

Handling Platinum Equipment

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However, when using platinum equipment it must be remembered that even platinum is not a universal wonder material which is resistant to everything. For instance, damage can result from elements which form low-melting phases with platinum, from very aggressive chemical media or from evaporation.

Damage to platinum by tin, lead and bismuth

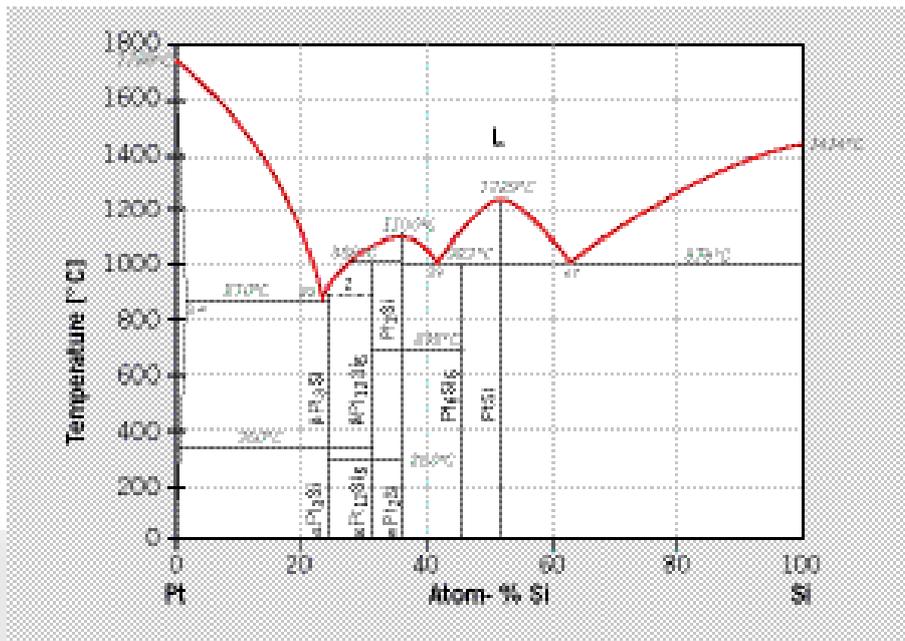
The formation of alloys with most metals leads to a reduction in the melting point of platinum, especially in the case of the low-melting metals tin, lead and bismuth. Thus, it is possible that even with low concentrations and at moderate temperatures the melting point can be exceeded in localised areas, which results in the destruction of the apparatus (see Table "Melting Temperatures of Low-Melting Precious Metal Alloys" on page 30).

It should be noted that, due to thermal decomposition and especially under reducing conditions, chemical compounds can dissociate and release these detrimental elements. Therefore, to avoid reduction, heating processes and ignitions should be carried out in oxidising atmospheres, i.e. in open crucibles. In this context it should be especially noted that hydrogen may be absorbed by platinum at 400° C, diffuse through the walls of equipment at higher temperatures and can reduce the material contained within.

Damage to platinum by carbon

Apart from reducing conditions in the environment, the presence of carbon or organic substances can also result in the reduction of chemical compounds and thus the release of elements which can damage platinum. Carbon itself can also cause damage to the structural integrity of platinum. Please take special care to adjust the flame when working with bunsen burners and ensure that gas-heated fusion equipment is adjusted to an oxygen-rich flame.

Phase diagram of the Pt-Si system

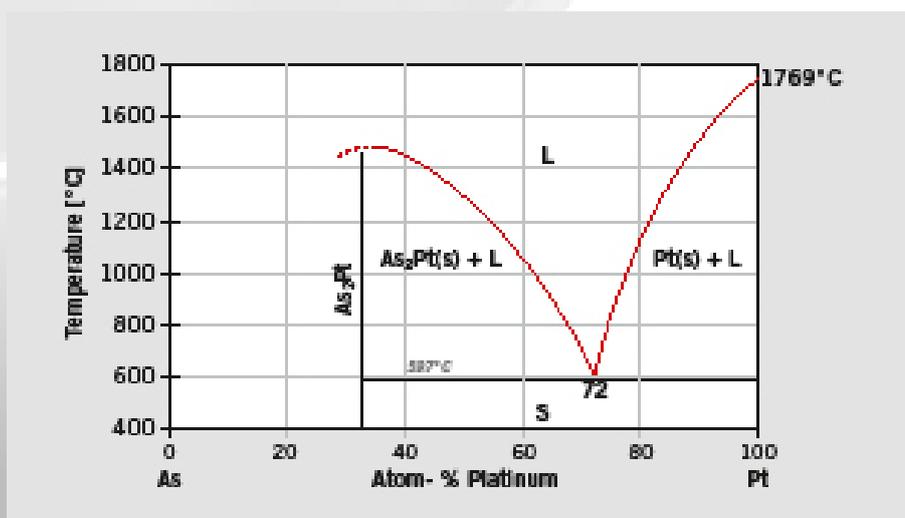


Damage to platinum by silicon, lead, antimony and phosphorus

A platinum alloy with a low melting point is formed when the elements silicon, antimony or arsenic are present in very small quantities. The alloy formation occurs preferentially at the grain boundaries. The embrittlement which is associated with this process can lead to the formation of cracks.

The effects are particularly hazardous when organic matter containing phosphorus is ignited, e.g. in flour ignition. Damage to apparatus by silicon corrosion can occur during heat treatment in furnaces with silicon carbide heating elements. Spalling of the exposed silicon carbide rods can lead to silicon being deposited on the platinum equipment or on the furnace floor which then diffuses into the platinum equipment.

Phase diagram of the Pt-As system



Damage to platinum by sulphur

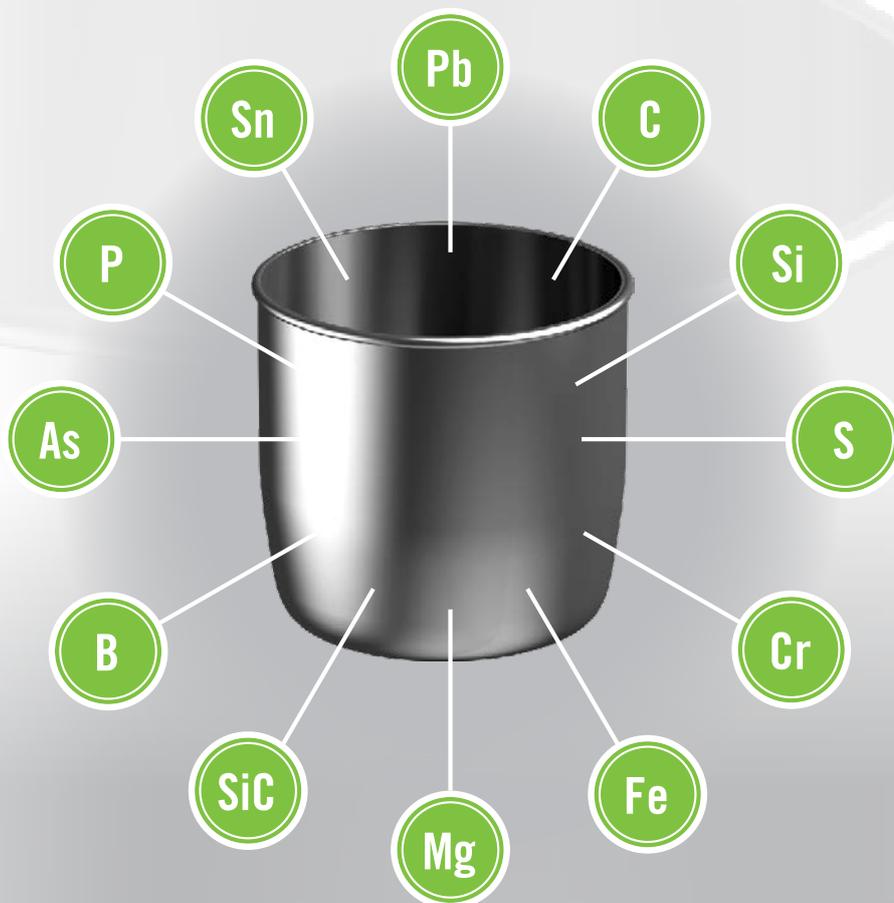
Sulphur can also cause platinum corrosion. This problem is encountered, for example, when preparing fused tablets for XRF from samples containing high levels of sulphur in the form of sulphides.

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Further potential hazards

A further potential hazard is contamination of the crucible on its external surface, for instance by placing it on a dirty surface. At elevated temperatures the contamination can then lead to one of the damage mechanisms described above. We recommend, therefore, that only crucible tongs or tweezers whose tips are protected with platinum should be used when handling hot crucibles. The crucible tongs must not be immersed into acids and alkalis beyond the platinum shoes, because of the danger that liquid could penetrate between the tongs and the shoe resulting in corrosion from within.

Naturally, care must also be taken that the triangles on which the laboratory equipment is usually heated are not contaminated by corrosive materials such as heavy-metal salts, phosphates, etc. Unprotected iron triangles or wire gauzes should not be used, but only those with platinum/iridium buttons, or those made of platinum wires. Alternatively non-precious metal wire triangles which are protected by oxide ceramic tubes at contact points may be used. Contact with ferrous materials should be generally avoided.



Heraeus has prepared a summary of the most important precautionary measures using actual case histories.¹⁾

The phenomenon which is commonly known as “platinum corrosion” is not corrosion in the usual sense of aqueous corrosion, rusting, etc. It is usually the formation of a compound which results from a reaction of platinum with another element. It has a low melting point, and results in the formation of a eutectic with an even lower melting point between the compound and the platinum.

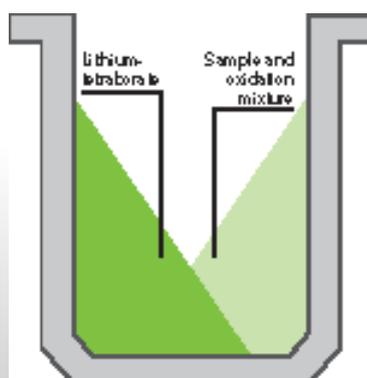
The inner surface of the crucible is more difficult to protect especially when samples to be prepared contain both “poisons” and carbon. Examples are ferro-alloys (ferro-silicon), carbides (grinding media containing silicon carbide), active carbon, spent catalysts from oil refineries.

Petin et al.²⁾ describe an elegant procedure for carrying out a combined oxidation-fusion treatment:

1.25 g of the following low melting oxidation mixture is prepared:

(60% NaNO_3 + 20% KNO_3 20% $\text{Sr}(\text{NO}_3)_2$) + 2 g Na_2CO_3 + 1.5 g $\text{Li}_2\text{B}_4\text{O}_7$, $\text{Li}_2\text{B}_4\text{O}_7$. The sample (250 mg) is mixed with this oxidation mixture and then added to the lithium tetraborate which is in the crucible. The oxidation mixture is composed in such a way that at the beginning of the fusion the components of the sample are encapsulated in a layer of molten salt before the nitrates decompose. In this way the platinum is protected from contact with the sample. The nitrates are selected so that they decompose over a broad temperature range starting with NaNO_3 at 380°C and continues up to $\text{Sr}(\text{NO}_3)_2$ at > 1100°C, in order to ensure that the oxidation media do not completely decompose before the sample oxidises and dissolves in the lithium tetraborate.

Although the techniques described above are only necessary for strongly reducing samples, they clearly show that, with appropriate care, platinum crucibles can be used reliably for the fusion of a very broad variety of XRF samples.



Charging a crucible for the fusion of ferro-alloy samples (Petin et al.²⁾)

The main precautionary measures

The main precautionary measures which must be observed when platinum equipment is used in an analytical laboratory are:

- Never touch the crucible with your bare hands
- Use Pt clad tongs
- Avoid mechanical damage of the crucibles
- Use separate crucibles for samples which are known to contain hazardous impurities (S, P, Pb, etc.)
- Never place the crucible on an SiC support
- Take care to keep sufficient distance between the crucibles and SiC heating elements
- Ensure strongly oxidising conditions for samples containing carbon (ferro-alloys, carbides, etc.)

1) J. Merker, F. Schölz, D. F. Lupton: “Correct Use of Platinum in the XRF Laboratory”, “Tricks of the Trade” at the 19th Durham Conference on X-ray Analysis, University of Durham, England, 18 – 21 September 1995

2) 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), 215-218

Damage to platinum by salts, halogen compounds and acids

Less critical than the damage mechanisms described above is corrosion due to salts, halogen compounds or acids. Normally the advantages of using platinum crucibles are greater than the risk of damage by corrosion. At room temperature platinum only dissolves slowly in aqua regia. Amongst the most severe effects are the melting of alkali metal hydroxides and alkali cyanides at high temperatures. Potassium compounds react more strongly than sodium compounds in such fusion preparations. Alkalis have the effect of being oxygen carriers and oxidise platinum to yellow-brown platinum oxide. For this reason molten salt preparations, above all in soda and soda-potash fusions, should always be carried out in covered crucibles. In this way the carbon dioxide released during the fusion can be retained as a protective gas over the melt and prevents the crucible from oxidation.

Evaporation losses

It is not always appreciated that a thin oxide film forms on platinum in air at room temperature and evaporates at elevated temperatures. The platinum loss which occurs as a result can lead to significant damage over very long operating periods, e.g. at 900° C in air. This effect can be counteracted to a limited extent by alloying with a few percent of rhodium.

Platinum-iridium alloys with higher iridium contents, on the other hand, suffer from evaporation losses which are very much greater than for other platinum alloys when exposed to air for long periods.³⁾

Cleaning crucibles

Crucibles and dishes of platinum or platinum alloys are cleaned by boiling in a suitable solvent. Platinum utensils can be cleaned very thoroughly by melting potassium pyrophosphate in them. For the removal of substances which have alloyed with the surface we recommend that the apparatus be scoured with alumina powder.

The use of grinding media containing carbon (e.g. SiC) should be avoided at all costs. Any remaining alumina residues should be removed with a hydrofluoric acid treatment. Contaminated utensils may not, under any circumstances, be cleaned by heating, because the impurities might thereby diffuse into the platinum.

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3) H. Jehn: "High Temperature Behaviour of Pt-Group Metals in Oxidizing Atmospheres", Journal of the Less Common Metals, 100 (1984), 321