

## The Correct Use of Platinum in the XRF Laboratory

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The use of crucibles and dishes of platinum and its alloys in the preparation of samples has become an essential feature of XRF analysis. Its broad application results from its near-perfect oxidation resistance and its excellent resistance to corrosive attack by metal oxide melts such as XRF fluxing agents. However, a few basic rules must be adhered to if platinum ware is to give satisfactory service. A number of “platinum poisons”, which are commonly encountered in samples, can cause destruction within a few sample preparation cycles. These “poisons”, the reasons for their corrosive effects, and techniques for minimising or eliminating their influence are outlined.

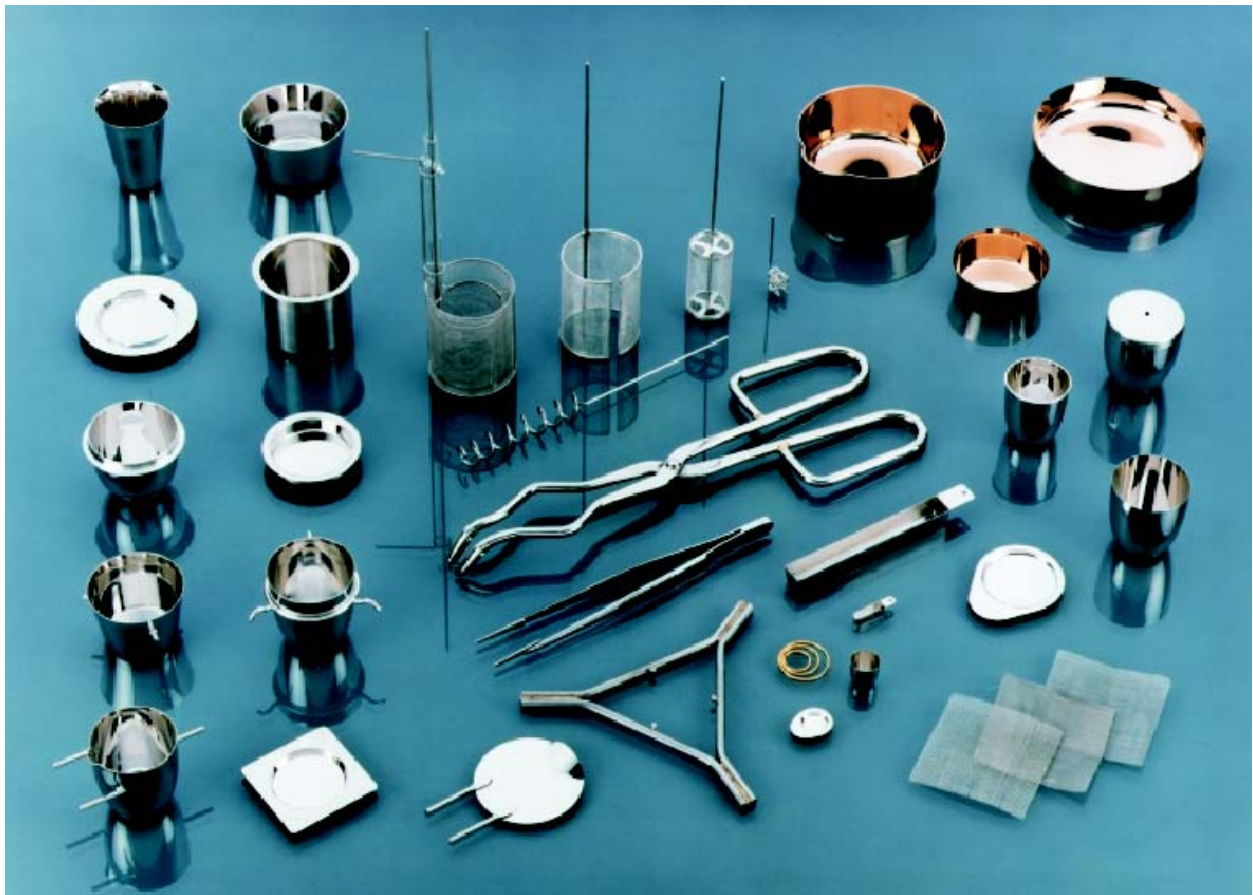
## INTRODUCTION

Modern chemical analysis would be unthinkable without the wide range of platinum apparatus and laboratory ware that is currently available (Figure 1). The range of products on the left have been specially developed for the XRF laboratory.

Platinum is used, of course, because it is essentially inert, does not contaminate the sample for normal analytical purposes and shows no significant weight loss even over prolonged periods of heating at temperatures over 1000°C in air.

However, the full benefits of using platinum can only be achieved if a number of simple basic precautions are observed in laboratory practice. The main risk is the “corrosion” of platinum which was described in detail nearly 20 years ago by Menzel [1].

It is the purpose of the present paper to summarise the most important precautions and to outline a number of case histories resulting from inadequate caution in practice

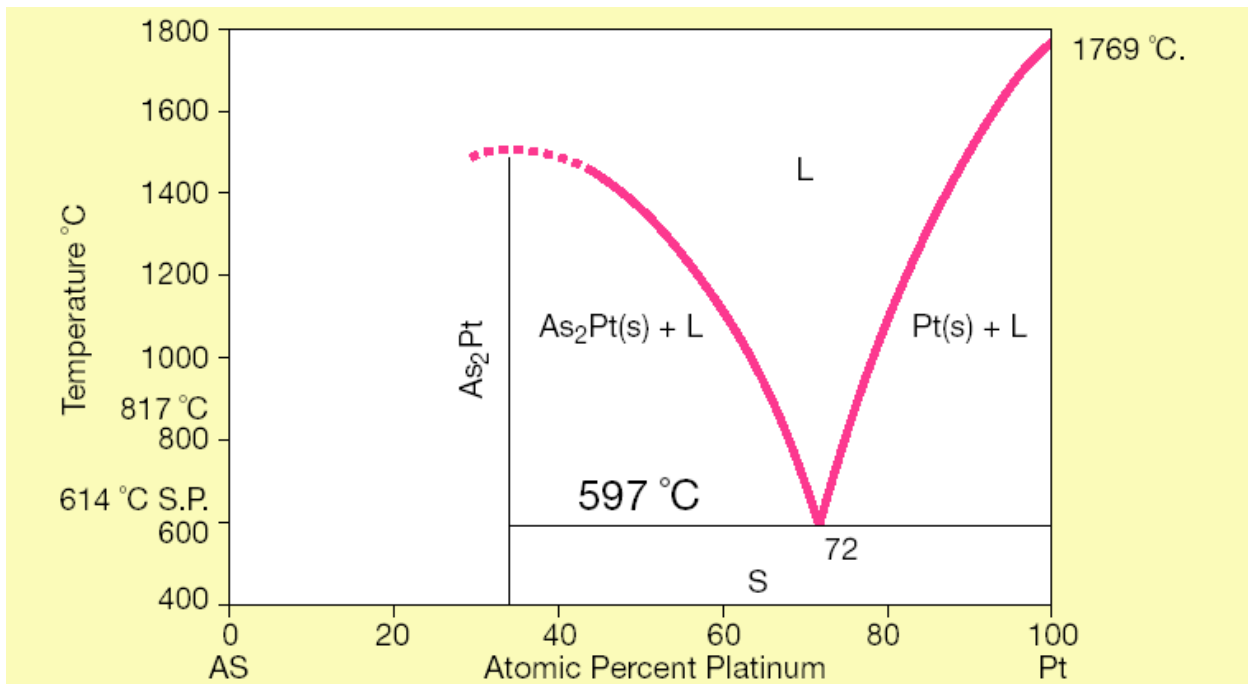


**Figure 1** Platinum laboratory apparatus

## PLATINUM “POISONS” AND OTHER HARMFUL ELEMENTS

The effect commonly referred to as “platinum corrosion” is not corrosion in the normal sense of aqueous corrosion, rusting, etc. It is usually the reaction of platinum with another element to form a compound with a lower melting point and the subsequent formation of a eutectic with an even lower melting point between the compound and platinum.

This effect is best demonstrated by the well known reaction of arsenic with platinum. Figure 2 shows the phase diagram of the Pt-As system (all phase diagrams are taken from [2]).



**Figure 2** Platinum-arsenic phase diagram.

Platinum (m.pt. 1769°C) reacts with arsenic to form the compound As<sub>2</sub>Pt (m.pt. 1500°C). This compound can then form a eutectic mixture with platinum containing 72 at.%Pt and melting at only 597°C.

Reactions of this type generally take place at the most reactive regions of the platinum, i.e. at the grain boundaries of the metal. Thus, the presence of even small amounts of arsenic in a sample can lead to localised attack of the grain boundaries and disintegration of the platinum at temperatures as low as 600°C. Arsenic is thus a particularly spectacular example of a “platinum poison”. Other examples of poisons are phosphorus, boron, bismuth, silicon, sulphur and a number of heavy metals, e.g. lead, zinc, tin, antimony. Even if these elements are only present at low concentrations they can diffuse gradually into the grain boundaries of the platinum where they lead to a loss of high temperature strength as shown by Fischer [3] for platinum exposed to phosphate glass melts.

A number of elements which do not form low melting compounds and eutectics with platinum can also have a detrimental effect on the integrity of utensils. Metallic elements such as silver, copper and nickel form alloys with the platinum, thus reducing both the melting point and the resistance to oxidation and corrosion. Furthermore, carbon can cause structural disintegration of platinum at elevated temperatures.

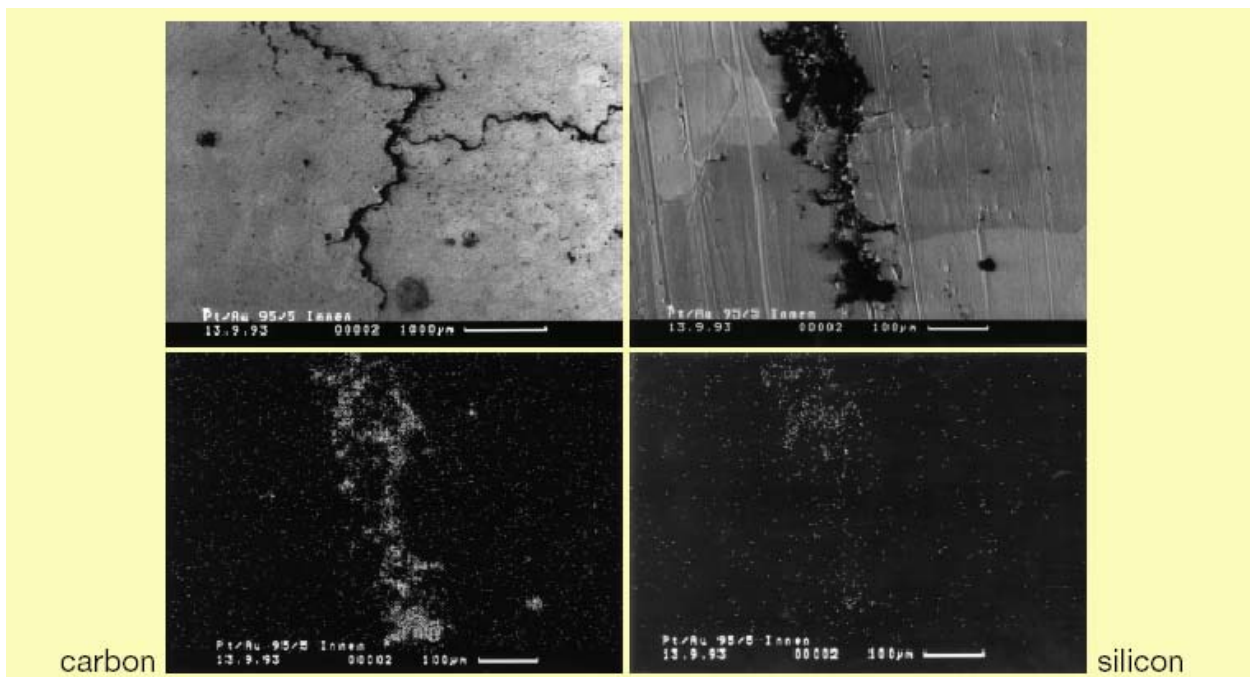
The poisons and other harmful elements mentioned above are only detrimental to platinum in their elemental state. Their oxides are normally harmless. The essential rule when preparing

samples in platinum utensils is, therefore, to ensure that the environment is sufficiently oxidising to prevent dissociation of any of the harmful oxides. Although it is usually adequate to carry out the sample fusion preparation by heating in air, there are a number of situations where additional precautions should be taken. These will be outlined in the following case histories.

## CASE HISTORIES

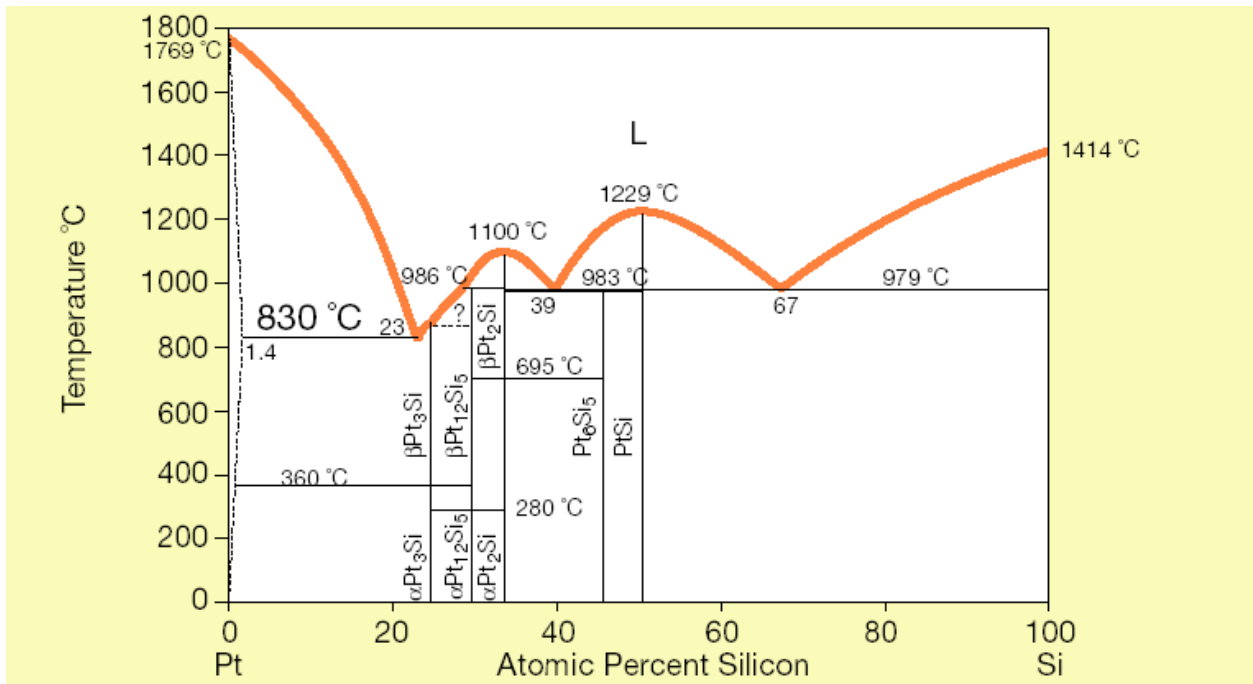
### Silicon Carbide

A common cause of damage to crucibles during sample fusion preparation in a furnace is contamination of the surface with silicon carbide either from the heating elements or supporting trays. Figure 3a (upper left) shows cracking in the base of a Pt-5%Au crucible that had been used for preparing cement samples. The micrograph shows the internal surface of the crucible - the outside was covered with a large number of pits and residues of samples and lithium tetraborate flux. Figures 3b - d show part of the crack at higher magnification and the local distribution of silicon and carbon.



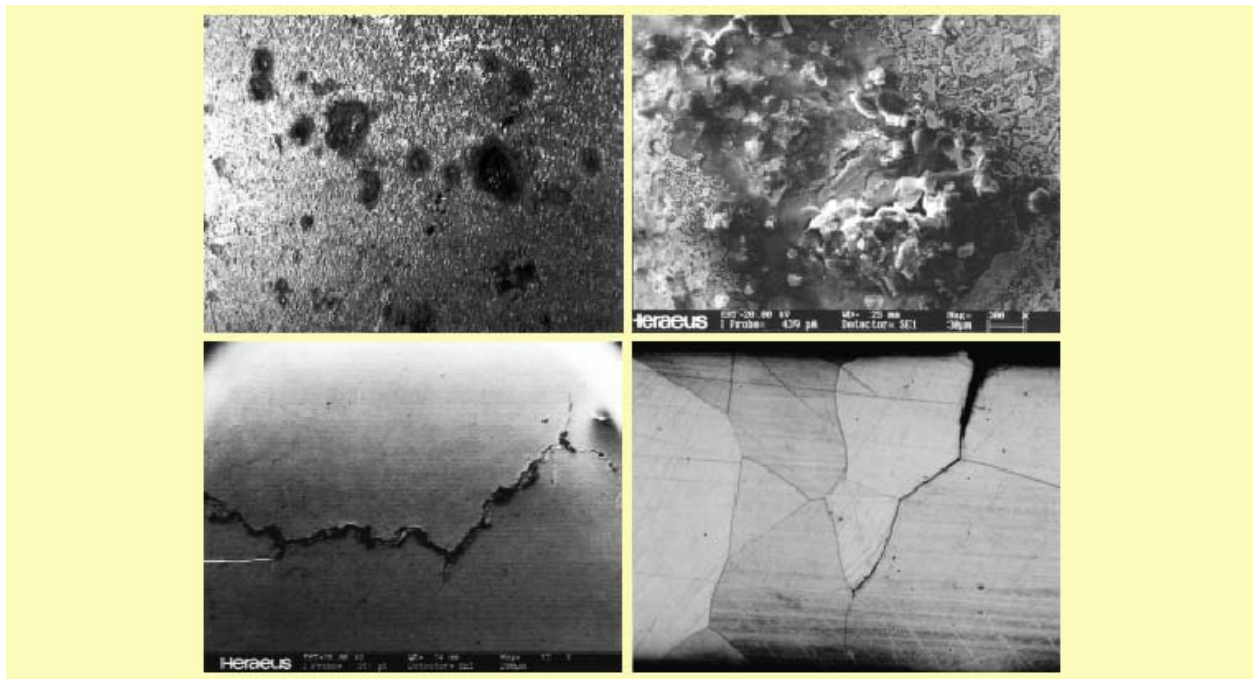
**Figure 3** Crack in Pt-5%Au crucible with C and Si enrichment.

The presence of silicon is not surprising, as this will be found at high concentrations in a large number of samples, usually in the form of SiO<sub>2</sub>. However, the presence of carbon is a clear indication that the damage has been caused by unoxidised silicon from a silicon carbide tray on which the crucible had been standing. Figure 4 shows the phase diagram of the Pt-Si system with 3 low melting eutectics. It can be seen that contact between platinum and unoxidised silicon can cause melting at temperatures well below 1000°C. We strongly recommend that platinum crucibles are never placed on a silicon carbide tray. Alumina or fused silica are greatly preferable.



**Figure 4** Platinum-silicon phase diagram.

A further danger is spalling of silicon carbide heating elements. Small particles of silicon carbide adhering either to the side of the crucible or accumulating on the floor of the furnace can lead to the same effect. Of course, it would be best to avoid using furnaces with silicon carbide heating elements. However, as these furnaces are readily available and relatively economic they are commonly used in analytical laboratories. It is important to ensure that platinum crucibles are positioned well away from the heating elements and that the supporting tray is cleaned of carbide particles after every fusion cycle.



**Figure 5** Cracks in Pt-5%Au crucible from cement works with Si-C contamination.

Another example of corrosion resulting from SiC is shown in Figure 5, although it is not clear whether the SiC came from the furnace or had been transferred accidentally to the outside of



the crucible because of inadequate cleaning after handling grinding media. The outer surface of the crucible base (Figure 5a, upper left) showed numerous pits which, on closer examination (Figure 5b, upper right), were found to be regions where localised melting had occurred. Substantial concentrations of both silicon and carbon were found in these pits. However, the actual cause of crucible failure was cracking, as shown in Figure 5c, lower left. The cracks were also found to have initiated on the inside surface of the crucible and showed distinct traces of carbon contamination (Figure 5d, lower right). It appears that carbon had been released by the dissociation of SiC on the outer surface and had then diffused through the full thickness of the base following the grain boundaries in the Pt-5%Au alloy. It was not possible to ascertain whether the cracking was caused by the presence of carbon itself at the grain boundaries or by the reduction of platinum poisons in the sample.

Figure 6 shows a particularly dramatic case of localised melting caused by SiC during sample preparation in a cement works. In this case, the crucible was heated in an induction coil. Traces of SiC had been present on the rim of the crucible. When this part of the crucible exceeded the melting point of the Pt-Pt<sub>3</sub>Si eutectic (830°C), the platinum started to melt. A large drop of molten Pt-Si eutectic, still containing particles of unreacted SiC, ran down the inside of the crucible and continued to melt the platinum as it descended. When the molten drop reached the surface of the flux, it dispersed to some extent and the SiC attacked a larger area on the inner surface of the crucible (Figure 6, right). However, the silicon content of the platinum was still sufficient for the melting process to continue until the base of the crucible was reached. Metallographic examination of the base showed particles of SiC embedded in resolidified platinum.

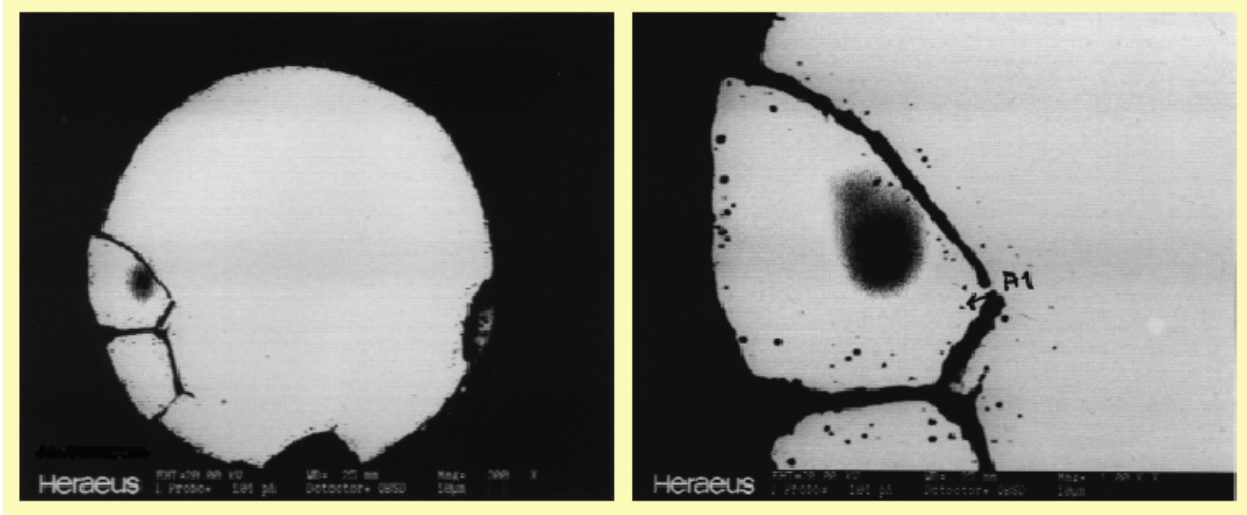


**Figure 6** Catastrophic melting of a Pt crucible caused by localised SiC contamination on top rim.

## Carbon

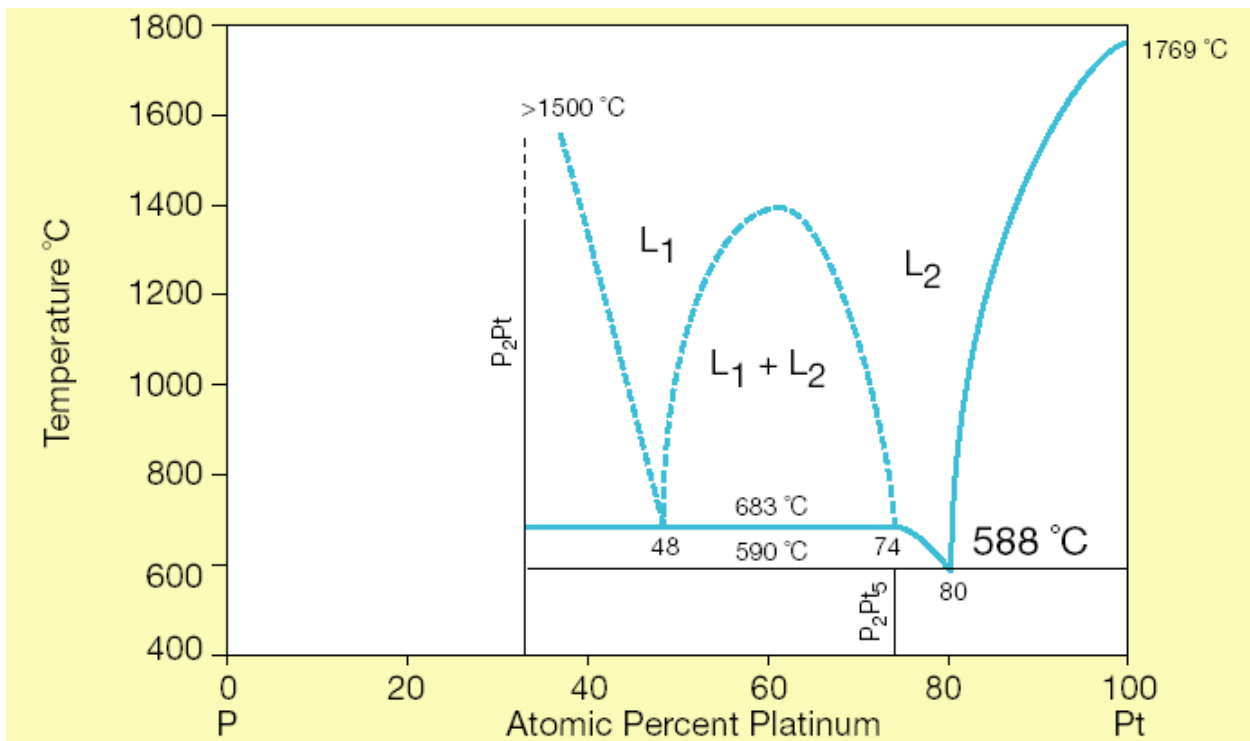
In addition to its influence in reducing oxides of platinum poisons, carbon itself can be severely detrimental to the structural integrity of platinum. Figure 7 shows a platinum wire that had been exposed to carbon at elevated temperatures. The carbon has diffused into the grain boundaries leading to grain boundary separation and porosity. The mechanisms of this process are not truly understood, but the effect is also observed in platinum catalysts exposed to atmospheres containing hydrocarbons.

It is essential that platinum crucibles and other utensils should not come into contact with carbon, for example by placing them on a graphite plate. Contact with carbonaceous materials should be avoided as much as possible or, if contact cannot be completely avoided - e.g. during the ignition of organic materials, the platinum should not be exposed to unnecessarily high temperatures until carbon combustion is complete.



**Figure 7** Disintegration of Pt wire exposed to carbon at high temperatures.

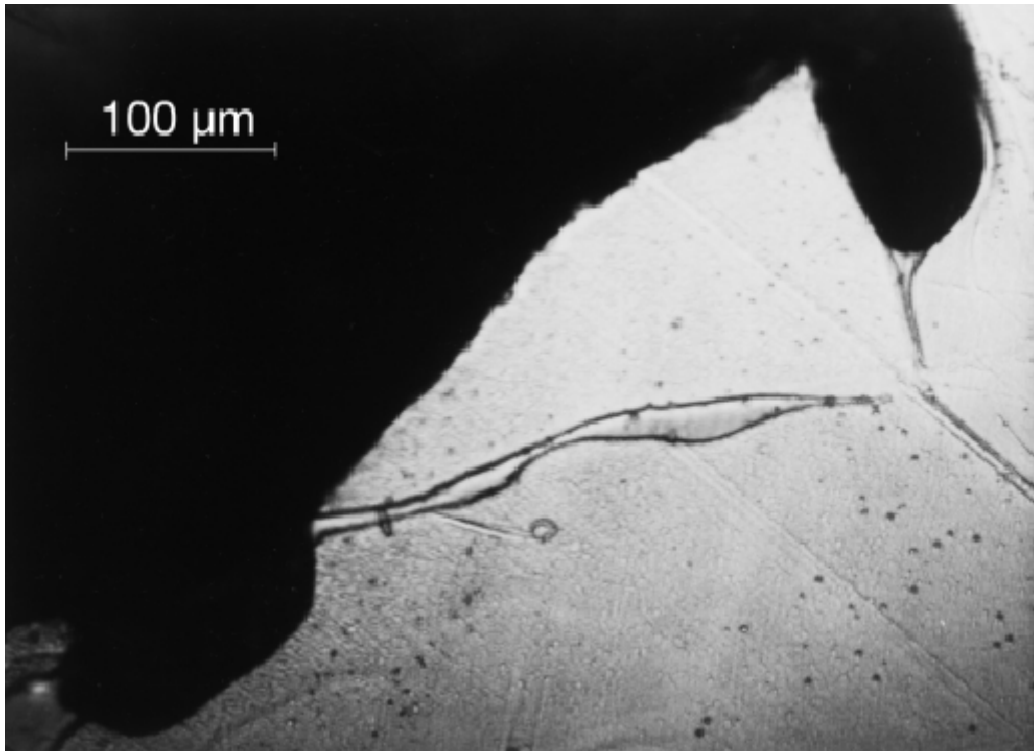
## Phosphorus



**Figure 8** Partial phase diagram of the Pt-P system.

Phosphorus is one of the classical platinum poisons with one of the lowest eutectic temperatures (588°C, Figure 8). Fortunately, phosphorus in most samples is present as a phosphate rather than in its elemental state. Phosphates do not usually cause catastrophic

corrosion but lead to a progressive surface roughening and mechanical embrittlement: Figure 9 shows the formation of brittle platinum phosphide at the grain boundary of platinum exposed to a phosphate glass melt [5].



**Figure 9** Brittle, low melting Pt phosphide at grain boundary of platinum after exposure to a phosphate glass melt [4].

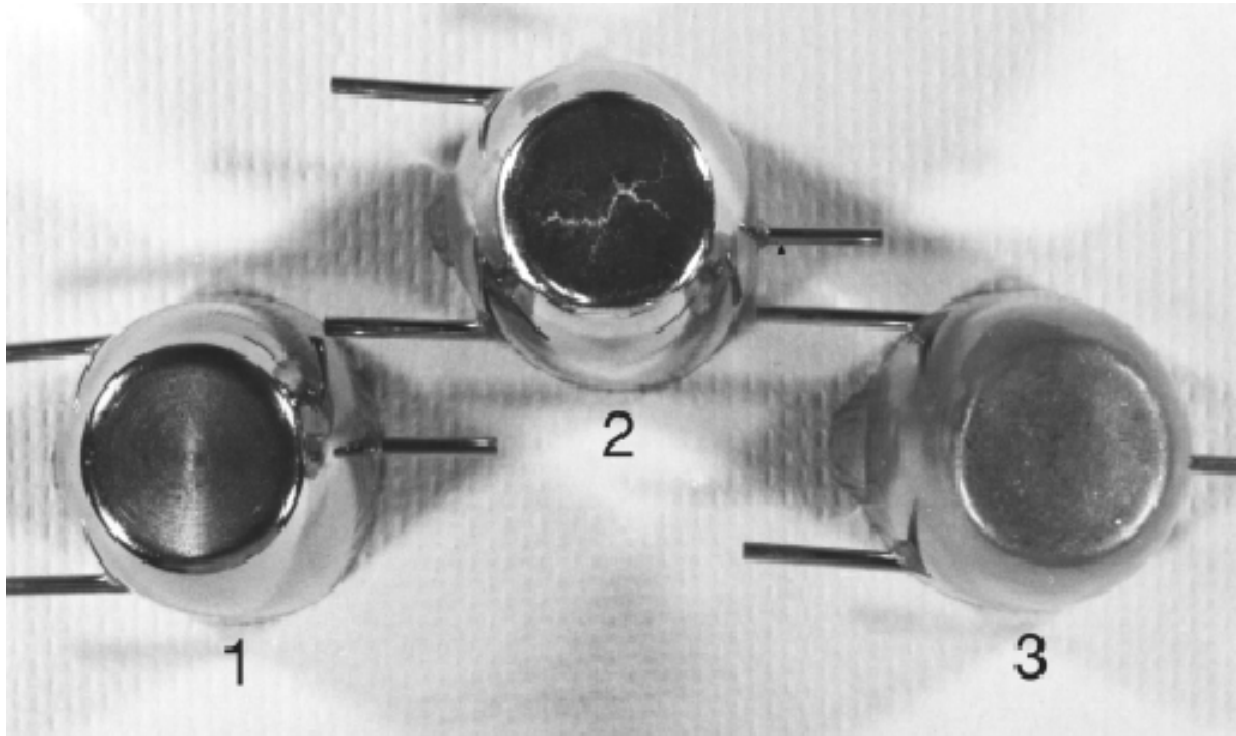
These corrosive effects can be minimised in crucibles for XRF sample preparation by ensuring that conditions are highly oxidising during the melting cycle, by keeping the melt temperature as low as possible and by mixing the sample with the flux in order to dilute the phosphorus-containing sample before it contacts the platinum.

The ignition of cereals and other foodstuffs containing phosphorus is best carried out in dishes of Au-10%Pt which is not prone to phosphorus corrosion. However, this alloy has lower mechanical strength and a considerably lower melting point than the platinum-base alloys and it is recommended not to heat it above about 900°C.

## Sulphur

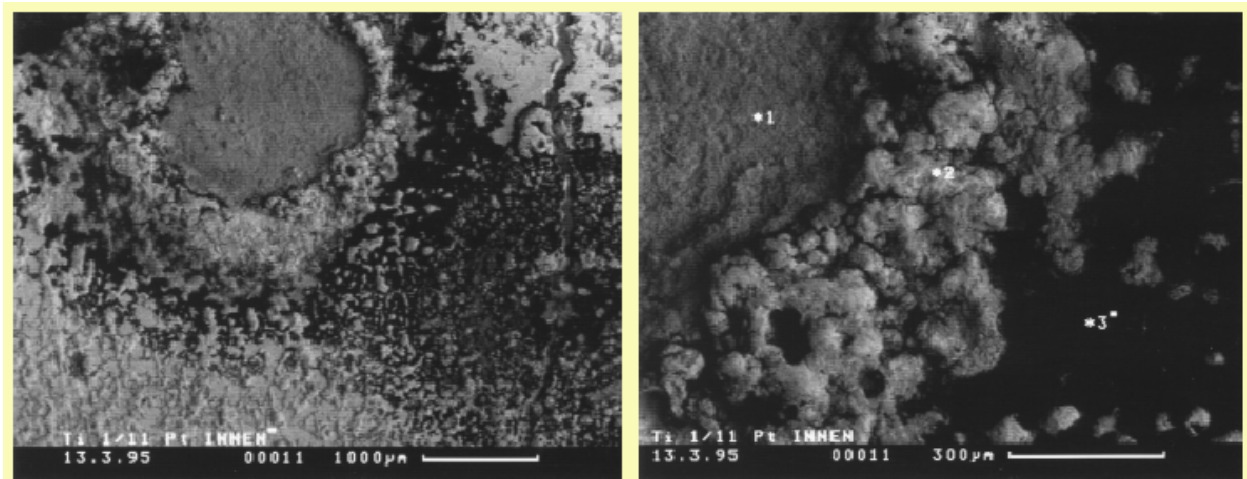
Whereas sulphur is relatively harmless in the form of sulphates, sulphides can cause serious embrittlement of platinum crucibles. Figure 10 is a photograph showing the bottoms of three crucibles. Crucibles 1 and 2 had been used for the preparation of XRF samples of blast-furnace slag containing 1 - 2% S with lithium tetraborate flux. After 27 samples the crucible was still intact (No. 1) showing only an abnormal degree of roughness on the inner surface. However, after 50 cycles the crucible failed by brittle cracking over the whole base. Similar crucibles used for low-sulphur samples, e.g. cement (No. 3) or steel slags, commonly achieve many hundreds of cycles.





**Figure 10** Cracking of pt-5%Au crucibles caused by 1 – 2% sulphur in blast furnace slag:  
 1) 27 slag samples – no cracking  
 2) 50 slag samples – severe cracking  
 3) 650 cement samples (no sulphur) – no cracking.

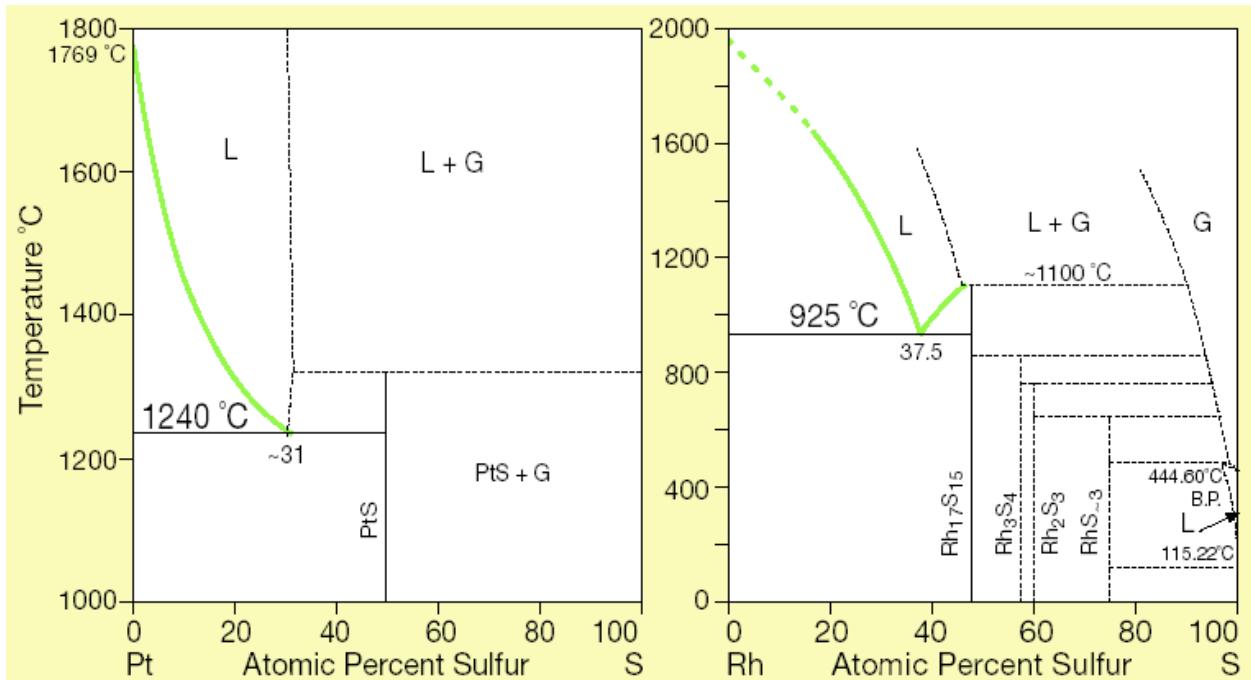
Figure 11 shows localised melting of a platinum crucible which was accidentally contaminated with sulphur when the analyst did not expect this element in the sample.



**Figure 11** Localised melting of Pt crucible due to accidental sulphur contamination.

The melting has been caused by the formation of a Pt-S eutectic with a melting point of 1240°C (Figure 12, left). As this temperature is considerably higher than the melting points of the eutectics described above, it is easier to avoid catastrophic corrosion failure by sulphur than in the case of other platinum poisons. We recommend using separate crucibles for the fusion of samples suspected of containing sulphur to minimise the risk of damage to crucibles which would otherwise be usable for very many sample preparations.

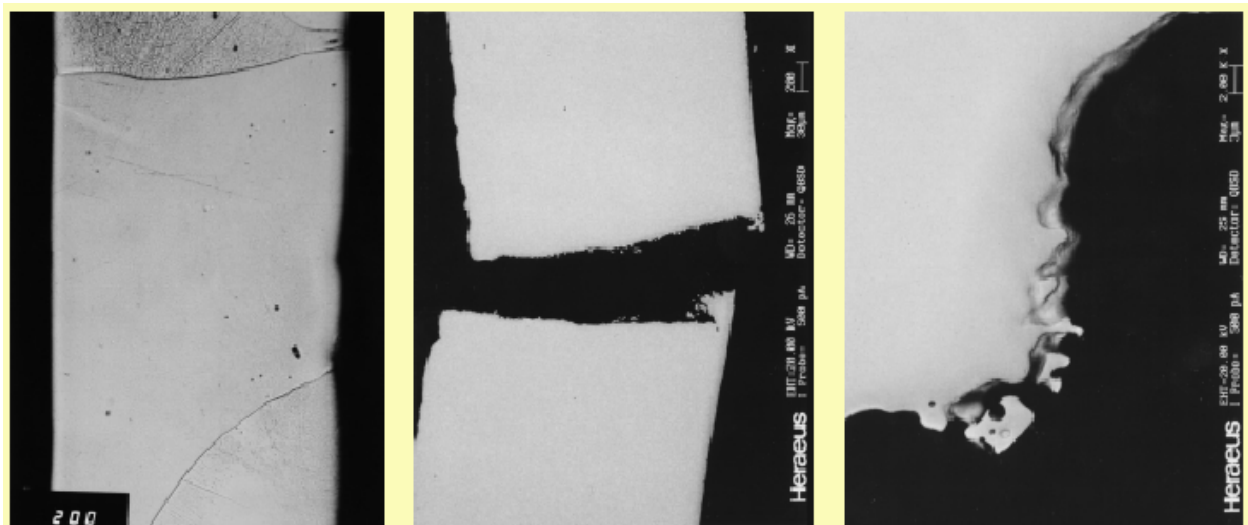
Platinum alloys containing rhodium are particularly prone to corrosive attack by sulphur because the Rh-S eutectic melts at only 925°C (Figure 12, right).



**Figure 12** Comparison of the eutectics in the Pt-S and Rh-S systems.

## Copper

Copper is not a platinum poison in the usual sense. However, copper oxides have only limited thermodynamic stability and great care must be taken to ensure that any copper present in samples is fully oxidised during the preparation treatment. Figure 13 shows the effect of inadequate copper oxidation. The sample preparation had been carried out at a very high temperature, as can be seen from the coarse grain structure in the base of the crucible, with grain boundaries across the whole thickness (Figure 13a, left).

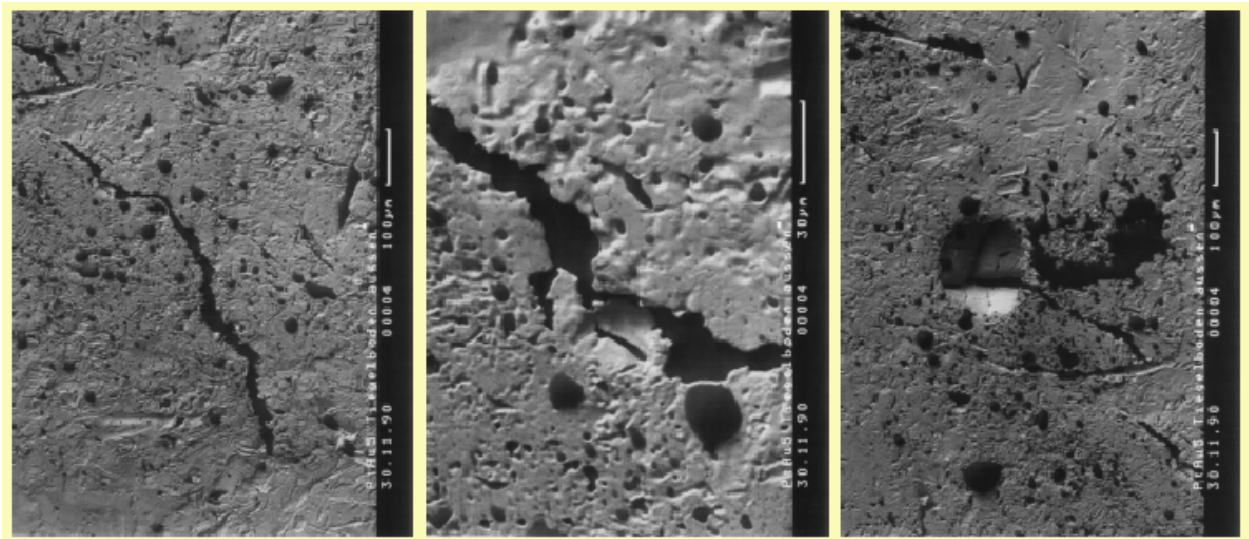


**Figure 13** Grain growth and local melting of Pt-5%Au crucible after fusion of copper oxide samples with carbon contamination.

Some of the grain boundaries had separated in a manner which appeared initially to be brittle fracture (Figure 13b, middle). However, closer examination showed the presence of a film rich in copper at the grain boundaries which had melted during the fusion operations (Figure 13c, right).

## Careless Handling

One of the most common causes of premature failure of platinum crucibles is careless handling. Figure 14 shows pitting and cracking of a Pt-5%Au crucible used for the fusion of china clay samples. The samples contain no significant quantities of platinum poisons and sample preparation was carried out under suitably oxidising conditions at moderate temperatures (approx. 1100°C). The damage in this case has resulted from touching the crucible with bare hands, placing the crucible on dusty surfaces and insufficient cleaning between preparation cycles. Within a relatively small number of cycles the outer surface was covered with very many firmly adhering lithium tetraborate droplets which served as nuclei for pits and subsequent cracks. Crucibles and dishes should only be gripped with platinum-tipped tongs. Furthermore, the practice of heating platinum in a Bunsen burner to clean it should be avoided. Although platinum can be made to appear clean in this way the impurities on the surface tend to diffuse into the platinum causing serious damage.



**Figure 14** Surface damage and cracking of Pt-5%Au crucible caused by careless handling.

## OXIDATION CONDITIONS

As the above case histories show, the most important measure to achieve long service life from platinum utensils is - apart from “good housekeeping” - to ensure sufficiently oxidising conditions both outside and inside crucibles and dishes.

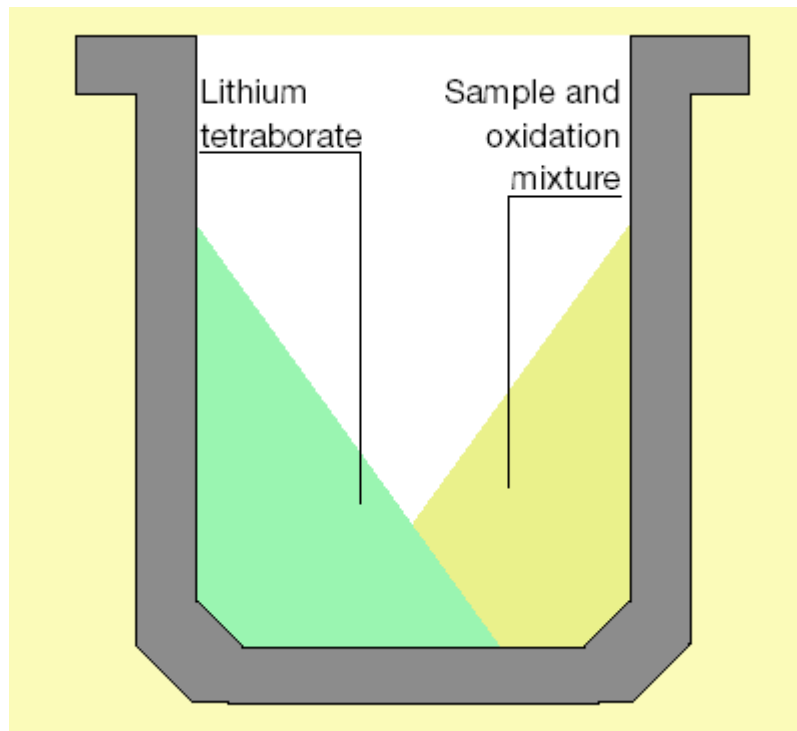
For the outside of the crucible it is usually adequate to prevent the platinum coming into contact with unburnt gas in burner flames and to avoid contamination with silicon carbide or carbon.

The inside of the crucible can, however, be more difficult to protect, especially if samples containing both poisons and carbon have to be fused. Examples are ferro-alloys (in particular ferro-silicon), carbides (in particular grinding media containing silicon carbide), active charcoal, spent catalysts from oil refineries. A number of procedures have been developed which permit the preparation of XRF samples from these materials in platinum crucibles, e.g. [7, 8].

Rutherford [7] describes a process for oxidising and fusing ferro-alloys in a furnace by first

forming a protective wall of lithium tetraborate on the inside surface of the crucible. The finely ground sample is first oxidised by treatment under flowing air and then by addition of lithium carbonate at temperatures below the melting point of the lithium tetraborate wall. Subsequently, the crucible is transferred to a furnace at 1200°C to complete the fusion process.

Petin et al. [8] describe an elegant technique for carrying out a combined oxidation/fusion treatment. Figure 15 shows the principle of this technique.



**Figure 15** Crucible charging for fusion of ferro-alloy samples according to Petin et al. [6].

A low-melting oxidation mixture is prepared comprising: 1.25 g nitrate mixture (60%  $\text{NaNO}_3$  + 20%  $\text{KNO}_3$  + 20%  $\text{Sr}(\text{NO}_3)_2$ ) + 2 g  $\text{Na}_2\text{CO}_3$  + 1.5 g  $\text{Li}_2\text{B}_4\text{O}_7$ . The sample (250 mg) is mixed with this oxidation mixture and then added to the crucible on top of the lithium tetraborate. The oxidation mixture is composed in such a way that fusion starts and the particles of sample are encapsulated in a layer of molten salt before the nitrates decompose, thus protecting the platinum from contact with the sample. The nitrates are chosen to decompose over a wide range of temperature starting with  $\text{NaNO}_3$  at 380°C and continuing to  $\text{Sr}(\text{NO}_3)_2$  at > 1100°C to ensure that the oxidant has not fully decomposed before the sample has been oxidised and taken into solution in the lithium tetraborate flux.

Although techniques such as those described above are only required for strongly reducing samples, they demonstrate clearly that, with appropriate care, platinum crucibles can be used reliably for the preparation of a very wide variety of XRF samples.

## THE MAIN PRECAUTIONS

The main precautions to be observed when using platinum utensils in the analysis laboratory are:

- Avoid reducing gas flames
- Never place crucibles on SiC trays
- Keep crucibles clear of SiC heating elements
- Ensure strongly oxidising conditions for samples containing carbon (ferro-alloys, carbides, etc.)
- Never touch crucibles with bare hands
- Use Pt-clad tongs
- Minimise mechanical damage to crucibles
- Never heat in a Bunsen burner to clean
- Use separate crucibles for samples containing known poisons (S, P, Pb, etc.).

## CHOOSING THE BEST PLATINUM ALLOY

There is a range of platinum alloys available for the various applications in the analysis laboratory. The main points to be considered in selecting the alloy are summarised below:

- Chemically pure Pt for simple routine preparations
- Pt-5%Au for reduced wetting
- Pt-5%Au DPH for high temperatures and in presence of unavoidable poisons
- Au-10%Pt if phosphorus unavoidable, but temperature limited to approx. 900°C
- Never use Rh-containing alloys if sulphur present.

## References

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6. J. Petin, A. Wagner and F. Bentz "Combination of Oxidation and Melt Treatment for a Rapid Preparation of Metallic and Other Oxidising Samples for X-ray Fluorescence Analysis", *Steel Research* **56** (1985) pp. 215-218.