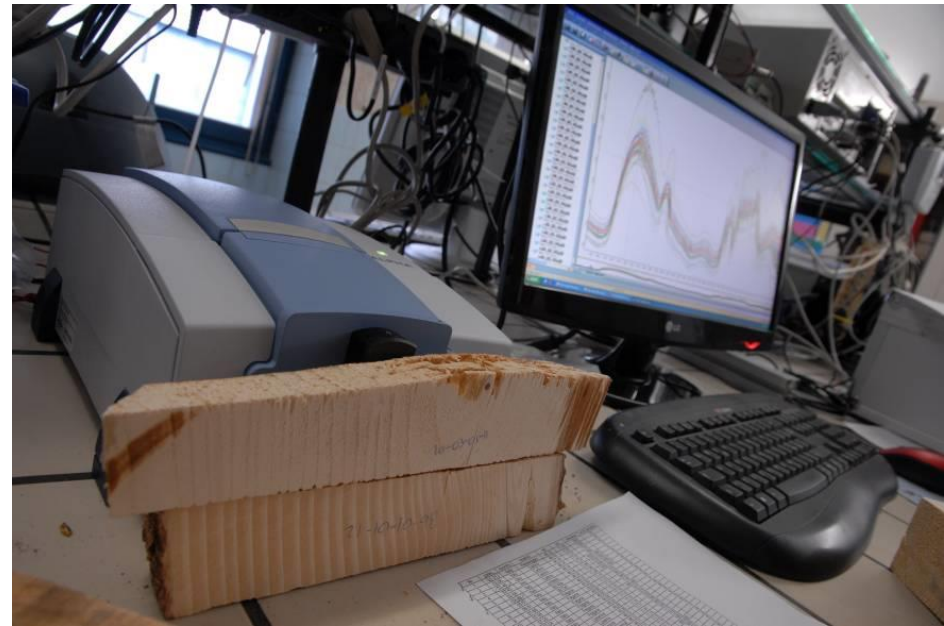
Sampling 4: common varnishes, coatings, glues, and preservatives

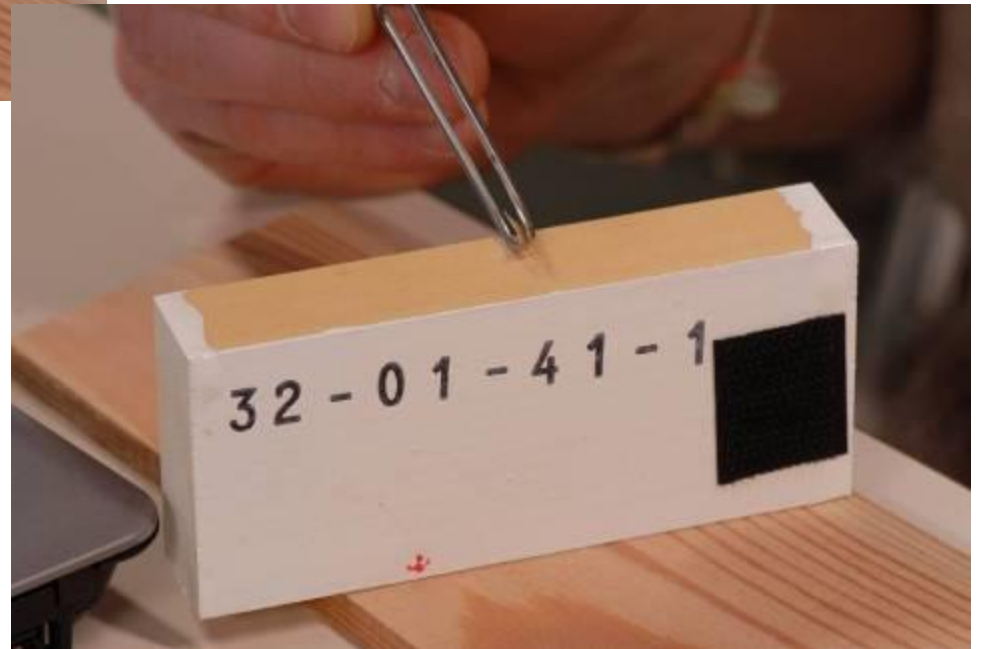
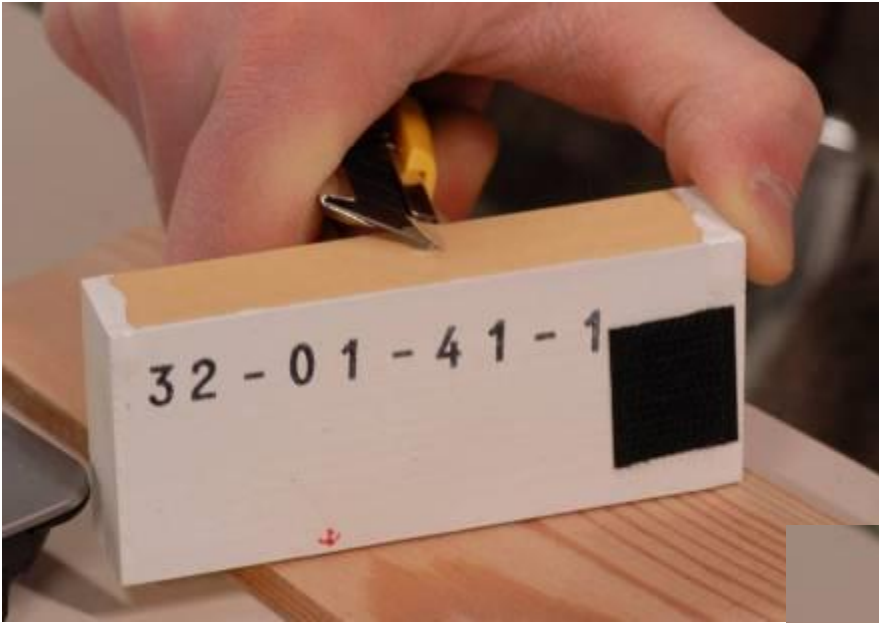


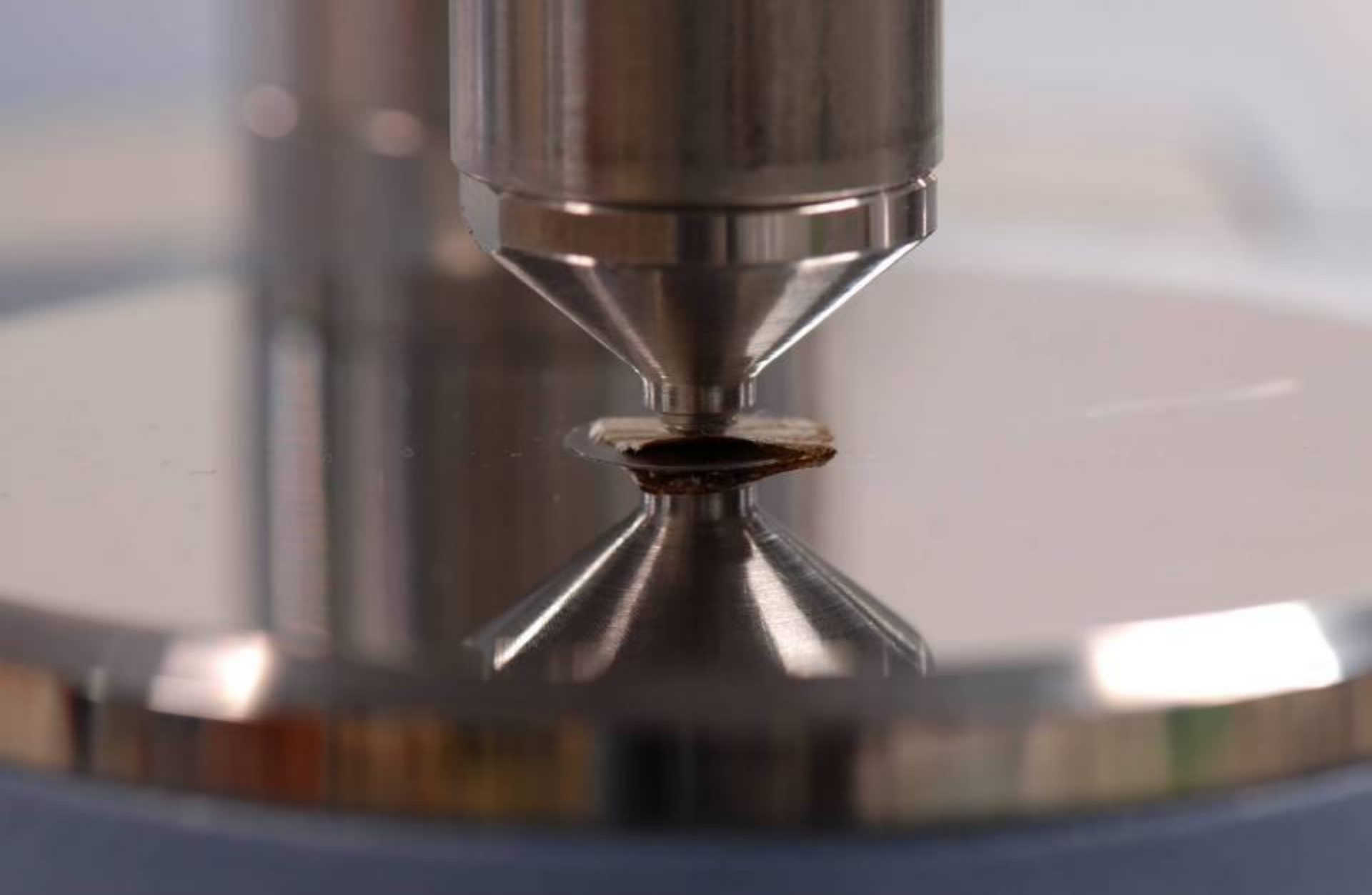
FT-IR-ATR measurements

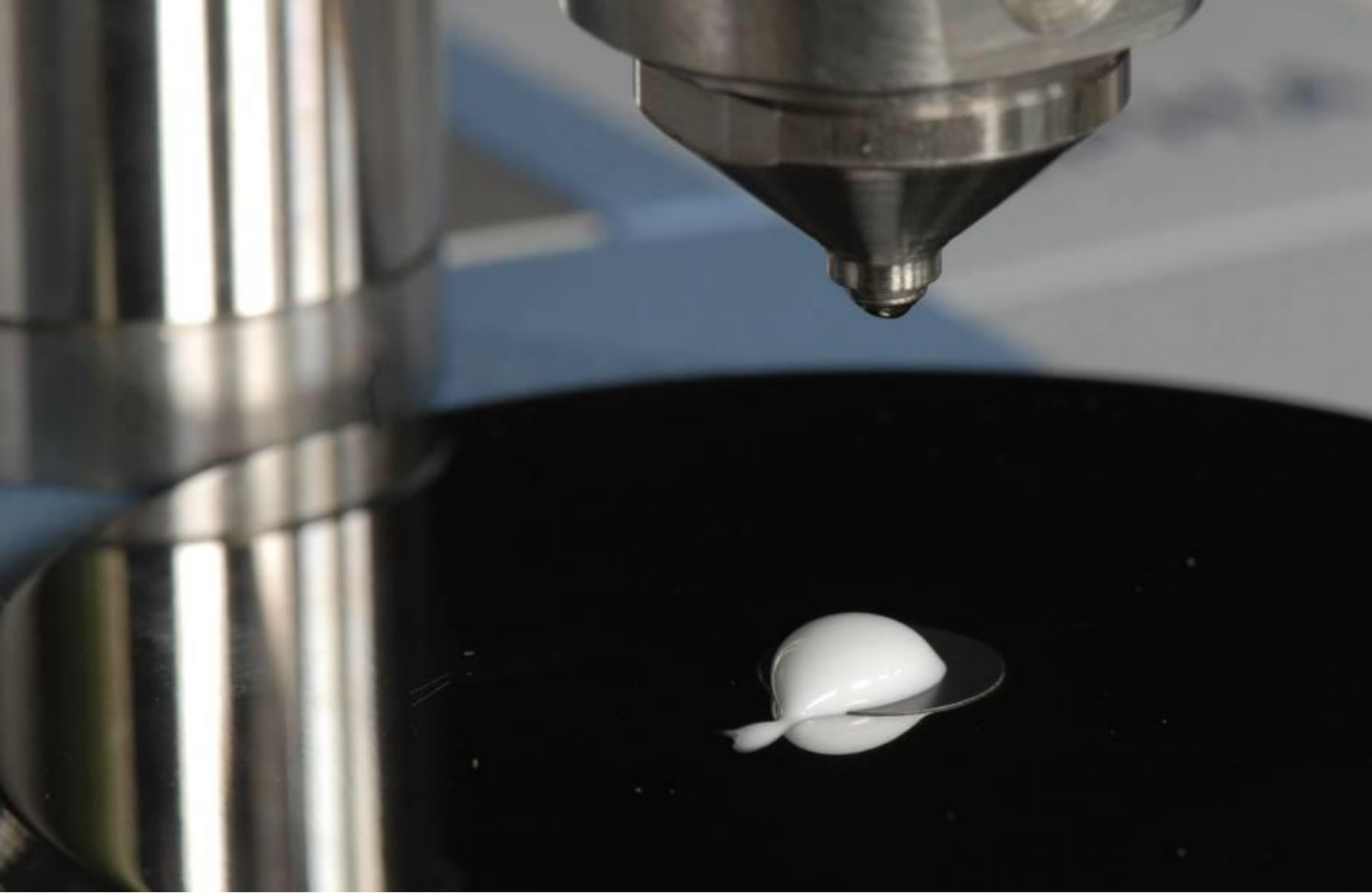
- Alpha by Bruker Optics GmbH with diamond ATR crystal (mainly) or non contact accessory.
- the spectral range: 4000 cm^{-1} - 600 cm^{-1}
- the spectral resolution: 4 cm^{-1}
- each spectrum: average of 64 scans
- 3 measurements per specimen

Non contact accessory

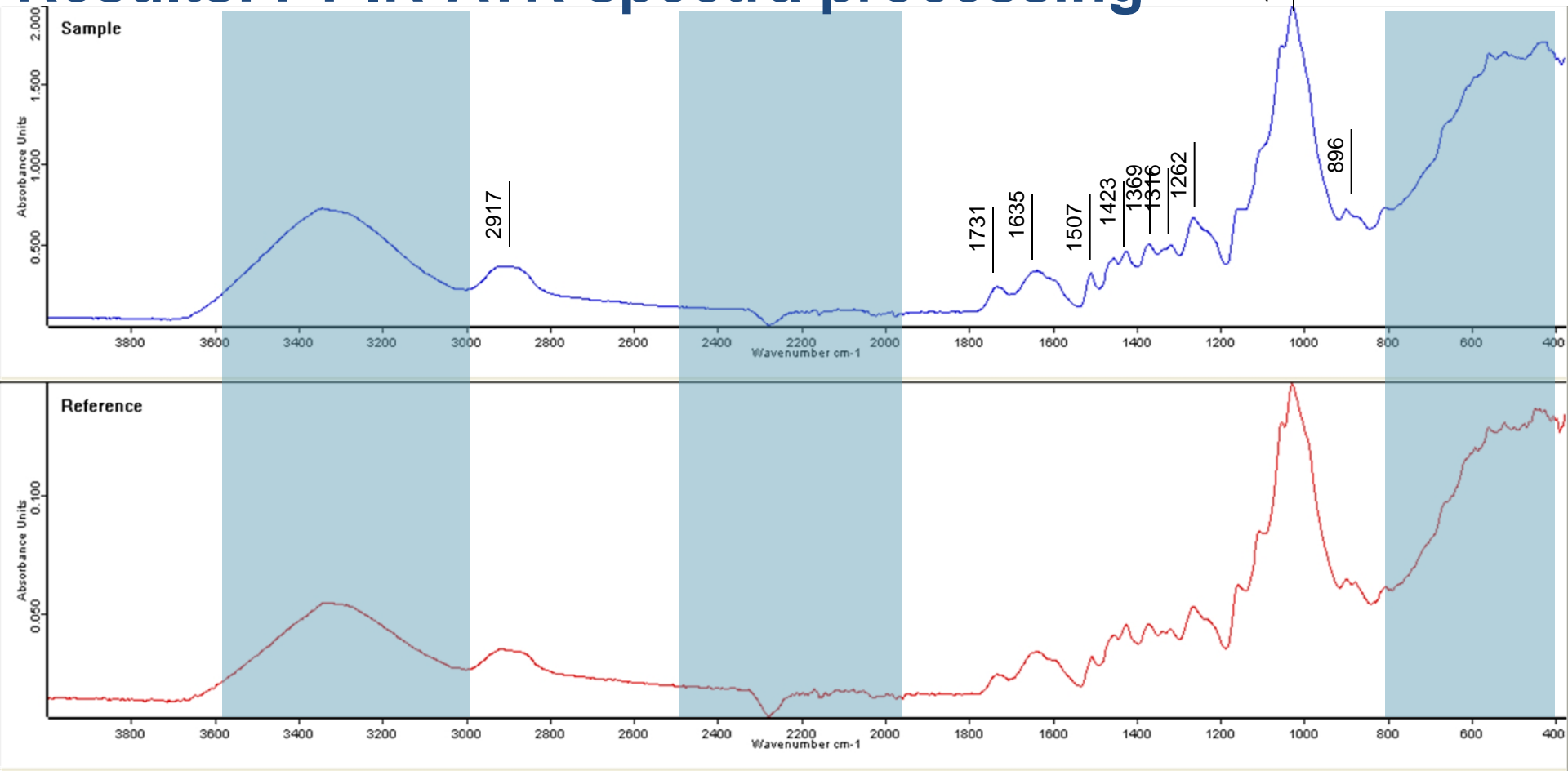


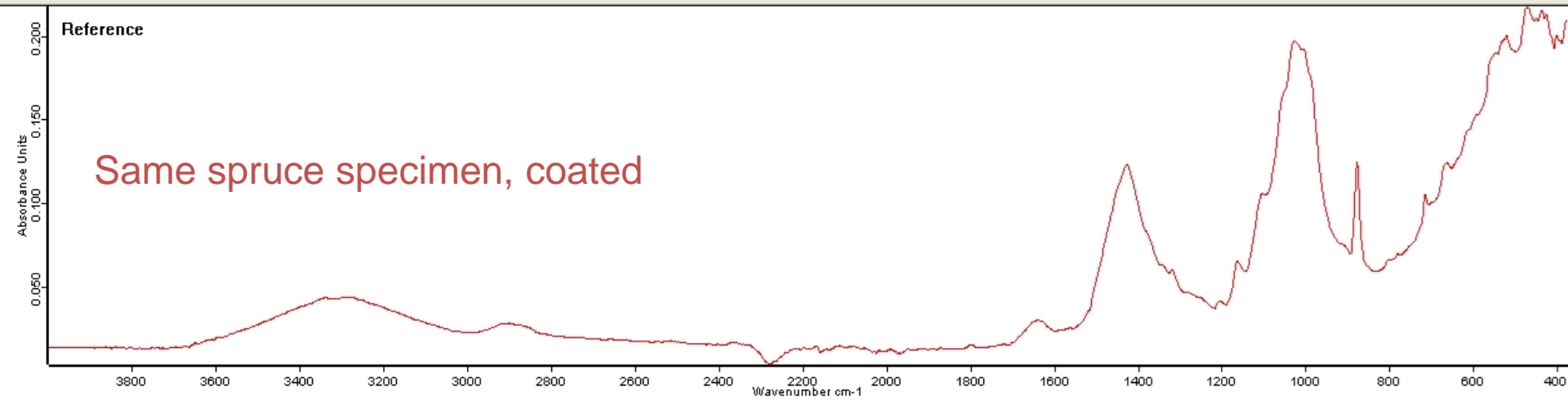
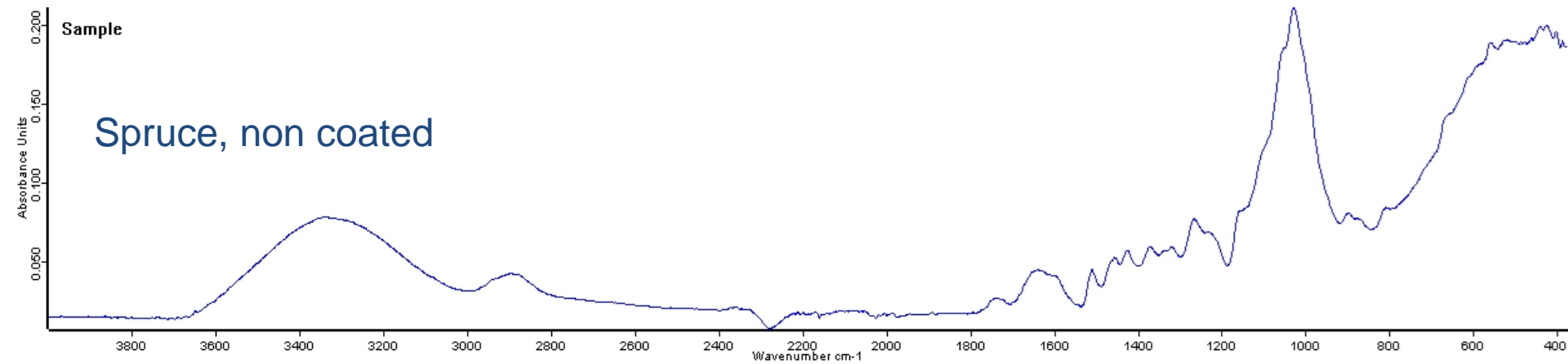






Results: FT-IR-ATR spectra processing





**NOT
OK**

Correlation: 91.03 %

Threshold: 98.00 %

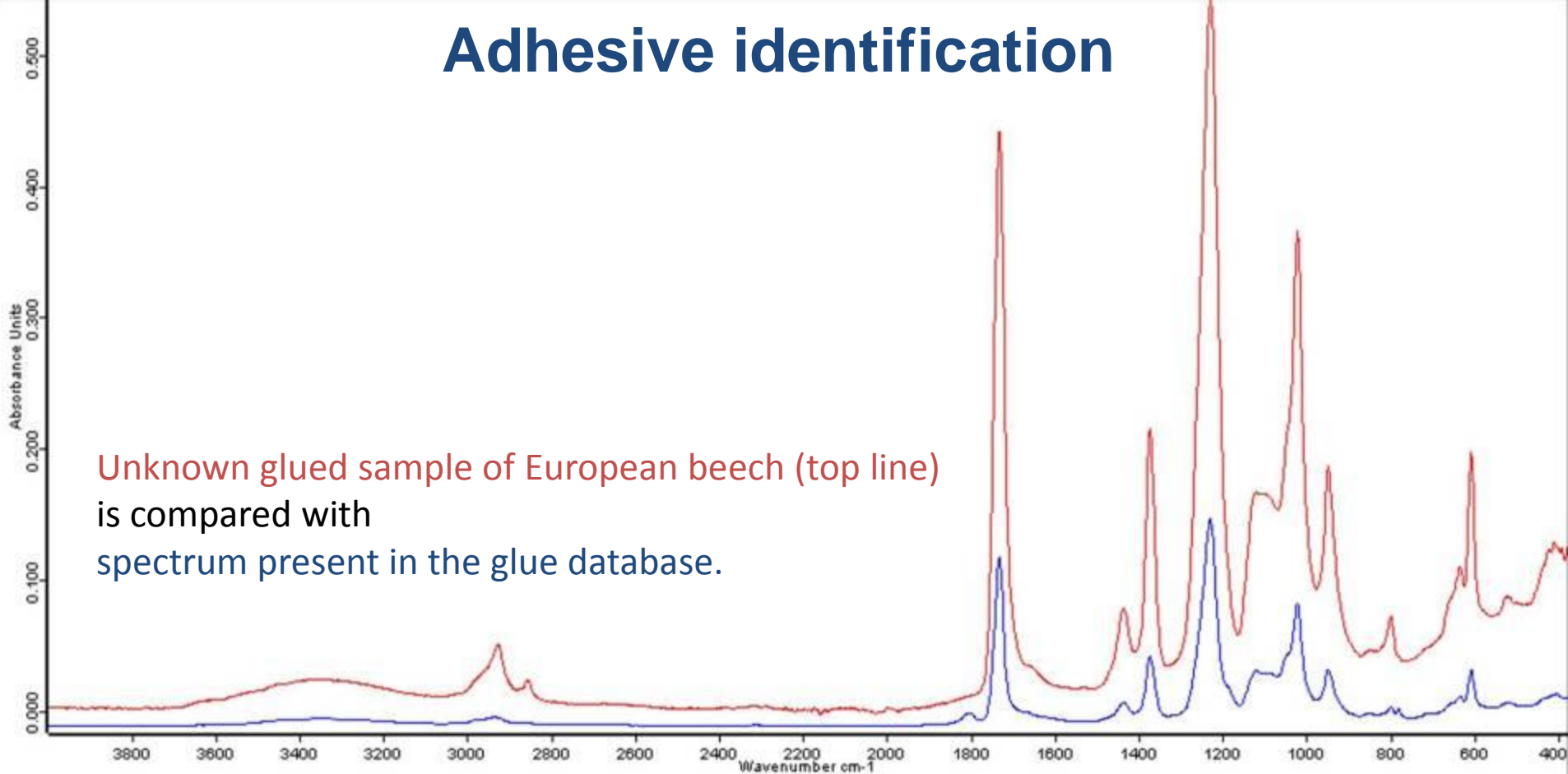
Sample: \\valsatn\Area Tematica 1\z_biqueen\MISURE FT-ATR\misure MIR maggio 2011\36 3 mm under surface NV.0

Reference: \\valsatn\Area Tematica 1\z_biqueen\MISURE FT-ATR\misure MIR maggio 2011\36 surface NV.0

Method file: C:\Programmi\OPUS_65\Methods\QC noCO2 noH2O noDi.qcm (2011/08/10 11:04:58 (GMT+2))

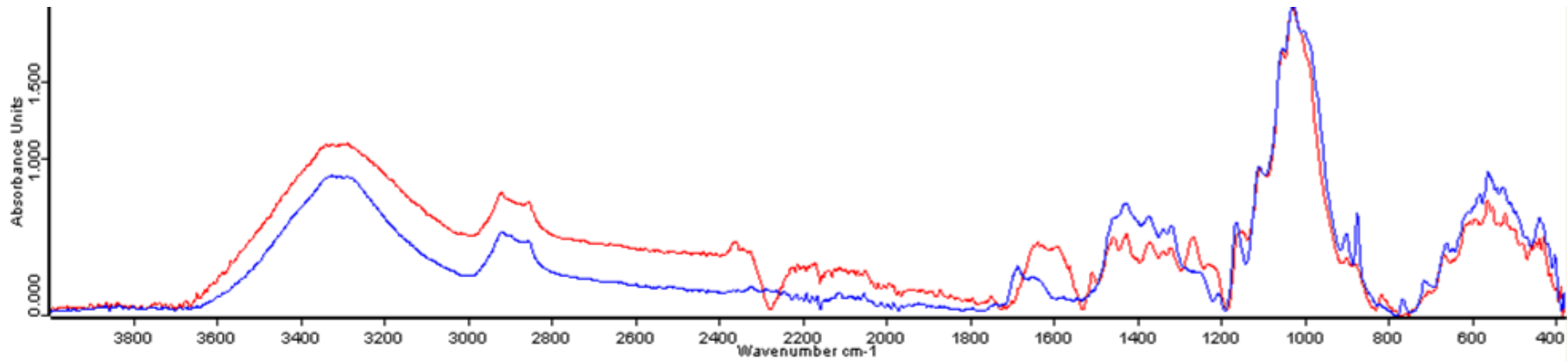
Adhesive identification

Unknown glued sample of European beech (top line) is compared with spectrum present in the glue database.



24 Hits	Hit Quality	Compound Name	Entry No.	Molecular formula	Molecular weight	CAS number
<input checked="" type="checkbox"/>	1.	711	PVAC2 24h	11		
<input type="checkbox"/>	2.	560	PVAC1	9		
<input type="checkbox"/>	3.	480	POLY(VINYL ACETATE)	340	C4H6O2	9003-20-7
<input type="checkbox"/>	4.	480	POLY(VINYL ACETATE)	340	C4H6O2	9003-20-7
<input type="checkbox"/>	5.	410	terracol plus protect fresca	25		
<input type="checkbox"/>	6.	340	VINYL ACETATE	124	C4H6O2	86.09 108-05-4
<input type="checkbox"/>	7.	340	VINYL ACETATE	124	C4H6O2	86.09 108-05-4
<input type="checkbox"/>	8.	326	BENZYLACETATE	13	C9H10O2	150.18 140-11-4
<input type="checkbox"/>	9.	326	MOWIOL 04	331		
<input type="checkbox"/>	10.	326	BENZYLACETATE	13	C9H10O2	150.18 140-11-4

Panel identification

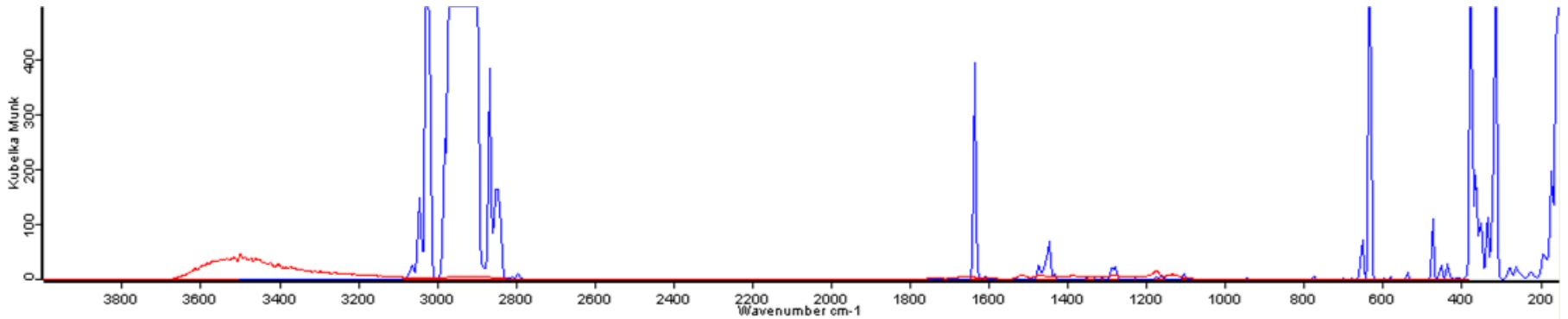


30 Hits	Hit Quality	Compound N...	Entry No.	Molecular formula	Molecular weight	CAS number
<input checked="" type="checkbox"/>	1.	468	glue R397 dry	42		
<input type="checkbox"/>	2.	462	[1a2]Uw2	52		
<input type="checkbox"/>	3.	447	[1a2]Um3	48		
<input type="checkbox"/>	4.	440	[1a10]Um3	23		
<input type="checkbox"/>	5.	440	23retro	11		
<input type="checkbox"/>	6.	435	[1a2]Uh1	46		
<input type="checkbox"/>	7.	435	[1a2]Um3	49		
<input type="checkbox"/>	8.	432	[1a10]Uh1	18		
<input type="checkbox"/>	9.	426	[1a10]Um3	24		
<input type="checkbox"/>	10.	424	[1a2]Um3	50		
...

Exit Hide Query Spectrum Help Collection of known adhesives
CNR IVALSÀ

Plywood panel (red) is correctly recognized for the presence of adhesive (blue)

Panel identification

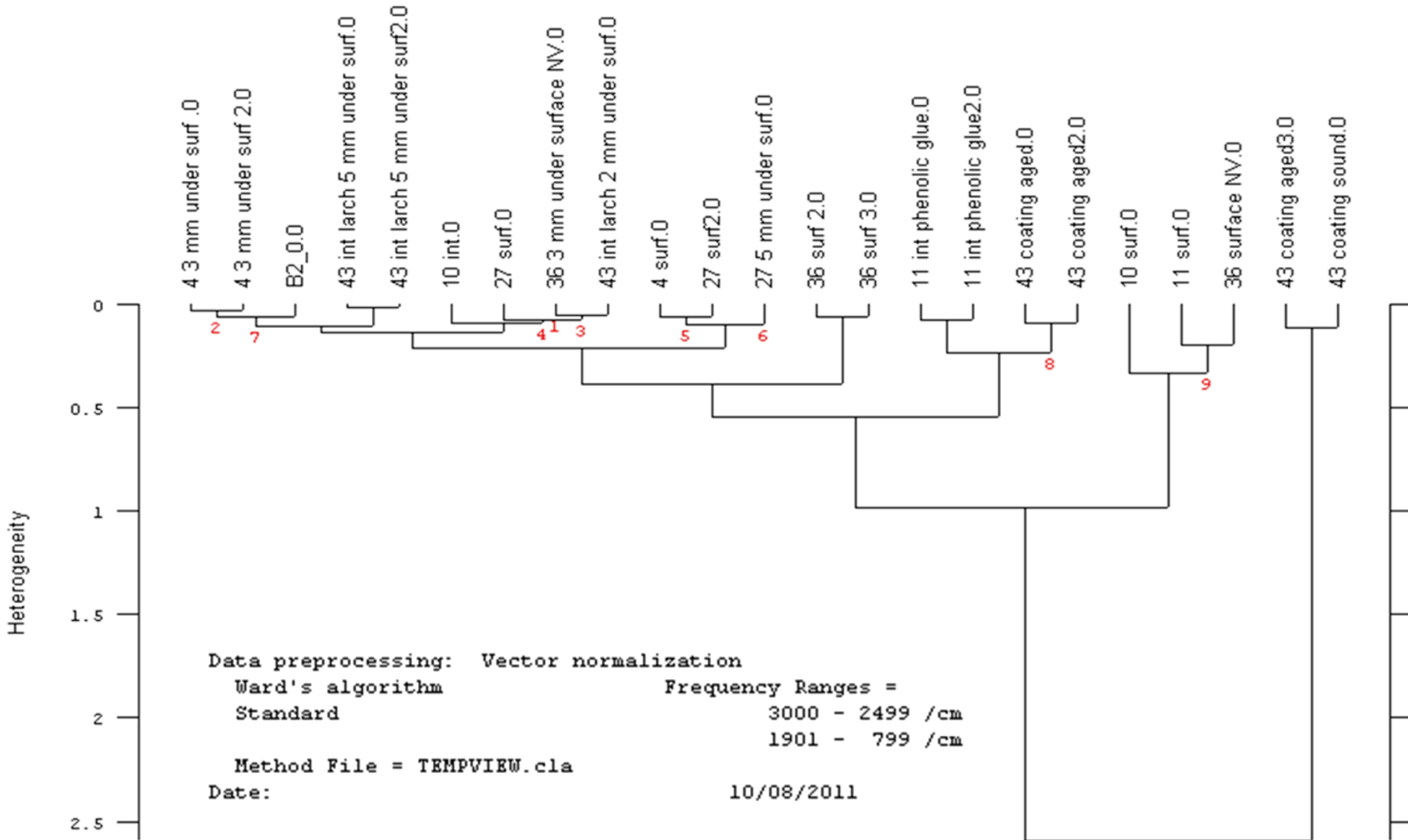


17 Hits	Hit Quality	Compound Name	Entry No.	Molecular formula	Molecular weight	CAS number
<input checked="" type="checkbox"/>	161	Codeine	67	C ₁₈ H ₂₁ N ₁ O ₃ *H...	317.39	
<input type="checkbox"/>	159	CHLORAMPHENICOL	70	C ₁₁ H ₁₂ Cl ₂ N ₂ O ₅	323.13	
<input type="checkbox"/>	159	CHLORAMPHENICOL	70	C ₁₁ H ₁₂ Cl ₂ N ₂ O ₅	323.13	
<input type="checkbox"/>	144	2-AMINOPHENOL	170	C ₆ H ₇ N ₁ O ₁	109.13	95-55-6
<input type="checkbox"/>	144	2-AMINOPHENOL	170	C ₆ H ₇ N ₁ O ₁	109.13	95-55-6
<input checked="" type="checkbox"/>	133	virgwo 2730 Tartu	1			
<input type="checkbox"/>	133	virgwo 2730 Tartu	1			
<input type="checkbox"/>	128	O-TERPHENYL	244	C ₁₈ H ₁₄	230.31	84-15-1
<input type="checkbox"/>	128	DIBENZOTHIOPHENE	317	C ₁₂ H ₈ S ₁	184.26	132-65-0
<input type="checkbox"/>	128	O-TERPHENYL	244	C ₁₈ H ₁₄	230.31	84-15-1
<input type="checkbox"/>	128	O-TERPHENYL	244	C ₁₈ H ₁₄	230.31	84-15-1

Exit Hide Query Spectrum Help Non contaminated spruce
CNR IV ALSA

Particleboard panel is wrongly recognized as *codeine*. The correct classification is the sixth most probable.

Cluster analysis of polluted and non-polluted wood.



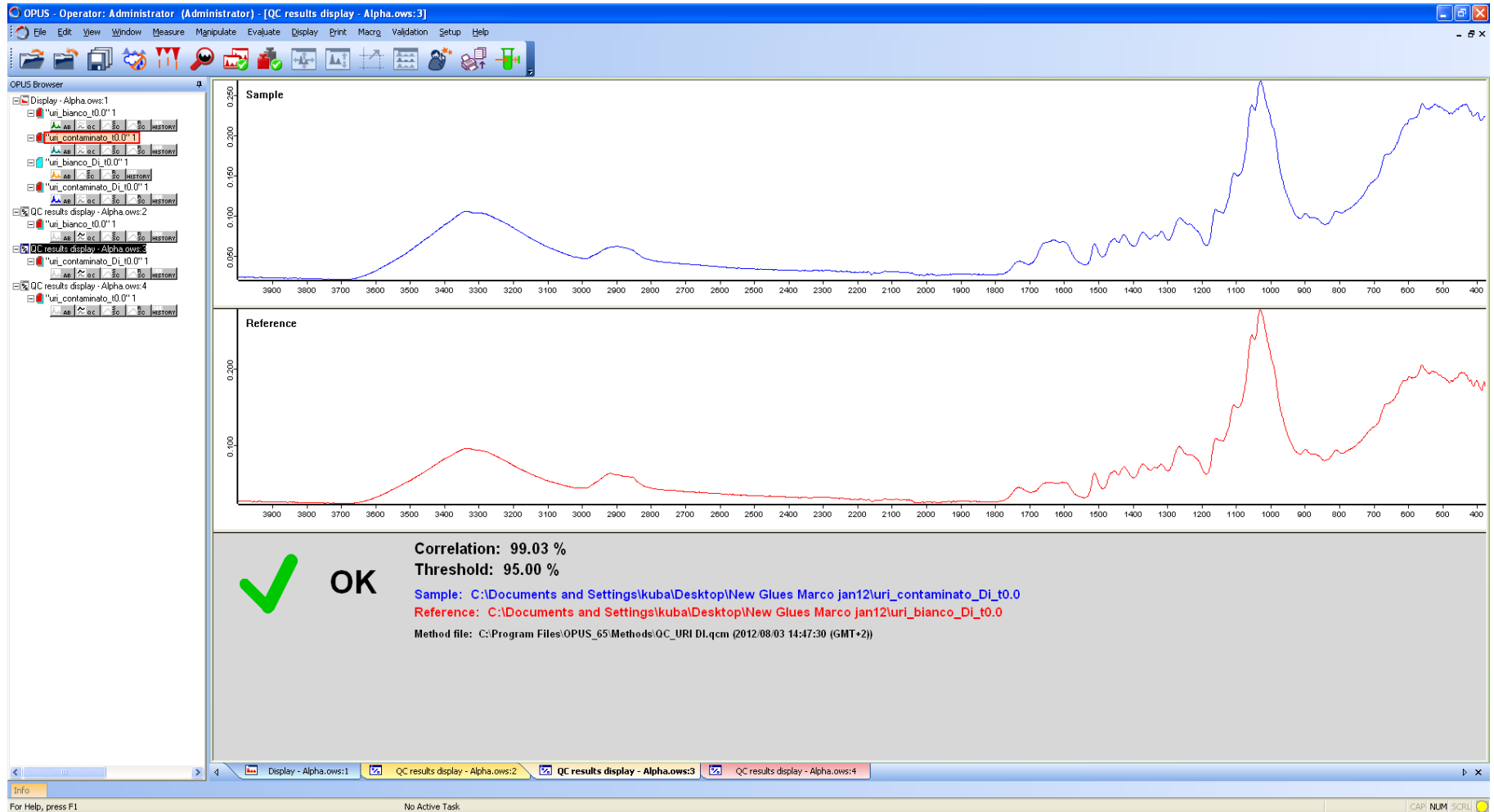
Cluster analysis to sort almost all kind of polluted/non polluted spectra.

Case study 1



Urine on wood

FT-IR, diamond accessory, 64 scans, 4 cm⁻¹ steps, 3 replica measurements



Case study 2

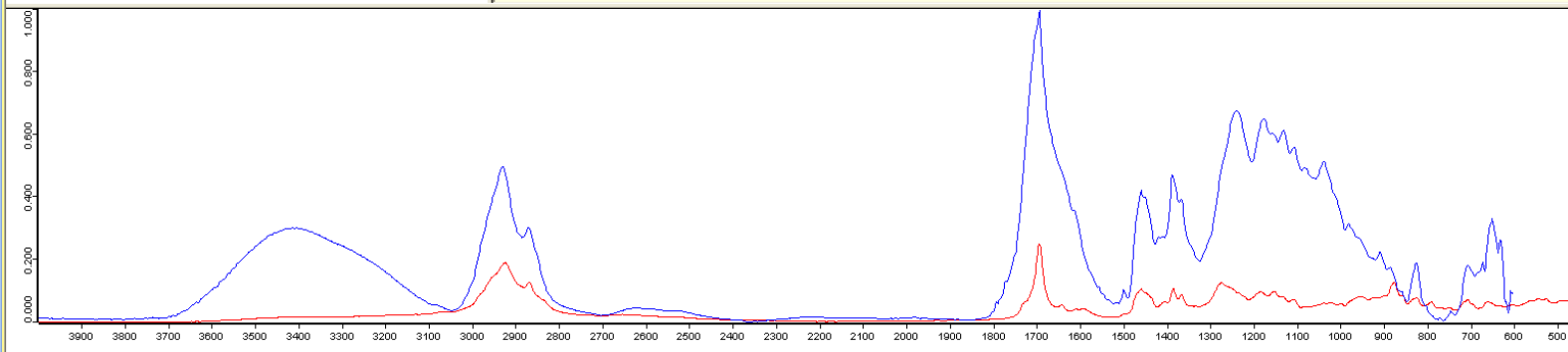
FT-IR, diamond accessory, 64 scans, 4 cm⁻¹ steps, 3 replica measurements



OPUS Browser

- Display - default.ows:1
 - "SGS ruggine.0" 1
 - "SGS ruggine.1" 1
 - "SGS ruggine.2" 1
 - "SGS resina.0" 1
 - "SGS resina.0" 1
- Search Results - default.ows:2**
 - "SGS resina.0" 1

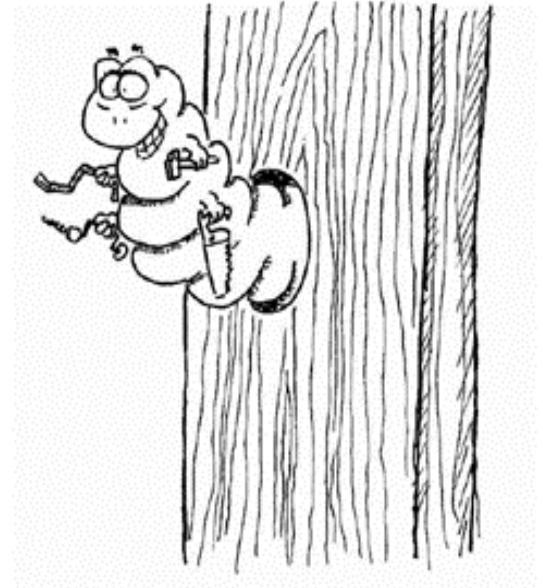
Compound information	
Compound Name	NATURAL RESIN, Binder for explosives
Molecular Formula	
Molecular Weight	
CAS Registry Number	
Sample Preparation	ATR single bounce
Manufacturer	© 2007 Nicodrom
Comment	NICO2831 / NX187



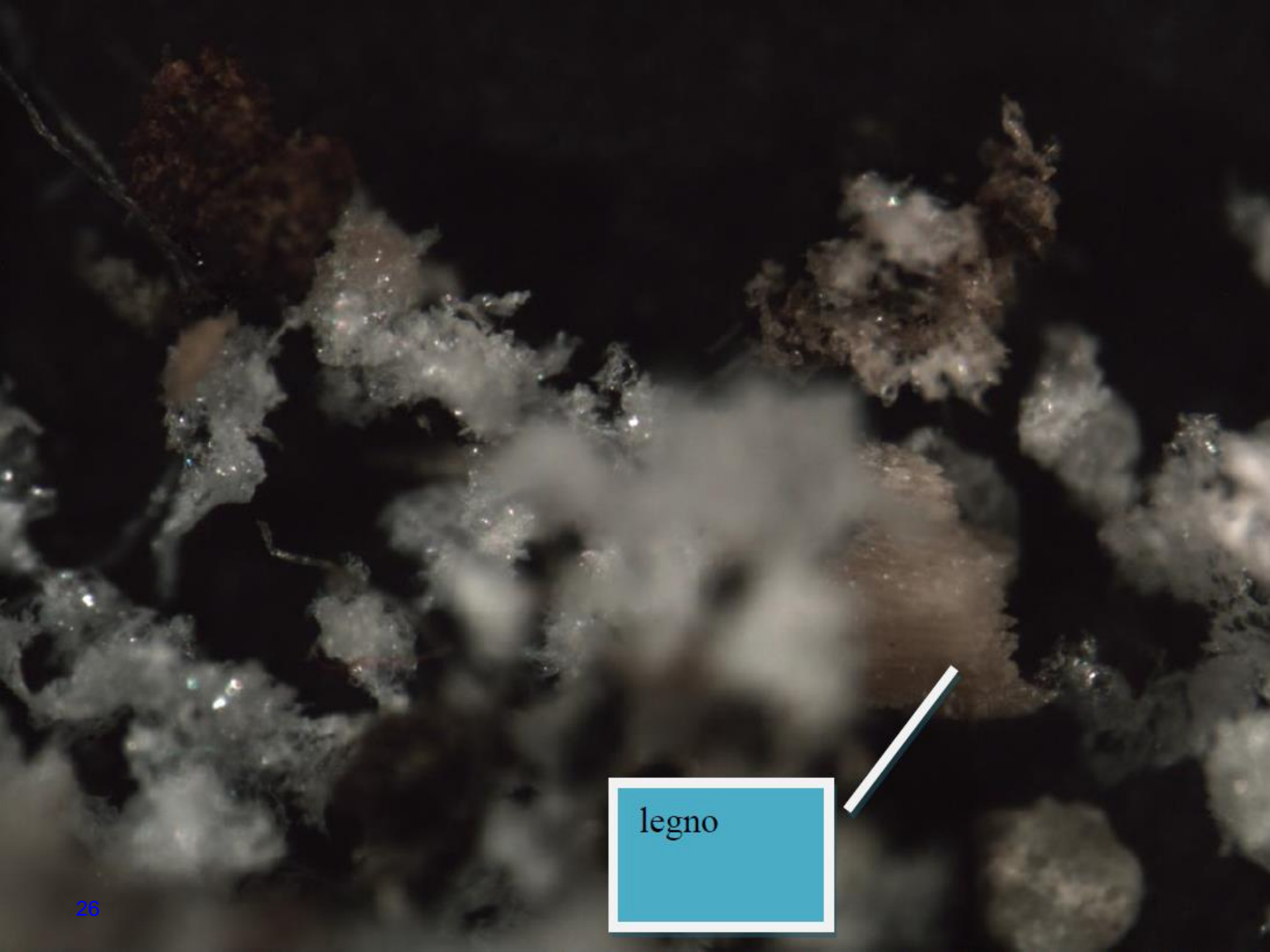
60 Hits	Hit Quality	Compound Name	Entry No.	Molecular formula	Molecular weight	CAS number
<input checked="" type="checkbox"/>	299	NATURAL RESIN, Binder for explosives	2691			
<input type="checkbox"/>	297	PINE RESIN, Natural based	2340			
<input type="checkbox"/>	262	OIL OF PINE, Excipient - Aromatic oil	2562			
<input type="checkbox"/>	246	POLY(1-BUTENE), isotactic	73	CH2Ch		8002-09-3
<input type="checkbox"/>	242	EPOXIDIZED LINSEED OIL	172			9003-28-5
<input type="checkbox"/>	240	NYLON, Nylon content > 85%, Benetton	2096			8016-11-3
<input type="checkbox"/>	239	RUSTICO, Acrylic 48%, Cotton 48%, Nylon 4%, SDS	2062			
<input type="checkbox"/>	235	POLY(DIMER ACID-CO-ETHYLENE GLYCOL), average Mn ~1,000, hydrogenated	1317			68855-78-7
<input type="checkbox"/>	230	EPOXIDIZED SOY BEAN OIL	173			8013-07-8
<input type="checkbox"/>	229	9-RK-156, NALCO VISCO CHEMICALS, Oil Additive, corrosion inhibitor, PVA based; manuf. in USA	2139			
<input type="checkbox"/>	227	ELJRA, PAN-VBR, MODACRYLIC FIBER	2767			
<input type="checkbox"/>	223	SILK MUD-MEE THAILAND, Silk, Ethno	2036			
<input type="checkbox"/>	218	SPHERON OXIN 1000 LC	2448			
<input type="checkbox"/>	217	2-ETHYLHEXYL EPOXYL GALLATE	174			61789-01-3
<input type="checkbox"/>	216	8-RK-344, NALCO VISCO CHEMICALS, Oil Additive, corrosion inhibitor, PVA based; manuf. in USA	2138			
<input type="checkbox"/>	212	ELECTRONIC BOARD, Product	2517			
<input type="checkbox"/>	210	POLY(3-OCTYLTHIOPHENE-2,5-DIYL), regioregular average Mw ~142,000 by GPC average Mn ~54,000 by GPC	1347			104934-51-2
<input type="checkbox"/>	210	COMBOLO, 66% Nylon, 30% Tactel, Plymouth Brand	1784			
<input type="checkbox"/>	210	ACRYLIC/POLYAMIDE, Mixed Yarn, C&A	1871			
<input type="checkbox"/>	209	POLYGLYCEROL POLYRICINOLEATE, Emulsifier	2610			107615-51-0

Case study 3

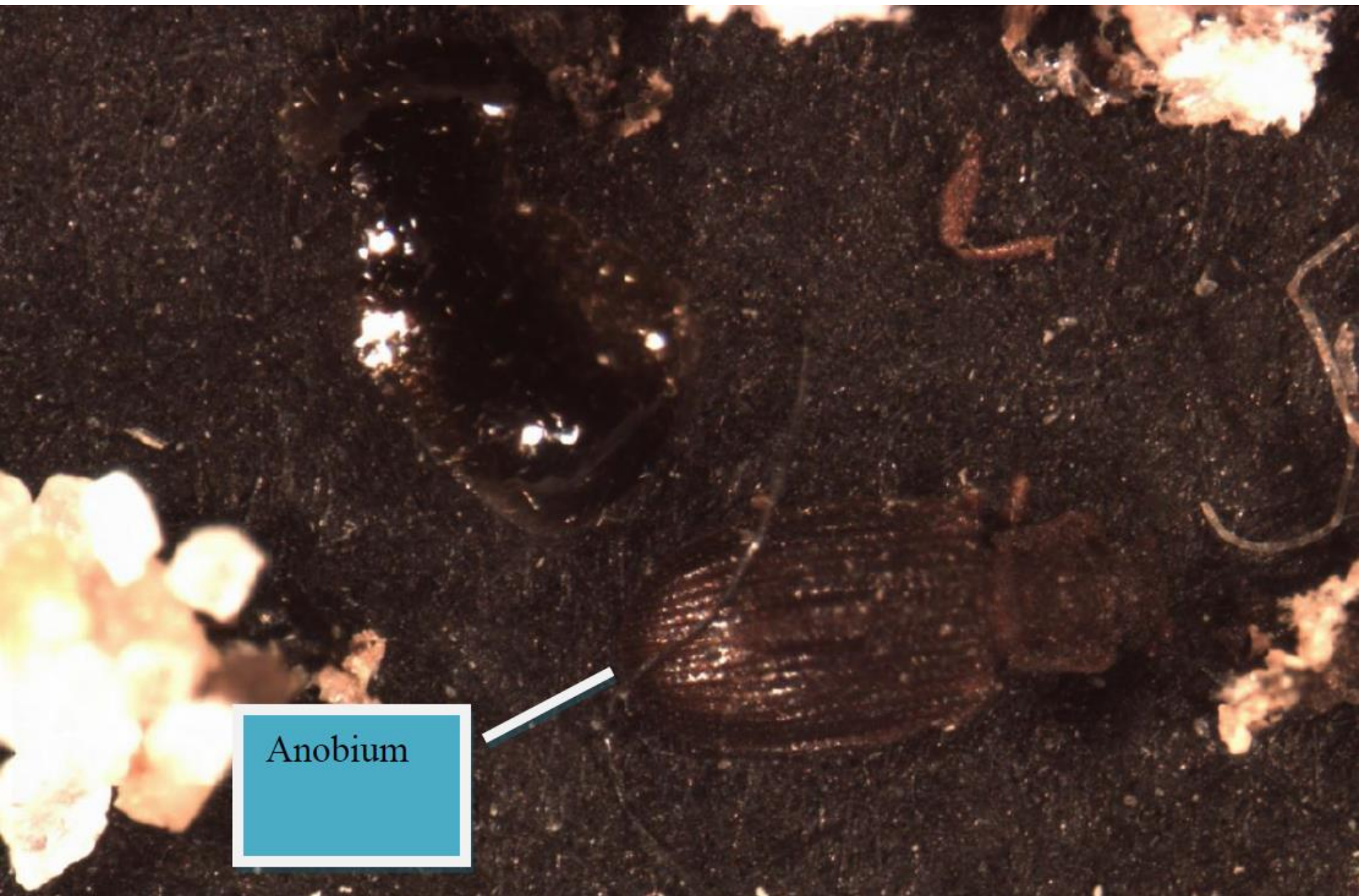
FT-IR, diamond accessory, 64 scans, 4 cm^{-1} steps, 3 replica measurements



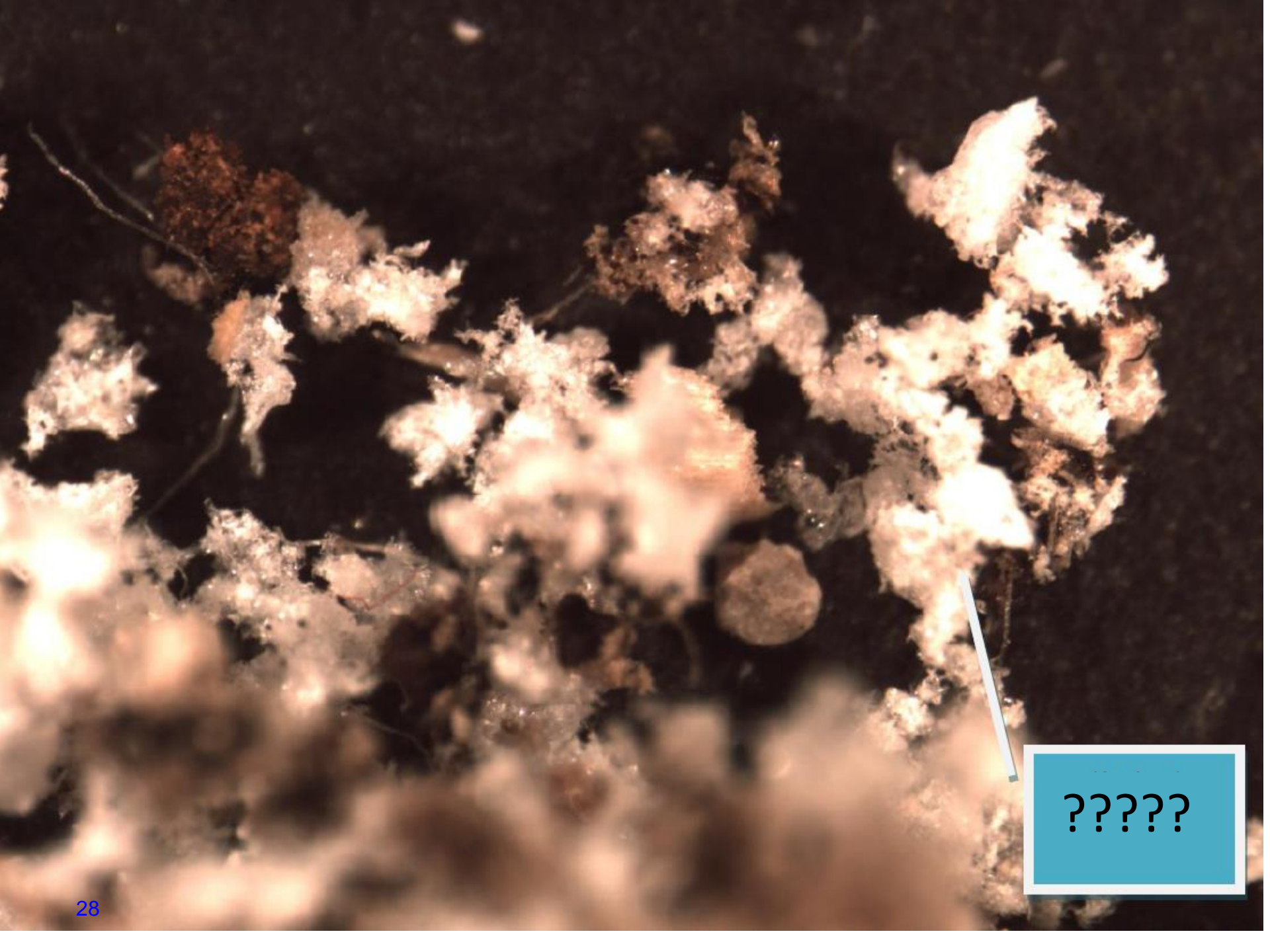
?????



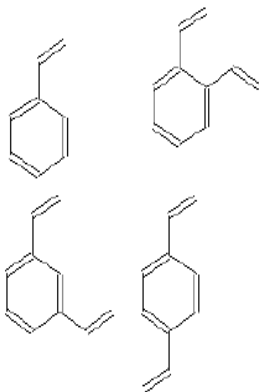
legno



Anobium

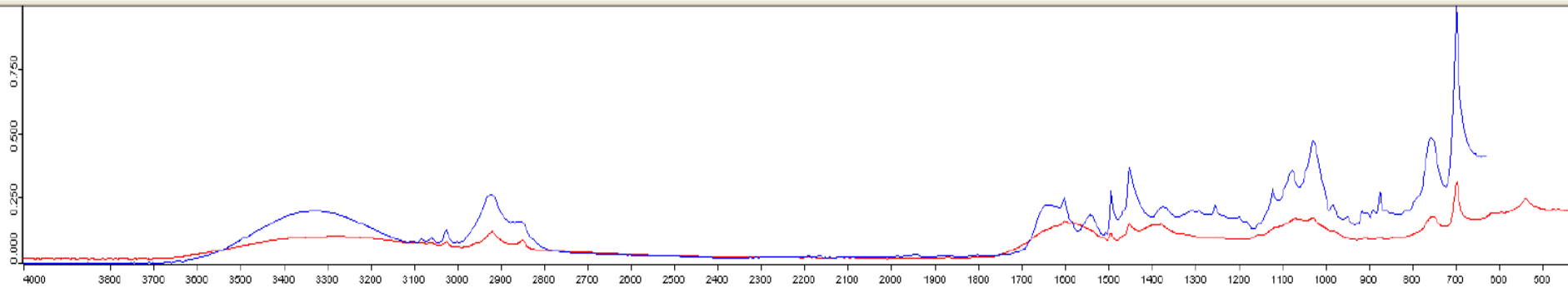


?????

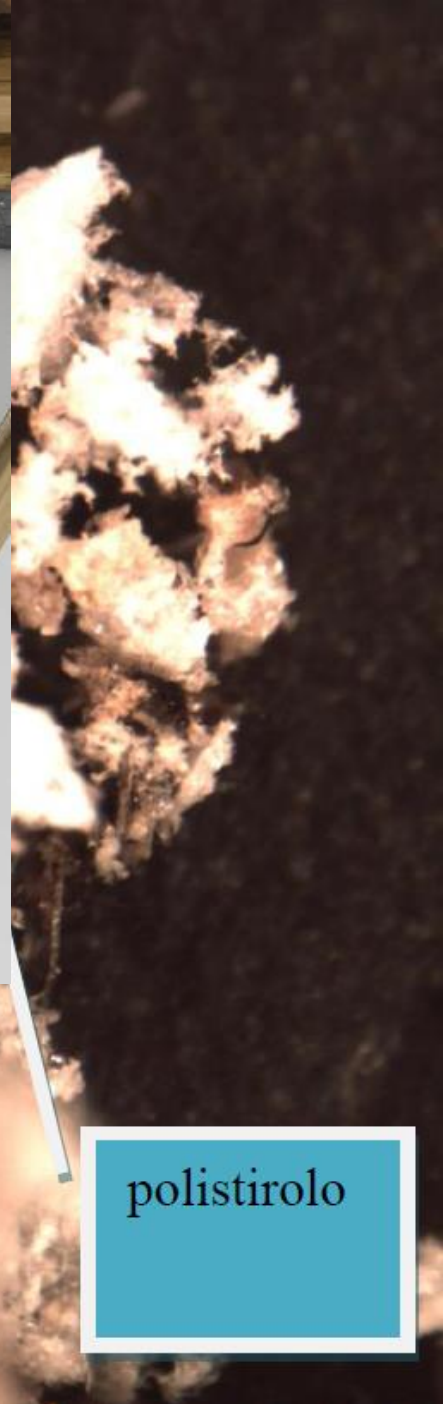


Compound information

Compound Name POLY(STYRENE-CO-DIVINYLBENZENE), CA. 1 mmol N/G, amino-methylated
 Molecular Formula
 Molecular Weight
 CAS Registry Number 69551-24-6
 Sample Preparation ATR, single bounce
 Manufacturer © 2003, 2004 Sigma-Aldrich, Co.
 Comment 34319 | U06398



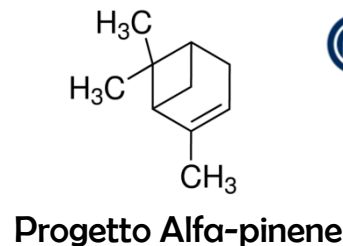
30 Hits	Hit Quality	Compound Name	Entry No.	Molecular formula	Molecular weight	CAS number
1	470	POLY(STYRENE-CO-DIVINYLBENZENE), CA. 1 mmol N/G, amino-methylated	1141			69551-24-6
2	467	COLOR MASTERBATCH POLY(STYRENE-CO-ACRYLONITRILE) + 50% WHITE PIGMENT, Color masterbatch	2129			
3	461	STYRENE/ALLYL ALCOHOL COPOLYMER, 5.4-6.0% HYDROXYL	114	(CH ₂ CHC ₆ H ₅) _x (...		25119-62-4
4	460	SBS BASED RUBBER, Binder for explosives	2686			
5	446	POLYSTYRENE, average Mw 1,000,000 (Typical)	1380			9003-53-6
6	439	DIETHYLAMINE, POLYMER-BOUND, Particle size 100-200 mesh	1398			
7	422	SIS BASED RUBBER, Mixture, Binder for explosives	2687			
8	417	ISOCYANATE, POLYMER-BOUND, Particle size 200-400 mesh	1377	C ₂₆ H ₂₅ N ₁	367.5	59990-69-1
9	410	POLYSTYRENE, Binder for explosives	2683			
10	408	COLOR MASTERBATCH POLYSTYRENE + 50% WHITE PIGMENT, Color masterbatch	2427			
11	402	STYRENE/ALLYL ALCOHOL COPOLYMER, 5.4-6% HYDROXYL	1558			25119-62-4
12	402	STYRENE/ACRYLONITRILE COPOLYMER, ACRYLONITRILE 25%	1602			9003-54-7



polistirolo



FONDAZIONE
CASSA DI RISPARMIO
DI TRENTO E ROVERETO



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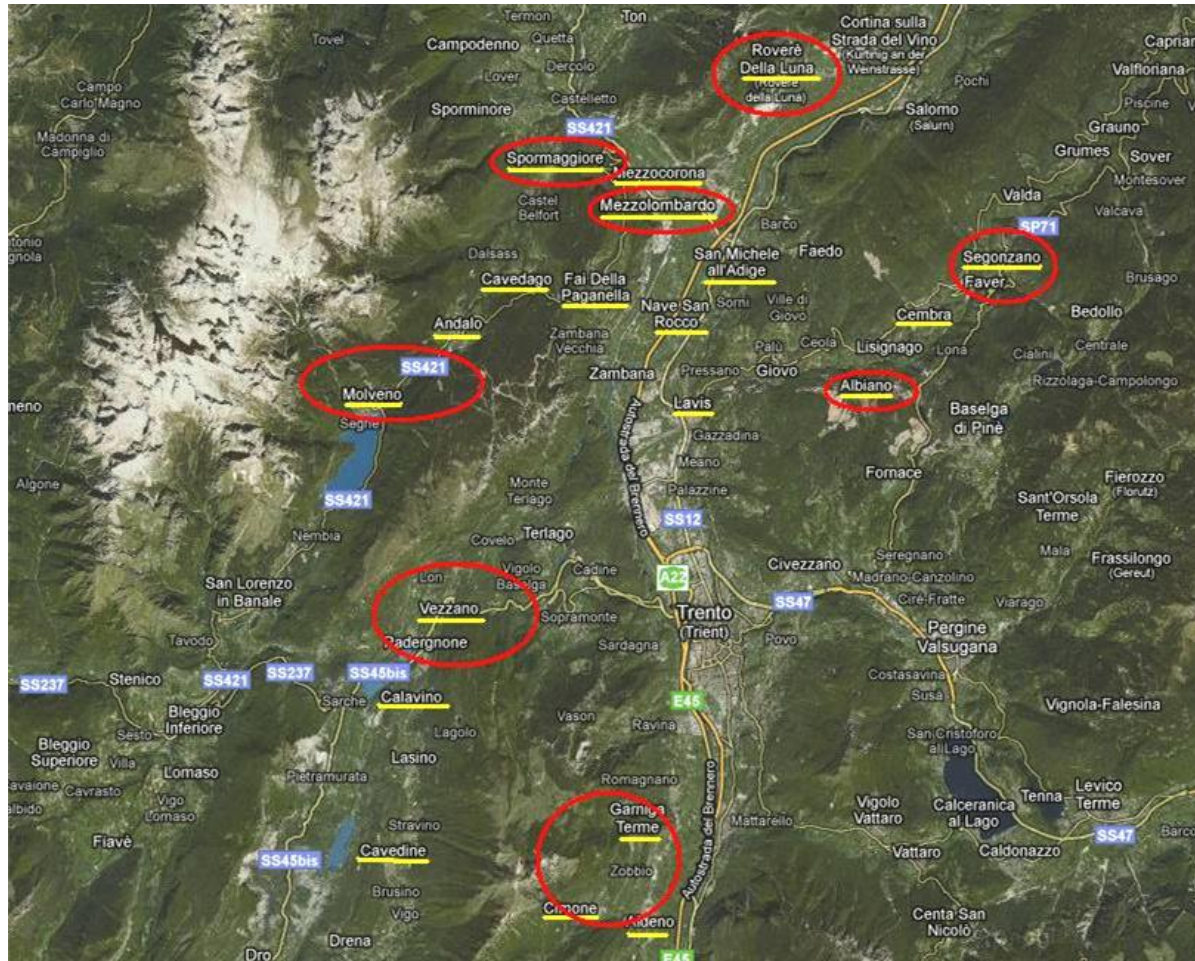
fellin@ivalsa.cnr.it

negri@ivalsa.cnr.it

Thanks for your attention

Conclusions

- Effectiveness of the monitoring tools.
- Presence and sometimes type of pollutants were successfully traced.
- The use of software functions like database search and “Quick compare” were effective to:
 - sort contaminated from non-contaminated wood
 - distinguish most of the times different types of pollutants.
- Cluster analysis method was found an useful tool to classify spectra in polluted vs. non-polluted classes.



Centri di raccolta legno dove si sono effettuati i campionamenti (cerchiati in rosso). Immagine ©2012 TerraMetrics, Map data ©2012 Google, Tele Atlas



For a total amount of:

- 336 samples polluted and non polluted wood from recycling facilities
- 21 varnishes, 18 glues, 4 preservatives for FT-IR database
- 2163 samples of virgin wood from stumps of spruce, beech, larch, sampled from 10 to 1900 m a.s.l. in 75 sites in 14 E.U. and not E.U. countries (not all measured)
- 450 spectra of evolution of pollution within time

All data are stored:
in a database for recycled wood
In FT-IR libraries



Further steps:

- Identify the final destination of pollutants
- Identify lacks on recycled wood management system
- Monitor the pollutants before and after process (both in particle board and combustion fumes and/or ash).
- Implementation of the system with feedbacks to government/scientific community
- Transfer information in real life recycle plants and administrative system.
- Design a automatic sorting system for recycling facilities.

Introduction

a problem driven research

Wood, since 400.000 years serving mankind

The sixties: wood engineerization

Today: welcome diffuse use of wood

Goals: extending natural lifespan without
compromising natural biodegradability

Challenge: correct end of life management

Exhausted wood: from garbage to resource

Experimental plan

Wood recycle management

- **Analysis of wood pollutants**
 - **in forest (biomass),**
 - **wood enterprises,**
 - **post consumer wooden goods (wood recycling platforms).**
- Analysis with FT-ATR.
- Analysis with XRF
- Analysis with ICP-OES

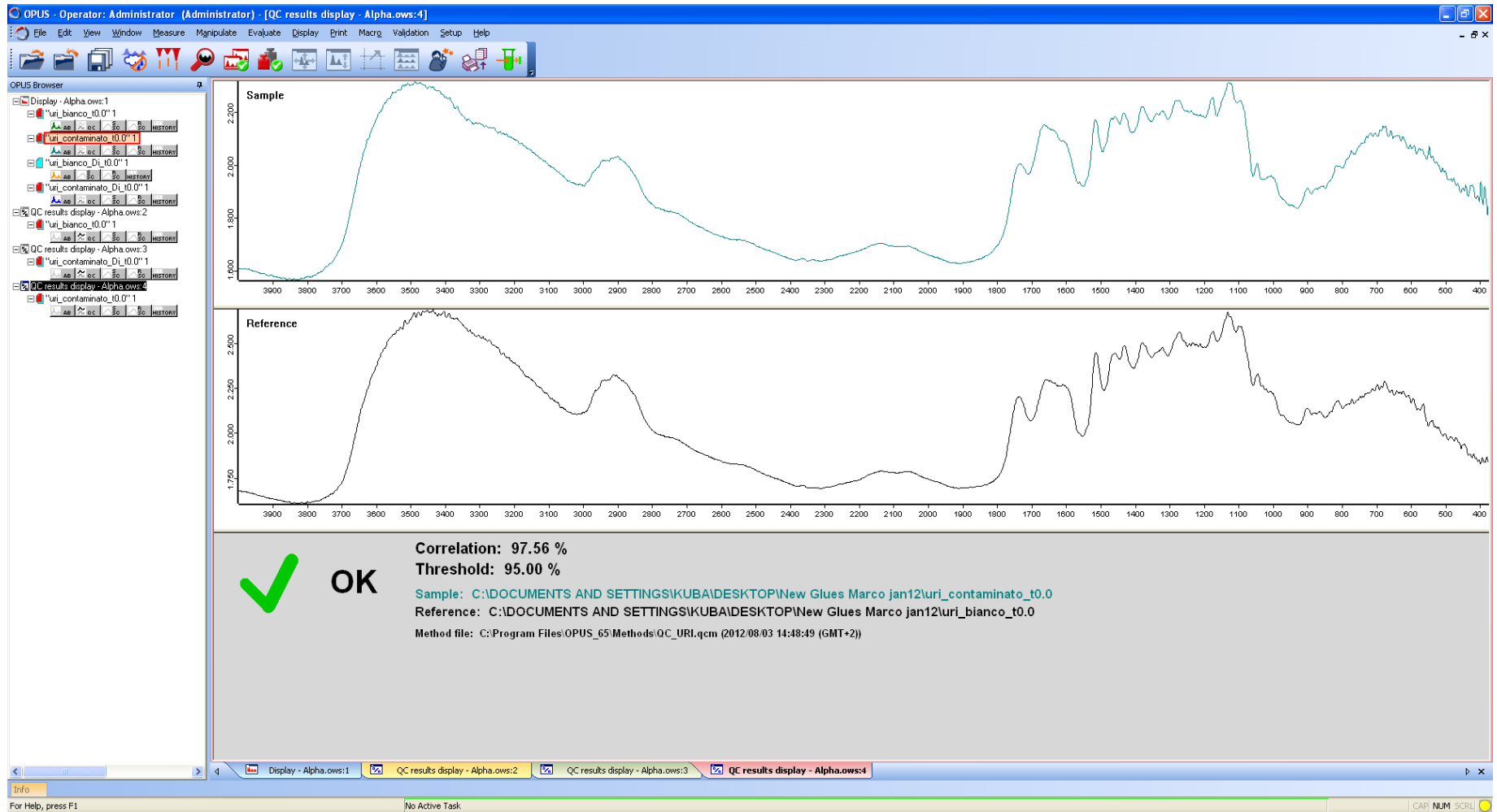
Solid pollutants

Application of FT-IR-ATR for:

- **recognition** of contamination presence in wooden based products
- **monitoring** concentration of pollution in wood chips, pellets, wastes
- **evaluation** of pollution dynamics within time

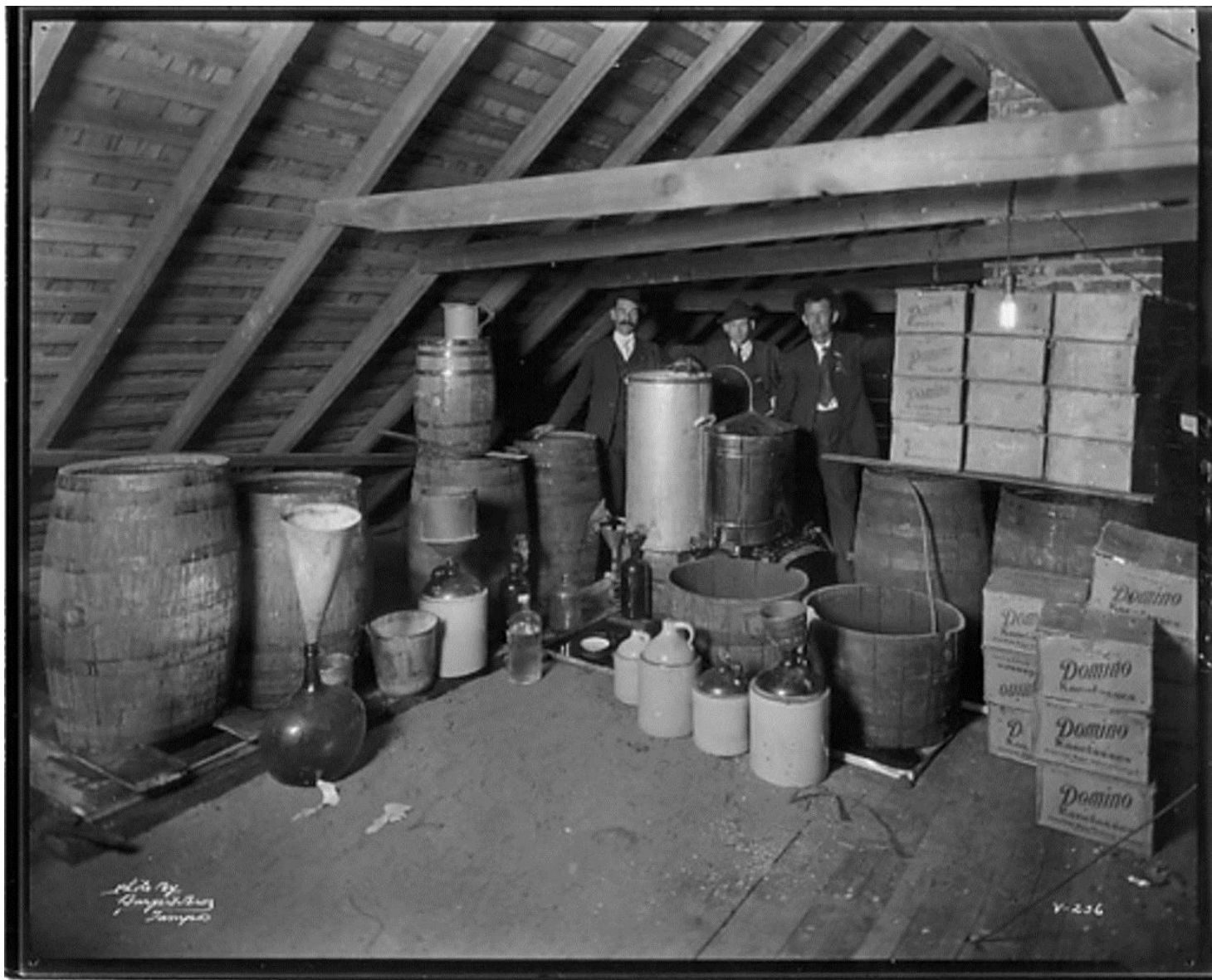
Urine on wood

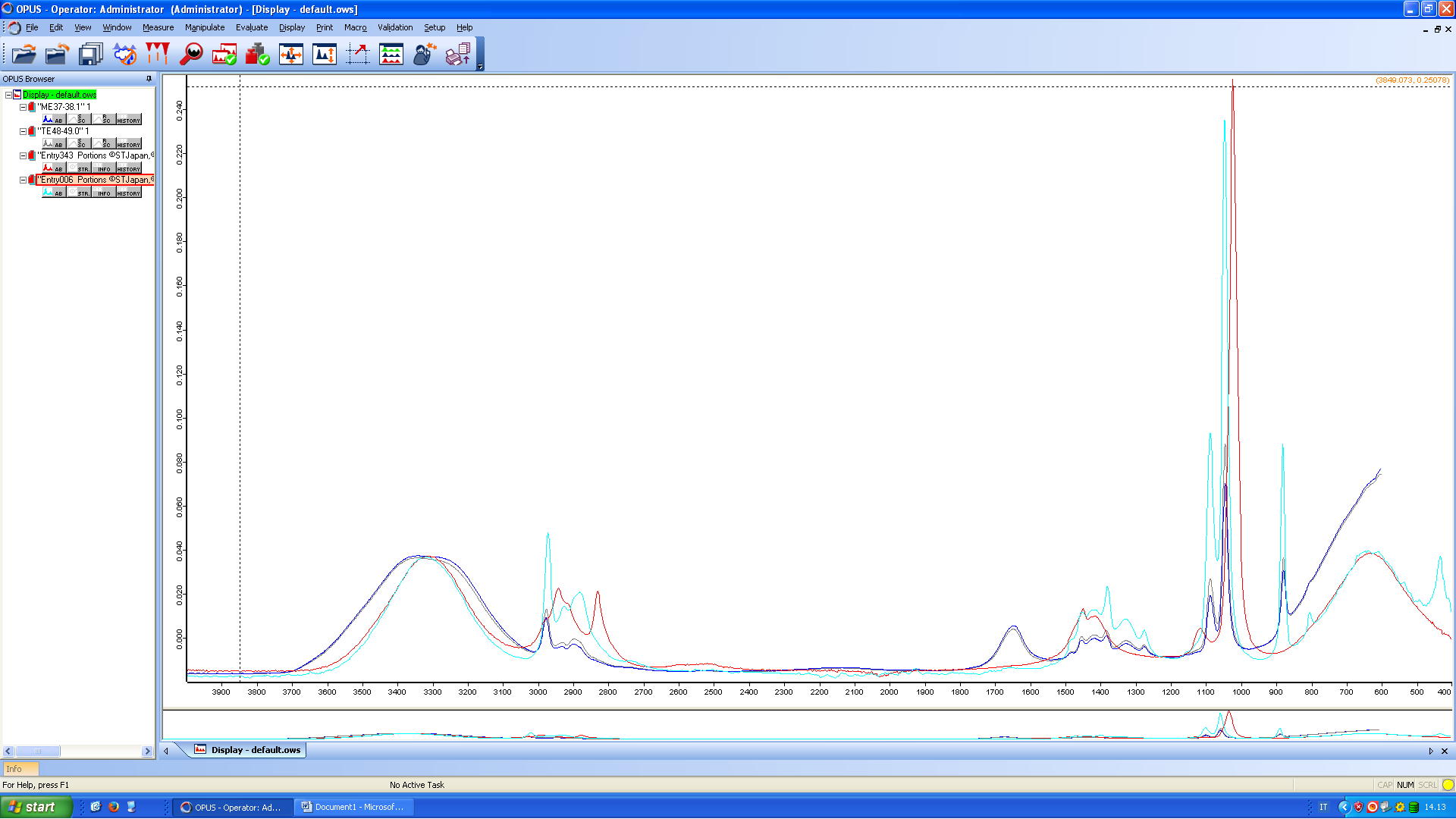
FT-IR, diamond accessory, 64 scans, 4 cm⁻¹ steps



Case study 4

FT-IR, diamond accessory, 64 scans, 4 cm^{-1} steps, 3 replica measurements





whole range 4000-600 cm-1
grappa Merlot 37-38
grappa Teroldego 47-48
database: 343 metilic alchool
database:006 etilic alchool

