Evidence of the state of pre-war German essay Michel Nr. 784 P9

An experimental SEM-EDX study for a Bi_2S_3 detection

by

Dr. U W Gross - Berlin

Introduction

By mere chance I became familiar with the title subject of this contribution when reading a German stamp auction catalogue. Surprisingly, I found a 5 Pf dark-green Adolf Hitler definitive stamp of Deutsches Reich 1941 (Fig. 1) specially recommended. This piece should be remarkable due to an outstanding bismuth sulphide, Bi_2S_3, addition to the printing colour pigment. This bismuth-compound immediately found my interest as a scientist and stamp collector.
After some time I was able to buy one exemplar with a certificate by the late German BPP Emil Ludin[+] in an internet shop for a moderate price, while by auction about 100. - Euro and more had to be paid.

Fig. 1a Deutsches Reich 1942 Mi 784 P7 ** 1b reverse, experts' mark

The certificate number 292 (later I found numbers in the row up to 499 as the highest[++]) states clearly:
The stamp is carrying the experts' mark Ludin BPP and is declared

- Genuine, limited edition
- Contains Bi_2S_3 , verified by chemical analysis
- Probably printed by the Reichsdruckerei Berlin for testing reasons
- The war-surviving stamps are probably war booty

Before starting more intensive chemical investigations, the circumstances of the fate of subject were checked.

I. Enquiries on the issue

1. Investigation of the stamps' history

To get more information of the scene I first contacted the Bundesdruckerei GmbH Berlin, which is the

[+]Ludin, Emil (1920-2006), BPP 1958-90, expert for test prints and essays of German Reich, German occupation Kotor, Zante, Zara
[++] I suppose there are probably existing 5 certified sheets with 10x10 stamps, altogether 500 specimen. The first that I have noticed is No 13 from 1.8.1981, the last one in the row No 499 dated 15.5.1982.

follower of the former Reichsdruckerei in the same compound in Berlin-Kreuzberg. The answer was short and disappointing: "No data and material, respectively, related to your problem do exist".
That's why February, 3, 1945 the centre of Berlin was heavily bombarded by the USAF air-raid in "operation thunderclap" and the buildings concerned were destroyed to more than 60 %.

This and following robbery is generally confirmed also by well-known Berlin-born philatelists. In this regard I interviewed also the legendary former BPP Wolfgang Jakubek.[1] I reached him by chance at phone and had a long talk on philately and his personal experiences after war in Berlin, talked on rarities, stories of stamp business and also BPP Ludin. Obviously, they were not big friends. He told me, Ludin in his later period was not always fully accepted with his philatelic decisions. With the expert article "Dienstpost Blaue Adria" published in Michel Rundschau[2] 1968 E. Ludin was involved in the Alpenvorland Adria stamp case.[3] He authenticated the corresponding edition as bogus and was accused in the Landgericht Karlsruhe trial in 1971, but was not found guilty[4].

I also contacted the German stamp trading house Richard Borek in Braunschweig. Obviously, this trader was involved in the marketing of the Ludin certified stamps. With my Internet acquisition I was provided also with a ticket of him

*Los-Nr B 61, Preis 190.- DM of Borek, Probedruck der Reichsdruckerei Berlin, Mi-Nr 784 x P9 **.*

They responded to my question that "years ago this stamp was actually offered. But now no information is available in our archive. We make the offer sending us the stamp back for examination."
Furtheron, I looked to philately forums and web sites of the internet and found in few of them sceptical discussions concerning the subject itself and also the expert certifier.

2. The certification of E.Ludin

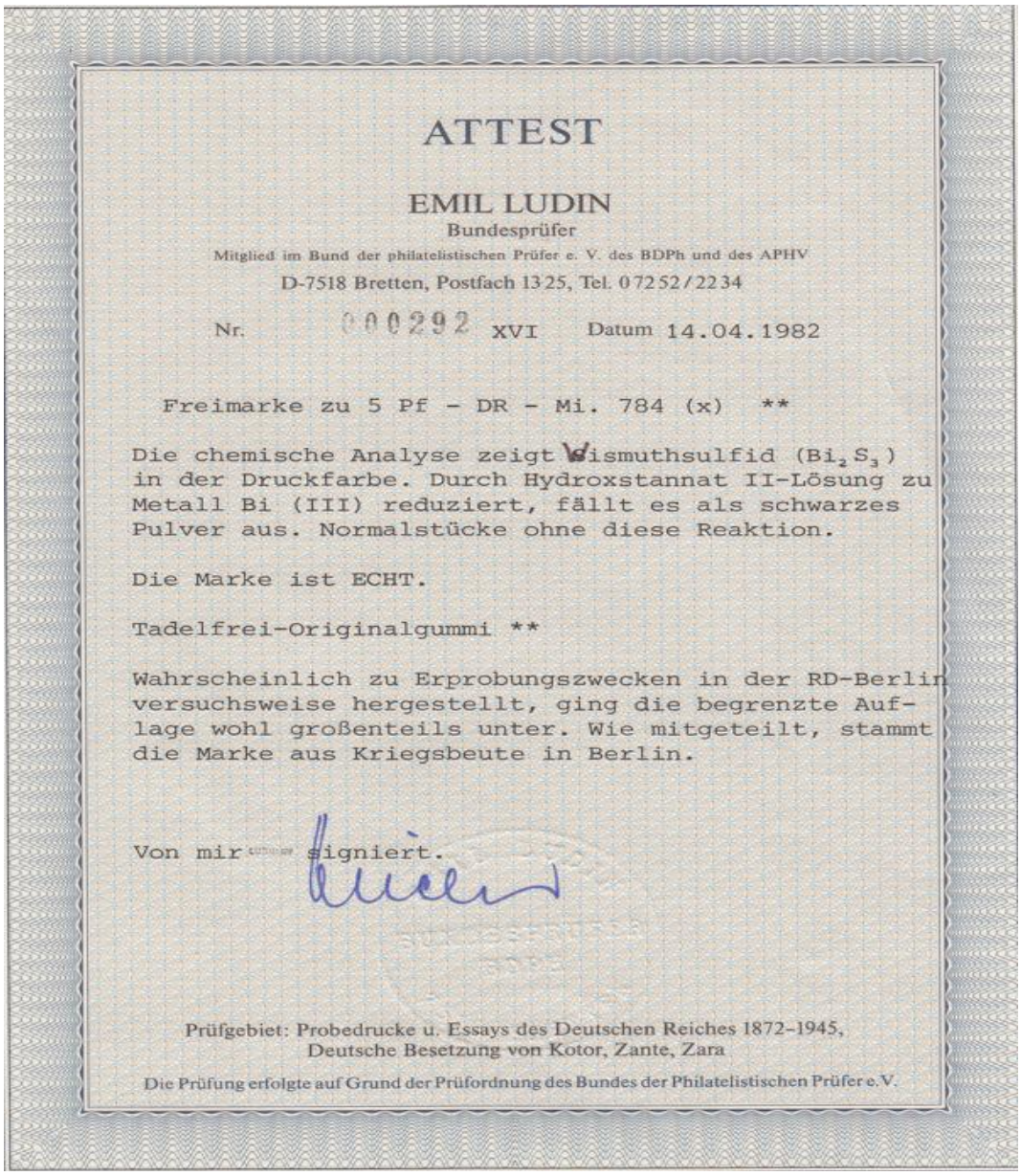
Bismuth sulphide: What is special and outstanding?
Bi_2S_3 is a dark-brown insoluble solid which was found useless as pigment. Unlike this, bismuth vanadate, $BiVO_4$, is a yellow pigment that has substituted the former widely used but toxic $PbCrO_4$ and CdS. Metal bismuth and bismuth compounds are outstanding due their strong diamagnetism expressed by a strong negative susceptibility $\chi_m = -0{,}24 \times 10^{-6}\ cm^3/g$.
Practically, this material is pushed out from a magnetic field. It is the quantum-chemical consequence of the fully occupied electron orbitals as it is existent in bismuth. If this physical property could be of practical use for post automation is unknown. May-be, this behaviour has lead to the core of the stamps' story.

According to Ludin the admixture of bismuth (III) sulphide was confirmed by a classical analytical reaction
known as "Bettendorfsche Probe" [5] according to the chemical equation

$$3\ Sn(OH)_3^- + 2\ Bi^{3+} + 3\ OH^- \longrightarrow 3\ Sn(OH)_6^{2-} + 2\ Bi\downarrow \text{ (black)}$$

equ. 1

Briefly, the bismuth $^{3+}$-ion (possibly) containing sample is reduced in an aqueous medium by Sn^{2+} to amorphous black Bi metal, which precipitates from the solution. Unfortunately, the stamp will be necessarily destroyed, because it must be fully dissolved in a strong acid for analysis. No question, this reaction needs a skilled chemist to be successful. But the chemical description at the certificate hints to an absolute layman in this respect.



ATTEST

EMIL LUDIN
Bundesprüfer
Mitglied im Bund der philatelistischen Prüfer e. V. des BDPh und des APHV
D-7518 Bretten, Postfach 1325, Tel. 07252/2234

Nr. 000292 XVI Datum 14.04.1982

Freimarke zu 5 Pf - DR - Mi. 784 (x) **

Die chemische Analyse zeigt Wismuthsulfid (Bi_2S_3) in der Druckfarbe. Durch Hydroxstannat II-Lösung zu Metall Bi (III) reduziert, fällt es als schwarzes Pulver aus. Normalstücke ohne diese Reaktion.

Die Marke ist ECHT.

Tadelfrei-Originalgummi **

Wahrscheinlich zu Erprobungszwecken in der RD-Berlin versuchsweise hergestellt, ging die begrenzte Auflage wohl großenteils unter. Wie mitgeteilt, stammt die Marke aus Kriegsbeute in Berlin.

Von mir signiert.

Prüfgebiet: Probedrucke u. Essays des Deutschen Reiches 1872–1945, Deutsche Besetzung von Kotor, Zante, Zara

Die Prüfung erfolgte auf Grund der Prüfordnung des Bundes der Philatelistischen Prüfer e.V.

Fig. 2 Original-Attest Nr 292 with expertise by Emil Ludin of 14.04.1982

"Wismutsulfid" as a German chemical term is sometimes wrongly written. The old German term Wismut (symbol Bi) was at that time officially substituted by Bismut (from lat. bismutum, engl. bismuth). Moreover, hydroxostannate is incorrectly written but most important, the formed metal bismuth possesses oxidation state zero (O) instead of three (III). It seems that the test reaction was taken over from a textbook of analytical chemistry[5], but without understanding the chemical background.
A more simple and thus advantageous bismuth check would be the reaction with iodide to give at first black
BiI_3, which is then complexed with excess I^- to give the orange-yellow BiI_4^-.
Secondly, the experimental detection of the very low amount of Bi-containing substance is questionable. A

rough calculation yields 1, 05 x 10^{-4}g Bi/per stamp which corresponds to 0,0001g (under the precondition of admixing 10 % Bi_2S_3 to the pigment and a total conversion of the above reaction). The absolute amount of 0.1 mg is at the limiting concentration for the reaction. Clearly, not only one but some more stamps must be sacrificed to establish the test and to ensure a positive result.

Of course, it is *a priori* strange to destroy a rare stamp because one wants to know its authenticity. This striking argument was raised by the highly accepted late Bundesprüfer BPP Hans-Dieter Schlegel in Berlin. Therefore Schlegel characterized the attest as "complete nonsense" and strongly recommended not to take up the stamp in the "Michel Katalog Deutschland-Spezial".[6]

3. **The "essay rarity" and its trade**

With a letter from 26.01.1982 to clients dealer R. Borek offered the stamp exclusively for sale in Germany. The provenance of only few sheets of 100 fresh stamps each is explained as stemming from a special chemical printing and treatment procedure at January, 8th in 1942. By a secret process the Deutsche Reichspost would improve post automation. At the end of war these stamps became war booty and many years later they were found in the USA. The story seems not convincing because any conformation of it did not happen.

Richard Borek, Braunschweig Gegründet 1930

Richard Borek GmbH · Bruno-Straße 25-26 · 3300 Braunschweig

Herrn

01-589-415
26.01.1982

Sehr geehrter Herr

als Anlage erhalten Sie eine besondere Rarität, die Ihre Sammlung um einiges bereichern wird.

Dem Briefmarkenhaus Richard Borek ist es gelungen, diese Marke exklusiv für Deutschland zu sichern und Ihnen heute zu einem noch relativ günstigen Preis zu liefern. Sie als Deutsches Reich - Sammler erhalten diese Ausgabe von 1942 als erster.

Am 8. Januar 1942 wurde eine Anzahl von Bogen zu je 100 Marken der 5-Pfg.-Hitler-Ausgabe in einem geheimen chemischen Prozeß behandelt. Eine eisenhaltige Zusammensetzung, die in den anderen Werten des Satzes nicht vorkommt, wurde dem Papier beigemengt. Sie sollte dazu dienen, bei den Abstemplungsmaschinen eine magnetische Reaktion auszulösen, die es ermöglicht, die Briefe automatisch zu "lesen" und zu bearbeiten. Mit diesen Automatisierungsversuchen hat die Deutsche Reichspost bereits vor dem 2. Weltkrieg begonnen.

Der Krieg ging vorüber und die Versuche gerieten in Vergessenheit. Wie sich herausstellte, wurden diese Marken als Kriegsbeute von einem amerikanischen Soldaten geschmuggelt und tauchten erst jetzt in Amerika auf.

Diese Marke wird im neuen Michel-Deutschland-Spezialkatalog aufgenommen, und die geringe Stückzahl der vorhandenen Marken wird den Preis sicherlich in die Höhe schnellen lassen.

Wir haben Ihnen diese Marke zugeschickt, weil wir der Meinung sind, daß sie in Ihrer Sammlung nicht fehlen darf. Sollten Sie jedoch aus irgendwelchen Gründen darauf verzichten wollen, so schicken Sie alles komplett mit beiliegendem Umschlag zurück. Rückporto haben wir ebenfalls beigefügt.

Mit freundlichen Grüßen

Richard Borek

RICHARD BOREK

PS.: Übrigens erhalten Sie zu dieser Marke ein Attest von dem unabhängigen, vereidigten Sachverständigen Emil Ludin. Die Einzelheiten dieser Ausgabe wurden darin bestätigt.

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Fig.3 Letter of 1982 of a stamp dealer (with permission for publishing by the addressee)

The latter has announced that this stamp will appear in the next “Michel Katalog Deutschland-Spezial”. Because of the small limited number of the rare pieces the price is expected to go up.

Indeed, then the Michel catalogue of 1987 mentioned the essay as follows: “At the end of war several definitive stamps e.g. Nr 784 were printed in a deviating colour pigment composition as compared with the usually known which only can be identified by (destructive) chemical analysis”.

In 1990 this passage was withdrawn from the catalogue. Nevertheless, the stamp was traded and offered by internet shops and in stamp auctions up to now.

4. **Legends, fraud, forgery**

With the information available the true state of the issue can not be explained.
Understandingly, the general impression on authenticity in the German philatelic community is sceptical. There are several facts of states to be discussed:
The stamp

- contains Bi_2S_3 as certified (legend tell the truth)
- does not contain any additional material (fraud)
- is forged according to legend in the time span up to publication in 1982 (forgery)

Forging of the unused stamp Mi 784** by a process to cover it by the chemical mentioned above is not yet
considered. How could it be possible? I was referred to the subject by a philatelic expert, who has details of such cases in the past. Such a forging is more critical because the gum of the unused fresh stamp must not be affected. That means aqueous media must be strictly excluded at any rate, and a possible chemical
treatment must take place in a free of water gas phase reaction. The chemical reactants could be gases as

- hydrogen chloride (HCl, acidic), chlorine (Cl_2, chlorinating, oxidative), sulphur dioxide (SO_2 ,
- acidic, reducing), ammonia (NH_3, basic), sulphur hydride (H_2S), and others.

According to my view, there is no corresponding bismuth compound available to follow the described pathway of forging.
Some of the above mentioned gases are extremely toxic. However, well educated and skilled chemists can handle it safely with convenient tools. Such considerations should not be extended at this point, because this is not a place giving a manual of forging by chemicals.

II. Experimental investigation by modern instrumental analysis methodology

SEM-EDX study as a non-destructive research tool

While we did not get suitable information from the routes of all the facts given above, a modern instrumental technique was arranged to shed light on title subject.
Unlike the classical analyses mentioned in Ludins' certificate, the method of choice must efficient and non-destructive. There are some powerful physical principles e.g. optical spectroscopy (Fourier-Transform Infrared FT-IR, Raman R-microscopy) and electron- or x-ray based microscopic/spectroscopic methods (SEM, EDX, XRF).
Raman-microscopy as well as the Laser FTIR register characteristic valence vibrations e.g. the Bi-S vibration for detection. It is successful in many cases, but problematic in our case because of disturbing and superimposing of mixtures.

In my eyes the electron microscope is of advantage in this case. SEM-EDX (scanning electron microscope –combined energy dispersive x-ray spectroscopy) is a special arrangement, where the scanning microscope is equipped with a detector for energy of emitted x-rays. Such facilities are principally rare, because they are expensive high-tech apparatuses that need specialised and educated operators.

Physical principle of SEM and methodology in brief

An electron beam with high energy (up to50 keV) is scanning the sample under vacuum. The analysed area can be varied in the range of about 5x5 mm (Magnification 20) up to about 2x2 µm (Magnification 200 000). The primary electrons PE interact with the atoms of sample in different ways. The reflected PE (called backscatter-electrons) are collected with a detector yielding the morphology-picture (SEM).
The PE can also remove electrons from inner shells of the atom of pigment. In this case the vacancy is filled with an electron from higher shells combined with the emission of X-ray radiation. Each element has characteristic lines in the X-ray spectra.
Analysing the energy of all lines in the spectra of the sample (EDX), one can see, if a certain element is present in the sample or not. There are different modes for analysing the emitted lines. The mode ”spectra” shows the lines and the quantitative amount of the elements which are present in the sample (detecting limit about 0.2%) at one look.
In the mode “mapping” the distribution of the elements within the sample is presented. For more information see e.g. [7]

Similar scientific studies by these non-destructive methods in the field of old paintings and philatelic subjects are published. R. Neunteufel[8] has investigated a handstamp of a historic philatelic document by X-ray excited X-ray fluorescence (XRF) analysis. Thus, evidence of the composition of inks and origin of the matter is verified. Recently, a convincing example is given by the group of Ludovico Valli[9] of the University in Lecce (Italy). In an extensive investigation the authors studied the entire Italian postage stamps of the last 150 years by means of FT-IR. They characterised in detail paper, use of kaolin filler and gum. A spectral database was created where stamp collectors can date any Italian stamp and detect fakes. One result was a “Gronchi rosa” fake of 1961 and a regummed stamp issued 1865.

The measurement of the Deutsches Reich definitive Mi 784** was carried out with a JEOL JSM-6060 equipment combined with Röntec (now BRUKER) EDX. The stamp was placed in the vacuum chamber and scanned with energies above 20 keV of the exciting electron beam. Spots all over the stamp surface were measured. Fig. 4 presents the spectra with signal intensity over the energy of x-ray photons.

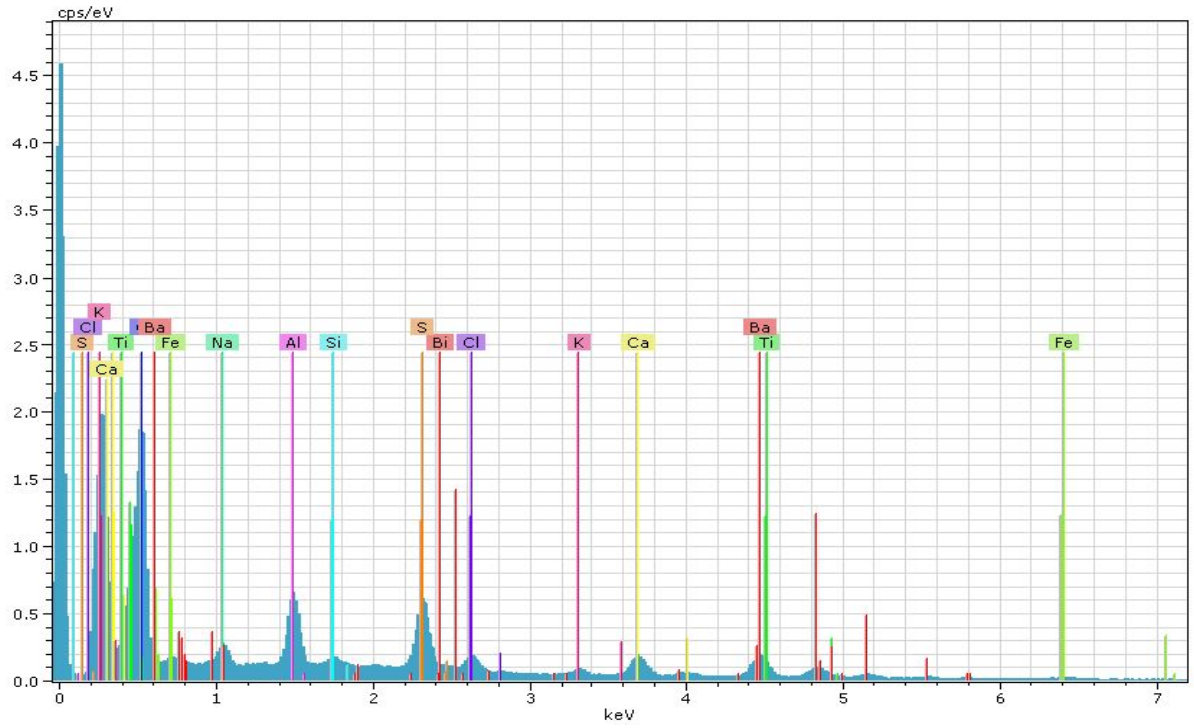

Fig. 4 EDX spectrum of Mi 784 certified by E. Ludin

The strongest signals are the elements Ca, Ba, S, Al, Ti resulting from filler and whitener barium sulphate, $BaSO_4$, aluminium oxide Al_2O_3, calcium carbonate $CaCO_3$, titanium dioxide, TiO_2. The light elements carbon C and oxygen O are also present at lower keV-values at the very left of the spectrum. They are a result of organic material and of carbonate and oxides. Bismuth is not present, its major peaks should be occur in the spectrum at 2.42 keV, 10.83 keV and 12.955 keV. (see Fig. 5 for comparison) To confirm the missing Bi as evident, a reference measurement of a Bi containing sample was carried out (Fig. 5).

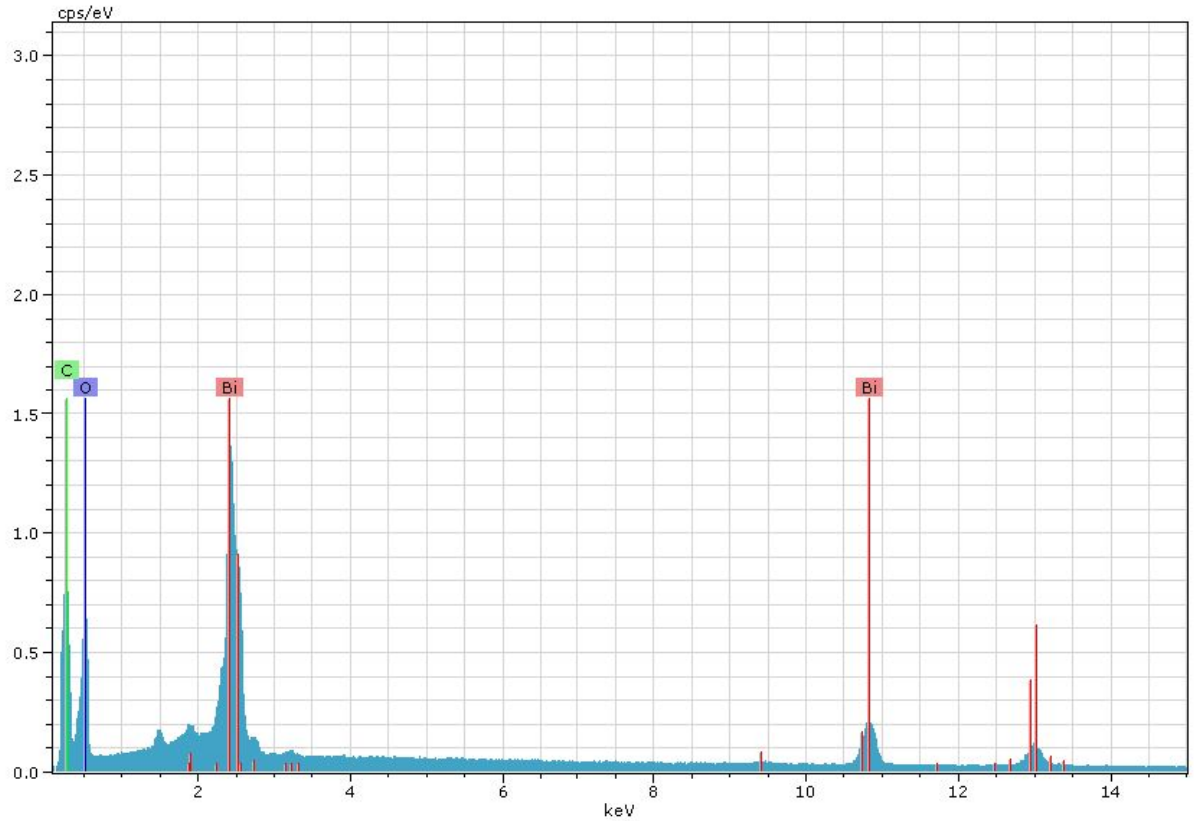

Fig. 5 EDX reference spectrum (paper sample treated with a aqueous solution of Bi $(NO_{3)})_3$ $5H_2O$)

Reference sample

To insure our results a reference sample containing the bismut^{3+} ion, a small piece of filter paper was wetted with an aqueous solution of bismuth nitrate penta hydrate (Aldrich, 98%) and then dried. As a chemist knows, the nitrate salt is easily hydrolysed to the oxy nitrate, which has a low water solubility. Thus, after treating the paper, the bismuth concentration is pretty low. Nevertheless, the EDX spectrum is convincing and of high intensity. The peaks of corresponding energy values in keV are due to the M-, L-series of the term scheme, known from theory.

Mapping - a mode of data processing

The mapping presentation of atoms and their corresponding compounds, respectively, show their distribution over the investigated stamp area and gives additional information: e.g. Ba ($BaSO_4$) is to be found in the printed picture of the stamp but not in the white side margins and perforation. This clearly confirms: barium sulphate is exclusively a constituent of the printing ink but not of the stamp paper. In contrast, Ca ($CaCO_3$) is only part of the paper as filler, to be seen only in the margins, not in the main part.

Not surprisingly, the Titanium mapping (not depicted!) is of the same kind as was found for Barium: TiO_2

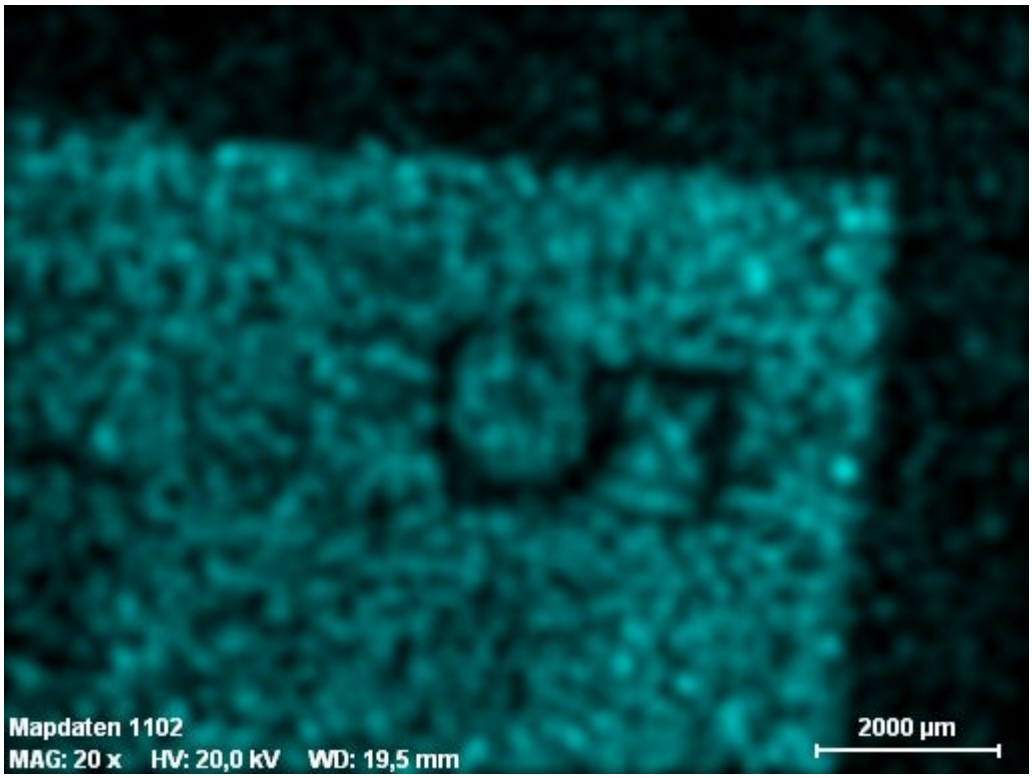

Fig. 6 Barium (Ba) mapping

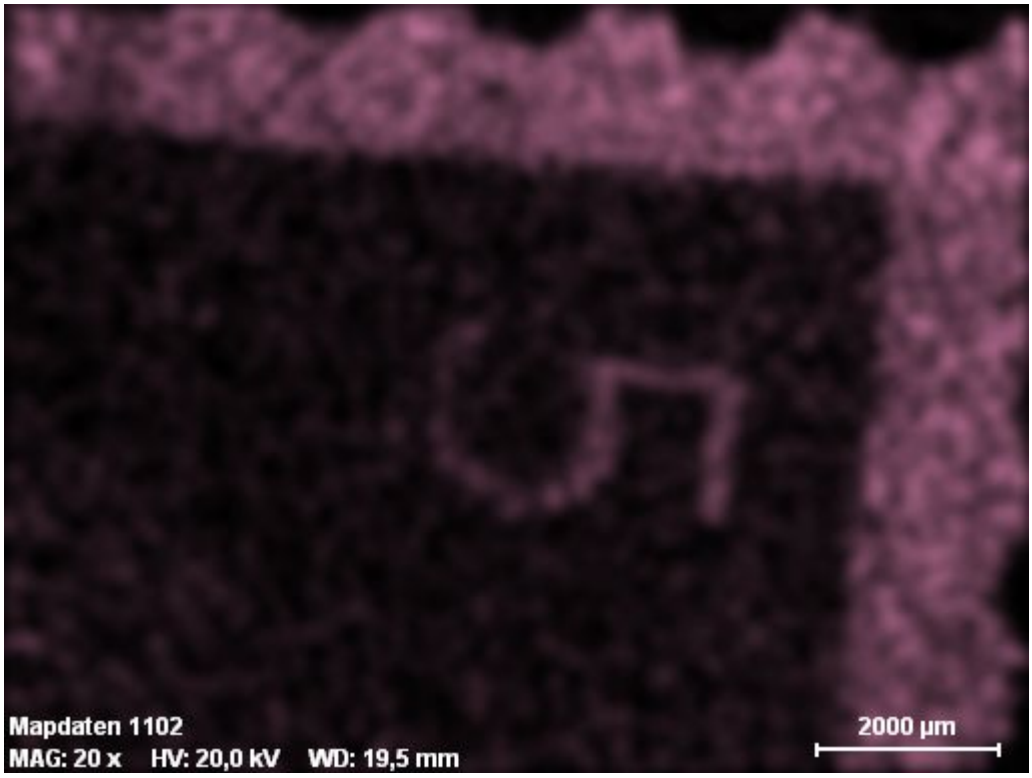

Fig 7 Calcium (Ca) mapping
only in the ink, not in paper.

Although, the Atanas-TiO_2 modification is industrially produced since 1916, the usage in paper was minor; it was at that time economically not competitive to the cheaper $CaCO_3$ as filler. The technological breakthrough of the "Chlorine Process" in the midth of the last century made the preferred Rutil-TiO_2 a mass product, nowadays available also for quality paper production.

III Final Result

From this investigation it is for sure: This single stamp does not contain bismuth and bismuth sulphide, respectively.

The green colour of the stamp is not to be seen by EDX, because of lack of inorganic material. Not knowing exactly the chemical origin of colour, it is thought to be synthetic organic Malachite green of the tri-phenyl methane structural group. These lighter atoms give no characteristic signals in the in the x-ray spectrum. The mapping of the green area confirms that no other additional element is present, i.e. the green colour is not generated by an inorganic pigment.

Fig. 8 SEM microscope

CONCLUSION

The results of the study of the Mi 784** in my hands do not agree with the facts of Ludins' attest. Although
carrying the backside expert label, this piece contains no measurable amount of bismuth (III) sulphide. Thus, this stamp is special in that: it is a rarity characterised by two certificates and two experts.
I have learned from W. Jakubek[1] to consider forgery also as special related to the origin, when he is quoted as saying "also forger are sometimes creative people (see the famous forgers in history) in their field and generate rare products, which one must accept also when illegal".

ACKNOWLEDGMENT

The author wishes to express his thanks to his colleagues Dr. G. Kauschka and Dr. A. Dimitrov, who were running the SEM equipment.

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