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To Professor Petar Pfendt, *In calidum, et plurium retributivus memoriae*: FTIR-ATR analysis of post stamps of the Principality of Serbia issued in 1866 and 1868 and their forgeries

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Abstract: In order to further define the potential use of FTIR-ATR spectroscopy, as a non-destructive and reliable technique, for the analysis of the characteristics of post stamps, certified originals of the Principality of Serbia stamps ("Prince Michael issues") issued in 1866 and 1868 as well as their forgeries were analyzed. Spectra enabling the comparison of the paper, dye and glue of stamps of so-called "Vienna issues", having denominations of 10 (orange-yellow), 20 (pink) and 40 para (blue) and "Belgrade issues" (1 para-green and 2 para-reddish brown), as well as 24 expert-certified forgeries, were taken. It was shown that the applied technology was, in most of the cases, a fast and suitable technique for establishing clear differences between the spectral characteristics of the paper and dye used for the original stamps, and forgeries that were most probably made decades after the printing of the genuine stamps. The differences between printings of the same issues of the genuine stamps were also elaborated. It is proposed, for the first time in philatelic history, the possibility that "Vienna issues" stamps may have been printed on two different papers, and, having in mind the technology of printing in the 19th century, potentially, not even at the same time or in the same printing house.

Keywords: philately; stamps of Serbia; Prince Michael; "Vienna Issues"; "Belgrade Issues".

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INTRODUCTION

Professor Petar Pfendt (Jaša Tomić 1934–Belgrade 2021) was the first author's teacher, with whom he shared not only the passion for chemistry, but also numerous other fields, history being among them. Their conversations, during active service of Professor Pfendt at the University, were often devoted to this subject, emphasizing especially regional contemporary history. Probably due to sad past of the population of German origin in the Danube Basin during and after World War Two,[1] these conversations were brief, with occasional reminiscences of the professor from his childhood. In most occasions, historical facts were only inspiration for more applicative ideas, elaborating and connecting history (and other topics) with chemistry, over viewing the potential application of chemical methods, including analytical ones, in other areas of contemporary life, such as art, archaeology or sport. His passion was not only history, it is the fact that the late Professor Pfendt was a person of different and wide areas of interest, and deep and profound knowledge of chemistry, with publication in chemistry of oil shales,[2] aquifers and alluvial sediments,[3] coal,[4] water quality,[5] environmental consequences of war activities,[6] laboratory equipment,[7] processes occurring in soil,[8] air[9] and chemical education.[10] For these reasons, the authors of this paper decided unanimously to devote the study below, which includes history and applied chemistry, to the memory of Professor Petar Pfendt, a scholar and teacher.

Almost from the very moment of their invention and beginning of use, post stamps became the subject of collection[11] and forging.[12] Their basic issues and numerous variations were attractive forging targets due to their nature, rareness and very often the unpredictability of variations caused, among other reasons, by imperfections of the printing process.[13] Political changes, including those provoked by wars,[14] increased number of post stamp issues printed in limited quantities and for very short periods of time, sometime counted in days.[15] Like in the case of other collectables, the number of stamps printed as well as their quantity and availability on the market determine their values.

For decades, practically more than a century, the comparison between original and forged stamps was realised without any analytical methods, and was subject to the judgement and expertise of verified experts. The quality of forgeries were, in some cases, very close to the originals,[16] thus leading to mistakes in certification and the building of collections or their substantial parts that were not based on originals. Certainly, the introduction of instrumental analytical techniques that are non-destructive and that can differentiate paper,[17–20] dye[21,22] or the glue used in the printing of post stamps (and other documents) could improve their analysis, eliminate, at least to the large extent, potential errors that were involuntarily made due to subjectivity of experts. FTIR-ATR spectroscopy is one of such methods that could be used for the analysis of post stamps. It has

been used for the analysis of the stamps from Germany,[23] the United Kingdom,[24] Italy[25] and other countries, thus joining other non-destructive methods, such as Raman spectroscopy,[26] PIXE…[27]

The Principality of Serbia issued its first post stamps in 1866 (so called "Grbuše"), used for post tariffs of newspapers. In July of the same year, three post stamps used for mailing common letters were also issued, portraying Prince Mihajlo Obrenović. They were printed in Vienna's "Die Kaiserliche Wiener Hof-Und Staatsdruckerei" and thus are known as "Vienna Issues", designed by Anastas Jovanović, with denominations of 10 (orange yellow), 20 (pink) and 40 (blue) para.

Stamps with same design were issued five more times by Belgrade's "Praviteljstvena knjigopečatnja" ("State Printing House") in November 1866–February 1867 (the 10 para stamp being orange-yellow, 20 para stamp pale pink and 40 para stamp – ultramarine), March 1867 (1 para stamp – light green, 2 para stamp – yellowish-olive brown), July 1868 (20 para – pink, 40 para – blue), November 1868 (1 para – dark green, 2 para – reddish-brown) and in still unknown month in 1868 (1 para – pale to dark olive, 2 para yellow-olive). All of them are known in literature as "Belgrade issues". Forgeries of all the Prince Mihajlo Obrenović portrait definitive stamps are plentiful.[28] Their market values are different, the most expensive being the 1 para pale to dark olive stamp (1868) having not more than twenty known genuine samples at the present time, with a catalogue value of 6000 EUR.[29]

In this study, the authors present the potential use of FTIR-ATR spectroscopy for the analysis of similarities and differences of post stamps of the so-called "Vienna issue" of 10, 20 and 40 para and stamps of 1 para and 2 para issued in 1868, as well as of 24 proven forgeries of these stamps, being obtained from the collection of the late Professor Jovan Veličković (1927–2012), official expert of the Union of Philatelists of Serbia.

EXPERIMENTAL

Photographs of the examined original stamps are shown in Fig. 1, while their characteristics are given in Table I.[27]

Fig. 1. 10, 20 and 40 para Prince Mihajlo "Vienna Issue" (1866) and 1 and 2 para "Belgrade Issue" (1868) post stamps.

Infrared spectra were recorded for all stamps from collections using Fourier transform infrared spectroscopy (FTIR) with attenuated total reflectance (ATR) at 4 cm^{-1} resolution

(Nicolet 6700 FT IR, software Omnic, Version 7.0, Thermo Scientific, USA). The spectra were recorded on a diamond crystal with signal beam in the range of 400 to 4000 cm^{-1}. Crystal was cleaned with alcohol between samples. The background was recorded with 50 and sepals with 100 scans. The differences in the collected spectrum were shown by automatic subtraction of the spectra in Omnic software.

TABLE I. Characterists of the 10, 20 and 40 para Prince Mihajlo "Vienna Issue" (1866) and 1 and 2 para "Belgrade Issue" (1868) post stamps

Stamp	Printing	Colour	Paper	Glue
10 para	1866, Vienna	Orange yellow	Regular, soft	White, cracked
20 para	1866, Vienna	Pink	Regular, soft	White, cracked
40 para	1866, Vienna	Blue	Regular, soft	White, cracked
1 para	1868, Belgrade	Dark green	Different thickness	Yellow-grey
2 para	1868, Belgrade	Reddish-brown	Different thickness	Yellow-grey

RESULTS AND DISCUSSION

The results obtained by FTIR-ATR spectroscopy of the described samples or original and forged post stamps are shown at Figs. 2–11.

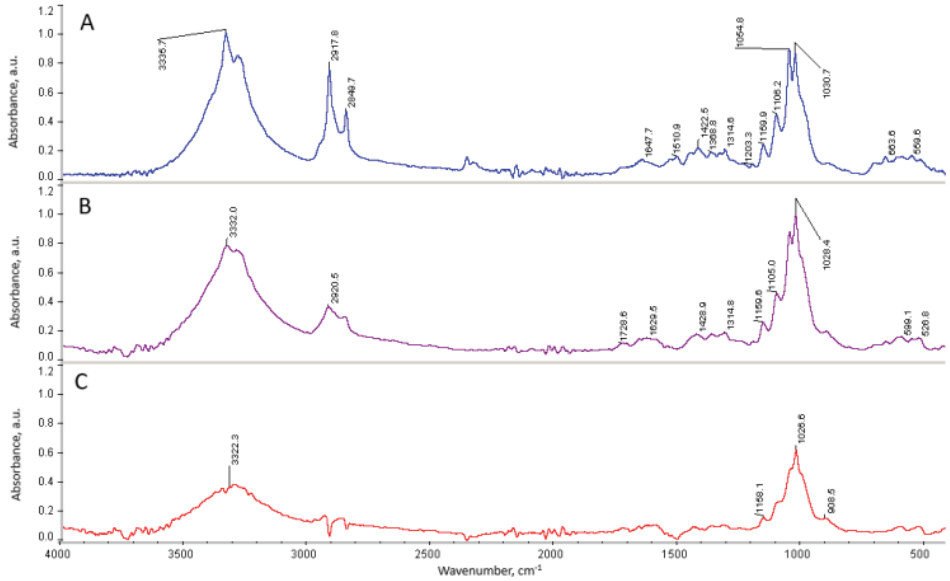

Fig. 2. FTIR spectra of: A) 10 para original stamps paper printed in Vienna 1866, B) 10 para confirmed forgery stamps paper and C) subtraction result of the original and the forgery stamp papers.

Comparison of certified original and forgery paper spectra revealed the differences between the paper used for printing of original and false stamps. This should not be a surprise, since certainly years if not decades elapsed between the

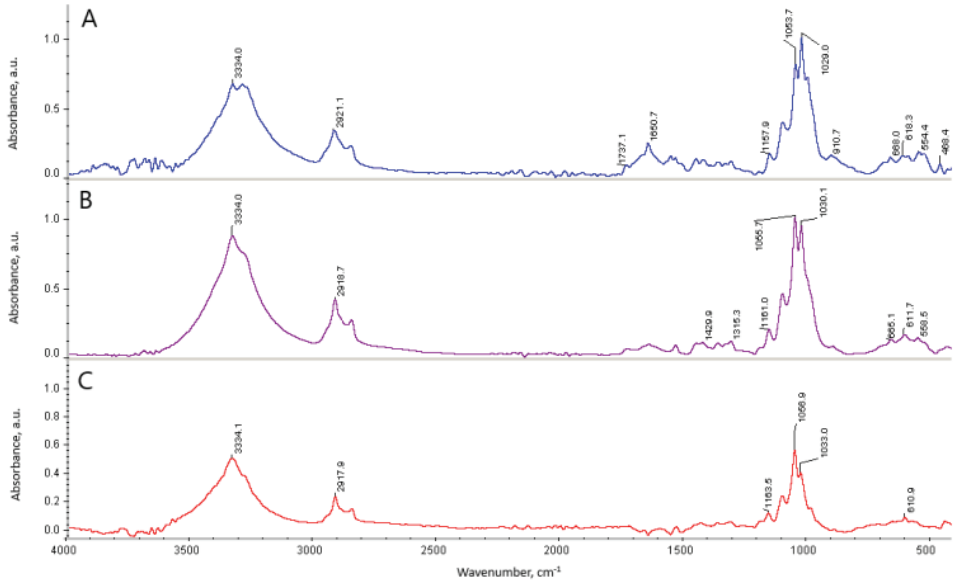

Fig. 3. FTIR spectra of: A) 20 para original stamps paper printed in Vienna 1866, B) 20 para confirmed forgery stamps paper and C) subtraction result of the original and the forgery stamp papers.

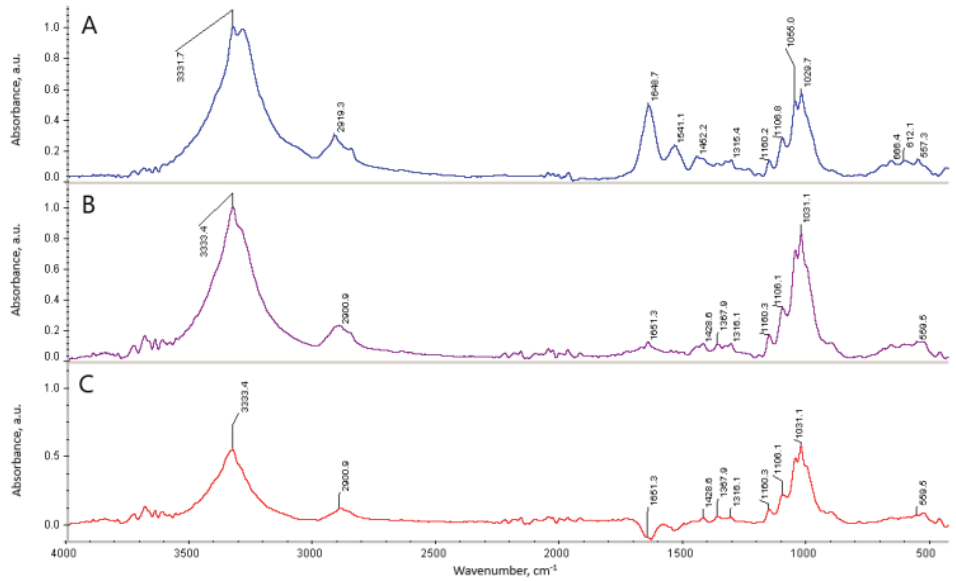

Fig. 4. FTIR spectra of: A) 40 para original stamps paper printed in Vienna 1866, B) 40 para confirmed forgery stamps paper and C) subtraction result of the original and the forgery stamp papers.

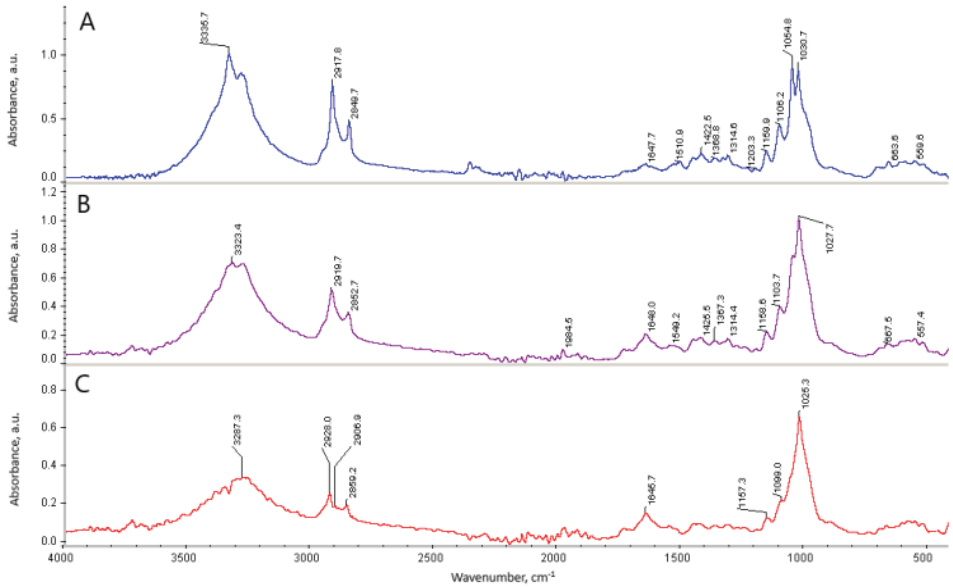

Fig. 5. FTIR spectra of: A) 10 para original stamps dye printed in Vienna 1866, B) 10 para confirmed forgery stamps dye and C) subtraction result of the original and the forgery stamp dyes.

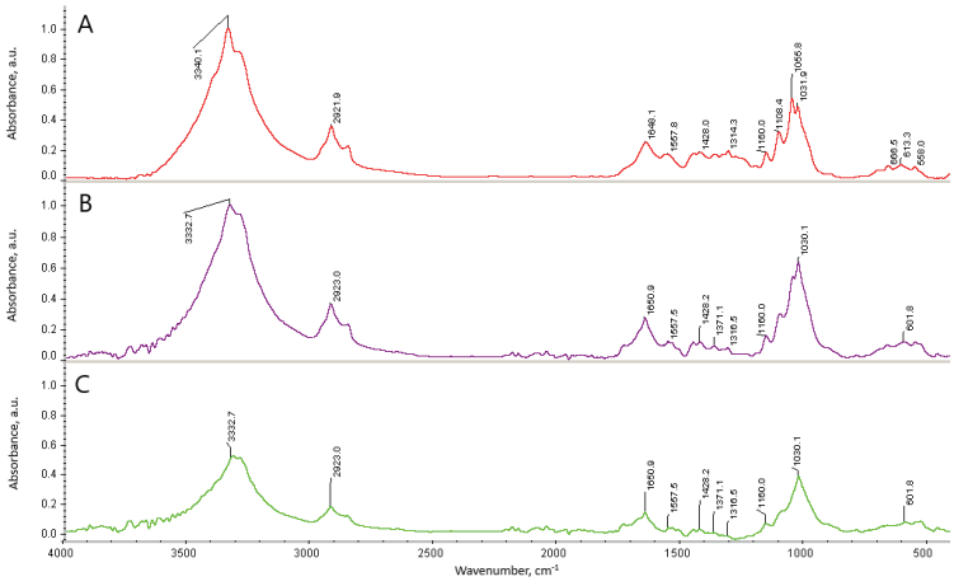

Fig. 6. FTIR spectra of: A) 20 para original stamps dye printed in Vienna 1866, B) 20 para confirmed forgery stamps dye and C) subtraction result of the original and the forgery stamp dyes.

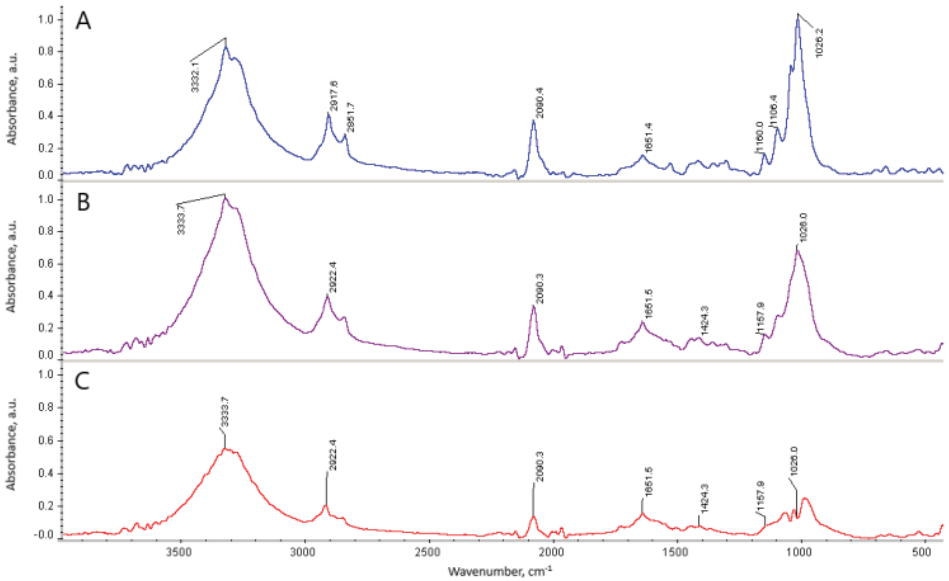

Fig. 7. FTIR spectra of: A) 40 para original stamps dye printed in Vienna 1866, B) 40 para confirmed forgery stamps dye and C) subtraction result of the original and the forgery stamp dyes.

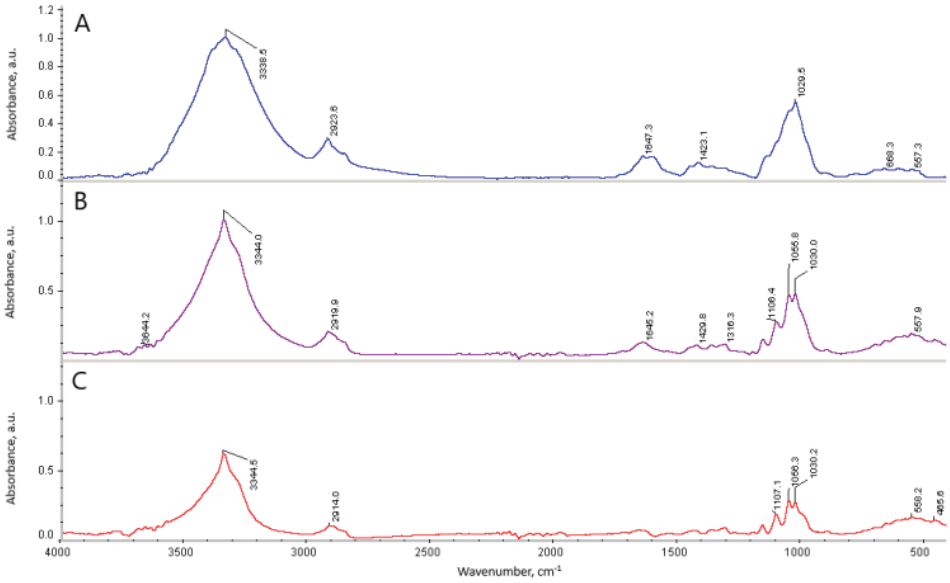

Fig. 8. FTIR spectra of: A) 1 para original dark green stamps paper printed in Belgrade 1868, B) 1 para confirmed forgery stamps paper and C) subtraction result of the original and the forgery stamp papers.

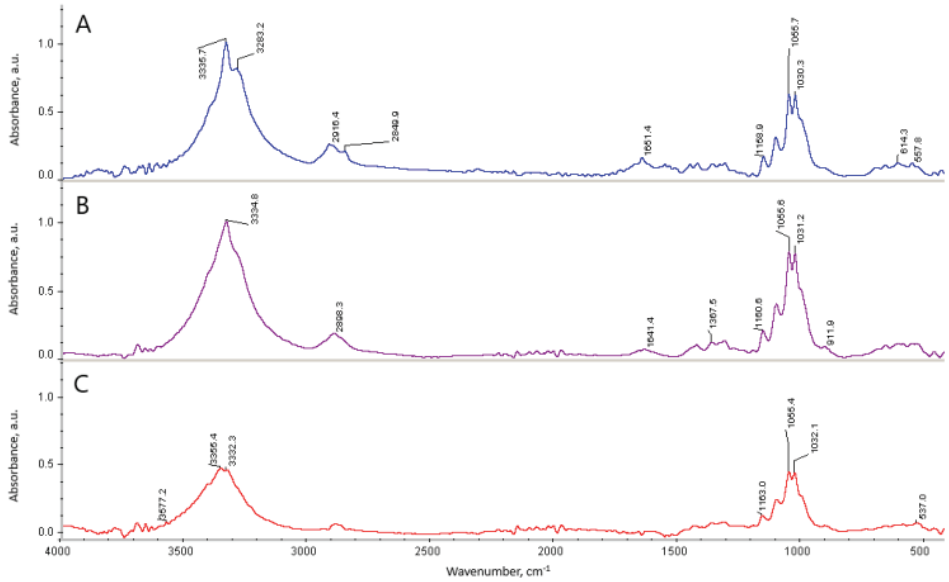

Fig. 9. FTIR spectra of: A) 2 para original stamps paper printed in Belgrade 1868, B) 2 para confirmed forgery stamps paper and C) subtraction result of the original and the forgery stamp papers.

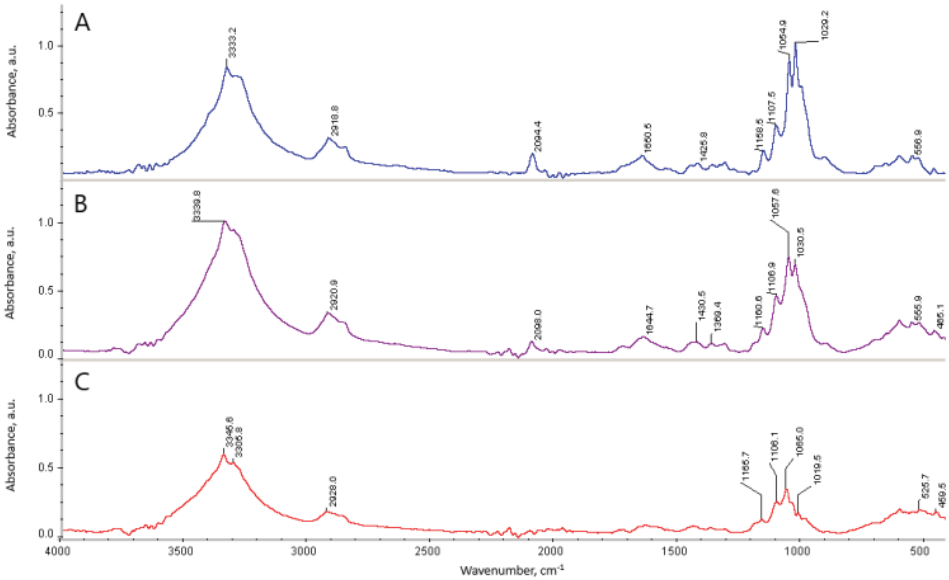

Fig. 10. FTIR spectra of: A) dye of 1 para original dark green stamp printed in Belgrade 1868, B) dye of 1 para confirmed forgery stamp and C) subtraction result of the original and the forgery stamp dyes.

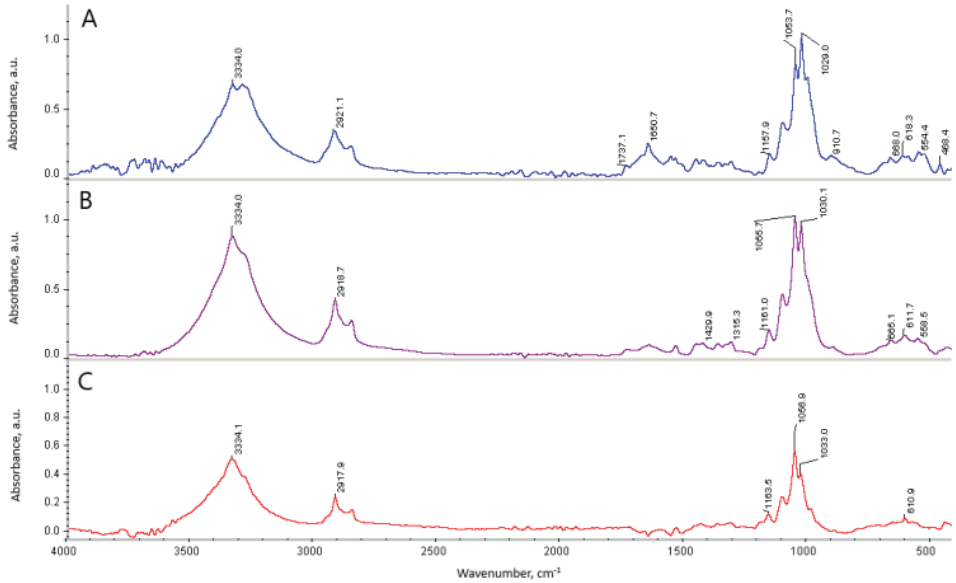

Fig. 11. FTIR spectra of: A) dye of 2 para original stamp printed in Belgrade 1868, B) dye of 2 para confirmed forgery stamps and C) subtraction result of the original and the forgery stamp dyes.

two processes, and it is not expectable that conspirators that produced false stamps could have the same paper available. In case of the 10 para stamp (Fig. 2), the intensity of peaks of the originals and fakes were different. In addition, the spectra of the genuine stamp exhibit a shoulder at 984 cm^{-1} that the forgeries do not have, while peaks at 533 or 910 cm^{-1} are absent in the spectra of the originals but are visible in the spectra of fake stamps. Differences also exist in the spectra of paper of the 20 para original and the certified forgeries (Fig. 3).

In the original stamp, the IR spectrum revealed the existence of a shoulder--like band at 3100 cm^{-1}, which is not seen in the spectrum of the fake stamp of the same denomination. On the contrary, the counterfeit exhibited a band at 1428 cm^{-1} not existing in the spectrum of the original stamp. Finally, the spectrum of the paper of the 40 para stamp (Fig. 4) was also different from those of known and proven forgeries. Its spectrum has a peak at 1542 cm^{-1}, not existing in the fakes, as well a peak at 1648 cm^{-1}, present in the spectra of some, but not all of the forgeries. However when present, they are never as intensive as in the spectrum of the original. Finally, forgeries exhibit different peaks not existing in the spectra of the originals, most commonly at 470 and 911 cm^{-1}.

Since the original stamps having denomination of 10, 20 and 40 para were, according to the available literature,[28,29] printed at the same time in the same printing house, it should be reasonable to expect that the spectra of their papers should match. However, although this is the case for 20 and 40 para stamps, the

one with denomination of 10 para does not have a band at 1551 cm^{-1} other two do. This raises the question of whether the 10 para orange-yellow stamp is original, as claimed by experts, and, if so, were two different sorts of papers used for printing the same set of stamps in Vienna?

If the spectra of the dyes of original and fake stamps are compared, in most, but not all cases, there are differences between the legal issues and those made for criminal purposes. When 10 para orange-yellow colour was compared (Fig. 5), ribbons existing in spectra of original stamp at 1510 and 1536 cm^{-1} do not exist in the spectra of the forgeries. The pink dye used for printing the 20 para stamp (Fig. 6) in Vienna exhibits peaks at 1284, 1253 and 1557 cm^{-1}, not seen in the forgeries, while some, but not all fakes, do have a specific peak at 1733 cm^{-1} not observed in the original. Minimal differences exist in the spectra of the blue dye used for the 40 para stamp, some of the peaks in original (1543 and 558 cm^{-1}) are more intense than in the forgeries (Fig. 7).

Comparison between spectra of original stamps of 1 para and 2 para, as well as between the certified originals and proven forgeries did not show such spectacular results as in case of the "Vienna issues". When the spectra of the paper of two originals were compared (Figs. 8 and 9), they did not show any differences, which is to be expected since they were printed in same printing house in Belgrade, and at the same time. However, more interesting and a bit unexpected is the fact that there is no differences between the original of 1 para and the compared fake, and between of original of 2 para and the analyzed fakes (Figs. 8 and 9). Bearing in mind that the stamps were issued in 1868 and that, most probably, the forgeries were made decades later, when philately and values of rare post stamps came into the focus of collectors worldwide, the credit is due to counterfeiters who used the same paper as the original one, at a time when analytical methods were not widely accessible.

Based on the information extracted from the IR spectra after their processing with PeakFit software, the values of the wavenumbers for dyes of 1 and 2 para originals stamps and proven forgeries were obtained and are shown in Tables II and III.

TABLE II. Wavenumber values (cm^{-1}) of dyes of original and forged 1 para green post stamps

Original	Forgery 1	Forgery 2	Forgery 3	Forgery 4	Forgery 5	Forgery 6	Forgery 7	Forgery 8
580	551	571	571	532	549	572	539	570
566	499	483	490	473	486	554	482	471
520	464	456	462		452	486		
501						473		
468								
428								

This information is compared to the spectral data of the most frequently used green (Table IV), red (Table V) and yellow (Table VI) pigments, and it was concluded that green malachite pigment ($CuCO_3 \cdot Cu(OH)_2$) was used for the 1 para stamps, while a mixture of lead contained red (Pb_3O_4), and yellow (PbO) pigments was used for the 2 para stamps.

TABLE III. Wavenumber values (cm^{-1}) of dyes of original and forged 2 para reddish-brown stamps

Original red	Original yellow	Forgery 1	Forgery 2	Forgery 3	Forgery 4
526	581	596	568	548	578
511	504	574	485	491	481
450	494	466		463	
440	482				
	466				
	413				

TABLE IV. Wavenumbers (cm^{-1}) of the most frequently used green pigments

Bohemian Green	Cr_2O_3	Cobalt Green (CoO·ZnO)	Malachite ($CuCO_3 \cdot Cu(OH)_2$)	Vagone Green Earth	Verdign Green ($Cu(CH_3COO)_2 \cdot 2Cu(OH)_2$)	Green ($Cr_2O_3 \cdot 2H_2O$)
497	571	409	581	519	561	570
462	445	327	571	498	521	559
437	416	250	523	465	460	496
397	307	230	501	415	374	477
	227		464	382	327	422
			427	315	271	386
			386		253	
			355			
			322			

TABLE V. Wavenumbers (cm^{-1}) of the most frequently used red pigments

Cadmium Red (CdS+ +CdSe)	Caput Mortuum Reddish (Fe_2O_3+silicate)	Cinabarite (HgS)	Red Earth (Fe_2O_3+ +kaoline)	Pompeiian Red (Fe_2O_3+ +kaoline)	Minium (Pb_3O_4)	Venetian Red (Fe_2O_3+ +gypsum)
272	528	342	537	534	528	460
268	458	301	467	466	513	446
258	379	284	431	428	454	422
230	294	280	396	334	442	377
		268	366	318	381	354
			344	300	334	301
			336	272	326	255
			321	234		237
			297			

The spectra of coloured sectors of the original stamps were different from the same spectra of the fake stamps, forged stamp of 1 para has a peak at 2099 cm^{-1}, not seen in the original (Fig. 10), while in case of the 2 para stamp, there are peaks at 910 and 2854 cm^{-1} which are not seen in the spectra of the fake stamps, while there is a band at 1005 cm^{-1} in the spectrum of original, while the forged stamp exhibited a shoulder (Fig. 11).

TABLE VI. Wavenumbers (cm^{-1}) of the most frequently used yellow pigments

Barium yellow ($BaCrO_4$)	Cadmium yellow (CdS)	Chromium yellow ($PbCrO_4$)	Lead yellow (PbO)
418	261	464	582
391	247	384	503
374		377	495
336		279	484
238		262	464
			415
			375

CONCLUSIONS

FTIR-ATR spectroscopy, as a non-destructive and reliable technique, was used for the analysis of certified originals of Principality of Serbia stamps issued in 1866 and 1868 and their forgeries. Differences between the paper used for original and fake stamps was, in most but not all examined samples, clearly established. Moreover, the applied spectroscopy was a powerful tool not only for differentiation of the dyes used for originals and fakes, but also, in cases of 1 and 2 para issues of 1868, a tool for identification of pigments used (green malachite ($CuCO_3 \cdot Cu(OH)_2$) for 1 para stamps, mixture of lead contained red (Pb_3O_4) and yellow (PbO) for the 2 para stamp). The difference between the papers used for the printing of 1866 issue has been established, and the possibility that the so-called "Vienna issues" may not have been printed at the same time or in the same printing house has been proposed. FTIR-ATR spectroscopy was proven to be valuable method for comprehensive analysis of potential philatelic forgeries.

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ИЗВОД

ПРОФЕСОРУ ПЕТРУ ПФЕНТУ, *IN CALIDUM, ET PLURIUM RETRIBUTIVUS MEMORIAE*: FTIR-ATR АНАЛИЗА ОРИГИНАЛНИХ ПОШТАНСКИХ МАРАКА КНЕЖЕВИНЕ СРБИЈЕ ИЗДАТИХ ИЗМЕЂУ 1866. И 1868. ГОДИНЕ И ЊИХОВИХ ФАЛСИФИКАТА

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Како би се утврдиле могућности коришћења FTIR-ATR као недеструктивне и поуздане технике за анализу поштанских марака, анализирани су оригинали и фалсификати марака Кнежевине Србије издате 1866. и 1868. године. Снимљени су спектри који су омогућили поређење папира, боја и гуме оригинала такозваних „Бечког издања“ вредности 10 (наранџасто-жута), 20 (ружичаста) и 40 (плава) пара, „Београдског издања“ (1 пара-светло и тамно зелена и 2 паре – црвенкасто-смеђа) као и 12 фалсификата, које су као и оригинале, сертификовали овлашћени испитивачи. Показано је да је примењена аналитичка метода у већини случајева погодна и да је њеним коришћењем могуће разликовати папир и боју оригинала од фалсификата који су, готово извесно, штампани неколико деценија касније. Утврђене су и разлике у папиру између оригинала истог издања, па је предложена могућност, по први пут у филателистичкој историји, да су марке „Бечког издања“ штампане на два различита папира, а имајући у виду тадашњу технологију штампања, могуће чак и у различито време или различитој штампарији.

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