Rediscovery of the Elements

The Curious Case of "Vestium"

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EDITOR'S NOTE: *This installment of the Rediscovery series is based in part on a recent publication[1] that appeared in the ACS Division of History, used with permission, that dealt with the historical controversy of the proposed new element "vestium."*

Introduction. In 1806 the Académie de France proclaimed that a new metal had been discovered in platinum:[2a] "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. . . ."

Three years later, in one of the shortest publications on record, it was announced by the Académie:[2b] "On Vestium. This new metal has been reported as being isolated from platinum, but the experiments are not reproducible. We await further work."

The case of vestium lay dormant in the main scientific literature until Mary Elvira Weeks (1892–1975) categorically stated in her celebrated *Discovery of the Elements*:[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." In spite of the fact that Karl Ernst Klaus (1796–1864) is the historically accepted discoverer[4d] of ruthenium (1844), scattered reports of Sniadecki's discovery persist to this day—for example, in *Przemysł chemiczmy [Industrial chemistry]* the author flatly states in a short letter that "a careful reading of the

Figure 1. Dr. Biruté Railiené (right), head of the Lithuanian Academy of Science Library in Vilnius, was extremely valuable in giving the authors useful information about Sniadecki. She has written[15] a 250-page biography of Sniadecki and also furnished unpublished notes on the famous scientist to the authors.

original manuscript . . . leaves no doubt . . . that Sniadecki discovered a new element now known as ruthenium."[5] The English Wikipedia says,[6] "Sniadecki may have been the original discoverer of the element ruthenium in 1807, 37 years before Karl Ernst Klaus." The Polish Wikipedia reports[7] "[Sniadecki] 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." None of these accounts includes details and it is impossible to evaluate their merit. Should Sniadecki, instead of

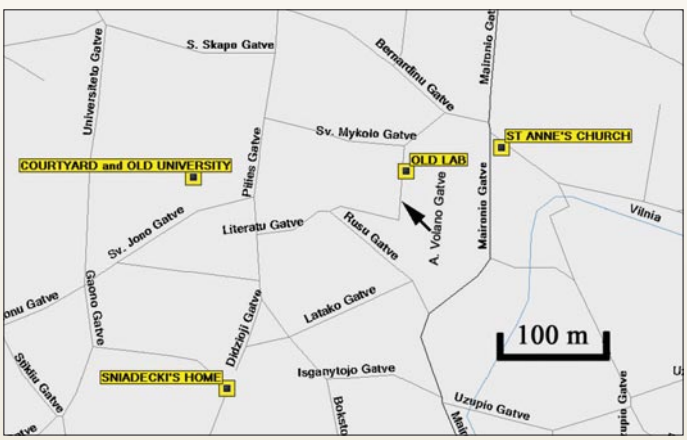

Figure 2. Map of Old University section of Vilnius, Lithuania:
Courtyard and Old University*, site of St. John's Church (Sv. Jonu Baznycia), Universiteto Gatve—N54° 40.96 E25° 17.29.*
Sniadecki's home*, 1 Didzioji Gatve, now a candy shop/apartment building—N54° 40.84 E25° 17.32.*
Sniadecki's laboratory*, now the Ministry of Science and Education, 2 A. Volano Gatve—N54° 40.96 E25° 17.49.*
St. Anne's Church (Sv. Onos Baznycia)*, 8 Maironio Gatve; there is a legend that Napoleon during the Franco-Russian War of 1812 said he thought the church was so beautiful that he "wanted to carry the church back to his home in his pocket"—N54° 40.97 E25° 17.58.*
Not shown*, modern Chemistry Faculty [Building] (Chemijos Fakultetas), located 1.2 km southwest of the University Courtyard at 24 Naugarduko Gatve–N54° 40.56 E25° 16.45.*

Figure 3. This is the building on A.Volano Gatve where Sniadecki had his laboratory on the second floor. The building is now the Lietuvos Respublikos Svietimo Ir Mosklo Ministerija (Ministry of Science and Education).

Figure 4. This was Sniadecki's home, now used as an apartment house and a confectionary shop. Notice the plaque on the corner (above the author's head), which commemorates (in both Lithuanian and French) Stendal (pen name of Henri-Marie Beyle 1783–1842), who participated in the ill-fated Napoleonic campaign of 1812 and stayed briefly in this house. In December of that year, Napoleon's tattered army in retreat from Moscow stumbled into Vilnius for rest before proceeding on to Paris. Recently mass, graves have been unearthed in Vilnius of French soldiers who survived the frozen march from Russia but succumbed to exhaustion.

Figure 5. The old courtyard of Vilnius University on Universiteto Gatve, founded in 1579 and built around the Sv. Jonu Baznycia (St. John's Church) which is straight ahead. 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.

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[8] that 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 Wollaston and Tennant.[4c] Sniadecki sent a report of his discovery in 1808 to the French Academy and to the Russian Academy of Sciences. The French Academy promptly published the preliminary account.[2a] 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,[9] and Sniadecki's claim was rejected.[2b] Meanwhile, the Russian Academy reported Sniadecki's claim with the comment that it could not be accepted without verification, but they did no experimental work in an attempt to confirm vestium.[10]

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,[11] the science citizenry outside Paris was well aware that the French Academy was not infallible in its chemical analysis. 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), "I can already see the French hurrying to deny the existence of [our molybdenum]."[12] Other hasty assessments of the French include Buffon's pronouncement that platinum was an alloy of iron, gold, and mercury[13] and Collet-Descotils' misidentification of del Río's "erythronium" as chromium after performing only three quick superficial experiments,[14] thus "undiscovering" vanadium.[4a] Unfortunately, Sniadecki himself could not reproduce the chemistry; before its reading in Paris he had attempted a retraction,[15] 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]."[12] After the French pronouncement, however, Jedrzej allowed the matter to drop, not even mentioning vestium in his own famous chemistry textbook, *Poczatki Chemii (Introductory Chemistry)*.[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 pro and con Kaczkowski's idea ensued in the Polish scientific community.[12] In 1937 Stanislaw Plesniewicz, a lecturer in the Warsaw Polytechnic Institute who wrote

Podrecznik Chemji [Handbook of Chemistry; 1931], urged Mary Elvira Weeks to include Sniadecki in her *Discovery of the Elements*.[12] Although Weeks had not mentioned Sniadecki in her original *Journal of Chemical Education* article on the platinum group,[17] a section about vestium was added in *Discovery of the Elements*[3] — but with no chemical details as was customarily done for other elements in her expansive book.

Rediscovering Vilnius and Vestium. To explore the question of vestium with hopes of settling the issue, the authors traveled to Vilnius, Lithuania. Here they visited the university where Sniadecki worked and they consulted with scholars familiar with Sniadecki's career (Figure 1).

The first task was to obtain an accurate translation of Sniadecki's work, which was written in old Polish presenting obstacles to clear understanding of the experimentation. Fortunately, three separate and independent translations became available[15] and furnished a dependable account of Sniadecki's laboratory observations:

First, Sniadecki boiled 400 grams of crude platinum in nitric acid to remove mercury. Following the previous procedures of Wollaston and Tennant,[4c] he dissolved the residual ore in aqua regia, obtaining a solution and a residue. In the residue he identified and verified Tennant's[4c] osmium and iridium. In the solution he identified contaminants iron, silver, lead, and the noble metals platinum and Wollaston's[4c] palladium and rhodium—and vestium. The vestium was isolated as "red needles" (vestium chloride) which were not soluble in "spirit of wine" (ethyl alcohol) and which remained after alcohol extraction. Sniadecki performed several chemical tests to characterize the "new metal" to fill out his 26-page treatise.[8]

Figure 7. Sniadecki's bust in St. John's exhibit room. The caption heralds him as "Vilnius professor of natural sciences 1797–1832, philosopher, head of the medical clinics. Artist Kazimieras Jelski. Terracotta."

Figure 6. Inside the St. John's Church is this beautiful exhibit room on the history of Vilnius University. The bust of Sniadecki is to the left; showcases include his famous chemistry book.

There exist irreconcilable differences between Sniadecki's vestium and ruthenium. The main problem is that vestium was found in the wrong fraction, i.e., in the aqua regia soluble fraction. Ruthenium is the least tractable of the platinum-group elements[18] — in fact, Klaus discovered ruthenium in the insoluble residue after aqua regia extraction. Even though ruthenium is *not* soluble in aqua regia, proponents of vestium have claimed 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[16] is at odds with the observation that unlike ruthenium chloride (either $RuCl_3$ or $RuCl_4$) which is readily *soluble* in ethyl alcohol,[13] vestium chloride[8] was *not* soluble (Note 1).

Additional differences are noticed, *e.g.*, vestium chloride reacts with ammonium chloride to form a lemon-yellow precipitate while ruthenium chloride forms a black precipitate[12] (Note 1). Arguments have been made that these discrepancies arise from Sniadecki's vestium being "impure,"[16] but Sniadecki's bright-yellow precipitate could, at the very best, contain only minute amounts of authentic ruthenium black compounds. In total, nine distinct differences between the chemical behavior of vestium and ruthenium have been documented.[12] Unfortunately, proponents of vestium were generally not knowledgeable in platinum chemistry and obvious problems with vestium were simply glossed over.

There were two notable experts in platinum chemistry during this period, and they did not support vestium: Orest Evgenevich Zvyagintsev (1894–1967) and James Lewis Howe (1859–1955). Zvyagintsev was editor of the leading Russian platinum journal,[19b] co-author of a series on ruthenium,[20] and author of many articles on platinum geochemistry (a mineral has been named after him[21]). 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.[12]

James Lewis Howe, the "one outstanding American authority on and bibliographer of the platinum metals in general,"[19a] never mentioned Sniadecki's work, not even in his comprehensive bibliography of the platinum metals covering over one and one-half centuries (1748–1917).[22] In his publication[23] *The Eighth Group of the Periodic System and Some of its Problems*, Howe recounted how Vauquelin (the discoverer of chromium[4c] and beryllium[4b]) in 1814 noticed a blue color when osmium solutions were reduced by zinc; Vauquelin was unaware that this color is not characteristic of osmium, but of the yet unknown element ruthenium, an impurity overlooked by Tennant during his original discovery of osmium[4c] (this blue color is a modern diagnostic test for

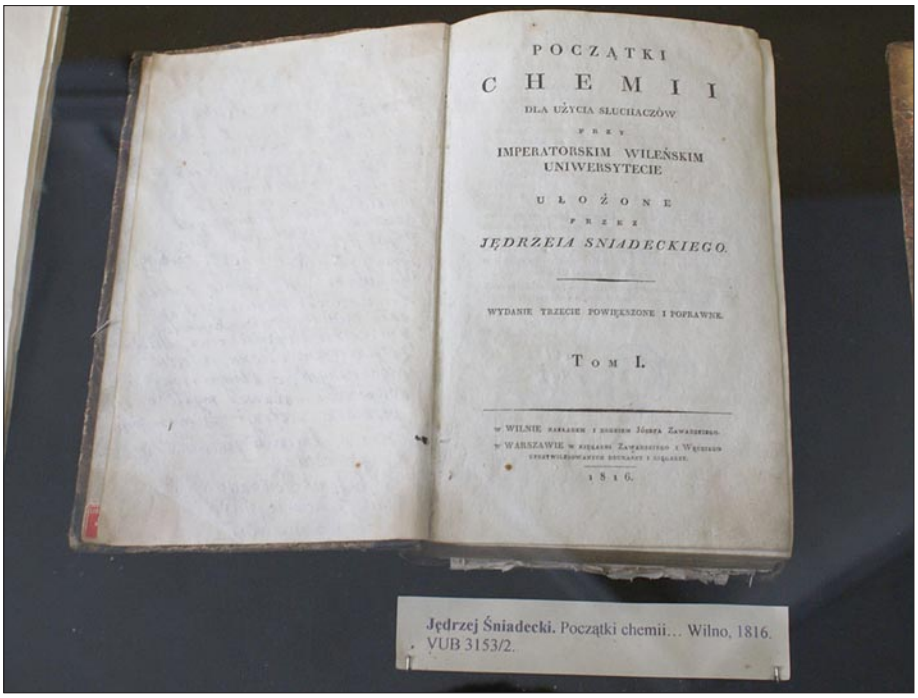

Figure 8. In the St. John's exhibit room is Sniadecki's famous introductory text, Sniadecki's famed book, Poczatki Chemii (Introductory Chemistry)*, first appeared in 1800 and used for over a century. It was the first general chemistry book written in Polish. Sniadecki developed the general Polish vocabulary for chemical terms and nomenclature. 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.*

ruthenium[18]). In the same publication, Howe described how Vauquelin and Collet-Descotils earlier in 1803 investigated the aqua regia insoluble residue from platinum[4c] and ascribed the orange-yellow color of the potash fusion product as due to chromium instead of the true cause, potassium ruthenate (K_2RuO_4). These examples underscore the fact that ruthenium has always resided in the least soluble aqua regia fraction instead of the *most* soluble fraction where Sniadecki found his vestium.

So — what did Sniadecki "discover"? The history of platinum is replete with erroneous discoveries; this list includes pluran, polinium, ilmenium, davyum, neptunium, uralium, amarillium, josephinite, canadium, plus others which were never named, all of which were impure 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] It would be desirable to reexamine Sniadecki's samples, but unfortunately they were shipped to the University of Kiev in 1840 (during Russia's annexation of Lithuanian territory), never to be seen again.[12]

What was "vestium"?— An educated guess. Laboratory experiments by the authors suggest that the "red needles" of Sniadecki were an artifact of palladium chloride. A sample of palladium chloride (which is red) behaved precisely as Sniadecki's vestium chloride — it was insoluble in ethanol, but dissolved in water to form a golden solution (Note 1). Palladium chloride also forms a yellow complex in ammonia, precisely as Sniadecki's vestium chloride (it is to be noted that of platinum group elements, the yellow color of the palladium complex is unique). Additionally, Sniadecki's vestium was found to be *more* soluble than platinum in aqua regia, and in fact was the most soluble component—just as palladium. The answer to the question "What was Sniadecki's vestium?" remains unanswered—except that it is certain it was *not* ruthenium—but apparently might have been an accidental residuum of uncomplexed palladium (Note 2).

Sniadecki's legacy. The legacy of Sniadecki lies in the many powerful contributions he made to the scientific community in Vilnius[15] (Figure 2). Sniadecki was born in Znin, Poland (halfway between Warsaw and Berlin), and studied medicine in Krakow, Poland, and then in Pavia, Italy, where he graduated in 1793. Although an ardent admirer of Lavoisier, he never met him. Sniadecki was professor of natural sciences 1797–1832 at Vilnius.[15] His laboratory and home still stand in Vilnius (Figures 3–4). He (and his brother) introduced Polish in the lectures at the University (Figure 5); he wrote the first chemistry text in Polish—his famed book, *Poczatki Chemii (Introductory Chemistry)*, first written in 1800 (Figures 6–8). On September 28, 2008, the Jedrzej Sniadecki Lecture Hall (Auditorija) was dedicated at the modern Chemistry Faculty Building, located a kilometer southwest of the University Courtyard.

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Notes.

Note 1. Ruthenium and palladium derivatives were investigated by the authors in their laboratory to determine, or confirm previously reported, behavior of solutions and precipitates of ruthenium and palladium group elements. The authors wish to thank Dr. Michael Richmond of UNT for furnishing ruthenium chloride ($RuCl_3$) and palladium chloride ($PdCl_2$) for these experiments.

Note 2. An analogous example of a known element being erroneously identified as "new" was a mixture of impure nickel (admixtured with cobalt and arsenic)—ironically also named "vestium" — discovered[25] in 1818 by the Austrian chemist Lorenz Chrysanth von Vest (1776–1840) of the University of Graz. This misidentification of von Vest was due to his lack of understanding of the dependence of metal sulfide solubilities upon pH, as shown[26] by the accomplished chemical manipulations of Michael Faraday (1791–1867) in the laboratory of Sir Humphry Davy (1778–1829). The examples of "vestium" described in this paper are only two of several hundreds of misidentifications — it is not an exaggeration to state that the number of elements "discovered" is triple the number that presently exist.[27]

References.

1. J. L. Marshall and V. R. Marshall, *Bull. Hist. Chem.*, **2010**, *35(1)*, 33–39.
2. _____, *J. phys. chim.* (a) **1808**, *67*, 71; (b) **1809**, *68*, 29 (translation by the authors).
3. M. E. Weeks, *Discovery of the Elements*, 7th ed., **1968**, *Journal of Chemical Education*, 418. Vestium was not included in earlier editions and did not appear until the extensively revised 7th edition.
4. J. L. Marshall and V. R. Marshall, *The HEXAGON of Alpha Chi Sigma*, (a) **2004**, *95(2)*, 24–28; (b) **2008**, *99(1)*, 8–11; (c) **2009**, *100(1)*, 8–13; (d) **2009**, *100(2)*, 20–23, 31.
5. R. E. Sioda, *Przemysł chemiczmy [Industrial chemistry]*, **2010**, *89(9)*, 1158 (translation by the authors).
6. *http://en.wikipedia.org/wiki*, entry on Jedrzej Sniadecki.
7. *http://pl.wikipedia.org/wiki*, entry for Sniadecki [Śniadecki]. (translation by the authors).
8. J. Sniadecki, *Rosprawa o nowym metallu w surowey platynie odkrytym [A treatise on a new metal discovered in crude platinum]*, **1808**, Vilnius [Lithuania].
9. W. Zacharewicz, *Jedrzej Sniadecki. His Life and Scientific Work*, in *Polish men of Science*, A. Plonka, trans., **1975**, Polish Academy of Sciences, Polish Scientific Publishers, Warsaw.
10. I. L. Znaczko-Jaworski, "Jedrzej Sniadecki. His Life and Scientific Work," *Quart. J. Hist. Sci. Tech.*, Warsaw, **1967**, *12(1)*, 48–59.
11. For a thorough description of the flow and ebb of French chemistry during the 19th century, see A.J. Rocke, *Nationalizing Science. Adolphe Wurtz and the Battle for French Chemistry.* **2001**, MIT Press, Cambridge, MA.
12. K. Sarnecki, *Problemy*, **1969**, *24(6)*, 342–349 [translation by W. Titow].
13. G.-L. Leclerc [Buffon], *Histoire Naturelle des Minéraux*, **1783**, *3*, 316-358.
14. H.-V. Collet-Descotils, *Ann. Chim.*, **1805**, *53*, 268–271.
15. B. Railiené, *Andrius Sniadeckis*, [in Lithuanian], **2005**, Vilniaus universiteto leidykla [Vilnius University Publishing House], Vilnius, Lithania. Additional unpublished information was also made available by Dr. Biruté to the authors.
16. W. Kaczkowski, *Chemik Polski*, **1907**, *7(15-17)*, 363–365 (translated by W. Titow).
17. M. E. Weeks, *J. Chem. Ed.*, **1932**, *9(6)*, 1017–1034.
18. F. P. Treadwell, *Analytical Chemistry*, translated and revised by W. T. Hall, Wiley, NY, 9th English edition, **1937**, Vol. 1, Qualitative Analysis, 521–539.
19. G. Kauffman, *Platinum Metals Rev.*, (a) **1972**, *16(4)*, 140–144; (b) **1974**, *18(4)*, 142–148.
20. O. E. Zvyagintsev, T. D. Avtokratova, T.D., A. A. Goryunov, et al., *Khimiya ruteniya* [The Chemistry of Ruthenium], Moscow: Nauka, 1965.
21. *Dana's New Mineralogy*, 8th Ed., John Wiley & Sons, N.Y. **1997**, 23–24. The mineral "Zvyagintsevite" has the principal formula Pd_3Pb.
22. J. L. Howe, *Bibliography of the Metals of the Platinum Group. Platinum, Palladium, Iridium, Rhodium, Osmium, Ruthenium 1748–1917*, **1919**, Smithsonian Inst., Washington, DC.
23. J. L. Howe, *Science*, **1900**, *11(287)* [June 29], 1012–1021.
24. W. P. Griffith, *Chemistry in Britain*, **1968**, *4(10)*, 430–434.
25. (Dr.) von Vest, *Ann. Phys.*, **1818**, *29*, 387–411; English translation (Dr.) Von Vest, *Ann. Philos.*, **1819**, *13* (Jan-Jun), 344–355.
26. M. Faraday, *J. Sci. Arts, R. Inst. Gr. Br.*, **1819**, *6*, 112–115; **1819**, *7*, 291–293.
27. P. van der Krogt, *http://elements.vanderkrogt.net.*