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Short communication

Mössbauer and X-ray fluorescence measurements of authentic and counterfeited banknote pigments

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ABSTRACT

Mössbauer and X-ray fluorescence studies revealed that a number of valuable monetary units (dollars, pounds, yen, old German marks, and others) are printed using pigments which contain considerable amounts of iron. Mössbauer spectroscopy has been applied to the analysis of the pigments that are used in both authentic and counterfeit currency notes.

1. Introduction

After the large counterfeiting of British currency in Germany during World War II, the major subject of forgery has been US paper money; the 100 USD Federal Reserve Notes (FRN) are most frequently falsified. The so-called "super hundreds" or "super dollars" are "very high quality" false banknotes printed probably on Giori presses by the intaglio method using iron-bearing pigments similar to those used by the Bureau of Engraving and Printing (BEP) in Washington DC [1]. The dollar color design is a comparatively simple one and includes two basic magnetic pigments namely a magnetite black pigment and chrome green dye on the backside (Fig. 1a). This simple color design is probably the main reason responsible for the repeated attempts to counterfeit dollar bills. To avoid further problems the BEP released enormous quantities of newly designed 100 USDs issued in the series of 1996 and after. Improved security features such as denim fibers, security thread, water mark, etc. have been added to the paper. This decision aimed to replace as rapidly as possible the old design of 100 USDs of the series up to 1993 [2]. Despite that the new design was immediately counterfeited, too. Some authors or commercial firms claim that their instruments can detect the magnetism of very small areas, for example the dot over the *i* in the signature on a US dollar bill [3] which is intensively used as a simple test for authenticity in the vending machines. However, the "high quality" forgeries are printed with magnetite Fe_3O_4 black pigment and on the green backside with another iron-bearing pigment and pass the magnetic test (Fig. 1b). There are many other forgeries printed with a simple carbon black pigment (carbon + $Ca_3(PO_4)_2$) (Fig. 1c); these are easy to distinguish from authentic banknotes and have not been subject of investigation in previous studies [4–6] or here. In this work we report summarized data for the Mössbauer parameters of the pigments used to print authentic and counterfeit USD banknotes. Initial results from the measurements of the pigments of the EURO banknotes are also presented [7].

2. Experimental section

In the concluding remarks of the Mössbauer conference in China, 1991, Gonser discussed the application of Mössbauer spectroscopy to the magnetite Fe_3O_4 that is used on one-dollar bills as a curious finding which seems that Mössbauer spectroscopy can tell us what is genuine currency and what is a fake [8]. Subsequently, a large number of authentic and counterfeit USD banknotes were studied by means of two experimental techniques, Mössbauer spectroscopy and Energy Dispersive X-Ray Fluorescence (EDXRF) analysis. In this work, the authentic 100

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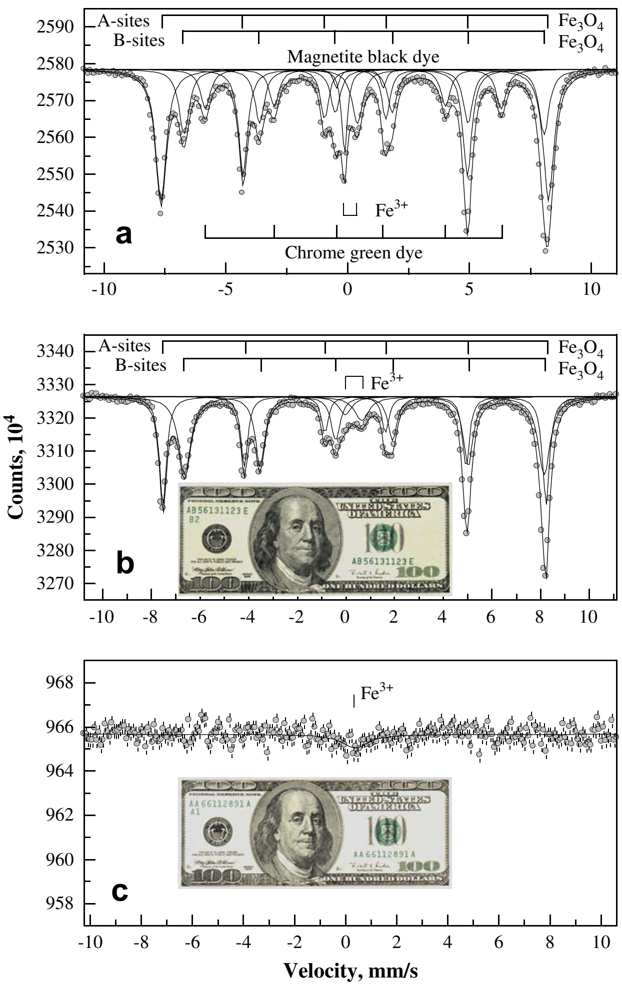

Fig. 1. Typical Mössbauer spectra obtained at room temperature from genuine 100 USD banknotes (a) shows that the two pigments used are magnetite black dye and chrome green dye. Mössbauer spectra obtained at room temperature from "high quality" counterfeit 100 USD banknotes (b) printed with iron-bearing pigments and counterfeit 100 USD banknotes (c) printed with simple carbon black dye. Adapted and extended from Ref. [4] with permission of Applied Spectroscopy.

USD banknotes were chosen at random while the counterfeit banknotes were kindly provided by Bulbank Ltd, Sofia, Bulgaria. For the Mössbauer investigations standard spectrometers working in transmission geometry, constant acceleration mode and equipped with a ^{57}Co[Rh] radioactive source of about 30 mCi activity were used. The isomer shifts are referred to α-Fe standard at room temperature. The parameters of the γ-pulse-height window must be optimally chosen since the concentration of iron in the sample is very small. The ratio signal/noise in the window of the differential discriminator must be better than 5:1 in order to obtain high quality Mössbauer spectra from a single banknote. The spectra with statistics of about 2×10^7 counts/channel have been accumulated for several days provided the banknotes were properly folded and rolled as already shown in a previous work [5]. For an estimate of the iron concentration in a banknote from the Mössbauer spectra the "area method" of Hafemeister and Brooks Shera [9] has been applied. The presence of iron in the printed inks was first checked with a simple homemade EDXRF spectrometer with isotopic (^{241}Am, 60 keV) excitation of the characteristic X-rays and an X-ray XR-100T/CR Si PIN detector Amtek Inc. Additionally, the iron concentrations and element composition have been precisely confirmed by EDXRF analysis using an electron probe microanalyzer JEOL Superprobe 733 with a Si(Li) detector Ortec 7986-P30.

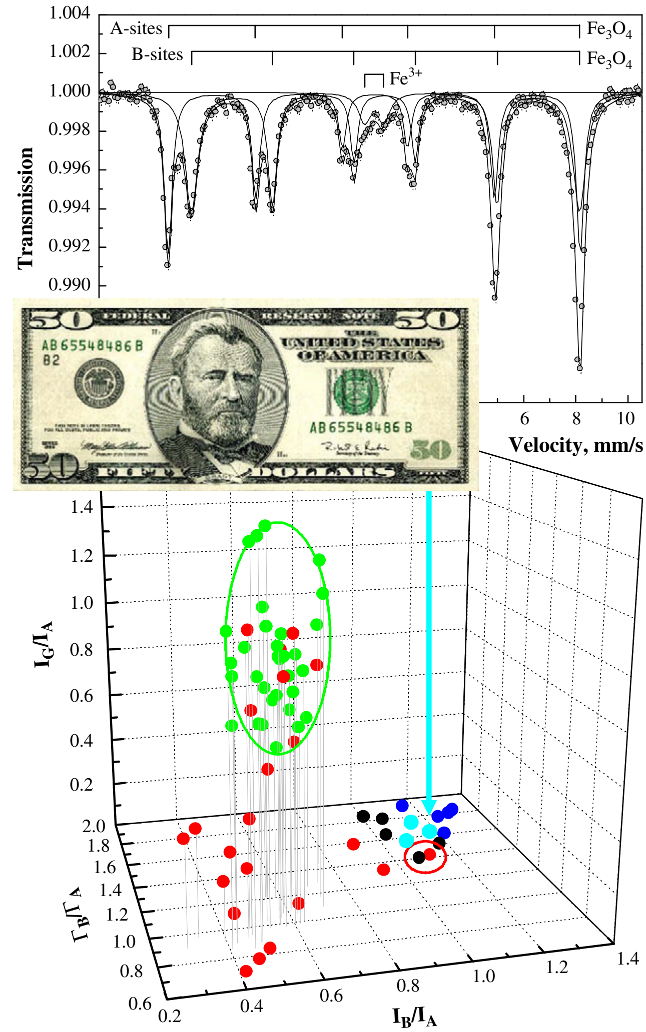

Fig. 2. (Top) Mössbauer spectrum obtained at room temperature from a single counterfeit 50 USD banknote. (Center) Photograph of the newly designed counterfeited 50 USD banknote from which the Mössbauer spectrum was obtained. (Bottom) Distribution of Mössbauer parameters of all banknotes measured in a coordinate system with the following three axes: first line area ratio of the B- and A-sites sextets in magnetite I_B/I_A; area ratio between the first line of the green dye sextet and the first line of the A-sites sextet in magnetite I_G/I_A; and ratio of the experimental line widths for the first lines of the B- and A-sites sextets of magnetite Γ_B/Γ_A. Red dots – genuine 100 USD issued between 1934 and 1993 (without the issue of 1990), green dots – genuine 100 USD issued 1990, and the boundary of the 1990 sample is marked with a green line. Black dots – counterfeit 100 USD old bill, blue dots – counterfeit 100 USD new bill, and cyan dots – counterfeit 50 USD new bill. Authentic and counterfeit banknotes with similar parameters are marked with a red line.

3. Results and discussion

The Mössbauer studies show that a number of valuable monetary units are printed using dyes which contain considerable amounts of iron [4–6]. Counterfeiting requires a reproduction of the properties of the pigments. For the most important pigments used for specific purposes the reproducibility of their properties should be high. Our systematic studies on different issues of authentic banknotes show that the composition of the black pigment (a mixture of two iron oxides – magnetite Fe_3O_4 and maghemite γ-Fe_2O_3) as well as the stoichiometry of the magnetite alone is consistent and stable. Surprisingly, the green pigment has less stable properties. The intensity of the subspectra of the green pigment (the Zeeman sextet and quadrupole doublet shown in Fig. 1a) varies greatly from nearly zero intensity to dominant subspectrum [4]. The large variations in the chemical composition of the green printing inks are amazing and difficult to explain. In the work of Hall and Chambliss [10] the green pigment was identified as C.I. Pigment Green 15, also known as Chrome Green, $PbSO_4 \times xPbCrO_4 \times yFe_4[Fe(CN)_6]$. Perhaps the BEP was experimenting with a substitute pigment for the green ink. The lead-based printing inks have been phased out due to health concerns. The lead–chrome oxide, which was probably partially substituted by iron (the sextet subspectrum), was changed to chemically pure chrome green, Cr_2O_3 precipitated onto $BaSO_4$. The lower quality and not lightfast iron blue in the form of Prussian blue $Fe_4[Fe(CN)_6]$ (the quadrupole doublet subspectrum) were changed to another non-iron pigment of high lightfastness. These considerable chemical changes are the reason why sometimes the Zeeman sextet subspectrum, the quadrupole doublet or both are absent in the Mössbauer spectra. In some cases the Mössbauer spectra of the authentic banknotes are visually similar to those of counterfeit money from Fig. 1b.

The instability of the green pigment is most probably another reason for the forgery of the newly designed 50 USD banknotes. In the last few years the "high quality" forgery of the new 50 USD banknotes has widely spread. Bank experts are concerned to identify another "high quality" forgery of the newly designed 20 USD, too. Here we present and discuss spectra taken from some of the "new" 50 USD forgeries [7]. The black pigment is again of the magnetite type with $I_B/I_A \cong 1.2$ as in the counterfeit 100 USD. The green pigment spectrum is without Zeeman sextet and the spectrum (Fig. 2, top) looks generally like the one in Fig. 1b. Summarized results from the measurement of 54 authentic and 13 forged banknotes are given in Fig. 2, bottom. Some important conclusions can be drawn: (1) The green pigment possesses unstable properties as already pointed out. The distribution of the parameters has a large dispersion (red and green dots) and the parameters of eight of the measured banknotes lie in the horizontal plane, which means zero intensity of the Zeeman sextet of the green pigment. Three of them exhibit parameters dangerously close to the forgeries, and one shows practically the same parameters as the counterfeit banknotes. (2) The issue of 1990 (and probably all later issues) have higher consistency and stability of the properties of the green pigment. It is obvious that in these issues (green dots) additional effort has been taken to improve the stability of the pigment properties. (3) All counterfeited banknotes (five 100 USD banknotes old bill, five 100 USD banknotes new bill and three 50 USD banknotes new bill) are grouped closely together with parameters $1.0 \le I_B/I_A \le 1.3$, $1.4 \le \Gamma_B/\Gamma_A \le 1.9$, and $I_G/I_A = 0$. Mean values of the Mössbauer parameters measured from all banknotes are summarized in Table 1. Some parameters such as the experimental line width, Γ_{exp} of the magnetite B-sites sextet and its relative intensity, I_{rel}, the absence of green dye sextet which are never observed in the forgeries and the new values of the green dye doublet (all given in bold) allow unambiguous discrimination of counterfeit banknotes from originals. On the other hand the parameters measured for all counterfeit banknotes: 100 USD all bill, 100 USD and 50 USD new bill do not differ greatly from one another.

For the calculation of the iron concentration the "area method" of Hafemeister and Brooks Shera [9] has been applied. In the authentic banknotes varying concentrations up to 10 $\mu g\,mm^{-2}$, typically 5–6 $\mu g\,mm^{-2}$, have been measured. Nearly the same values were found by the EDXRF method [10]. In the false banknotes the concentrations were measured to be 2–3 times lower. The concentrations obtained are mean averages and semi-quantitative because the printed ink area is irregular and smaller than the area of measurement covered by the γ-beam.

The iron concentration and chemical element composition in EURO banknotes have first been determined by simple homemade Energy Dispersive X-Ray Fluorescence spectrometer (Fig. 3). A simple set up was created for the purpose of comparatively fast semi-quantitative control of iron concentration and of the concentration of the other chemical elements in the samples with unknown origin. This allowed optimizing the sample thickness for further Mössbauer spectroscopic investigations. Iron was detected in all EURO banknotes, the highest being in 5 EURO (Fig. 3), twice lower in 50 EURO and four times less in 20 and 100 EURO banknotes. Ca and Ti were the other elements detected. All other lines

Table 1
Mean values for the Mössbauer parameters of the spectra of all authentic and counterfeited 100 USD banknotes. Isomer shift IS relative to α-Fe at room temperature; quadrupole splitting ΔE_Q (peak separation); hyperfine magnetic field H_{hf} in the iron nucleus; experimental line width Γ_{exp} of the first line of the sextet or a doublet; partial intensity of the subspectrum I_{rel}. In brackets the uncertainty of the last digital is given. In eight of the 54 measured authentic 100 USD a green dye sextet has not been observed. Only in 19 spectra of the authentic 100 USD banknotes a green dye doublet has been observed. The mean values for the subspectra are calculated from 46 and 19 measurements respectively, which is why the sum of I_{rel} for the authentic 100 USD banknotes is more than 100%. All parameters of the counterfeited banknotes, with values different and out of the uncertainty ranges observed for authentic ones are given in bold.

Banknotes	Parameters				
	IS [mm/s]	ΔE_Q [mm/s]	H_{hf} [T]	Γ_{exp} [mm/s]	I_{rel} [%]
Authentic 100 USD					
Black dye, magnetite A-sites	**0.294**(**3**)	−**0.015**(**5**)	**49.3**(**3**)	**0.43**(**1**)	41(2)
Black dye, magnetite B-sites	**0.667**(**5**)	−**0.016**(**9**)	**45.9**(**6**)	**0.45**(**2**)	24(2)
Green dye, sextet	**0.371**(**5**)	−**0.281**(**7**)	**37.7**(**4**)	**0.48**(**2**)	39(2)
Green dye, doublet	**0.15**(**5**)	**0.54**(**8**)	**–**	**0.43**(**3**)	7(1)
Counterfeited 100 USD old bill					
Black dye, magnetite A-sites	**0.28**(**1**)	**0.00**(**1**)	**49.0**(**5**)	**0.38**(**1**)	41(2)
Black dye, magnetite B-sites	**0.65**(**1**)	**0.00**(**1**)	**45.9**(**8**)	0.66(2)	**49**(**2**)
Green dye, sextet	Not observed	Not observed	Not observed	Not observed	**Not observed**
Green dye, doublet	0.33(1)	0.79(1)	**–**	0.55(3)	10(1)
Counterfeited 100 USD new bill					
Black dye, magnetite A-sites	**0.28**(**1**)	−**0.02**(**1**)	**49.1**(**5**)	**0.35**(**1**)	40(2)
Black dye, magnetite B-sites	**0.66**(**1**)	**0.01**(**1**)	**46.1**(**8**)	0.60(2)	**54**(**2**)
Green dye, sextet	Not observed	Not observed	Not observed	Not observed	**Not observed**
Green dye, doublet	0.26(1)	0.72(1)	**–**	0.59(3)	6(1)
Counterfeited 50 USD new bill					
Black dye, magnetite A-sites	0.27(1)	−0.03(1)	49.0(5)	0.36(1)	43(2)
Black dye, magnetite B-sites	0.67(1)	0.03(1)	46.0(6)	**0.60**(**2**)	**51**(**2**)
Green dye, sextet	**Not observed**	**Not observed**	**Not observed**	**Not observed**	**Not observed**
Green dye, doublet	**0.25**(**1**)	**0.74**(**1**)	–	**0.57**(**3**)	6(1)

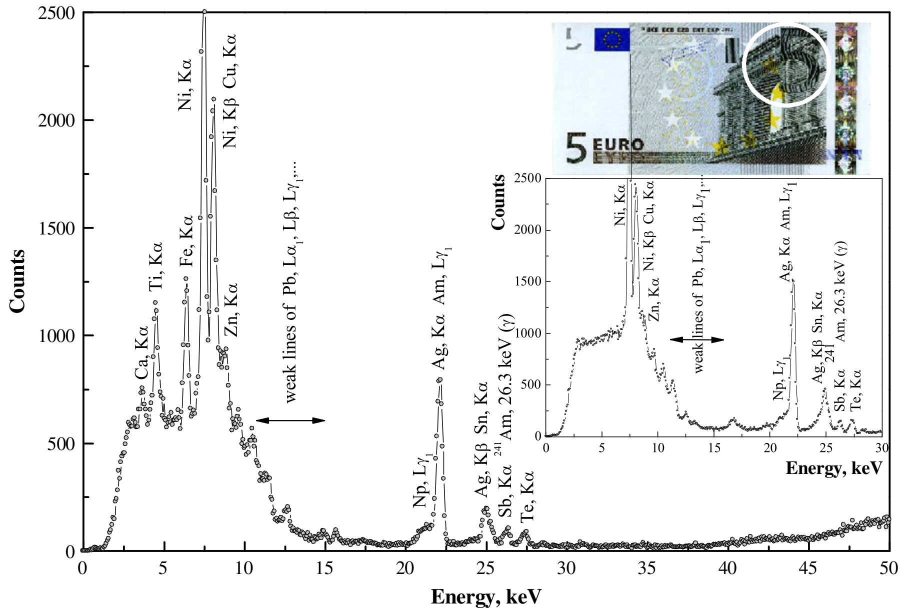

Fig. 3. X-ray spectrum of 5 EURO banknotes. The approximate area from which the spectrum was accumulated is marked with a circle. The background spectrum is given in the inset. It is accumulated without any sample in the experimental set up.

are artefacts related to: the ^{241}Am source holder (Ni), the brass container (Cu, Zn), the lead shield (Pb), some characteristic X-rays of Am, the daughter decay nuclide Np, the Ag protecting layer evaporated over the active ^{241}Am area, or from the construction materials of the X-ray detector and cooling Peltier element where the Si PIN detector is mounted (Sn, Sb, Te) [11].

A second set of measurements by EDXRF analysis using an electron probe microanalyzer JEOL Superprobe 733 with a Si(Li) detector Ortec 7986-P30 confirmed the sample element composition (Fig. 4). It is related to chemical compounds added to the paper as whitening and filler agents like Ti_2O, $CaCO_3$, $Al_2Si_2O_5(OH)_4$, and some calcination $CaSO_4$ or precipitation $BaSO_4$ products. Measurements showed comparatively high concentration of iron in the 5 EURO banknote, very small concentration in the 10 and 50 EURO banknotes, and practically zero concentration in 20 and 100 EURO.

Additionally, a set of Mössbauer measurements were carried out using EURO banknotes (Fig. 5). Only the €5 and €50 banknotes showed small quantities of iron in the form of magnetite Fe_3O_4 and α-Fe. The iron concentrations were very low (0.36 and 0.09 μg mm^{-2}) for the €5 and €50 banknotes, respectively. In the €10, €20 and €100 banknotes iron was not detected even in trace

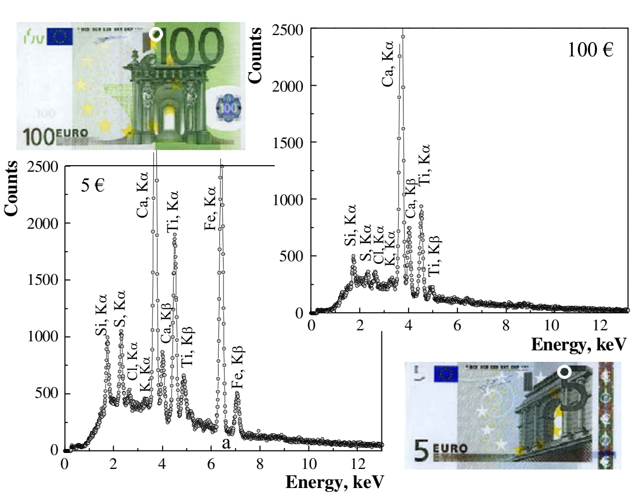

Fig. 4. X-ray spectra of the studied EURO banknotes obtained by EDXRF analysis using an electron probe microanalyzer. The white circles on the banknotes show the site of sampling.

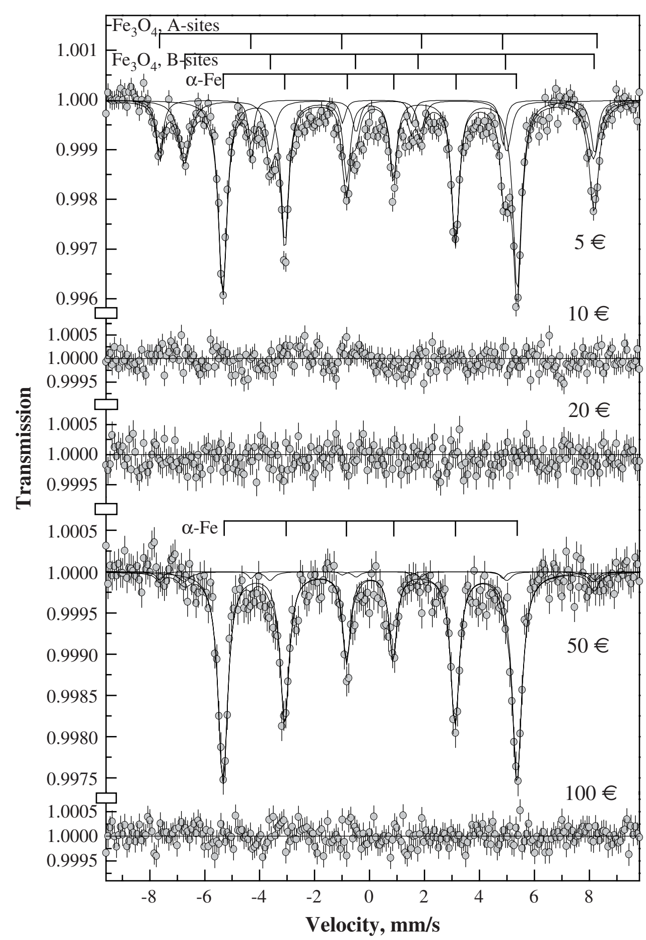

Fig. 5. Mössbauer spectra obtained at room temperature from genuine 5, 10, 20, 50 and 100 EURO banknotes.

concentrations (Figs. 4 and 5). The pigments used to print these banknotes are chemically pure compounds with very low iron concentration [7]. Evidently, other improved security features, which make falsifying difficult, such as a complicated design and printing technique, water- and hologram mark, security metal thread, luminescent area, etc., have been used. The differences between the X-ray and Mössbauer results are most likely due to the different areas used to accumulate the spectra of the complicated color surface of the EURO banknotes.

4. Conclusion

Mössbauer spectroscopy has been used as an analytical, nondestructive and informative method of analysis in the field of currency authentication not just as de Waard [12] claims "to provide fun for ingenious people, who suggest a way for Mössbauer spectroscopists to make money". The Mössbauer parameters of the pigments used in 13 different counterfeit banknotes printed in different years are very similar. This is evidence that if not all pigments have the same source of dissemination then at least they have been prepared using quite similar constituents. The observed instability of the authentic green pigment is surprising; their common feature is their green color. Mössbauer spectra permit the sensitive differentiation of the chemical differences between pigments at a molecular level. The method can be used for quality control of the manufactured pigments, their properties consistency and stability, and for monitoring any alterations and deterioration during circulation. A new set of measurements made using a synchrotron X-ray fluorescence microprobe [13], which will allow estimation of chemical elements with atomic numbers between 20 and 92 at very low detection limits, will be subsequently provided. The common use of iron-bearing pigments and iron oxides, carbonate and phosphate compounds as fillers and anti-corrosion components may well broaden the applications of Mössbauer spectroscopy to fine art, archeology, as well as the automobile and aeroplane industries [14].

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