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Session Four:

Assaying

USE of ICP – Mass Spectrometry for Precious Metals

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I. Introduction

Good morning everyone. I am Satomi Tabuchi, and I am in charge of quality control and process control at the Japan Mint. Thank you for giving us the chance to make a presentation today. I am going to talk about the use of ICP mass spectrometry for precious metals.

First of all, let me introduce the Japan Mint, then I am going to explain ICP-MS features, and finally, I will report the analysis of our refined silver with ICP-MS.

II. Introduction of Japan Mint

We have three offices and factories in Japan: our headquarters are in Osaka, and two branches in Tokyo and Hiroshima.

Next, I would like to show you our products. On the upper left are our Japanese circulation coins. The material, colour and size of these coins are different by denomination, so it is easy to distinguish coins for children and for blind people. Here is a 500 yen coin; it is one of the highest value in the world as a circulation coin. Here is a one yen coin: its diameter is just two centimetres and its weight is just one gram.

Next, we have a proof coin set for collectors; in the lower left we have some examples of commemorative coins. The coin on the left is a gold coin; the middle coin is a silver coin with a print, and the one on the right is bicolour-clad coin. The bicolour-clad structure is used in euro coins as well, and it is very effective against counterfeiting.

Finally, we also produce decorations and medals. On the left is the Order of Sacred treasure, made of pure silver, and, next to it is a Gold Medal with a hologram, its centre shines like a rainbow.

At the Japan Mint, we refine gold and silver and make Good Delivery bars, we check the fineness of precious metal wares, and certify them by stamping hallmarks on them. In order to support these businesses, we do assaying for precious metals.

This picture shows the LBMA and Good Delivery referees evaluating our gold and silver bars when they visited the Japan Mint in November last year. You can find Dr Murray, Ms Theron, Mr Harby, Dr Jodry, and Dr Ruffoni. We are very glad that they enjoyed the Mint tour, especially the refining and the assaying processes.

III. Analysis for Precious Metals

Gold coins are made of pure gold over three-nines, so we usually use the fire assay. Our silver coins are made of silver of 925, so we usually use a potentiometric method. The fineness of our refined bullion is over four-nines, so we usually use ICP-OES for gold and ICP-MS for silver. Actually, we have ICP-OES and ICP-MS, so we can use them properly. We use aqua regia to dissolve gold, silver chloride precipitate, and adhere to the path of ions in ICP-MS. It results in decrease of sensitivity, so we must exchange many parts when we analyse silver after analysing gold. In order to avoid such contaminations, we use the ICP-OES for refining gold and we use the ICP-MS for refining silver.

The precious metal products for certification refer to gold and silver medals and the precious metal wares such as necklaces or rings. Basically, we use fire assay for gold and use the potentiometric method for silver.

IV. ICP Mass Spectrometer

Now, I would like to explain the ICP-MS. This is the ICP Mass Spectrometer we use now; it is made by Agilent Technologies. Its advantages are as follows: first, it has a high sensitivity of the PPT level; second, it enables a high-matrix analysis; third, it enables a wide dynamic range analysis; fourth, it enables a multi-elemental analysis. On the other hand, its disadvantages are as follows: firstly, we have to avoid isobaric interferences; secondly, we have to be aware of polyatomic interferences; and, thirdly, we need ultra-pure water and reagents.

I would like to explain the greatest advantage of ICP-MS: its sensitivity. Please take a look at this periodic table. In it we have highlighted elements based on the range of detection limits for each element for both ICP-MS and ICP-OES. As you can see, the detection limits of almost all elements for ICP-OES are three orders lower compared to those for ICP-OES. For example, in the case of iron, the detection limit for ICP-MS is below ten ppt, but it is below ten ppb for ICP-OES.

V. Structure

Next, I would like to show you the structure of ICP-MS. When you see the structure, I am sure you will see the principle of ICP-MS and how the polyatomic interferences are removed. The ICP, which is shown as part one here in the figure of ICP-MS, is the same principle as ICP-OES. The sample is ionised by high temperature plasma at ICP. Compared to ICP-OES, ICP-MS delivers simple spectra; however, the argon gas in the plasma, solvent and sample-matrix, give rise to polyatomic interference in many analytes. Modern ICP-MS instruments make use of a collision reaction cell (CRC), which is shown as part four, to reduce these polyatomic interferences. After that, analyte ions are separated by atomic number, in the quadrupole mass spectrometer, which is shown as part five. Finally, the numbers of ions are measured with a detector, which is shown as part six. I will touch on the polyatomic interference and the collision reaction cell later.

VI. Isobaric Interferences

Before I talk about polyatomic interferences, let me explain the isobaric interferences, which is one of the disadvantages of ICP-MS. As you know, each element exists by the peculiar natural isotope ratio. Here is an extract from the relative isotopic abundance table. For instance, manganese, in the first row, has only one mass number, 55, but iron, in the second row, has four mass numbers, including 54, 56, 57 and 58. Also, nickel has five mass numbers: 58, 60, 61, 62 and 64. This means that the peaks of iron and nickel of mass number 58 overlap. Equally, in the peaks of nickel and zinc of mass number 64 overlap. Peak overlap like this is called 'isobaric interference'. We can measure iron by mass number 56, due to its high natural abundance; however, we should measure nickel by mass number 60, which has lower abundance than mass number 58. Equally, we should measure zinc by mass number 66, which has a lower sensitivity than mass number 64. What this means is that we select mass numbers of lower sensitivity to avoid the isobaric interferences.

VII. Polyatomic Interferences

I will now explain polyatomic interference. Please look at the table. From the left, each column represents element, mass number, abundance, polyatomic ion coming from argon gas, and detection limit, respectively. The detection limits are different due to the attachment to ICP-MS, such as normal plasma. As you can see, a polyatomic ion composed of argon and nitrogen has mass number of 54 – it is the same as iron 54 – and polyatomic iron, composed of argon and oxygen, has mass number 56 – it is the same as iron 56. Thus, the overlap of spectra on element and polyatomic ion due to the same mass number is called 'polyatomic interference'. Argon polyatomic ions interfere with any sample because it is plasma gas; in addition, it forms a background. Argon polyatomic ions have an especially great influence on potassium, calcium and iron; therefore, the detective limits of these elements are in the order 1,000 of ppt.

This is a measurement method with cool plasma in order to reduce the argon polyatomic interference. Cool plasma has a lower temperature than normal plasma. Under the cool plasma it is difficult to generate argon polyatomic ions, and as a result analysis in ppt order is enabled because of the low background. Otherwise, the detection limits depends on the equipment. To tell you the truth, when we initially purchased the ICP-MS, it only had normal plasma, so, when we measure calcium we select the mass number 44, but the ICP-MS we use now has a CRC and it can remove polyatomic interferences. We now measure calcium using mass number 40, which has a higher sensitivity than mass number 44. Equally, when we measured iron in the past, we selected mass number 57 – now we use mass number 56, and we can analyse calcium and iron in ppt order.

1. Polyatomic Interference Removal

Now, I would like to tell you about the mechanism of interference removal with CRC. This is CRC and helium gas is introduced in it. Helium gas collides with both analyte ions and polyatomic ions in this cell. At the cell entrance their kinetic energy distribution overlaps when their mass number is the same – energy loss from each collision with helium atoms is the same for analyte ions and the polyatomic ions; but polyatomic ions are bigger, and so collide more often with analyse ions. Therefore, by cell exit, these ions' energies no longer overlap, and polyatomic ions with low energy are rejected using a bias voltage.

VIII. Analysis for Refined Silver with ICP-MS

I will tell you about our analysis for refined silver with ICP-MS. First, we put the silver sample weighing 100 milligrams into the disposable bottle. Then we add five millilitres of nitric acid to the bottle, and dissolved using a heater at 100 degrees. Finally we make this up to 50 millilitres with water. In order to avoid contaminations, we use a disposable bottle, reagent for precision analysis and ultrapure water.

When we use ICP-OES to analyse silver we add hydrogen chloride into the silver solution to remove silver matrix from the solution, but when we use ICP-MS, we can analyse the silver solution directly without filtration.

Advantages of ICP-MS are as follows: first, we can avoid the impurities to absorb on silver chloride; second, we can minimise contaminations after dissolution; third, we save time by not having to deal with precipitation or filtration.

Now here is a flow chart of analysis for refined silver. First, we determine the impurity elements for ICP-MS by qualitative analysis with DC-Arc-OES. In the case of our refined silver, we selected the 13 elements as shown here. Second, we make standard solutions for each element, with silver matrix and yttrium as internal standard. Using the standard solutions, we plot the calibration curves. Thirdly, by means of the calibration curves, we do quantitative analysis of impurities in samples with ICP-MS. It takes about five minutes for each measurement. Finally, the fineness of silver is obtained by the subtraction of the total contents of impurities from 1000.

IX. Results for Refined Silver with ICP-MS

Here are the results of analysis of refined silver with ICP-MS. I will show you examples of calibration curves for iron, nickel, and zinc. We obtained linear calibration curves for all elements.

This table shows the result of quantitative analysis for 13 elements. It is found that the fineness of these refined silvers is five-nine. Thus, they confirm the fineness of silver Good Delivery bars with ICP-MS.

X. Conclusions

To summarise, we introduced the features of ICP-MS. It is important to eliminate interferences. Then we introduced the analysis of refined silver with ICP-MS. ICP-MS is very useful to analyse our refined silver over four-nines by recent technological advances.

Thank you for your attention. We hope you have found the presentation informative. Thank you.