The Minting of Platinum Roubles

PART I: HISTORY AND CURRENT INVESTIGATIONS

By Professor Christoph J. Raub
Waldsiedlung 17, D-73525 Schwäbisch-Gmünd, Germany; E-mail: ChrisRaub@t-online.de

Nineteenth century Russian roubles are collectors items, but because of their history, there is a question over each one whether it is a genuine Russian rouble or a forgery. There has been some prior research and analysis on the platinum used to make these roubles and on their method of manufacture. As W. C. Heraeus and Johnson Matthey both hold small collections of roubles never before investigated, it was decided to see what could be found out about them and what this could tell us about their origins. This is the first of a three part series and begins with some of the background history to the work. Part II appears later in this issue and Part III will be published in July.

Although there had been rumours in the early 1800s that platinum was to be found in Russia (1), it was not until 1819 that small pieces of white metal, "panned" with gold and other minerals of high density, in the gold fields in the Urals, south of the city of Ekaterinburg, were noticed by the authorities and taken for examination to laboratories in Ekaterinburg. (Alluvial platinum nuggets had been found earlier in Colombia, and later examples have been found in other regions, for example, in the Far East. Even in the river Rhine nuggets of platinum and platinum group metals have been reported.)

By 1825 large quantities of the native metal had been collected from several areas around Ekaterinburg and sent to St. Petersburg. The increased volume of metal was noticed by the Imperial Russian Government and resulted in them declaring a State Monopoly on all platinum dealings – except under licence – with no export of native metal being allowed. The poor administration of this Monopoly in the remoter areas of the country promoted smuggling and this distorted the published statistics for Russian output of platinum, even after the State Monopoly had ceased (1).

Early Platinum Refining in Russia

On analysis, the samples of platinum from the Ekaterinburg region were also found to contain iridium, osmium, iron, gold, sometimes osmiridium, and sometimes copper and rhodium. These samples were refined by Janety's process and by a process developed in 1827 by Peter G. Sobolevsky. Sobolevsky's process involved boiling the native metal with four times its weight of *aqua regia*. Malleable platinum was produced from the calcined chloroplatinate. In the final stages, the platinum sponge was cold pressed, then heated to whiteness and further compressed. The granular structure became dense and malleable by this final compression (1). The malleable metal was hammered for fabrications. Platinum was thus available in pieces of any required size. The platinum was made into medals, wires, dishes, crucibles, ingots and other artifacts (1).

As there seemed to be plentiful amounts of platinum, Count Egor F. Kankrin, Minister of Finances to Tsar Nicholas I, and Head of the Department of Mining, suggested its use as coinage. Kankrin brushed aside words of caution from the German naturalist and traveller, Alexander von Humboldt, who had travelled in Colombia and was knowledgeable about Colombian platinum. He had advised that as Colombian platinum was available there would be difficulty in controlling the platinum price sufficiently to prevent depreciation and counterfeiting. In spite of this in 1828 Kankrin issued first 3 rouble platinum coins, and later 6 and 12 rouble platinum coins.

In 1846, due to the falling price of platinum outside Russia, "cessation of coining and withdrawal of the whole platinum currency" was

Coin	Inscription
3 rouble	2 zol. 41 dol.
6 rouble	4 zol. 82 dol.
12 rouble	9 zol. 68 dol.
1 zol. ≈ 4.26 g	1 dol. ≈ 0.044 g

ordered. In fact, the platinum price had fallen to a lower level than the exchange value of the Russian platinum coins (1).

All the coins that were minted bore, curiously, the same inscription on the reverse. In the centre of the face was the denomination, the date, and the mint mark: SPB for St. Petersburg. Around the edge was the mass of pure Urals platinum in zolotnik (zol.) and dolya (dol.).

The coins, minted for eighteen years, numbered in total: 1,373,691 3-rouble; 14,847 6-rouble; and 3474 12-rouble. The total weight of platinum used in their production was 485,505 troy ounces (1, 2).

The Purity of the Platinum

It was soon realised that the native platinum was rather impure, so samples were sent to the famous chemists of the time: Berthelot, Berzelius and Döbereiner, asking for help with analysis and refining. While the Russian efforts and achievements in platinum chemistry at that time have been extensively discussed, the contemporary work of Berzelius in Stockholm, Döbereiner Senior in Jena, and Osann, Klaus and Döbereiner Junior in Dorpat has been neglected (1).

Johann Wolfgang Döbereiner (Senior) was the towering figure in chemistry at the beginning of the 19th century, issuing final verdicts on the work of his contemporaries (3). He confirmed the discoveries of other platinum group materials: pluran (Platina + Ural) platinum, polin (probably iridium oxide) by Gottfried Wilhelm Osann, and ruthen (ruthenium) by Karl Klaus in the residues of the St. Petersburg platinum refinery.

Johann Wolfgang Döbereiner

Döbereiner's connections with the platinum industry were arranged by Maria Pavlovna, a daughter of Tsar Paul I, who had married Carl Friedrich von Weimar in 1804. She financed much of the scientific work in Jena, not only that of Döbereiner but also, for instance, work by J. W. Goethe on mining in Thüringen. Indeed, she may be considered to have provided the venture capital for the upcoming German chemical (catalysis) and optical (Zeiss/Schott/Abbe – glass) industries. Maria Pavlovna believed that by cooperation with Döbereiner the work of Count Kankrin and Sobolevsky in St. Petersburg might advance faster.

However, Döbereiner had no wish to leave Jena for St. Petersburg and instead sent his son, Franz. On his way to St. Petersburg Franz stayed for a while in Dorpat, in the laboratory of Osann where he and a Dr F. Weiss worked on the platinum problem (1).

In 1836, F. Wöhler's translation of J. J. Berzelius' "Lehrbuch der Chemie" appeared in its 4th Edition, extensively discussing the state of knowledge of the platinum group metals based on work on Russian platinum (4). Wöhler, the favourite pupil and collaborator of Berzelius, was the discoverer of aluminium. On the cover sheet of this first chemistry textbook in Swedish/German he proudly states: "translated from the Swedish handwriting of the author" (4). He mentions that Alexander von Humboldt brought back from America a nugget of 1080.6 "gram" weight and that in Tagilsk in the Urals, a nugget of 10 and another of 3.5 "Pfund" weight were found. These platinum nuggets contained mostly platinum and iron, less copper, palladium, rhodium and nearly always some iridium. Wöhler states that:

> *...some of these nuggets contain so much iron, that the greater part of it can be dissolved in nitric acid and one can consider the iron as present in elementary form. Many of the smaller platinum grains are attracted by a magnet... The most iron-rich platinum occurs near Nischne-Tagilsk. It is dark grey and has between 11 and 13% iron. Some grains are not attracted by a magnet. This is caused less by a lower iron content but more by a higher iridium concentration. The platinum in Goroblagodat in the Urals is, more than others, free of iridium in the state in which it is co-dissolved (with platinum). Therefore this ore produces the purest platinum.*

In the book, Berzelius/Wöhler discusses details of the raffination of the nuggets. Basically it is the classical method used before the introduction of the liquid-liquid extraction processes. The precipitate was called by Berzelius/Wöhler "Platinsalmiak" (4). Later is mentioned:

> *...if one does not care much for the purity of platinum it can be precipitated with 'Salmiak' (ammonium chloride) immediately after dissolution...* (most platinum is currently produced this way). *It therefore contains iridium in all cases...*

He then describes compacting and sintering of platinum sponge and states:

> *If it (platinum) is free of iridium it can be drawn into fine wire, like gold and silver.*

From the work of Berzelius we must conclude that the main impurities to look for in Russian platinum coins will be iridium and iron. However, it will be difficult to discern between the use of a natural high-grade alluvial platinum powder with low iridium and iron content and a well refined one, due to the large variations in the contents of their ore.

Forged Russian Coins by 'Novodel' Mintings

Russian platinum roubles are now collectors' items (5). After the coinage was withdrawn, additional mintings took place ('Novodel' mintings) until 1890, and for a while after that other forgeries were made. The original coins were made from natural platinum alloys containing ~ 75 wt.% platinum. This was refined to obtain a technically pure platinum powder for forging and minting. This powder also contained additional material, such as gold- and copper-rich inclusions.

However, one 'Novodel' coin, dated 1828, has been shown to consist of technically pure platinum, and was probably struck at the end of the 19th century (5, 6). In a textbook on chemical technology published in 1900 (7), the impurity concentration of platinum for crucibles was listed as Ir 2.56%, Rh 0.20%, Pd (trace), Ru 0.02% and Fe 0.20%. It is thought that some of the coins may have been 'mechanically' diluted by inclusions of natural platinum alloys, containing gold. Genuine Russian roubles contain iron impurities up to 4 weight percent. In fact, a compilation of the composition of the platinum from Russian placer deposits shows that the iron content varies between 2.3 and 18.9% and iridium between traces and 5.32%. Coins analysed so far contain iron: 0.5 to 1.4%, and iridium: undetected to 0.85 to 1.06% (6, 8). (XRF-surface analyses) confirm Berzelius' remark on iridium.

It is interesting to note that metallography shows that one coin (6) has a surface area rich in platinum. This might indicate the use of better grade platinum for the surface than for the centre of the coin. This would not be a problem for the sintering method used for the coins. However, the use of chemical/electrochemical enrichment, "platinising", by pickling in acids must be excluded for platinum and its alloys.

Depending on the process parameters of the sintering process, the coins will:

[a] have a density less than that of platinum produced by the melt-solidification process. This is caused by "rest porosity" (voids, bubbles, pores, defects between sintered grains, etc.). Impurities may also reduce the density;

[b] possess a certain striated structure seen in microsections;

[c] and, depending on their sintering, show a "snake skin" surface structure (irregularities in the surface). This is observed on the surface of pieces, sintered, annealed and deformed from powders.

A microsection of one coin confirmed the sintered structure. Surface irregularities of coins typical for sintered and deformed metals ('snake skin') were observed (6, 8).

The densities of the roubles investigated until now vary between 20.7 and 20.03 to 21.32 g cm^{-3} (4, 6, 8), all less than the currently accepted value for the density of platinum of 21.45 g cm^{-3}. Values for the density for platinum known at that time were (in g cm^{-3}): Wollaston 21.53; Berzelius 21.45 (J. R. Bréant, Paris); and Klaproth 21.47.

First Indications of Ferromagnetism

The ferromagnetism of platinum nuggets and coins was noted very early. Berzelius attributed it to the presence of metallic iron (4). Platinum nuggets display ferromagnetism at room temperature, irrespective of their origins. Recently the (B×H) (magnetic energy product) was measured semiquantitatively (6).

Magnetic measurements on synthetic platinum-iron alloys, in thermodynamic equilibrium, are somewhat inconclusive (9, 10). Platinum-rich alloys (above 90% Pt) in disordered f.c.c. solid solution are not ferromagnetic at room temperature. The ordered Pt_3Fe phase seems to be antiferromagnetic. Cold-working disorders the phase and generates strong ferromagnetism as does ion beam irradiation (11).

However, neither the effects of heat treatment nor of cold working on the magnetic properties have been properly investigated. Cabri and Feather have proposed a partial phase diagram in the regions Fe-PtFe (10). They postulate "that the composition has a greater effect on their crystal structure (assuming no cold-working effects) than their annealing histories ...". It may therefore be assumed that in coins that have regions which contain ~ 12 wt.% Fe (30 at.%) or a little less, iron, at least to some extent, may be in the form of partially disordered Pt_3Fe.

Lattice constant measurements were used to try to decide if the iron was in solid solution with platinum, but the method was insensitive and the conclusions not convincing as the authors did not observe any ordering, only line shifts in their X-ray patterns from their ferromagnetic coins (6). Furthermore, true disordered f.c.c. solid solutions at low iron concentrations, even if cold deformed, are not ferromagnetic. This might support the chemical observation of Berzelius that iron, at least to some extent, is present in elementary form.

We have to expect changes in the magnetic properties of the coins compared with the starting powder. These will be due, for example, to composition changes, disorder-order phenomena by heat treatment and/or deformation during sintering. Indeed, it has not been established how nuggets and/or coins are in thermodynamic equilibrium, as synthetic alloys are.

After the cessation of circulation the platinum coins, together with native platinum, were sent for refining to European refineries, such as Johnson Matthey, W. C. Heraeus, Hanau, and W. Sieber, Hanau, Frankfurt (later Degussa, now Umicore). The Sieber coins were investigated some short while ago (8). The coins investigated in (6) came from private collections. Experimental results of investigations on coins in the possession of W. C. Heraeus (Hanau) are published later in this Journal and results on Johnson Matthey's roubles will be published in the July issue.

Acknowledgement

The investigations would be impossible without the generous support of the companies W. C. Heraeus, Hanau, Germany, and Johnson Matthey, Sonning Common, Reading, U.K.

References

1 D. McDonald and L. B. Hunt, "A History of Platinum and its Allied Metals", Johnson Matthey, London, 1982, pp. 239, 241–247, 280
2 E. K. Fritsman, *Ann. Inst. Platine*, 1927, **5**, 23–74
3 G. B. Kauffman, *Platinum Metals Rev.,* 1999, **43**, (3), 122–128
4 J. J. Berzelius, "Lehrbuch der Chemie", aus der schwedischen Handschrift des Verfassers übersetzt von F. Wöhler, 4 verbesserte original-Auflage, 3 und 4. Band Dresden und Leipzig, in der Arnoldischen Buchhandlung, 1836
5 K. Janssens, G. Vittiglio, I. Deraedt, A. Aerts, B. Vekemans, L. Vincze, F. Wei, I. De Ryck, O. Schalm, F. Adams, A. Rindby, A. Knöchel, A. Simionovici and A. Snigirev, *X-Ray Spectrom.*, 2000, **29**, 73
6 E. Auer, Th. Rehren, A. von Bohlen, D. Kirchner and R. Klockenkämper, 'Über die Hertstellung und Zusammensetzung der ersten Platinmünzen in Russland', *Metalla (Bochum)*, 1998, **5.2**, 71–90
7 F. Fischer, "Handbuch der chemischen Technologie", Leipzig, Verlag von Otto Wigand, 15. umgearbeitete Auflage, 1900, 787 Seiten, S. 305
8 H.-G. Bachmann and H. Renner, 'Nineteenth Century Platinum Coins', *Platinum Metals Rev.*, 1984, **28**, (3), 126–131
9 M. Hansen and K. Anderko, "Constitution of Binary Alloys", 2nd Edn., McGraw-Hill Book Co. Inc., New York, 1958
10 L. J. Cabri and C. E. Feather, 'Platinum-iron alloys: a nomenclature based on a study of natural and synthetic alloys', *Can. Miner.*, 1975, **13**, 117–126
11 S. Maat, A. J. Dellock, D. Weiler, J. E. E. Baglin and E. E. Fullerton, *J. Magn. Magn. Mater.,* 2003, **265**, (1), 1–6

The Author

Professor Raub is retired from the Forschungsinstitut für Edelmetalle und Metallchemie, Schwäbisch Gmünd where for many years he was its Director. He is now interested in the history of precious metals, especially of the platinum group metals, and their geology, and in iron smelting in southern Germany.