REINVESTIGATING VESTIUM, ONE OF THE SPURIOUS PLATINUM METALS

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Introduction

In 1806 the Académie de France proclaimed that a new metal had been discovered in platinum (1):

> One writes from Germany that a chemist has discovered a new metal in small amounts in platinum. It was named Vestium from Vesta, the last planet [asteroid] discovered by Olbers. Consequently, platinum contains, 1. platinum. 2. palladium. 3. rhodium. 4. osmium. 5. iridium. 6. vestium. Other impurities were gold, iron, copper, titanium. . . . [authors' translation]

Three years later, in one of the shortest publications on record, it was announced by the Académie (2):

> On Vestium. This new metal has been reported as being isolated from platinum, but the experiments are not reproducible. We await further work. [authors' translation]

The case of vestium essentially lay dormant in the scientific literature until Weeks categorically stated in *Discovery of the Elements* in the mid-twentieth century (3):

> The Polish chemist, Jedrzej (Andrei) Sniadecki was the first to isolate the element now known as ruthenium, which he called vestium, though he later became convinced that this was not a new metal. . . . In Paris. . . a commission composed of Berthollet, de Morveau, Fourcroy, and Vauquelin was unable to detect the new metal in their platinum. This so discouraged Sniadecki that he dropped all his claims and carried out no further experiments. There is no doubt, however, that he had isolated ruthenium.

One can search contemporary literature for details regarding vestium, but they are lacking. Nevertheless, the layman's literature accepts Sniadecki's discovery; for example, the Wikipedia entry is as follows (4):

> Sniadecki may have been the original discoverer of the element ruthenium in 1807, thirty-seven years before Karl Klaus.

(Karl Ernst Klaus, 1796-1864, is the historically accepted discoverer of ruthenium (5)). According to the Polish Wikipedia entry for Sniadecki (6):

> He discovered ruthenium (called vestium in an 1808 presentation about his work where he discovered it in crude platinum) only to find it was not officially confirmed. [author's translation]

Note there is no mention of Klaus. Should Sniadecki, instead of Klaus, in fact be credited with the the original discovery of ruthenium? What is the story?

The Rebirth of Vestium—How it Happened

In 1808 Jedrzej (Andrew) Sniadecki (1768-1838), a Polish scientist at the University of Vilnius (now Lithuania, formerly in the Polish-Lithuanian Commonwealth), published his paper (7), in which he described a "new metal" that he found in crude platinum in addition to the four (palladium, rhodium, iridium, and osmium) just discovered by the English scientists. He named this element vestium ("West" in Polish) in observance of the asteroid just discovered (Vesta, in 1807). After his discovery Sniadecki sent his 1808 report to the

French Academy and to the Russian Academy of Sciences. The French Academy promptly published the preliminary account (1). To validate his claim Sniadecki sent a sample of platinum ore to Paris, which was analyzed by Guyton, Fourcroy, and Berthollet (and nominally Vauquelin); but they could not reproduce the work (8), and Sniadecki's claim was rejected (2). Meanwhile, the Russian Academy reported Sniadecki's claim with the comment that it could not be accepted without verification, but no one did experimental work in an attempt to confirm vestium (9).

Figure 1. *Sniadecki's bust. The caption heralds him as "Vilnius professor of natural sciences 1797-1832, philosopher, head of the medical clinics. Artist Kazimieras Jelski. Terracotta."*

The French rejection did not really settle the issue. In spite of the grand reputation of French science at the beginning of the 19th century, the science citizenry outside Paris was well aware that the French Academy was not infallible in its chemical analysis (10). After Cronstedt discovered nickel in 1751, Sage and Monnet opined that the "new metal" was merely a mixture of cobalt, arsenic, iron, and copper—prompting Scheele (who discovered molybdenum in Köping) to write to Hjelm (who prepared an ingot of it on his forge in Stockholm) (11):

> I can already see the French hurrying to deny the existence of [our molybdenum].

Other hasty assessments of the French include Buffon's pronouncement that platinum was merely an alloy of iron, gold, and mercury (12) and Collets-Descotils' misidentification of del Río's "erythronium" as chromium after performing only three quick superficial experiments (13), thus "undiscovering" vanadium (14).

Unfortunately, Sniadecki could not reproduce his own chemistry (15). Before the initial reading in Paris he had attempted a retraction, but his brother Jan Sniadecki (1756-1830), who was rector of Vilnius University 1807-1815, urged him to persist. In a speech at a public meeting of the university, Jan boasted of this chemical achievement which elevated Jedrzej to the level of Klaproth and Vauquelin, the two best laboratory chemists in the world, and of Bergman (the mentor of Scheele) (11). After the French pronouncement, however, Jedrzej allowed the matter to drop, not even mentioning vestium in his own chemistry textbook (11, 15).

A century later, in 1907, Waclaw Kaczkowski, a dyestuff technologist from Warsaw, reopened the question and wrote an article (16) arguing that Sniadecki should have persisted in his claim. In fact, Kaczkowski contended, vestium was ruthenium, which by then had been known for six decades. A debate for and against Kaczkowski's idea ensued in the Polish scientific community (11). In 1937 Stanislaw Plesniewicz, a lecturer in the Warsaw Polytechnic Institute, urged Mary Elvira Weeks to include Sniadecki in her *Discovery of the Elements*. Although Weeks had not mentioned Sniadecki in her original article on the platinum group (17), she did add a paragraph about vestium in her book (3)—but with no chemical details, as she customarily did for other elements in that expansive book.

Reinvestigating Vestium

To explore the question of vestium with hopes of settling the issue, the present authors traveled to Vilnius, Lithuania. Here they visited the university where Sniadecki worked, and they consulted with scholars (15) familiar with Sniadecki's career. The first task was to obtain an accurate translation of Sniadecki's work, written in old Polish, which presented obstacles to a clear understanding of the experimentation. Fortunately, three separate and independent translations became available (15) and furnished a dependable account of Sniadecki's procedure:

First, Sniadecki boiled 400 g of crude platinum in nitric acid to remove mercury. Then he dissolved the residual ore in aqua regia, obtaining a solution and a residue. In the residue he identified and verified osmium and iridium. In the solution he identified contaminants iron, silver, lead, and the noble metals platinum, palladium, and rhodium—and vestium. The vestium was isolated as "red needles" (vestium chloride), which were not soluble in "spirit of wine" (ethanol) and which remained after alcohol extraction. Sniadecki performed several chemical tests to characterize the "new metal" to fill out his 26-page treatise (7). One who carefully reads Sniadecki's original paper finds irreconcilable differences between vestium and ruthenium. The main problem is

that vestium was found in the wrong fraction, i.e., in the aqua regia-soluble fraction. It is to be remembered that Klaus discovered ruthenium in the insoluble residue. Today ruthenium is known to be the least tractable of the platinum-group elements (18). Despite the fact that ruthenium is not soluble in aqua regia, proponents of vestium have claimed that Sniadecki's observations could be rationalized by the fact that Sniadecki "had only a small quantity of the metal at his disposal," and hence the minute quantity could be dissolved in aqua regia (16). Unfortunately, this argument of low concentration solubility is diametrically opposed to the fact that ruthenium chloride (either $RuCl_3$ or $RuCl_4$) is readily soluble in ethyl alcohol (11), whereas vestium chloride was not soluble (19).

Additional disparities are noticed, such as the reaction of vestium chloride with hydrogen sulfide to form an orange precipitate, whereas ruthenium chloride reacts to form a black precipitate (11, 19); and its reaction with ammonium chloride to form a lemon-yellow precipitate, while ruthenium chloride forms a black precipitate (11, 19). Arguments (16) have been made that these discrepancies arise from Sniadecki's vestium being "impure," but Sniadecki's orange and bright-yellow derivatives could, at the very best, contain only minute amounts of authentic ruthenium compounds which are black. In total, nine distinct differences between the chemical behavior of vestium and ruthenium have been documented (11), leading one to read with astonishment and amusement such comments as (16):

> . . comparison of the reactions of the two metals provides grounds for identifying vestium as ruthenium and thus crediting our great naturalist with yet another achievement in the field of science.

It is regrettable that proponents of vestium were generally not knowledgeable in platinum chemistry and that obvious inconsistencies with vestium were simply glossed over. It would be helpful to involve a specialist in platinum ore analysis in the debate, and as a matter of fact there was one, and he was outstanding: Orest Evgenevich Zvyagintsev (1894-1967), editor of the leading Russian platinum journal (20), coauthor of a series on ruthenium (21), and author of many articles on platinum geochemistry [a mineral has been named after him (22)]. Zvyagintsev's contribution to the debate was his matter-of-fact statement in 1957 that there was simply no similarity between vestium (whatever it was) and ruthenium (11).

So, what did Sniadecki have? The behavior of vestium does not correspond to that of any known element; instead it mirrors a combination of several substances. Indeed, the history of platinum is replete with "discoveries" from platinum ore which were misidentifications, all mixtures. The list of mistakes includes not only Osann's irreproducible discoveries of four new elements [polinium, pluranium, two different rutheniums (23)] but also ilmenium, davyum, neptunium, uralium, amarillium, josephinite, and canadium, plus others that were never named—all of which were mixtures of metals and oxides of titanium, zirconium, silicon, iron, niobium, tantalum, tellurium, lead, tin, copper, the platinum-group metals, and perhaps other elements (24). The possibility of new element discoveries has always been alluring. Unfortunately, all too frequently elements have been identified without critical examination, even 20th-century "discoveries" such as alabamine, virginium, and illinium (25). The answer to the question "What is vestium?" remains unanswered—except one can say with certainty it is not ruthenium (26).

Sniadecki's Legacy

The legacy of Sniadecki lies in the many powerful contributions he made to the scientific community in Vilnius (8, 15). Born in Znin, Poland (half-way between Warsaw and Berlin), Jedrzej Sniadecki studied medicine in Krakow, Poland, and then in Pavia, Italy, where he graduated in 1793. Sniadecki admired Lavoisier and adhered to his principles; he wanted to meet Lavoisier but the French Revolution prevented this; instead he studied with Joseph Black in Edinburgh, Scotland in 1794. He was professor of natural sciences 1797-1832 at Vilnius (15). He and his brother introduced Polish into the lectures at the university; he wrote the first chemistry text in Polish. His famed book, *Początki chemii* (Introductory Chemistry), first written in 1800, has been used over a century (15). Sniadecki was a strict anti-phlogistonist and was informed about modern chemical theories. In his textbook he developed the general Polish vocabulary for chemical terms and nomenclature which are still used today (15). His laboratory and home still stand in Vilnius.

On September 28, 2008, the Jedrzej Sniadecki Lecture Hall (Auditorija) was dedicated at the Chemistry Faculty (Chemijos Fakultetas) at Vilnius University (Fig. 3). In the grand exhibit hall of St. John Church (Sv. Jonu Baznycia), the site of the original Vilnius University (Fig. 4), Sniadecki's bust (Fig. 1)is prominently displayed, as well as his famous Początki chemii (Fig. 2).

A Second "Discovery" of Vestium

In 1818, ten years after Sniadecki's claim, the German editor Ludwig Wilhelm Gilbert (1769-1824) announced (27) a new element discovered by Lorenz Chrysanth von Vest (1776-1840) of Graz, Austria. Vest was professor of botany and chemistry at the University of Graz (1812-1828) and later (1829-1840) Protomedicus (Chief Government Medical Officer) of Steiermark (Styria, in southeast Austria), attaining lasting recognition for his writings in botany and his contributions to public medical health in Steiermark (28). His "new element" was found in a nickel ore of Schladming, Austria (27), 140 km west of Graz. Vest had originally proposed the name Sirium but adopted Vestium upon Gilbert's suggestion. [Gilbert was unaware of Sniadecki's work (29)]. Vest's article followed with a detailed analysis of his new metal (30), with an addendum that Sir Humphry Davy (1778-1829) had visited during his continental tour and had briefly studied the "new metal." Davy initially thought it might be tantalum but then changed his mind and took a sample away for further analysis in London (30). Thomson, editor of *Annals of Philosophy*, was quick to note that the discovery was in question because Vest had never obtained vestium free from arsenic, cobalt, and nickel (31); and in 1819 Michael Faraday (1791-1867), Davy's assistant, published an article announcing that vestium was only impure nickel (32), with minor amounts of cobalt, iron, and arsenic. Promptly, this "second" vestium was "utterly forgotten," never to be revived again (33).

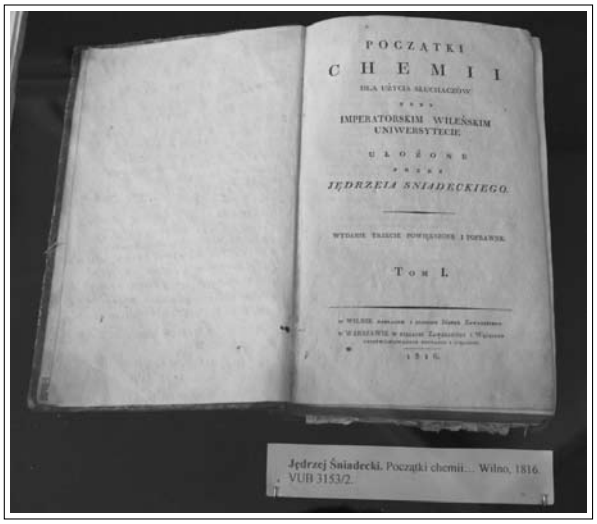

***Figure 2**. In the St. John's exhibit room is Sniadecki's famous introductory text, Sniadecki's famed book, Poczatki Chemii, first appeared in 1800 and used for over a century. It was the first general chemistry book written in Polish.*

Lessons from Vestium

In the excellent website Elementymology & Elements Multidict by the author Peter van der Krogt (34) lists over 200 "Names that did not make it," i.e., elements and/or element names which we do not recognize today as valid. Some of the names are archaic (e.g., columbium for niobium), but the majority are erroneous claims. Why were there so many? A more detailed analysis of the second vestium (sirium) may give us insight. A French editor observed, immediately after Vest's announcement (35):

> ..as it now stands, nobody can give credit to M. Vest's Sirium, but must rather be impressed with his want of experience. As he appears not to know that nickel is not precipitated from its solutions by sulphuretted hydrogen [hydrogen sulfide], when they are acid, and that it is partially precipitated when they are neutral, we must beg him to repeat his experiments in order to discover whether his Sirium be not merely very impure nickel.. . .

Indeed, a chemist versed in inorganic qualitative schemes knows very well that the selective precipitation of metal ions with hydrogen sulfide—especially the nickel-cobalt subgroup—requires a very carefully adjusted pH (36). After ascertaining the major components (37), with his wry sense of humor Faraday described his analysis of 4.9 g of ore, how he carefully removed the arsenic, then the cobalt, finally the nickel, only to find that, "My Vestium entirely disappeared (38)."

Three years later Berzelius (1779-1848), the master assayer in Sweden, published an insightful discussion of the difficulties of analyzing ores of nickel (39). In this work, he advanced the art of nickel ore analysis to a sophisticated level, as Klaus had done for platinum ores. Berzelius studied the reasons why not only vestium, but also two additional substances from nickel ore had been misidentified as new metals. These two substances were "wodanium," from a Hungarian ore (40), and "nicolanum," observed "only in the presence of nickel ores (41)." He pointed out that not only alloys of two or more different metals, but also compounds of metals with arsenic or sulfur, can appear as unique metals. Consider, for example, niccolite (NiAs), a reddish-brown mineral with a metallic luster (42), which was originally confused with copper until Axel Fredrik Cronstedt (1722-1765) discovered nickel in 1751 (43).

Berzelius' treatise underscores the difficulties of analyzing new materials in the early years of qualitative analysis, during the late 1700s and the early 1800s, before sophisticated schemes were worked out and when

Figure 3*. The old courtyard of Vilneus University, founded in 1579 and built around the Sv. Jonu Baznycia (St. John's Church) which is straight ahead. The location is on Universiteto Gatve. The building to the right has an old auditorium, akin to the one where Jedrzej Sniadecki's brother Jan, rector of the university, extolled the virtues of Jedrzej's vestium. Sniadecki, the "discoverer of vestium," had his laboratory 250 m to the east (straight ahead, past the church, out of view), on 2, A.Volano Gatve on the second floor of a building which is now the Lietuvos Respublikos Svietimo Ir Mosklo Ministerija (Ministry of Science and Education).*

Figure 4. Grand Exhibit Hall, St. John Church

it was unknown which, and how many, elements were yet to be discovered. Even in the hands of experienced chemists, mistakes were easily made. This difficulty was understood by the broad scientific community, and it was common to send a specimen to experts for confirmation— and ideally to the masters, Klaproth of Berlin, Vauquelin of Paris, or Berzelius of Stockholm. In the case of Lorenz von Vest, there was good reason why he observed that the properties of vestium "were too much like those of nickel and cobalt to be separated (30)," for the "vestium" was a mixture of nickel and cobalt.

With the platinum group analytical difficulties were even sharper, and Sniadecki, a more experienced chemist, did not understand the mutual interferences of the chemically similar platinum metals that hindered quantitative separations. This research had to await Klaus, four decades later, who was able to work out simple, efficient separation schemes for their various combinations (44).

For Vest we understand the source of his errors, because several accomplished chemists studied his "vestium" and we have access to their analytical results. Regrettably, for Sniadecki's vestium careful analysis was never repeated with his ore. Furthermore, one cannot reexamine his chemical samples, because they were shipped to the University of Kiev (during Russia's annexation of Lithuanian territory), never to be seen again (11)— and we shall never know the identity of his "red needles."

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been named after the first two asteroids, Ceres and Pallas); Vest hesitated, fearing he might be accused of intentionally lending his own name to his new metal, but he relented and accepted Gilbert's suggestion. The English continued to use vestium and sirium interchangeably.
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