APPLICATION NOTE

# Analysis of copper alloys

# ARL OPTIM'X WDXRF Spectrometer

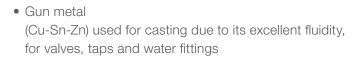
### **Key words**

ARL OPTIM'X, brass, bronze, copper, XRF

## Copper alloys

Pure copper is mixed with other elements to produce a wide range of alloys:

- Brasses (Cu-Zn)
- Bronzes (Cu-Sn)



- Manganese bronzes (Cu-Zn- Mn) are not true bronzes as Sn is not the essential constituent. Used for rudders, propellers and ship fittings
- Cupro-nickel (Cu-Ni) used for coins, tubes, wires, electrical resistances and thermocouples
- Nickel silver (Cu-Ni-Zn) used for marine applications, car radiators and fittings

#### **Brasses**

One the most important non-ferrous engineering alloys. They cover a large range of physical properties and their applications are multiple.

Copper is capable of holding about 39 % of zinc in solid solution. Alloys containing less than 39 % Zn are known as  $\alpha$ -brasses. This brass (70/30) is very widely employed for cartridge, cases, condenser tubes, etc.

From 39 % to 46 % of Zn, a  $\beta$ -solid solution gives  $\alpha\beta$ -brass. This alloy (60/40) is found in extensive engineering applications with enhanced corrosion resistance used in marine applications. Alloys containing more than 49 % Zn are very hard and only used for brazing brasses.

#### **Bronzes**

Bronzes are used for bearing and gears. There are a wide variety of bronze alloys containing various elements such as phosphorus, beryllium, silicon, etc.:

- Leaded bronzes (Cu-Sn-Pb) are mainly used for bearings due to their good wear resistance
- Aluminum bronzes (Cu-Al) have good corrosion resistance but are difficult to cast. Used for pumps rods, diecastings, etc.
- Silicon bronzes (Cu-Sn-Ni) have high electrical conductivity and are used for wires
- Phosphor bronzes (Cu-Sn-P) are used for valves, bearings and gears. Cold worked into rods and sheets

#### **Received samples**

Four samples were submitted in order to test the performance of the Thermo Scientific ARL OPTIM'X for the analysis of copper base samples. The samples belong to various qualities of copper: phosphorus bronze, silicon bronze, nickel silver and brass. Results are shown in Tables 2 to 5.

# **Analytical request**

In order to assess the performance of the ARL OPTIM'X for the analysis of these various copper base materials, the instrument has been calibrated with a General Copper calibration. This calibration covers large ranges of concentrations for the elements generally found in copper base materials.

The four "unknowns" have then been analyzed against this general calibration in order to get concentrations values. It must be stressed that this general calibration is not specifically adjusted for any of the four types of copper alloys submitted. Such specific adjustment of a calibration known as Type standardization would be normally used in order to get the best accuracy of analysis.



Nevertheless the General Copper Calibration allows to do repeatability tests in concentration for the various elements in order to assess the precision of analysis of the instrument for a total counting time of 10 minutes.

#### Instrument

An ARL OPTIM'X XRF spectrometer has been used to derive these results. It is fitted with an Air-cooled Rh End-Window Tube with thin Be window (0.075 mm) and has a maximum power of 50 Watts. Thanks to close coupling between the X-ray tube anode and the sample the performance of the ARL OPTIM'X is equivalent to a 200 W conventional



WDXRF instrument. The instrument can be equipped with the unique SmartGonio<sup>™</sup>, a series of Multichromators<sup>™</sup> or both. Wavelength dispersive XRF ensures a very good stability of analysis, both in long term and short tenn. Ease of operation is obtained through the state-of-the-art OXSAS software.

### Sample preparation

The samples have been milled prior to analysis.

### **Analysis and results**

As the maximum analysis time allowed seems to be around 10 minutes we have used a counting time of 36 seconds per element. This counting time might be too short for some elements that are present as traces or that are less sensitive like arsenic for example. For other elements the precision obtained with this counting time can be sufficient and the counting time could

be shortened. Depending on the alloy quality and the analysis requirements, the required counting time can be adjusted for each element. This adjustment can be done depending on the customer's requirement of analysis.

The X-ray tube excitation conditions are 50 kV - 1 mA. The analytical conditions are shown in Table 1.

The analytical lines are K alpha lines unless stated. The copper concentration is obtained by difference to 100 %.

| Element<br>K alpha<br>line<br>unless<br>Stated | Analytical<br>device | Crystal | Detector      | Counting<br>time used<br>for this<br>preliminary<br>test |  |
|--|----------------------|---------|---------------|--|--|
| Sn   | SmartGonio           | LiF200  | Scintillation | 36s  |  |
| Zn   | SmaliGonio           | LiF200  | Scintillation | 36s  |  |
| Pb La  | SmartGonio           | LiF200  | Scintillation | 36s  |  |
| Fe   | SmartGonio           | LiF200  | Flow prop     | 36s  |  |
| Ni   | SmartGonio           | LiF200  | Scintillation | 36s  |  |
| Al   | SmartGonio           | PET     | Flow prop     | 36s  |  |
| Р  | SmartGonio           | PET     | Flow prop     | 36s  |  |
| Si   | SmartGonio           | PET     | Flow prop     | 36s  |  |
| Mn   | SmartGonio           | LiF200  | Flow prop     | 36s  |  |
| S  | SmartGonio           | PET     | Flow prop     | 36s  |  |
| Bi La  | SmartGonio           | LiF200  | Scintillation | 36s  |  |
| Cr   | Cr SmartGonio        |         | Flow prop     | 36s  |  |
| Sb   | SmartGonio           | LiF200  | Scintillation | 36s  |  |
| AsKb   | SmartGonio           | LiF200  | Scintillation | 36s  |  |
| Со   | SmartGonio           | LiF200  | Flow prop     | 36s  |  |

Table 1: Analytical conditions

| Run | Sn    | Zn    | Pb     | Fe    | Ni    | Al    | Р     | Si    | S     | Bi    | Sb    | As    | Cu_<br>Diff |
|-----|-------|-------|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------------|
| 1>  | 0.504 | 32.85 | 0.251  | 0.066 | 0.123 | 0.022 | 0.06  | 0.097 | 0.007 | 0.023 | 0.119 | 0.046 | 65.83       |
| 2>  | 0.493 | 32.91 | 0.247  | 0.065 | 0.122 | 0.019 | 0.062 | 0.093 | 0.007 | 0.02  | 0.119 | 0.046 | 65.79       |
| 3>  | 0.494 | 32.86 | 0.247  | 0.063 | 0.122 | 0.016 | 0.061 | 0.09  | 0.006 | 0.019 | 0.123 | 0.048 | 65.85       |
| 4>  | 0.496 | 32.9  | 0.254  | 0.065 | 0.122 | 0.023 | 0.064 | 0.092 | 0.006 | 0.022 | 0.125 | 0.044 | 65.79       |
| 5>  | 0.498 | 32.9  | 0.251  | 0.064 | 0.122 | 0.017 | 0.07  | 0.1   | 0.006 | 0.02  | 0.12  | 0.035 | 65.8        |
| 6>  | 0.499 | 32.9  | 0.255  | 0.064 | 0.122 | 0.016 | 0.07  | 0.095 | 0.006 | 0.021 | 0.119 | 0.045 | 65.79       |
| 7>  | 0.498 | 32.89 | 0.257  | 0.064 | 0.122 | 0.027 | 0.057 | 0.093 | 0.007 | 0.016 | 0.122 | 0.013 | 65.84       |
| 8>  | 0.499 | 32.86 | 0.257  | 0.066 | 0.122 | 0.014 | 0.056 | 0.082 | 0.007 | 0.019 | 0.12  | 0.036 | 65.86       |
| 9>  | 0.498 | 32.86 | 0.253  | 0.065 | 0.123 | 0.011 | 0.058 | 0.094 | 0.005 | 0.022 | 0.121 | 0.042 | 65.85       |
| 10> | 0.501 | 32.86 | 0.253  | 0.064 | 0.121 | 0.012 | 0.055 | 0.091 | 0.005 | 0.019 | 0.118 | 0.019 | 65.88       |
| 11> | 0.503 | 32.88 | 0.253  | 0.065 | 0.122 | 0.022 | 0.059 | 0.087 | 0.007 | 0.019 | 0.12  | 0.051 | 65.81       |
| Avg | 0.498 | 32.88 | 0.253  | 0.065 | 0.122 | 0.018 | 0.061 | 0.092 | 0.006 | 0.02  | 0.121 | 0.038 | 65.83       |
| Sd  | 0.004 | 0.02  | 0.0033 | 0.001 | 0.001 | 0.005 | 0.005 | 0.005 | 0.001 | 0.002 | 0.002 | 0.012 | 0.03        |

Table 2: Repeatability test on a brass sample using a counting time of 36 s per element

| Run | Sn    | Zn    | Pb    | Fe    | Ni    | Al    | Р     | Si    | s     | Bi    | Sb    | As    | Cu_<br>Diff |
|-----|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------------|
| 1>  | 4.74  | 0.373 | 0.736 | 0.145 | 0.083 | 0.018 | 0.082 | 0.103 | 0.071 | 0.023 | 0.061 | 0.024 | 93.54       |
| 2>  | 4.757 | 0.375 | 0.739 | 0.146 | 0.082 | 0.012 | 0.073 | 0.1   | 0.072 | 0.023 | 0.065 | 0.054 | 93.5        |
| 3>  | 4.745 | 0.373 | 0.743 | 0.146 | 0.083 | 0.017 | 0.092 | 0.099 | 0.071 | 0.024 | 0.065 | 0.018 | 93.52       |
| 4>  | 4.755 | 0.371 | 0.736 | 0.143 | 0.084 | 0.015 | 0.083 | 0.104 | 0.072 | 0.024 | 0.066 | 0.039 | 93.51       |
| 5>  | 4.778 | 0.373 | 0.732 | 0.145 | 0.083 | 0.016 | 0.079 | 0.102 | 0.07  | 0.02  | 0.066 | 0.027 | 93.51       |
| 6>  | 4.768 | 0.371 | 0.749 | 0.144 | 0.081 | 0.009 | 0.089 | 0.1   | 0.071 | 0.024 | 0.061 | 0.038 | 93.49       |
| 7>  | 4.754 | 0.37  | 0.746 | 0.143 | 0.083 | 0.012 | 0.083 | 0.101 | 0.074 | 0.026 | 0.062 | 0.029 | 93.52       |
| 8>  | 4.759 | 0.372 | 0.739 | 0.144 | 0.083 | 0.022 | 0.094 | 0.101 | 0.071 | 0.022 | 0.063 | 0.023 | 93.51       |
| 9>  | 4.735 | 0.373 | 0.742 | 0.144 | 0.082 | 0.012 | 0.086 | 0.1   | 0.071 | 0.023 | 0.069 | 0.038 | 93.52       |
| 10> | 4.768 | 0.369 | 0.746 | 0.144 | 0.085 | 0.011 | 0.09  | 0.099 | 0.071 | 0.022 | 0.063 | 0.033 | 93.5        |
| 11> | 4.753 | 0.372 | 0.746 | 0.146 | 0.083 | 0.016 | 0.085 | 0.101 | 0.069 | 0.02  | 0.06  | 0.014 | 93.53       |
| Avg | 4.756 | 0.372 | 0.741 | 0.144 | 0.083 | 0.015 | 0.085 | 0.101 | 0.071 | 0.023 | 0.064 | 0.031 | 93.51       |
| Sd  | 0.013 | 0.002 | 0.005 | 0.001 | 0.001 | 0.004 | 0.006 | 0.001 | 0.001 | 0.002 | 0.003 | 0.011 | 0.02        |

Table 3: Repeatability test on a phosphor bronze sample using a counting time of 36 s per element

| Run | Sn    | Zn     | Pb    | Fe    | Ni    | Al    | Р     | Mn    | Cu_<br>Diff |
|-----|-------|--------|-------|-------|-------|-------|-------|-------|-------------|
| 1>  | 0.028 | 28.5   | 0.068 | 0.028 | 12.79 | 0.015 | 0.116 | 0.666 | 57.58       |
| 2>  | 0.028 | 28.5   | 0.072 | 0.027 | 12.79 | 0.022 | 0.11  | 0.661 | 57.77       |
| 3>  | 0.029 | 28.5   | 0.07  | 0.027 | 12.78 | 0.016 | 0.105 | 0.663 | 57.81       |
| 4>  | 0.026 | 28.52  | 0.075 | 0.027 | 12.77 | 0.02  | 0.108 | 0.661 | 57.79       |
| 5>  | 0.03  | 28.5   | 0.07  | 0.028 | 12.78 | 0.019 | 0.114 | 0.665 | 57.79       |
| 6>  | 0.027 | 28.5   | 0.07  | 0.026 | 12.78 | 0.019 | 0.108 | 0.666 | 57.79       |
| 7>  | 0.025 | 28.51  | 0.071 | 0.027 | 12.76 | 0.015 | 0.113 | 0.665 | 57.79       |
| 8>  | 0.027 | 28.49  | 0.075 | 0.027 | 12.78 | 0.015 | 0.119 | 0.661 | 57.79       |
| 9>  | 0.029 | 28.49  | 0.073 | 0.027 | 12.78 | 0.016 | 0.113 | 0.666 | 57.8        |
| 10> | .023  | 028.48 | 0.071 | 0.026 | 12.77 | 0.015 | 0.115 | 0.67  | 57.82       |
| 11> | 0.027 | 28.49  | 0.067 | 0.025 | 12.78 | 0.023 | 0.112 | 0.67  | 57.79       |
| Avg | 0.027 | 28.5   | 0.071 | 0.027 | 12.78 | 0.018 | 0.112 | 0.665 | 57.79       |
| Sd  | 0.002 | 0.01   | 0.002 | 0.001 | 0.01  | 0.003 | 0.004 | 0.003 | 0.01        |

Table 4: Repeatability test on a nickel silver sample using a counting time of 36 s per element

| Run | Sn    | Zn    | Pb    | Fe    | Ni    | Al    | Р     | Mn    | Cu_<br>Diff |
|-----|-------|-------|-------|-------|-------|-------|-------|-------|-------------|
| 1>  | 0.029 | 0.032 | 0.007 | 0.039 | 0.013 | 0.014 | 2.918 | 0.892 | 96.04       |
| 2>  | 0.029 | 0.033 | 0.004 | 0.038 | 0.014 | 0.011 | 2.945 | 0.895 | 96.04       |
| 3>  | 0.032 | 0.034 | 0.004 | 0.04  | 0.015 | 0.017 | 2.942 | 0.899 | 95.98       |
| 4>  | 0.031 | 0.03  | 0.005 | 0.039 | 0.014 | 0.015 | 2.965 | 0.892 | 96          |
| 5>  | 0.03  | 0.03  | 0.008 | 0.038 | 0.015 | 0.02  | 2.92  | 0.893 | 96.04       |
| 6>  | 0.031 | 0.032 | 0.005 | 0.038 | 0.015 | 0.014 | 2.942 | 0.895 | 96.01       |
| 7>  | 0.031 | 0.032 | 0.007 | 0.038 | 0.014 | 0.012 | 2.929 | 0.893 | 96.03       |
| 8>  | 0.034 | 0.034 | 0.007 | 0.038 | 0.014 | 0.015 | 2.943 | 0.893 | 96.01       |
| 9>  | 0.029 | 0.031 | 0.007 | 0.038 | 0.014 | 0.013 | 2.939 | 0.899 | 96.02       |
| 10> | 0.029 | 0.032 | 0.004 | 0.039 | 0.015 | 0.017 | 2.94  | 0.902 | 96.01       |
| 11> | 0.032 | 0.032 | 0.006 | 0.039 | 0.014 | 0.014 | 2.959 | 0.895 | 95.99       |
| Avg | 0.031 | 0.032 | 0.006 | 0.038 | 0.014 | 0.015 | 2.938 | 0.895 | 96.02       |
| Sd  | 0.002 | 0.001 | 0.002 | 0.001 | 0.001 | 0.003 | 0.015 | 0.003 | 0.02        |

Table 5: Repeatability test on a silicon bronze sample using a counting time of 36 s per element

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#### Conclusion

The precision obtained on the four samples is quite acceptable for copper base analysis for practically all elements. For zinc, iron and nickel, the counting time could be practically halved to 20 seconds while still getting a very good precision. On the contrary for arsenic and aluminum at low levels, precision can be improved by increasing the counting time to 60 seconds each or more. If arsenic must be controlled at high precision at low level, a fixed channel for As could be used such as to be able to have a parallel analysis on As during 10 minutes. In such case the total time of analysis remains at 10 minutes as the SmartGonio is analyzing on the various elements while the fixed channel of As is doing its analysis. This would improve the standard deviation on arsenic by a factor of at least 4.

The long experience of our company in metals analysis comes from an installed base of over 1,000 XRF spectrometers worldwide. The ARL OPTIM'X is the answer to your metallurgical analysis needs; whether they be incoming material control, metal QC or production analysis. Working 24 hours a day and 7 days a week, the ARL OPTIM'X delivers dependable performance year after year.

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