New forensic insight into Carl Auer von Welsbach's 1910 observation of induced radioactivity: theoretical, experimental and historical approaches

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Abstract

In 1910, Carl Auer von Welsbach noted that he had made an observation of a radioactive substance inducing radioactivity to an inactive substance. From today's point of view, this could have been the first observation of neutron activation. Herein, we present new insights into our investigation of this "mysterious observation" as Auer von Welsbach termed it. We believe that one of the activated objects was a platinum-iridium crucible. The dominating activation product of the crucible could have been iridium-194. We have discovered several platinum crucibles from Auer's heritage and investigated them by gamma-spectrometry and, one of them, by SEM/EDX. In the EDX investigations, however, no iridium was found in the most promising crucible. Hence this particular crucible was probably not the activated object. In any case, gamma-ray spectrometry revealed very low but detectable amounts of natural radionuclides. This indicated that these crucibles were used by Auer von Welsbach for his radioactive work and that these crucibles were bought prior to World War I. Hence Auer von Welsbach somehow managed to save these crucibles from the noble metal collections during the war. Auer's 1910 publication carried the suffix "Part I", however, Part II was thought to be lost. In our recent work, however, we rediscovered a hand-written manuscript of Part II, in which the peculiar observation is mentioned vaguely. Lastly, we converted Auer's uranium standard into becquerels. Based on this conversion, we estimated that Auer von Welsbach observed an ^{194}Ir activity of the crucible of 500 kBq. It is further estimated that a (thermal) neutron flux density of approximately 8E+4 $cm^{-2}s^{-1}$ was needed to activate the crucible in a way to meet Auer's description.

Introduction

Carl Auer von Welsbach (1858-1929) was one of Austria's most renowned and prolific scientists in the late 19th and early 20th century (Fig. 1). He discovered four elements (praseodymium, neodymium, ytterbium, and lutetium) and revolutionized illumination technology by several outstanding inventions making him a successful entrepreneur of his time. Auer von Welsbach was well-known as a hard worker who would spend days and nights in his laboratory. Nonetheless, he rarely focused on the active development of a specific, practical solution to a specific technical problem; he did not regard himself as an engineer but as a scientist. Rather, he would continue his research efforts on fundamental science and develop solutions to existing problems through sole observation of chemical or physical phenomena during this fundamental research. For example, he became acquainted with the problems of poor light sources during his military service in the artillery, when strategic maps and written orders were difficult to read with the poor light sources of his time, especially at night in the field. Many years later, he recalled the need for better and more intense lighting when he observed the bright incandescence of rare earth salts when sprayed into the flame of a gas Bunsen burner. This scientific observation led him to the development of the incandescent gas mantle which was one of Auer's key inventions.

Auer's main specialty was the separation of rare earth elements (REE) which are known to exhibit much related chemical properties. In the course of these studies he developed chemical separation skills that were often unmatched by other researchers of his time. It was this specific chemical knowledge that introduced him to a different field where people with Auer's specific skills were needed: radioactivity research. In the early days of radioactivity research and the hunt for new, radioactive elements, chemical separation techniques were the key to success. It is no surprise, therefore, that Auer von Welsbach dedicated some of his time to the isolation of radioactive elements from radioactive raw materials that were derived from uranium ores. Since, at least by comparison to his work in REE chemistry, he was not overly successful in this area, Auer's involvement in radioactivity research in the beginning of the 20th century is somewhat less known.

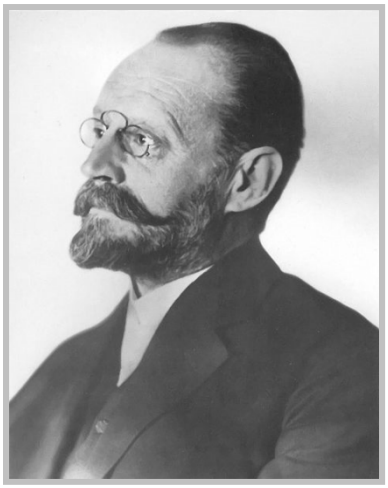
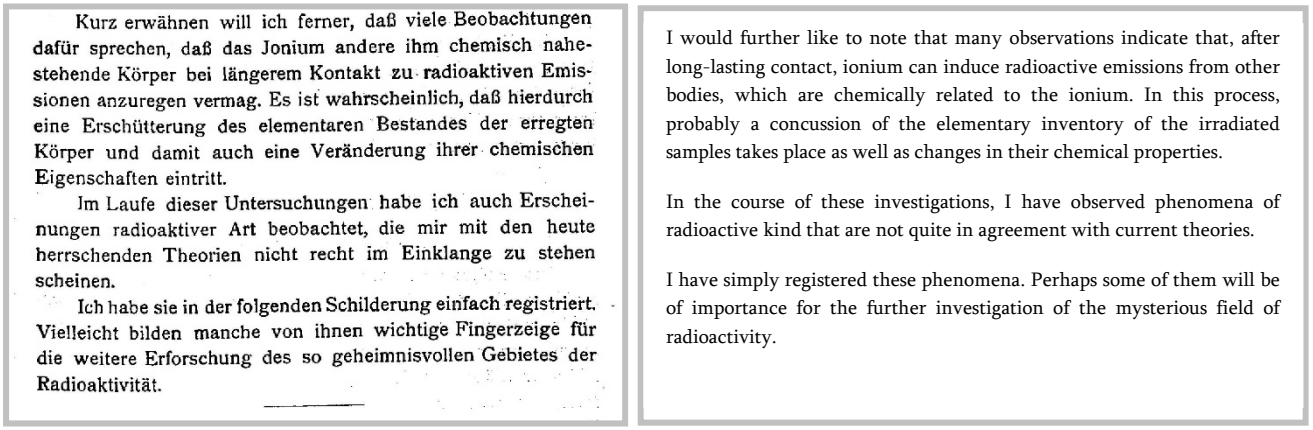


Fig. 1 Carl Auer von Welsbach (1858-1929). Bildarchiv der Österreichischen Nationalbibliothek.

Physical and chemical sciences in the early 1900s were dominated by the discovery of radioactivity, especially the discovery of radium by Marie and Pierre Curie. In the light of the French dominance of this new field, scientific leaders in the Austrian-Hungarian Empire (in particular the newly founded Radium-Commission of the Austrian Imperial Academy of Sciences) realized the need for a large-scale, industrial production of radium. Marie and Pierre Curie only used manual or semi-technical separation methods (at best) for the work-up of the uranium ore residues. Thus it was thought that

70 the production on an industrial scale would yield higher amounts of the precious new element
71 radium, which would fuel the scientific progress in this field in the Danube Monarchy. Auer von
72 Welsbach offered his gas mantle factory in Atzgersdorf (near Vienna) for this industrial endeavor. He
73 expected to receive a fraction of the produced radium for his own research, however, as described
74 previously (Steinhauser, Löffler, and Adunka 2013), his requests for some of the radium were turned
75 down. Instead, Auer von Welsbach was offered the residues of the radium production: water-rich
76 filter cakes (water content 77.5%) that were termed "hydrates" and contained both radioactive and
77 not radioactive substances. Despite his major disappointment, Auer von Welsbach agreed to further
78 work up these hydrates, hoping he might isolate known or new radioactive substances from them.

79 In the course of his work, Auer von Welsbach made a very strange but fascinating observation that is
80 the basis of our study. In a 1910 publication (Auer von Welsbach 1910a, b), he described how a
81 radioactive substance, namely thorium/ionium (Th/Jo) (today known as thorium-230), was capable
82 of activating non-radioactive substances (Fig. 2). The ionium was a major constituent of the hydrates.



Kurz erwähnen will ich ferner, daß viele Beobachtungen dafür sprechen, daß das Jonium andere ihm chemisch nahestehende Körper bei längerem Kontakt zu radioaktiven Emissionen anzuregen vermag. Es ist wahrscheinlich, daß hierdurch eine Erschütterung des elementaren Bestandes der erregten Körper und damit auch eine Veränderung ihrer chemischen Eigenschaften eintritt.

Im Laufe dieser Untersuchungen habe ich auch Erscheinungen radioaktiver Art beobachtet, die mir mit den heute herrschenden Theorien nicht recht im Einklange zu stehen scheinen.

Ich habe sie in der folgenden Schilderung einfach registriert. Vielleicht bilden manche von ihnen wichtige Fingerzeige für die weitere Erforschung des so geheimnisvollen Gebietes der Radioaktivität.

I would further like to note that many observations indicate that, after long-lasting contact, ionium can induce radioactive emissions from other bodies, which are chemically related to the ionium. In this process, probably a concussion of the elementary inventory of the irradiated samples takes place as well as changes in their chemical properties.

In the course of these investigations, I have observed phenomena of radioactive kind that are not quite in agreement with current theories.

I have simply registered these phenomena. Perhaps some of them will be of importance for the further investigation of the mysterious field of radioactivity.

83

84 **Fig. 2.** A document of a peculiar observation: Activation processes (Auer von Welsbach 1910b, a)

85 Under normal circumstances, ionizing radiation, in particular α-particles emitted from thorium-230,
86 cannot make their targets radioactive (there are, however, some exceptions to this general rule,
87 which do not seem to apply here). Therefore, only one reasonable explanation for this phenomenon
88 appeared obvious at Auer's time: one might only conclude that the "long-lasting contact" of ionium
89 had caused a contamination of the surface of the seemingly activated objects. Auer von Welsbach
90 was well aware of this simple explanation for his "mysterious" observation. Later he describes, how
91 he attempted to decontaminate the activated object: a platinum crucible (Fig. 3). In his (unpublished)
92 lab journal he even notes that "glowing to red heat does not help".

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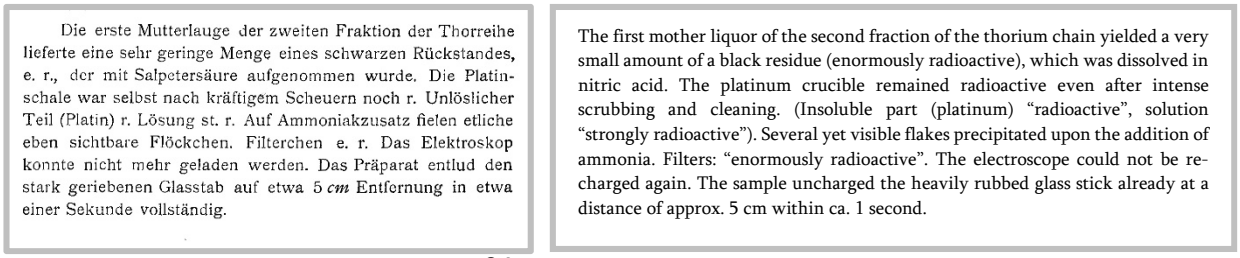


Die erste Mutterlauge der zweiten Fraktion der Thorreihe lieferte eine sehr geringe Menge eines schwarzen Rückstandes, e. r., der mit Salpetersäure aufgenommen wurde. Die Platinschale war selbst nach kräftigem Scheuern noch r. Unlöslicher Teil (Platin) r. Lösung st. r. Auf Ammoniakzusatz fielen etliche eben sichtbare Flöckchen. Filterchen e. r. Das Elektroskop konnte nicht mehr geladen werden. Das Präparat entlud den stark geriebenen Glasstab auf etwa 5 *cm* Entfernung in etwa einer Sekunde vollständig.

The first mother liquor of the second fraction of the thorium chain yielded a very small amount of a black residue (enormously radioactive), which was dissolved in nitric acid. The platinum crucible remained radioactive even after intense scrubbing and cleaning. (Insoluble part (platinum) "radioactive", solution "strongly radioactive"). Several yet visible flakes precipitated upon the addition of ammonia. Filters: "enormously radioactive". The electroscope could not be recharged again. The sample uncharged the heavily rubbed glass stick already at a distance of approx. 5 cm within ca. 1 second.

94

95 **Fig. 3** Facsimile of Auer's publication: Failed elimination of a possible contamination (Auer von Welsbach 1910b, a)

In our previous report (Steinhauser, Löffler, and Adunka 2013) we already outlined that there are several reasons to believe that Auer von Welsbach incidentally observed neutron activation. Neutron radiation is the only type of ionizing radiation that can activate stable nuclei under the "normal" circumstances that prevailed in Auer's laboratory and experimental setup. The neutrons are believed to originate from a nuclear reaction of beryllium with α-particles: $^{9}Be(\alpha,n)^{12}C$. In this nuclear reaction, a beryllium-9 nucleus captures an alpha particle and yields both a carbon-12 nucleus and a neutron that is emitted as radiation. We speculate that beryllium was incorporated into the hydrates as a contamination in the course of the radium production in Auer's incandescent gas mantle factory in Atzgersdorf. In that factory, large amounts of beryllium salts were used for the production of the gas mantles (Steinhauser, Löffler, and Adunka 2013).

Neutron activation would follow the physical laws of the activation equation (1):

$$A = N_0 \Phi \sigma (1 - e^{-\lambda t_{irr}}) \qquad (1)$$

where A is the resulting activity after neutron irradiation, N_0 is the number of target atoms of the activatable isotope, Φ is the neutron flux density under which the target is exposed to neutrons, σ is the cross section for neutron capture in the target nucleus, λ is the decay constant (defined as $\lambda = \ln(2)/T_{1/2}$), and t_{irr} is the irradiation duration. One reason, why we believe that neutron activation is the key to the mystery is that Auer von Welsbach explicitly mentions the "duration" of the contact between the radioactive sample and the activated object ("long-lasting contact"). This is one major indication that the platinum crucible experienced more than a sole contamination.

The neutron was finally discovered by James Chadwick only in 1932 (Chadwick 1932b, a), also taking advantage of the nuclear reaction $^{9}Be(\alpha,n)^{12}C$. Not only did Auer von Welsbach have no idea of the existence of the neutron. At the time of his peculiar observation, he had a very different view of the constitution of matter in general since Bohr published his model of the atom only three years later in July 1913 (Bohr 1913). Auer von Welsbach likely still had Thomson's model of the atom in mind ("plum pudding model").

Even after our previous report (Steinhauser, Löffler, and Adunka 2013), many questions remained open. For example, why was not there any "Part II" of the mysterious publication (Auer von Welsbach 1910b, a)? What happened to the platinum crucible as it seemed to have disappeared? How radioactive was the "activated" object and what neutron source strength would be needed to produce this activity? In the current paper, we report on new insight into these questions, and we conducted further historical research as well as forensic investigations to gain more knowledge on what happened more than 100 years ago.

Methods

This project is a continuation of our continuing interest in forensic history of science (Steinhauser, Löffler, and Adunka 2013, 2014, Steinhauser et al. 2008). For the historic investigations we rely on original objects and documents collected at the Auer von Welsbach-Museum in Althofen, Austria, or provided by the heirs of Carl Auer von Welsbach.

Several objects were investigated by γ-spectrometry at the low-level HPGe Canberra™ γ-counting facility of the Atominstitut. Specifics of the detector can be found elsewhere (Steinhauser et al. 2013). The objects included a total of 11 platinum crucibles and 6 platinum spatulas from the heritage of Carl Auer von Welsbach. The six spatulas were counted together with nine crucibles in one batch

measurement (duration more than 15 days) for an overview on possible radionuclide contaminations (a picture of these objects is available from the authors upon request).

The most interesting object, however, was an original platinum crucible which was also provided for the purpose of investigation in this study by inheritors of Carl Auer von Welsbach. It was counted separately on the γ-detector for more than 11 days. The crucible has a mass of approx. 330 g and a diameter of 17 cm. It is special because, on the interior, it shows characteristic scratches (see Fig. 4) – scratches that may have occurred in decontamination attempts. We were also allowed to apply scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM/EDX) at Treibacher Industrie-AG for information on the bulk elemental composition of this particular crucible.

Fig. 4 A platinum crucible for Auer's heritage. It shows very distinct scratches under right illumination (picture on the right).

Rediscovery of the Seemingly Lost Part II of Auer's Publication

Auer's 1910 publication was published twice; once in Sitzungsberichte der mathematisch-naturwissenschaftlichen Klasse (Auer von Welsbach 1910a) and once in Mitteilungen der Radium-Kommission der Kaiserlichen Akademie der Wissenschaften, Chemie-Heft (Auer von Welsbach 1910b). It carries the name "Über die chemische Untersuchung der Actinium enthaltenden Rückstände der Radiumgewinnung (I. Teil)" [On the chemical investigation of the actintium-containing residues of the production of radium (Part I)]. The second part was never published. Until recently, there was no indication of the existence of a draft of this second part. Finally, we can report that a hand-written and rather rough draft of the second part was rediscovered in the archive of the Auer von Welsbach-Museum in Althofen (Fig. 5).

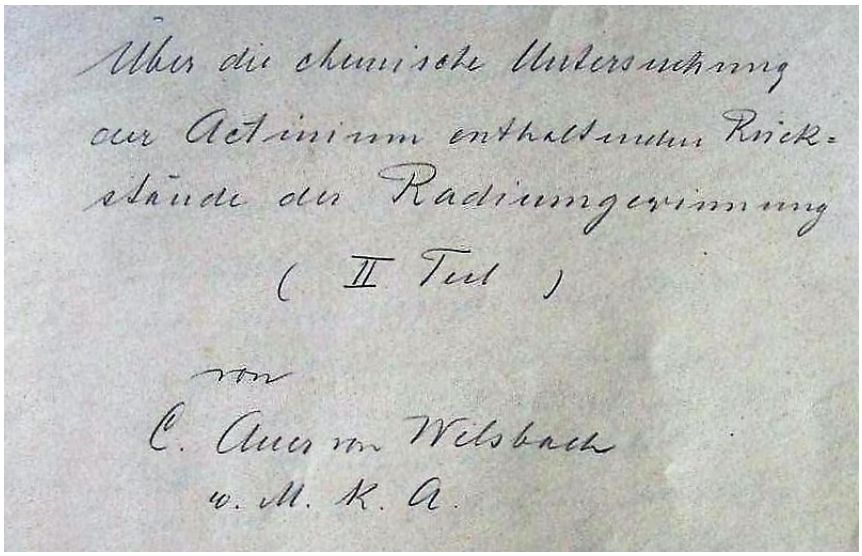


Fig. 5 Title page of the hand-written draft of the manuscript entitled "Über die chemische Untersuchung der Actinium enthaltenden Rückstände der Radiumgewinnung (II. Teil)" von C. Auer von Welsbach w.M.K.A. [On the chemical investigation of the actintium-containing residues of the production of radium (Part II) by C. Auer von Welsbach w.M.K.A. (*full member of the Imperial Academy*)]. Apparently Auer von Welsbach had intended submission of the manuscript to the Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften.

On pages 3 and 4 of this manuscript, Auer von Welsbach once again mentions the peculiar observation:

"Da ich bei der ersten Reindarstellung der Th(Jo)salze aus Roh-Th(Jo)oxalat nach dem Ammoniumoxalat u. Ammoniumnitratverfahren auf sehr merkwürdige Erscheinungen gestoßen bin, deren quantitative Erforschung nicht in mein Arbeitsgebiet fällt, so unterließ ich diesmal die Durchführung des im übrigen ganz einfachen und [*unreadable*] Trennungsprozesses und übergab das Präparat im ungereinigten Zustande [*dem*] Institut für Radiumforschung – Wien.

Es wurde später, wie ich nicht unerwähnt lassen will, von F. Exner u. E. Haschek spektrographisch geprüft, jedoch, insoweit das Jo-Spektrum in Betracht kommt, mit völlig negativem Resultat."

[I encountered very peculiar phenomena during the first preparation of pure Th(Jo)-salts from the raw Th(Jo) oxalate using the ammonium oxalate and ammonium nitrate process. Since quantitative investigation of these phenomena did not fall into an area of my own expertise, I skipped this separation process now which is, by the way, very simple and [*unreadable*], and transferred the substance in its unpurified state to [*the*] Institut für Radiumforschung – Vienna.

I shall mention that the substance was investigated spectroscopically by F. Exner and E. Haschek, but, as far as the Jo-spectrum is concerned, with an entirely negative result.]

It is interesting to learn that Auer von Welsbach realized that the analytical methods in his lab did not suffice to answer the question raised by the mysterious observations he had made. However, being a chemist at heart, Auer von Welsbach apparently only asked his collaborators at the Institut für Radiumforschung to check the material for impurities by means of spectroscopic investigations. He did not suspect a new type of radiation that may be responsible for his observations. It is unlikely that Exner and Haschek observed anything unusual in the spectroscopic investigations of this raw material. Their measurements probably revealed the presence of many (stable and unstable) elements so that even impurities with beryllium would not have raised a "red flag".

As far as we can tell at the very moment, Auer von Welsbach did not further specify the nature of the peculiar observations in this manuscript of Part II beyond the above statement.

Auer's Radioanalytical Equipment and Radioactivity Standard

Auer von Welsbach used an electroscope (Fig. 6) as an activity detector. He quantified activity by comparison to a uranium standard that had a defined activity of "1 Uran-Einheit (Ur.E.)" (uranium-unit). It is obvious that this standard was frequently used at the beginning of the 20th century, because Auer von Welsbach does not specify the composition and the specifics of this standard. Today this unit is no longer used. Stefan Meyer and Egon Schweidler (Meyer and Schweidler 1927), however, describe this uranium standard in great detail. According to them, the uranium-unit goes back to Henri Becquerel who had defined the activity of 1 g metallic uranium as 1 uranium-unit. However, since pure uranium metal is difficult to produce, to characterize and to maintain (as it oxidizes fairly quickly), later modifications of the uranium-unit replaced the metallic uranium by uranium oxides (UO_3, UO_2 or U_3O_8), after thorough removal of the radioactive progeny of the ^{235}U and ^{238}U decay chains. This was a reasonable modification, especially because in the early days of radioactivity research, mainly α-radiation was used for many experiments and a solid block or cylinder of metallic uranium would shield most of its own α-rays. Instead, 15-20 mg of fine U_3O_3 powder were suspended in ethanol or chloroform and applied to a metal plate to cover an area of 1 cm² (or more) upon drying of the organic solvent. Auer's uranium standard (as shown in the right top of Figure 7), encompassed an area of 3 cm² (note: "3 □ cm").

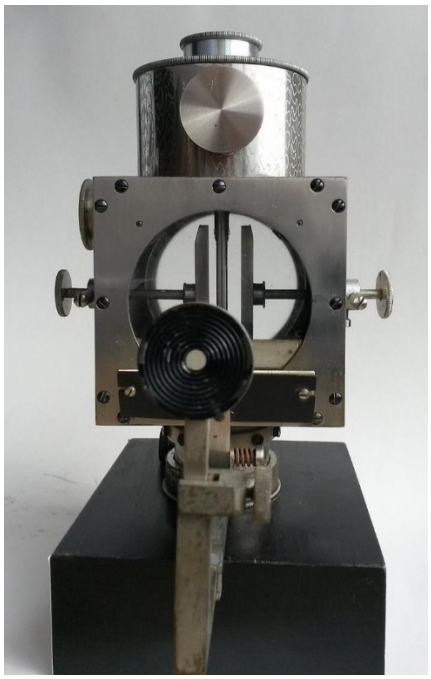


Fig. 6 The electroscope Auer von Welsbach used for activity measurements.

Auer von Welsbach used a uranium-unit based on U_3O_8. He defined activities via the discharge time of the plates of his electroscope. The definition of his activity units are shown in Figure 7 and summarized in English in Table 1. Natural uranium is constituted by three uranium isotopes: ^{238}U, ^{235}U (both mothers of their decay chain), and ^{234}U (daughter nuclide of the ^{238}U decay chain) with a natural abundance of 99.2742%, 0.7204%, and 0.0054%, respectively. All three uranium isotopes are virtually pure α-emitters, however three β^- daughter nuclides will grow quickly into secular radioactive equilibrium: ^{234}Th ($T_{1/2}$ = 24.1 d), ^{234}Pa ($T_{1/2}$ = 6.7 h), and ^{231}Th ($T_{1/2}$ = 25.5 h). Even a thoroughly purified uranium sample will therefore also emit β^- particles of various energies within a time range of a couple of months. The ingrowth of further progeny will be hampered by longer-lived daughter nuclides down the decay chain, which will prevent a purified uranium sample to reach anything close to equilibrium of the entire chains within a human life-span and beyond. Based on the information provided by Meyer and Schweidler [1927], we can assume that Auer's 3 cm² uranium

standard consisted of 60 mg U_3O_3 with all non-uranium progeny fully removed (see our estimate of the activities of Auer's reports converted to SI-allowed units in Table 1).

Table 1: Auer's definition of radioactivity units and estimated conversion to SI-allowed units.

Uranium-Units (Ur.E.)	**Time to discharge the electroscope (s)**	**Symbol**	**Characterization**	**Estimation of the activity in SI-allowed units**
1 Ur.E.	1800	f.i.a.	almost inactive (fast inaktiv)	ca. 2.6 kBq (1300 α particles per second; 1300 β^- particles per second)
10 Ur.E.	180	s.w.r.	very little radioactive (sehr wenig radioaktiv)	26 kBq
10-20 Ur.E.	90	w.r.	little radioactive (wenig radioaktiv)	26 – 52 kBq
20-50 Ur.E.	36	r.	radioactive (radioaktiv)	52 – 130 kBq
50-100 Ur.E.	18	st.r	strongly radioactive (stark radioaktiv)	130 – 260 kBq
100-1000 Ur.E.	2	s.st.r.	very strongly radioactive (sehr stark radioaktiv)	260 – 2.6 MBq
1000-10,000 Ur.E.	0.2	h.r.	highly radioactive (hochradioaktiv)	2.6 MBq – 26 MBq
> 10,000 Ur.E.	electroscope cannot be charged and discharges the glass rod within seconds	e.r.	enormously radioactive (enorm radioaktiv)	> 26 MBq

It is interesting to note how the perception of radioactivity changed throughout the decades since Auer's time based on the improvement of radioanalytical techniques. Naturally, Auer's electroscope was a rather primitive analytical device compared to modern radiation detectors. Nevertheless, Auer von Welsbach described an activity of 2600 Bq as "almost inactive", which is actually a rather considerable activity by today's standards. For a better illustration, this activity is higher by a factor of 26 than the regulatory limit for radiocesium in normal food (100 Bq/kg) after the Fukushima nuclear accident (Merz, Shozugawa, and Steinhauser 2015).

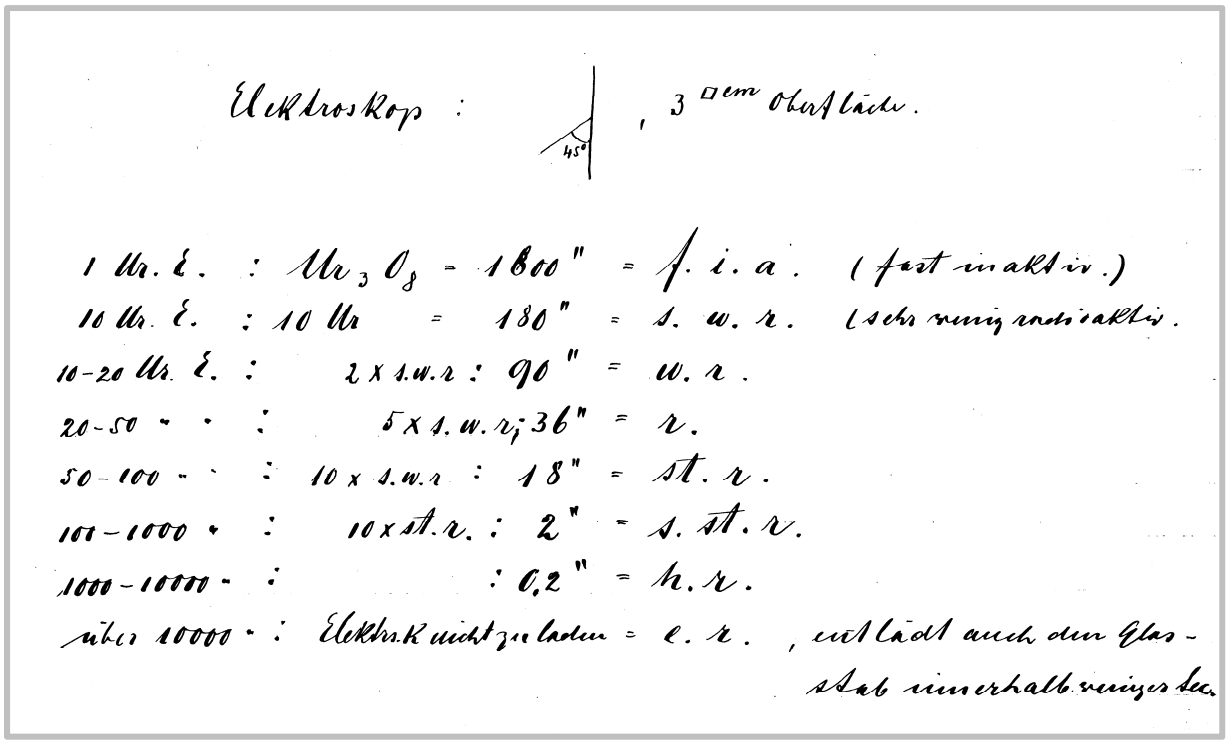


Fig. 7 Auer's chart of definitions of activities

Theoretical Considerations of the Activation of the Platinum Crucible

Auer's observation was clearly described for a platinum crucible. Therefore, our interest focuses on trying to identify the platinum crucible that showed signs of activation. We regard this object as key to possibly solving the forensic question whether or not Auer von Welsbach had incidentally discovered neutron activation in 1910. For many years, it has been believed that any platinum crucibles and other platinum objects from Auer's private property had been donated/confiscated in the course of noble metal collections of World War I in order to support the war efforts of the Austrian-Hungarian Monarchy. However, recently, we have been in contact with inheritors of several platinum objects from Auer's collection which somehow could be saved from the confiscation or which were purchased after the war.

Given the assumption that Auer von Welsbach really had observed neutron activation processes back in 1910, what was the dominating radionuclide after the "long-lasting" contact with the hypothetical neutron source? Platinum consists of several stable or quasi-stable nuclides (mass numbers 190, 192, 194, 195, 196, and 198) that all show some significant drawbacks for the "neutron activation" hypothesis. Most of these (quasi)stable nuclides have relatively low cross sections (i.e. a low affinity) for significant neutron capture of a presumably low-intensity neutron source; or they yield less suitable activation products. It can be assumed that the activation product generated by neutron capture should have had a half-life of at least a couple of hours to remain detectable throughout Auer's cleaning procedures in which it proves to be "difficult" to remove. The half-live of the activation product, however, should not be too long either, in order to yield high specific activities. Lastly, in order to be detectable for Auer's electroscope, the activation product should be a β-emitter (and not just a photon emitter which causes much less ionization events in air). It shows that no platinum nuclide or activation product of platinum is a promising candidate under these prerequisites.

Literature, however, teaches us that "platinum crucibles" at the end of the 19th century were preferably made of alloys of platinum and iridium, with iridium contents up to 30% (Meyers Konversations-Lexikon 1877, Ullmann 1930a). In contrast to platinum, iridium is easily activated. For the following scenario, therefore, we will assume an iridium content of the crucible of 30%.

A comparison of the activities of every possible neutron activation product (see Fig. 8) of a hypothetical platinum crucible with an iridium content of 30 wt.% shows that iridium-194 is the most promising candidate for Auer's observation. It is reasonably long-lived ($T_{1/2}$ = 19.15 hours) and a powerful beta emitter. Although it yields even higher activities, iridium-192m is too short-lived to be a good candidate ($T_{1/2}$ = 1.4 min). Iridium-194 is activated 100 times more readily than the most promising activation product of platinum (^{197}Pt with $T_{1/2}$ = 18.3 hours). Generally, the most "prominent" activation product of iridium is ^{192}Ir. The target nuclide ^{191}Ir has a much higher (by approx. a factor of 10) cross section for neutron capture than the respective target nuclide ^{193}Ir in the nuclear reaction ^{193}Ir(n,γ)^{194}Ir. In this nuclear reaction, stable iridium-193 catures a neutron and yields radioactive iridium-194 under emission of a prompt gamma photon. However, ^{192}Ir has a much longer half-life, so it takes much longer to reach saturation upon irradiation with a neutron source.

With respect to exposure duration, we do not know what Auer von Welsbach termed as "long-lasting contact". Therefore, we have chosen a duration of activation of 24 hours on an arbitrary basis. It is possible, if not likely, that Auer von Welsbach exposed the platinum crucible for more than 24 hours to the radiation of his jonium sample, but we wanted to keep our approach rather conservative. However, we calculated that it would take a staggering number of 131 days for the constantly increasing activity of ^{192}Ir to finally exceed the activity of ^{194}Ir. Since Auer von Welsbach was a very productive, almost restless character, it seems very unlikely that he "forgot" about the jonium for more than four months before he continued with his separation work.

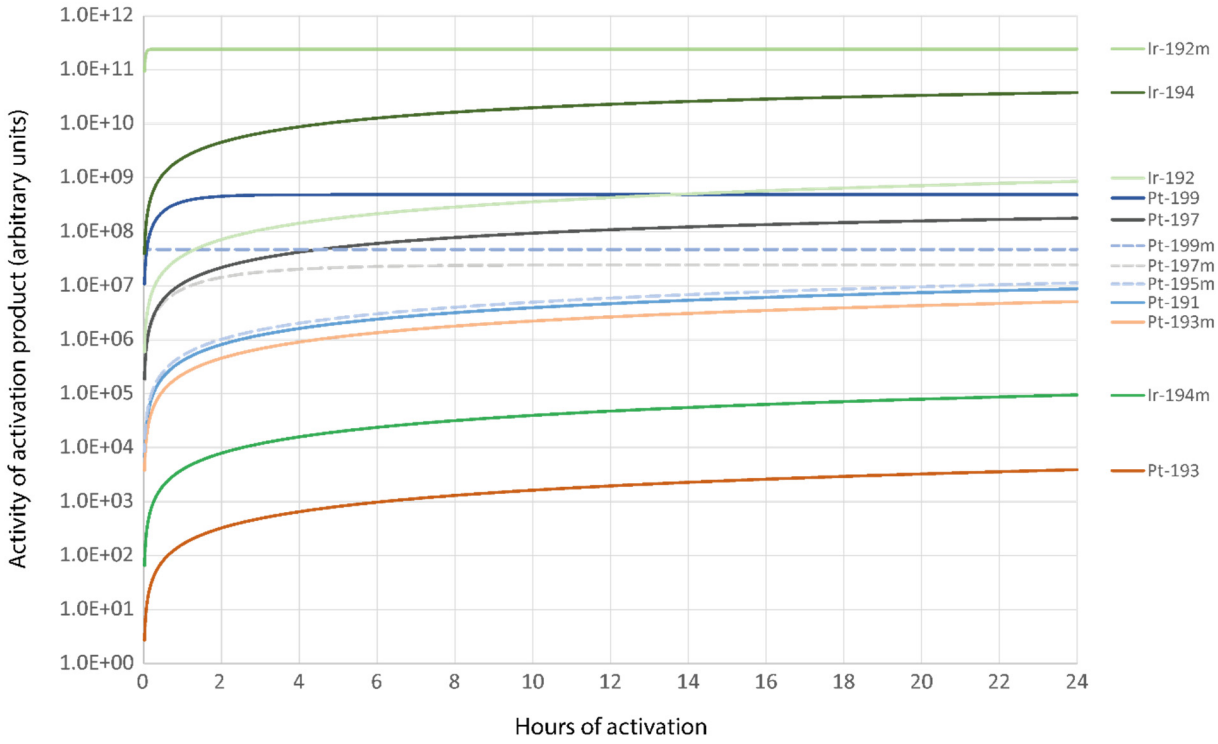
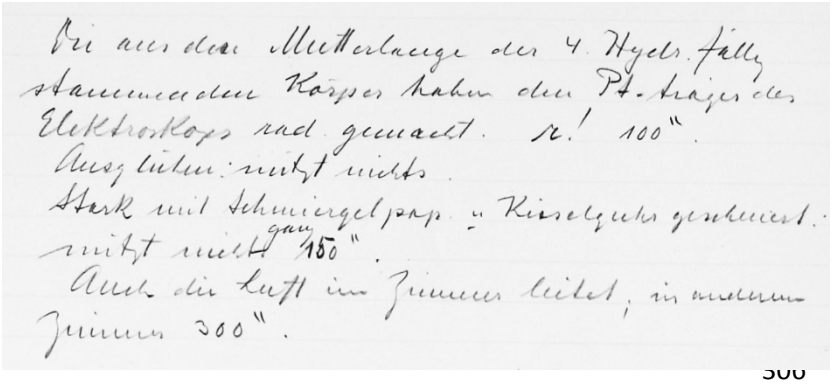


Fig. 8 Relative neutron activatability of the constituents of a Pt-Ir alloy with the composition of 70% Pt and 30% Ir in a 24 h activation cycle. For this model, we used thermal neutron energy cross sections, which is the simplest approach. Pure photon emitters are shown in dashed lines.

The very high β^- energy of iridium-194 ($E_{\beta, max}$ = 2.2 MeV) is another striking argument in favor of the "iridium hypothesis" since Auer von Welsbach writes a note in his lab journal (see Fig. 9):



[The bodies that originate from the 4th hydr[ate] precipitation have made the Pt carrier of the electroscope radioactive. r! 100''
Glowing out does not help.
Heavily rubbed with sandpaper and diatomite: does not help (*unreadable*) 150''.
Also the air in the room becomes conductive; in the other room 300''.]

Fig. 9 Note taken from Auer's lab journal "Notizen über die radioaktiven Arbeiten", dated 26 XI 1913 (three years after the 1910 publication)

It is not entirely clear what Auer von Welsbach described as "Pt carrier" in Fig. 9. In any case, only powerful, highly energetic β^- rays of more than 1 MeV have a range of several meters that would allow the observation of air becoming conductive in the entire room and also the adjacent room. This is another powerful argument why ^{194}Ir is the more likely activation product than the more prominent ^{192}Ir. The statement of "heavy scrubbing" and the use of sandpaper triggered the hypothesis that the crucible with the scratches from Fig. 4 may be identical with the platinum carrier Auer von Welsbach described in this lab note. Therefore we focused our investigation on this object.

Auer von Welsbach noted that the platinum crucible remained "r." (radioactive). According to his uranium standard-based definition (Fig. 7), "r." would correspond to an activity of his uranium standard of approximately 52-130 kBq (see Table 1). From this value we can roughly estimate the activity of the crucible and the neutron flux density of the neutron source that would have been necessary to activate the platinum/iridium crucible to reach a matching iridium-194 activity. The various types of radiation emitted by the uranium standard are not equally capable of ionizing surrounding air. Assuming an average energy loss of 34 eV per ion pair formed in air, the α-radiation emitted from Auer's purified uranium standard will contribute 10 times more to the ionization of air than the β^- rays emitted from the standard. A sample with the classification "r." will produce approximately 10^{10} ion pairs per second in air. In order to reach the same ionization of air, an activity of $5 \cdot 10^5$ Bq ^{194}Ir would be needed.

Several assumptions have to be made to estimate the neutron flux density of Auer's neutron source to reach an activity of ^{194}Ir of $5 \cdot 10^5$ Bq. In order to keep this estimate simple, we will assume a thermal neutron energy, negligible neutron self-absorption, negligible contribution to the ionization of air through γ-radiation, and negligible geometric effects affecting the activation process. We further assume that the "long-lasting contact" lasted for 24 hours and that half of the crucible was exposed to neutrons whereas the other half remained unirradiated. With all these assumptions, the neutron flux density needed to cause an activity of 500 kBq of ^{194}Ir would be about $8 \cdot 10^4$ cm^{-2}s^{-1}. The question of neutron energy remains a big challenge. Neutrons produced from the ^{9}Be(n,α)^{12}C reaction are fast (Q-value 5.7 MeV). Fast neutrons have significantly lower cross sections for neutron capture in most materials. In order to cause significant irradiation, they need to be thermalized first. We have no idea what a possible moderator could have been. Auer von Welsbach mentioned that he measured the

activities of two bodies, the platinum crucible on the one hand and "solution" on the other. If the crucible was filled with water or any form of aqueous medium, this would probably have shielded the α-rays before they could have reacted with the beryllium nuclei.

Alternative Explanations of Auer's Observation

Neutron activation is only one of several possible explanations for Auer's description of the unusual phenomena. The other, probably more obvious explanation, would have been a contamination of the crucible with radioactive substances on its surface. Auer von Welsbach was well aware of this simple explanation to the "mysterious" observation. As shown before, Auer von Welsbach tried everything to remove contaminations from the surface of the crucible. Generally, platinum surfaces are easy to clean as they are chemically inert and can be treated with harsh chemicals without being attacked. We have learned that Auer von Welsbach tried "heavy scrubbing" and "glowing" of the crucible, but it is likely that he had tried several other methods (probably boiling with acids etc.) to remove any contaminants from the surface. Being a brilliant and experienced chemist, we can safely assume that Auer von Welsbach would probably have succeeded in removing the contaminants or at least reducing their amounts significantly. None of this seemed to be the case.

Another theory that needs to be considered, therefore, is the implantation of radioactive recoil nuclei into the crucible matrix. For example, it may be possible that the ^{222}Rn-emanation of radium-226 on the surface of the platinum crucible may have caused the implantation of ^{218}Po into the platinum/iridium matrix upon α-decay, from where it would be difficult or even impossible to remove. However, this hypothesis is limited primarily by half-lives of polonium-218 and its progeny. Polonium-218 has a half-life of 3.05 min; lead-214 (26.8 min) and bismuth-214 (19.9 min) are only marginally longer-lived. If this was the sole cause for the peculiar phenomena, physical decay would probably have pretended to Auer von Welsbach that his laborious and time-consuming efforts to remove the alleged contamination (by washing, scrubbing, glowing to red heat etc.) would have been effective. The next radionuclide in the decay chain, lead-210, is much longer-lived ($T_{1/2}$ = 22.3 a), but emits β^- particles with a very low energy. This radionuclide would barely have caused significant ionization of the air in order to be detectable by Auer's electroscope, especially not in the "adjacent room." This certainly had to be a very powerful beta emitter, which is another strong argument in favor of the "neutron activation hypothesis."

Results of the Experimental Investigation of the Platinum Crucibles

Two gamma-ray measurements were done: (1) a measurement of multiple platinum objects placed on top of the gamma detector and (2) a separate measurement of the scratched platinum crucible that was thought to be of particular interest (because the scratches may have resulted from decontamination attempts as described by Auer von Welsbach). Gamma-ray spectrometry revealed presence of elevated levels of natural radionuclides in both measurements of platinum objects. Interestingly, in both cases, the platinum objects showed minute contaminations of daughters of ^{227}Ac ($T_{1/2}$ = 21.8 years; member of the ^{235}U decay chain) and ^{226}Ra ($T_{1/2}$ = 1600 years; member of the ^{238}U decay chain) and its radioactive progeny, but no traces of their mother(s), including the γ-emitting nuclides ^{231}Pa and $^{234m+g}$Pa, respectively. All γ-emitting daughter nuclides of these nuclides (^{227}Ac and ^{226}Ra) could be detected in amounts that suggests the presence of the radioactive progeny in equilibrium with their mother nuclides (see Fig. 10). This includes ^{227Th}, ^{223}Ra, ^{211}Pb and ^{211}Bi as the daughters of ^{227}Ac as well as ^{214}Pb and ^{214}Bi as the daughters of ^{226}Ra (the gamma peak of ^{226}Ra itself can also be seen in the spectrum, see Fig. 10).

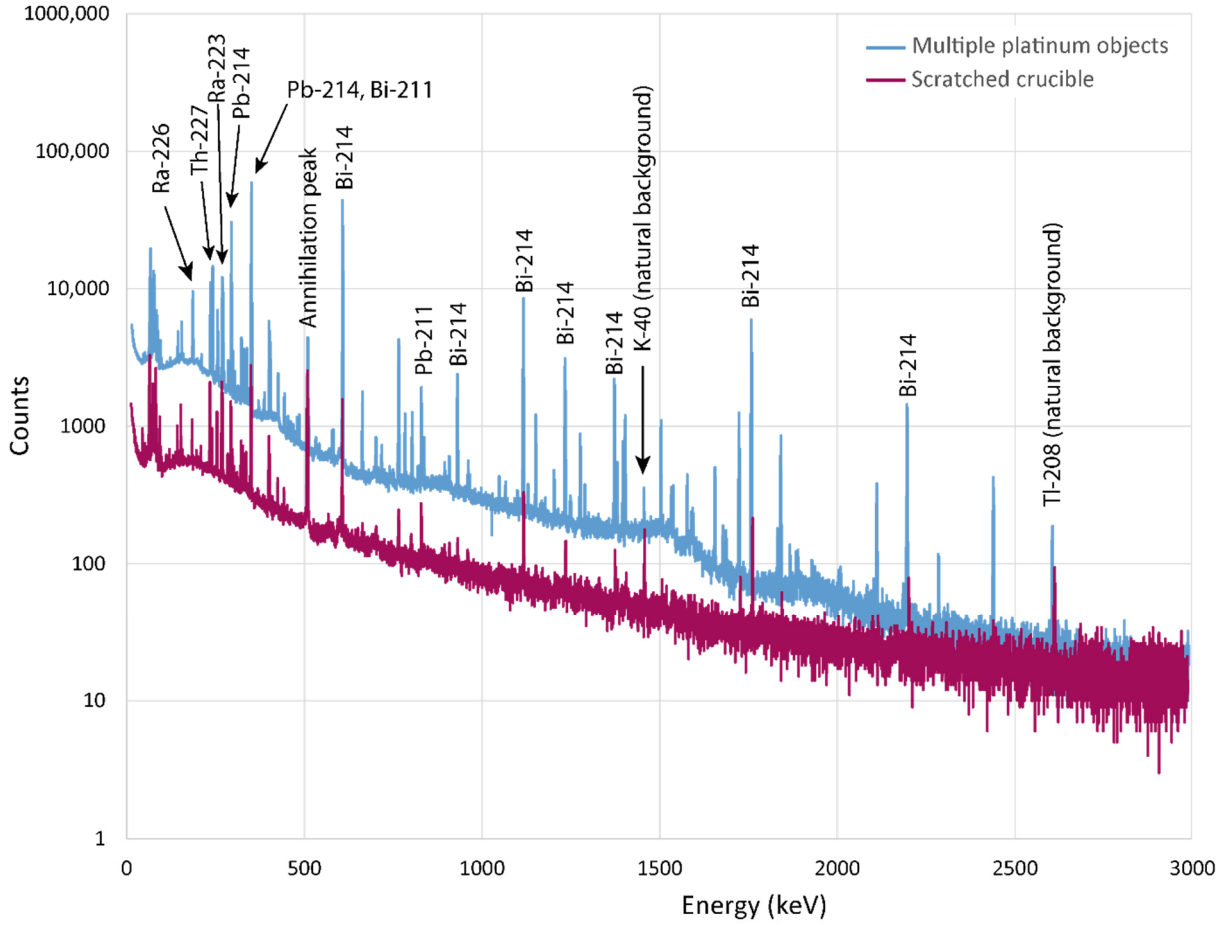


Fig. 10 Gamma spectra of several platinum objects (combined for the measurement) (blue) and the scratched crucible (purple). The most important/relevant peaks were labeled.

Quantification of the contamination could not be performed because the distribution of the radionuclides on the surface of the platinum objects could not be determined. Hence the measurement took place with unknown geometry. Also, for historical reasons, we decided not to not remove the contamination as it also has historical value. In any case, the activities were well in the sub-becquerel range. This explains why Auer von Welsbach did not spot them using his electroscope that naturally lacked the necessary sensitivity.

Interesting insight can be derived from the ratio of radionuclides. We observed that the measurement with the multiple platinum objects (1) revealed higher activities of radium-226 and its progeny compared with actinium-227 and its progeny. The scratched crucible (2), however, had a higher activity of the actinium-227-decay-chain compared with radium-226 and its decay products (see Fig. 10). At this point it should be noted that more than 5 half-lives of actinium-227 have passed since 1910, so this fraction was more than 30 times higher when Auer von Welsbach had worked with the objects. However, is not it remarkable that Auer von Welsbach isolated significant activities of radium-226 from that residues of the radium-production? The materials were significantly depleted in radium, but Auer von Welsbach isolated even visible amounts of radium as discussed in (Steinhauser, Löffler, and Adunka 2013).

This results clearly shows that Auer von Welsbach used these platinum crucibles in the work-up of the “hydrates”, and also that they were contaminated in a least two independent steps, because in the separation actinium and radium performed in different steps. The contamination also is a clear indication that these crucibles were used at a time when Auer von Welsbach dedicated most of his time to radioactivity research, which was the time before the First World War (the lab journal “Über die radioaktiven Arbeiten” [On the radioactive works] does not include any entries dated later than 1913). Therefore it appears likely that these platinum objects were saved from the noble metal collections of World War I and rather not purchased after 1918.

No activities of possible (both γ-emitting and sufficiently long-lived) activation products were found in any of the measurements.

The question whether or not the scratched crucible was the one of Auer’s 1910 observation remained open. Since we believe that neutron activated iridium was the main culprit of the mysterious observation, we asked the owner of the scratched crucible for permission to investigate the chemical composition of this crucible. Hence several flakes from the scratched crucible (shown in Fig. 4) were investigated with SEM/EDX (Fig. 11).

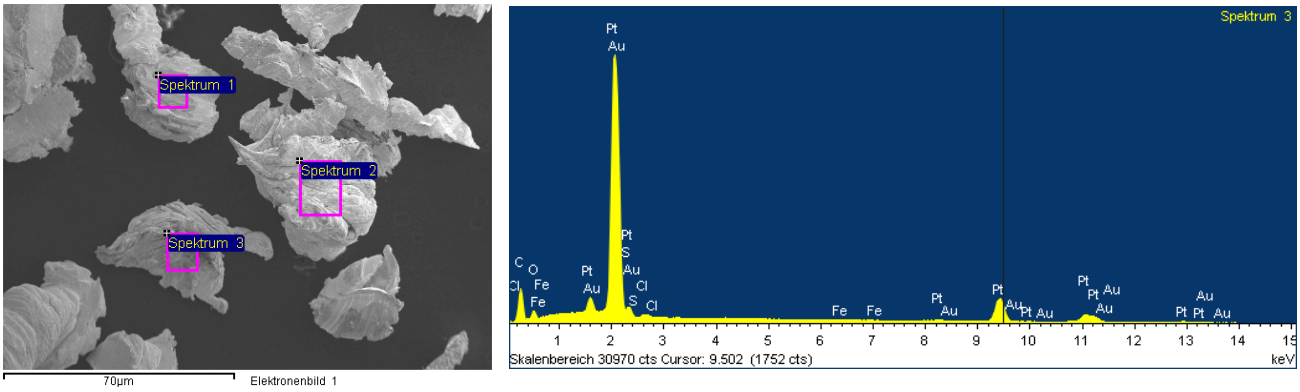


Fig. 11 SEM images of flakes from the scratched crucible (left) and EDX spectrum of these flakes (right).

EDX analysis revealed that the matrix of the crucible does not contain any macroscopic amounts of iridium. The detection limit in this case is about 0.2 wt.%. In addition to platinum (which is, of course, is the dominating constituent), traces of gold and carbon (probably stemming from soot of the burners used and which is known to aggressively corrode platinum (Mylius and Hüttner 1916, Ullmann 1930b)). In some flakes also cerium was found. Presence of lanthanides such as cerium can easily be explained by the intensive work of Auer von Welsbach in rare earth element chemistry. Unfortunately, the lack of iridium makes it rather unlikely this particular crucible was the one that showed signs of neutron activation. If it really was neutron activation of platinum/iridium, we have not found yet the right crucible. We will continue our search for platinum crucibles and hope for permission of the owners to investigate the objects further with respect to their chemical composition.

Possible Implications of Auer’s Observation

The discovery of the neutron is not “just another milestone” in physics and our view of nature on an atomic and subatomic level. The discovery of the neutron marks the starting point of nuclear technology and the nuclear age. After Irène and Frederic Joliot-Curie had discovered artificial radioactivity by bombarding aluminum with alpha particles in December 1933 (Joliot and Curie 1934),

Enrico Fermi realized that neutrons would be even better suited to yield artificial radionuclides as the neutrons would not have to overcome the Coulomb barrier before being captured by the target nucleus. Within one year, Fermi had tested numerous elements and their activation products upon neutron bombardment (Fermi 1934). In total he tested more than 60 elements and characterized their neutron activation induced radioactivity. In most cases, neutron activation yields an activation product that exhibits the characteristics of a beta-minus emitter. These nuclides are characterized by neutron excess in their nuclei. In the course of beta-minus decay, a neutron is transformed into a proton, hence yielding the element with the next-higher atomic number. This offered a completely new perspective on the known and unknown elements. The story says that Fermi gave his assistant, later Nobel laureate Emilio Segrè a 1000 dollars with the order "Get the whole Mendeleyev table" (Kubešová 2016). Thanks to the neutron, science suddenly had a tool to explore unknown regions of the periodic table. Therefore it was no surprise that scientists also wanted to explore a completely unknown terrain: the production of elements heavier than uranium which was the heaviest known element back then. Since irradiation of uranium with neutrons not only induces activation processes but also fission processes, it was only a matter only few years until nuclear fission was (or virtually rather "had to be") discovered. In fact, induced fission of uranium was discovered only six years after the neutron in December 1938 (Hahn and Strassmann 1938, 1939, 2016, Steinhauser 2016).

History of science is generally rather reluctant to make "what - if" assumptions. Speculations about possible implications of an earlier discovery of the neutron are hence difficult to make. Nonetheless, it is obvious that especially the military application of nuclear power and the nuclear arms race was only possible because essential discoveries were made only months before World War II or during the war. All the important milestones towards the atomic bomb happened within a very short time span. In particular, this includes the discovery of nuclear fission (Hahn and Strassmann 1938), a deeper understanding of the energy budget involved in a fission cycle (Meitner and Frisch 1939), the confirmation of the possibility of a nuclear chain reaction (Anderson, Fermi, and Szilard 1939), the discovery of plutonium by Glenn T. Seaborg, Joseph W. Kennedy, Edwin M. McMillan, and Arthur Wahl in December 1940, the launch of the Manhattan project in 1942 (triggered by Albert Einstein's letter to President Franklin D. Roosevelt on August 2, 1939) and lastly the production of nuclear war heads that would be tested in New Mexico and deployed over Japan in 1945. This impressive chain of discoveries was triggered by Chadwick's discovery of the neutron in 1932. Hence there is reason to believe that an earlier discovery of the neutron is likely to have triggered some of these discoveries at an earlier stage that would have allowed other nations and military powers to scrutinize the applicability of nuclear power for military purposes. We do not know exactly how – but the world and the warfare of World War II would probably have evolved differently if not only the United States had been in possession of this extremely powerful new weapon type at the time of World War II.

Whether or not Auer's observation has been the first observation of neutron activation, why did not anybody uncover the solution to the mystery? Auer von Welsbach certainly felt that there was something unusual going on with the ionium sample in his experiment. Unfortunately, however, he apparently did not feel qualified to further scrutinize this mysterious observation by himself. From Part II of his publication, we have learned that he suspected rather a chemical anomaly than a new type of radiation. He submitted it to Vienna for further spectroscopic investigations, which did not reveal any unusual composition. Even if beryllium was found in the sample, it would probably not have been a sufficiently unusual observation to have rung any alarm bells. So we learn that Auer von Welsbach did ask colleagues of his time for help, but none of them (including Auer von Welsbach) put enough effort into this question to finally solve it. It is also probably due to the largely lacking echo within the scientific community that Auer von Welsbach eventually let this issue rest. We only know of one comment from the scientific community in response to the short note of Fig. 2. The

German chemist Bruno Keetman sent a letter to Auer von Welsbach, congratulating him on this spectacular result. Unfortunately this letter was lost in the second half of the 20th century. Keetman had earned his doctoral degree in 1909 in Berlin for the retrieval of ionium from uranium ores. Later he took the lead of the Laboratory of Radioactivity of the Auer-Gesellschaft in Berlin. It seems he was naturally intrigued by the observation of Auer von Welsbach involving ionium. In any case, Keetman died on April 13, 1918 at the age of 34, which explains why this trace was lost, too (Wichelbaus 1918).

A deeper discussion within the scientific community or a wider dissemination of the reported observation, however, may not have been the sole key to solving the mystery because the composition of Auer's crude ionium oxalate would have been difficult to repeat by others; especially keeping in mind that beryllium impurities would have been the key constituent of such mixture. Therefore one would have had to investigate the original ionium substance produced by Auer von Welsbach himself which might have been difficult. Auer von Welsbach was a deeply generous person and scientist who worked for the advancement of science, who shared his knowledge with everyone who asked for his advice, and who donated more than 500 samples of precious, purified substances to other researchers. Nonetheless, he was not what one would regard as a "team player" in modern scientific terms. For his own research, Auer von Welsbach accepted little assistance by others. He even preferred to wash his laboratory glassware manually by himself rather than letting anybody assist him with such back-work. For a deeper understanding of Auer's character, we must understand that he was deeply traumatized in the course of the discovery of the elements 70 and 71 in the year 1907. Although Auer von Welsbach is generally believed to have been the first who isolated these elements in pure form (Kragh 1996), a fierce controversy between Auer von Welsbach and Georges Urbain about the priority of this discovery had erupted, which he finally lost. After such bad experience, Auer von Welsbach was probably even less likely to share a sample of his substance (which he truly believed to be of importance for the further investigation of the field of radioactivity) with others outside the Austrian "radium circle", before having had the possibility of claiming his own full priority of the discovery. Therefore, it rather appears unlikely that he would have given this mystery completely out of his own hands and let somebody else than his closest colleagues study the mysterious ionium sample.

Conclusions and Summary

Although our recent investigations have not been sufficient to fully answer the question whether or not Auer von Welsbach really observed neutron activation processes back in 1910, we still believe that neutron activation is the most likely explanation for the "peculiar observation" Auer von Welsbach described in his 1910 publications (Auer von Welsbach 1910b, a). Above we have described some major new steps that can be summarized as follows:

- We have discovered a hand-written manuscript of Part II of the key publication. It is a rather rough hand-written draft, on which Auer von Welsbach shortly mentions the "peculiar observations" and how he did not feel qualified to investigate the phenomenon further. He states that he transferred a second fraction of raw thorium/ionium oxalate to F. Exner and E. Haschek at the Institut für Radiumforschung in Vienna. Auer von Welsbach reported that they could not report any insightful result from their investigation. It seems that they rather analyzed the chemical composition of the sample with spectroscopical methods, but there is no indication that they investigated it for a possible new type of radiation (neutron radiation?).
- Theoretical considerations revealed that neutron activation remains more likely a plausible scenario for the peculiar phenomenon than surface contaminations or implantation of recoil nuclei from radon-222 or other α-emitters into the metallic matrix of the platinum crucible.

- We attempted the “translation” of Auer’s activity units (Uran-Einheit, Ur.E.) to modern Si-allowed units (becquerel). It turned out that what Auer defined as “almost inactive” was in fact an activity as high as 2600 becquerels.
- We identified iridium as a possibly very important constituent of the crucible material which Auer von Welsbach terms “platinum crucible”. Presence of iridium in the crucible would increase the likelihood to observe neutron activation processes by a factor of 100 compared with pure platinum. It is the much higher cross sections of the stable iridium nuclides, the suitable half-live of the activation product iridium-194 and its very high β^--energy which make iridium a much more promising candidate than platinum.
- In order to make iridium-194 appear “r.” (“radioactive”, according to Auer’s definition), it would have had to have an activity of ~ 500 kBq.
- Based on the assumption that Auer’s crucible contained some 30% iridium, we estimated the neutron flux density that was necessary to sufficiently activate the object to roughly $8 \cdot 10^4$ $cm^{-2}s^{-1}$. This is a rather high neutron flux density for a “coincidental”, not designed neutron source.
- Gamma spectrometry of the platinum crucibles investigated in this study reveals that Auer succeeded repeatedly in separating actinium-227 and radium-226 from the “hydrates”. This is even more remarkable as the hydrates were already depleted in radium as they constitute the *residues* of the radium production. The fact that the platinum crucibles were contaminated with actinium and radium allows the conclusion that Auer von Welsbach saved these platinum objects from the noble metal collections of the Austrian-Hungarian Monarchy during World War I because most of his “radioactive works” were conducted before 1914.
- SEM/EDX analyses revealed that the most promising crucible (the scratched one) did not contain any iridium. It is therefore questionable (if not unlikely) that this crucible was the one that Auer von Welsbach noted his peculiar observations with (provided that Auer von Welsbach indeed incidentally had observed neutron activation processes).

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References

Anderson, H. L., E. Fermi, and L. Szilard. 1939. "Neutron production and absorption in uranium." *Physical Review* 56 (3):284-286. doi: 10.1103/PhysRev.56.284.

Auer von Welsbach, Carl. 1910a. "Über die chemische Untersuchung der Actinium enthaltenden Rückstände der Radiumgewinnung (I. Teil)." *Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften* 119 (6):1011-1054.

Auer von Welsbach, Carl. 1910b. "Über die chemische Untersuchung der Actinium enthaltenden Rückstände der Radiumgewinnung (I. Teil)." *Mitteilungen der Radium-Kommission der kaiserlichen Akademie der Wissenschaften, Chemie-Heft* 10:1159-1202.

Bohr, Niels. 1913. "On the constitution of atoms and molecules." *Philosophical Magazine* 26:1-25.

Chadwick, James. 1932a. "Existence of a neutron." *Proc. R. Soc. London, Ser. A* 136:692-708. doi: 10.1098/rspa.1932.0112.

Chadwick, James. 1932b. "Possible existence of a neutron." *Nature (London)* 129:312.
Fermi, Enrico. 1934. "Radioactivity induced by neutron bombardment." *Nature (London, U. K.)* 133:757. doi: 10.1038/133757a0.
Hahn, O., and F. Strassmann. 1938. "Über die Entstehung von Radiumisotopen aus Uran durch Bestrahlen mit schnellen und verlangsamten Neutronen." *Naturwissenschaften* 46:755-756.
Hahn, O., and F. Strassmann. 1939. "Über den Nachweis und das Verhalten der bei der Bestrahlung des Urans mittels Neutronen entstehenden Erdalkalimetalle." *Naturwissenschaften* 27 (1):11-15.
Hahn, O., and F. Strassmann. 2016. "On the production of radium isotopes from uranium caused by irradiation with fast and decelerated neutrons." *The European Physical Journal H*:in press. doi: 10.1140/epjh/e2016-70025-1.
Joliot, F., and I. Curie. 1934. "Artificial production of a new kind of radio-element." *Nature (London)* 133:201-202.
Kragh, H. 1996. "Elements 70, 71 and 72, Discoveries and Controversies." In *Episodes from the History of the Rare Earth Elements*, edited by C. H. Evans, 67-89. Dordrecht: Kluwer Academic Publishers.
Kubešová, M. 2016. "Neutron Activation Analysis - History." accessed September 2016. http://www.naa-online.net/theory/history/.
Meitner, L., and O. R. Frisch. 1939. "Disintegration of Uranium by Neutrons: a New Type of Nuclear Reaction." *Nature (London)* 143:239-240.
Merz, Stefan, Katsumi Shozugawa, and Georg Steinhauser. 2015. "Analysis of Japanese radionuclide monitoring data of food before and after the Fukushima nuclear accident." *Environmental Science & Technology* 49:2875-2885. doi: 10.1021/es5057648.
Meyer, S., and E. Schweidler. 1927. *Radioaktivität*. Wiesbaden: Springer Fachmedien Wiesbaden GmbH.
Meyers Konversations-Lexikon. 1877. Platinlegirungen. Leipzig: Verlag des Bibliographischen Instituts.
Mylius, F., and C. Hüttner. 1916. "Platin und Leuchtgas." *Zeitschrift für anorganische und allgemeine Chemie* 95 (1):257-283. doi: 10.1002/zaac.19160950118.
Steinhauser, Georg. 2016. "Hahn and Strassmann's first credible, yet erroneous approximation to the discovery of nuclear fission." *The European Physical Journal H*:in press. doi: 10.1140/epjh/e2016-70043-y.
Steinhauser, Georg, Jürgen Evers, Stefanie Jakob, Thomas M. Klapötke, and Gilbert Oehlinger. 2008. "A review on fulminating gold (Knallgold)." *Gold Bulletin (London, United Kingdom)* 41 (4):305-317.
Steinhauser, Georg, Gerd Löffler, and Roland Adunka. 2013. "The possible discovery of neutron activation in 1910." *Journal of Radioanalytical and Nuclear Chemistry* 296 (1):157-163. doi: 10.1007/s10967-012-2065-7.
Steinhauser, Georg, Gerd Löffler, and Roland Adunka. 2014. "Eine unentdeckte Entdeckung?" *Nachrichten aus der Chemie* 62:1073-1076.
Steinhauser, Georg, Stefan Merz, Dieter Hainz, and Johannes H. Sterba. 2013. "Artificial radioactivity in environmental media (air, rainwater, soil, vegetation) in Austria after the Fukushima nuclear accident." *Environmental Science and Pollution Research* 20 (4):2527-2537. doi: 10.1007/s11356-012-1140-5.
Ullmann, Fritz. 1930a. Iridium. In *Enzyklopädie der technischen Chemie*. Berlin/Wien: Urban & Schwarzenberg.
Ullmann, Fritz. 1930b. Platin. In *Enzyklopädie der technischen Chemie*. Berlin/Wien: Urban & Schwarzenberg.
Wichelbaus, H. 1918. "Sitzung vom 15. April 1918." *Berichte der deutschen chemischen Gesellschaft* 51 (1):689-695.