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LETTER TO THE EDITOR

Author's response

See Original Article *here*.
See Commentary on *here*.

Editor,

At first, I was skeptical of a letter, so well structured, being written by Ms. Bittencourt, a restorer with an impeccable resume, but with no academic experience. Also, if every reader's questions, of each published report, were directed to the editor, there would be no need of referees or corresponding author.

Before getting into responding the requested technical aspects, I would like to reaffirm the main goal of the published technical report: demonstrate the availability of nondestructive analytical techniques for the identification of materials of artistical and forensic interest. This is precisely the reason we decided to offer our contribution to the *Journal of Forensic Sciences*.

As response for her requests, I list the following.

1 | INFRARED SPECTRUM

Infrared spectroscopy is an excellent instrumental technique for characterizing *pure* substances. The farther we stray from pure, the greater the chances of misinterpreting the spectra. Therefore, a dedicated spectroscopist is of vital importance, as well as employing complimentary techniques for characterization.

Any experienced vibrational spectroscopist will tell you that analyzing samples in reflectance (ATR) mode is already prone to changes in spectrum appearance (peak intensity, shape, and position). The greater the difference between the refractive index from sample and the ATR crystal, the more evident these changes are.

Lastly, considering the nature of the photographic samples, one should consider that working with a private collection has challenges of its own, such as sample conservation (these photos might have been stored in a shoe box for 100 years).

Regarding the IR spectrum presented in Figure 7, we propose the presence of collodion *along* with silver gelatin. From the intensity ratio, we assume that the collodion layer is very thin (probably because of improper storage), since the peaks for nitrocellulose are present. It is evident that the cellulose from paper would overcome the intensities of the nitrogenated groups in collodion ($\nu_s NO_2$ ~1272 cm^{-1} and $\nu_s NO$ ~840 cm^{-1}). We can still see a small contribution of an overtone of $\nu_s NO_2$ at around 2500 cm^{-1}. Gelatin and cellulose have no nitrogenated groups, hence collodion *is* present. Being an extraordinary restorer will not make you see the infrared spectrum with the eyes of a trained spectroscopist, this is why this area (forensic) must be multidisciplinary.

2 | MICROSCOPIC ANALYSIS

As already explained in the technical report's text, micrographs of *our samples* are a criterion of exclusion, not inclusion in the identification process.

3 | TONING/COLOR

Figure 3 is not a black/white reproduction, but a colored one (in RGB model 8 bit/channel). The use of documentation targets is beyond the scope of this work, since we did not address the toning as a differential aspect of identification. Perhaps, reading Ms. Bitterncourt's future publications, me and the coauthors of this paper can start employing this method of differentiation in forensic works.

4 | TARGET ELEMENT FOR EDXRF

It is essential to point out that Ag has a relevant presence in the photographic analysis (photosensitive layer with silver particles) as well Ba and S (baryta). When choosing the target, we considered the feasibility of being able to measure Ag, Ba, and S (simultaneously) without interference. The Au target proved to be suitable for this purpose. Figure 5 of our published report shows distinct and well resolved peaks for Ag, Ba, and S in the samples employing the Au target. The increase of the Au peak on the photographic paper, compared with the spectrum obtained without it, is evident.

Figures 1 and 2 (below) present the spectra of the samples employing Ag and Rh targets, respectively. These were initial tests, mostly to decide upon instrumental parameters. From literature and our past experiences, we expected the Au target to be the most suitable for these analyses. Figure 1 (Ag target) shows a lot of noise in the sulfur and calcium area, besides the low resolution of barium peaks. Figure 2 also shows noise in the same area as Figure 1, but with greater interference from rhodium on peaks for silver this time.

At this point, I imagine Ms. Bittencourt misunderstands the purpose of our paper. If we were to detail, explain, and reconstruct every step employed to produce the photographs, this report should have been published in a *Technical Art History* journal. The aim of our

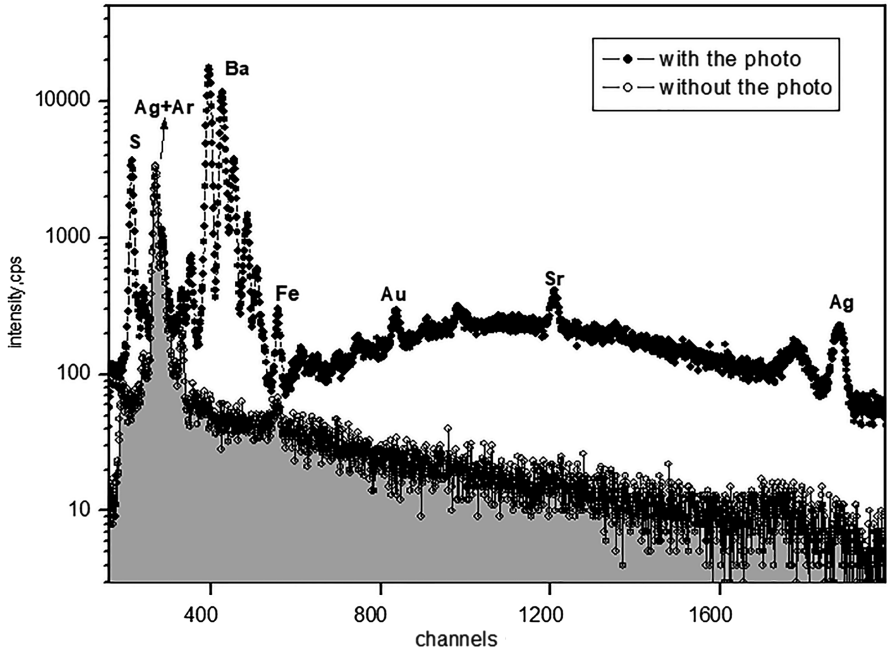

FIGURE 1 XRF spectrum with Ag target

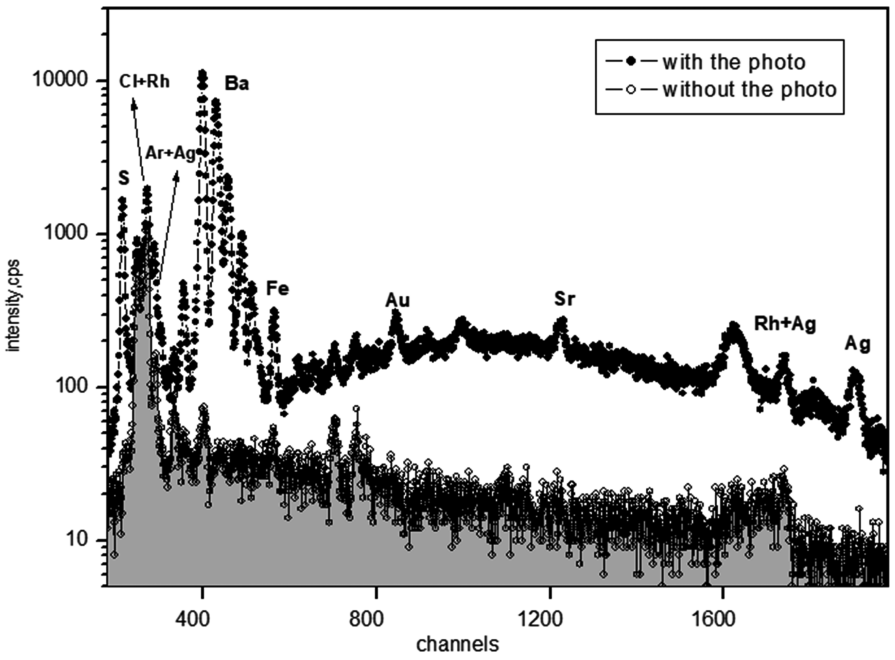

FIGURE 2 XRF spectrum with Rh target

work was to portrait the nondestructive techniques as capable of aiding photographers, auctioneers, forensic experts, as well as conservators, identifying historical photographs.

As a final technical consideration, I would like to point out that employing Py-GC/MS or stratigraphic microscopy on the samples would settle this discussion and show the presence of collodion. However, this technical report is based on *nondestructive* analyses as an important path to characterizing samples of forensic interest.

Based on the explanations presented, we understand that there is no need for any complement to our text. We thank the editor for consulting us and patiently waiting for our comments. We agree that the discussion of paper/reports is essential to the progress of scientific research.

Finally, me and the co-authors of this paper would like to thank Ms. Bittencourt for her interest in our work and her time devoted to this matter.

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