

# Resistance Ratio and Purification of Platinum

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*Accurate correlation between the purity and the properties of platinum is essential both to quantify the properties of the metal with a view to its practical applications and to establish the behaviour of platinum as a representative metal for various physical and chemical measurements. The authors of this paper describe the systematic purification of a platinum bar by vacuum-melting and zone-refining. The final residual resistance ratio obtained was very high. The purity of the platinum, as indicated by optical and mass spectrography, then compared well with the best values previously reported.*

The importance of reducing the impurity content in platinum metal hardly needs to be emphasised, as the demand is growing for high purity platinum for industrial usage, such as thin film deposition in micro-solid state electronic circuits and thermometry. Indeed, it appears from a recent detailed account of the impurity concentrations by Chaston (1) that we have made considerable progress since the days of Chabaneau, Achard, Janety and Wollaston (2, 3). It should, however, be pointed out that the purity of the presently available bulk platinum is inadequate to perform some experiments in electron physics of the metal. This paper is essentially a part of the progress report of a systematic investigation of ways and means of obtaining ultra-pure platinum.

One of the most direct methods of determining the purity of a relatively pure metal (particularly for the assessment of the suitability of the metal for experiments to determine electronic properties) is the measurement of the ratio of the resistance (or resistivity) of the metal at room temperature to that at liquid helium temperature, i.e.:

$$S_{4.2} = \frac{\rho_{300\text{K}}}{\rho_{4.2\text{K}}} \quad (1)$$

This ratio increases with the purity of the metal. The precise relationship between the impurity content and the resistance ratio can be shown to stem from the well known Matthiessen's rule which states that the observed resistivity  $\rho(T)$  of a metal at any temperature  $T$  consists of a temperature independent part  $\rho_0$ , known as the residual resistivity, and a temperature dependent part  $\rho_i(T)$ , i.e.:

$$\rho(T) = \rho_0 + \rho_i(T) \quad (2)$$

It is known that Matthiessen's rule is not strictly obeyed in platinum. The argument pertaining to the residual resistivity however is valid. The residual resistivity arises because of the scattering of electrons by impurities and other lattice defects. It can be shown that commonly observed values of the residual resistivity of platinum are unlikely to be limited by dislocation-type defects. The contribution to the residual resistance by point defects other than impurities can be eliminated by annealing.  $\rho_i(T)$ , however, rapidly approaches zero at low temperatures and one can reasonably assume that at 4.2 K,

$$\rho(4.2 \text{ K}) \ll \rho_0 \quad (3)$$

Thus it can be seen that  $S_{4,2}$  in well annealed samples would directly vary with the impurity content of the specimen.

The resistance ratio of a 6 mm diameter cylindrical bar of "Thermopure"\* grade platinum is typically in the range 80-100. This particularly low value can be attributed to a high density of point defects arising from the cold work in the forged bar. The value of  $S_{4,2}$  can be raised fourfold, by a simple vacuum annealing treatment at a relatively low temperature ( $\sim 973$  K). For instance, Flynn and O'Hagan (4) have reported a value  $S_{4,2} = 393$  in a platinum bar of diameter 20 mm, after the annealing treatment.

For "Fermi surface" determination of the metal a much higher resistance ratio is required. For instance, the de Haas-van Alphen (dHvA) effect, in which one endeavours to detect variations in the diamagnetic susceptibility with the variations in the applied magnetic field at low temperatures, is dependent upon the impurity content. The effect arises due to the variations in free electron energy in the course of electron orbits as Landau energy levels cross Fermi energy. (In the space of this article it is impossible to define fully the various terms used here. A detailed description of the various phenomena may be found in Ziman (5)). To observe the effect it is necessary to fulfil certain conditions so that electrons have a reasonable chance of completing an orbit in the magnetic field without being scattered. The above conditions can be specified by the inequality

$$\omega_c \tau > 1 \quad (4)$$

where  $\tau$  is the scattering time in an orbit, and  $\omega_c$  is a characteristic cyclotron frequency of electrons describing orbits and is defined by

$$\omega_c = \frac{eH}{m^*c} \quad (5)$$

where  $e$  is the electronic charge,  $c$  is the velocity of electromagnetic radiation,  $H$  is the applied magnetic field, and  $m^*$  is the

effective (cyclotron) mass of the electrons.

The value of  $\tau$  is directly dependent upon the impurity scattering; it is necessary to have high purity. The dHvA effect may be observed in platinum with relative ease (6, 7, 8, 9) if  $S_{4,2} \sim 3000$ . For the observation of another phenomenon known as Azbel'-Kaner cyclotron resonance (AKCR) (10) one requires even higher resistance ratio. In this experiment one applies a magnetic field precisely parallel to the surface of the metal specimen together with an imposed radio frequency (r.f.) alternating field. Under these conditions electrons travel in helical orbits. If the frequency ( $\omega_{imp}$ ) of the r.f. field is such that

$$\omega_{imp} = n \omega_c \quad (6)$$

where  $n$  is an integer and  $\omega_c$  is the cyclotron frequency defined by (5), then electrons are able to absorb energy from the r.f. field and one observes anomalies in the surface impedance in the direction of the field. The strength of the signal in the above-mentioned resonance phenomenon is dependent upon the magnitude of  $\omega_{imp}\tau$ . In the case of platinum, to observe the AKCR phenomenon arising due to electrons with heavier effective masses, a resistance ratio of the order of 5000 is required. Furthermore, it is also necessary to have a perfectly flat specimen area of a relatively larger ( $\sim 6$  mm) diameter to observe the effect at an easily attainable frequency of the imposed r.f. field.

High resistance ratios can be obtained in specimens of small diameter ( $< 1$  mm). For instance, Jackson (11) and Huebener (12) were able to achieve resistance ratios  $> 7000$  in wires of diameter 0.6 mm and 0.25 mm respectively, by a series of annealing treatment in air (temperature range 1673 to 773 K) followed by quenching and/or etching. The purification effect of air annealing in small diameter wires is also described by Misek (13) and by Polk and Kunz (14). Ketterson and Windmiller (9) have reported resistance ratios between 2000 and 3000 in float-zone

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grown crystals of diameter  $\sim 0.92$  mm after a similar treatment. To date, the resistance ratio achieved in larger diameter rods ( $\sim$ several mm) are much smaller than the above-quoted values.

The detailed mechanism of the purification by annealing in air has not been investigated. It may, however, be suggested from the descriptions of the treatments that in the course of annealing, oxygen 'combines' with impurity atoms in platinum to render them ineffective or less effective as electron scattering centres. The reaction may take place either (i) because oxygen diffuses into the metal or (ii) because the impurity atoms diffuse out at the surface. The product of the reaction is either driven away because of high volatility, or because the end products of oxygen impurity combination are incapable of diffusing back into the metal, or because the presence of the above products does not contribute to the scattering as substantially as that due to original impurity atoms. In any case, following the approximate diffusion equation,

$$\bar{x}^2 = 2 Dt \quad (7)$$

where  $\bar{x}^2$  is the mean square distance covered by diffusing atoms in time  $t$ , and  $D$  is the diffusion coefficient of the diffusing species, it is easy to see that the length of the time required to complete the combination of oxygen with impurities in a large diameter platinum bar may be prohibitively long.

It was, therefore, decided to adopt a new approach based on combined zone refining and chemical treatments and to investigate correlation of impurity removal for each treatment with the aid of emission spectrographic and mass spectrometric analyses.

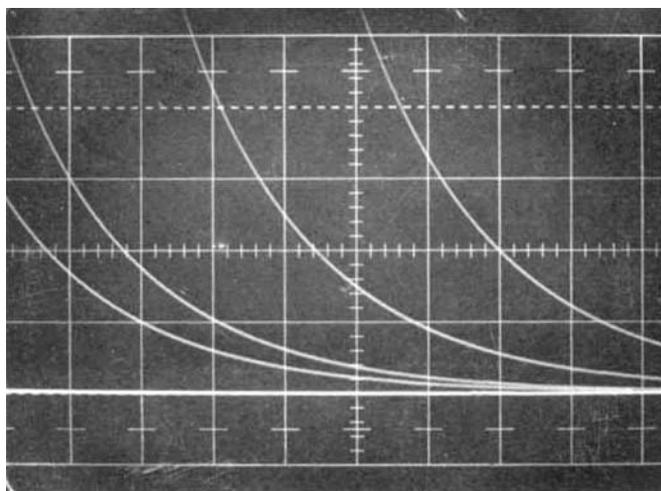
A nominally 99.999 per cent pure platinum rod (6 mm diam  $\times$  200 mm long) fabricated from a "high alpha" platinum with resistance ratio (i.e.  $\rho_{373K}/\rho_{273K}$ ) of 1.39227<sub>7</sub> was supplied to us by Johnson Matthey Metals Ltd. In Table I the mass spectrographic analysis and the emission spectrographic analysis of the supplied material are presented. It is to be noted

Table I Analyses of the As-supplied Bar $\left(\frac{\rho_{373K}}{\rho_{273K}} = 1.39227_7\right)$		
Element	Mass Spec. Deter.	Emission Spec. Deter.
Pb	<0.4	N D
Au	0.3	1
Pt	Base	Base
W	<0.04	N D
Ta	<0.3	N D
Pd	2.7	20
Ag	0.06	<2
Rh	0.3	
Cu	0.05	2
Ni	1.5	N D
Fe	20	20
Cr	1.2	N D
Ti	<1.4	N D
Ca	3	<4
S	3	N D
P	1	N D
Si	7	7
Al	10	N D
Mg	3	<8
Na	1	N D
O	30	N D
N	10	N D
B	4	N D

Notes: (1) All figures are in parts per million atomic  
 (2) N D—Not detected  
 (3) In the mass spectrometric analyses determination elements with <0.1 p.p.m. concentration are not included.

that contrary to the customary practice, the impurity concentrations in all the tables presented here are quoted in parts per million atomic (p.p.m. atomic) since it is more sensible to relate the resistance ratio  $S_{4.2}$  to the atomic concentrations of impurities. Attention is also drawn to the fact that the iron group impurities in the platinum lattice will act as very strong scatterers because they are ferromagnetic and their presence

Fig. 1 Resistance ratios for platinum were measured by an eddy current decay method in which the resistance is measured by observing the time decay of the potential generated by an induced current due to the magnetic flux penetration in a metal specimen. The voltage function approaches a simple exponential form and some typical voltage-time traces are shown here (time along the horizontal axis)



would set up large localised magnetic moments. It is therefore evident that the resistance ratio in the main is limited by the major impurities Fe, C and Pd. It is clear that particularly in the case of Pd the discrepancy between emission and mass spectrometric analysis is the largest. It is, however, not unusual in platinum to have Pd content  $\sim 20$  p.p.m. atomic.

The resistance ratios in the entire work were measured by the eddy current decay method originated by Bean, De Blois and Nesbitt (15). Briefly, in this method the

resistance is measured by observing the time decay of the potential generated by an induced current due to the magnetic flux penetration in a metal specimen. The voltage function  $V(t)$  can be shown to approach a simple exponential of the form

$$V(t) = A \rho(T) \exp(t/\tau(T)) \quad (8)$$

where  $A$  is a constant for a given geometry,  $\rho(T)$  is the resistivity of a sample at a temperature  $(T)$  and  $\tau(T)$  is a time constant of the decay function. Some typical traces of the above function are shown in Fig. 1.

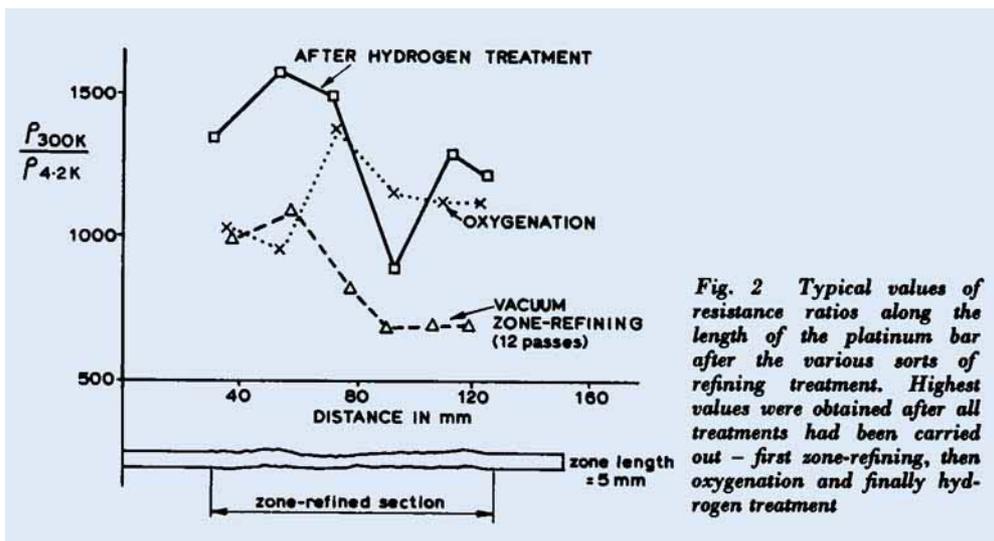


Fig. 2 Typical values of resistance ratios along the length of the platinum bar after the various sorts of refining treatment. Highest values were obtained after all treatments had been carried out - first zone-refining, then oxygenation and finally hydrogen treatment

**Table II**  
**Emission Spectrographic Analyses of Platinum Before and After Melting and Zone Refining**

Element	In Vacuum-heated Pt	In Vacuum-melted Pt	In Pure Zone-refined Section (Z.R.I.)	In the End of Zone-refined Section
Pd	10	8	N D	N D
Rh	4	2	N D	N D
Al	10	N D	N D	N D
Cu	3	3	N D	3
Fe	14	4	<4	4
Mg	8	<8	<8	<8
Si	7	<7	<7	<7
Ag	2	2	N D	N D

Notes: (1) All concentrations are in p.p.m. atomic  
(2) N D—Not detected

The value of  $S_{4,2}$  can be simply obtained by measuring the time constants  $\tau_{(T)}$  at the two temperatures, i.e.:

$$\frac{\rho_{300K}}{\rho_{4,2K}} = \frac{\tau_{(4,2 K)}}{\tau_{(300 K)}} \quad (9)$$

$$\therefore t \gg \tau_{(T)}$$

Resistance ratio of the as-supplied bar was 90. It was then annealed at 1273 K, in a vacuum at the pressure of  $6.65 \times 10^{-5}$  Pa ( $5 \times 10^{-7}$  mm Hg) for a period of 24 hours. The resistance ratio after this treatment was raised to 750. It was inferred from the presence of a very thin layer of blackish deposit on the colder part of the vacuum chamber that the somewhat greater improvement was due to evaporation of volatile impurities besides the removal of other point defects.

### Zone Refining and Chemical Treatment

The platinum bar was then zone-refined in an electron beam float-zone refiner, manufactured by Japan Electron Optics Laboratory Ltd., at a pressure of  $1.33 \times$

$10^{-4}$  Pa. After a zone-refining operation the whole of the zone-refined section bar was converted with its growth axis showing a preference for <100>. The emission spectrographic analyses of the vacuum-heated, vacuum-melted and two zone-refined sections are (after 12 passes) presented in Table II. The typical values of resistance ratios along the length of the bar are presented in Fig. 2. Table III presents the mass spectrometric analysis of the higher purity section of the bar (i.e. sample Z.R.I. in Table II). (Analysis performed after oxygenation.) It is evident from Tables II and III that the iron group impurities can be reduced by melting and zone-refining. They cannot, however, be completely removed by zone-refining operations. (It should be emphasised at the same time that the iron content in the zone-refined section is roughly one-fifth of that in the as-supplied bar). It seems almost certain from Table III that the effective segregation coefficient of carbon is approximately 1, as it has been hardly shifted by zone-refining.

**Table III**  
**Mass Spectrometric Analysis of the Specimen Z.R.I.**

Element	Concentration p.p.m. atomic
Pd	<0.04
Rh	0.3
Au	0.2
Al	1
Bi	<0.1
Cu	<0.05
Fe	3
Pb	<0.6
Mg	<0.1
Si	<2
Ag	<0.02
Ti	<0.13
W	0.07
Cr	0.4
Ni	0.15
O	30
C	100

Note: Many elements with concentration <0.05 p.p.m. have been omitted from the above list.

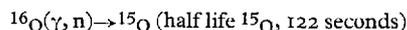
Further improvement of the resistance ratio was then sought by chemical treatments. Since air annealing of thin wires has proved to provide dramatic improvement in the resistance ratio, it was decided to give oxygenation treatment by giving two more zone passes in the residual oxygen environment at a pressure of  $1.33 \times 10^{-2}$  Pa, the upper pressure limit at which the electron gun may be operated. The resistance ratio measurements after oxygenation are given in Fig. 2. One interesting observation here was that the resistance ratio of the polycrystalline section (not melted) of the bar after oxygenation shot up from 750 to 1100.

Heating of an 8 mm diam.  $\times$  30 mm single crystal of platinum in air for 150 hours at K in a separate experiment had shown no improvement in resistance ratio in accordance with the findings of Norton (16) that no appreciable quantity of oxygen is able to

diffuse into single crystal in the above time period. The improvement in the resistance ratio of the polycrystalline section suggests relatively rapid grain boundary diffusion followed by slower diffusion in the individual grains.  $\gamma$ -photon activation analysis of the polycrystalline section showed oxygen concentration of around 30 p.p.m. Furthermore, the rapid grain boundary diffusion in platinum is supported by the findings of Selman, Ellison and Darling (17), who in the course of heating Pt-C alloys in air found porosity - a result of carbon-oxygen reaction - confined to the grain boundaries.

### Mass Spectrometric Analysis

The mass spectrometric analysis of the zone-melted platinum showed the presence of oxygen at about 30 p.p.m. and of carbon (see Table III). It is known that both oxygen and carbon can be accommodated on the platinum surface due to the phenomenon of adsorption. To eliminate the surface contamination each specimen for mass spectrometric analysis was washed in acetone and rinsed in distilled water, etched in Aristar grade HCl and rinsed in distilled water, etched in Aristar HNO<sub>3</sub>, rinsed in distilled water and finally rinsed in deionised water. The specimen was then dried under an infra-red lamp. To avoid the possibility of contamination from the source of the mass spectrograph the electrodes were set up (i.e. the specimen) in the source and it was then evacuated and baked at 373 K for 12 hours. An additional check on the oxygen determination by mass spectrometric analysis was obtained by the technique of  $\gamma$ -photon analysis, performed by Analytical R and D Unit AERE, Harwell. Briefly in this method the platinum sample is irradiated to induce the nuclear reaction.



The <sup>15</sup>O is then chemically separated by inert gas fusion after the specimen is subjected to the etching treatment by aqua regia to remove superficially active oxygen.

Further the  $^{15}\text{O}$  is separated from  $^{13}\text{N}$ ,  $^{11}\text{C}$  and  $^{16}\text{O}$  by an isotopic exchange of  $^{15}\text{O}$ . The accuracy of the oxygen determination by the above method is around  $\pm 1$  p.p.m. (wt./wt.).

In view of the above results and the argument that the diffusivity of oxygen in liquid platinum should be considerably higher it is apparent that the oxygen had diffused through the bulk of the platinum during oxygenation. Accepting the above argument, the fact that the resistance ratio of the polycrystalline platinum improved considerably more than that of the zone-refined section can only be explained by assuming that oxygen-iron interaction is responsible for the improvement in the polycrystalline material. The iron content in the polycrystalline material is much higher than that in the molten section. It must also be accepted that carbon, which is probably in solution, cannot be driven away by oxidation reaction.

A possible method of reducing the effect of carbon is hydrogen reduction. Two further zone passes were carried out in the residual hydrogen pressure  $1.33 \times 10^{-2}$  Pa. The resistance ratio measurements are given in Fig. 2. Thus after all the treatment listed above the resistance ratio achieved was  $S_{4.2} = 1600$ . It is of interest to record that by combining further treatment, to be described in a future article elsewhere, with the chemical treatment described here, it has been possible to achieve  $S_{4.2} = 3200$ . For the moment, however, it may suffice to say that both emission spectrographic and mass spectrometric analyses compare favourably with the purity obtained elsewhere. For instance, that of N.B.S. Std. 681 ( $S_{4.2} = 2.110$  measured on 0.51 mm diameter wire) (18) and other zone-refined platinum (19).

## Conclusions

The main conclusions of the foregoing study can be summed up as follows:

- (1) The major impurities limiting resistance ratio in commercially available

99.999 per cent pure platinum are iron, carbon and palladium.

- (2) Palladium concentrations can be substantially reduced by melting and zone-refining.
- (3) Iron content can be reduced by zone-melting.
- (4) The electron scattering due to iron can be reduced by oxygenation.
- (5) Carbon content cannot be reduced by zone-refining.
- (6)  $S_{4.2}$  may be significantly improved by hydrogenation. (It is premature to discuss in detail the effect of hydrogen treatment here as it is hoped to present more conclusive evidence pertaining to the individual purities in the near future.)

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## References

- 1 J. C. Chaston, *Platinum Metals Rev.*, 1971, **15**, 122
- 2 D. McDonald, 'A History of Platinum', 1960, London
- 3 D. McDonald, *Platinum Metals Rev.*, 1968, **12**, 142
- 4 D. R. Flynn and M. E. O'Hagan, *J. Res. Nat. Bur. Stds.*, 1967, **71C**, 255
- 5 J. M. Ziman, Ed., 'Physics of Metals 1', 1969, C.U.P.
- 6 M. D. Stafflau and A. R. De Vrooman, *Phys. Lett.*, 1965, **19**, 81
- 7 J. B. Ketterson, M. G. Priestley and J. J. Vuillman, *Phys. Lett.*, 1966, **20**, 452
- 8 L. R. Windmiller and J. B. Ketterson, *Phys. Rev. Lett.*, 1968, **20**, 324
- 9 J. B. Ketterson and L. R. Windmiller, *Phys. Rev. B*, 1970, **2**, 1483
- 10 M. Ya. Azbel' and E. A. Kaner, *Sov. Phys. J.E.T.P.*, 1957, **5**, 533
- 11 J. J. Jackson, *Proc. Internat. Symp. 'Reinstoff in Wissenschaft und Technik'*, Dresden, 1965
- 12 R. P. Huebener, *Phys. Rev.*, 1966, **146**, 490
- 13 K. Misek, *Czech. J. Phys.*, 1967, **17B**, 647
- 14 J. Polk and L. Kunz, *Czech. J. Phys.*, 1971, **21B**, 269
- 15 C. P. Bean, R. W. De Blois and L. B. Nesbitt, *J. Appl. Phys.*, 1959, **36**, 1976
- 16 F. S. Norton, *J. Appl. Phys.*, 1958, **29**, 1122
- 17 G. L. Selman, P. J. Ellison and A. S. Darling, *Platinum Metals Rev.*, 1970, **14**, 14
- 18 Private communication: U.S. Department of Commerce, Nat. Bur. Stds., 1970. See also *Platinum Metals Rev.*, 1968, **12**, 45
- 19 G. T. Murray, *Platinum Metals Rev.*, 1970, **14**, 42