



Ink analysis using reflectance spectrophotometry

The reflectance **spectrophotometer** (called reflectance **SPF**) was invented to obtain the **chromatic characterization of inks** outside the laboratory.

This device makes it possible to discover anomalies deriving from fraudulent tampering of documents by acquiring technical data in digital format.

The following are the most frequent cases which can be ascertained:

- *Texts falsified by additions or changes;*
- *Blank documents signed first and then filled out;*
- *Altered private deeds;*
- *Promiscuous filling in of forms by inking;*
- *Wills that are partially or totally forged;*
- *Identification, travel documents, etc. that have been forged;*
- *Abrasions, erasures, corrections of dates and amounts;*
- *Ungluing of documents, substitution of photographs;*
- *Gluing of new elements onto paper, stapling, etc.*
- *Falsification of seals, stamps, etc;*
- *Tampering with checks, bank documents, Post Office deposits, etc.*

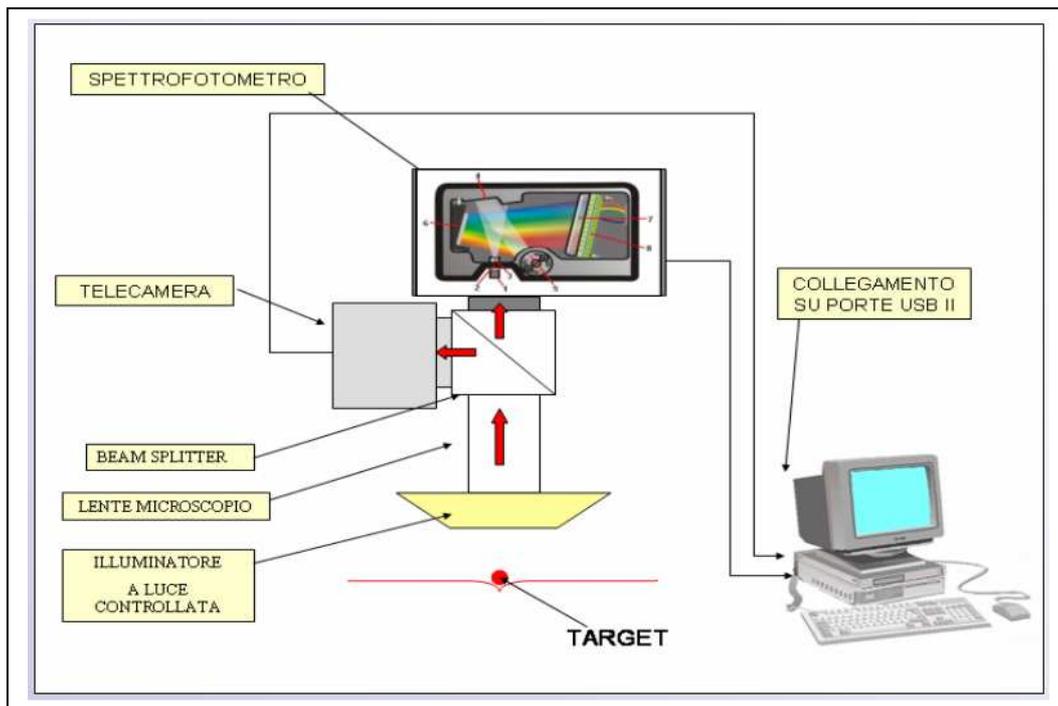
In these cases the spectral comparative analysis (between the ink pigments or between different parts of the paper texture surface, if it has undergone alterations) makes it possible to evidence and demonstrate the anomalies.

The most standard application involves examining the text to single out possible additions; if the suspicious parts of the writing have been applied with the same pen, the spectral responses will give the same results. Otherwise the document may have been altered.

Brief description of the SPF for in loco uses

The device is made up of the following components:

- A generator of controlled solid-state artificial lighting and a source of incandescent light that can cover the range between ultraviolet (UV), visible spectrum (VIS) and near infrared spectrum (NIR).
- An imaging system composed of a CCD matrix solid-state color with integration times that varies within the range of 500 us - 40 ms. The sensor is equipped with a high performing anti-blooming function and the diffusion of inter-pixel charges, medium sensitivity and low noise for low levels of the luminance and high dynamics.
- A lens for optical microscopy having an extension to operate in macro mode for strong magnification acquisition of the graphisms to be examined
- An SPF having a linear CCD array of 650 Pixels and a 12-bit A/D converter; Electrical output signals from the array, proportionate to the intensity of the flow in the various spectral areas, are digitalized and then processed by a computer.
 - A software module to compare the digital color values of the ink sample with the signals produced by a standard reference white (naturally in addition to the "white" of the paper texture of the document being ascertained) previously acquired.



Spectroscopy: Basic Concepts

White light, according to Newton's theory, can be seen as:

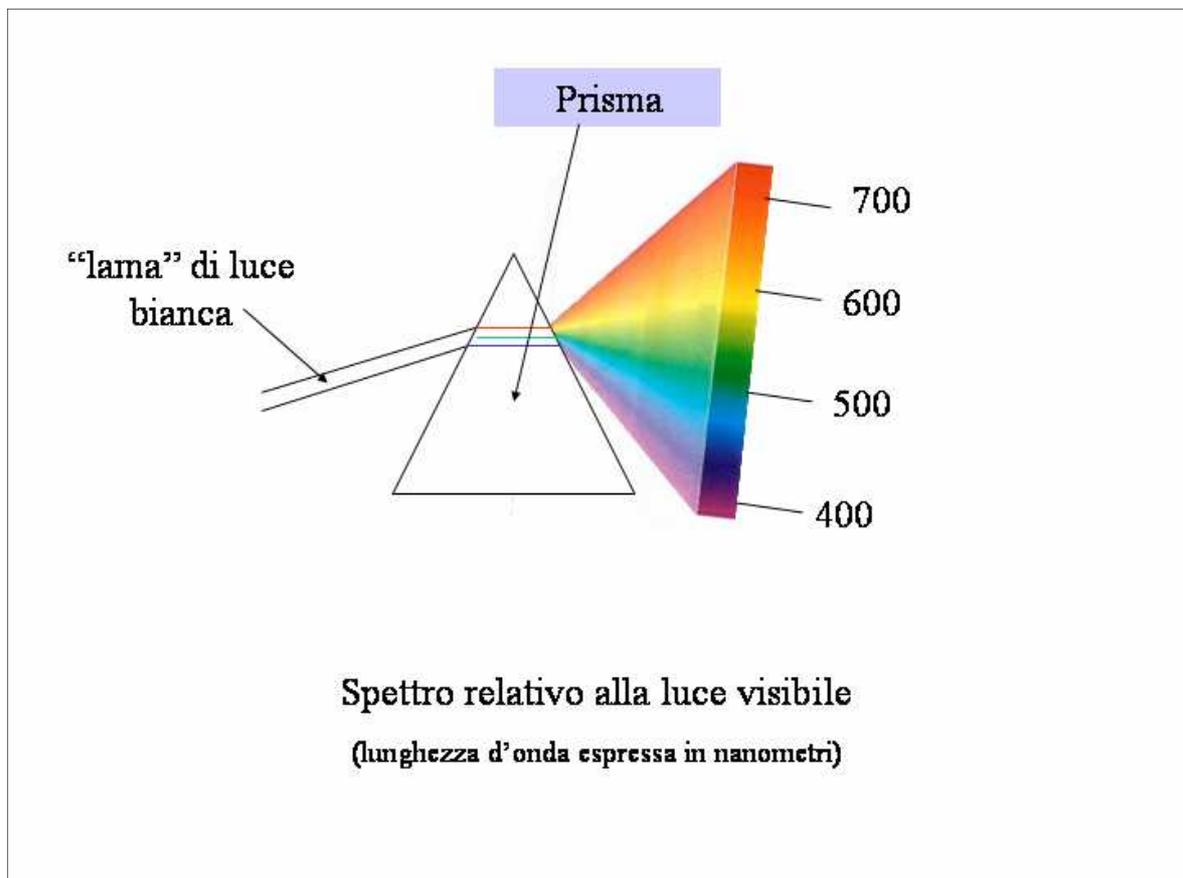
- A group of photons having a certain amount of energy that allows them to move;

or

- A group of electromagnetic waves, each having a well-defined wavelength that determines the color we perceive;

The **visible waves** are the ones between 380-780 nanometers, i.e. between violet and red, passing through light blue, green, yellow-green (approximately 550 nanometers, where the sensitivity of the human eye is at its maximum), yellow and orange. Less than 380 nm is **ultraviolet light** and above 780 nm is **infrared**.

The figure below shows the breaking up of white light (in the visible spectrum):



Didascalia della figura sopra: lana di luce bianca = beam of white light

Prisma = prism

Spettro relativo alla luce visibile = Spectrum of visible light

Lunghezza d'onda espresso in nanometri = Wavelength expressed in nanometers

Brief description of the functioning of the spectrophotometric technique in the analysis of inks

A spectrum is made up of a series of luminous or dark bands of a variable intensity. The spectrum is formed when a light source is intercepted by a device (prism) that is capable of dividing the light into the various wavelengths that make it up. Spectrophotometry is the field that studies and elaborates methods for measuring the reflectance or transmittance of an object at the various wavelengths, or a particular type of spectroscopy that deals essentially with the visible part of the spectrum, the areas near the infrared and the ultraviolet spectrum (UV/VIS/NIR).

Absorption spectroscopy

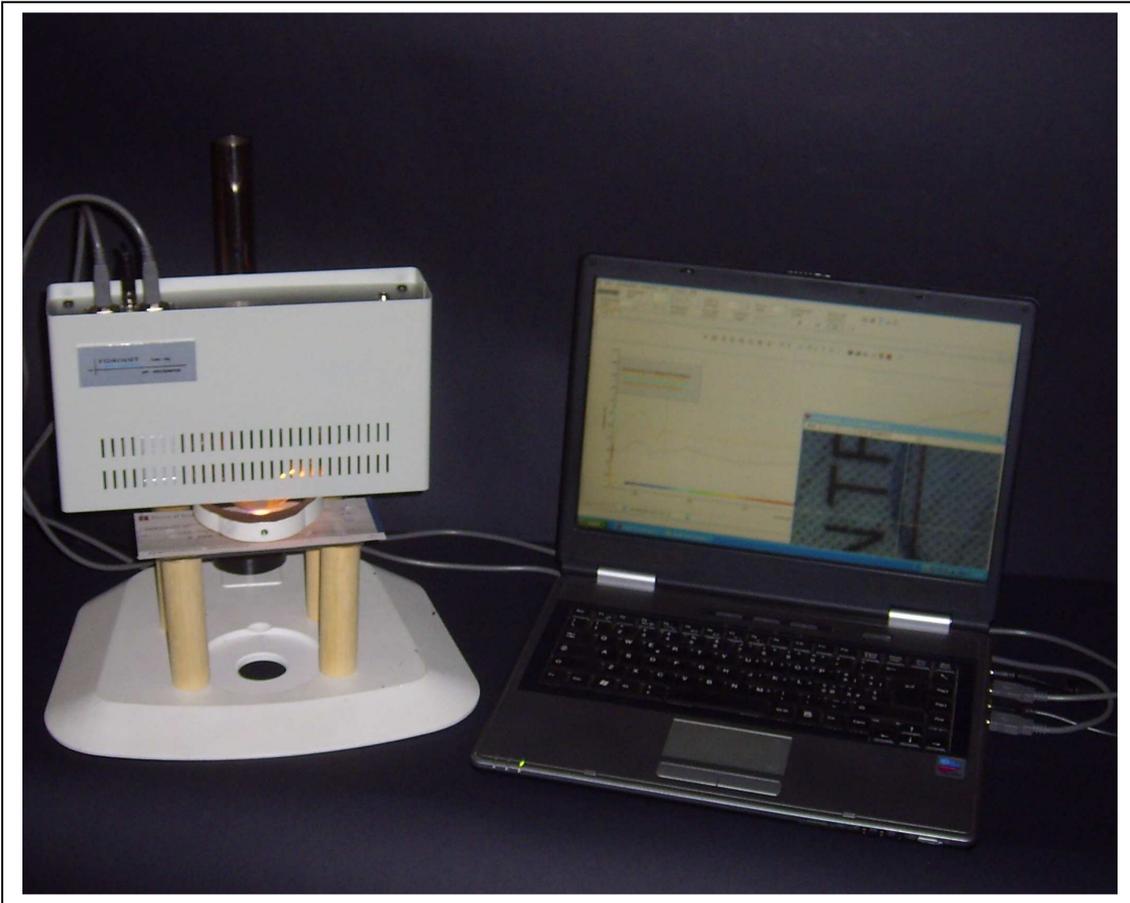
When the light is radiated on a surface, the molecules that make up the surface texture of the material can absorb part of the radiation. The energy absorbed in the form of photons causes the passage of molecules from their fundamental state to an excited state. This occurs when the energy associated with the photons (quanta) corresponds to the difference between the energy pertaining to the electrons in the excited state and the fundamental state. The absorption spectrum represents the probability that the photons having a certain amount of energy are absorbed by the molecules of a given substance and it shows the energy situation of the electrons of those molecules. On this basis the absorption spectrum can be considered a parameter that is characteristic of any substance, i.e. it can be used to identify said substance. This type of spectroscopy is used frequently in the chromatic components of a specimen and the absorbency spectra are measured with an SPF.

Reflectance spectroscopy

When examining two specimens that are totally opaque, the absorption measurements cannot be made directly. In this case we use reflectance spectroscopic techniques. The reflectance of a material is correlated to the absorption properties because in a certain sense reflectance is the opposite of absorption. Reflectance is lower at wavelengths where absorption is higher.

This type of spectroscopy gives us indications of the chromatic characteristics of the specimen. Nonetheless it should be taken into consideration that the reflectance properties of a specimen do not depend merely on its absorption characteristics but are affected by the nature of its surface and illumination conditions.

The SPF spectrophotometer for measuring documents being investigated is the type that measures reflectance; it is easy to operate and does not require physical removal of the inked parts of the exhibit. Consequently the analysis is repeatable and nondestructive.



The SPF spectrophotometer

The physical-chemical characteristics of the inks

The spectroscopic techniques used in forensics can give important indications on the authenticity of a document by characterizing the product analysis properties of the main ingredients, mainly paper and inks, but also any other type of material, even traces, that can be measured on the exhibit.

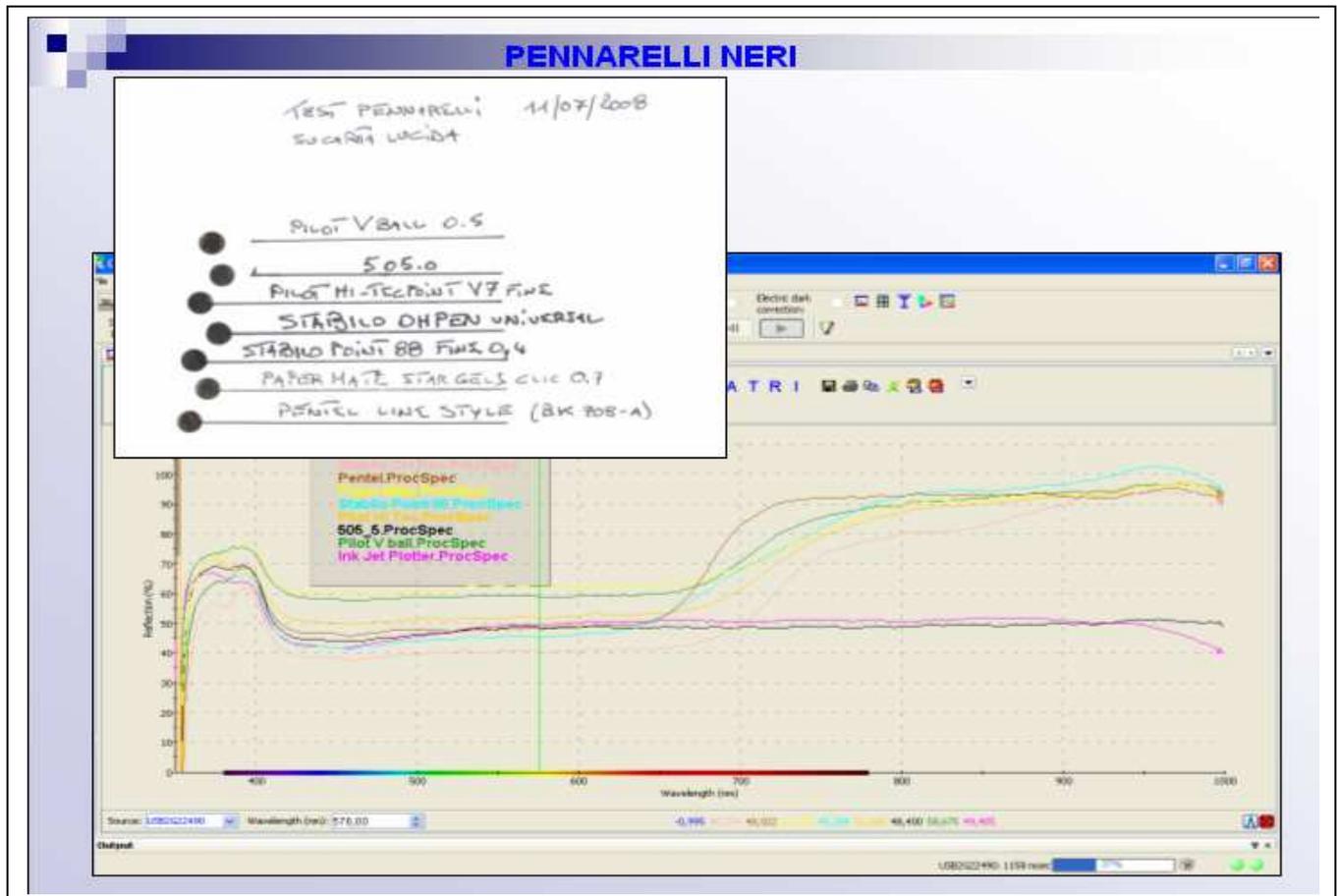
The inks can be considered a mixture of dyes and pigments dissolved or dispersed in a solvent with characteristics that allow a continuous and homogenous flow from the pen to the paper or other material and adequate penetration into the paper.

The most important ink ingredient in terms of product analysis is the chromatic one, obtained from blends of pigments and dyes. From their combination it is possible to obtain the desired color, a good covering effect, and the nuances and brightness that most suitably match the market demand.

The presence of several chromatic ingredients in the composition of an ink plays an important role in the spectroscopic analysis. In fact a highly structured spectrum – due to the simultaneous presence of several superimposed absorption bands – provides more reference elements when comparing inks.

Comparison example of inks generated by seven different writing instruments

The diagrams below give an example of the absorption spectra of black traces impressed by different felt-tip pens).



The spectral analysis shows the presence of different absorption bands by position and relative amplitude which make it possible to discriminate between them.

Note:

The SPF spectrophotometer is the subject of a thesis titled: "Sviluppo di un sistema basato sulla spettrofotometria per l'analisi di inchiostri di strumenti scrittori" [The development of a system based on spectrophotometry for the analysis of inks of writing instruments] (Evouna Essengue Hugues Joel, Supervisor: Prof. Nello Balossino University of Torino, Faculty of Mathematics, Physics and Natural Sciences, Major in IT. Academic year 2006 – 2007)