

IN SWITZERLAND

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ASSAYING GOLD



Although centuries old, the cupellation or fire assay method for determining the fineness (purity) of gold articles is highly accurate. It is extensively used not only for hallmarking purposes but also in the gold mining industry, and for the control of the purity of the world's bullion supply. In this article, the authors give a step by step account of the way in which the test is carried out in the Swiss federal offices for the control of precious metals.

Introduction

We gave an account of the assaying of precious metals by the touchstone method, a relatively quick and simple procedure for the determination of

fineness but which, at best, cannot enable accuracies better than 10 to 20 parts per thousand to be achieved*.

The cupellation assay method described here, although somewhat more expensive to carry out, is much more exact, being accurate

to 0.1 parts per thousand. It is the classical, standard technique used throughout the world for the reliable and precise determination of the gold content of jewellery and other gold items. It is today still carried out in essentially the same way as in antiquity. The method was further improved during the Middle Ages through the use of nitric acid and brought to its present state of development thanks to advances in chemistry and modern technology.

The first mention of an early form of assaying by cupellation goes back to Babylonian times (tablets of cuneiform script from Tel-el-Amarna, Egypt, dating from about 1380 BC). An allusion to the technique is made in the Bible (Jer. 6:27-30) and it was known to the Egyptians, Phoenicians, Greeks and Romans.

Although it is a very old method of assaying, cupellation is able to provide the necessary precision in almost all cases. It is economic, relatively simple to carry out and (most important), as far as accuracy is concerned, is at least as good as and frequently better than modern techniques using expensive optical or X-ray fluorescent spectrophotometers.

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Fields of Application

The cupellation assay is suitable for the determination of the fineness of all precious metal alloys in solid form (such as ingots or other cast products, semi-finished products, finished articles, etc.).

For the assay of precious metal ores, cinders, dross, sludge, slag, sweepings, etc., non-metallic impurities must be removed before cupellation. This is usually done by heating the material with borax and lead, which results in the pre-

vious metals being concentrated in the lead.

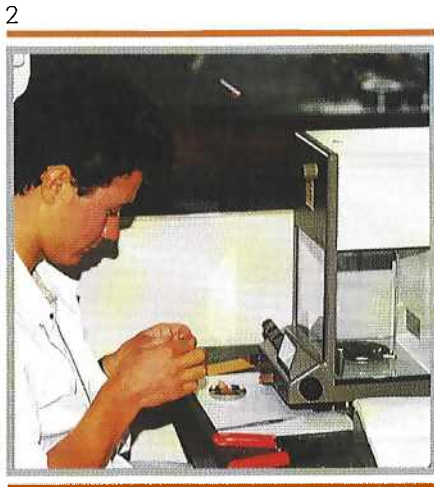
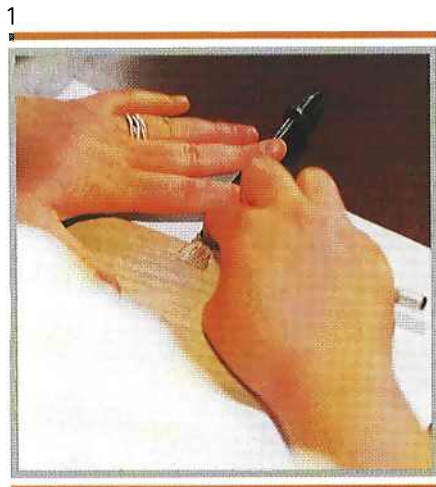
In principle, the cupellation assay enables the perspective contents of gold and silver in their alloys to be found; in combination with gravimetric analysis techniques, it is also possible in principle to determine gold, silver, platinum or palladium in the presence of the other three.

In this account, however, only the assay of gold by cupellation is described.

Figure 1 Using a triangular scraper to remove traces of solder from the region of an article from which the sample for analysis is to be taken

Figure 2 Weighing the sample on an analytical balance

Figure 3 Wrapping gold sample and parting silver in lead foil



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Basic Principles of the Cupellation Assay

The cupellation assay (fire assay) is based on the fact that unlike base metals, noble metals like gold, platinum and silver essentially do not oxidise at high temperatures. The sample to be analyzed is therefore melted together with lead at 1150°C. All the base metals present in the alloy, as well as the lead that was added to assist melting of the sample and extraction of base metals from it, combine with the oxygen in the air, and the oxides thus formed are absorbed by the porous crucible or cupel. The gold and other noble metals remain behind as a pellet or button at the bottom of the crucible. Finally, the silver is separated from the gold by dissolving in nitric acid.

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Description of the Cupellation Assay for Gold

A. Preliminary Assay

As will be explained later, for var-

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ious reasons it is essential that we know as accurately as possible the composition of the material to be assayed before actually performing the analysis. An expertly performed touchstone assay (see AURUM 24) is therefore an indispensable first step if little is known about the sample. In addition to the gold content, we are also interested in whether the alloy contains silver and, if so, approximately how much. In the case of items in white golds, we must also know whether the alloy is a nickel- or palladium-based white gold.

B. Sampling

The material required for the assay – at most 250 milligrams – is removed from the articles to be assayed by cutting, scraping, sawing or drilling (sampling). Since the object of the assay is to find out the fineness of the alloy from which the bulk of the article is made, soldered regions must be avoided, and surface coatings (gilding, rhodium plate, etc.), traces of soldering and other impurities must be filed off or scraped off with a triangular scraper before sampling (Figure 1).

C. Weighing of the Material to be Assayed

Between 245 and 255 mg (milligrams) of sample is weighed out on a high precision analytical balance (Figure 2) to an accuracy of at least 0.02 mg (the most modern analytical balances have a sensitivity of one millionth of a gram). The result is noted and the weighed material is packed in a piece of thin lead foil weighing 2 g that has been previously folded into an envelope. Also inserted in this envelope is the 'inquartation' or parting silver (Figure 3), i.e. the amount of additional high purity silver required to bring the ratio of gold to silver to

Figure 4 Cupellation furnace

Figure 5 Temperature controller used for maintaining cupellation furnace at 1150°C

about 1:3 (after allowing for the silver content of the alloy to be assayed). For the weighing of the silver, whose role will be explained later, an accuracy of ± 10 per cent is sufficient, since later in the process it is dissolved out again.

The envelope of lead foil is now closed; more lead to assist melting of the sample is added in the form of small blocks of 1, 2, 3 or 4 g.

D. The Amount of Lead Required

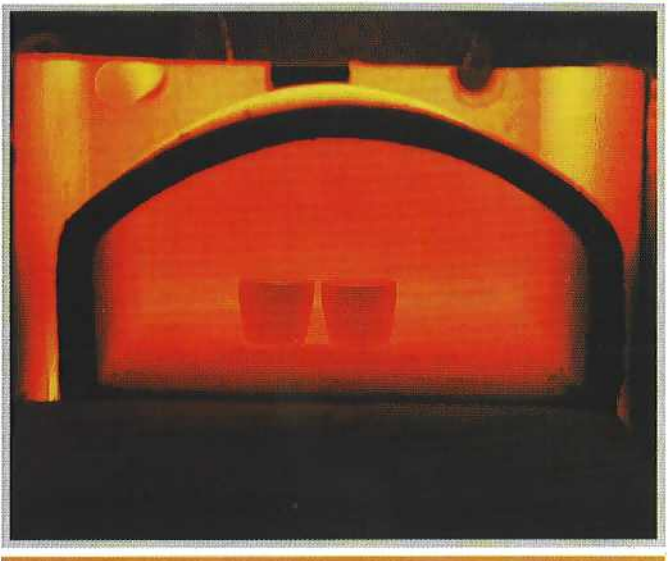
The amount of pure lead (free from any traces of precious metals) that must be added is proportional to the base metal content of the sample. When assaying 18 carat yellow gold, for example, about 4-5 g of lead is required for a 250 mg sample. For a 14 carat alloy sample, the corresponding amount of lead is about 7 g.

E. The Cupellation, or Refining Process

During the preliminary tests and sampling, the assay furnace, as well as the porous crucible or cupel, which is usually made of magnesium oxide, have been allowed to heat up to the cupellation temperature of 1150°C (Figures 4-5). The size of the cupel used depends on

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the amount of base metals and added lead to be eliminated during the cupellation process.

The assay sample in its lead envelope together with the required amount of additional lead are now carefully placed in the pre-heated crucible in the furnace, using long tweezers or tongs (Figure 6). Unless the furnace is equipped with an air circulation system, the door should be left partly open to allow entry of oxygen from the air.

As soon as the sample has melted, the cupellation process begins. The base metals in the gold alloy, as well as the added lead, combine in the molten state with oxygen in the air to form oxides (Figure 7). A visible first sign of the process taking place is the occurrence of oil-like drops of lead oxide that float to the edge of the cupel and are absorbed. Towards the end of the separation, these droplets completely disappear and are replaced by a rainbow coloured opalescent lead oxide skin over the remaining metal. In the end this skin also disappears and the melt remains bright and still – an indication that the cupellation process has run its course.

The cupel with the molten metal in it is now removed from the furnace using tongs and left to cool on a metal plate (Figure 8). As it solidifies, the melt first glows for a few moments as a result of the re-

Figure 6 Placing lead envelope containing gold sample and parting silver in pre-heated cupel

Figure 7 The cupellation process begins as soon as the sample has melted

lease of its latent heat of solidification, and then takes on a matt appearance.

F. Separation of Gold from Silver

a) The Role of the Added Silver

At this point, the reason for adding silver to the sample (parting silver) needs to be explained. The cupellation process has removed the base metals from the original alloy. In the next step, the silver in it must be separated from the gold using nitric acid. However, without the addition of the parting, or inquartation silver, the excess of gold in the sample would prevent the silver from being dissolved out. The parting silver changes the gold/silver ratio so that there is three times as much silver as gold in the metal. This ensures that the silver is completely eliminated during the parting step and that the gold is left behind in a compact state.

b) Handling of the Gold-Silver Bead Before Parting

After cupellation, the silver bead containing all the original gold is removed with tongs from the cupel, which has been coloured a dirty green by the absorbed base metal oxides (Figure 9). The bead is freed from any adhering crucible sand using a stiff brush with natural or synthetic bristles (Figure 10).

In order to facilitate attack by the parting acid, the bead is first flattened by hammering to a disk of about 10 mm in diameter (Figure 11). After annealing, the disk is rolled down to give a strip of about 0.12 mm in thickness (Figures 12-13) which is also annealed to enable it to be coiled up into an approximately B-shaped 'scroll', or 'cornet' (Figure 17). Care must be taken to ensure that the inner surfaces of the metal do not touch, since otherwise the acid attack would be locally hampered. Annealing is done at 800-1000 °C simply with a torch or bunsen burner (Figures 14-15).

c) The Parting Process

Depending on the gold content of the sample, the parting process involves two or three dissolution steps using nitric acid.

In the first step (Figure 18), the cornet is put in a flask containing 25-30 ml of cold nitric acid of relative density 1.18 (22° Bé) and a

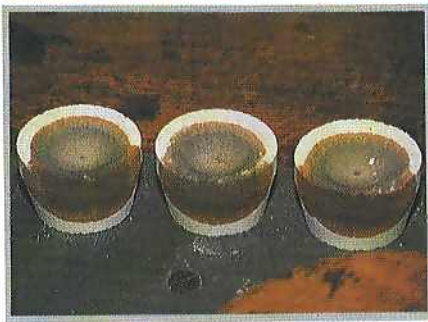
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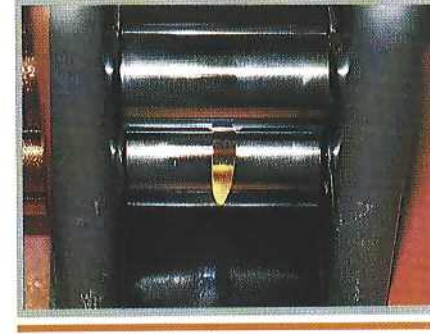
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'boiling stone' (these are chips of pumice, coke, calcined peas or peppercorns that prevent bumping and splashing of the acid during boiling). The flask is heated slowly to the boiling point and held at temperature for 10 minutes. The acid is then decanted, taking care to ensure that the boiling stone remains in the flask (Figure 20).

For the second step, the flask is again filled with 25-30 ml of nitric acid, but this time of relative density 1.284 (32° Bé), and again heated to the boiling point where it is held for 10 minutes.

If the estimated fineness of the sample is greater than 800/000, then the second step must be repeated at least once more to make certain that all the silver has been dissolved out.

At the end of the parting process, the acid is decanted together with the boiling stones (Figure 20) and the flask is washed two or three times with distilled water and then filled to the brim with cold water (Figure 21). Next, a crucible for melting gold is inverted over the mouth of the flask and then the assembly is turned over so that the cornet sinks into the crucible (Fig-

ure 22). By means of a brief tilting movement, the flask and the crucible are separated and the water in the crucible is removed by decanting (Figure 23).

G. Annealing the Gold Cornet

The gold cornet, which has a dull brown appearance, is dried together with the crucible by slow heating before being annealed at 800-1000 °C. After annealing, the gold takes on a matt fine-gold colour (Figure 24).

H. Weighing and Fineness Calculation

The annealed gold cornet is carefully weighed on an analytical balance (Figure 25). The result is the weight of fine gold in the sample. A simple calculation of the ratio of the final weight to the original weight, multiplied by 1000, gives the fineness of the sample in parts per thousand.

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The Influence of Alloying Elements on the Gold Assay

Most gold alloys used in jewellery are based on the ternary system gold-silver-copper, although smaller amounts of other metals are often added also. Some of these alloying elements can have a greater or lesser effect on the gold assaying process. A brief account of the most important of these interfering effects is given below, with particular emphasis on the white gold alloy components nickel and palladium.

Figure 8 Cooling down after cupellation

Figure 9 Base metals, in the form of oxides, are absorbed by the porous cupels

Figure 10 Cleaning the gold-silver bead with a stiff brush

Figure 11 Flattening the gold-silver bead

Figure 12 Rolling the flattened bead

Figure 13 Gold-silver strip emerging from rolls

A. Nickel

Nickel is only partially soluble in molten lead and therefore floats to the top of the melt. It frequently remains in the cupel as an unmeltable black scale that can hold back some of the gold. We try to prevent this scale formation by increasing the amount of lead and adding 20-40 mg of copper; if this does not work, the problem is usually solved by reducing the size of the sample (e.g. taking 100 mg instead of 250 mg).

B. Palladium

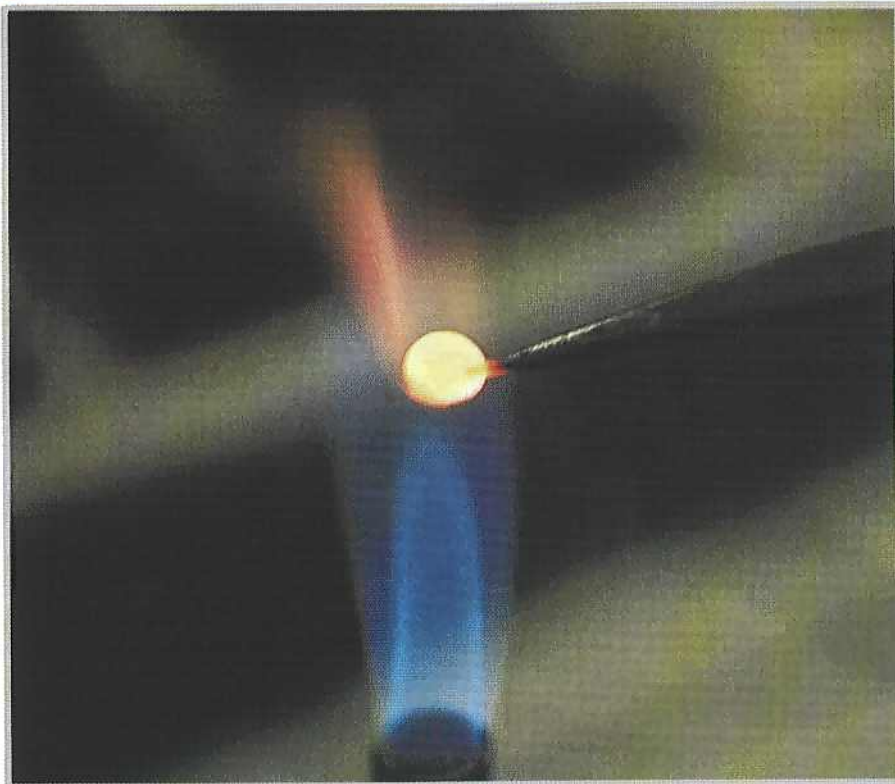
In the cupellation process, any palladium present in the sample is not extracted but remains in the bead. During the parting step, the palladium certainly goes into solution together with the silver, turning the nitric acid a characteristic orange to reddish brown colour. With samples of high palladium content, however, some palladium is retained in the gold cornet, giving erroneous figures for the gold content.

To ensure accuracy, a second cupellation and parting cycle is therefore necessary.

C. Other Elements

Small zinc additions have no effect on the cupellation assay but larger amounts can lead to scale formation with some retention of gold.

In the assay, platinum essentially behaves like palladium. But the other metals of the platinum group – rhodium, iridium and ruthenium – cannot be separated from gold



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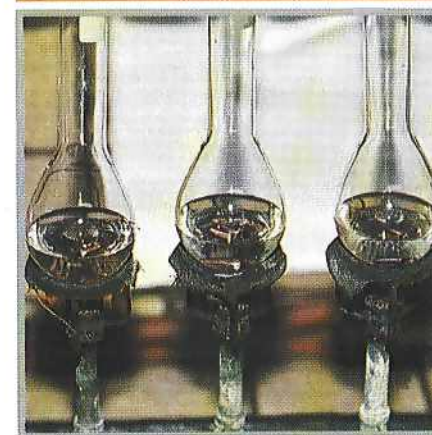
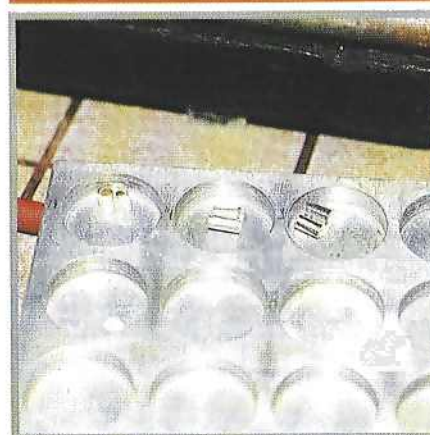
Figure 14 Annealing flattened gold-silver bead

Figure 15 Annealing rolled strip

Figure 16 Coiling strip to produce 'cornet'

Figure 17 Gold-silver cornets in sample tray

Figure 18 Flasks containing cornet and nitric acid ready for the parting step



by the methods described here, and their presence in a sample renders the cupellation assay invalid.

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The Reference Assay

The reference assay is carried out using samples made from pure metals representing as closely as possible the composition of the test sample. A reference assay is always necessary when it is important to determine the fineness with the greatest possible accuracy, since it is subject to the same influences and errors as the assay sample, and provides independent evidence of the accuracy of the assay.

Pure precious metals are used for making up reference samples.

The gold is weighed out very accurately to match as closely as possible the composition of the sample to be analyzed, which has been estimated by touchstone testing. The other alloying elements can be weighed with less precision.

The deficiency or excess of gold in the reference sample, in comparison with its original, known, gold content, is taken into account when calculating the fineness of the assay sample.

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Summary of Assay Operations

The various steps involved in the cupellation or fire assay of gold are summarized in the flowchart on p. 64.

Figure 19 During the parting step, the silver is dissolved out by boiling nitric acid

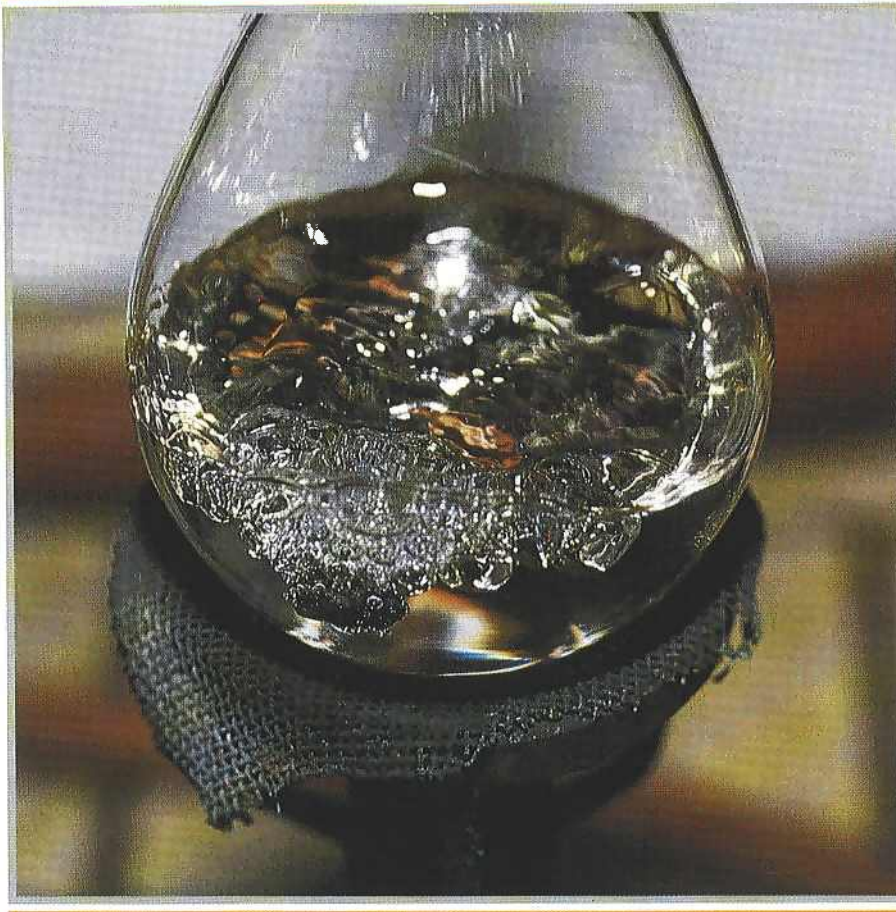
Figure 20 Decanting the acid after the parting step

Figure 21 Washing flask and gold cornet with distilled water

Figure 22 Transferring gold cornet to annealing crucible

Figure 23 Decanting water from crucible containing gold cornet

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Equipment and Materials Required

A. Sample Preparation

Depending on how the material necessary for carrying out the fire assay is to be taken from the article under assay, a saw (hacksaw or jeweller's saw), tin-snips, a triangular scraper or a drill will be needed. For cleaning the surface of the sample, a scraper or needle file is required.

B. Weighing

The most important item of equipment required for carrying out an accurate assay is a good modern analytical balance with a sensitivity of 0.000001 g or better.

A supply of fine silver foil is helpful when weighing out the parting silver, and a handy supply of fine gold, palladium, copper and nickel foil is essential for the preparation of reference samples.

Lead foil is needed for wrapping up the assay sample, and lead pellets or plaquettes in the form of 1, 2 or 4 g pieces should be at hand when additional lead is to be added to the sample.



Tin-snips are used for cutting up the metal foil prior to weighing, whilst a needle file is useful for making slight weight adjustments. The sample itself should not be touched with fingers but should be handled with a pair of tweezers. Before weighing, the sample is freed of dust or other contaminants with a fine camel-hair brush. A glass laboratory specimen dish is very useful for transporting the samples at all stages of the assay procedure. Finally, an electronic calculator is required to facilitate the fineness calculations.

C. Furnace Operations

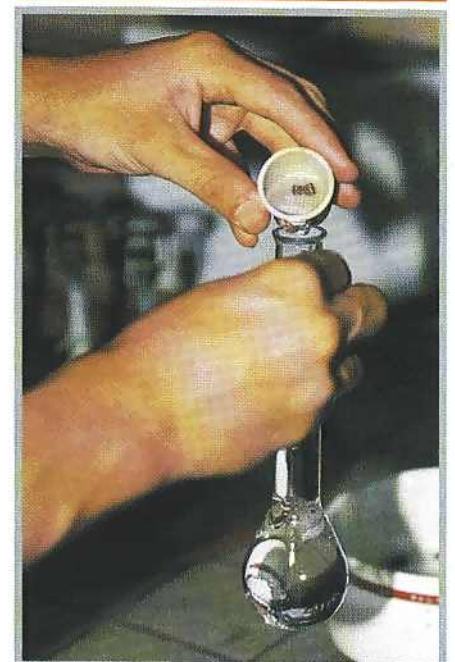
The most important requirement for the assay furnace is that it be lined with materials like fire-brick. Generally, such a furnace has a rectangular base and a flat or semi-circular roof. It should be possible to leave the furnace door open, closed or partly closed as required.

The cupels (crucibles) have the form of a truncated cone with an approximately hemispherical depression for the sample. Originally, they were made of bone ash and leached wood ash but today are mostly of magnesium oxide or magnesite. These can absorb between 60-70 per cent of their weight of molten base metal oxides. The size of the cupels is determined by the quantity of base metal to be driven out and the amount of lead added.

For handling the cupels and putting the samples in them, furnace tongs (cupel tongs) 60-70 cm long are required. They are best used together with high temperature oven gloves.

D. Production of the Cornet

A pair of tweezers is required for removing the silver-gold bead from the cupel, and for cleaning it, a stiff brush (with natural or synthetic bristles). A polished steel anvil and a domed hammer are used for flattening the bead. For rolling, a small



hand- or electrically-powered rolling mill is required.

E. Parting

The parting operation with nitric acid should be carried out only in a well-ventilated fume-cupboard. The gas or electrical heater for the boiling flask must have provision for temperature control.

Nitric acid of relative density 1.18 (22° Bé) and 1.284 (32° Bé), as well as distilled water are necessary for making up the parting acid.

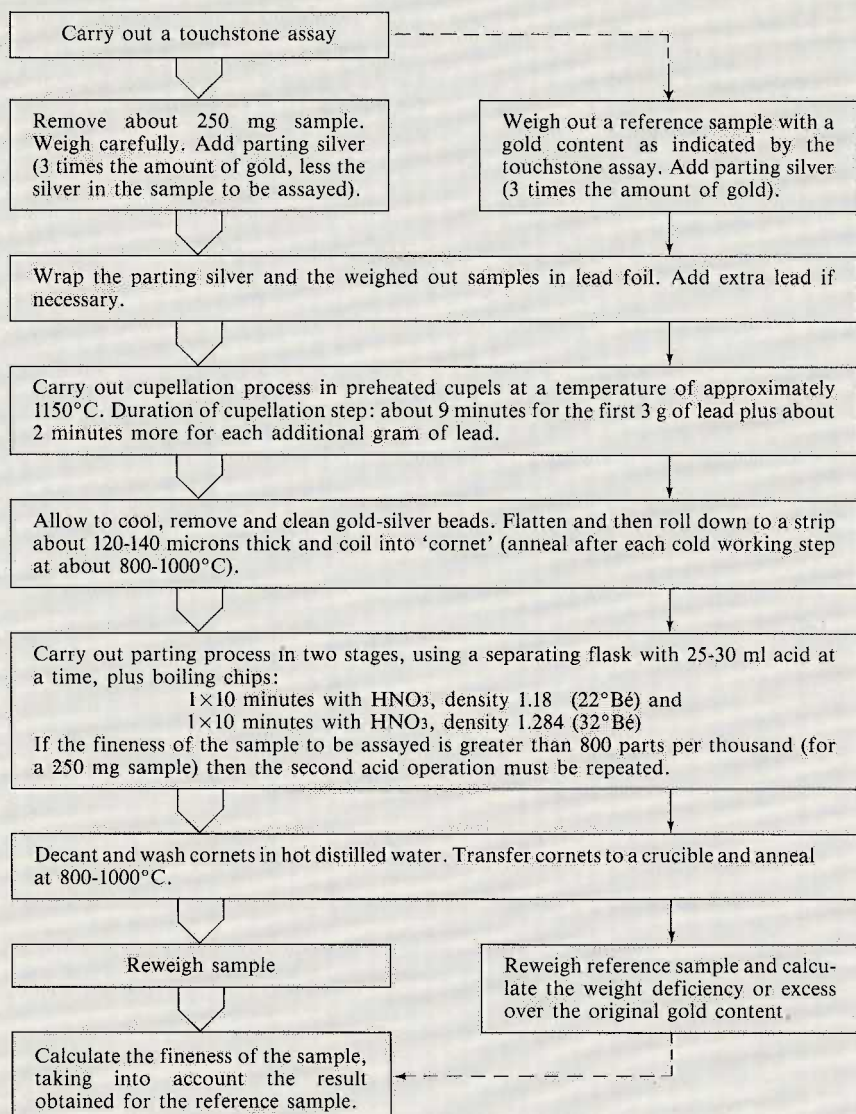
For boiling the cornets in the



Figure 24 Gold cornet before annealing (left) and after annealing (right)

Figure 25 Final weighing of pure gold cornet after the parting step

Flowchart of Operations Involved in the Cupellation Assay for Gold



parting acid, long-necked glass flasks about 20-25 cm long with a pear-shaped bulb at the bottom are required. Boiling stones help to avoid bumping and splashing of the acid during boiling. For manipulating the flasks, wooden tongs are most suitable.

The cornets can be annealed in unglazed fire-clay or quartz crucibles.

A stopwatch is useful for timing the various operations.

Photographs by Urs Bangerter