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METALLURGY IN NUMISMATICS 5

NC EDITORS' NOTE

THE RNS held a conference at the Society of Antiquaries in London on 14-16th September 2000 entitled 'Counterfeiting: Ancient and Modern'. It was the intention to publish the contributors' papers as the fifth monograph on metallurgy in numismatics within the Special Publications series. For various reasons the publishing project was beset by delays, and, given the timescale, several of the papers were either withdrawn or not considered suitable for publication. Eventually eight papers remained, but their combined length was insufficient to justify publication in monograph form. It was therefore decided that MIN 5 should be published as a separate enclave within *NC* 2012.

The eight papers which follow were edited by M.R. COWELL and J. ORNA-ORNSTEIN, with support from D.R. HOOK and G. WILLIAMS.

The Chemical Composition of Early Russian Platinum Coins

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[PLATE 29]

Introduction

THE FIRST decades of the nineteenth century saw the mastery of platinum refining and the development of a number of different methods to produce malleable platinum sponge.[1] Initially, this metal was extracted from native South American platinum and used in the manufacture of chemical apparatus and laboratory equipment. The discovery in the early nineteenth century of large deposits of platinum in the Urals led to the introduction of a platinum coinage, issued in denominations of three roubles (**Pl. 29**), six roubles and 12 roubles.[2] To this end, General Sobolewsky of the Royal Mint in St Petersburg developed the refining procedures of the time to produce platinum on an industrial scale.[3] Native platinum consists primarily of metallic platinum. However, due to the presence of other metallic elements in the ore mineral, the average platinum concentration even in high grade concentrates rarely exceeds 80 wt% Pt. In order to obtain a malleable metal, the platinum had to be separated from its companion elements in the ore, notably iron and the other platinum-group elements, such as iridium, osmium, rhodium, ruthenium and palladium. The process consisted basically of the dissolution of the native platinum in *aqua regia*, followed by decantation of the solution from the insoluble residue and the selective precipitation with salammoniac of ammonium hexachloroplatinate. This precipitate, however, still contained a considerable amount of other metals, particularly iron, iridium and rhodium, making it more difficult to consolidate and hammer the refined platinum into shape without cracking. A number of procedural variants were in use during the first half of the nineteenth century to maximise the platinum yield from the ore, and to reduce the amount of impurities in the precipitate.

Despite the importance of early nineteenth century platinum as surviving evidence for the invention and development of powder metallurgy in general,[4] we found very few systematic studies of early platinum in the literature. Bachmann and Renner published a semi-quantitative analysis of an early coin, done by X-ray fluorescence

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[1] D. McDonald and L.B. Hunt, *A History of Platinum and its Allied Metals* (London, 1982), pp. 55 ff.

[2] McDonald and Hunt, *History of Platinum*, pp. 241-7; H.G. Bachmann and H. Renner, 'Nineteenth century platinum coins – an early industrial use of powder metallurgy', *Platinum Metals Review* 28 (3) (1984), pp. 126-31.

[3] P.G. Sobolewsky, 'Über das Ausbringen des Platins in Russland', *Annalen der Chemie und Pharmazie* 13 (1835), pp. 42-52.

[4] Bachmann and Renner, 'Nineteenth century platinum coins', p. 127.

(XRF) with an energy-dispersive spectrometer, and Kaim[5] described the composition of Russian platinum metal used in coinage, but without further specifying the source of his data or the analytical method used. The most detailed account of early nineteenth century platinum compositions was published by Kronberg and co-workers,[6] who analysed by mass spectrometry samples of platinum wire made by Wollaston[7] possibly in the 1820s, and now held at the Science Museum in London.

During an earlier investigation of Russian platinum coins by some of the current authors,[8] the surfaces of nine nineteenth century coins were analysed by XRF, using several different methods and instruments. All coins were pieces of three roubles with dates between 1828 and 1842. The 1828 example was the only one in mint condition and was considered to be a *novodel* issue, probably struck in the late nineteenth century; all the other coins showed signs of wear and circulation. In that investigation, initially, a Philips PW 1400 XRF with wavelength dispersive spectrometer (WD-XRF) was used on seven coins to scan over the energy range from 6 KeV up to 12 KeV, and again from 15 KeV up to 24 KeV. Then, an X-ray microprobe was used to analyse specifically a gold-rich inclusion on the surface of one of the coins (see below).[9] More recently, as reported here, we re-analysed all seven coins and analysed a further two (dated 1829 and 1831), with other XRF equipment, namely a Spectro X-LAB 2000, applying polarised X-rays via a number of secondary targets and analysing the characteristic radiation with an energy-dispersive spectrometer. By these means we were able, for the first time to evaluate the coins against reliable reference materials for a quantitative analysis of a number of minor and trace elements.

Wavelength dispersive spectrometry

The first sequence of analyses allowed us to detect a number of elements present in most of the seven original coins, most notably iron, copper, nickel and iridium, in some of them also manganese, zinc, silver and gold, and in one instance palladium (Fig. 1). Of these, only iridium and gold were quantified, on the basis of a straightforward peak area comparison with the dominant platinum peak and the fact that those X-rays lines are well known in position and relative intensities.[10] We believed that this was justifiable for these two elements, since they are immediate neighbours of platinum in the periodic table of the elements.

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[5] R. Kaim, *Die Münzen des Zaren Nicolaus I. 1825-1855* (Russland-Serie Spezial, 5), (Hagen, 1982).

[6] B.I. Kronberg, L.L. Coatsworth, and M. C. Usselman, ‘Mass spectrometry as a historical probe: Quantitative answers to historical questions in metallurgy’, in J. Lambert (ed.), *Archaeological Chemistry* 3 (Washington, 1984), pp. 295-310.

[7] A pioneer of platinum refining, see McDonald and Hunt, *History of Platinum*, pp. 147-77.

[8] E. Auer, Th. Rehren, A. von Bohlen, D. Kirchner and R. Klockenkämper, ‘Über die Herstellung und Zusammensetzung der ersten Platinmünzen in Russland’, *Metalla* 5 (1998), pp. 71-90.

[9] The results of XRD and metallographic studies are given in Th. Rehren, D. Kirchner and E. Auer, ‘The metallography of early Russian platinum coins’, in P. Northover (ed.), *Founders, Smiths and Platers* (Oxford, forthcoming).

[10] Auer *et al.*, ‘Platinmünzen in Russland’, pp. 80-3.

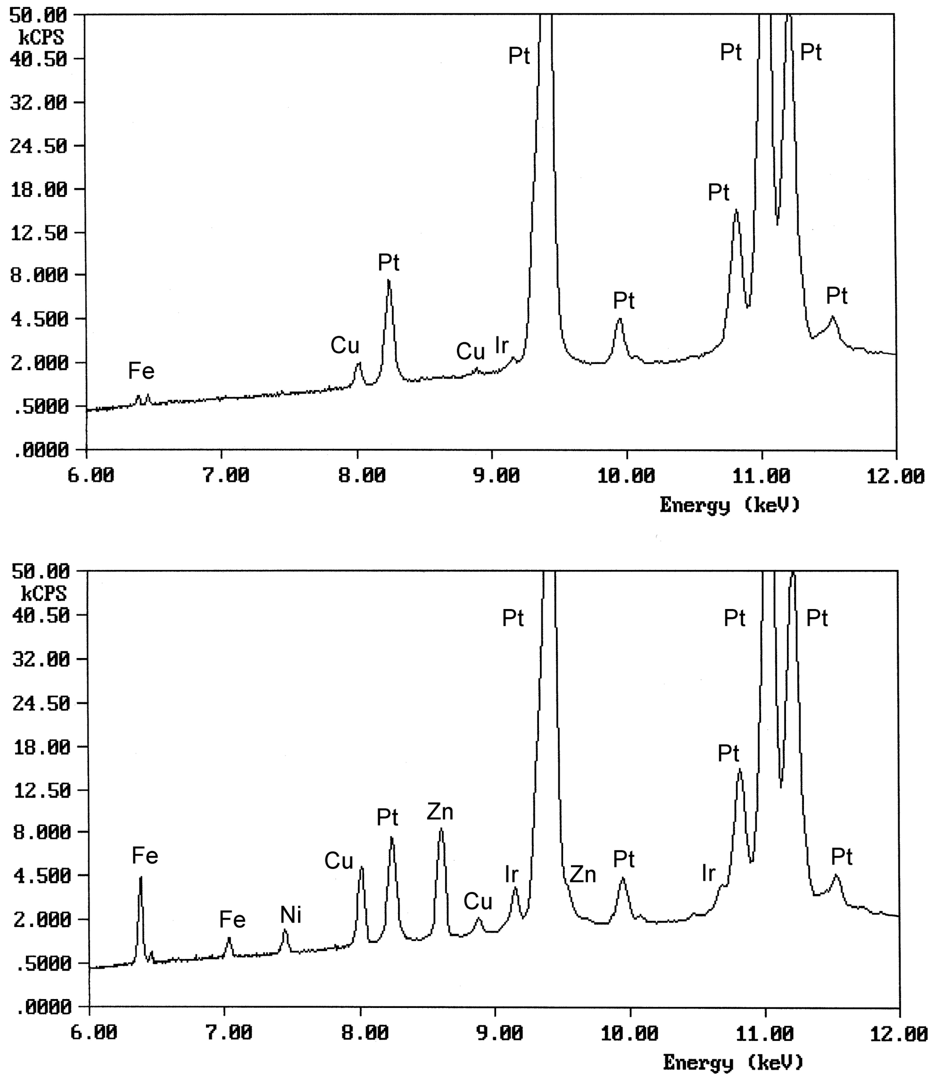

Fig. 1. Juxtaposition of spectra for the novodel issue (obverse; top) and the 1837 issue (obverse; bottom), using the Philips PW1400 instrument at Dortmund.

Table 1. Qualitative assessment of trace and minor elements in Russian platinum coins (WD-XRF). (r = reverse, o = obverse; x = trace; xx = clearly present; xxx = present at high level).

	Mn	**Fe**	**Ni**	**Cu**	**Zn**	**Pd**	**Ag**	**Ir**	**Au**
1828 r								0.15%	
1828 o		x			x			0.1%	
1832 r	x	xx	x	xx				0.8%	
1832 o		xx	x	xx				0.8%	
1835 r	x	x						0.5%	0.05%

	Mn	**Fe**	**Ni**	**Cu**	**Zn**	**Pd**	**Ag**	**Ir**	**Au**
1835 o		x			x			0.5%	0.05%
1836 r	x	xx	x	xx			x?	0.7%	
1836 o	x	xx	x	xx			x?	0.8%	
1837 r	x	xx	xx	xx	xxx		xx?	0.5%	0.05%
1837 o	x	xx	x	xx	x			0.8%	
1838 r		xx	x	xx	x		xx	0.8%	0.50%
1838 o		xx	x	x				0.8%	0.05%
1842 r		x		x	x	xx		1%	0.05%
1842 o		x	x	x		xx		1%	

Six of the coins had concentrations of iridium between 0.5 and 1 wt%; only the coin considered to be a *novodel* issue (coin date 1828) had a far lower level, of 0.1 to 0.15 wt%. Gold was identified only in four of the coins studied, and estimated at 0.05 wt%, although one surface of the coin dated 1838 gave a much stronger gold signal, estimated at about 0.5 wt%: this was likely to be due to the presence of several gold inclusions on the coin's reverse surface.[11]

Unfortunately, because we had no calibration standards available for estimating low concentrations of the transition metals in a platinum matrix, only a qualitative interpretation of the concentration levels for these elements was possible. Iron, copper and nickel were the elements most frequently found; they all occurred in most of the six non-*novodel* coins except the 1835 example, which showed only a relatively weak iron peak on both surfaces, some manganese and zinc on opposite sides, but neither nickel nor copper. The 1828 *novodel* coin gave a weak iron and zinc signal on one surface only, and no signal for either nickel or copper.

X-ray microprobe

A laboratory energy dispersive X-ray microprobe (Fig. 2) assembled at ISAS (Dortmund) was used for the local analyses of gold inclusions. The probe consists of a 2 kW fine focus X-ray tube with Mo anode, a high voltage generator ISO-DEBYEFLEX 1001 (Seifert and Co., Ahrensburg, Germany) and a Si(Li) detector with analyser QX 2000 (Oxford Instruments, High Wycombe, England). The stand, sample chamber and the sample positioning system were built in the mechanical workshop of ISAS. For X-ray optics we used different commercially available thermometer capillaries of borosilicate glass with inner diameters ranging between 10 μm and 1 mm (Glaswerke Wertheim GmbH, Wertheim, Germany). A 45°/45° geometry was chosen for excitation and detection, i.e. the exciting beam and the beam of detected fluorescence X-rays were both adjusted at 45° normal to the sample plane (cf. Fig. 2). The X-ray tube was operated at 58 kV and 30 mA and the fluorescence radiation was collected at a spectral width of 40 eV per channel and a time of 300 seconds for each spectrum. The analyses were performed at normal atmospheric conditions, i.e. no vacuum was applied and no special gas was flushed into the sample chamber. Acceptable spatial resolution and a reasonable time of analysis were achieved by using a capillary of 200 μm aperture and of 160 mm length. X-ray fluorescence radiation of elements with atomic numbers ≥ 14 (silicon) can be recorded simultaneously with this laboratory device.

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[11] Ibid.

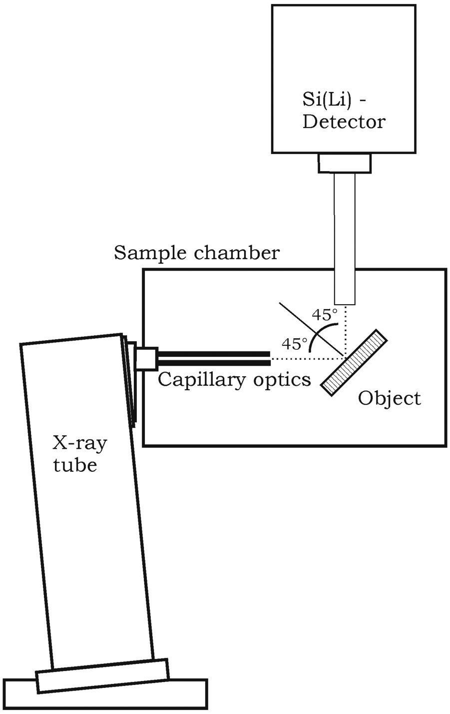

Fig. 2. Schematic drawing of ISAS' X-ray microprobe.

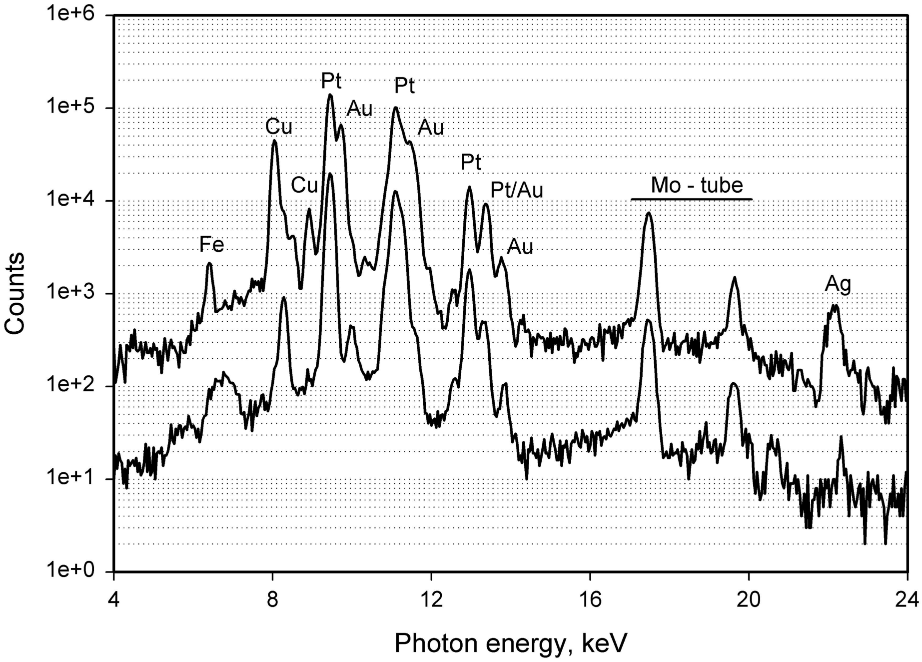

Fig. 3. Juxtaposition of X-ray spectra for the gold inclusion (top) of coin 1838 and a pure platinum substrate (bottom).

Only qualitative information was gained from the recorded spectra. In Fig. 3 two of them are shown, representing the signals of a gold inclusion of the coin minted in 1838 (above) and the signal of modern platinum foil (below). When comparing the upper spectrum (shifted for better interpretation) to the lower, peaks additional to those of platinum can be observed. They are related to the iron, copper, gold and silver X-ray fluorescence radiation. The clear presence of significant amounts of copper with the gold indicates that the inclusion is an artificial alloy, and not unrefined native gold. The presence of platinum lines in the spectrum indicates that the gold inclusions are of limited thickness, estimated to be only a few microns. Otherwise, the heavy gold matrix would have absorbed completely the incident beam, or at least the platinum fluorescence radiation.

Polarised energy-dispersive spectroscopy

The second approach, using the energy-dispersive spectrometer Spectro X-LAB 2000 with a 400 W X-ray tube with Pd anode, several secondary and polarisation targets and a Si(Li) detector, revealed the presence of a number of additional elements in the coins. In particular it produced data on titanium, tin, ruthenium, rhodium and palladium, reflecting the excellent peak to background ratio of this method as well as the purity of the spectra. In contrast to the former investigation with a WD-XRF spectrometer, element-specific signals from the X-ray tube anode material (Pd in this case) were eliminated completely by the use of a corundum target placed in a cartesian geometry between tube and sample (Fig. 4).

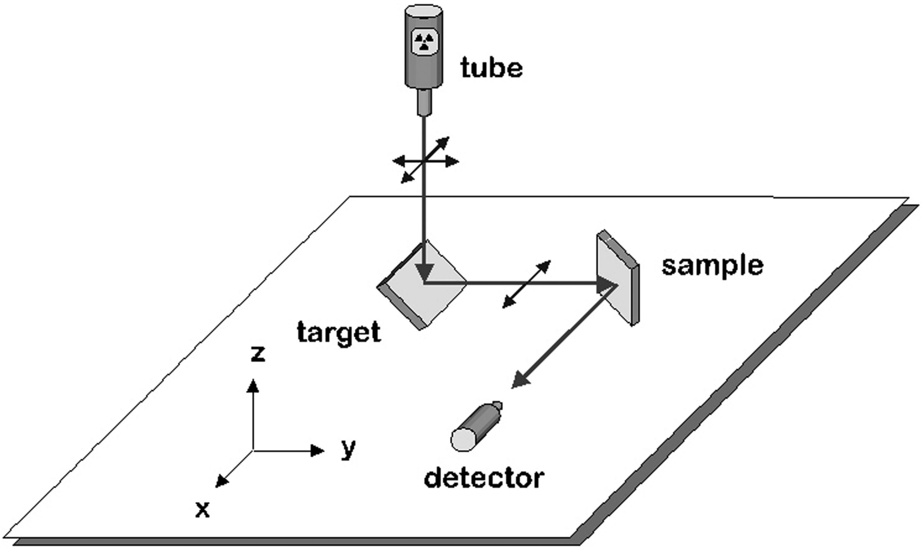

Fig. 4. Schematic drawing of Specto's X-LAB 2000 arrangement of tube, targets and samples.

Using a series of six multi-element platinum-base standards as well as three binary and ternary platinum-alloy standards we were able to build up a calibration to quantify several of the elements identified. The calibration used was based on a fundamental parameter model which combined theoretically and empirically determined physical constants to perform an accurate matrix correction with regard to the varying compositions of the coins. For the light platinum-group elements (PGEs) ruthenium, rhodium and palladium as well as tin the detection limits were determined in the range of 5 to10 µg/g. The limits of detection (LODs) for the heavy PGEs, osmium, iridium and gold, are between 150 and 300 µg/g, due to considerable overlap with the Pt-signals. Transition elements can be determined at levels of ≥ 20 µg/g. In addition to the elements listed in the table, we analysed for vanadium, chromium, molybdenum, cadmium, antimony, rhenium and osmium, but could not detect any of them.

Table 2. XRF analyses of Russian platinum coins, measured using a Spectro X-LAB 2000 and several reference materials to calibrate the method. All data are in µg/g.

Coin	Ti	Mn	Fe	Ni	Cu	Zn	Rh	Pd	Sn	Ir	Au
1829	120	<20	12100	40	2600	590	1100	1370	20	3300	1150
	100	<20	12500	80	3000	290	1150	1270	<5	3700	1050
1831	40	<20	6700	250	1600	70	790	540	<5	9400	1100
	300	<20	6900	230	1850	70	770	530	10	9200	850
1832	60	<20	15800	680	4200	<20	1100	760	10	13200	510
	180	180	14300	600	5100	50	1050	710	10	12100	280
1835	140	<20	5700	125	1200	240	520	210	30	9200	630
	240	620	5200	140	1050	100	610	260	30	8400	1000
1836	140	100	13800	470	3100	<20	1400	610	60	14100	220
	280	480	14500	410	4200	50	1400	590	20	13300	190
1837	50	190	10600	440	5900	650	870	570	15	14100	550
	25	180	13700	1540	7300	11300	890	550	850	10800	430
1838	530	<20	11800	340	2850	160	760	290	60	12200	1100
gold specks	280	<20	11300	440	10300	850	760	280	80	15100	13200
1842	50	<20	7000	340	2900	170	1500	1380	30	16700	950
	160	70	5100	230	2250	370	1650	2000	75	18700	1050
1828	520	90	6100	50	290	610	90	140	10	2250	20
novodel	<20	<20	130	<20	260	130	85	140	5	2300	<300
1977	<20	<20	480	<20	110	150	60	140	<5	<300	<300
	<20	<20	650	<20	170	170	50	90	<5	<300	<300

The data

Table 2 lists the values for each coin in chronological sequence, with the upper row giving the values found on the obverse and the lower row those on the reverse. Marked discrepancies between opposite faces of individual coins are obvious particularly for titanium, manganese, zinc and tin, while for the other elements there is generally a good agreement in composition between opposite surfaces. An exception to this is the 1838 coin with much higher concentrations for copper and gold on the reverse; this clearly is due to the visually obvious inclusions of gold particles.

The list of elements found as impurities in the coins can be divided into those resulting from incomplete chemical separation and those present as mechanical inclusions. The former include the PGEs, notably iridium, rhodium and palladium, but also iron and nickel, and possibly copper and gold; the problems and developments in nineteenth century chemical separation of platinum from its contaminants are discussed in considerable detail by McDonald and Hunt.[12] Titanium and tin are likely to be mechanical impurities; both oxides are known to be chemically refractory, and common impurities in the placer deposits which provided the platinum ore. Not analysed by XRF, but clearly present in the metallographic section, are mechanical inclusions of silica dust, confirming in principle the existence of such mechanically introduced impurities among the dense scatter of chemically introduced iron-nickel oxides.[13] Given the frequent concentration discrepancies found at opposite faces of individual coins for manganese and zinc, a mechanical factor may be responsible here as well.

The gold inclusions found at the surface of the 1838 coin (**Pl. 29, 3**) remain enigmatic. They appear to be far too coarse to be a mechanical contamination through incomplete decantation of platinum-rich solution from the insoluble residue at an early stage of the refining. Furthermore, their analysis by X-ray microprobe revealed a copper content much higher than typically known from placer gold. They seem to be rather thin, in the range of a few microns only, to judge from the presence of characteristic platinum X-ray emission lines in the spectrum, even when only the gold inclusion is irradiated by the focussed incident beam. The difference in design between these platinum coins and contemporary gold roubles makes it unlikely that the gold is due to an attempt to gild the platinum coin, when platinum was less valuable than gold, as was the case during most of the nineteenth century. This relative cheapness of platinum also makes it unlikely that the gold was deliberately added to dilute the refined platinum.

Examination of the overall level of contaminations in each coin reveals clear differences among the genuine coins struck between 1829 and 1842, the late nineteenth century *novodel* issue ('1828'), and the 1977 commemorative coin. Not unexpectedly, the 1977 coin shows the least contaminations, with about 550 µg/g iron as the major impurity, followed by 100 to 200 µg/g each copper and palladium, but no detectable titanium, nickel, tin, iridium and gold. The *novodel* issue, in contrast, has about 2000 µg/g iridium, and between 100 and 500 µg/g each of titanium, copper, iron, palladium and rhodium. This is, however, still a considerably lower level of impurities than those found in the genuine coins. They have on average between 0.3 and 1.5 wt% each of iron and iridium, between 0.1 and 0.4 wt% copper, and between 100 and 1500 µg/g rhodium, palladium, gold, nickel and titanium.

Sobolewsky mentions various improvements in the refining procedure followed at the Royal Mint in St Petersburg.[14] The period of minting of platinum coinage covers the time after the death of Wollaston and the publication of Sobolewsky's superior procedure. Improvements in the refining procedures and hence a reduction of overall impurity levels among the coins over the time of Russian production would thus be expected. No pattern of decreasing impurities, however, is apparent from the data for the genuine coins, spanning more than a decade. The three coins with the lowest

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[12] McDonald and Hunt, *History of Platinum*.

[13] Rehren *et al.*, 'The metallography', n. 9.

[14] Sobolewsky, 'Platin in Russland' , n. 3.

impurity levels are those minted in 1831, 1835 and 1842. In particular iron, the element most critical for the malleability of the refined platinum, shows no decrease over the period concerned.

The results of the various methods used in the analyses of these coins show very good agreement between the quantification of gold and iridium concentrations based on the two XRF instruments used. We estimated a level of 500 µg/g gold for those four coins which had clear gold peaks in the WD-XRF spectra, and 0.5 wt% for the gold-rich surface of the 1838 issue. The iridium level was estimated at between 0.5 and 1 wt% for the genuine coins, and 0.1 to 0.15 wt% for the *novodel* coin. The calibrated values obtained by the second instrument are between 500 and 1000 µg/g gold in the richer coins, and 1.3 wt% in the one side showing gold inclusions. The iridium levels were determined at between 0.9 and 1.7 wt% in the genuine coins, and 0.2 wt% in the *novodel* coin; the 1829 issue, with only about 0.3 wt% iridium, was not part of the initial series analysed by WD-XRF.

The presence of considerable quantities of rhodium in these coins, undetectable by the Philips PW 1400 instrument (WD-XRF) due to interference from the X-ray tube emission lines, was already indicated by the investigation of a metallographic section of one of them. The analysis of this section by electron microprobe with a wavelength dispersive spectrometer gave a concentration of about 0.5 to 0.6 wt% rhodium for the interior of the 1837 coin.[15] Analysis using Spectro's X-LAB 2000 found about 900 µg/g (equivalent to about 0.09 wt%) rhodium on the surface, i.e. almost an order of magnitude less. There were also discrepancies in iron and nickel, which were found at considerably lower levels by the microprobe than by XRF. Here, the difference is likely to be due to the particulate nature of the oxide inclusions, which contain a great deal of the total iron and nickel content of the coins. They were excluded from microprobe analysis, but of course included in the XRF analysis. The iridium level, finally, is similar for both instruments. Clearly, the agreement between XRF and microprobe data is less good for rhodium than for the other elements.

Discussion

The refining of platinum during the nineteenth century relied primarily on a complex, and at the time only partly understood, sequence of dissolution and precipitation operations. The primary consideration for the purpose of the Royal Mint in St Petersburg was the malleability of the resulting metal (i.e. how easily blanks could be manufactured and struck) balanced against the overall costs of the operation at an industrial scale. The analyses of the genuine coins of the first half of the century give a fairly accurate image of the tolerated level of impurities, particularly in respect of iron and iridium. For both elements, typical concentrations were found to be in the one percent range, only slightly worse than in Wollaston's contemporary metal which was refined in the laboratory with the opportunity for more careful control of the process than on an industrial scale.[16] The relatively wide scatter in impurity concentrations found among the seven coins analysed so far suggests that a certain

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[15] Auer *et al.*, 'Platinmünzen in Russland', p. 85.

[16] Kronberg *et al.*, 'Mass spectrometry', p. 308.

amount of latitude was tolerated in the refining at St Petersburg. The *novodel* issues, produced by the Russian mint at the end of the century to satisfy demand from collectors, and using the original dies, are apparently of a considerably higher purity than even the best genuine coins for a number of critical elements, among them gold, iridium, copper, nickel and iron. At present, we are only able to give data for a single *novodel* coin which may not be characteristic of the whole issue. A marked improvement in the quality of the refining operations is to be expected over the fifty years between the production of the original and the *novodel* issues. The Russian 1977 Olympic medal in contrast, analysed as an example of modern platinum used for commemorative coins and medals, is almost pure platinum with only minute concentrations of iron, palladium, rhodium and copper. It is very obviously different from the nineteenth century metal.

Future work should concentrate on characterising the *novodel* issues more fully, by their chemical composition and some physical properties such as magnetic response and density. This would greatly enhance our ability to tell them apart from the original genuine series which are otherwise almost indistinguishable. Furthermore, it would be of interest to study the homogeneity of individual metal batches of the genuine coinage, e.g. on a year to year basis. This could allow us to identify whether any of the recorded changes in the refining at St Petersburg resulted in systematic shifts in composition, if not in improvements in quality, or whether any variability in the composition is random and simply reflects individual batch preparations.

Acknowledgements

Dr E. Auer (Wertheim) provided most of the coins analysed, and initiated the series of investigations into their magnetism and composition. We gratefully acknowledge Prof. R. Klockenkämper's support of this study through access to the analytical facilities of the Institut für Spektrochemie und Angewandte Spektroskopie in Dortmund, and valuable discussions regarding the interpretation of the wavelength-dispersive XRF results. Prof. H.G. Bachmann kindly provided one coin for analysis, and was helpful in facilitating access to a series of reference materials from Degussa (Hanau). Degussa Hüls AG and W.C. Heraeus GmbH & Co. KG are thanked for providing reference materials for this study.

Key to Plate 29.

A sample of the coins analysed. The reverse of the 1838 coin has gold inclusions (darker, lower right hand corner, near the last '8'). Except for the 1828 issue, they all show signs of wear. Not to scale. Diameter of coins is 23 mm. Photos E. Auer.

3 Roubles 1828

3 Roubles 1842

3 Roubles 1838 (with gold inclusions)