Database of Raman Spectra of Inks Used on Banknotes

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Abstract: - Based on the characteristic Raman spectra of note materials, paper and inks, the authenticity assessment of Czech banknotes is presented. Raman spectroscopy has by its nature a potential to recognize different substances, even their structural modifications. That is why it is a powerful method for relatively rapid material identification. On the basis of Raman spectra is possible to determine whether the questioned banknote is genuine or a forgery. Popularization and availability of digital technology shifts the level of counterfeits at a higher level and we need to have effective means for the detection. This paper is focus on systematic experimental examination of inks used on all Czech banknotes in order to obtain a spectral response of the composition, although it is a manufacturing secret, and create database of Raman spectra for the purpose of further verification of banknotes.

Key-Words: - Czech banknotes, Database, Raman spectroscopy, Raman spectra, authenticity, identification

1 Introduction
Raman spectroscopy is an innovative analytical tool that becomes a valuable part of laboratories around the world lately. This modern analytical method allows an insight into the structure of materials on a molecular level and enables an evaluation of their composition based on the characteristic vibrations of these molecules caused by monochromatic light. It is a powerful tool for material identification. Applications of Raman spectroscopy comprise increasing number of scientific and technical fields in recent years. As an example may be mentioned following: material sciences, nanotechnology, semiconductors, chemistry, biology, pharmaceutical industry, medicine, area of arts and cultural heritage, last but not least also forensic analysis [1], criminology and interests of the security.

Raman spectroscopy has a potential of an effective tool for quite fast identification [2]. The key importance for the identification of materials consists in Raman spectra. Every single chemical substance, its modification or compound has its unique set of molecular vibrations, which can be recorded as Raman spectrum that is characteristic purely for the appropriate substance. Essentially it is analogical to the human fingerprints. Every single human being on Earth has its own unrepeatable set of fingerprints which can be used for his/her identification. The method is also non-destructive, what is a one of the basic requirements for forensic examination. Researched notes may be after the measurement, if genuine, return back into circulation.

Banknotes as a universal mean of payment are used worldwide. Also, the effort for enrichment can be found all over the world. Being not unusual this desire is accompanied by illegal activity comprising forgery of money. To prevent counterfeiting banknotes, most of banknotes contain different numbers and more or less successful security features. Many of them are recognizable to the naked eye, some can be verified using e. g. UV light, but some require more advanced analytical tools.

Using mentioned fundamental features of Raman spectroscopy, the possibility of the assessment of the authenticity of Czech banknotes has been investigated. Raman spectroscopic analysis of the used inks and the paper can be conductive to reveal the crime against the currency. Any differences in the composition of the inks or in the paper should appear in their Raman spectra as a presence or an absence of particular peaks and their distribution in spectrum.

2 Scope of the research
The focus of this paper is to introduce a using of Raman microscopy to distinguish genuine Czech banknotes and the counterfeits. Second base is the...
creation of database of Raman spectra of inks used on Czech banknotes. This database can serve for relatively rapid evaluation of spectral data of examined banknotes.

3 Theory
3.1 Czech Banknotes
There is six banknotes currently in the circulation of currency in the Czech Republic, valid since 1993. The nominal value of these banknotes are 100 CZK, 200 CZK, 500 CZK, 1000 CZK, 2000 CZK and 5000 CZK. The Author of all Czech banknotes is Oldrich Kulhanek, Czech painter, graphic and stage designer. 1000 CZK banknote with innovative security features was in 2008 selected as the banknote of the world.

3.2 Statistics counterfeits
An occurrence of counterfeits of Czech Banknote has according to Czech National Bank (CNB) rather decreasing trend since 2003. Nevertheless 3586 notes in the in a cash value 3,739 million CZK was captured in 2012. The most often faked are 1000 CZK (41,6 %) and 500 CZK (29,9 %) notes. Absolutely predominant (84,5 %) forgery technique in the long term is inkjet print, as is shown in Fig.1 Color copying was used for 15,3% revealed fakes. On a five-grade scale of danger (1 very dangerous - 5 primitive) the most is graded as 4 (less successful) And even the count of grade 2 (dangerous) decreased from 21,8 % of all Czech falsified notes in 2011 to 9,1 % in 2012. [3]

3.3. Raman spectroscopy
Raman spectroscopy has recently become a popular method for material identification. This analytical method provides very specific chemical “fingerprint” of every single chemical substance in the form of the Raman spectrum. Raman spectroscopy is based on so called Raman scattering. Raman scattering is an inelastic scattering resulting from an interaction of a photon and a molecule. Inelastic scattered photons have slightly changed wavelengths. These changes are characteristic for specific bonds in surveyed material. Since most photons are on molecules scattered elastically (Rayleigh scattering i.e. without changing the wavelength), it is necessary to filter out of the spectrum the strongly present wavelength of laser. Raman and Rayleigh scattering are shown schematically in Fig. 2. Although the fundamental

![Fig. 2 Energy level diagram of Rayleigh and Raman scattering](image)

phenomenon was discovered almost 85 years ago, its effective use in Raman spectroscopy occurs in about last decade. The rebirth of this method goes hand in hand with advances in technology: powerful lasers as sources of monochromatic light, efficient Notch filters transmitting all the wavelengths except the excitation wavelength of the laser, sensitive detectors and last but not least computer technology. Raman spectroscopy has many advantages. The method is:
• Non-destructive what allows undergoing investigated samples further analyses or simply repeat Raman analyses.
• Relatively rapid, Raman spectra can be acquired within seconds.
• Contactless what is convenient, samples are not contaminated, also it is advantageous when toxic, dangerous samples or those with strong aroma are measured. There also exists a possibility of measuring samples through transparent glass or polymeric covering layers or containers. Raman spectra of the covered sample and the cover can be then subtracted via software.
• Applicable to all states of matter and different its forms (crystals, powders, fibers, solutions, etc.).
• Without special requirements for sample preparation, what is convenient and prompt.
• Usable as in situ analysis.

The greatest drawback of the method is the fact that Raman scattering is a weak effect. Luminescence as much stronger quantum effect with bigger intensity can overlap Raman spectra and mask spectral information. Another disadvantage is eventual degradation of a sensitive sample when using intense laser beam [4].

4 Experimental part
All Czech banknotes were analyzed by Raman spectroscopy. The procedure is demonstrated on 200 CZK note in this paper, but the same routine was applied on all banknotes. On each note 23 points were picked on the face and the reverse side as is shown in Fig. 3. The criterion of performance consists in a color layout and also distribution of methods used during the production of the notes and application of protecting elements.

To study the diversity of the results two types of notes imitation were created – by the inkjet printer and by color print. These are the most often methods for counterfeiting.

4.1 Materials
The most important aspect of the analysis notes using Raman spectroscopy are used inks and paper.

4.1.1. Inks
By a comprehensible reason a specific composition of inks used on banknotes is not publically known. Although the composition is a manufacturing secret, using Raman spectroscopy does not suffer from absence of this concrete information. Original banknotes provide corresponding data which will serve as a standard for comparison. Colors occurring on all notes together with number of protective elements are listed in Table 1.

Table 1 Inks and security features on banknotes

<table>
<thead>
<tr>
<th>Value [CZK]</th>
<th>No. of measured points</th>
<th>Inks - colors</th>
<th>No. of security features</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>23</td>
<td>green, red, yellow, black</td>
<td>6</td>
</tr>
<tr>
<td>200</td>
<td>23</td>
<td>brown, orange, green, black</td>
<td>6</td>
</tr>
<tr>
<td>500</td>
<td>23</td>
<td>brown, yellow, red, orche, green, black</td>
<td>7</td>
</tr>
<tr>
<td>1000</td>
<td>23</td>
<td>violet, orche, pink, blue, black</td>
<td>8</td>
</tr>
<tr>
<td>2000</td>
<td>23</td>
<td>green, violet, yellow, pink, black</td>
<td>8</td>
</tr>
<tr>
<td>5000</td>
<td>23</td>
<td>blue, red, yellow, pink, black</td>
<td>8</td>
</tr>
</tbody>
</table>

4.1.2. Paper
Banknotes are print on high quality paper, which is most commonly based on cotton and contain characteristic fibers (several mm long) and watermarks to prevent the imitation. More stringent requirements are laid on this paper in comparison with ordinary consumer paper. Banknote paper must have greater strength and flexibility, must be resistant to bending, breaking and tearing (even the wash in a washing machine). Czech banknotes are printed on natural colored paper. This means that the paper is not pure white, but has a very weak light – ocher tint.

One of the easiest ways of fake’s recognition is its sound of wrinkling or friction (the acoustic safety feature). It is influenced by appropriate composition of the paper fibers. The paper notes sounds different than writing paper, the sound is tougher.

4.2 Raman spectroscopy
InVia Basis Raman microscope from Renishaw was used for recording Raman spectra of inks and the paper of Czech banknotes. Argon ion laser with the excitation wavelength 514nm and maximum output power of 20 mW and 785 nm NIR diode laser with maximum output power 300mW were used as light sources. A Leica DM 2500 confocal
microscope with the resolution up to 2µm was coupled to the Raman spectrometer. All measurements were collected at 20x - 50x magnification, with 15 s exposure time and 10 accumulations. Powers of lasers were from 0.1% to 5% of the output laser power. The samples were scanned in range 200 to 3200 cm\(^{-1}\) with 2 cm\(^{-1}\) spectral resolution.

5 Results
Czech banknotes and their imitations were measured using visible laser light with the wavelength 514 nm and NIR laser with 785 nm. Some of the inks exhibit luminescence and its Raman spectrum was poor quality or was not possible to acquire by visible laser. In these cases most of them were acquired by NIR laser. High level of luminescence was also present with imitations. This behavior is also a partial result indicating the presence of luminescent element which is missing in originals. In Fig. 4 Raman spectra of green ink in 200 CZK gained by two lasers is shown.

![Fig. 4 Raman spectra of green ink in 200 CZK gained by two lasers](image)

Raman spectra of banknote paper and ordinary office paper used for imitations are displayed in Fig. 5. Spectrum of paper confirms the presence of viscose fibers recovered from cellulose that are similar in structure to fibers of cotton from which are divergent mainly by the presence of the peak at 650 cm\(^{-1}\) for C-S-C vibrations. This peak is also missing in spectrum of ordinary paper.

![Fig. 5 Raman spectra of banknote paper and ordinary office paper](image)

Noticeable differences in Raman spectra are recorded for genuine banknotes and reproductions as is shown in Fig 6 and Fig 7 for orange and green ink in 200 CZK notes. Different layout of Raman peaks and their intensities clearly demonstrate various compositions of used inks.

![Fig. 6 Raman spectra of orange ink on genuine 200 CZK note and two imitations](image)

![Fig. 7 Raman spectra of green ink on genuine 200 CZK note and two imitations](image)
6 Database of Raman spectra
More than 500 Raman spectra were acquired from specified points from all Czech original banknotes using both lasers. On all spectra was performed baseline correction. These data were used to create Raman spectral database of inks used in Czech banknotes in Spectra ID, which is a rapid and robust application for spectral searching needs. Created database offers the possibility of full spectrum search, peak search or text searches with searching algorithms including Correlation, Absolute Value, Least Squares and their 1st Derivatives, and Euclidean for full spectral search. This spectral library is a valuable tool in the authentication of banknotes.

6 Conclusion
Raman spectroscopy was used as an innovative tool for analyzing inks and paper used on Czech banknotes. These features may due to the characteristic Raman spectra provide information about the authenticity of banknotes and point out any successful forgeries, which are not possible to distinguish with the naked eye. For the purpose of further verification of banknotes was created Raman spectral database of inks measured on all Czech banknotes using two different lasers. Further procedure will be focused on the expansion of library by Raman data of banknotes of different series.

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