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The use of Raman and laser-induced breakdown spectroscopy for the study of iron-containing inks

O.S. Gribovskaya[1]✉, N.A. Sharkova[1], A.V. Vasilieva[1], V.A. Parfenov[1]

[1] St. Petersburg Electrotechnical University "LETI", St. Petersburg, Russia

✉ fen.tefal2@gmail.com

Abstract. The paper presents experimental results of combined use of Raman and laser-induced breakdown spectroscopy (LIBS) for determining elemental composition of iron-containing inks. It was shown that proposed approach allows to solve the problem of iron-containing components identification for paper artifacts.

Keywords: iron gall ink, Raman spectroscopy, laser-induced breakdown spectroscopy, LIBS, chemical composition analysis

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Использование Рамановской и лазерно-искровой эмиссионной спектроскопии для исследования железосодержащих чернил

О.С. Грибовская[1]✉, Н.А. Шаркова[1], А.В. Васильева[1], В.А. Парфенов[1]

[1] Санкт-Петербургский государственный электротехнический университет «ЛЭТИ» им. В.И. Ульянова (Ленина), Санкт-Петербург, Россия

✉ fen.tefal2@gmail.com

Аннотация. В статье представлены экспериментальные результаты совместного использования методов Рамановской и спектроскопии лазерно-индуцированной плазмы (LIBS) для определения элементного состава железосодержащих чернил. Показано, что предложенный подход позволяет решить проблему идентификации железосодержащих компонентов для бумажных артефактов.

Ключевые слова: железосодержащие чернила, Рамановская спектроскопия, спектроскопия лазерно-индуцированного пробоя, лазерно-искровая эмиссионная спектроскопия, LIBS, исследование химического состава

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Introduction

Iron gall ink is one of the earliest materials used by humans for writing, which is made from iron salts (most commonly from vitriol) and a mixture of organic colorants and tannins. Comparing with inks, containing copper salts as a base, iron gall inks can eventually cause damage to paper [1], which is a significant obstacle to preserving paper manuscripts and ancient books. In order to address the issue of detecting iron and other chemical elements within ink, it becomes necessary to develop techniques for its detection in various ways.

One of the modern methods for study chemical composition of different materials is Raman spectroscopy. Despite the fact that Raman spectroscopy is a highly effective, non-invasive technique, working with inks can be challenging [2]. This may be due to the complex nature of inks and the presence of fluorescent additives that can hinder the detection of weaker band intensities [3, 4]. That is why it is necessary to create an investigation technique for inks, which includes some alternative methods of identification.

Laser-induced breakdown spectroscopy (LIBS) technique, unlike many others, can detect the presence of specific elements in a material's composition. The method is not completely nondestructive, but it does allow for measurements with minimal damage to the surface of the sample [5]. Thus, in this work chemical composition of model ink sample is studied with Raman spectroscopy and LIBS to create a technique for paper artifacts investigation.

Materials and Methods

In experiments we used model sample imitation the sheet of manuscript. The model sample was created in a cellulose paper, where the inks, made by hot infusion of gall nuts, iron vitriol, cherry resin and drinking water were put with the brush.

For this work a Raman Confocal microscope Confotec MR350 (SOL instruments Ltd., Germany) with 785 and 850 nm working wavelength and 1 micron laser spot was used. The detector had special cooling system to increase temperature up to −30 °C. In order to avoid the thermal heating of the paper by laser and the destruction of the sample, the ND filter (absorber) was installed either. The sample was placed on the working surface, then it was pressed with a weight to avoid fluctuations. Spectral range for Raman spectra detection was from 99 cm^{-1} to 1734 cm^{-1} with spectral resolution of at least 0.145 cm^{-1}.

For the study, LIBS setup (Onteko, USA) was employed. A pulsed Nd:YAG nanosecond laser with focal spot size up to 30 microns operated at a wavelength of 1064 nm with a maximum pulse energy of 28 mJ. USB4000 spectrometer (Ocean Insight, USA) operated in the spectral range of 200−1100 nm with spectral resolution ranging from 0.1−10 nm and an integration time ranging from 3.8 milliseconds to 10 seconds. Additionally, part of the setup included the following software programs: OceanView (a specialized spectrometer software), and LIBS Identification Software for processing the acquired spectra. The sample was placed at 7 cm from the laser outlet. A two-pulse laser mode with pulse energy of 5 mJ was used for measurements.

In both cases, for Raman and LIBS, measurements of paper uncoated with ink and paper covered with ink were carried out, when subtracting the first measurement from the second, a spectra of pure ink were obtained.

Results and Discussion

Analysis of Raman spectrum (Fig. 1) showed no peaks of iron-containing components, however clear peaks corresponding to glucose and fructose, as well as peaks corresponding to tannin, were detected in the spectrum, making possible the identification of cherry resin (1400 cm^{-1}) and gall nuts (550 cm^{-1}).

It is worth noting that to interpret the Raman spectra of ink, a personal library of Raman spectra of some substances typical for ink composition was created. More details about this study are shown in the previous work [6].

The obtained LIBS spectrum (Fig. 2) was compared with the National Institute of Standards and Technology (NIST) database [7]. Peaks corresponding to iron at wavelengths of 274.7, 357.8, 374.1, 382.4, 385.6 and 393 nm, as well as sodium at 589 nm, were detected in the spectrum.

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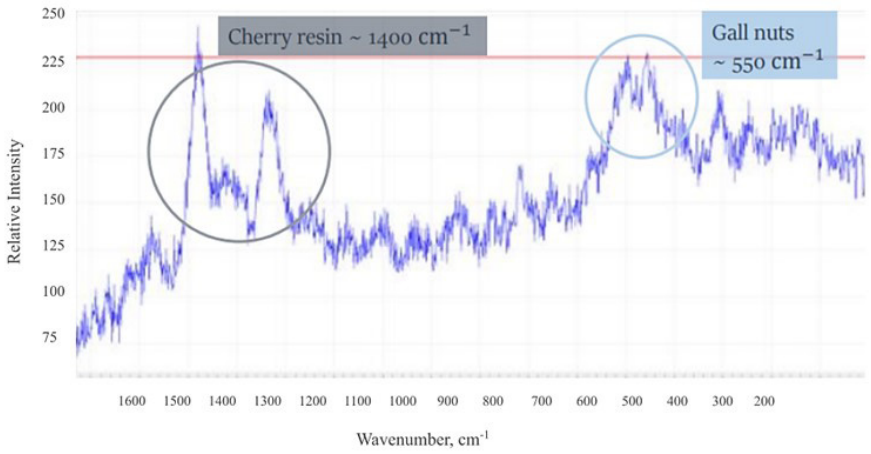

Fig. 1. Raman spectra of iron gall ink

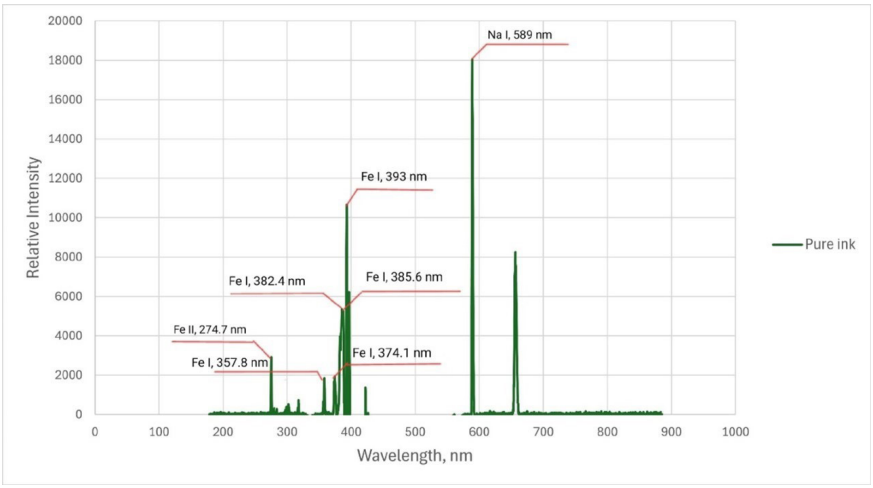

Fig. 2. LIBS spectra of iron gall ink

After reviewing relevant literature [8, 9, 10], it was determined that the spectral data obtained from LIBS method agrees with reference data, indicating that the method can detect iron and sodium in various compounds.

Conclusion

The problem of iron-containing components identification in Raman spectroscopy could be explained by alternative prohibition rule: in a molecule with an inversion center, all infrared bands will be prohibited in the raman spectrum and all Raman bands will be prohibited in the infrared ranges. This study showed that combined use of LIBS and Raman spectroscopy techniques for the ink investigation allows neglecting this problem. The Raman spectroscopy is suitable for identifying organic components of inks such as gall nuts and cherry resin, while LIBS peaks indicated the presence of iron and sodium. Sodium could be referring to contaminations or hand marks. In both spectral measurements no paper destroy was observed. Therefore, the combination of Raman and LIBS methods is a very effective analytical technique which can be recommended for paper artifacts studies.

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THE AUTHORS

GRIBOVSKAYA Olga S.
fen.tefal2@gmail.com
ORCID: 0009-0009-7765-2609

VASILIEVA Anastasia V.
anastasiastru@mail.ru
ORCID: 0000-0002-5317-3322

SHARKOVA Natalia A.
nasharkova@stud.etu.ru

PARFENOV Vadim A.
vadim_parfenov@mail.ru
ORCID: 0000-0002-2048-4677

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