

Gottfried Wilhelm Osann and ruthenium

Helvi Hödrejärv

Tallinn Pedagogical University, Narva mnt. 25, 10120 Tallinn, Estonia

Received 6 January 2004

Abstract. Gottfried Wilhelm Osann (1797, Weimar – 1866, Würzburg) was chemistry professor at Tartu University (Universitas Dorpatensis) in 1823–1828. In that period he analysed the crude platinum received from the Ural Mountains and discovered a new platinum metal. He named this metal ruthenium after the medieval name of Russia in Latin. As the quantity of the new element he had was small he could not isolate the metal. This was done several years later and published in 1844 by Carl Claus in Kazan, Russia. Claus is often mentioned as the discoverer of ruthenium and G. W. Osann is forgotten.

Key words: G. W. Osann, ruthenium, discovery of chemical element.

At the turn of the 18th and 19th centuries platinum ores were found in many places of the world and the interest of chemists in their exploitation was great. Many if not most well-known chemists started to analyse the ores and soon four new elements very similar to platinum were discovered. In 1803–1804 Smithson Tennant (1761–1851) discovered osmium and iridium, and William Hyde Wollaston (1766–1828) found rhodium and palladium. The great chemical and physical similarity of platinum metals makes the separation of pure elements from platinum ore an extremely complicated process. For that reason some decades passed before the sixth and last platinum metal was discovered. Gottfried Wilhelm Osann, chemistry professor of Universitas Dorpatensis¹, took successfully part in that research.

¹ Now the University of Tartu, Estonia. In the 19th century it was a Baltic German university in the Russian Empire.

LIFE AND ACTIVITIES OF GOTTFRIED WILHELM OSANN BEFORE HIS TARTU PERIOD

Gottfried Wilhelm Osann was born in Weimar, Germany, on 27 (26) October 1797 as a son of Friedrich Heinrich Gotthelf Osann (1753–1803), State Councillor of Saxony [1]. His mother was Amalie Caroline Friederika, born Hufeland (1766–1843). After the early death of her husband she married the Secretary of State of Weimar Christian Gottlieb von Voigt. Osann's stepfather belonged to the famous circle of literates, the men of letters, led by J. W. Goethe, which formed in a great deal the further life of young Osann and his two brothers. The eldest brother Emil Osann (1787–1842) became a well-known specialist of curative mineral springs and was medical professor of Berlin University. Friedrich Gotthilf Osann (1794–1858) was an expert of ancient languages and professor of philology, first at Jena University and then until his death at Giessen University [2].

G. W. Osann's interest in physics and chemistry was encouraged mostly by J. W. Goethe, who had given an essential contribution to the development of chemistry at Jena University and studied himself the relationship between light and colour. Osann started to study chemistry at Berlin University, but after a year and a half continued alternately at the universities of Jena, Erfurt, and Erlangen. He graduated in Jena in 1819. After graduation he was employed as docent of theoretical and experimental chemistry, physics, and stoichiometry at Erlangen University. In that period his first printed paper was published – a speech held on 18 June 1819 at a festival on the sports ground of Erlangen [3]. In 1821 Osann returned to Jena University and graduated there as doctor of philosophy. His dissertation was about the nature of chemical affinity – *Natura affinitatis chemicae* (Fig. 1). In 1821–1823 Osann worked at the philosophical faculty of Jena as a docent. That was the period when pure chemistry was separated from pharmacy and pharmaceutical chemistry. Osann delivered lectures on theoretical physics and chemistry and taught also experimental chemistry. He based in his work on the textbooks by E. G. Fischer² (*Lehrbuch der mechanischen Naturlehre*, second edition, Berlin and Leipzig, 1819) and J. W. Döbereiner³ (*Anfangsgründe der Chemie und Stöchiometrie*, Jena, 1819) [4].

In 1821 Osann completed his monograph *Beiträge zur Chemie und Physik* and published it in Jena [5]. The “rediscovered” platinum⁴ and its catalytic properties investigated by professor Döbereiner attracted Osann's interest. This evidently inspired him in his later work with platinum ores in Tartu.

In 1823 Osann returned to Erlangen where he gave lectures on physics. He refused the offer from Königsberg University to take the post of professor of physics and mineralogy, mostly due to the lack of interest in mineralogy. In

² Ernst Gottfried Fischer (1754–1831) was professor of physics at Berlin University from 1810.

³ Johann Wolfgang Döbereiner (1780–1849) was professor of the philosophical faculty at Jena University in 1810–1849.

⁴ Platinum was first mentioned in Europe at the end of the 17th century by a Bohemian Jesuit, who described the metal as white gold. In 1751 the Swedish scientist Scheffer categorized platinum as a precious metal as it dissolves only in aqua regia.

DISSERTATIO PHILOSOPHICA
DE
NATURA AFFINITATIS CHEMICAE

QUAM
RECTORE ACADEMIAE MAGNIFICENTISSIMO
AUGUSTO ET POTENTISSIMO PRINCIPE AC DOMINO
DOMINO
CAROLO AUGUSTO
MAGNO DUCE SAXONIAE VIMARIENSIVM ET ISENACENSIVM PRINCIPE
LANDGRAVIO THURINGIAE MARCHIONE MISNIAE PRINCIPALI DIGNITATE
COMITE HENNEBERGAE DYNASTA BLANKENHAYNII NEOSTADII ET
TAUTENBURGI REL.

AUCTORITATE
AMPLISSIMI PHILOSOPHORVM ORDINIS
D. XII M. SEPT. MDCCCXXI
PRO VENIA DOCENDI RITE IMPETRANDA
PUBLICE DEFENDET

AUCTOR
GODOFREDUS GUILIELMUS OSANN,
VIMARIENSIS
PHILOSOPHIAE DOCTOR ET SOCIETATIS MINERALOGICAE IENENSIS AB
EPISTOLIS.

IENAE,
PROSTAT IN LIBRARIA GROECKERIA
IN COMMISSIS.

Fig. 1. Title page of the dissertation of Gottfried Wilhelm Osann, Jena, 1821. Bayerische Staatsbibliothek, Id.n.00070370974.

autumn 1822, Gustav Ewers, Rector of Tartu University, came to Jena University looking for a new chemist. Jena University had already graduated three later chemistry professors of Tartu University: Erdmann Heinrich Gottlob Artzt, Alexander Nicolaus Scherer, and David Hieronymus Grindel [6, 7]. In his letter to Tartu from 23 November 1822 Ewers reported to the Curator of Tartu University that the possible candidate was private docent G. W. Osann [8]. After some hesitation Osann accepted the professorship of general chemistry and pharmacy at Tartu University.

The reasons of his hesitation were the unknown living conditions in Tartu and his private life. Young Osann was in love with Adele Schopenhauer (1797–1849), the sister of the philosopher Arthur Schopenhauer, but his love was not returned and so he uneagerly left Germany. A written proof of this is the following fragment from the letter of his mother to his brother Friedrich:

An mich wiederholt er abermals die Abneigung, nach Dorpat zu gehen, und warum? Weil es ihm unangenehm wäre, das er ohne Frau käme, da er das so gesagt habe, und da wolle er nach Jena gehen. [1]⁵

Despite the refused proposal of marriage, in 1823 he travelled to Tartu. Forseeing what would happen later, on 26 November 1826 he married Katharina Christine Stolz, a daughter of a landlord in Schwarzburg-Sondershausen in Germany. The marriage was harmonious and they had four sons, Friedrich, Hermann, Wilhelm, and August, and the daughter Julia [1].

PEDAGOGICAL AND SCIENTIFIC WORK OF G. W. OSANN IN TARTU (1823–1828)

The investigations of platinum metals

Osann started in Tartu successfully. In 1824 he published the second edition of his book *Beiträge zur Chemie und Physik* in Jena [5]. In the same year his portrait was painted by the Baltic German painter Carl (Johann Karl Emanuel) Ungern-Sternberg and lithographed (Fig. 2). In 1825 he published in Tartu *Messkunst der chemischen Elemente*, whose second edition was published in Jena in 1830 [9]. In 1827 the first volume of his *Handbuch der theoretischen Chemie* [10] appeared. His scientific interests concentrated on platinum ores. In 1819 large deposits of platinum ores were discovered in the Ural Mountains in Russia. The Imperial Government decreed that all mines in the Urals should submit any samples of platinum-bearing ore to St. Petersburg for analysis and in 1825 a government monopoly on the metal was declared.

This discovery made the problem of the separation of platinum from the other platinum metals topical not only in Europe but also in Russia. Difficulties were

⁵ Translation: He had mentioned me time and again his unwillingness to go to Dorpat and why? That it was unpleasant for him to go without a wife he had already stated, and therefore he will go to Jena.



Fig. 2. Doctor and ordinary professor of chemistry Gottfried Osann, 1825. Initials of the author of the lithography: C.v.U.S. EAA, f 402, n 3, s 1237, 1. The author is Carl (Johann Karl Emanuel) von Ungern Sternberg, a Baltic German painter (1773–1830).

caused by the great amount of residue left by platinum separation. The Finance Minister, Count Egor Kankrin (1775–1845), became worried about the possible loss of platinum in the residue and sent samples of native platinum to eminent persons and institutions both at home and abroad. One of the participants in the research was J. J. Berzelius⁶ in Sweden, who analysed the raw platinum in the

⁶ Jöns Jacob Berzelius (1779–1848), professor of chemistry at Karolinska Institutet in Stockholm, honorary doctor of Tartu University from 1827. He had high reputation in the whole of Europe and several well-known chemists used the opportunity to work in his laboratory: F. Wöhler, G. Rose, G. Magnus, and others.

classical way and determined the content of platinum and the other known platinum metals [11].

Osann decided to visit Berzelius during the summer vacation and he asked in his letter of 22 April 1825 from the University Government permission to travel to Sweden:

Schon längst war es mir Wunsch ein Sommerferien zu einer Reise nach Stockholm zu machen, um mich mit dem ausgezeichnetesten jetzt lebenden Chemiker J. Berzelius über mancherlei Gegenstände der Wissenschafts zu berathen, meine eigenen Arbeiten hierdurch zu fördern und um so wirksamer und thätig auf hiesiger Universität zu werden. [12]⁷

He travelled to Sweden in spring 1826 and Berzelius wrote to F. Wöhler on 25 April that Osann was already in Stockholm [13]. Osann asked in his letter of 9 May 1826 [14] the University Government to give him some more time for his vacation. This letter reveals that he had health problems and that he tried to heal himself in a Swedish spa. He promised to return at the beginning of the next semester. Berzelius, who was known by his biting remarks, wrote to the German chemist Friedrich Wöhler (1800–1882) about Osann:

Osann ist nicht beneidenswert. Der arme Mann ist so schrecklich hypochondrisch, dass er früher oder später vollkommen melancholisch wird. Er sollte bei Mosander Wasser trinken und wurde richtig verrückt; sobald er sich etwas besser befand, reiste er flugs nach Hause. – Er ist ein gutmütiger Mensch, aber ein Chemiker wird er wahrscheinlich niemals, denn er kann nie das, was möglich, von dem, was zu erforschen unmöglich ist, unterscheiden und hält sich stets vorzugsweise an das Unmögliche, indem er sich Subtilitäten verwickelt. [15]⁸

Osann met Berzelius once more when Berzelius visited him in Würzburg in 1845. In spite of Berzelius' prognosis Osann started immediately after his return to Tartu analysis of native platinum. On 16 September 1826 Tartu University received a letter from the Finance Minister Kankrin asking that somebody was sent to St. Petersburg to get the "gold crystals" (platinum was called white gold, H.H.) designated for chemical analysis. Osann mentioned in his paper in 1827 [16] that Tartu University obtained four pounds (Russian) of platinum ore used in St. Petersburg to make coins. In that paper Osann described the mineralogical analysis of the ore and treatment with a mixture of nitric and hydrochloric acids. A thorougher review of the analysis of crude platinum is given in his two papers published in *Poggendorff's Annalen* in 1828 [17, 18].

⁷ Translation: For a long time I have had a wish to travel in my vacation to Stockholm to discuss with one of the most outstanding among the now-living chemists J. Berzelius several scientific problems concerning my own work to advance that and to be more useful and active to the university here.

⁸ Translation: We cannot envy Osann. The poor man is so awfully hypocondric that sooner or later he will be melancholic. He had drunk water by Mosander [in a spa, H.H.] and got really mad; as soon as he felt himself a little better he hurried home. – He is a good-natured man, but he will most likely never become a chemist. He cannot separate that what is worth to investigate from that what is unworth. He prefers rather the unworthy and involves himself in small details.

In the Ural Mountains osmium–iridium ore was first found in 1819 and at the beginning of the 1820s a very rich deposit of platinum ore was discovered in Nizhni Tagil, central part of the Urals. The centre of the investigation of platinum metals in the Russian Empire was the united laboratory of the Mining Department and the Mining Cadets Corps (later institute) in St. Petersburg. The leading role in these investigations was played by the mining engineers Vassili Lyubarskij (1795–1852) and Petr Sobolevskij (1789–1841), whose method for the separation of platinum from ore was introduced into practice in 1827–1828. This method⁹ was used to produce the metal for coins [19].

Analysis of ore from Nizhni-Tagil [17]

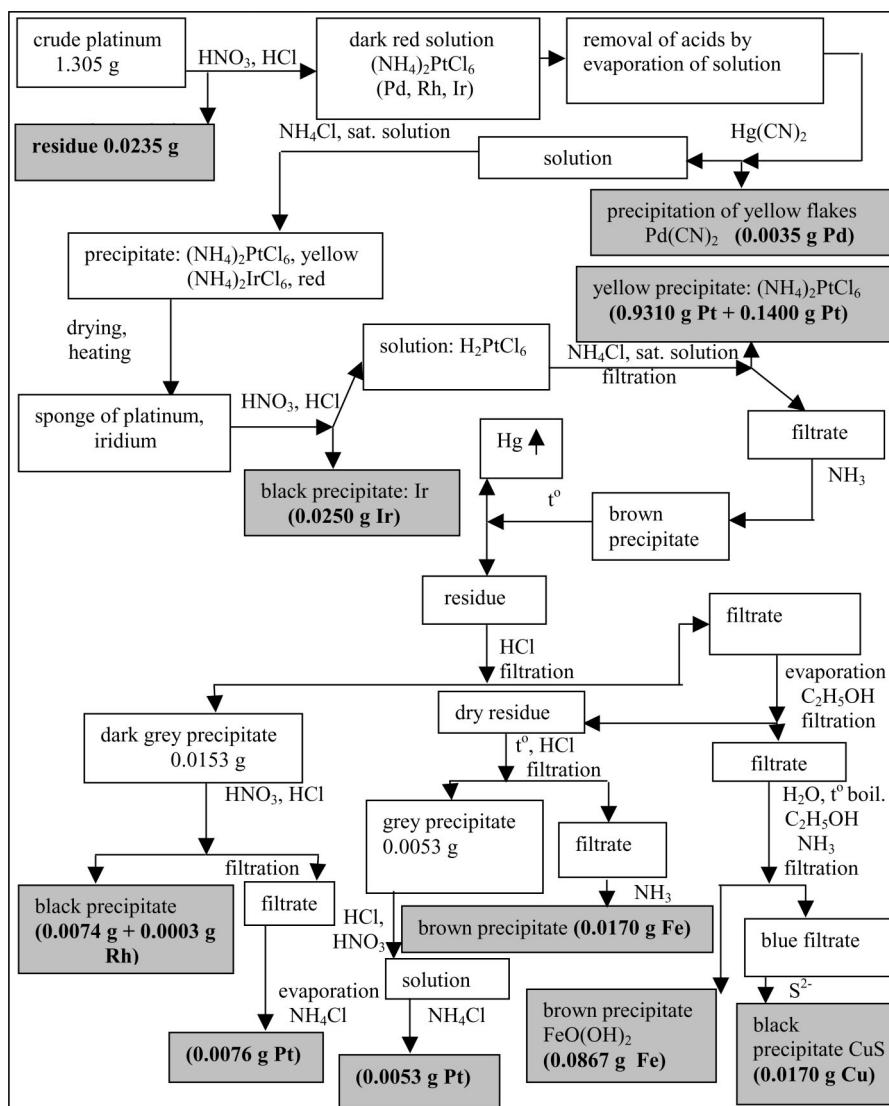
Beginning the analysis with 1.305 g of ore Osann used the well-known in Europe scheme by which the platinum metals were dissolved by treatment with a mixture of nitric and hydrochloric acids. The indissoluble residue (0.0235 g) was left aside and the solution was analysed. The course of the analysis is shown in Scheme 1.

The composition of the ore (Fig. 3) received by Osann and calculated in % by H.H. was: 83.06% Pt, 10.80% Fe, 1.92% Ir, 1.30% Cu, 0.59% Rh, 0.27% Pd, and 1.80% indissoluble residue [17]. The loss at analysis was 0.26%. For detailed analysis of indissoluble residue more primary matter was needed. Osann ordered from St. Petersburg a new portion of crude platinum and used 100 g of it for the next course of analysis paying greatest attention to the indissoluble residue.

Analysis of residue indissoluble in acids [17]

After treatment of crude platinum with nitric and hydrochloric acids the indissoluble residue was separated. The residue was treated by potassium hydroxide solution, dried, three crystals of potassium nitrate were added, and then melted. Some water was added to the cooled melt and after the partial dissolution of the melt, nitric acid was added. A black precipitate was formed and the mixture had an unpleasant smell. According to Osann, that smell indicated the presence of osmium in the mixture. The mixture was distilled in a retort to evaporate the gaseous osmium oxide (OsO_4 , H.H.). The distillation was interrupted when half of the mixture was left, and the remainder was cooled. After 24 h Osann discovered there long prismatic white slightly pink crystals with a specific lustre. The crystals dissolved when water was added to the distillation residue, but formed again after the residue was warmed and cooled. Osann made three tests with crystals and found that (1) the crystals partly sublimated at heating with blowpipe on charcoal, (2) from the solution in hydrochloric acid a dark grey layer was formed on a zinc stick, (3) the heating test in a glass pipe with both ends fused showed that the

⁹ The ore was treated with aqua regia, the indissoluble part was filtered, and platinum was precipitated from the received solution as chlorocomplex of ammonia. By thermal decomposition of the precipitate platinum formed a porous spongy mass. Pressing the sponge yielded a well malleable platinum. The method used in Europe was introduced by Wollaston and was kept secret for a long time but did not differ very much from the Russian method used in St. Petersburg.



Scheme 1. Analysis of the platinum ore from Nizhni-Tagil [17]. (According to the description of the analysis, H.H.)

crystals in the one end of the pipe vaporized (sublimized) fully forming in the other end of the pipe small lustering needles. Osann was convinced that no known substance behaved similarly. He excluded osmium because the substance did not smell and distil as a liquid. It did not resemble oxides of bismuth, tellurium, or antimony either.¹⁰

¹⁰ It was later found that ruthenium solution when treated with nitric acid forms by hydrolysis several hydroxocomplexes with a coordinated NO group, which are indissoluble in the region of pH 2–9 [20].

Gemessene Zugabe
 gelöst
 von
 G. Osann.

Zugabe von 29 Nov 1827.

Wie ein Springel Pflanz. Es sind 2. gezogen. so Gewicht be.
 29 ~~Nov~~ 0, 0213. wurde mit dem Wasser aufgelöst
 und weiter einige Stunden abgedunstet. Dagegen war. die letzten
 abgedunstet, was sich ein Dillmehl.

Was diese Untersuchung angiebt für die Zusammensetzung
 dieser Pflanzenbestandteile:

Zu Pulver - Dillm.	
zusätzliche zu Menn	0, 0255
Phosphor	0, 0035
Kalk	0, 9510
	0, 1400
	0, 0076
	0, 0055
Kalk.	0, 0024
	0, 0005
Faser	0, 0867
	(ausgewaschen 0, 1255 FO^3)
Faser	0, 0213
	(ausgewaschen 0, 0170 FO^3)
Längstfaser	0, 0542
	(ausgewaschen 0, 0785 FO^3)
Lüster	0, 0170
	(ausgewaschen 0, 218 CuS)
	<hr/> 1, 2765 ausgew. 0, 0295

$$\begin{array}{r} 1, 3080 \\ - 0, 0315 \\ \hline 1, 2765 \end{array}$$

Fig. 3. Chemistry diary held by G. Osann 29 Nov. 1827-[1828]. TU f 55, n 4, s 91.

Osann had used for the analysis 0.1 g of the produced crystals and decided that it would be most reasonable to send the left 0.3 g to Berzelius. In the same paper where Osann describes the analysis [17] he presents also the answer from Berzelius:

Stockholm d. 10. April 1828. Soviel ich daraus ersehen kann, haben Sie darin einen neuen Stoff gefunden. Denn ich kann aus den kleinen sublimirbaren Krystallen nichts Bekanntes bekommen.¹¹

Berzelius had made with the crystals the test with ammonium sulphide and had a precipitate of easily melting grey sulphide turning transparent and yellowish red at heating. At cooling the substance changed again grey and nontransparent. He made also a sublimation test with the crystals.

Repetition of the analysis of residue [17]

After Berzelius had confirmed the presence of an unknown element, Osann ordered again 100 g of the same kind of platinum from St. Petersburg and repeated the analysis applying the same method as earlier. Yet after the treatment with nitric acid only a very small amount of crystals similar to those received in the earlier analysis were found. The amount of crystals was too small to identify them. However, Osann made here an essential conclusion, supposing that if the new substance formed a volatile oxide like osmium did, it could go over into the distillate together with osmium.¹²

The distillate received by Osann smelled like an osmium compound and it turned dark blue at the addition of gallnut tincture. At saturation with sodium chloride an osmium salt of gallic acid¹³ precipitated. The precipitate was filtered and ammonium sulphide was added to the filtrate. By that a small amount of grey precipitate formed, which could be a sulphide of a new metal. These tests convinced Osann that a new metal was present. He named the metal ruthenium, obviously in honour of Russia after its medieval Latin name. At the end of his paper [17] he mentioned that there was another element in a larger amount present, and that he intended to name it pluran:

Dieses Wort ist zusammengesetzt aus den Anfangsbuchstaben des Platins und der Urals.¹⁴

Detailed analysis of platinum residue

In 1828 Osann published also another paper in *Poggendorff's Annalen* [18], where he discussed the analysis of the residue of the treatment of crude platinum

¹¹ Translation: As much as I can understand you have found a new substance and I cannot detect in the little crystals, which are able to sublime, any familiar [substance].

¹² RuO₄ is volatile but needs for forming a stronger oxydant than OsO₄ does; its boiling point is lower, H.H.

¹³ *Gallussaure osmiumoxide* by Osann, H.H.

¹⁴ Translation: That word is put together of the initial letters of platinum and Urals.

by acids in detail. Osann modified only a few details in the preliminary course of analysis. However, the changes made caused essential changes in the results. The description of the whole qualitative analysis is very capacious and it is convenient to follow its course in Scheme 2. In the scheme only the operations that were repeated many times one after another, caused by the occurrence of after-precipitation, are omitted. For clarity the scheme is divided into seven steps.

Step I. First the platinum residue was mixed with potassium hydroxide and heated in the presence of potassium nitrate as oxidant. The melt was digested by water and the alkaline sample was distilled in the retort until a dry residue formed. (In the first analysis the alkaline solution was acidified before distillation.)

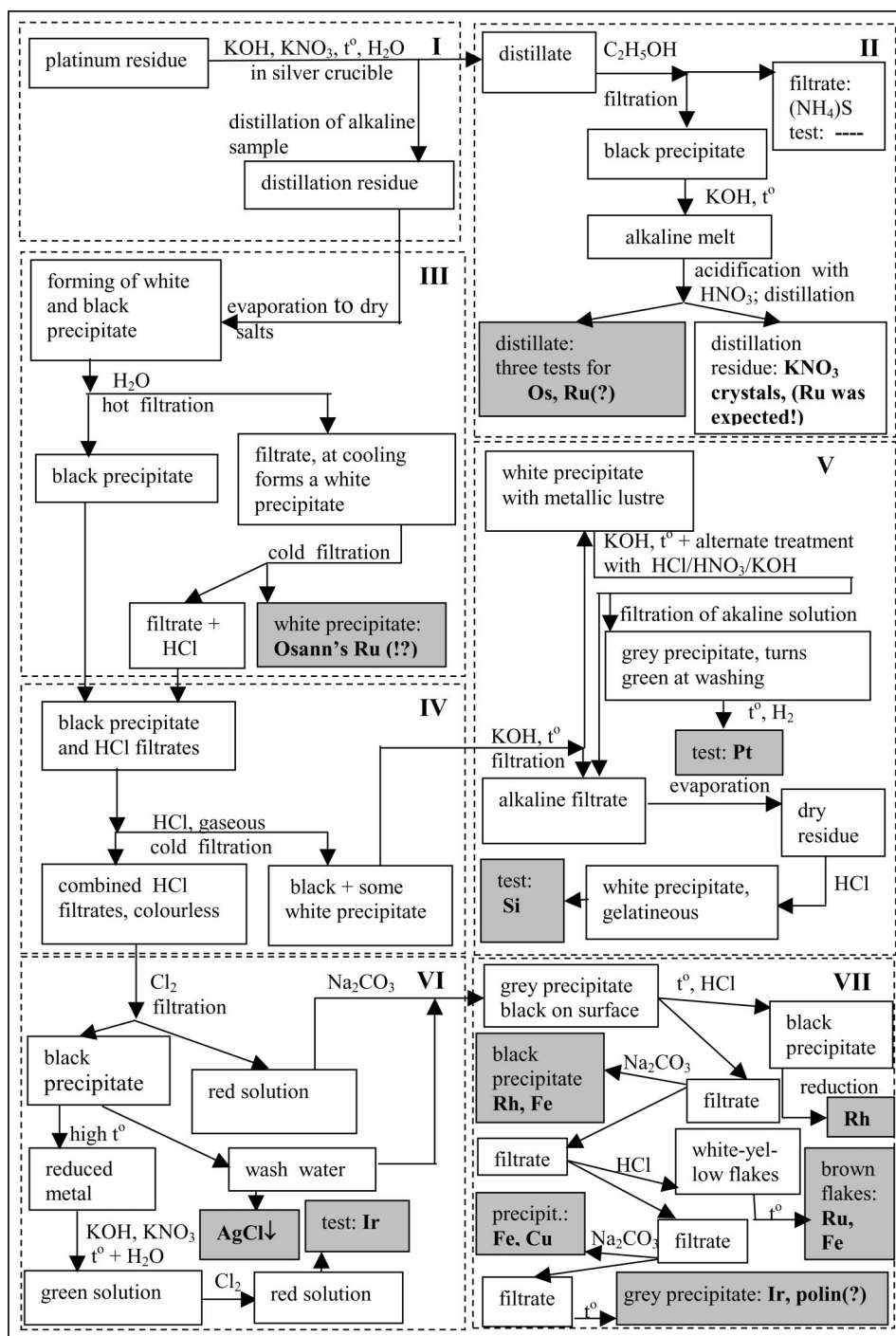
Step II. Great attention was paid to the analysis of the distillate from Step I. Ethyl alcohol was added to the distillate as reductant, and a black precipitate formed. The precipitate was filtered and melted with potassium hydroxide. Nitric acid was added to the melt and the acidified sample was distilled. Osann expected that pink crystals would form in the distillation residue as had happened in his first analysis but could not find them. He concluded that if the new element had formed a volatile compound (as he had stated already earlier) it had gone to the distillate. He made with the distillate the tests known for osmium and had positive results. (Actually ruthenium has very similar reactions: it colours the solution with tannic acid bluish green and reduces with ethyl alcohol as well as with zinc forming a black precipitate. H.H.)

Step III. The alkaline distillation residue was evaporated to dry, and a mixture of white and black precipitate formed. At hot filtration the white precipitate dissolved and the black precipitate remained on the filter. When the filtrate was cooled a white precipitate formed again. Osann was convinced that it was a compound of a new element. Here Osann was mistaken. He made numerous chemical and blow-pipe tests with the white oxide with a grey tint and could not detect any known element. He tried to reduce the oxide to metal and obtained a tiny gold-yellow grain. He wrote [18, p. 339]:

Da dieses Metall, welches ich nach den so eben beschriebenen Eigenschaften als ein neues glaube annehmen zu müssen, sich in grösserer Menge als das früher erwähnte in dem uralschen Platin befindet, und auch durch seinen schönen, dem Golde ähnlichen metallischen Glanz sich mehr empfiehlt, so glaube ich, das der Vorschlag, das zuerst aufgefundene neue Metall Ruthenium zu nehmen, besser auf dieses angewendet werden können.¹⁵

In a later paper, published in 1829 [21], he confessed that the white precipitate was mainly silicium oxide, which precipitated from the solution at the repetition of the acid-alkali treatment and he eliminated the presence of a new metal in the white precipitate.

¹⁵ Translation: As the metal that by tests seems to be a new element occurs in a bigger amount in platinum from the Ural than the earlier one, and also has a golden metallic lustre, I think that the name ruthenium that was used for the metal found earlier fits better for the element found later.



Scheme 2. Detailed qualitative analysis of platinum residue (indissoluble in acids) [18]. (According to the description of the analysis, H.H.)

Step IV. The black precipitate received in Step III was added to the combined hydrochloric filtrates and the mixture was saturated with gaseous hydrochloride. The black precipitate was now separated by filtration.

Step V. The black precipitate was treated alternately with alkali and acids and finally platinum and silicious oxide were detected.

Steps VI and VII. In combined hydrochloric filtrates Osann detected several metals: Ir, Fe, Cu, Rh, Fe–Rh, Fe–Ru, and Ir or a questionable new element polin. Prof. Carl Claus¹⁶, who analysed the platinum ores about 20 years later in Kazan University, Russia [22], was of the opinion that Osann could not have discovered ruthenium because he had not examined the hydrochloric filtrates carefully enough. In his latest paper about platinum analysis Osann refuted Claus's accusation referring to steps VI and VII of the scheme. He wrote in his paper in *Poggendorff's Annalen* 1845 [23]:

Wenn der Hr. Prof. Claus angiebt, es sey mir die Entdeckung des Rutheniums entgangen, weil ich die salzsauren Auszüge des weissen Oxyds nicht untersucht hätte, so irrt er sich. In meiner Abhandlung über den Platinrückstand, welche in den *Annalen von Poggendorff*, Bd. 14 (1828) abgedruckt ist, wird er die Untersuchung der salzsauren Auszügen S. 349 bis 352 finden.¹⁷

In step VI gaseous chlorine as oxidant was passed through the combined hydrochloric filtrates. As a result, the solution coloured red, and a black precipitate formed. In that precipitate iridium was found. In the washing water of the precipitate whitish yellow silver chloride fell down and was filtered. Silver evidently came from the silver crucible used for melting the sample with potassium hydroxide and nitrate. After the filtration of the silver chloride the hydrochloric filtrates were alkalized with soda. After some days (Step VII) a grey precipitate with a black surface appeared. The precipitate was dried and digested with hydrochloric acid. A small amount of a black powder was left, filtered, and reduced to metal, which was evidently rhodium.

The hydrochloric filtrate was alkalized with soda. A black precipitate, which evidently belonged to rhodium and iron, formed. The alkaline filtrate was acidified with hydrochloric acid. In the solution whitish yellow flakes formed. The precipitate was filtered and dried. The dry residue had a reddish brown colour and was identified as a compound of ruthenium and iron. The acidic filtrate was neutralized with soda and a brownish grey precipitate of iron and copper compounds was formed. To identify the precipitate it was filtered and dissolved in hydrochloric acid. Ammonia was added to the solution, and iron precipitated as oxihydroxide. Copper stayed in the solution forming a blue complex with ammonia. The alkaline

¹⁶ Carl Claus (1796–1864) was born in Tartu to a Baltic German family. He was educated and started to work at Tartu University. He worked also at Kazan University and later until his death again at Tartu University.

¹⁷ Translation: If Mr. Prof. Claus refers that I have missed the discovery of ruthenium as I have not investigated the hydrochloric extract of the white oxyde, he deceives himself. In my treatment of the platinum residue, printed in *Poggendorff's Annalen*, Vol. 14 (1828), he can find the investigation of hydrochloric extract from p. 349 to p. 352.

filtrate received by filtration of iron and copper compounds was evaporated to dry. A grey residue that reminded sponged platinum formed. Osann made eleven different tests but did not get a clear enough answer about the character of the grey powder. Osann declared:

Obwohl nun dieses Metall sich durch seine Auflöslichkeit in Säuren, so wie durch die Eigenschaft, keinen orangefarbenen Platinsalmiak zu geben, wesentlich vom Iridium unterscheidet¹⁸ so bin ich doch der Meinung, berücksichtigend das Mangelhaft unserer Kenntnisse der Eigenschaften des Iridiums, mit dem Ausspruch der Neuheit dieses Metall, zurückhalten, bis unsere Kenntnisse über diesen Gegenstand eine grössere Erweiterung werden erlangt haben. Sollte sich der aufgefundenene Unterschied bewähren, so schlage ich den Name Polin vor (von πολιοζ grau). Bis dahin nehme ich es einstweilen als Iridium an. [18]¹⁹

Osann could now summarize the elemental composition of the platinum residue as follows: osmium, ruthenium, silica, iridium, iron, platinum, copper, and traces of rhodium. He calculated an approximate quantitative relationship of the constituents: osmium, ruthenium, and iridium each made up 25% and the remaining 25% consisted of the other elements.

Complementary analysis of the part of platinum ore dissoluble in acids

Osann made a complementary analysis [18] for the part of platinum ore dissoluble in nitric and hydrochloric acids mainly to check the content of rhodium. After the evaporation of the excessive acid in solution, palladium dicyanide was precipitated. The difference from the earlier analysis [17] was that the filtrate was saturated with soda instead of ammonium chloride (Scheme 1). At saturation a dark brown precipitate was formed. The sublimation test of the precipitate in a glass tube gave two sublimes. The one formed first was taken from the glass tube together with the residue of soda and sublimized again in another glass tube. That sublimate proved to be mercury. The second sublimate (0.0012 g) was dissolved in hydrochloric acid. The solution was saturated with ammonia, and when sulphide ammonia was added a greyish brown precipitate formed. Based on these two properties – sublimation and formation of an insoluble sulphide – Osann concluded that he had here the “new” element mentioned already earlier and named pluran.

The final results of the analysis of platinum ore received by Osann were: the part soluble in acids: Pt 80.87%, Fe 10.92%, Rh 4.44%, Cu 2.30%, Pd 1.301%, pluran 0.06%, and traces of S, Ti, and Os; the insoluble part (0.113%): Os, Ru,

¹⁸ Osann used a test where in the presence of iridium the nitric and hydrochloric acid solution of platinum coloured orange when ammonium chloride was added. H.H.

¹⁹ Translation: Although this metal substantially differs from iridium by its solubility in acids as well as by the property not to form any orange-coloured compound of platinum and ammonia¹⁸ I am still of the opinion that looking back at our deficient knowledge about the properties of iridium, we must restrain from declaring the novelty of that metal until our knowledge in that field extends. But, if the determined differences are valid, I propose the name polin (πολιοζ, grey). Until then I will regard it temporarily as iridium.

and Ir 0.081%; silica, Fe, Pt, Cu, and traces of Rh 0.027% (the missing 0.005% is evidently a mistake caused by the rounding of numbers, H.H.) [18].

G. W. OSANN LEAVES TARTU AND SETTLES IN WÜRZBURG

Looking back at the years Osann spent in Tartu it seems that he was there unwillingly, waiting for an opportunity to return to Germany. His letter to J. B. Trommsdorff²⁰ in 1825 [24] reveals that Osann planned to establish in Germany a factory to produce tartaric acid and potassium hydroxide from the potassium tartrate forming in the wine industry. He wrote that he had no expectations for a sufficient heritage and so he hoped that that idea could provide a source of an additional income in the future and asked for advice. His project was never realized as we know and his career remained academic.

In 1828 Osann was invited to Würzburg University to become professor of physics and chemistry. In his letter of 12 March 1828 to the Council of Tartu University he asked to relieve him of his post at the University in connection with his moving to Würzburg [26]. The same day Osann wrote to the apothecary Burchard in Reval²¹ that he was leaving Estonia and asked him to give his best greetings to his friends in Reval:

Meinen Freunden in Reval, gibt es andere dergleichen... Reval mit seinen schicken Umgebungen werde ich daher nicht wieder sehen. [27]²²

Osann had a good reputation as a productive writer of textbooks and he was known, with some reservations, as the discoverer of a new platinum element – ruthenium. Some confusion about that fact was caused by his hurriedly made announcement of the discovery of two other elements – pluran and polin. In 1829 he answered in *Poggendorff's Annalen* [21] to the letter published by Prof. Berzelius, who was suspicious about the occurrence of a new element in the white oxide received by Osann in the analysis of the platinum residue. Osann agreed with Berzelius that the white oxide he received in the analysis of platinum residue was really a combined precipitate of titanium acid, zirconium oxide, and silica and not a new element. In 1841–1842 Prof. Carl Claus at Kazan University in Russia began to research the platinum metals and after successful separation of pure ruthenium in 1844 identified its properties. Claus was everywhere noted as the discoverer of ruthenium. However, he used the name given by Osann – ruthenium. Osann wrote in his paper in 1845 [23] that it was excellent for science if the same discovery had proof by two scientists. Osann himself repeated in

²⁰ Johann Bartholomäus Trommsdorff (1770–1837) is founder of scientific pharmacy. He published a critical review about Osann's book *Beiträge zur Chemie und Physik* [4] in the *Taschen-Buch für Chemiker und Apotheker* [25] in 1825. He approved Osann's text-book and said that he was a sharp-sighted naturalist and a good experimentator.

²¹ Now Tallinn, the capital of Estonia.

²² Translation: My friends in Reval, does anywhere exist any similar... Reval with its marvellous surroundings that I can never see again.

Würzburg the analysis of platinum residue received from St. Petersburg, but received nothing new.

Osann began an effective work in educational and scientific fields. His attention was attracted increasingly more by problems of physics such as electrical phenomena, electromagnetism, electroinduction, and light phenomena. He published nearly 50 papers (see for examples Fig. 4), mostly in K. W. G. Kastner's journal *Archiv für die gesammte Naturlehre* and O. L. Erdmann's *Journal für technische und ökonomische Chemie* [28, 29].

Some papers from the Würzburg period [30] are given as examples:

- 1843–1846 “Neue Beiträge zur Chemie und Physik”
- 1836 “Analyse des Mineralwassers vom Ludwigs-Brunnen zu Gross-Karben in der Wetterau... in Oberhessen”
- 1847 “Grundzüge der Lehre von dem Magnetismus und der Electricität” (Fig. 4)
- 1849 “Programm über die Bedeutung der Naturlehre unter den allgemeinen Wissenschaften”
- 1849 “Darlegung mehrere neuer Versuche über Gassäulen und das Ozon”
- 1852 “Erfahrungen in dem Gebiete des Galvanismus gesammelt. Für Physiker, Chemiker und Techniker”

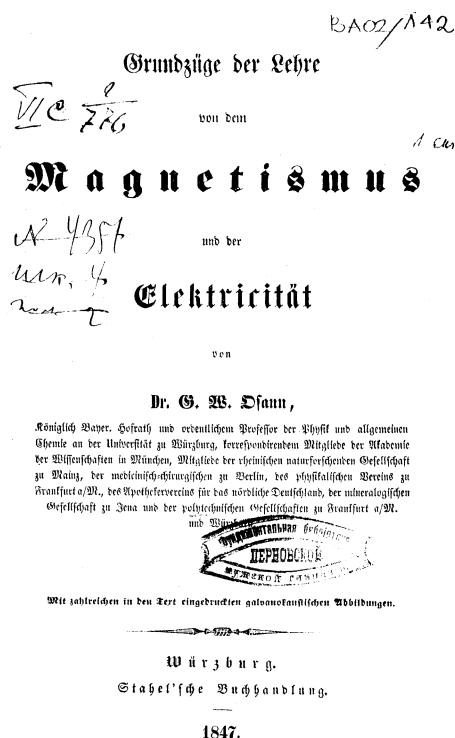
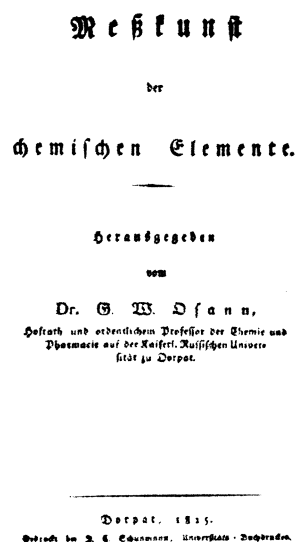


Fig. 4. Examples of publications by G. W. Osann.



Fig. 5. Rector of Würzburg University Dr. G. W. Osann. From: Koschel, K. & Sauer, G. *Zur geschichte des Chemischen Instituts der Universität Würzburg*, 1968; original in the Institute of Pharmacy of Würzburg University. The oil painting is not signed, but the probable name of the painter and date are found on its back side: J. Hahn, 1863. The author is grateful to the colleagues from Würzburg University, chair of pharmaceutical technology, who discovered that fact.

Osann took actively part in the academic life. He belonged as a foundation member to the society Physikalisch-medizinischen Gesellschaft zu Würzburg, was Royal Bavarian privy councillor, corresponding member of Munich Academy of Science, and member of many other societies. In 1840/41 Osann was elected dean and in 1848/49, rector of Würzburg University (Fig. 5). The subject of his promotion speech was the significance of the natural studies among the sciences. He said:

Die Kunst Beobachtungen zu verstehen, macht den Naturforscher. Es gehört Kenntnis und Urtheil dazu, in einer Beobachtung das heraus zu finden[!], was bekannt und was neu ist. Mitunter waren es ganz geringfügige von Vielen übersehene *Umstände*, welche zu den grössten Entdeckungen geführt haben. [31]²³

The last paper by Osann was published in the journal *Würzburger Naturwissenschaftliche Zeitschrift* in 1866. It was about the thunderclap into the tower of a church in Würzburg on 6 January 1865 [32].

Gottfried Wilhelm Osann died in Würzburg on 10 August 1866 [1, 8].

DISCUSSION

The question about the priority of the discovery of ruthenium can be answered only on the ground of a thorough study of the analysis and conclusions made by Osann using the modern knowledge about the chemistry of ruthenium.

Following Osann's analysis we must agree that the properties of the new element described by him belong to ruthenium: mineral acids do not affect the metal and it is dissolved by alkaline oxidizing fusion (Scheme 2, Step I). As a result ruthenium forms soluble ruthenate (VII, VI)-ions, staying in distillation residue (Step III) and/or forms volatile ruthenium (VIII) tetroxide RuO_4 , which is detected in the distillate (Step II). Tetroxide is usually reduced by hydroxide ion and it forms ruthenate ions. It is easily reduced also by ethyl alcohol forming oxides such as black ruthenium sesquioxide Ru_2O_3 or brownish black dioxide RuO_2 . Hydrous oxides are commonly precipitated in alkaline solution. When freshly precipitated, they may be soluble in acids, but after aging only with great difficulty or not at all (Steps IV–VII) [33].

It must also be taken into consideration that Carl Claus left the name of the element given by Osann – ruthenium – unchanged. Thus he indirectly recognized the rights of Osann to the discovery.

We must remember that after analysing the pink crystals received by Osann Berzelius declared that nothing already known could be found and consequently the crystals had to belong to a new element.

The trouble of Osann was that he could not repeat his results and was not sure in his conclusions. As Berzelius said – he involved himself in details. The “discovery” of two other elements, polin and pluran, caused misunderstanding and overshadowed the discovery of ruthenium. Osann had serious difficulties to analyse the too small quantities of samples for the determination of the element accounting for 1–2%. It was not always possible to make enough tests with the received compounds.

²³ Translation: The art to understand the observations will make the naturalist. For that we need the knowledge and ability to distinguish between what is new and what is already known. Sometimes there are absolutely insignificant details among the facts of the case that will lead to the great discovery.

Claus analysed platinum residue 16 years later. He had at his disposal enough substance and the experiences of Osann. Prof. Carl Claus had worked in the same laboratory where Osann had worked earlier. Claus has the honour of isolating ruthenium as a pure element and determining the properties of the new element.

Concluding finally all the for and against arguments we can attribute the priority of the discovery of ruthenium to G. W. Osann.

REFERENCES

1. Plückhan, A. Transkription und Kommentierung der Briefe von Gottfried Wilhelm Osann (1797–1866) und Emil Osann (1787–1842) an Johann Bartholomäus Trommsdorff (1770–1837): Brief von Amalie von Voigt/Weimar an Friedrich Osann – vom 8. Mai (1826?). Diploma paper, Ernst-Moritz-Arndt-Universität, Greifswald, 1998.
2. *Allgemeine Deutsche Biographie*, Vol. 24. Dunckler & Humblot, Leipzig, 1887.
3. Osann, G. W. *Rede zur Feier des 18. Junius: auf dem Turnplatze zu Erlangen gehalten*. Erlangen, 1819.
4. Chemnitz, F. *Die Chemie in Jena von Rolfink bis Knorr (1629–1921)*. Jena, 1929.
5. Osann, G. *Beiträge zur Chemie und Physik*. Jena, 1822–1824.
6. Siilivask, K. (Comp.) *Tartu ülikooli ajalugu, II, 1798–1918*. Eesti Raamat, Tallinn, 1982.
7. Hödrejärvi, H. History of analytical chemistry in Estonia (1800–1950). *Fresenius J. Anal. Chem.*, 1997, **357**, 191–196.
8. Letter of G. Ewers to the Curator of Tartu University 23. Nov. 1822. EAA, f 402, n 3, s 1237, 3.
9. Osann, G. W. *Messkunst der chemischen Elemente*. Dorpat, 1825; 2nd edn., Jena, 1830.
10. Osann, G. W. *Handbuch der theoretischen Chemie*, Vol. I. Dorpat, 1827.
11. Griffith, W. P. Spurious platinum metals. *Chem. Brit.*, 1968, **4**, 430–434.
12. Letter of G. Osann to the Council of Tartu University, 22 April 1825. EAA, f 402, n 3, s 1237, 29.
13. Holmberg, A. *Bibliographie de J. J. Berzelius*. Stockholm, 1953.
14. Letter of G. Osann to Tartu University, 9 May 1826. EAA, f 402, n 3, s 1237, 65.
15. Wallach, O. *Briefwechsel zwischen J. Berzelius und F. Wöhler*. Leipzig, 1901.
16. Osann, G. Analyse des Platins vom Ural. *Poggendorff's Annalen der Physik und Chemie*, 1827, **XI (87)**, 311–322.
17. Osann, G. Fortsetzung der Untersuchung des Platins vom Ural. *Poggendorff's Annalen der Physik und Chemie*, 1828, **XIII (89)**, 283–297.
18. Osann, G. Fortsetzung der Untersuchung des Platins vom Ural. *Poggendorff's Annalen der Physik und Chemie*, 1828, **XIV (90)**, 329–357.
19. Ključevič, A. S. Carl Carlovich Claus. *Izd. Kazanskogo universiteta*, 1972.
20. Nikol'skij, B. P. & Il'enko, E. I. Investigation of the hydrolysis of nitrate complexes of nitroruthenium. *Radiokhimiya*, 1966, **8**, 2.
21. Osann, G. Berichtigung, meine Analyse des uralischen Platins betreffend. *Poggendorff's Annalen der Physik und Chemie*, 1829, **XV (91)**, 158.
22. Claus, C. Über die Platinrückstand. *Bull. Acad. Sci. St. Petersb.*, 1844, **3**, 37–48; Fortsetzung der Untersuchung des Platinrückstandes nebst vorläufiger Ankündigung eines neuen Metalls. *Bull. Acad. Sci. St. Petersb.*, 1844, **3**, 353–371.
23. Osann, G. Analyse des in Salpeter-Salzsäure unauflöslichen Rückstands des uralischen Platins (neue Bearbeitung). *Poggendorff's Annalen der Physik und Chemie*, 1845, **64 (140)**, 197–208.
24. Letter of Gottfried Wilhelm Osann/Dorpat an Trommsdorff, 12 January 1825. Staatsbibliothek zu Berlin, Preussischer Kulturbesitz, Handschriftenabteilung, Nachlass 259 J. B. Trommsdorff und Nachf. 19, Nr. 696–717.
25. Trommsdorff, J. B. (Comp.) *Taschenbuch für Chemiker und Apotheker*, Vol. 46. Weimar, 1825.

26. Letter of G. Osann to the Council of Tartu University of 12 March 1828. EAA, f 402, n 3, s 1237, 62.
27. Letter of G. Osann to J. Burchard. Estonian History Museum, "D" fond, f 54, n 1.
28. *J. C. Poggendorff's Biographisch-literarisches Handwörterbuch zur Geschichte der exacten Wissenschaften*, Vol. II. Leipzig, 1863; Vol. III, Part II, Leipzig, 1898.
29. Levitskij, G. V. *Biographical Glossary of Professors and Teachers of the Imperial Yur'ev, Formerly Derpt University*, Vol. 1. Yurjev (Tartu), 1902.
30. Bibliotheks Verbundes Bayern-Kurzanzeige. Datenbank: Bibliotheks Verbund Bayern Treffer 1–17. <http://www-opac.bib-bvb.de/>
31. *Rede zur Antritte des Rectorats von Dr. G. W. Osann gehalten am 2. Januar 1849 in der Universitäts-Aula*. Würzburg, 1849.
32. Osann, G. Ueber den Blitzschlag, welcher am 6. Jan. 1865 den Thurm der Neubaukirche in Würzburg traf. *Würzburger Naturwissenschaftliche Zeitung*, 1866/1867, **6**, 38–42.
33. Cotton, F. A., Wilkinson, G., Murillo, C. A. & Bochmann, M. *Advanced Inorganic Chemistry*. John Wiley & Sons, New York etc., 1999.

Gottfried Wilhelm Osann ja ruteenium

Helvi Hödrejärvi

Gottfried Wilhelm Osann (1797, Weimar–1866, Würzburg) oli Tartu ülikooli (*Universitas Dorpatensis*) keemiaprofessor aastatel 1823–1828. Sel perioodil analüüsis ta Uurali mäestikust pärit toorplaatinat, avastas uue plaatinametalli ja nimetas selle Venemaa ladinakeelse nime järgi ruteeniumiks. Kuna Osann sai uut elementi väheses koguses, ei õnnestunud tal seda metallina isoleerida. Selle saavutas mitmeid aastaid hiljem ja avaldas 1844. aastal Venemaal Kaasanis tegutsev Carl Claus, säilitades Osanni poolt antud nimetuse. Carl Clausi nimetatakse sageli ruteeniumi avastajaks, unustades märkida G. W. Osanni osa.