LBMA Reference Materials Update

By Stewart Murray, Chief Executive, LBMA

The origins of the project go back to the Assaying and Refining Seminar held in London in March 2007. There it was agreed that the LBMA should evaluate the possible demand for solid samples reference materials for use in spectrographic analysis.

After carrying out a survey of all Good Delivery List refiners, it was clear that there was sufficient demand to justify such a project, and a Steering Committee was established under the Chairmanship of Dr. Mike Hinds of the Royal Canadian Mint to guide the project to completion. During the remainder of 2007, the foundations of the project were laid. This included establishing the size and composition of the materials, the companies who would be involved in manufacturing them and a larger group of companies which would be involved in analysing the materials once they had been manufactured. Most importantly, the Steering Committee also had to set the price of the materials that would cover the costs of manufacture based on the advance orders which were received.

In early 2008, the Steering Committee appointed the manufacturers of the gold and silver reference materials (Tanaka of Japan and Krastsvetmet of Russia for gold and silver respectively). Inspection visits to the facilities of the two manufacturers were carried out by Dr. Hinds and the LBMA Chief Executive in March 2008. Discussions during these visits allowed the manufacturing parameters to be agreed. Soon after this, the two companies began their exploratory research into the best way of meeting the considerable challenge of producing completely homogeneous large ingots containing approximately 20 impurity elements within the target ranges in each ingot (see table). In passing, it might be remarked that producing homogeneous ingots in the size sufficient to meet the projected demand for reference materials is by no means easy. This is especially because a number of the elements included are quite volatile and, as the melting has to be carried out in a vacuum furnace, these tend to be lost during the process of melting and equilibration before casting. In addition, when a large ingot of metal is cast, there is a natural tendency for some elements to segregate during the solidification process. This can be minimised by rapid cooling in the mould. To meet these challenges, each manufacturer developed its own strategy, employing the best available technology and the initial manufacture of master alloys containing various combinations of the desired impurities, which could then be combined together in the final melting stage.

The master alloys used in manufacturing the gold reference materials at Tanaka KK.

Rather than repeating in full here how this was achieved, details of the procedures used at Tanaka can be found on the LBMA website (www.lbma.org.uk/events/assay2009) in the form of the presentation which was made by members of the Tanaka team at the recent LBMA Assaying and Refining Seminar. By the end of 2008, both the Tanaka ingots had been produced and rolled to the final thickness and divided into units corresponding to the final product size (20x20x6mm, weighing 50 grams each). A semi-random selection of these units was then analysed both at the surface and at depth for each of the 22 impurity elements. The same units were sent to the Rand Refinery, which carried out the same analysis. These results were then submitted to the Chairman of the Steering Committee, who subjected them to a homogeneity check using an ANOVA statistical package. In early February 2009, Dr. Hinds was able to report that the two ingots were judged to be completely homogeneous in respect of all the impurities. This in effect meant that the gold materials are usable and that in due course they will be shipped to those companies which have placed orders for them. The penultimate phase of

Target Concentrations (ppm)

Gold Reference Materials

Element	Au-RM1	Au-RM2
Ag	20±10	100±50
Al	10±5	30±15
As	12±6	40±20
Bi	30±15	10±5
Ca	10±5	30±15
Cr	10±5	30±15
Cu	10±5	30±15
Fe	10±5	30±15
Mg	30±15	10±5
Mn	10±5	30±15
Ni	10±5	30±15
Pb	10±5	30±15
Pd	10±5	30±15
Pt	10±5	30±15
Rh	10±5	30±15
Sb	30±15	10±5
Se	12±6	40±20
Si	10±5	30±15
Sn	10±5	30±15
Te	40±20	12±6
Ti	10±5	30±15
Zn	10±5	30±15

For gold, there will be a difference of at least 10 ppm between the concentrations in RM1 and RM2.

Silver Reference Materials

Element	Ag-RM1	Ag-RM2
Al	5-10	20-40
As	20-40	5-10
Au	5-10	20-40
Bi	10	50
Cd	5-10	20-40
Cr	5-10	20-40
Cu	20	100
Fe	5-10	20-40
Mg	20-40	5-10
Mn	5-10	20-40
Ni	5-10	20-40
Pb	50	10
Pd	5-10	20-40
Pt	5-10	20-40
Rh	5-10	20-40
Sb	5-10	20-40
Se	20-40	5-10
Si	5-10	20-40
Sn	20-40	5-10
Te	5-10	20-40
Zn	20-40	5-10

the project is now well advanced in respect of the gold materials. The most important aspect of this has been the production of shavings for distribution to a total of 10 laboratories around the world, each of which will determine the content of the 22 impurities independently and report these findings to the Executive. The Executive will tabulate the analytical results, with each participating laboratory being shown only as a code number, and then circulate these to the Steering Committee, which will decide whether any of the results should be excluded as outliers and thus determine the reference value for each contained element. These reference values will be shown in the certification for the materials.

The final phase will consist of invoicing those companies which have placed orders and shipping the materials to them. Invoices for the manufacturing cost element of the overall price will be issued shortly to those companies which placed orders. Once the certification stage has been completed, companies will be informed about the variable element of the price (this being dependent on the price of gold when the material is available for shipment, the weight of each individual sample and the shipping cost). Purchasers will be required to pay for all costs before the materials are shipped.

Following despatch of the materials to meet the orders already received, there will be a small number of materials left, which can be purchased from the LBMA. The price of the reference materials is shown in the box to the right.

Shavings – For ICP Users

The original purpose of the solid sample reference materials was for use with machines such as spark spectrometers. Companies which use wet ICP methods of analysis would have to produce shavings from the materials in order for them to be used in this equipment. Responding to requests from such users, the LBMA and Tanaka have agreed to produce a certain quantity of the reference materials in the form of shavings. The method of shipping these shavings will be in tamper proof plastic containers each containing 50 grams of the materials. The materials sold in the form of shavings will be sold at a premium of US$600 per set, reflecting the cost of producing the shavings.

Fixed part of price per set of two blocks

LBMA Good Delivery Refiners, Members and Associates:	US$3,750
Other purchasers:	US$4,500

The Silver Project

Progress at Krastsvetmet has gone along similar lines to that at Tanaka. However, the initial ingot produced turned out to be not totally homogeneous in respect of all impurity elements. This is probably due to the fact that because of silver's lower density and the need to produce a greater volume of metal, the cooling rate during the solidification of the ingot was insufficient to prevent the segregation of some impurities. Krastsvetmet will therefore recast the ingot using enhanced cooling to minimise and hopefully avoid detectable segregation. A further update on the progress with the silver materials will be included in the next edition of the *Alchemist*. ■