Tecnologie e Metodi Avanzati per il Recupero e il Riciclo dei Materiali

Case Study:

Glass Recycling Industry

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Case study

Glass and ceramic glass recognition in recycling plants

In glass recycling plants, the presence of ceramic glass contaminants in the cullet strongly affects the quality of production. Ceramic glass fragments, presenting melting points higher than that of glass, are responsible for:

- **reduction of the production rate of the furnace,**
- **damages of the furnace,**
- **presence of defects in the glass products.**

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Damaged recycled glass

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What is ceramic glass?

Ceramic glass offer the possibility of combining the special properties of conventional sintered ceramics with the distincitve characteristics of glasses. Ceramic glass are obtained by controlled crystallization of a base glass. Glasses are melted, fabricated to shape and thermally converted to a predominantly crystalline ceramic.

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Ceramic glass products

The presence of ceramic glass inside waste glass products strongly increased in these last years, due to the introduction on the market of a large amount of ceramic glass manufactured goods (stove tops, cooking surfaces, plates, cups, bowls, etc.).

Ferrous metals, opaque ceramics, plastics or paper contaminants are commonly removed adopting different on-line sorting strategies, but are unable to separate ceramic glass.

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Ceramic glass characteristics

Ceramic glass are nowadays not only opaque white colored, but also translucent and highly transparent, following market rules.

They are not recognized inside the cullet stream by the equipment commonly utilized in the recycling plants as they are chracterized by **physical properties similar to those of glass.**

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Ceramic glass characteristics

Campione	Peso specifico (g/cm^3)
vetro sodico-calcico	2,51
vetroceramica	
marrone	2,56
gialla	2,53
bianca	2,52
nero-marrone	2,56
nero-viola	2,58

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Ceramic glass characteristics

Chemical composition (oxides weight %)

	Neoceram™	Ceran®	Glass
SiO_2	65.7	64.0	71-73
Al_2O_3	22.0	21.3	0-2.4
Li_2O	4.5	3.5	
ZnO	-	0.1	
P_2O_5	1.0	1.5	
Na_2O	0.5	0.6	12-14
K_2O	0.3	0.5	0-1.1
BaO	-	2.5	
CaO	-	0.2	10-12
ZrO_2	2.0	2.3	
TiO_2	2.5	1.6	

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Ceramic glass manual sorting

Trained personnel manually remove ceramic glass trying to evaluate their reflective characteristics.

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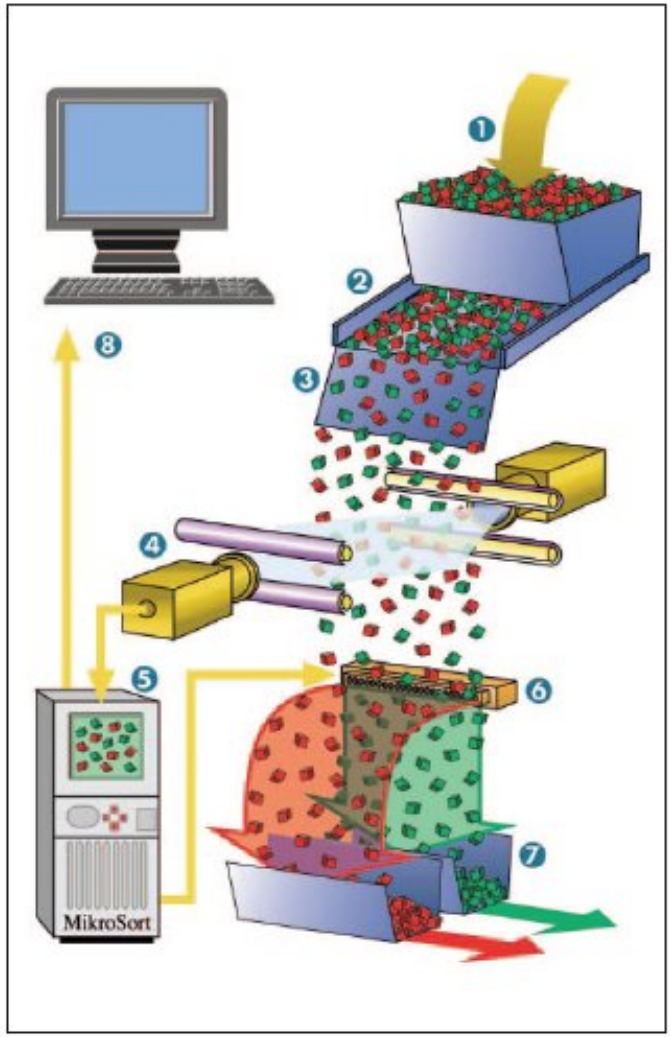
Glass color sorting



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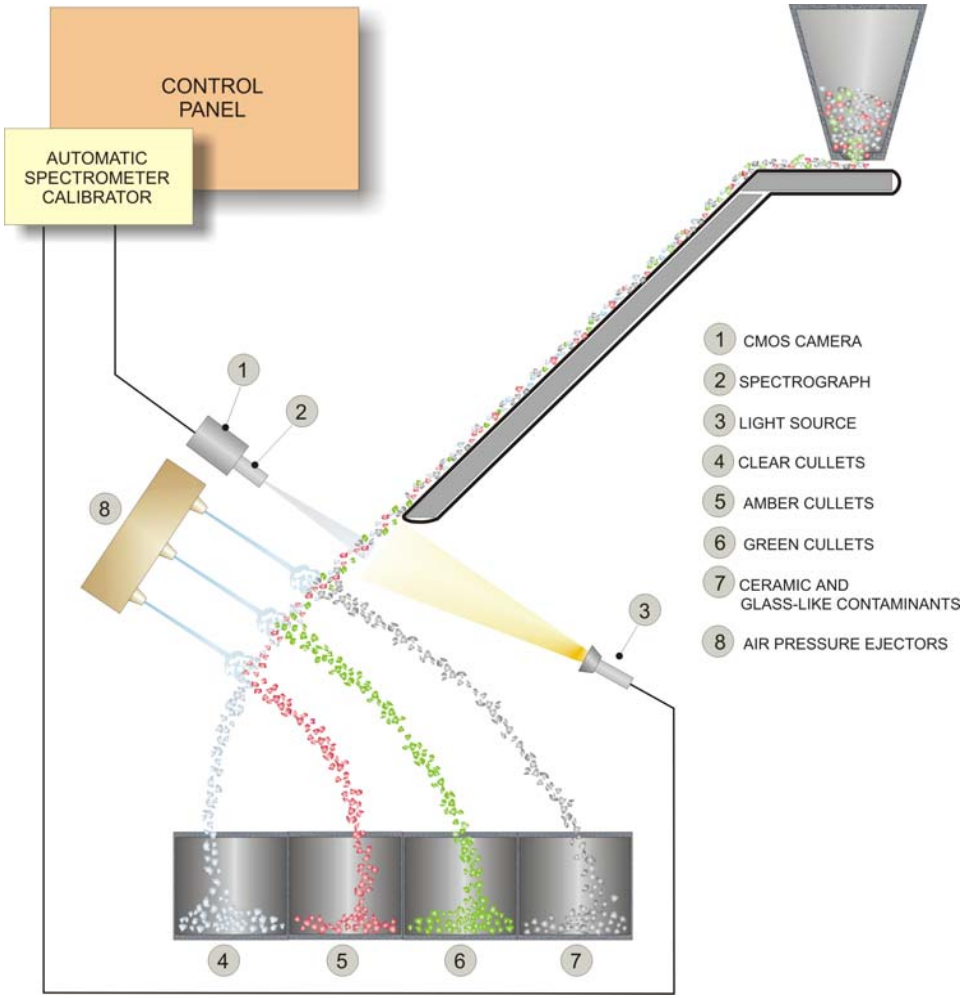
Ceramic glass sorting

Architecture se-up



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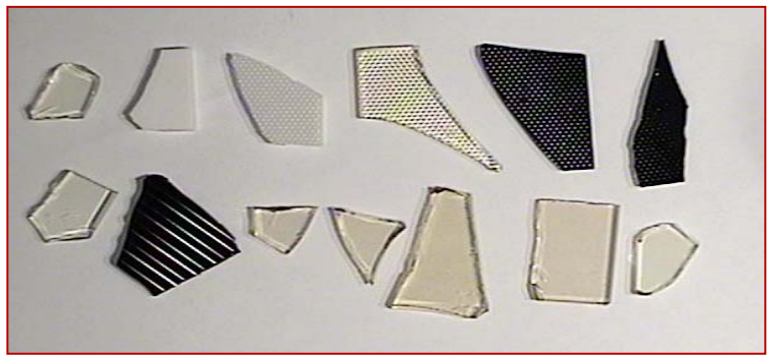
Glass and ceramic glass

The analyzed samples

Representative samples of container glass and ceramic glass have been collected at Reiling Glass Recycling Gmbh plant (Marienfeld, Germany). They are characterized by different color, thickness, manufacturing and shape.

Glass Samples



Ceramic Glass Samples

3 color classes of glass:
clear, green and amber

3 color classes of ceramic-glass:
clear, opaque white and amber

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List of glass samples

Glass samples characteristics

Ref. code	Description	Colour	Average thickness (mm)	Average size (cm)
V01	Bottom of bottle	Dark green transparent	7.30	3.5x2.8
V02	Neck of bottle	Greenish, transparent	3.18	2.6x2.5
V03	Bottom of bottle	Dark green transparent	6.59	5.8x2.5
V04	Bottom of bottle	Transparent, white	8.54	4.5x4.3
V05	Bottle body	Greenish, transparent	5.30	2.2x5.0
V06	Bottom of bottle	Dark brownish, transparent	5.80	4.7x3.4
V07	Bottom of bottle	Transparent, white	9.38	3.8x2.3
V08	Bottom of bottle	Transparent, white	5.32	2.9x3.6
V09	Neck of bottle	Transparent, white	3.64	3.2x2.4
V10	Bottom of bottle	Transparent, white	6.66	4.0x2.0
V11	Bottom of bottle	Greenish, transparent	5.60	2.0x3.2
V12	Bottle body	Greenish, transparent	3.18	3.3x1.8

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List of ceramic glass samples

Ceramic glass samples characteristics

Sample	Description	Colour	Average thickness (mm)	Average size (cm)
Arctic Fire	Scattered	White	3.90	10x10
Ceran Color	Scattered	Dark Amaranthine	3.94	10x10
Ceran Hightrans	Scattered	Dark Brown	4.00	10x10
Neoceram N0	Smooth	Transparent, yellowish	3.80	10.3x15.3
Neoceram N11	Scattered	White	3.92	5x5
Robax	Scattered	Transparent, yellowish	3.98	10x10
C01	Smooth	Transparent, yellowish	3.98	10.5x7.5
C02	Scattered	Dark brown	4.89	10x4
C03	Smooth	Transparent, brownish	4.11	6x3.4
C04	Smooth	Transparent, yellowish	4.42	10.7x3.2
C05	Smooth	Transparent, yellowish	5.92	5x2.7
C06	Smooth	Transparent, brownish	5.80	5.2x6
C07	Smooth	Transparent, yellowish	3.11	8.2x3.3

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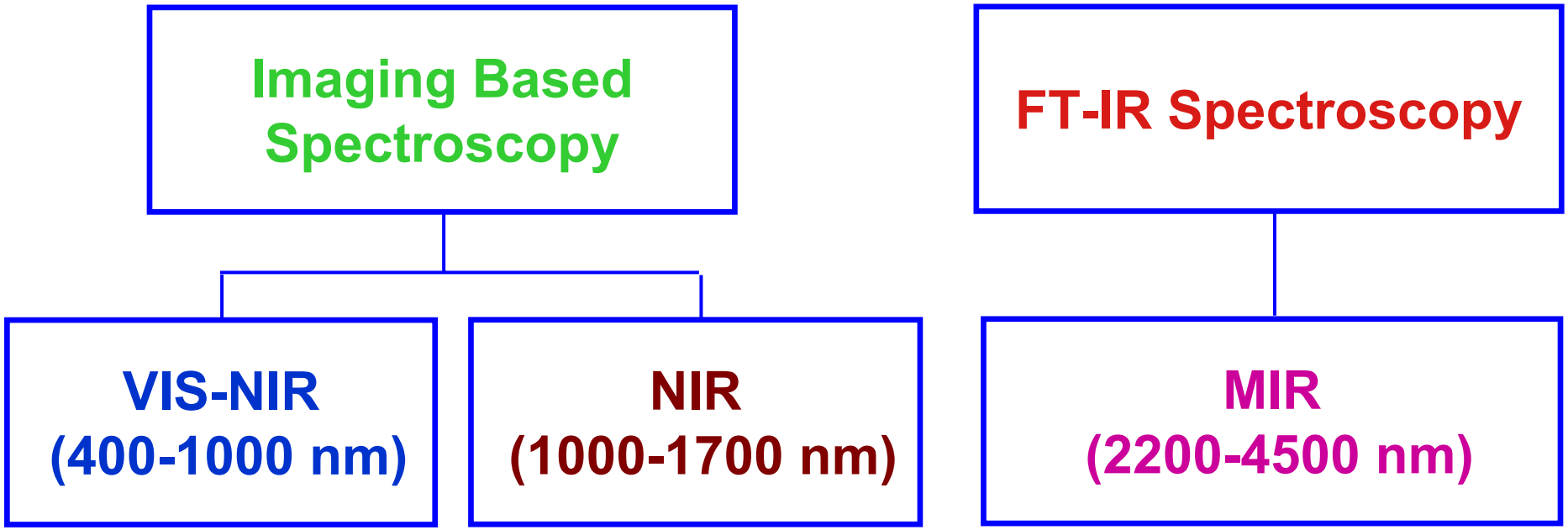
Spectral analyses

Spectral analyses of glass and ceramic glass samples have been carried out by different techniques and covering a wide range of wavelength:



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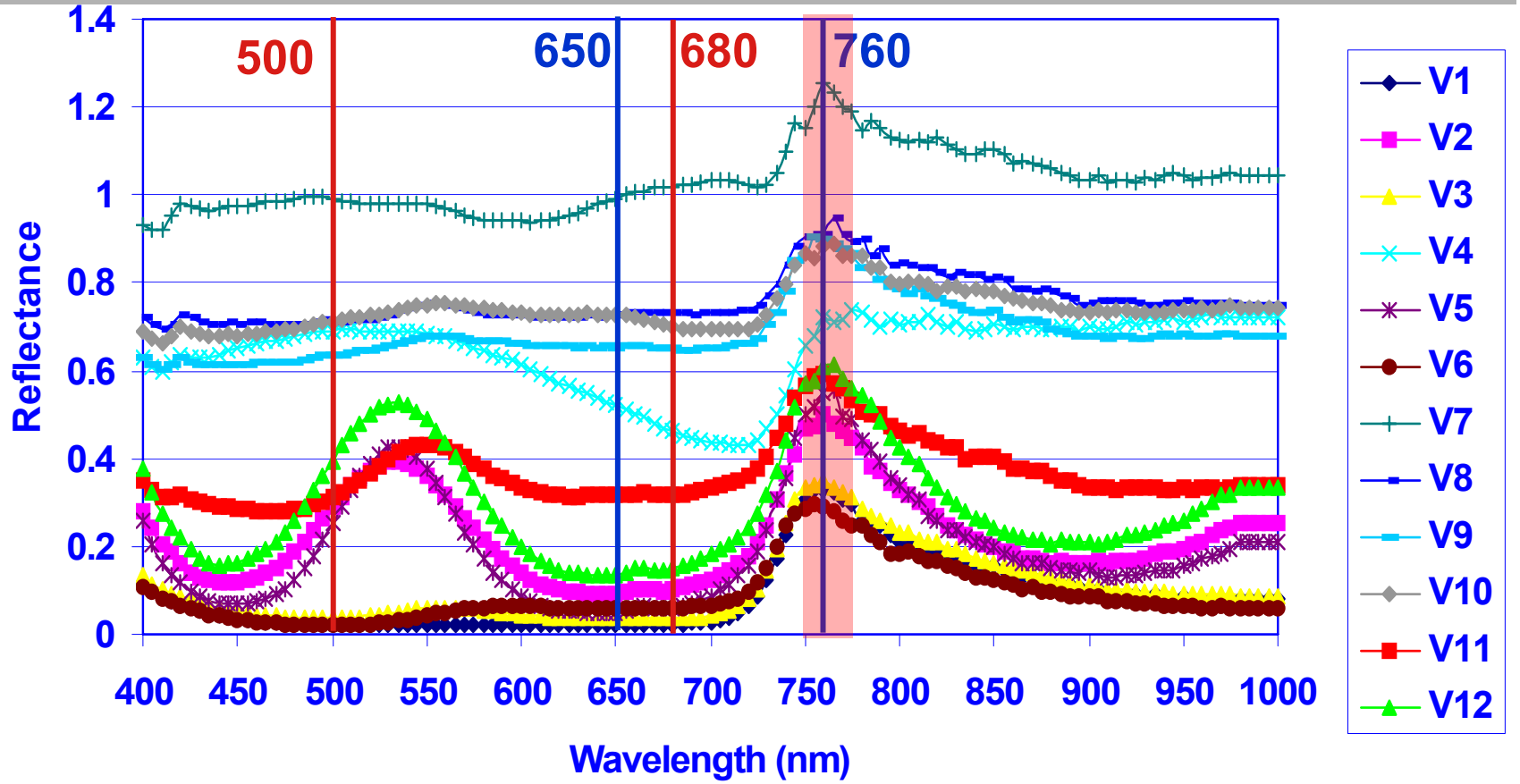
VIS-NIR Field (400-1000 nm)

Glass spectra



In the visible field (400-700 nm) the spectral behavior is influenced by color of samples (clear, green or amber). In the NIR field the spectra of all samples show a peak in the range 750-760 nm.

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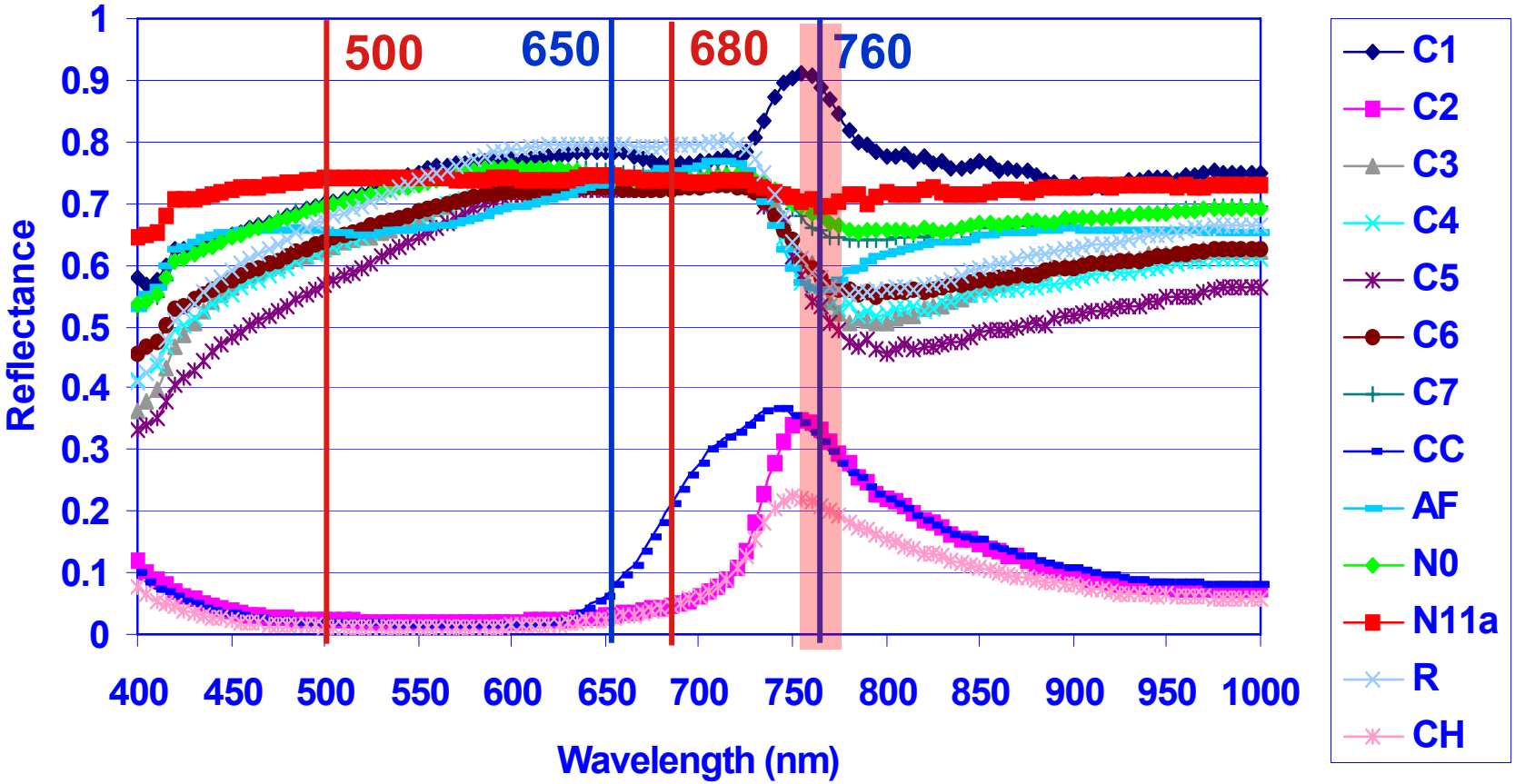
VIS-NIR Field (400-1000 nm)

Ceramic glass spectra



Ceramic glass are characterized by similar spectral signature, with the exception of dark samples and sample C1. The 700-1000 nm range present useful information for samples recognition.

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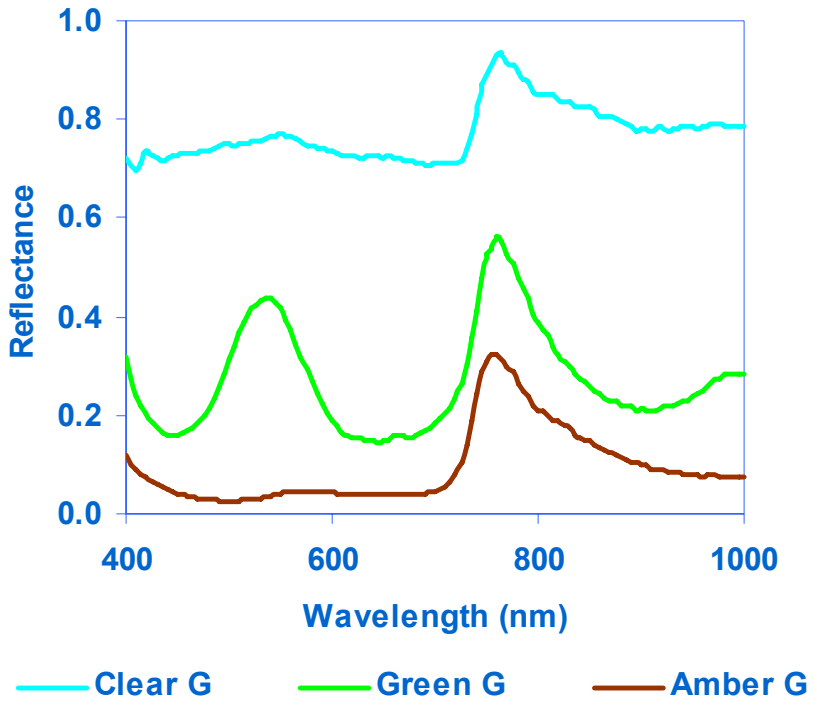
Experimental results

Average reflectance spectra of glass



Green cullet show a peak at 500-550 nm, corresponding to the green wavelength. Clear and amber cullet show spectral profiles with constant values but differences in reflectance level. In the near-infrared field (700-1000 nm) the curves are characterized by similar shape for all the samples.

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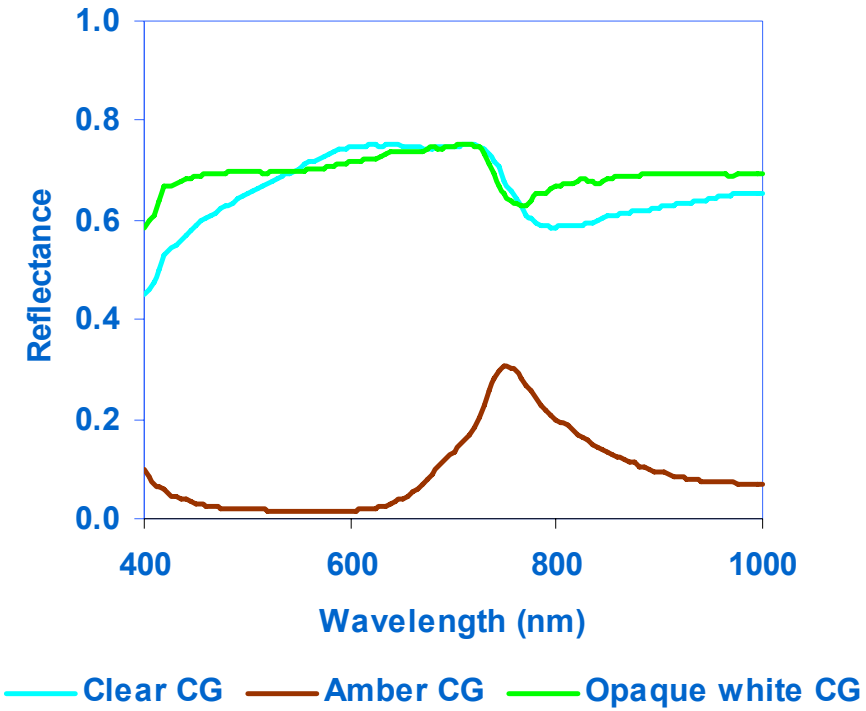
Experimental results

Average reflectance spectra of ceramic glass



Clear and opaque white CG samples show higher reflectance values compared to amber CG samples. The latter are characterized by a peak at 750-760 nm whereas clear and opaque white CG show a valley in the same wavelength region.

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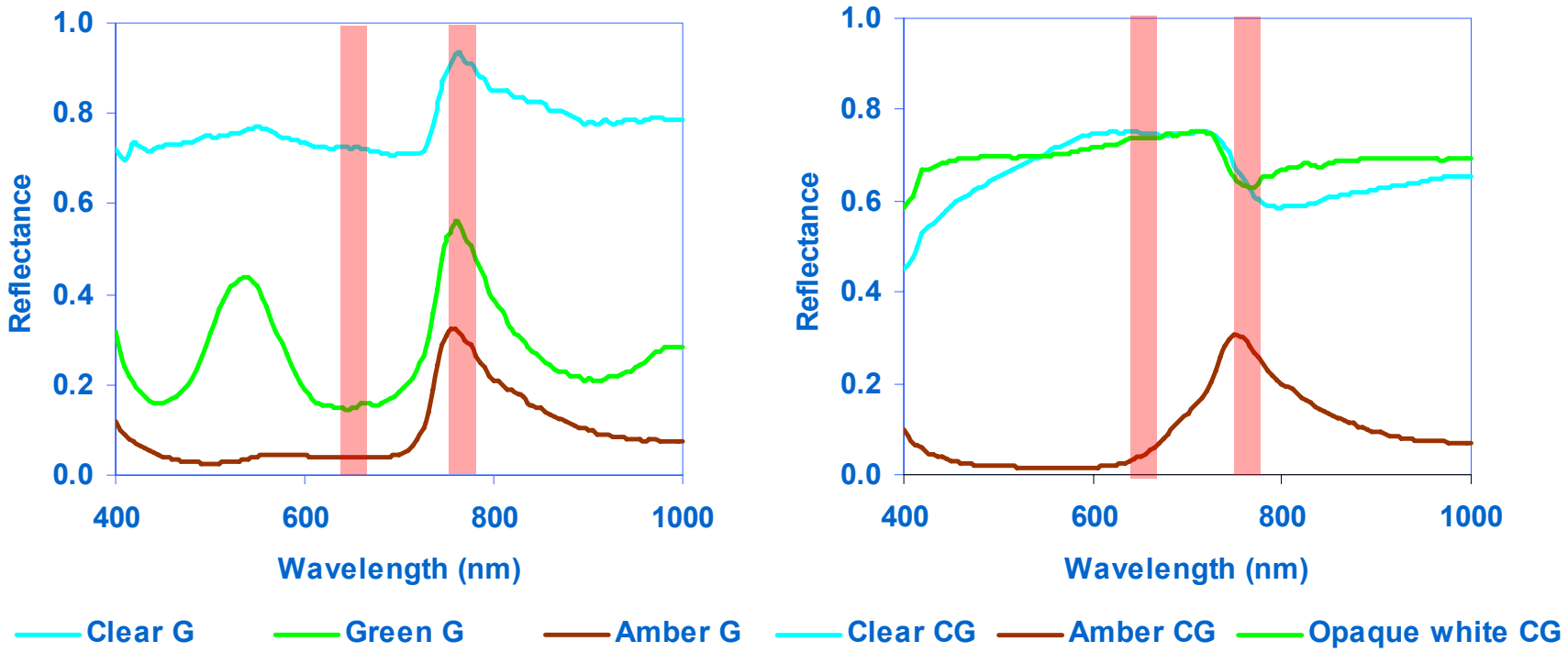
Experimental results

Average glass and ceramic glass reflectance spectra



Some parameters, as for example the ratio between the reflectance values at two different and pre-established wavelengths, can be adopted in order to realize the recognition between glass and ceramic glass fragments.

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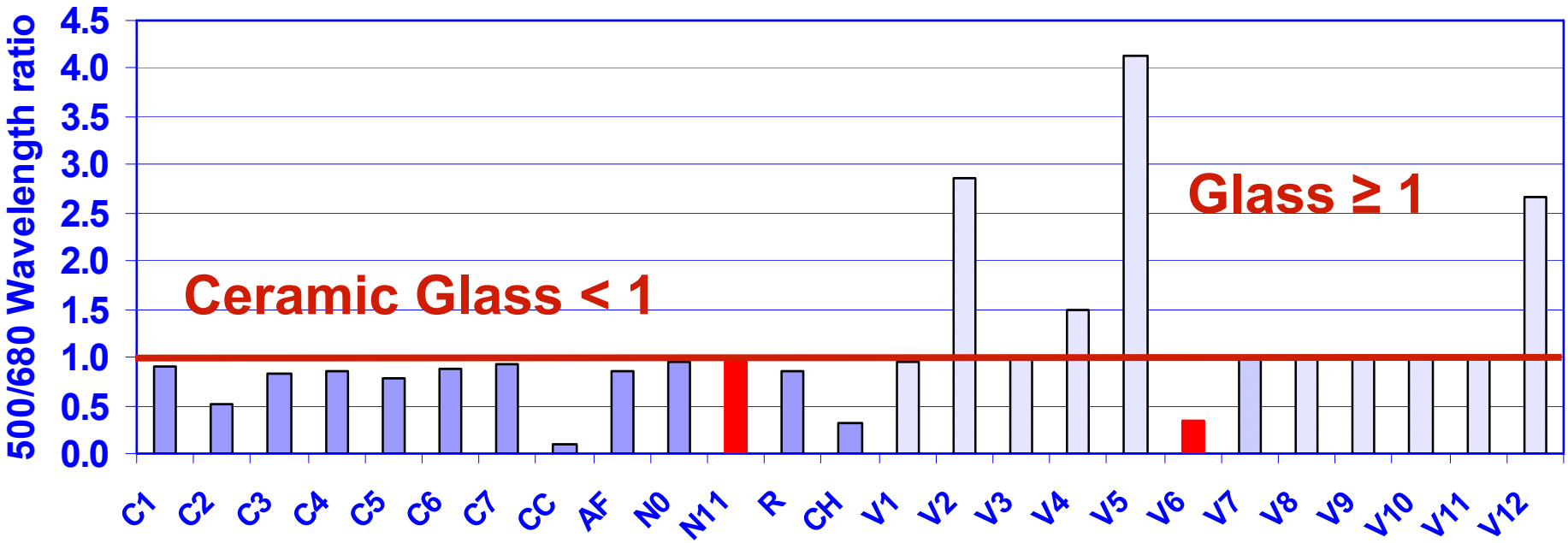
500/680 wavelength ratio



Using the ratio between the reflectance values at 500 and 680 nm, the recognition of most of ceramic glass and glass samples is performed, with the exception of two samples (N11 and V6).

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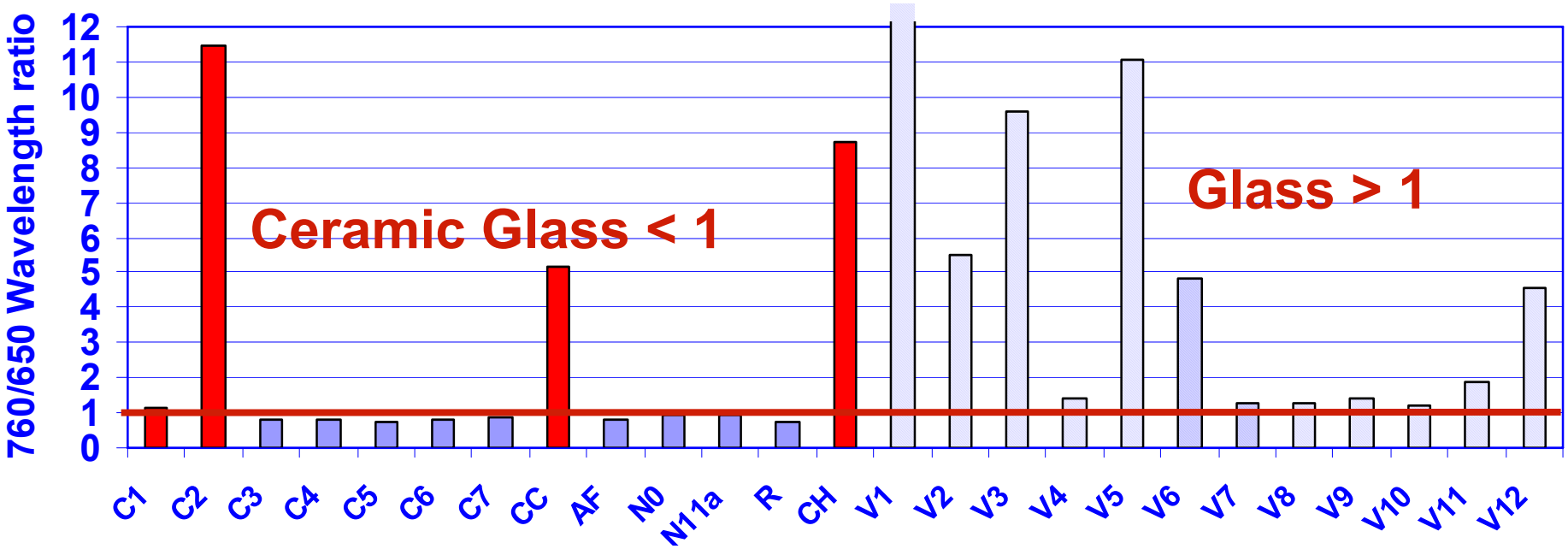
760/650 wavelength ratio



Using the ratio between the reflectance values at 760 and 650 nm, the recognition of most of ceramic glass and glass samples is performed, with the exception of four ceramic glass samples (the dark ones and C1).

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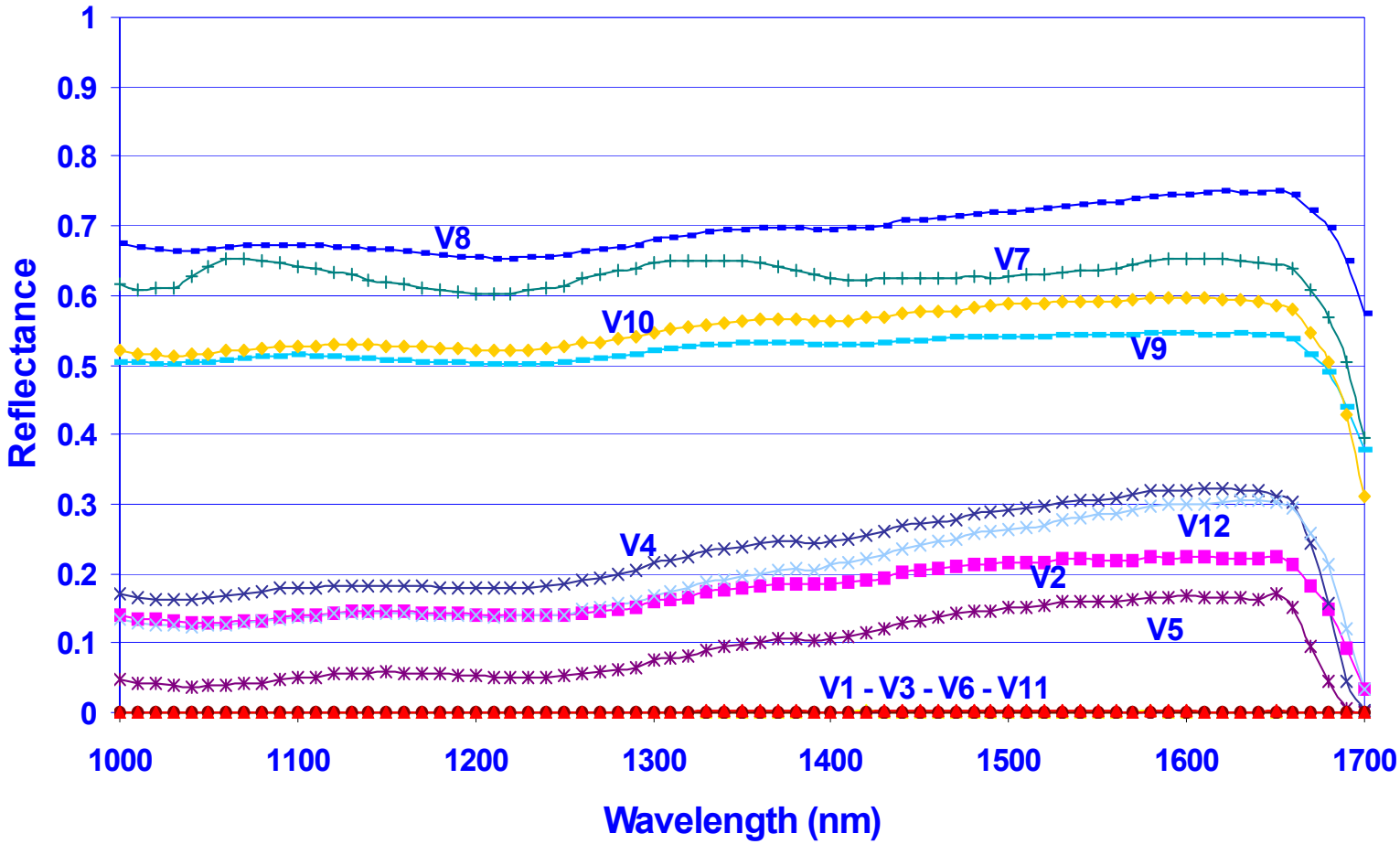
Near infrared field (1000-1700 nm)

Glass spectra



Glass cullets show similar shape of the curves, with the exception of dark samples that have poor reflection.

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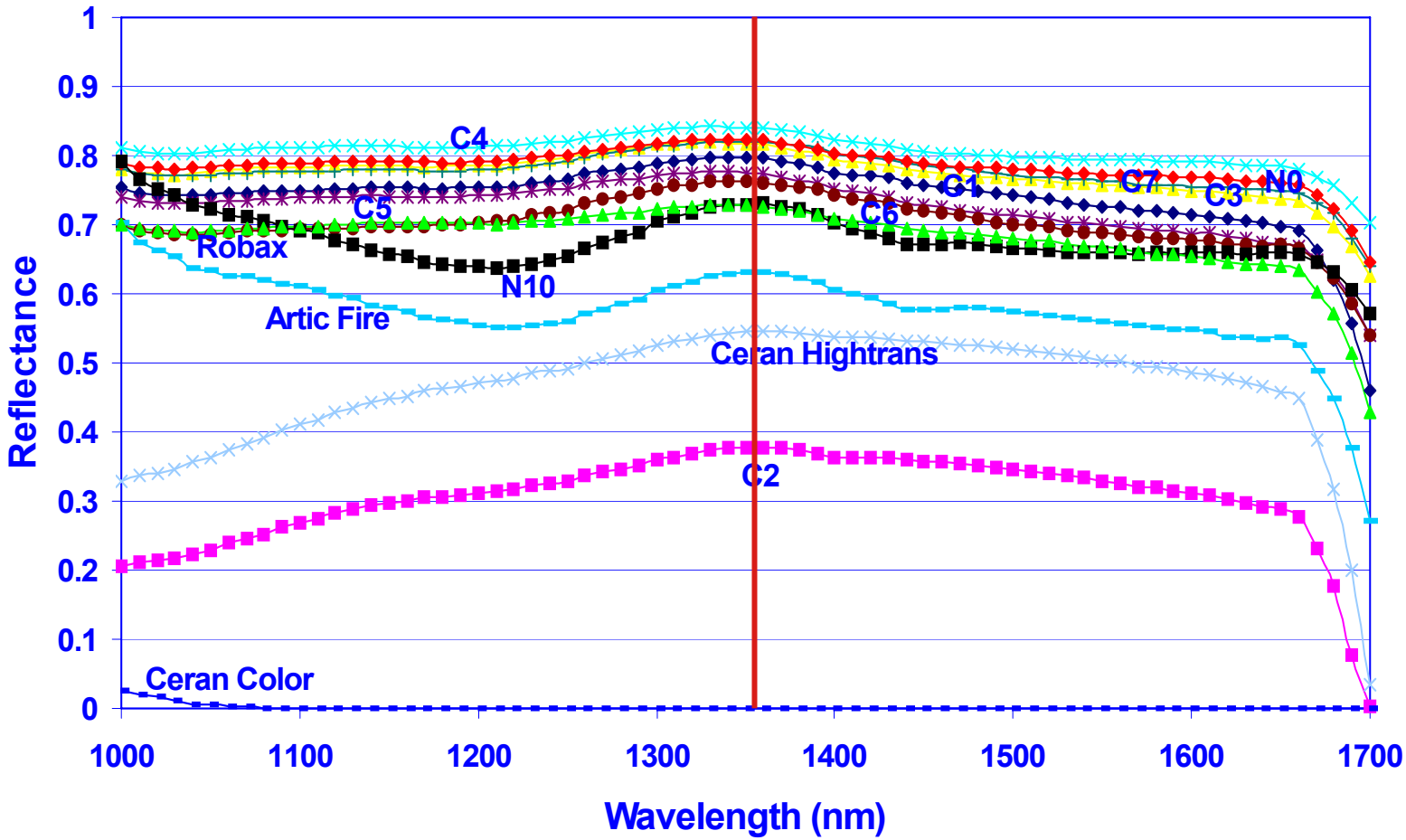
Near infrared field (1000-1700 nm)

Ceramic glass spectra



Ceramic glass show similar spectral signature, especially in the range 1300-1700 nm, with the exception of one dark sample (CC), not reflecting.

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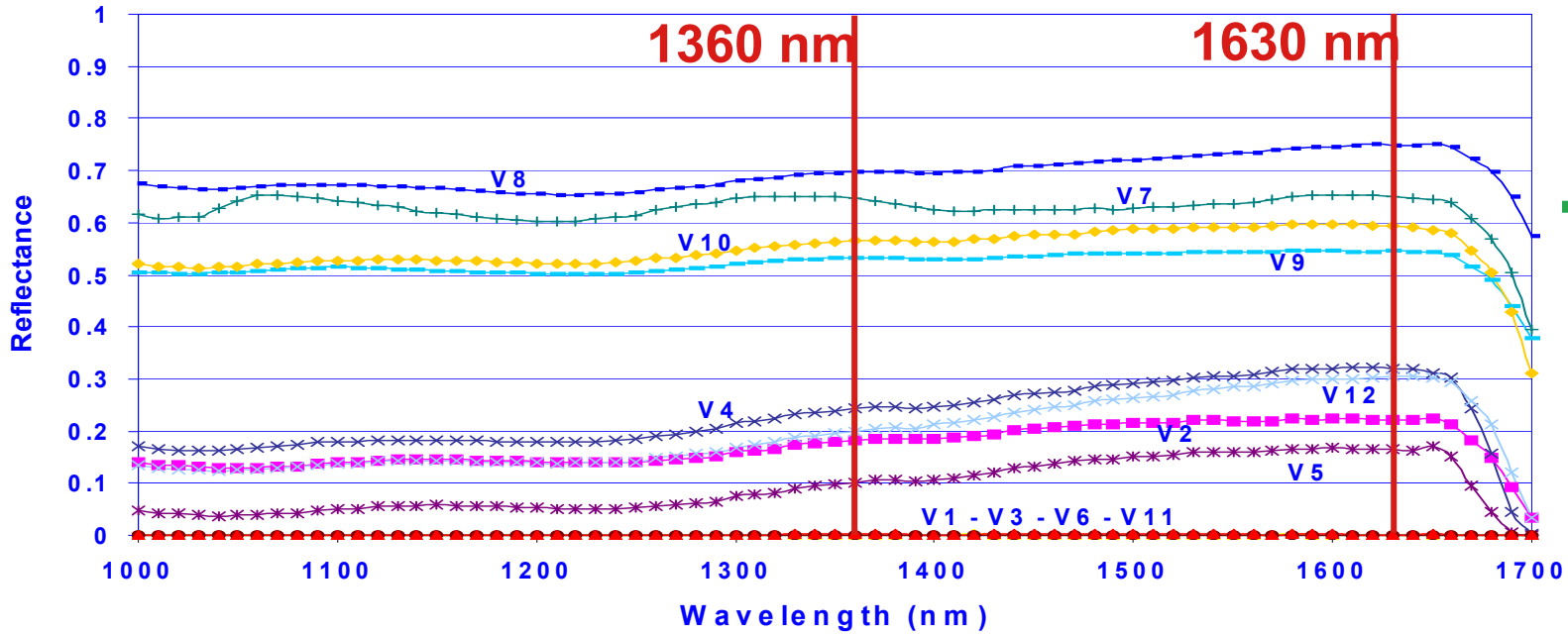

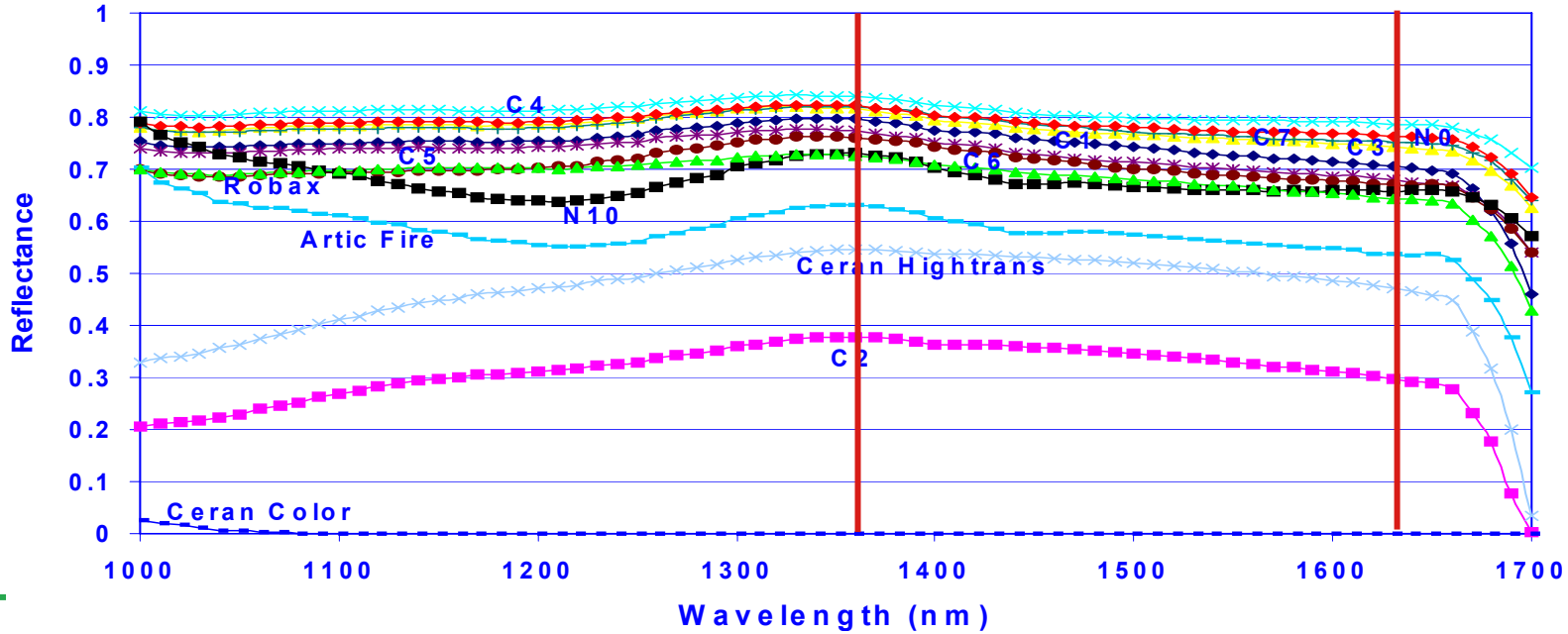

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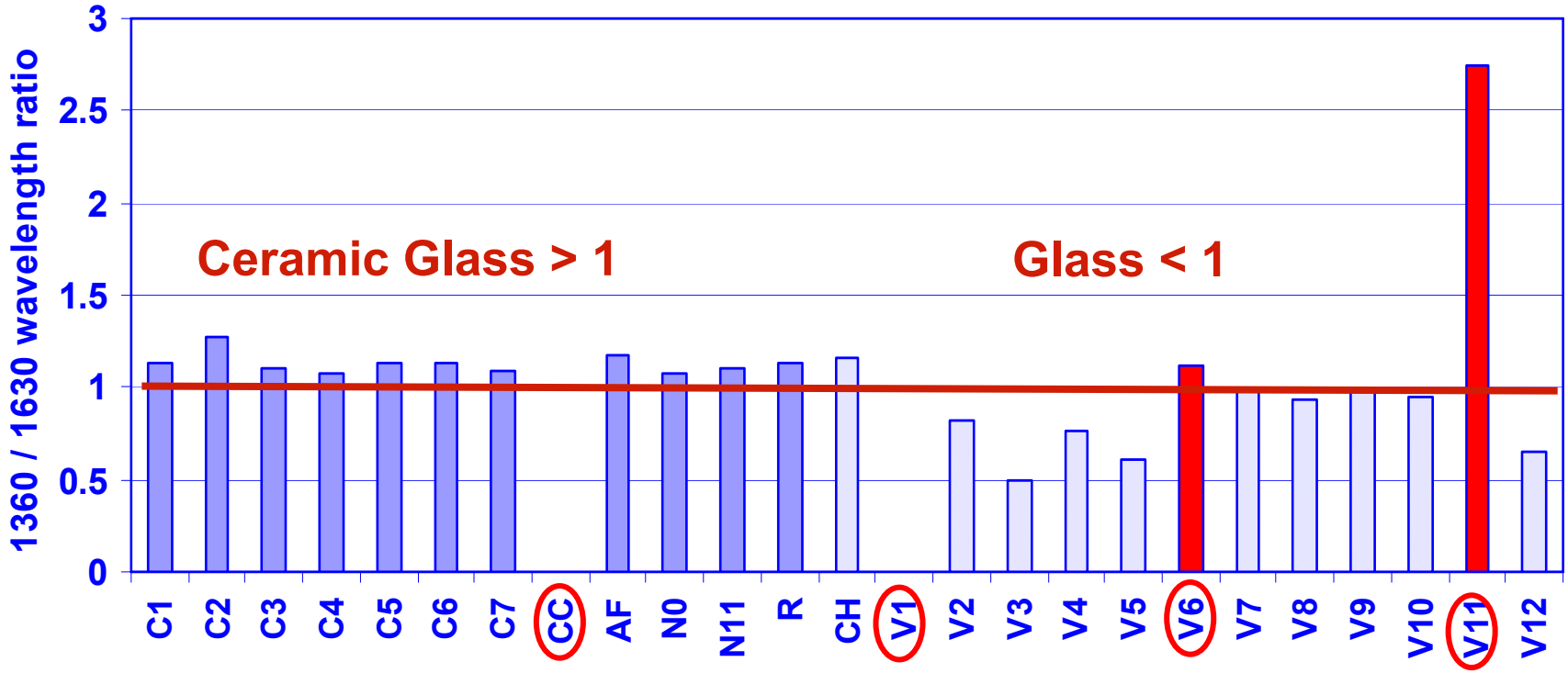
1360/1630 wavelength ratio



Using the ratio between the reflectance values at 1360 and 1630 nm, the recognition of most of ceramic glass and glass samples is performed, with the exception of four samples (CC, V1, V6, V11).

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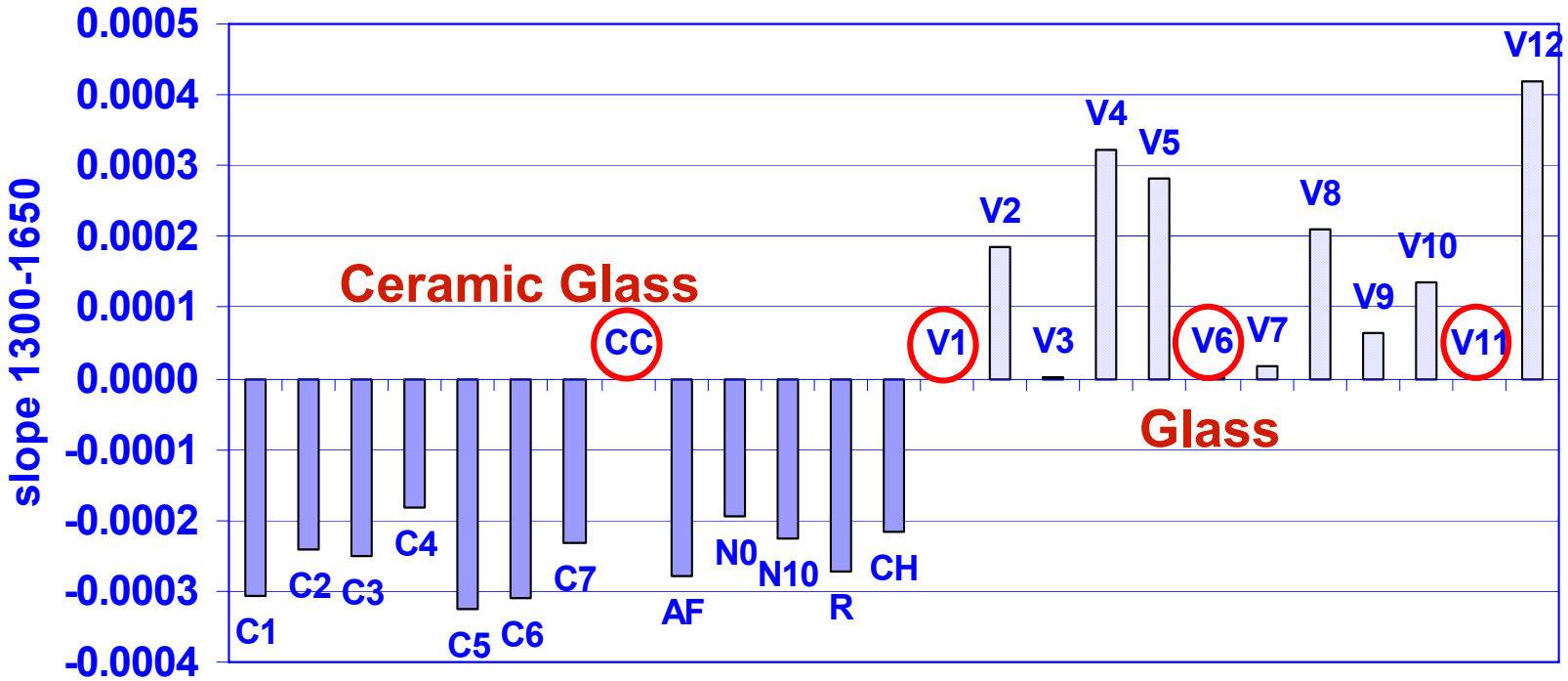
Slope from 1300 to 1650 nm



Using the slope of the curve in a predefined wavelength range, in this case from 1300 to 1650 nm, the recognition between glass and ceramic glass fragments is realized, with the exception of four samples (CC, V1, V6, V11).

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Summary of results

All samples

Wavelength ratio	Errors	
	Ceramic glass	Glass
500/680	N11	V6
760/650	C1 C2 CC CH	-
1360/1630	CC	V1 V6 V11
Slope 1300-1630	CC	V1 V6 V11

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Summary of results

No dark samples

Wavelength ratio	Errors	
	Ceramic glass	Glass
500/680	N11	-
760/650	C1	-
1360/1630	-	V11
Slope 1300-1630	-	V11

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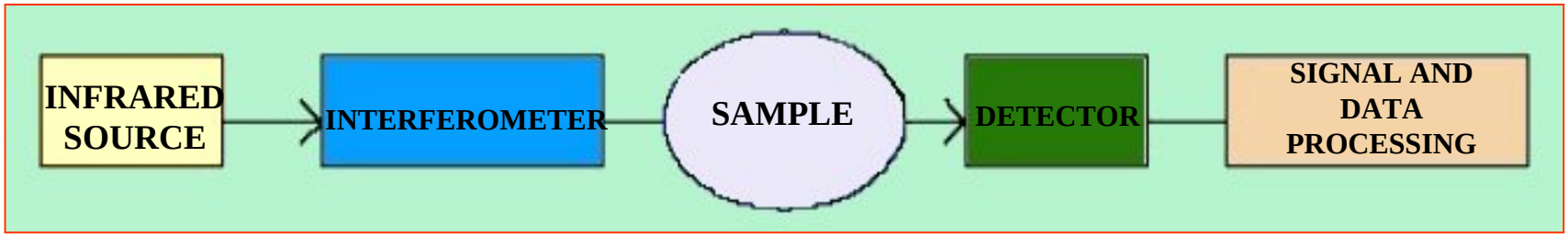
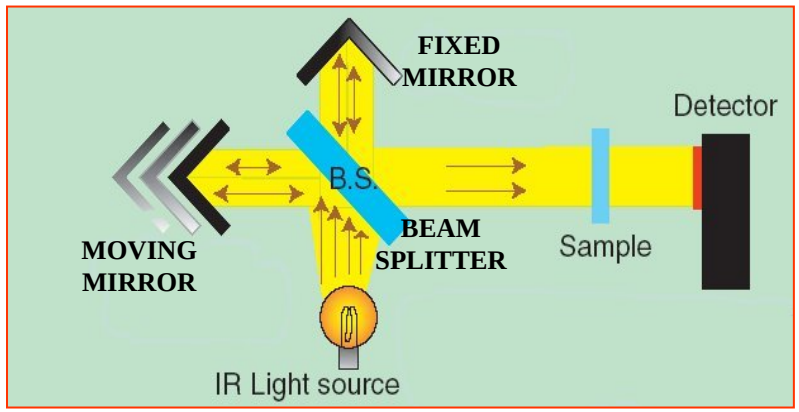
FT-IR Spectroscopy



A typical FT-IR spectrometer consists of a radiation source, a modulator (interferometer), a sample compartment, a detection unit and an electronic and computing unit.



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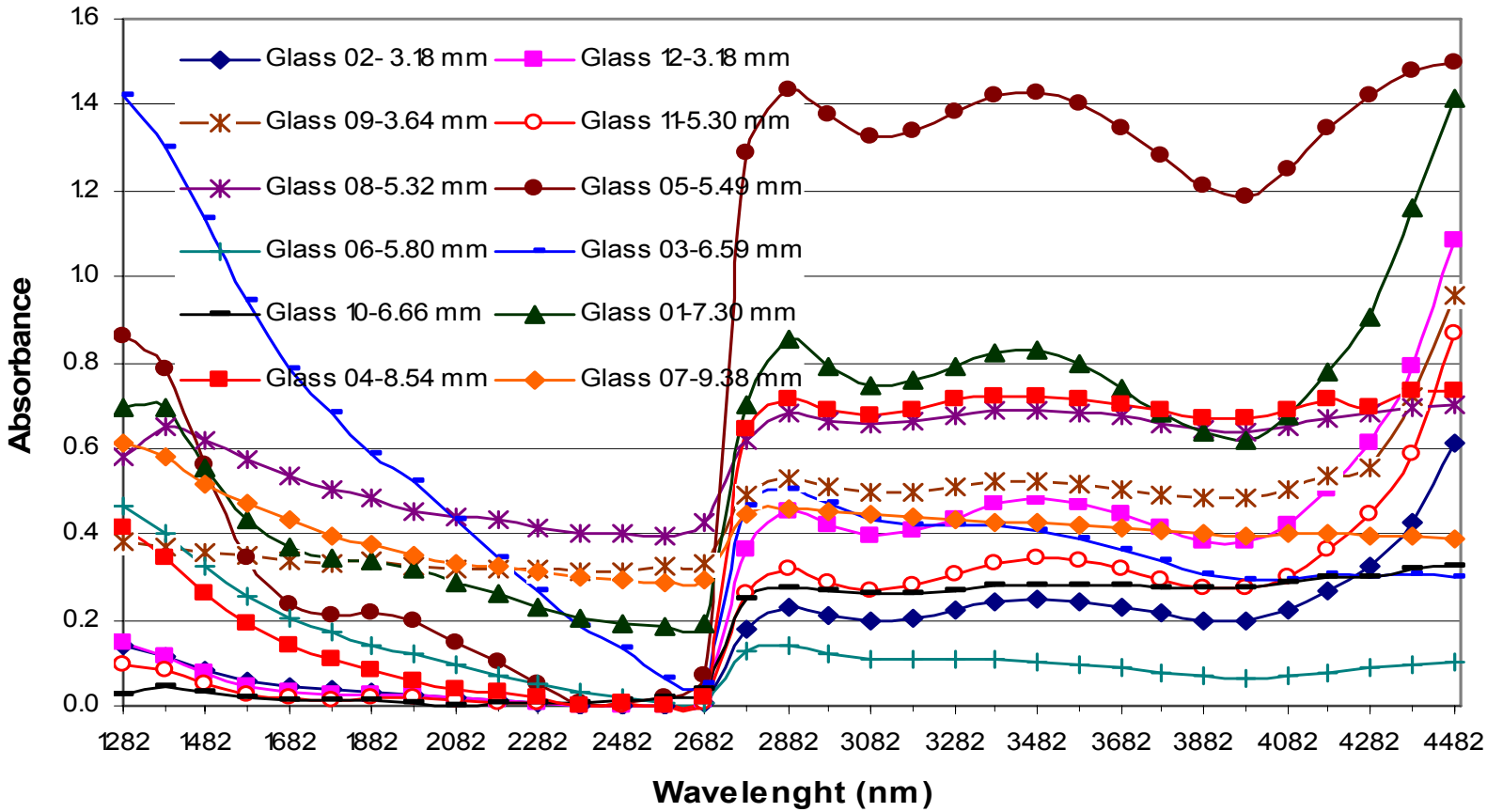
NIR-MIR field (1300-4500 nm)

Glass spectra



The absorbance spectra of glass cullets present a marked decrease of values up to 2700 nm, then a rapid increase, maintaining a constant value up to about 4500 nm.

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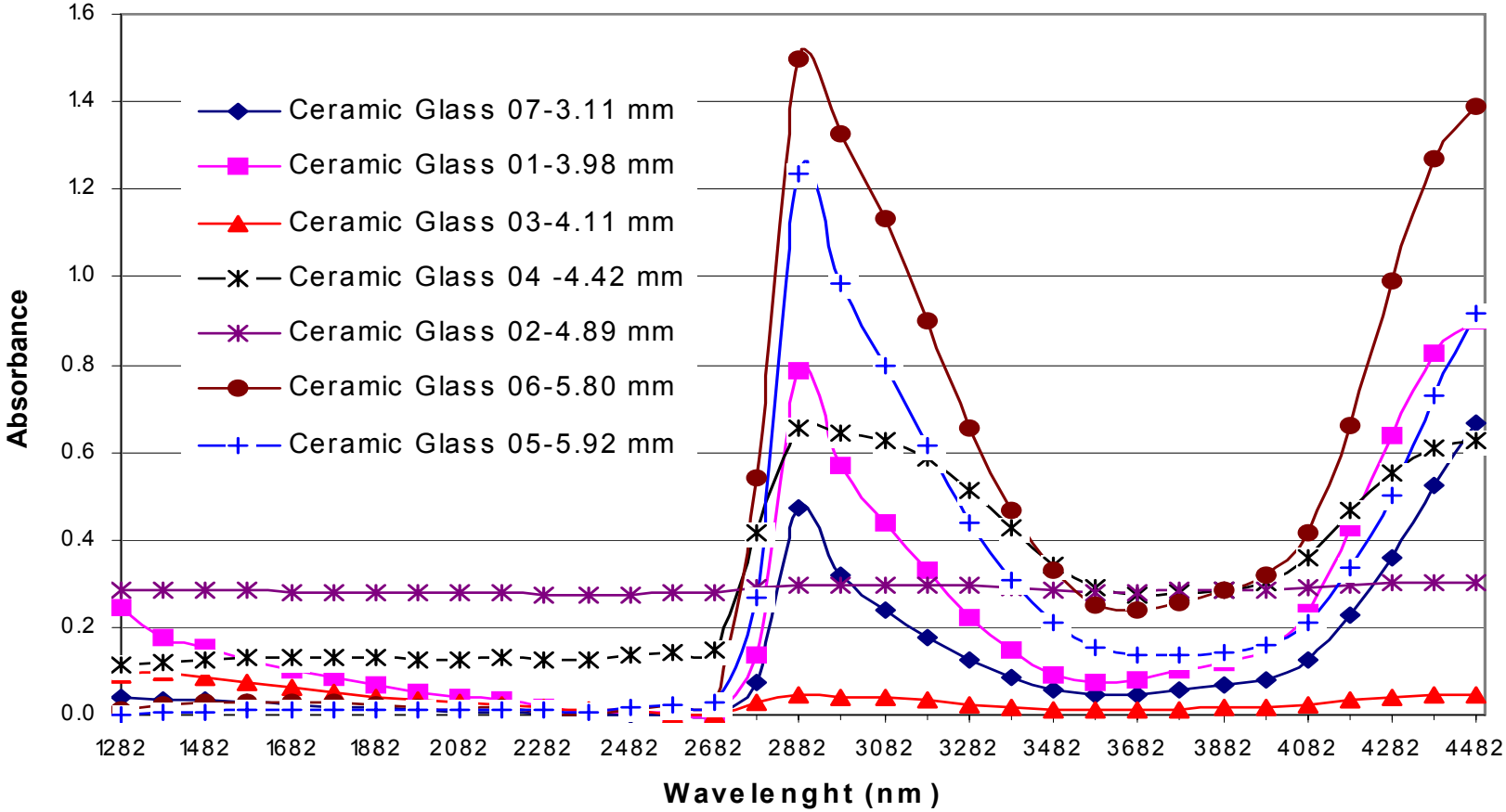
NIR-MIR field (1300-4500 nm)

Ceramic Glass spectra (1)



Ceramic glass fragments present a constant low value up to 2700 nm, then there is a marked peak (at about 2900 nm) and a second peak is detectable around 4500 nm.

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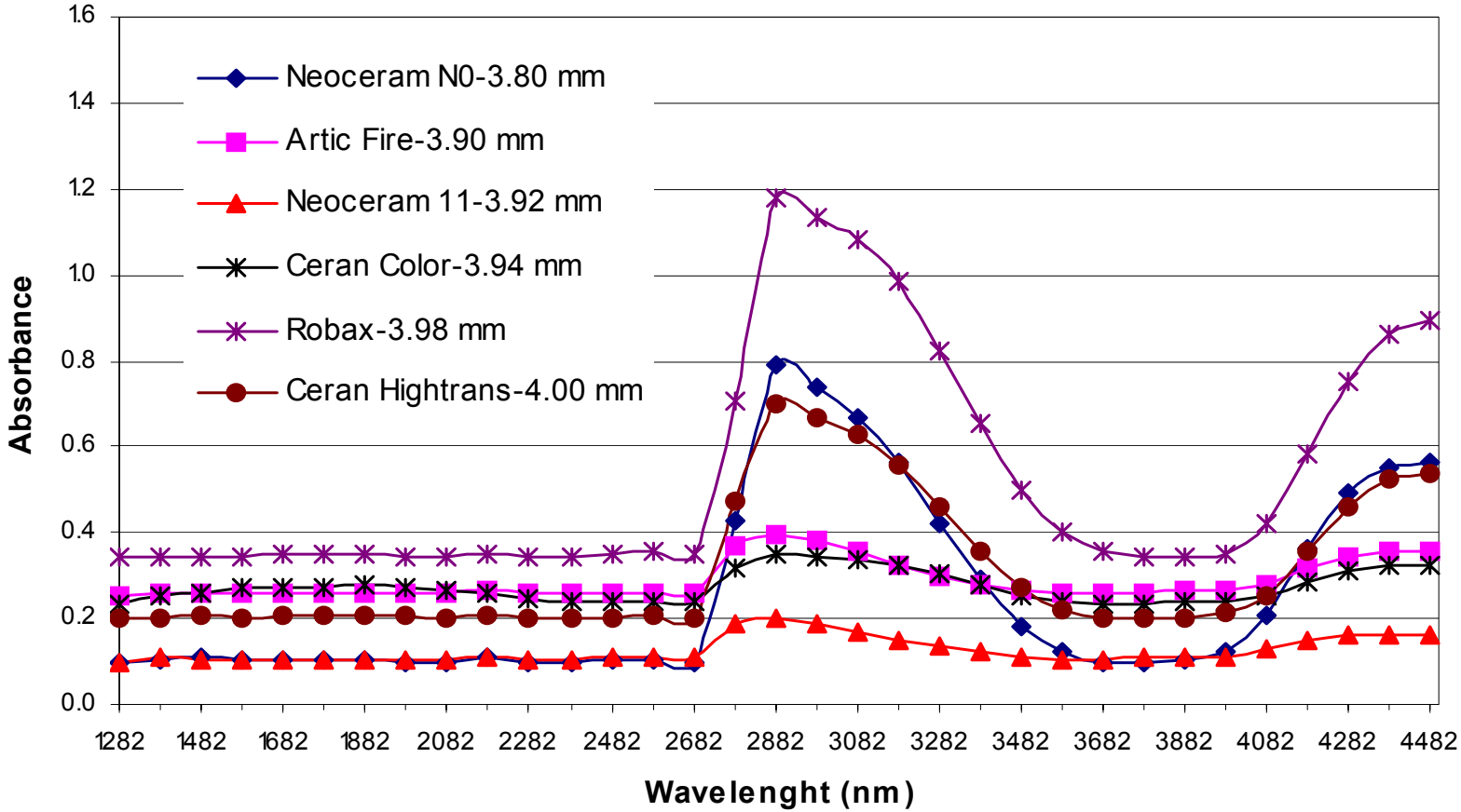
NIR-MIR field (1300-4500 nm)

Ceramic Glass spectra (2)



Ceramic glass fragments present a constant low value up to 2700 nm, then there is a marked peak (at about 2900 nm) and a second peak is detectable around 4500 nm.

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New collected samples

The following typologies of glass and ceramic glass samples have been collected inside the glass recycling plant by Reiling Glass.

- **Flat-Glass (FG)**
- **Coloured Container-Glass (CG)**
- **White Container-Glass (WG)**

- **White ceramic glass (GC-A)**
- **Amber ceramic glass (GC-B)**

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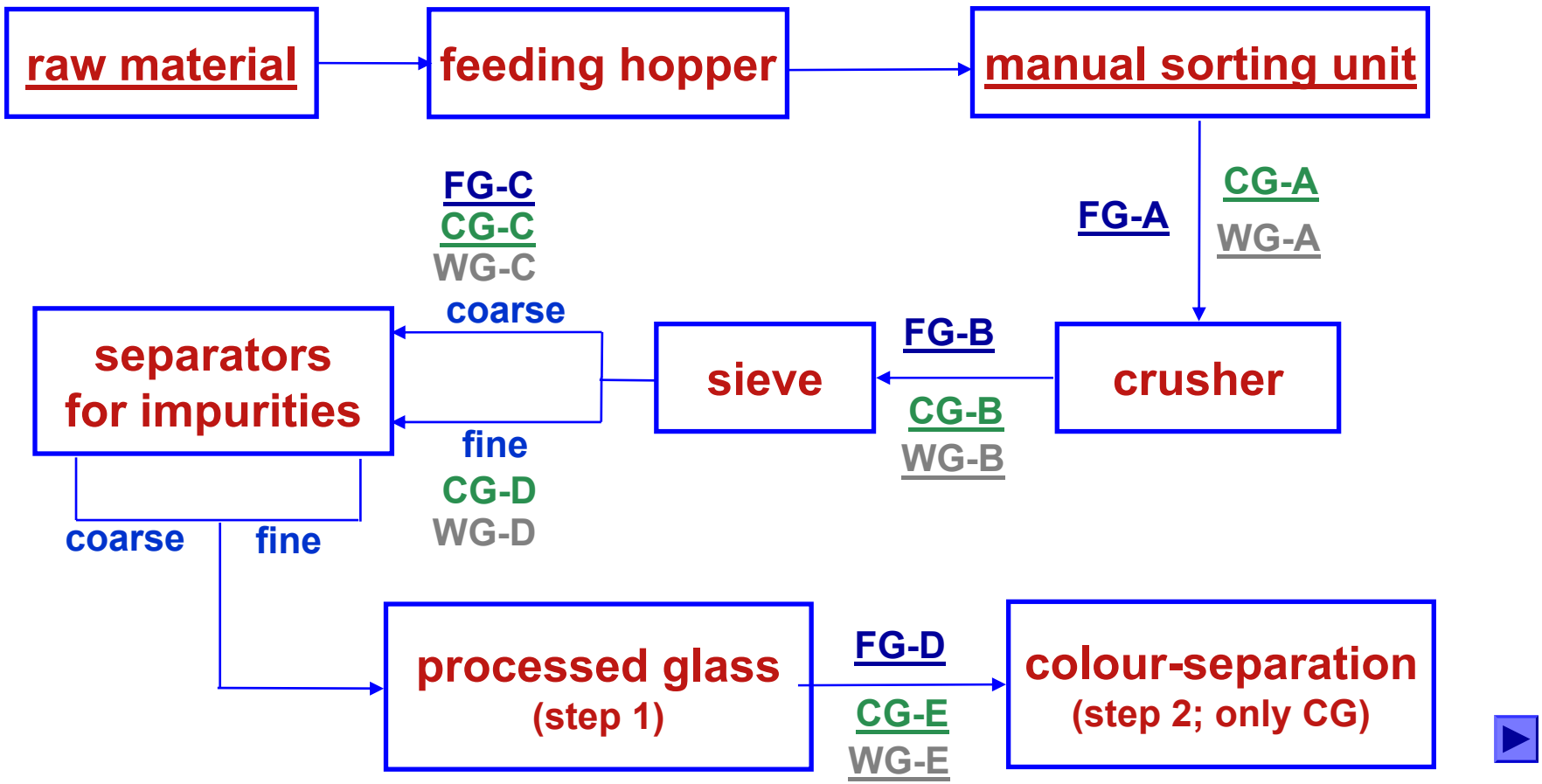
The sample collection points



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Sample Collection

Raw Material

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Sample Collection

Manual sorting

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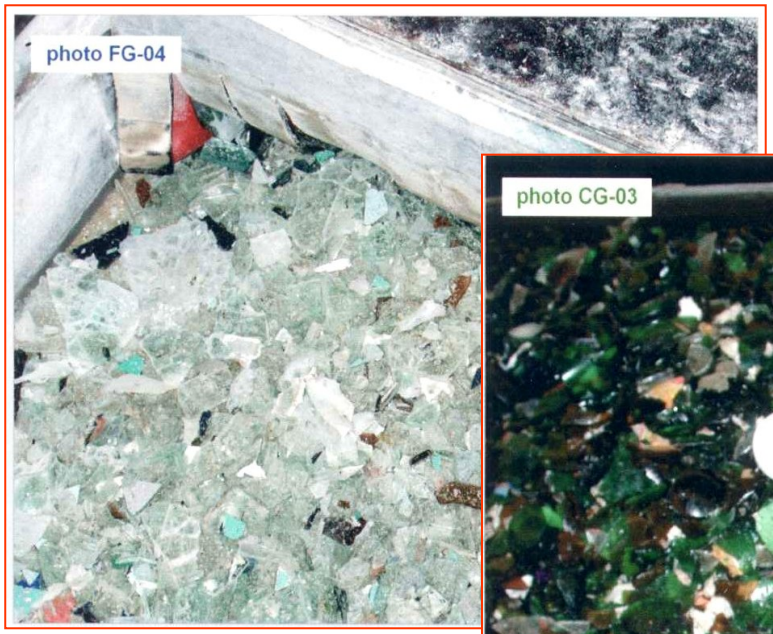
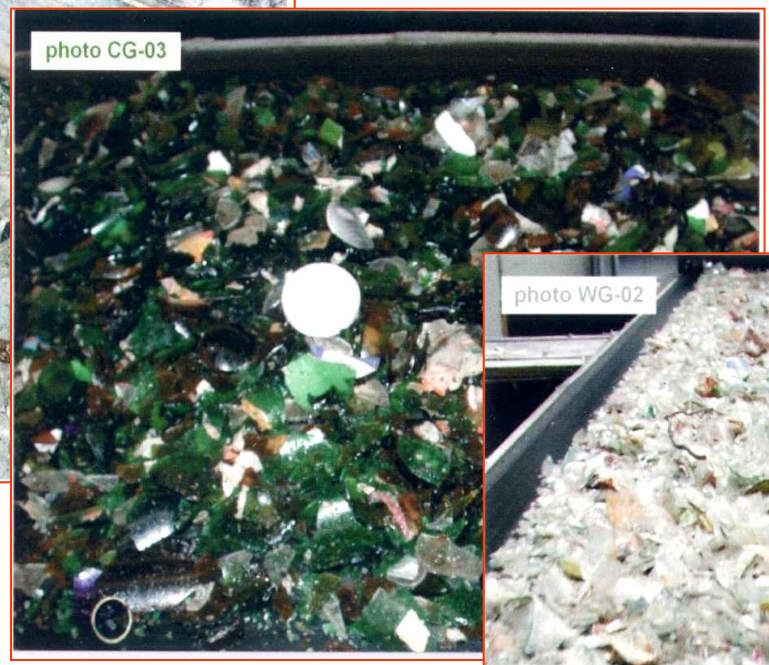
Sample Collection

Before the Crusher





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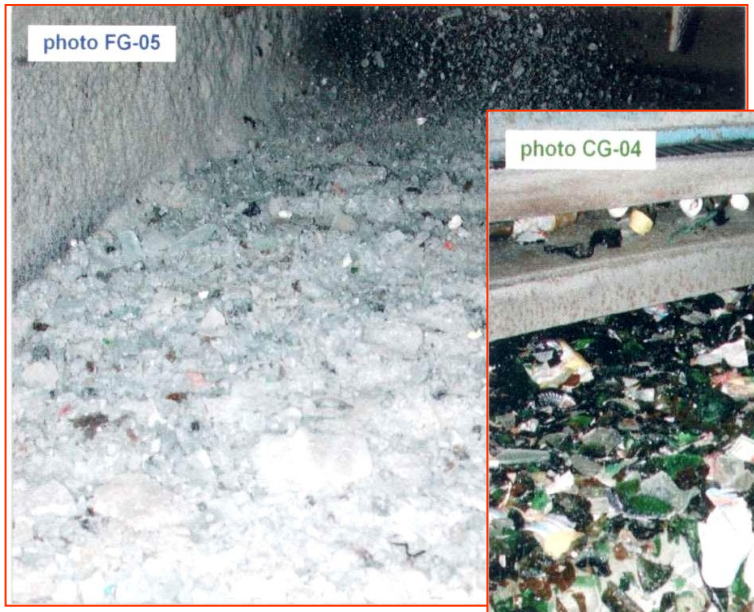
Sample Collection

After the Crusher



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Sample Collection

Before Separator Sections

flat glass
coarse grain

coloured container glass
coarse and fine grain

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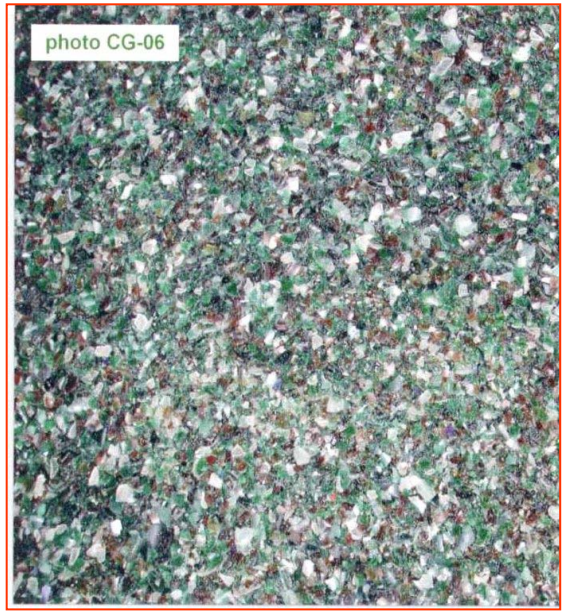
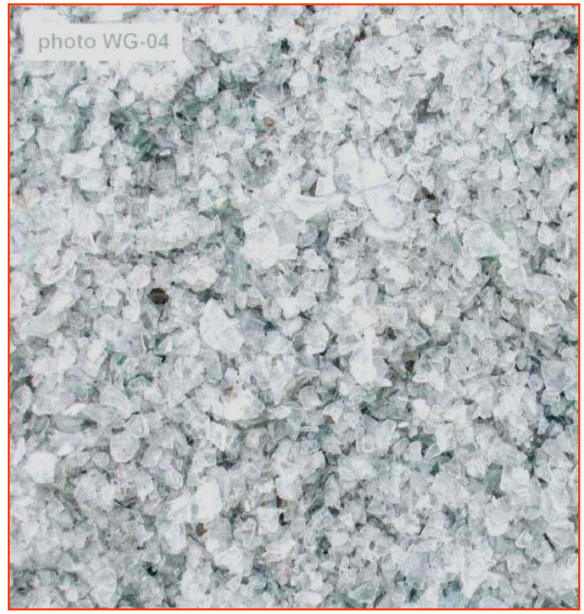
Collection of Processed Glass

flat glass



coloured container glass



white container glass

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Sample Selection

A total of 176 samples have been selected and analysed by FT-IR:

- **10 representative glass fragments for each cullet typology and for each sampling position for a total of 110 samples**
- **2 sets of 6 glass samples of similar green colour but different thickness from coloured container glass CG-C and CG-E**

- **40 representative samples of transparent white ceramic glass**
- **14 representative samples of amber ceramic glass**

The absorbance spectra have been acquired first on dirty glass and ceramic glass samples and after washing them (338 spectra have been acquired and analysed).

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Flat Glass FG-A

Source Glass

Selected Samples

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Coloured Container Glass CG-A

Source Glass

Selected Samples

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Coloured Container Glass CG-B

Source Glass

Selected Samples

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Coloured Container Glass CG-C

Source Glass

Selected Samples

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Coloured Container Glass CG-D

Source Glass

Selected Samples

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Coloured Container Glass CG-E

Source Glass

Selected Samples

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White Container Glass WG-A

Source Glass

Selected Samples

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White Container Glass WG-B

Source Glass

Selected Samples

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White Container Glass WG-C

Source Glass

Selected Samples

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White Container Glass WG-D

Source Glass

Selected Samples

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White Container Glass WG-E

Source Glass

Selected Samples

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Ceramic Glass RC-A

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Ceramic Glass GC-A

Source Glass

Selected Samples

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Ceramic Glass GC-B

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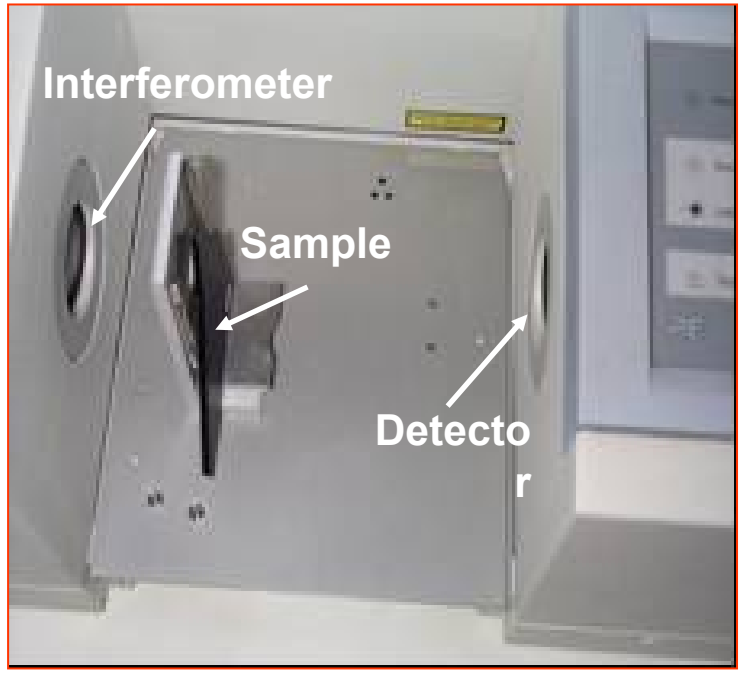
Utilized Equipment

Absorbance spectra have been acquired using an FT-IR spectrometer SPECTRUM-ONE™ by Perkin Elmer, selecting the wavelength range 2200-4500 nm.



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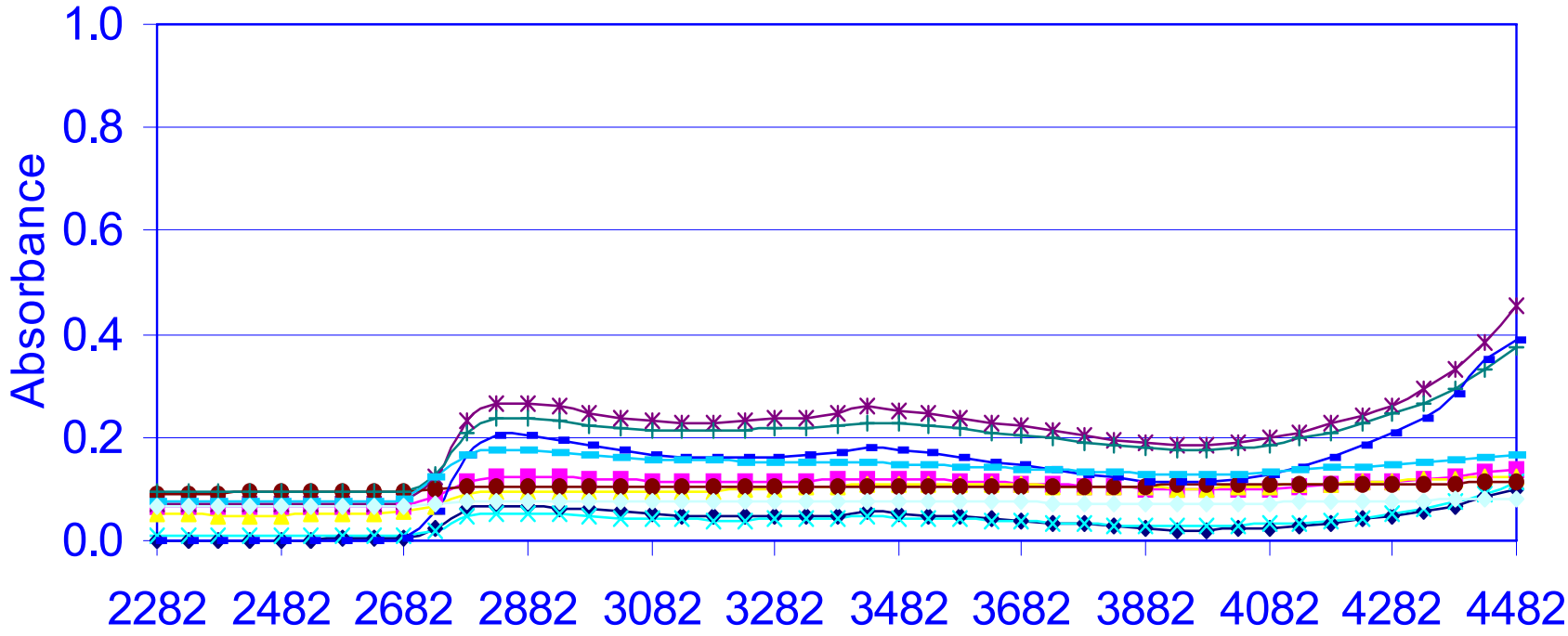
Absorbance Spectra

Glass Cullet

Dirty coloured container sample CG-B



The absorbance spectra of glass cullets are characterized by constant values up to 2700 nm, then they increase, maintaining more or less a constant value up to about 4500 nm.

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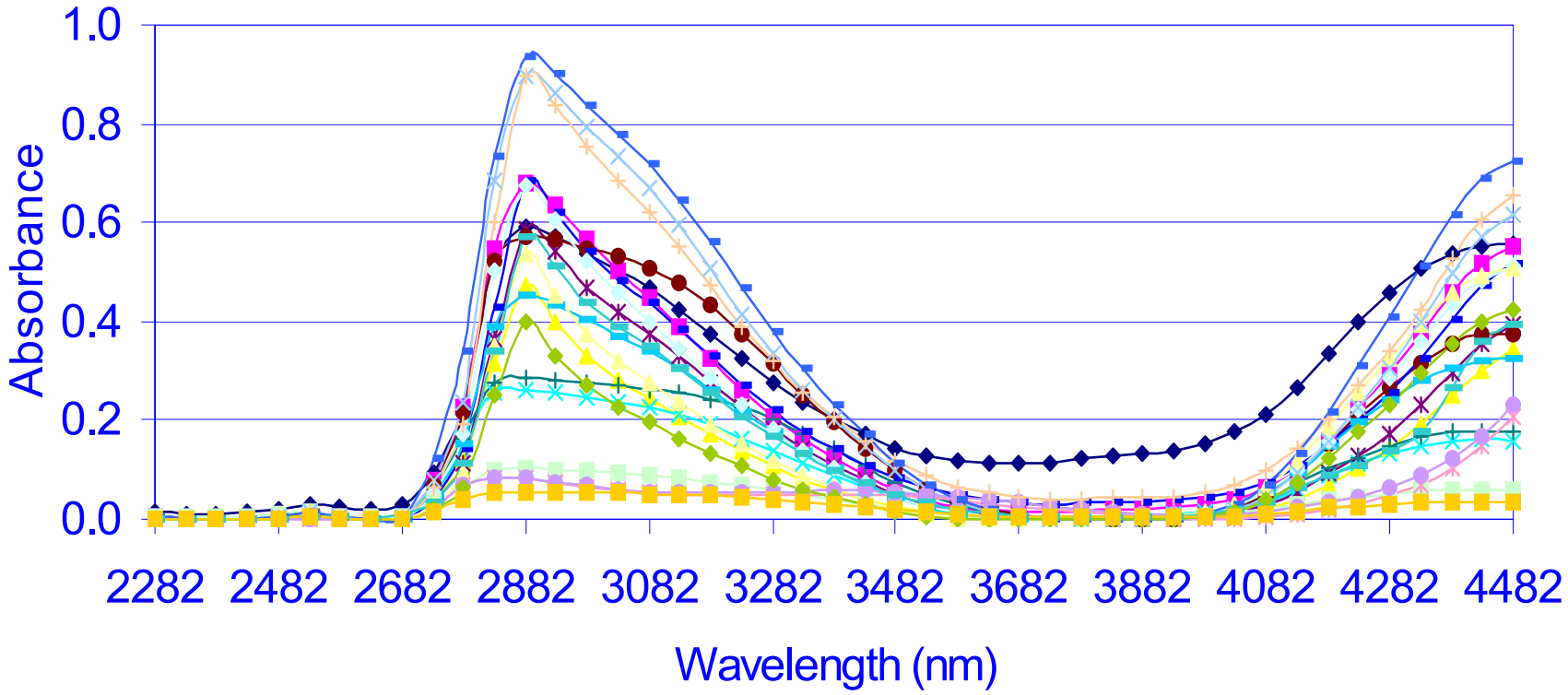
Absorbance Spectra

Ceramic Glass

Dirty white sample RC-A



The absorbance spectra are characterized by constant values up to 2700 nm, then there is a marked peak (at about 2880 nm) followed by a valley (3500-4000 nm) and a second peak moving towards 4500 nm.

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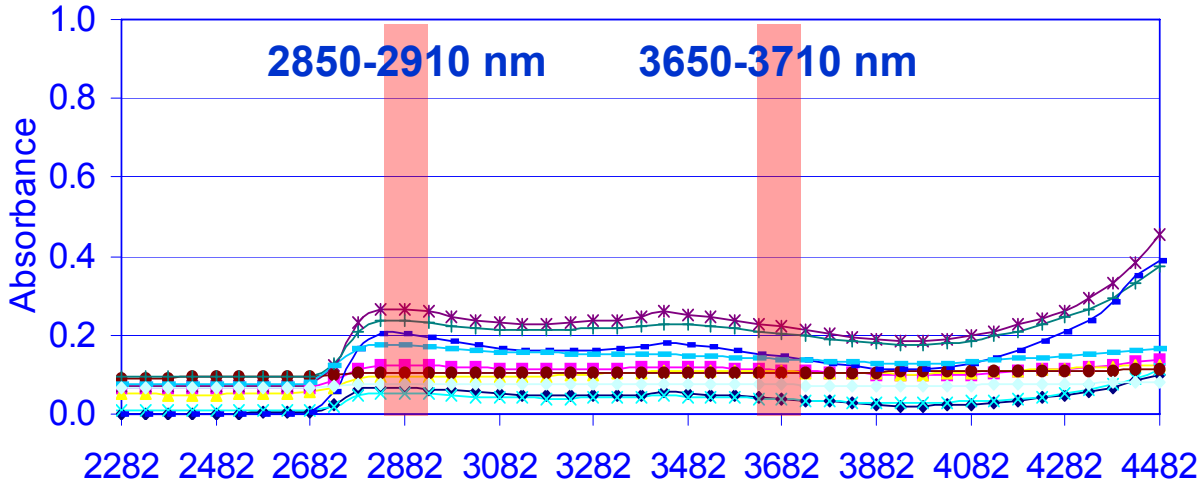
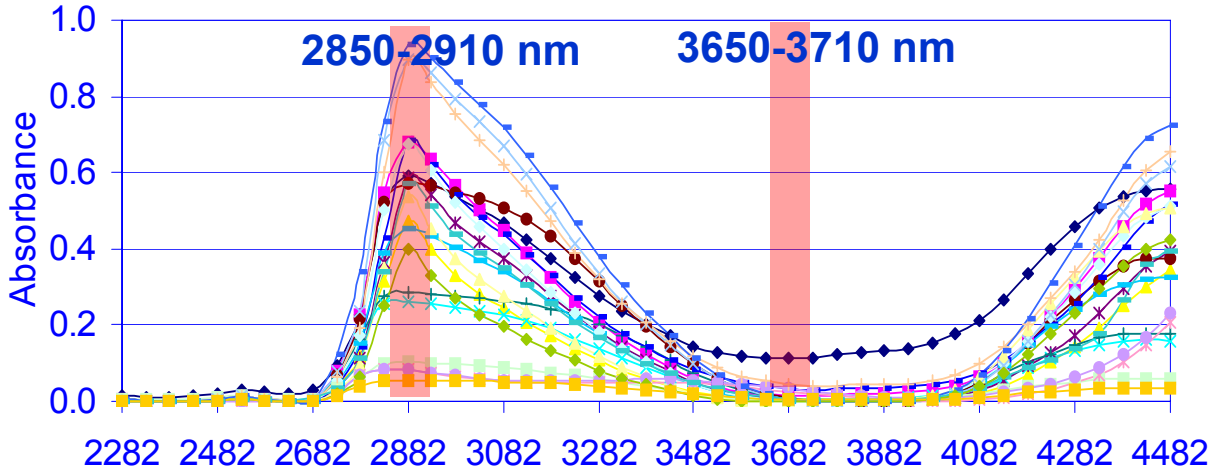
Absorbance Spectra

Glass and Ceramic Glass Comparison

Glass



Ceramic glass



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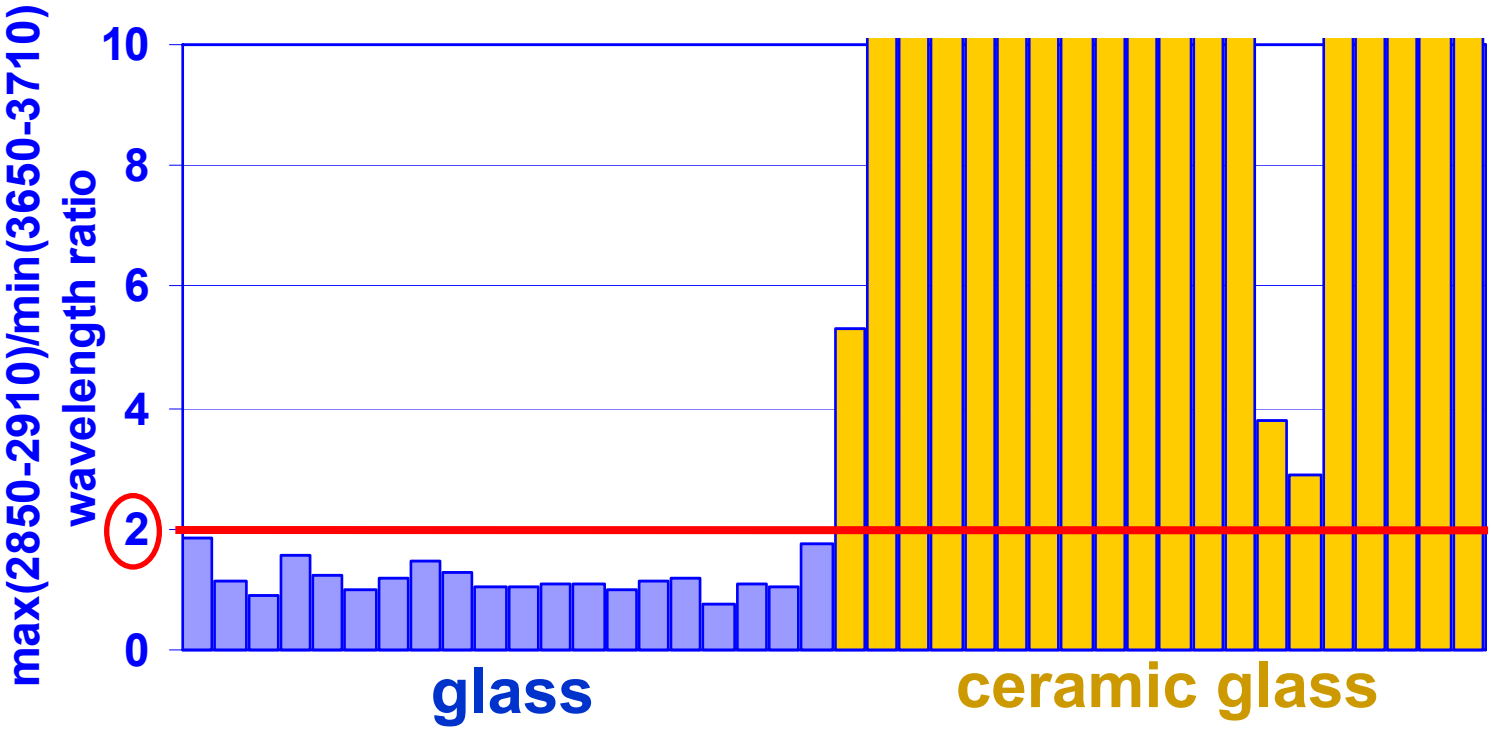
Glass and Ceramic Glass

Wavelength ratio: max 2850-2910/min 3650-3710



Glass samples are characterised by the wavelength ratio < 2 and ceramic glass samples by the wavelength ratio >2. Such result is valid for all the typologies of glass (white and coloured container and flat) and ceramic glass (white and amber).

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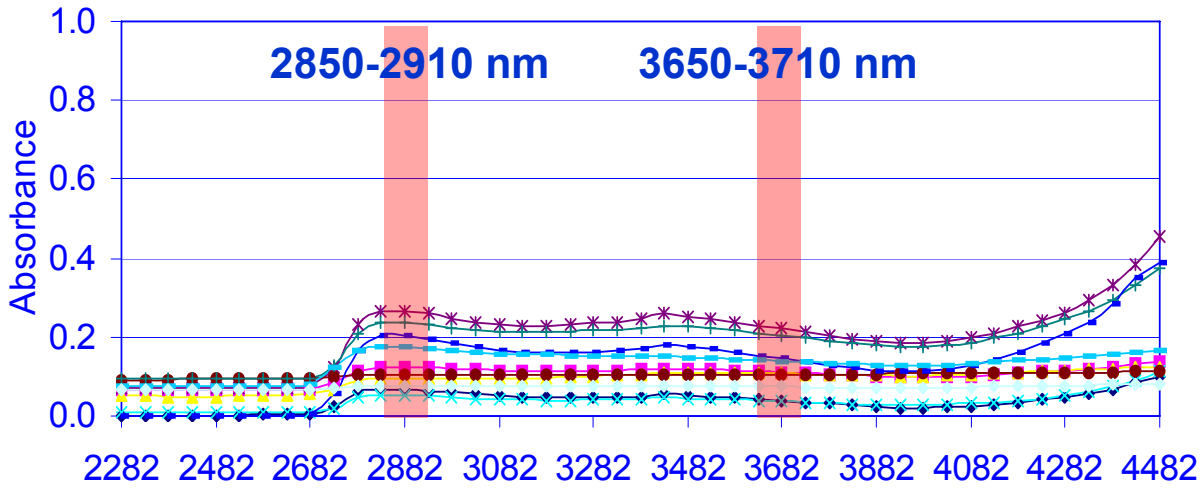
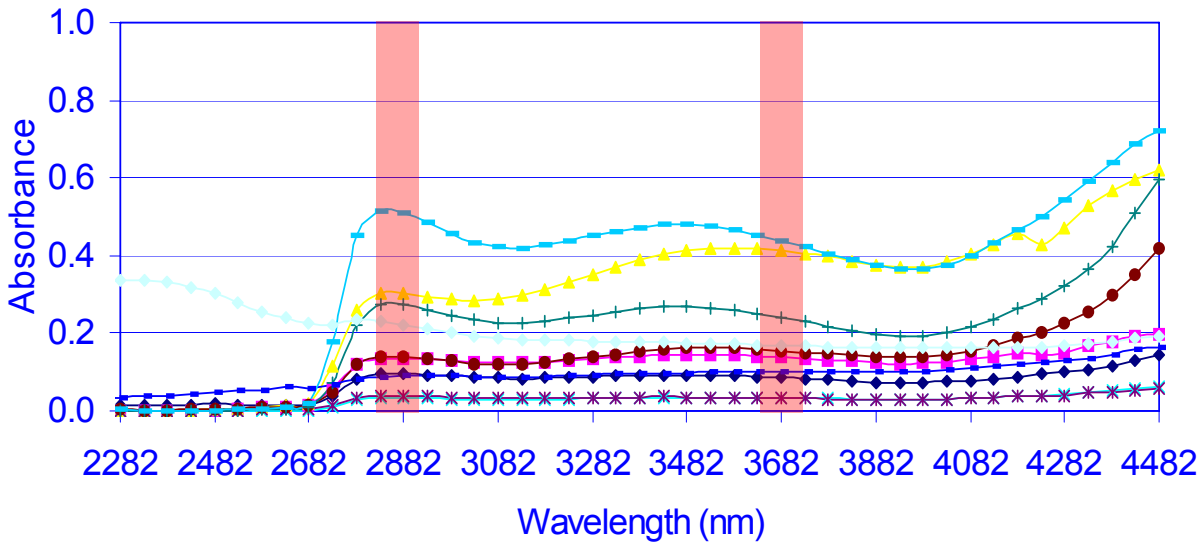
Absorbance Spectra

Dirt and clean glass fragments comparison

Dirty cullet



Clean cullet



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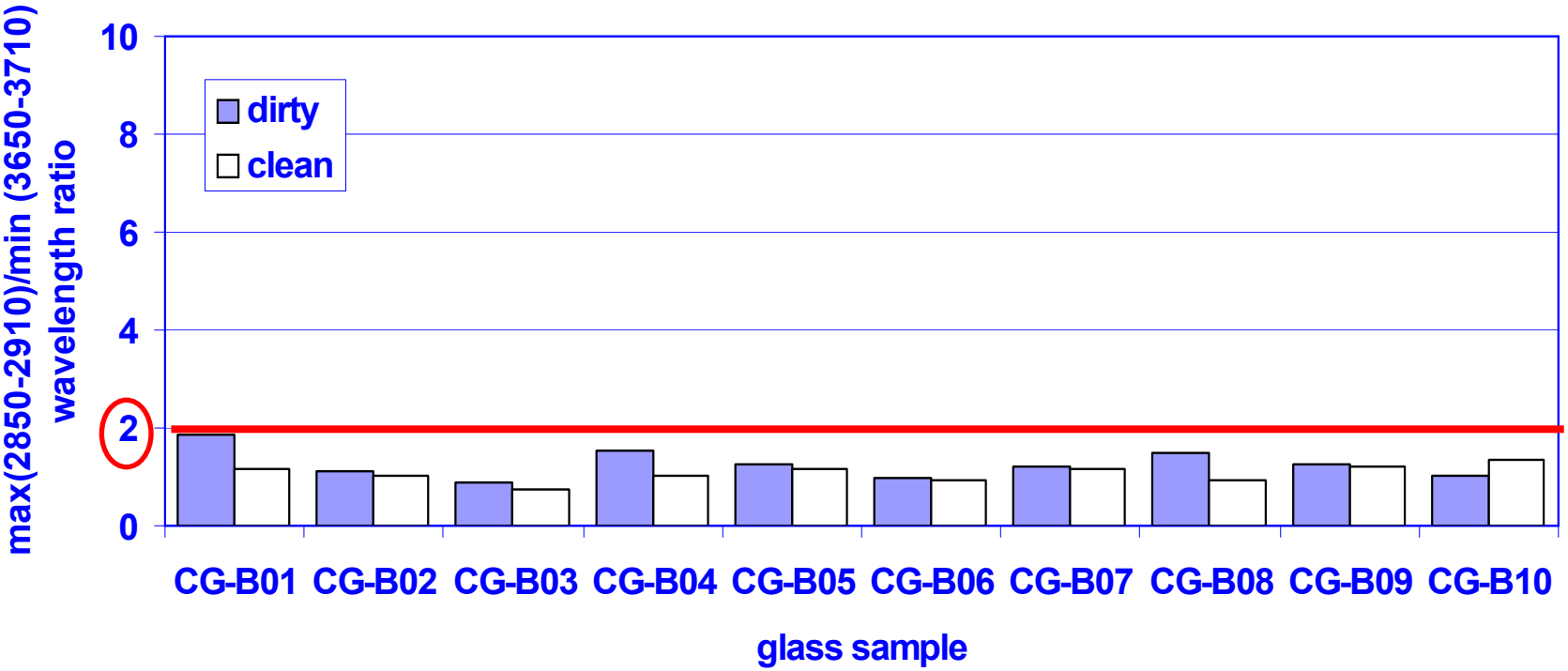
Dirty and clean glass cullet

Wavelength ratio: max 2850-2910/min 3650-3710



Both dirty and clean glass cullets are characterised by wavelength ratio between max value in the range 2850-2910 nm and min value in the range 3650-3710 nm < 2. Such result is confirmed for all the typologies of glass (white and coloured container and flat).

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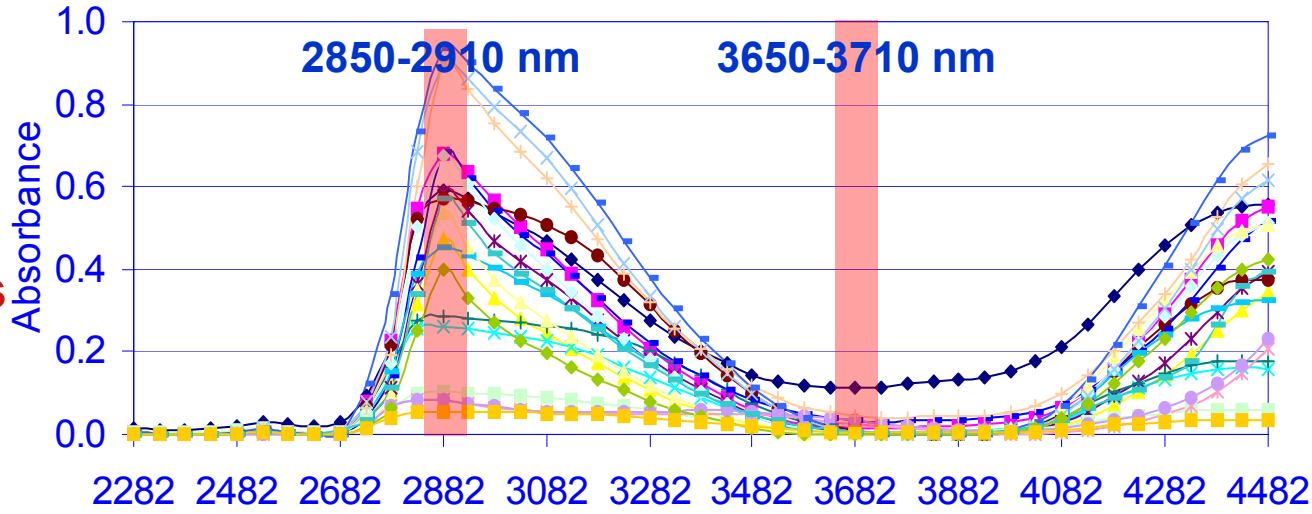
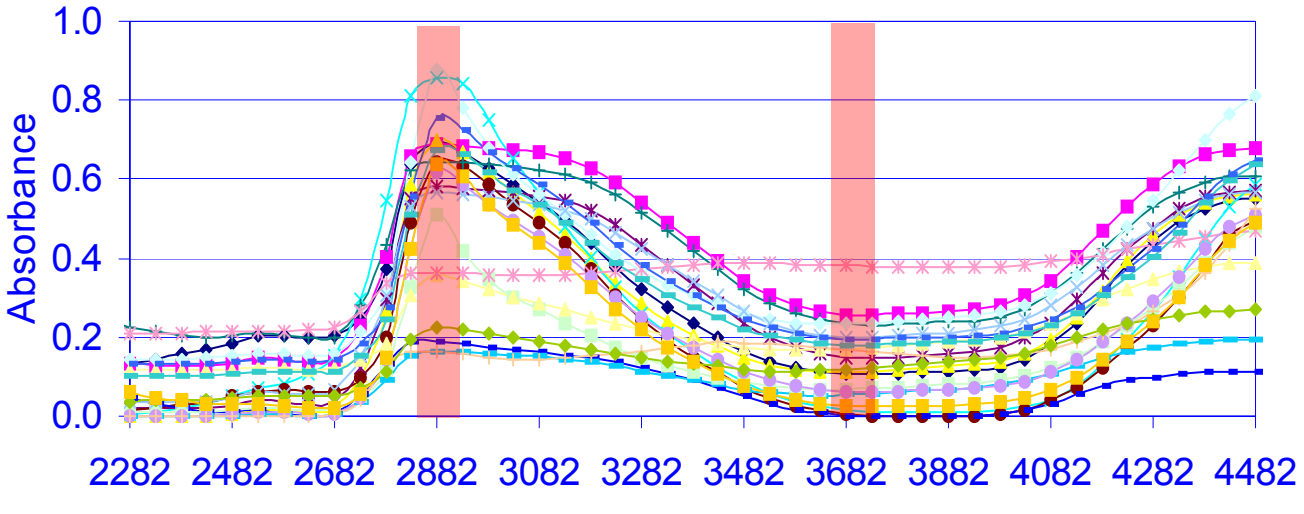
Absorbance Spectra

Dirt and clean white ceramic glass fragments comparison

Dirty white ceramic glass



Clean white ceramic glass



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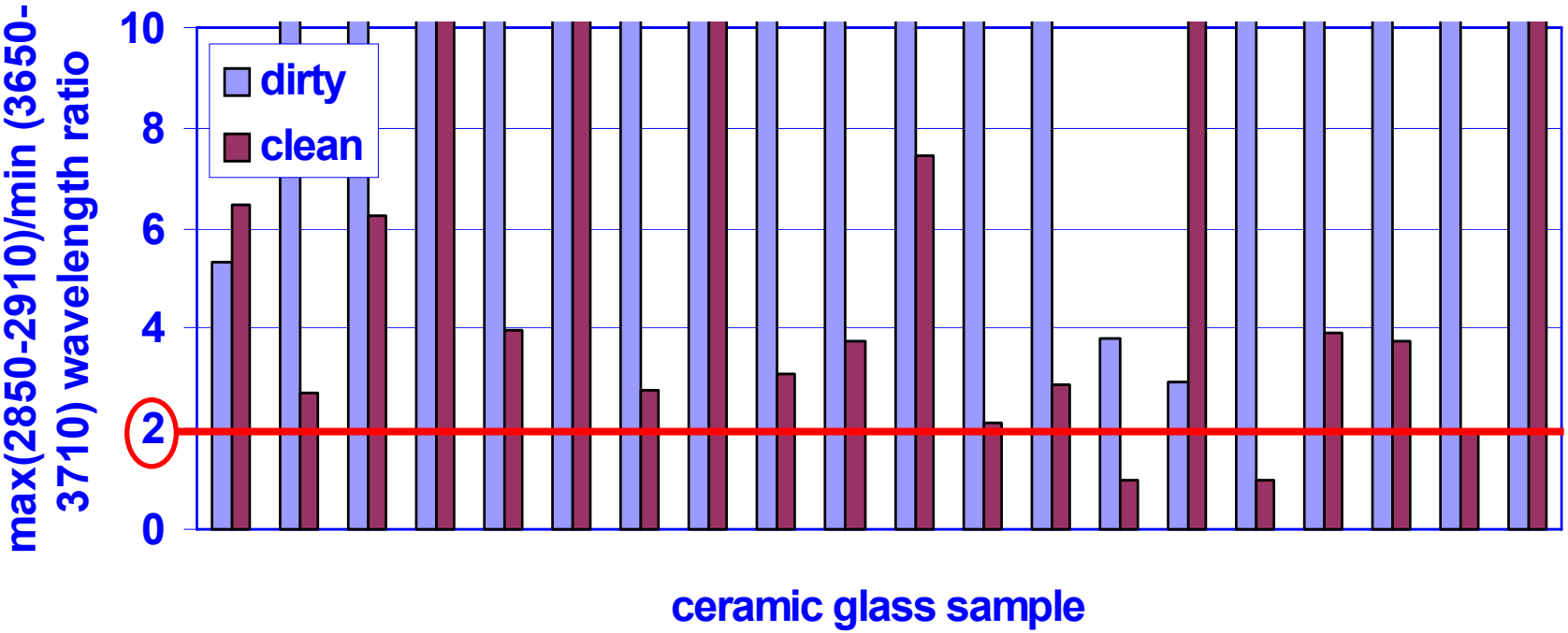
Dirty and clean white ceramic glass

Wavelength ratio: max 2850-2910/min 3650-3710



Both dirty and clean white ceramic glass samples are characterised by wavelength ratio between max value in the range 2850-2910 nm and min value in the range 3650-3710 nm > 2.

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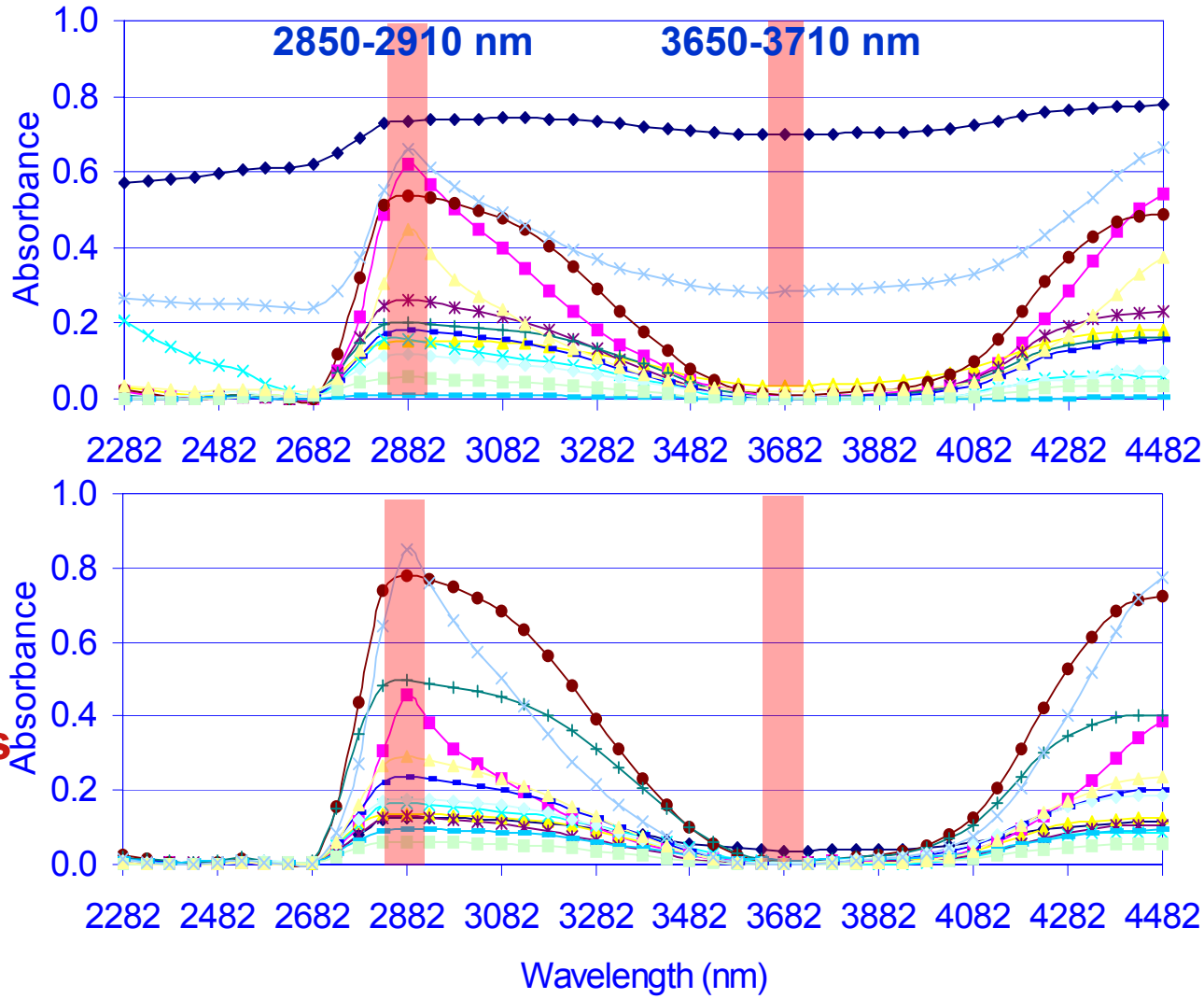
Absorbance Spectra

Dirty and clean amber ceramic glass fragments comparison

Dirty amber ceramic glass

Clean amber ceramic glass



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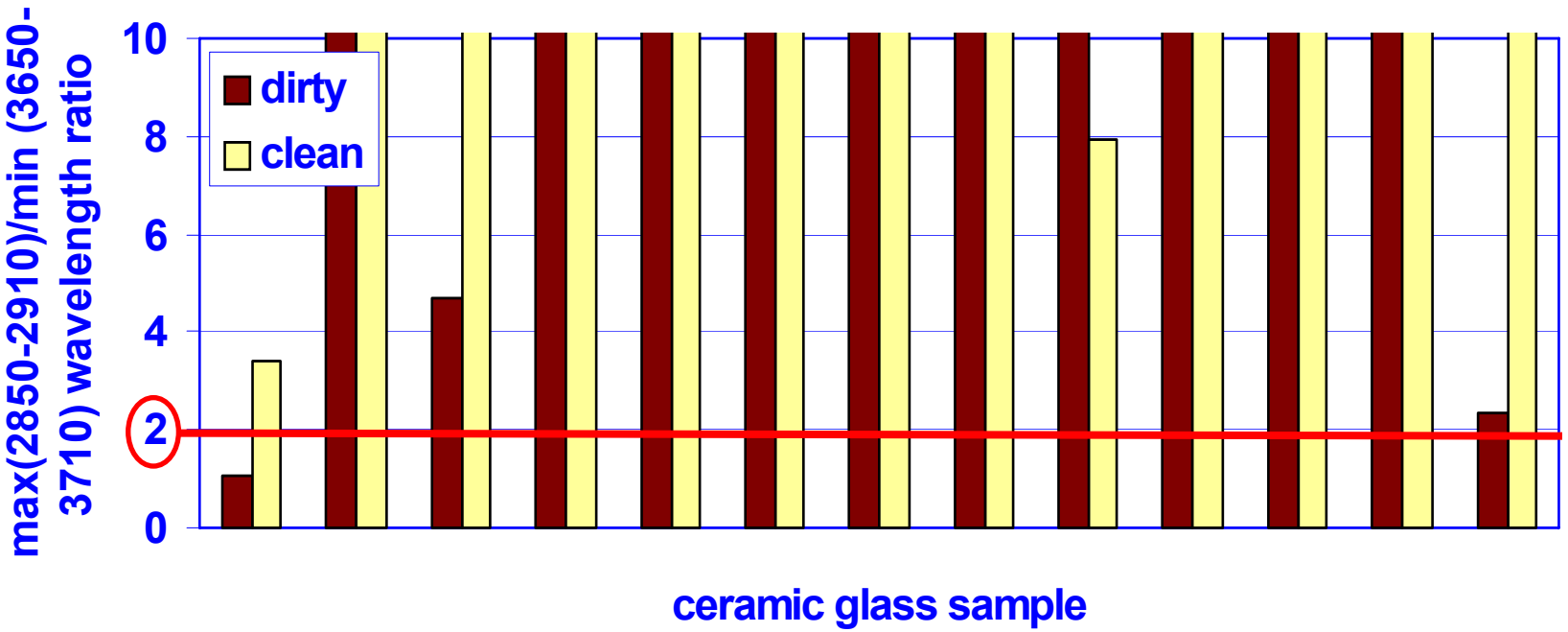
Dirty and clean amber ceramic glass

Wavelength ratio: max 2850-2910/min 3650-3710



Also amber ceramic glass samples are characterised by wavelength ratio between max value in the range 2850-2910 nm and min value in the range 3650-3710 nm >2.

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Summary of results

All samples

	Error dirty (%)	Error clean (%)
CG-A	10	20
CG-B	0	0
CG-C	6	19
CG-D	10	10
CG-E	6	0
Total CG	6	10
WG-A	0	10
WG-B	0	0
WG-C	0	10
WG-D	0	0
WG-E	0	30
Total WG	0	10
Total Glass	4	10

	Error dirty (%)	Error clean (%)
RC-A	0	15
GC-A	15	nd
Total GC White	7.5	nd
GC-B	7	0
Total Cer-Glass	7	nd

A total error on dirty glass of 5.5% means that just 6 out of 100 samples are rejected mistaking them for cer. glass.

In the same way, just 7 out of 100 ceramic glass samples could not be rejected and could be processed as glass.

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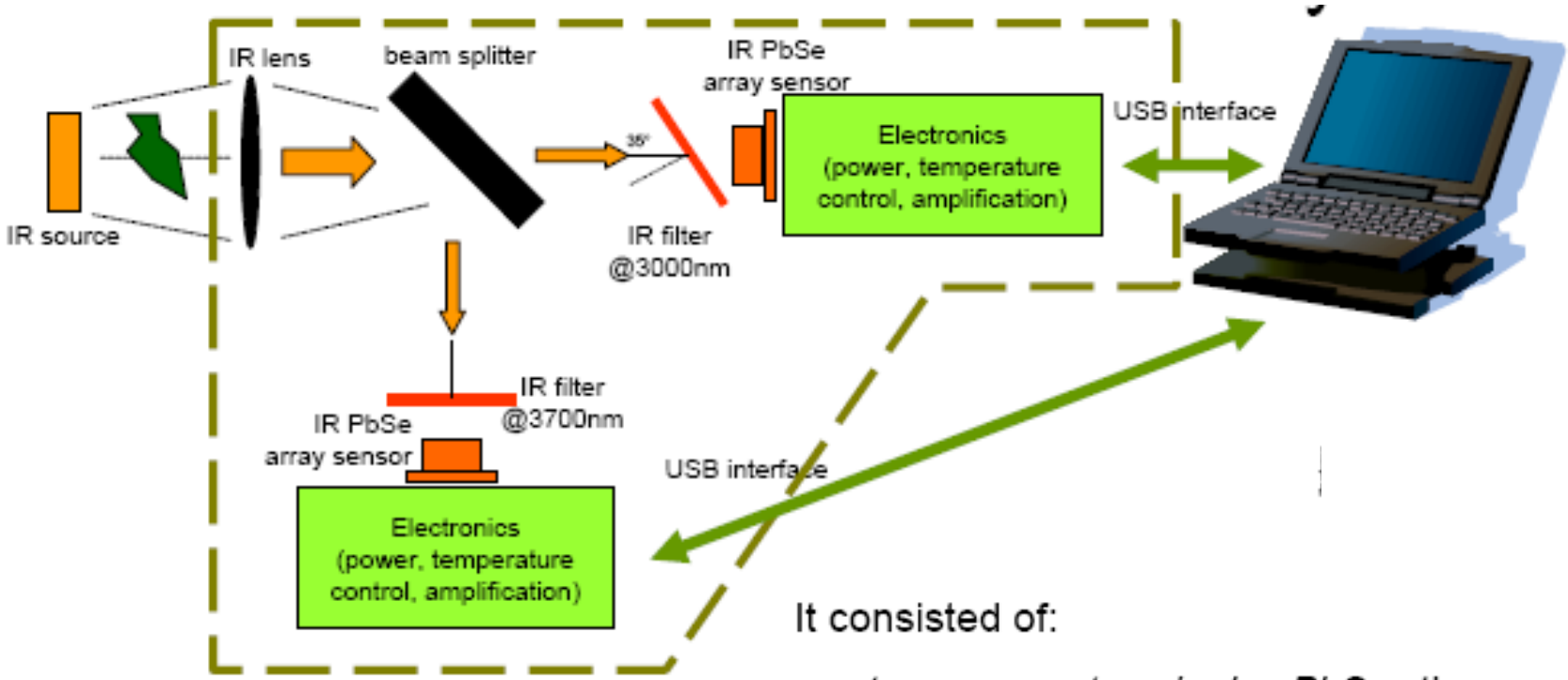
The developed prototype



It consisted of:

- *two separate single PbSe* thermo-electrically cooled single sensors
- *two different separate IR narrowband-bandpass filters*, centred in the two wavelength of interest
- a common *IR source*

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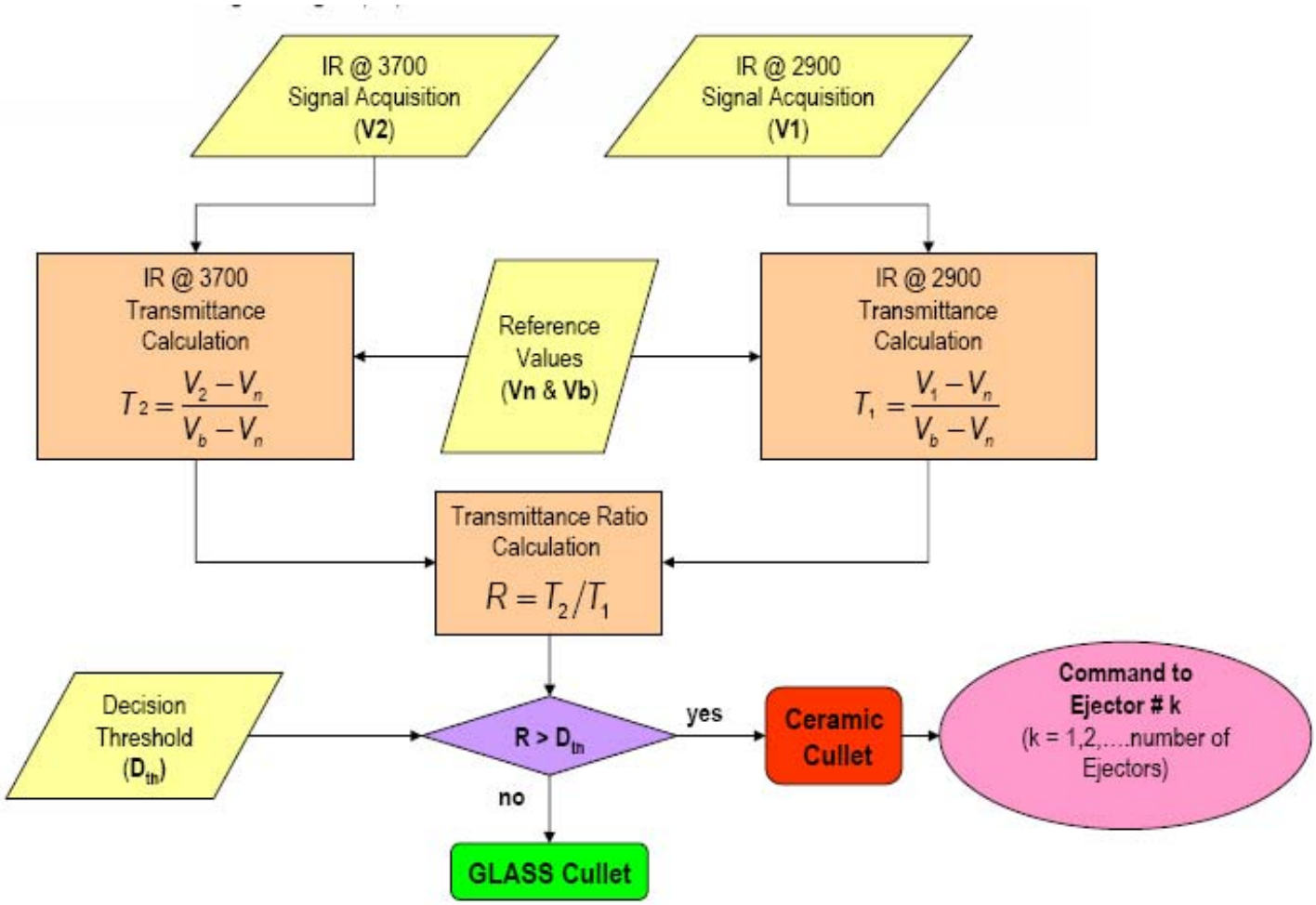
Selection logic



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