Laboratory of Inorganic and Analytical Chemistry
School of Chemical Engineering
National Technical University of Athens

Characterization of Refuse Derived Fuel using Thermogravimetric analysis and Chemometric techniques

Panagiotis Danias and Stylianos Liodakis

Laboratory of Inorganic and Analytical Chemistry, NTUA

- Inorganic Chemistry
  - Chemistry and technology of aluminosilicate compounds, cement and ceramics.
  - Chemistry high temperatures.
  - Chemistry and powder technology.
  - Recovery of metals from industrial waste.
  - Chemistry and manufacturing superconductors.
  - Use of industrial byproducts in the production of inorganic materials.
  - Use of inorganic materials in the environment.

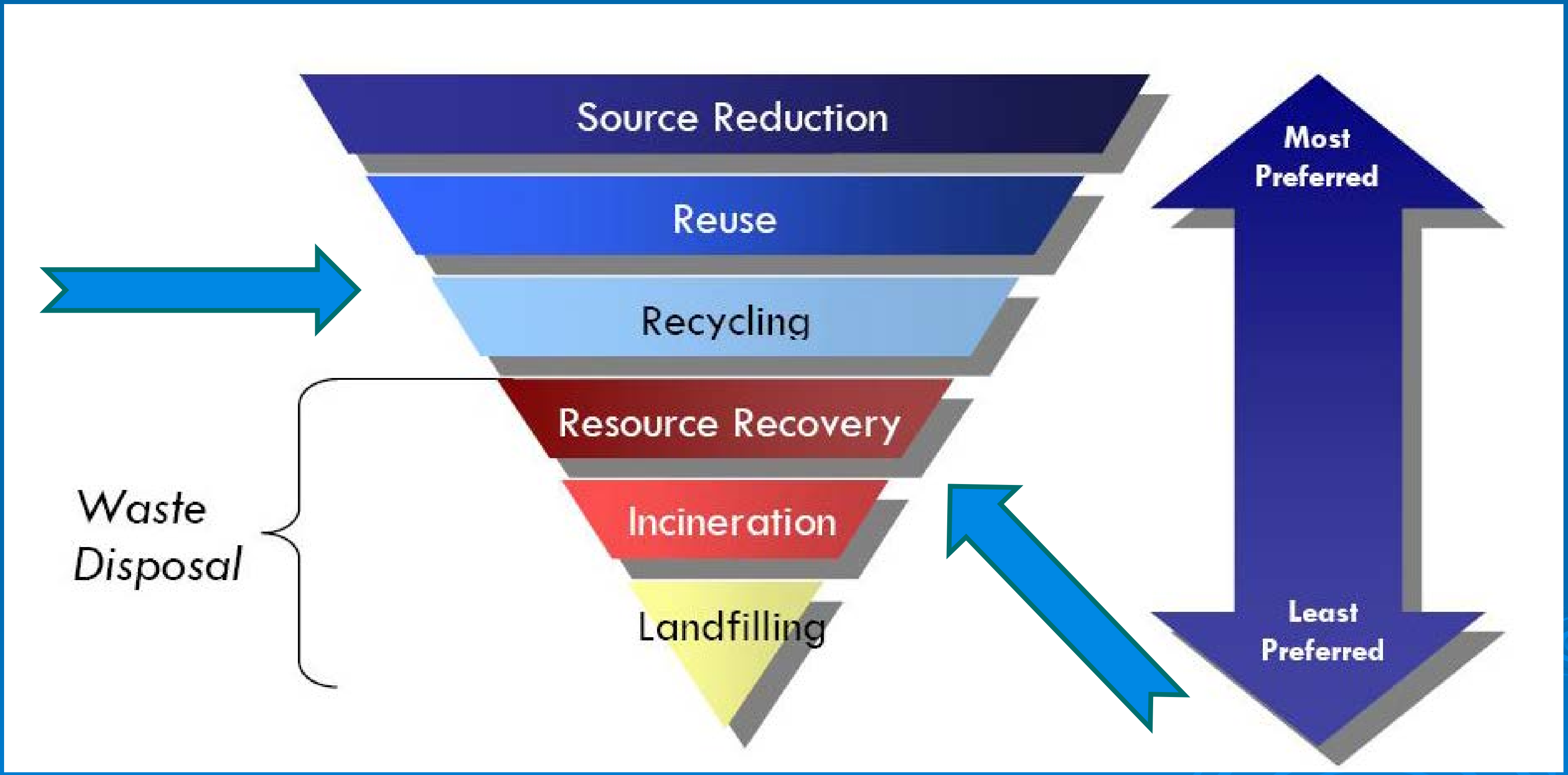
- Analytical Chemistry
  - Development of new analytical methodologies of materials properties with modern analytical techniques.
  - Using combined analytical techniques in complex analytical problems.
  - Analyses of environmental interest, such as field analyzes.
  - Design and assembling pieces of analytical instruments.

CATEGORIES OF SOLID WASTES

Most common waste streams produced from anthropogenic activities:

- paper
- cellulosic cloth
- yard waste
- food
- plastic
- leather and rubber
- metals
- glass
- ceramic and earthen materials

MUNICIPAL SOLID WASTE



Categorization of Solid Wastes

- Lignocellulosic residues (physical polymers),
- Plastics residues (chemical polymers),
- Refuse derived fuel (RDF) (mixture of physical and chemical residues).

Refuse Derived Fuel (RDF): “A nearly unlimited broad range of solid, liquid and gaseous waste materials from household, commerce, forestry, agriculture and industry, which have a certain calorific value, may be applied as ‘‘waste fuel’’ or ‘‘Refuse Derived Fuel’’ (RDF) in Waste to Energy (WtE).’’ (R. Sarc, K.E. Lorber).

Main characteristic is the high calorific fractions of the materials.

CHARACTERIZATION OF RDF

Tools and Analyses which have been used for the Characterization of RDF:

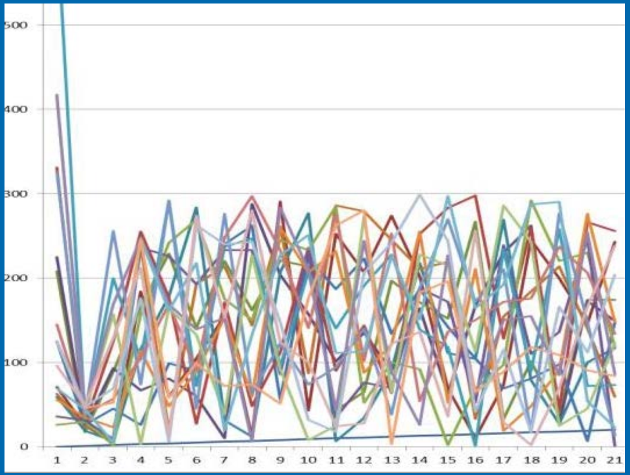
- Thermogravimetric Analysis **with**
- Ultimate Analysis
- Proximate Analysis
- Thermodynamic Modeling
- Gas , Liquid, Char Analysis
- Particle Size categorization
- Chemometric Technics

THERMOGRAVIMETRIC ANALYSIS (TGA)

- TGA offers the advantage to quantify the wood flour and polymer contents without the need to establish calibration curves, however, knowledge about the composition of the formulation is required.
- Reviewed literature indicate that a proper thermal pyrolysis method may be used for resolving the disposal problems and making an energy conversion from MSW.

MULTIVARIATE ANALYSIS (DATA MINING)

Why? If we have many data it is difficult to explain them.
Applications: Metabolomics (metabolic profile of humans), Drug Design, Toxicology, Process optimization, Ranking of microroganisms, materials, etc.



- Principal Component Analysis (PCA).
- Hierarchical Cluster Analysis.
- Non- linear mapping.

} Unsupervised

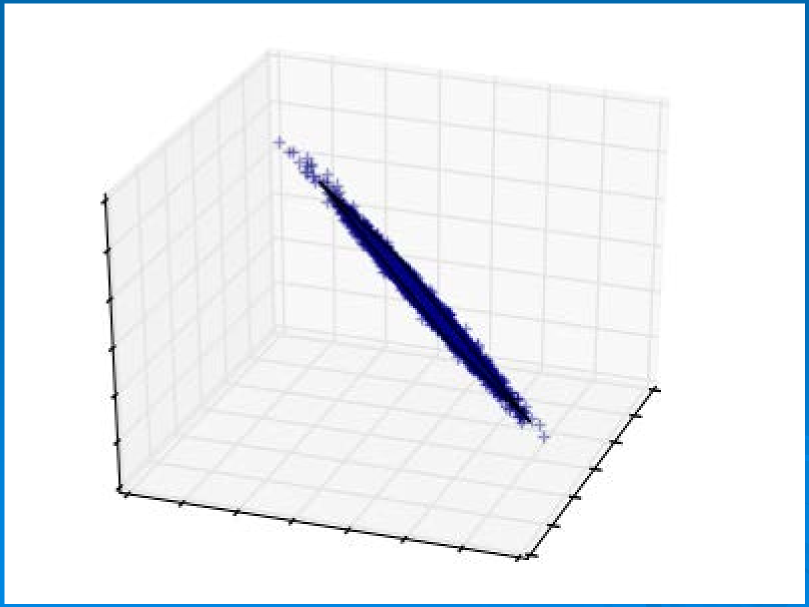
- Partial Least Square (PLS) Analysis.
- Partial Least Square Discriminant Analysis (PLS-DA)
- Neural Networks.

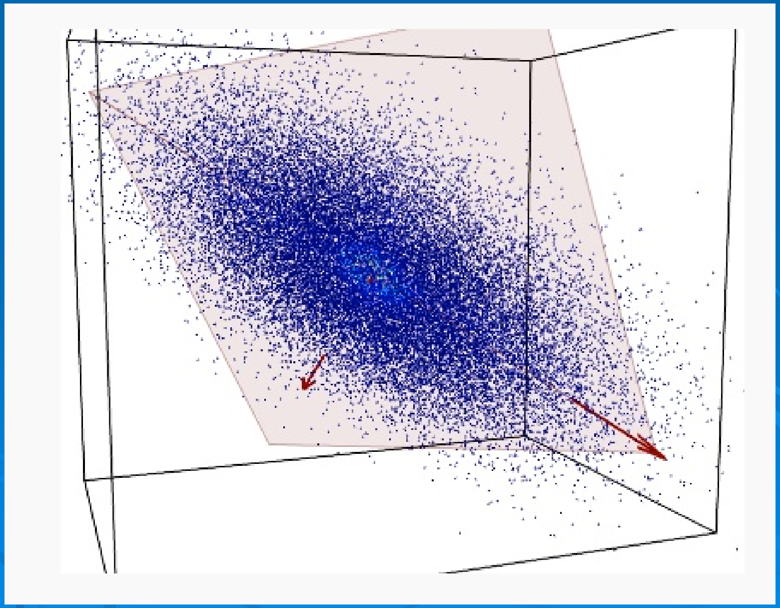
} Supervised

PRINCIPAL COMPONENT ANALYSIS

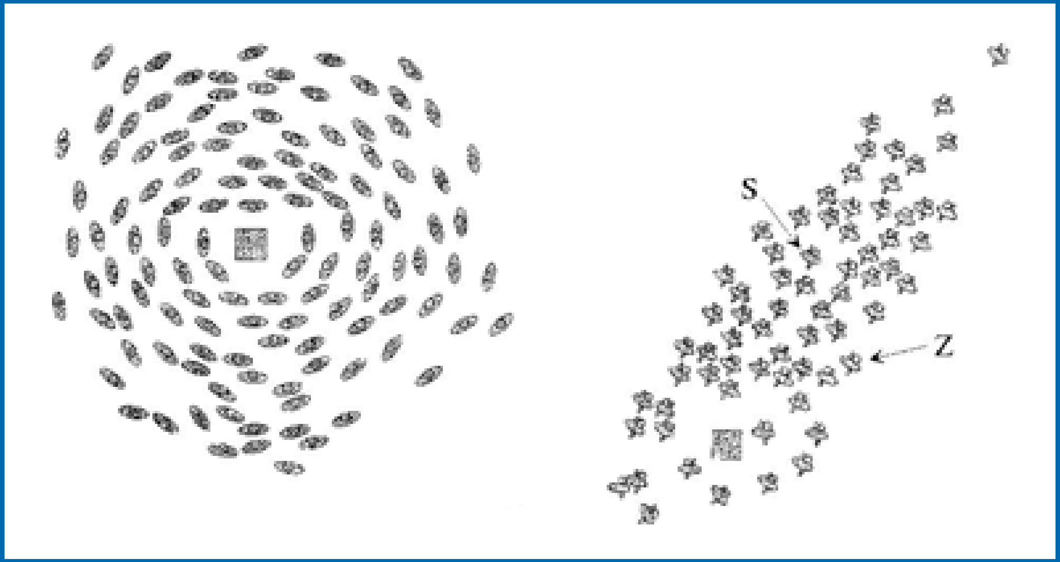
General principles:

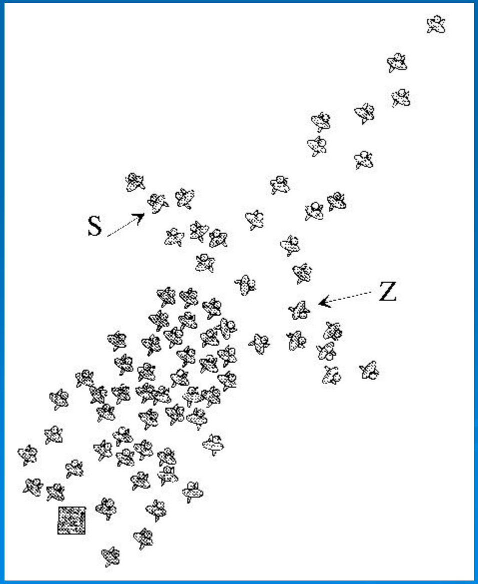
1. Nature mixes data structures into a composite of correlation sets and multivariate data analysis aims at decompositing this composite into its components.
2. If a process influences a system, then it generates a data structure. Example: A disease makes a certain structure in metabolic profile of a human.

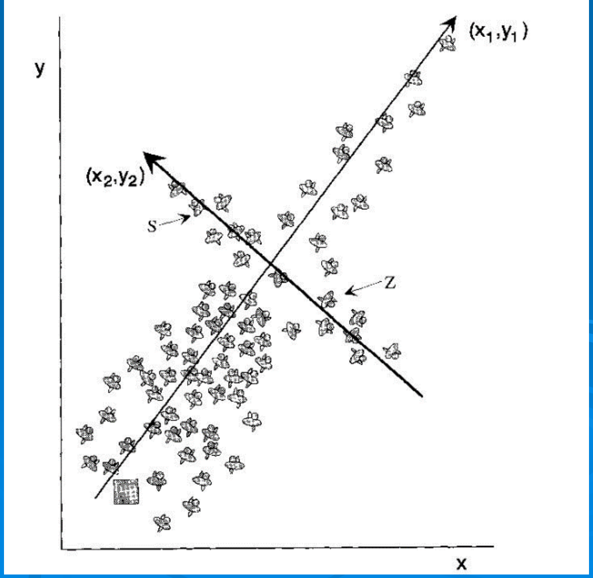




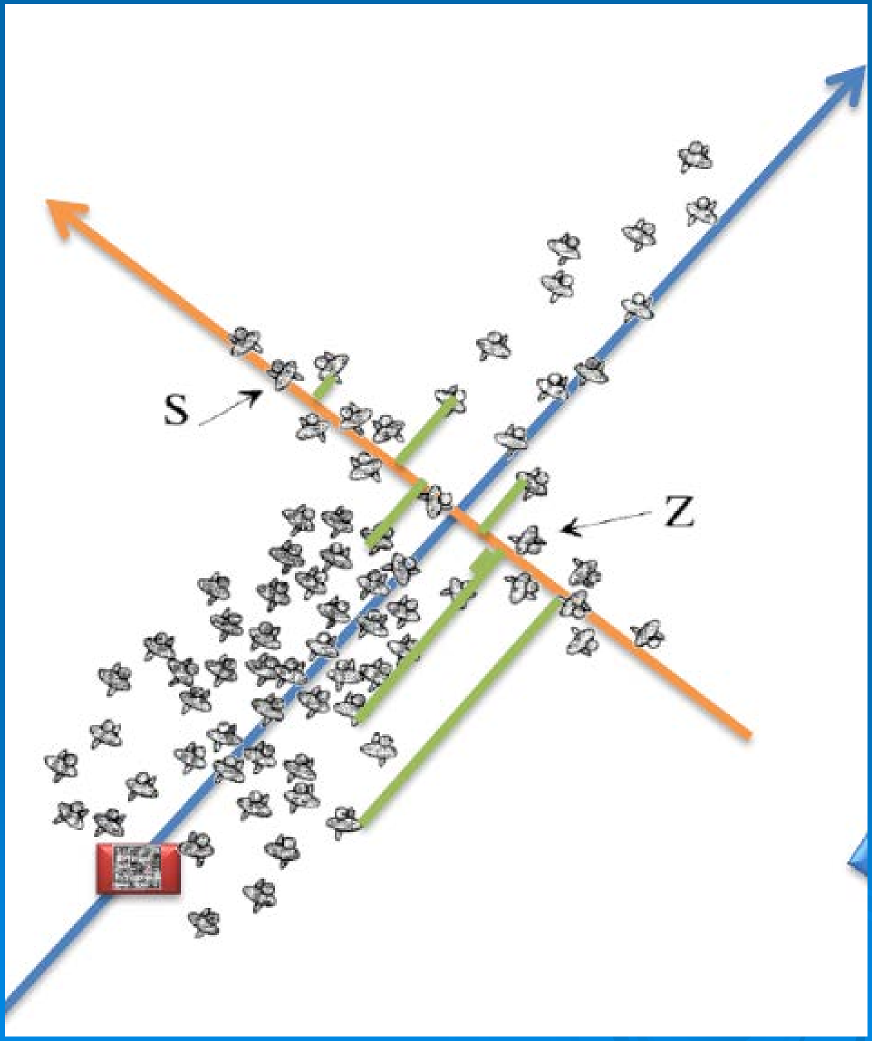
THE YELTSIN EXAMPLE

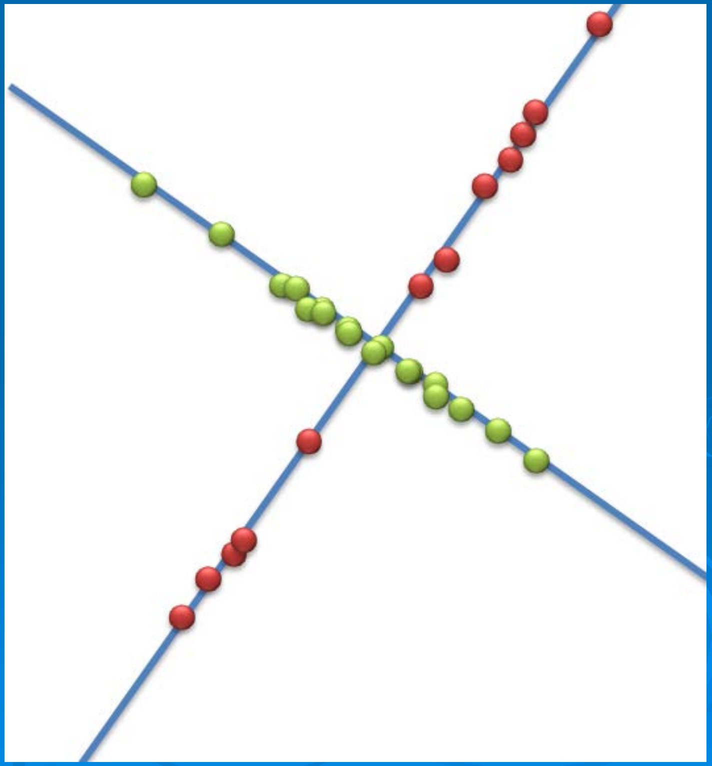




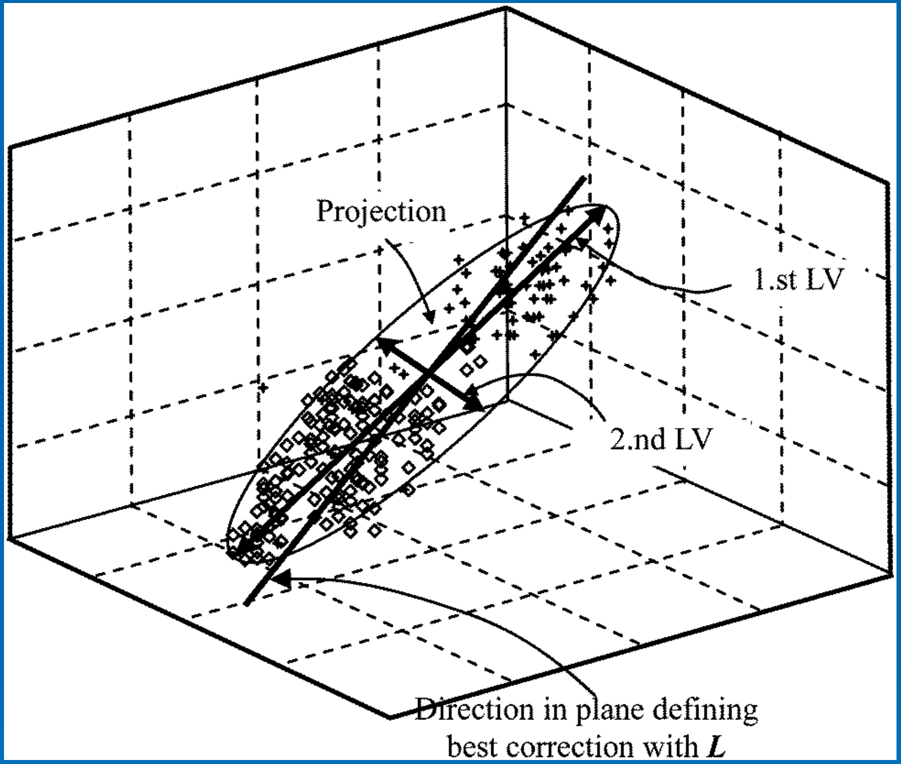


VECTORS AND SCORES





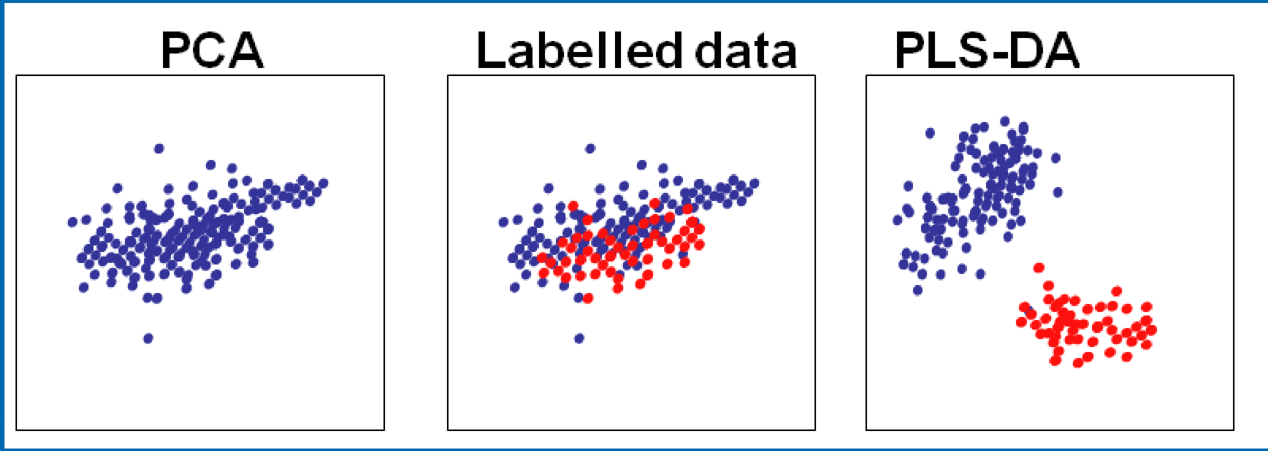
PARTIAL LEAST SQUARE ANALYSIS (PLS)



It is used to find hyperplanes of maximum fitting between response and independent variables (principal components). It finds a linear regression model by projecting the predicted variables and the observed variables to a new space. In addition to independent variables used in PCA, PLS uses a matrix of responses (Y axis).

PARTIAL LEAST SQUARE- DISCRIMINANT ANALYSIS

PLS-DA uses "labeled" data while PCA uses no prior knowledge
PLS-DA enhances the separation between groups of observations by rotating PCA components such that a maximum separation among classes is obtained



Validation of models

R^2 is the correlation index and refers to the goodness of fit or the explained variation (range = 0-1)
Q^2 refers to the predicted variation or quality of prediction (range = 0-1)
Typically Q^2 and R^2 track very closely together

CHEMOMETRIC ANALYSIS

Data submitted: Thermogravimetric analysis (25-800^{o}C) from:

- 15 paper samples.
- 15 newspaper samples.
- 15 cardboard samples.
- 15 wood samples.

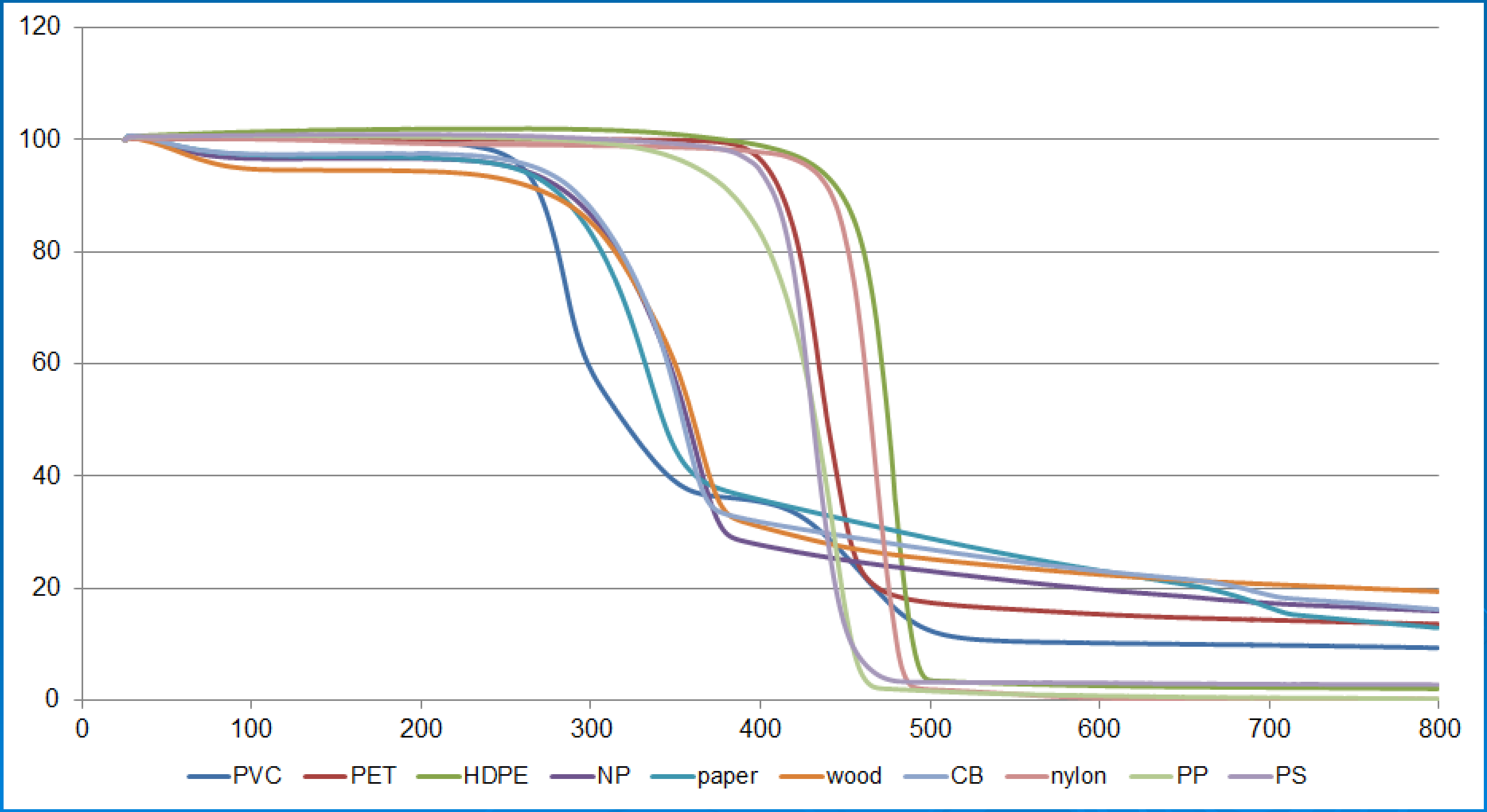
} Natural Polymers

- 10 PET samples.
- 10 PVC samples.
- 10 PP samples.
- 10 PS samples.
- 10 Nylon samples.
- 10 HDPE samples.

} Plastics

- 1 sample- mixture of natural polymers, 1 sample mixture of synthetic polymers.
- 1:1 mixtures of natural samples with PET, PVC, PP, PS, Nylon and HDPE.

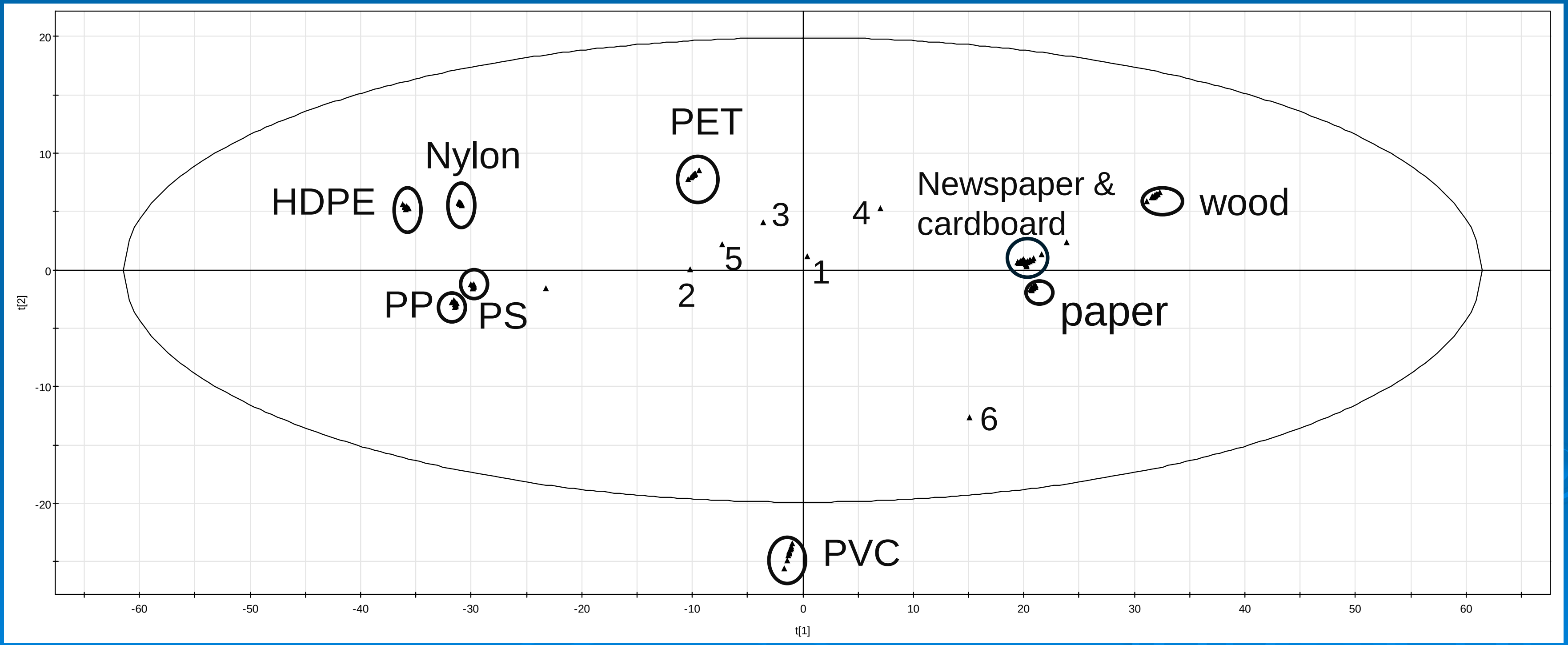
THERMOGRAVIMETRIC ANALYSIS



PRINCIPAL COMPONENT ANALYSIS

3 principal components were extracted with cumulative correlation coefficient R^2=0.925 and cross- validated correlation coefficient Q^2= 0.922.

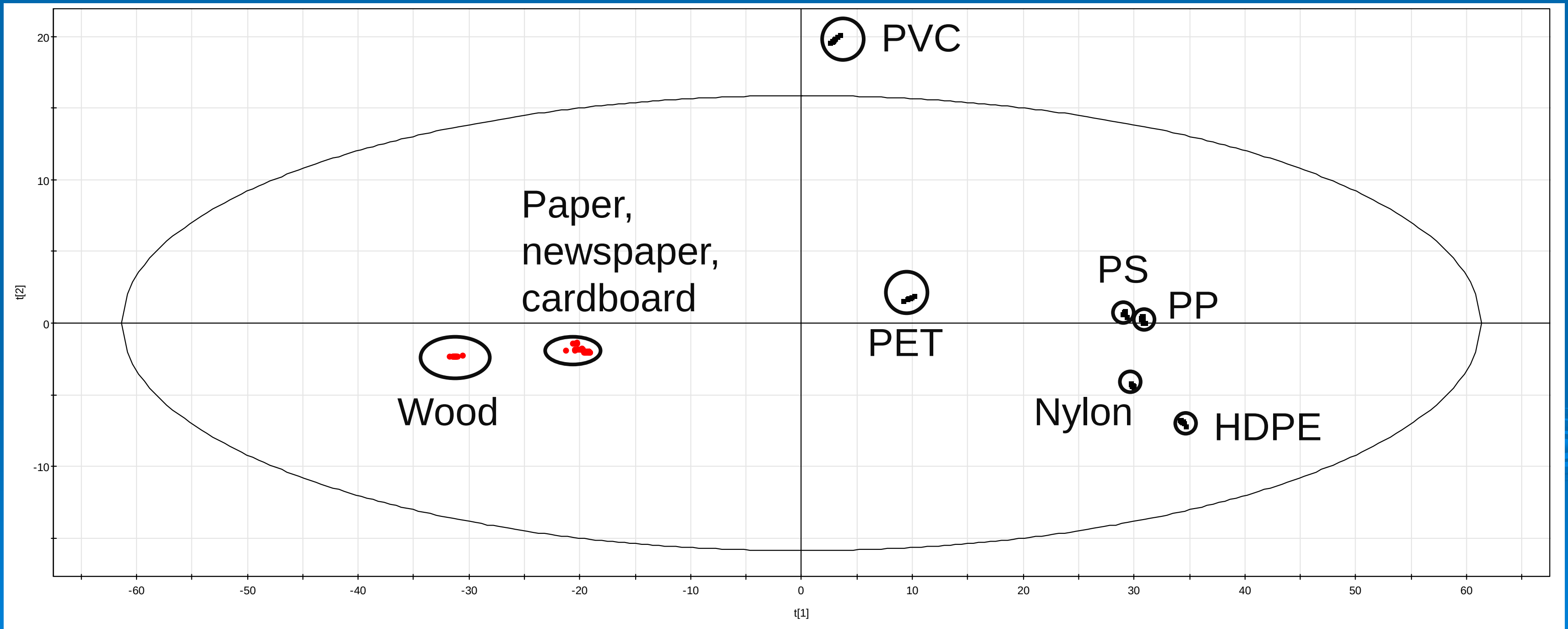
Score plot of the first 2 principal components → overview of lignocellulosic materials and plastics. Main component: Classification to two temperature ranges: a) 33-469^{o}C (p<0) and b) 25-32^{o}C and 470-800^{o}C (p>0).



Mixtures of natural polymers with HDPE(1), PS(2), Nylon (3), PET(4), PP (5) and PVC(6).

PARTIAL LEAST SQUARE-DISCRIMINANT ANALYSIS (PLS-DA)

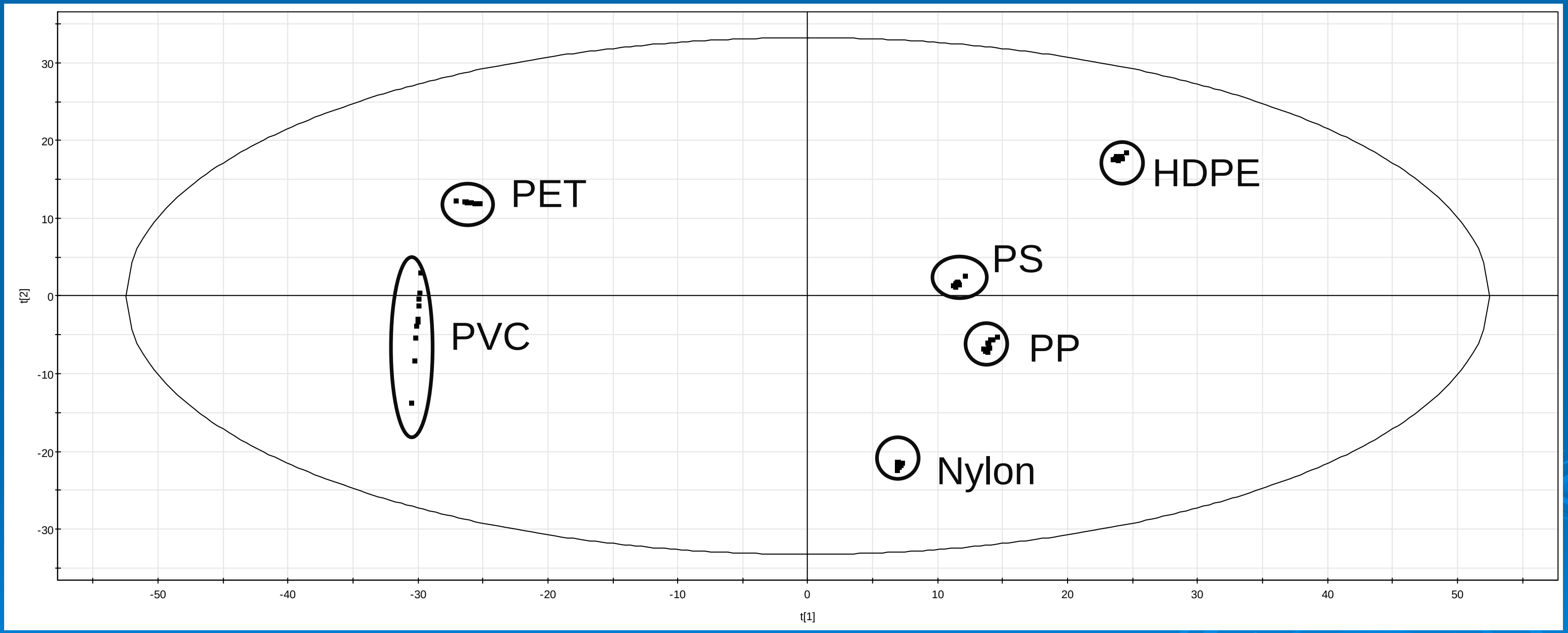
Cumulative correlation coefficient R^2= 0.895, Cross- validated correlation coefficient Q^2= 0.943.



Main component: Classification to two temperature ranges: a) 35-466ºC (p>0) and b) 25-34ºC and 467-800ºC (p<0).

PRINCIPAL COMPONENT ANALYSIS OF PLASTICS

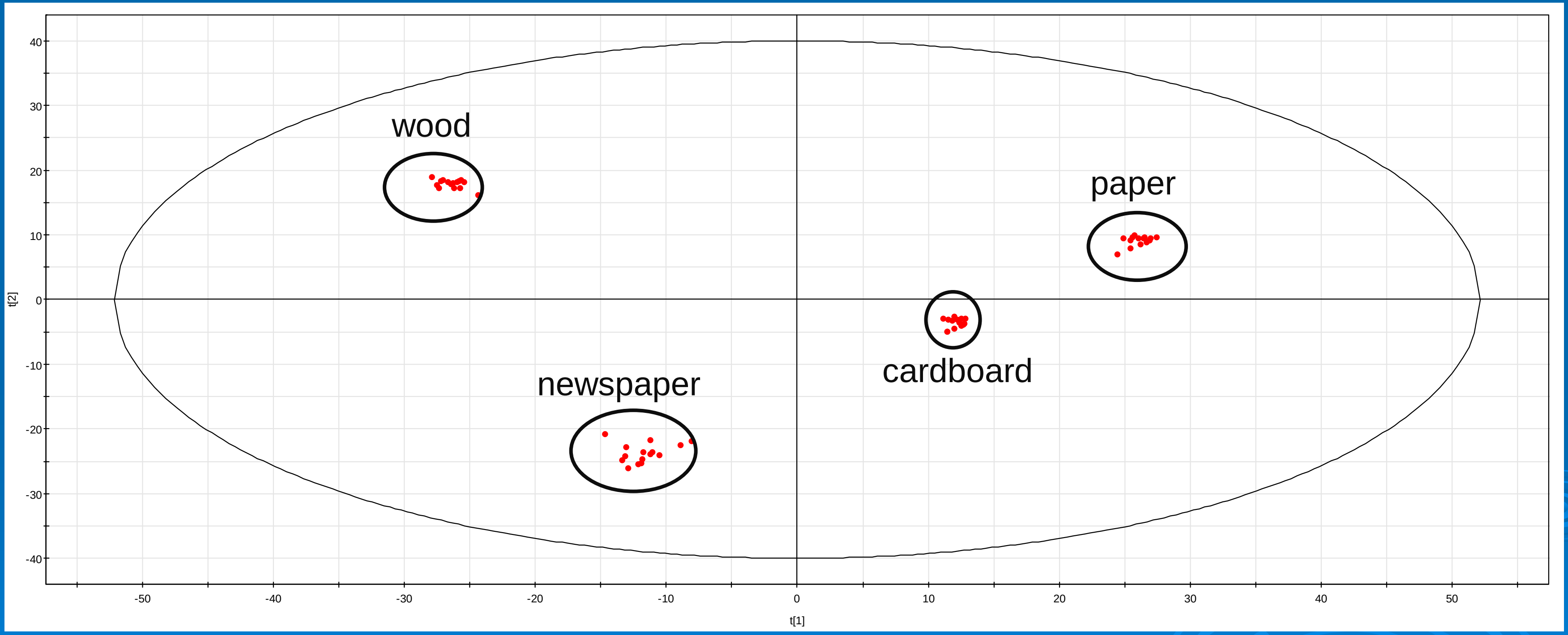
4 main principal components: coefficient R^2=0.998 and cross-validated correlation coefficient Q^2= 0.973.



Main component: Corresponds to the differences between the temperature ranges 25-479ºC (p>0) and 480-800ºC (p<0).
Second component: Differences in 436-452ºC.

PRINCIPAL COMPONENT ANALYSIS OF NATURAL POLYMERS

3 principal components: coefficient R^2=1.00 and cross- validated correlation coefficient Q^2= 1.00.

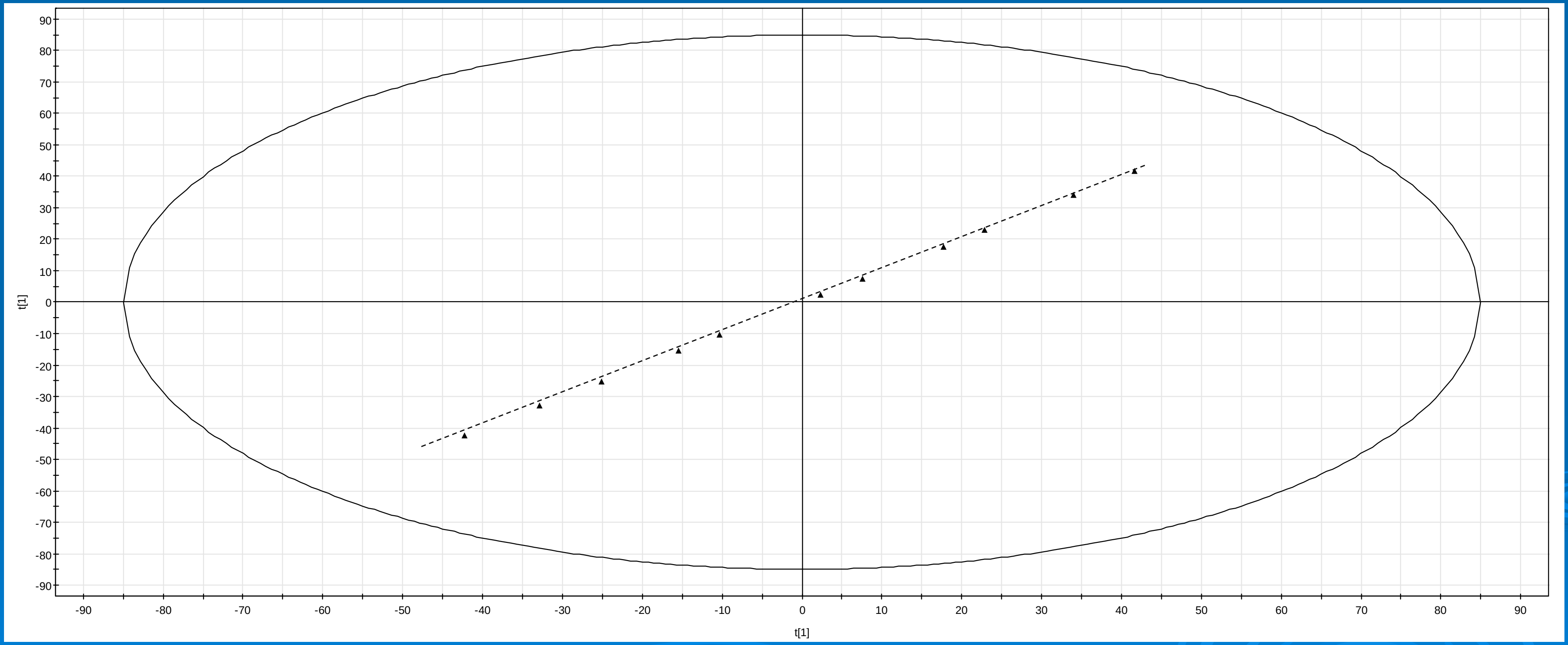


Main component: Corresponds to the differences in the temperature ranges 293-371ºC and 666-800ºC (p<0) compared to the other temperatures (p>0). Second component: Divide the temperature range in 25-357ºC and 358-800ºC

PARTIAL LEAST SQUARE ANALYSIS

Data used: Mixtures of natural polymers and synthetic polymers in (w/w) ratios 100:0, 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, 10:90 and 0:100.

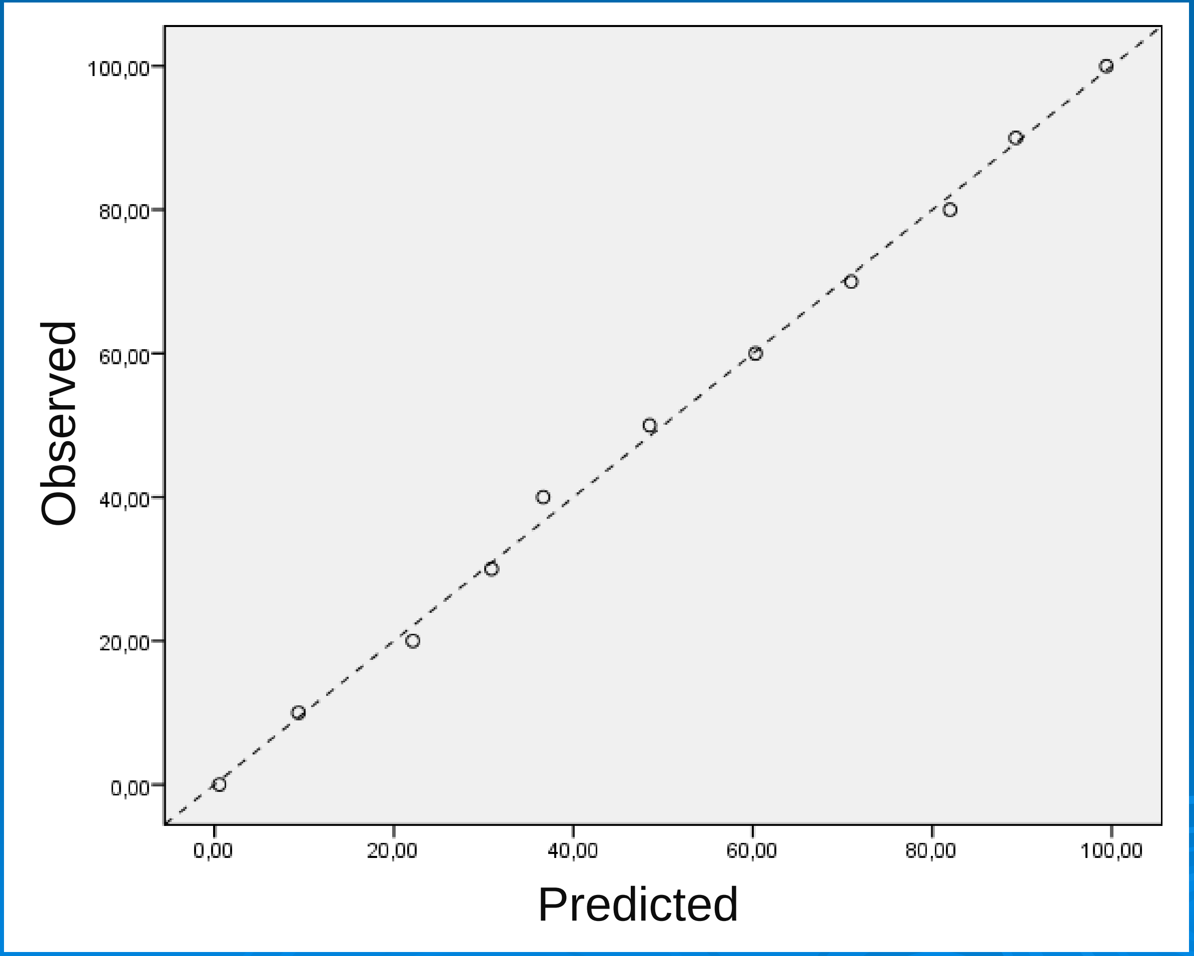
Statistics: R^2= 0.987, Q^2= 0.997.



Single component: Classification to two temperature ranges: 25-470ºC and 470-800ºC.

VALIDATION OF PLS MODEL

A. USING MIXTURES OF SYNTHETIC AND NATURAL POLYMERS



VALIDATION OF PLS MODEL

B. USING RDF SAMPLES RDF SAMPLES.

Fraction	Particle size (mm)	% (w/w)	% lignocellulosic content (PLS model)
1	1	17.1	64.7%
2	0.25	18.2	66.9%
3	0.09	15.6	73.2%
4	0.07	20.0	74.7%
5	0.056	13.4	81.1%
6	0.032	9.2	83.2%
7	<0.032	6.5	83.0%

RDF SAMPLE 1: proximate- ultimate analysis

Moisture (%)(r,m)	8.4
Proximate Analysis (% dry basis)	
Vollatile matter	64.1
Fixed Carbon	24.3
Ash	11.6
Ultimate Analysis (% dry basis)	
C	62.8
H	16.6
N	0.9
O	19.5
S	0.13
Cl	0.07
LHV (MJ/kg)	22.7

RDF SAMPLE 2

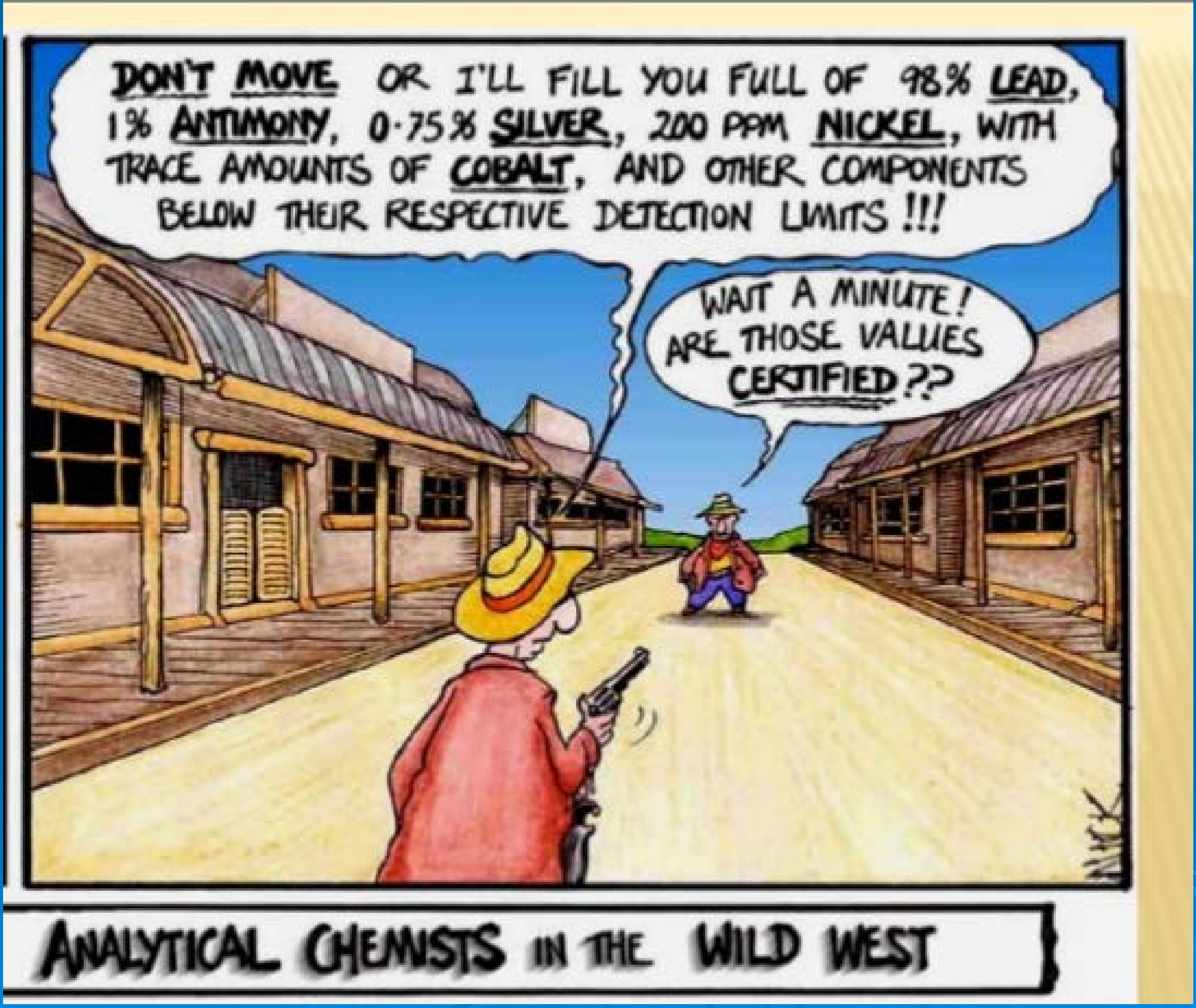
Fraction	Particle size (mm)	% (w/w)	% lignocellulosic content (PLS model)
1	1	15.7	70.5%
2	0.25	17.4	72.3%
3	0.09	21.3	71.8%
4	0.07	16.8	77.8%
5	0.056	12.6	81.8%
6	0.032	8.4	82.0%
7	<0.032	7.8	81.7%

RDF SAMPLE 1: proximate- ultimate analysis

Moisture (%)(r,m)	9.2
Proximate Analysis (% dry basis)	
Vollatile matter	70.6
Fixed Carbon	14.5
Ash	14.9
Ultimate Analysis (% dry basis)	
C	64.7
H	12.7
N	1.15
O	21.4
S	0.09
Cl	0.05
LHV MJ/kg	21.6

CONCLUSIONS

- Different behavior of lignocellulosic metarials and plastics in thermogravimetric analysis.
- Chemometric techniques can be used for the classification and quantification of such mixtures.
- The method was successfully validated using synthetic mixtures of natural polymers and synthetic polymers.
- The developed technique was applied to different fractions of RDF samples → Results consistent with elemental analysis.
- Fine fractions of RDF are enriched in natural polymers.
- The developed method can be useful in order for the characterization of RDF samples and relevant products.


DON'T MOVE OR I'LL FILL YOU FULL OF 98% LEAD, 1% ANTIMONY, 0·75% SILVER, 200 PPM NICKEL, WITH TRACE AMOUNTS OF COBALT, AND OTHER COMPONENTS BELOW THEIR RESPECTIVE DETECTION LIMITS !!!
WAIT A MINUTE! ARE THOSE VALUES CERTIFIED ??
ANALYTICAL CHEMISTS IN THE WILD WEST