



Non invasive micro-Raman spectroscopy for investigation of historical silver salt gelatin photographs



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ABSTRACT

At the end of the 19th century, photography rapidly spread and technical developments allowed for a wide range of artistic expressions. The application of micro-Raman spectroscopy on historical photographs permitted to identify the silver salt gelatin process and to characterize a typical surface alteration, known as "silver mirroring" or "silver tarnish". The Raman spectra show diagnostic peaks of silver halide as an evidence of the use of the silver salt gelatin technique, whereas on the areas that are affected by silver mirroring the presence of silver sulfide could be attested by comparison with standards. This application resulted especially useful for those photographs with no evidence of silver tarnish although a silver salt technique had been used. Moreover, this study proves the suitability of micro-Raman spectroscopy on fragile materials such as photographs, without causing any damage.

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1. Introduction

Photographic images may be considered cultural objects with a triple role, being of historical, technical, and artistic value. Photography, as we know it today, is the result of scientific efforts that have been made throughout the nineteenth century, both in the field of optics, with the development of the dark room, and of chemistry, in studying photosensitive substances [1]. The silver salt gelatin [1], platinum [2], and palladium [3] processes, the numerous-pigment method, and the cyanotype [4] were the most commonly used techniques in the 19th and 20th century.

From 1880 ca. the silver salt gelatin process was the most widespread. The photographs that were obtained with this technique consist of three layers: a paper support, a preparation layer, and a binder layer. The latter is composed of a photosensitive emulsion (actually a dispersion) of silver halides (AgBr and/or AgCl) in a collagen based gelatin. The photographic process is based on the reduction of the silver salts into metallic Ag grains due to the exposition to light. This results in the production of a latent image, which needs a development process that makes use of a reducing agent. The development is then followed by a washing and fixing bath which removes the residues of the unreacted silver halide grains.

The application of diagnostic techniques to photographic materials is documented in the literature, but the study of these particular and fragile items has still to be increased. The most frequently used

techniques are Fourier transform infrared (FTIR) spectroscopy [5], and scanning electron microscopy in combination with energy dispersive spectroscopy (SEM-EDS) [5–7]; both techniques, however, require sampling of material. X-ray diffraction has also been applied for investigation of photographic materials [7], but it is a destructive technique as well. X-ray fluorescence (XRF) is used too: it is not invasive, but it is limited to the analysis of elements with an atomic number higher than 12 [5]. A combination of different analytical techniques has been used for investigation of historical photographs which had been treated with high frequency plasma [6].

To our knowledge, only one application of Raman spectroscopy to photographic materials can be found in the literature, where it was used to identify pigments on pictures developed with the gum dichromate technique [8].

In this study the suitability of micro-Raman spectroscopy for the investigation of historical photographs was verified. Information on techniques and alteration phenomena may be essential for a correct conservation treatment and storage policy.

The photographs that were examined belong to the Pelloux's collection of the Earth Sciences Museum of the Geo-environmental and Earth Sciences Department of the University of Bari (Italy).

The mineralogical collection "Pelloux" is considered to be one of the richest and most beautiful collections conserved in Italian museums. It also includes different types of documents, such as historical catalogs, geological maps, field notes, many black and white pictures, as well as official documents and private papers relative to the collection acquisition. Among the pictures of the collection there are some photographs representing Marie Curie. One of these and two other pictures were

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chosen for investigation. The selection was performed in order to include pictures with different degrees of alteration and presence of superficial tarnishing.

The aim of the study was to identify the development technique and to study the chemical alteration phenomenon of silver mirroring by applying a non invasive analytical method such as micro-Raman spectroscopy. An in-depth study on this phenomenon [7] reports on a four-step process: (a) oxidization of the metallic silver which forms the latent image, (b) migration of the silver ions toward the surface of the gelatin layer, (c) reaction with environmental sulfur compounds, and (d) dimensional growth of the silver sulfide particles. The presence of silver sulfide in silver mirroring areas has been ascertained with analytical techniques such as XRF, SEM-EDS, XRD and X-ray photoelectron spectroscopy (XPS) [5,7,9].

2. Experimental

2.1. Photographic samples

2.1.1. Photo No. 1: Madame Curie, Lurisia 1918 (12.5 × 17.5 cm)

The black and white picture (Fig. 1) was taken during Marie Curie's visit in Italy, in the mine of Lurisia (Cuneo, Italy) in the summer of 1918 [10]. Macroscopic observations of the tarnish effect, known as "silver mirroring", on the edges and in the darkest portions of the picture (Fig. 2), were the most characteristic identifying factor to suggest the developing technique to be the gelatin silver process [11]. In fact, the use of this technique would be in agreement with the historical period.

2.1.2. Photo No. 2: mine entrance, Lurisia 1918 (12.5 × 17.5 cm)

The picture shows the gallery's entrance of the mine in Lurisia (Fig. 3). It is contextual to Photo No. 1 [10] and it is therefore reasonable to hypothesize that the same development process was used. Indeed, the photo presents the same type of silver mirroring, although more widespread (Fig. 4).

2.1.3. Photo No. 3: the lode (8 × 10 cm)

The black and white picture, dated to the beginning of the 20th century, represents a lode. It does not show any silver mirroring (Fig. 5).

2.2. Mineral samples from the Pelloux collection

Some minerals from the Pelloux collection were chosen in order to be used as standards for comparison with the materials identified in the photographs. In particular, the attention was focused on silver



Fig. 2. Photo No. 1 – detail of the silver mirroring in the upper left corner.

salts, because of the occurrence of the superficial tarnish effect, recognizable as silver mirroring.

2.2.1. Bromargyrite, AgBr

Silver bromide naturally occurs as a mineral named bromargyrite, member of the chlorargyrite group. It belongs to the isometric system and appears as a transparent, translucent yellowish mineral. The sample that was chosen from the Pelloux collection is a crystalline specimen, labeled no. 4266/11.

2.2.2. Chlorargyrite, AgCl

Silver chloride naturally occurs as a mineral named chlorargyrite, and gives the name to the chlorargyrite group. Also known as cerargyrite, it belongs to the isometric system exhibiting cubic crystals. The sample that was chosen from the Pelloux collection is labeled No. 4062/13; it is not a monocrystalline sample, but rather a mineral accretion on rock.

2.2.3. α -Argentite, Ag₂S

There are two mineralogical phases for silver sulfide. At room temperature, it occurs as α -argentite, known also as acanthite, showing a gray-black color and a metallic luster. The crystal system is monoclinic. At temperatures higher than 177 °C β -argentite is the stable phase. The sample analyzed in this study is labeled no. 530/19.



Fig. 1. Photo No. 1 – measurement points MC_1 and MC_2.



Fig. 3. Photo No. 2 – measurement points ME_1 (silver mirroring), ME_2 (black area without silver mirroring), and ME_3 (light area).

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