X-ray fluorescence

Analysis of copper alloys with ARL X900 XRF Spectrometer and its goniometer

Goal

Describe the analytical performance of Thermo Scientific™ ARL™ X900 Series Spectrometer for copper alloys analysis using the Moiré fringe goniometer. A separate application note will describe the results obtained with fixed monochromator channels.

Introduction

Copper alloys are very important products because they are used for many applications and many manufacturing processes as described in the next few paragraphs. It is important to accurately analyze these materials to confirm compliance with their chemical specifications that imply physical properties, like conductivity, compressive strength, hardness, resistance to traction and to abrasion. High product quality and efficient production can be ensured with accurate analysis results.

Copper alloys

Pure copper is mixed with other elements to produce a wide range of alloys: Brasses (Cu-Zn), bronzes (Cu-Sn), gun metal (Cu-Sn-Zn) used for casting due to its excellent fluidity, for valves, taps and water fittings. 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) is used for marine applications, car radiators and fittings.

Figure 1: ARL X900 Series Simultaneous-Sequential X-ray Fluorescence Spectrometer.

Brass

Brass is one of the most important non-ferrous engineering alloys. It covers a large range of physical properties with multiple applications.

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

From 39 % to 46 % of Zn, a β-solid solution gives αβ-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.

Figure 2: Brass, bronze and copper samples.

Bronze alloys

Bronzes are used for bearings 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.
- Aluminium bronzes (Cu-Al) have good corrosion resistance but difficult to cast. Used for pumps rods, die castings, etc.
- Silicon bronzes (Cu-Sn-Ni) have high electrical conductivity and used for wires.
- Phosphor bronzes (Cu-Sn-P) are used for valves, bearings and gears. Cold worked into rods and sheets.

Instrument parameters and conditions

The ARL X900 XRF Spectrometer can be equipped with the unique proprietary Moiré fringe goniometer. Speed, flexibility and reliability of analysis are guaranteed thanks to the ingenious friction-free positioning system. Up to nine crystals and four collimators can be fitted. With the two detectors (flow proportional and scintillation counters) precise elemental analysis from boron to californium is possible. Additionally, the spectrometer can accommodate up to 24 fixed monochromator channels alongside the goniometer or up to 32 fixed monochromator channels when no goniometer is fitted.

The ARL X900 XRF Spectrometer can be calibrated using commercially available CRM (certified reference materials) standards or well analyzed user samples.

It should be stressed that an XRF spectrometer is a very accurate comparator, the accuracy of the final analysis is entirely dependent on the quality of the standards used for calibration and on the care and reproducibility of sample preparation. This preparation must be identical for CRMs and for routine samples as well.

Typical performance in copper base alloys using the goniometer

Table 1 provides a summary of typical limits of detection. Calibration was performed using a set of international copper-based CRM standards (low alloy copper), with recommended goniometer parameters for the choice of crystal, detector, and collimator. X-ray tube settings were set at 50 kV and 70 mA. Phosphorus was measured with a PET crystal to avoid fluorescence of the crystal, that would result in higher spectral background.

All elements from B to Cf can be analyzed if needed, but Table 1 includes a selection of common elements measured in copper alloys. Limits of detection (LoD) are calculated from the calibration curve for comparison, using 20 seconds and 100 seconds counting time per element. As the goniometer measures sequentially, one element after the other, it is often beneficial to use shorter counting times in order to produce a final result within a few minutes.

Table 1. Typical limits of detection in copper base matrix for the goniometer at 20 s and 100 s counting time. (PBF = primary beam filter).

Element	Line	Detector	Goniometer Collimator	Filter	LoD (ppm) In 20 s	LoD (ppm) In 100 s
Ag	Kα	Scintillation	0.25°	PBF Cu	21.7	9.7
Al	Kα	FPC	0.6°	-	3.9	1.7
As	Kβ	Scintillation	0.25°	-	20.9	9.3
Bi	Lα	Scintillation	0.25°	-	6.1	2.7
Cd	Kα	Scintillation	0.25°	PBF Cu	36.1	16.1
Co	Kα	FPC	0.25°	-	3.2	1.4
Cr	Kα	FPC	0.25°	-	3.9	1.7
Fe	Kα	FPC	0.25°	-	4.5	2.0
Mg	Kα	FPC	0.6°	-	82.9	37.1
Mn	Kα	FPC	0.25°	-	4.1	1.8
Ni	Kα	Scintillation	0.25°	-	14.5	6.5
P	Kα	FPC	0.6°	-	15.3	6.8
Pb	Lβ	Scintillation	0.25°	-	24.7	11.0
S	Kα	FPC	0.6°	-	2.9	1.3
Sb	Kα	Scintillation	0.25°	-	29.5	13.2
Se	Kα	Scintillation	0.25°	-	5.8	2.6
Si	Kα	FPC	0.6°	-	11.2	5.0
Sn	Kα	Scintillation	0.25°	-	28.7	12.8
Te	Kα	Scintillation	0.25°	-	31.6	14.1
Ti	Kα	FPC	0.25°	-	4.2	1.9
Zn	Kα	Scintillation	0.15°	-	8.8	3.9
Zr	Kα	Scintillation	0.25°	-	4.8	2.1

LOD = limit of detection (3 sigma) = $3\sqrt{\frac{B}{QT}}$

where Q = counts per second per 1 % element

B = background equivalent concentration

T = time of analysis in seconds

The limits of detection are determined with low alloy copper samples. In practice, these values should agree with values measured practically, using the mathematical derivation of standard deviation (3 sigma) at low concentration level on a “blank” sample. In this case, we would use a pure copper sample.

3 sigma = $3\sqrt{\frac{\Sigma(X-\bar{X})^2}{n-1}}$

where X= the individual readings

X = the arithmetic mean of the individual values

n = number of determination (normally ≥10)

For guaranteed values, the values of precision and LODs should be multiplied by factor 2.

Typical precision tests

The stability of an instrument reflects the precision that can be obtained. Short-term repeatability tests, consisting of eleven runs on several copper base samples, were performed for an hour and a half. A 20 second counting time was used for all elements in each run. A power level of 3500W was used for these tests. Generally, the Kα line is used for the analysis, except for Pb (Lβ), for As (Kβ) and Bi (Lα).

Table 3a: Short term precision test over one hour and a half using the goniometer – cupro-nickel sample.
Note: for further improvement of precision on Zn and Cu in brass, the Bäkerud method is recommended.

	Sn	Pb	Ni	Fe	Al	Si	Mn	As	Co	Te	Ti	Cu
	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	Diff
	%	%	%	%	ppm	%	%	%	%	%	ppm	%
Run 1	0.0052	0.0011	20.09	0.981	49	0.5353	0.7995	0.0169	0.0675	0.0047	10	77.53
Run 2	0.0069	0.0006	20.15	0.980	56	0.5368	0.8016	0.0163	0.0674	0.0076	10	77.46
Run 3	0.0048	0.0020	20.11	0.982	50	0.5373	0.8037	0.0178	0.0679	0.0062	11	77.50
Run 4	0.0049	0.0004	20.11	0.982	52	0.5371	0.8011	0.0200	0.0675	0.0060	8	77.49
Run 5	0.0051	0.0017	20.13	0.982	53	0.5377	0.8030	0.0189	0.0673	0.0055	7	77.46
Run 6	0.0059	0.0008	20.06	0.982	51	0.5369	0.8003	0.0187	0.0680	0.0043	7	77.55
Run 7	0.0067	0.0013	20.14	0.981	55	0.5410	0.8024	0.0203	0.0673	0.0069	8	77.47
Run 8	0.0059	0.0012	20.15	0.982	55	0.5397	0.8018	0.0192	0.0668	0.0059	7	77.45
Run 9	0.0043	0.0013	20.11	0.981	50	0.5378	0.8019	0.0193	0.0678	0.0040	8	77.50
Run 10	0.0059	0.0010	20.14	0.981	43	0.5387	0.8011	0.0185	0.0674	0.0049	9	77.46
Run 11	0.0076	0.0013	20.10	0.982	50	0.5406	0.8021	0.0155	0.0673	0.0071	8	77.50
Average	**0.0057**	**0.0012**	**20.12**	**0.982**	**51**	**0.5381**	**0.8017**	**0.0183**	**0.0675**	**0.0057**	**8**	**77.49**
Std Dev	0.0010	0.00047	0.028	0.0008	3.5	0.0017	0.0012	0.00153	0.00034	0.0012	1.3	0.031

Table 3b: Short term precision test over one hour and a half using the goniometer – brass sample.
Note: for further improvement of precision on Zn and Cu in brass, the Bäkerud method is recommended.

	Zn	Sn	Pb	Ni	Fe	Al	Si	Mn	P	S	Bi	Sb	As	Cu
	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	Diff
	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Run 1	14.57	0.1902	0.1653	0.1924	0.1032	0.2202	0.1947	0.1600	0.1179	0.1326	0.2272	0.1815	0.1439	83.389
Run 2	14.62	0.1916	0.1631	0.1923	0.1028	0.2212	0.1959	0.1597	0.1174	0.1318	0.2267	0.1817	0.1464	83.331
Run 3	14.56	0.1864	0.1655	0.1930	0.1028	0.2195	0.1970	0.1600	0.1167	0.1314	0.2286	0.1837	0.1438	83.394
Run 4	14.62	0.1913	0.1639	0.1915	0.1028	0.2207	0.1958	0.1594	0.1186	0.1324	0.2270	0.1822	0.1470	83.333
Run 5	14.61	0.1911	0.1643	0.1923	0.1029	0.2208	0.1964	0.1593	0.1163	0.1318	0.2302	0.1824	0.1477	83.341
Run 6	14.58	0.1898	0.1653	0.1931	0.1029	0.2223	0.1969	0.1599	0.1190	0.1317	0.2284	0.1852	0.1441	83.369
Run 7	14.64	0.1884	0.1633	0.1925	0.1025	0.2210	0.1977	0.1599	0.1176	0.1316	0.2292	0.1831	0.1456	83.321
Run 8	14.58	0.1925	0.1642	0.1923	0.1029	0.2219	0.2007	0.1600	0.1173	0.1329	0.2300	0.1865	0.1452	83.365
Run 9	14.63	0.1911	0.1644	0.1925	0.1028	0.2196	0.1983	0.1598	0.1190	0.1329	0.2280	0.1847	0.1448	83.317
Run 10	14.64	0.1882	0.1635	0.1922	0.1031	0.2205	0.1983	0.1600	0.1177	0.1323	0.2253	0.1850	0.1485	83.314
Run 11	14.59	0.1927	0.1641	0.1935	0.1031	0.2201	0.1983	0.1593	0.1174	0.132	0.2289	0.1829	0.1466	83.359
Average	**14.60**	**0.1903**	**0.1643**	**0.1925**	**0.1029**	**0.2207**	**0.1973**	**0.1598**	**0.1177**	**0.1321**	**0.2281**	**0.1835**	**0.1458**	**83.349**
Std Dev	0.028	0.0020	0.0008	0.0005	0.0002	0.0009	0.00163	0.0003	0.0009	0.0005	0.0015	0.0016	0.00158	0.028

Table 3c: Short term precision test over one hour and a half using the goniometer – cupro-aluminum sample.

	Zn	Sn	Pb	Ni	Fe	Al	Si	Mn	Cr	Sb	As	Co	Te	Mg	Zr	Cu
	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	Diff
	%	%	%	%	%	%	%	%	%	%	%	ppm	%	%	ppm	%
Run 1	0.805	0.0566	0.0536	3.740	5.985	11.035	0.1089	0.4234	0.0891	0.0119	0.0202	89	0.0167	0.0163	17	77.67
Run 2	0.803	0.0561	0.0546	3.737	5.975	11.007	0.1074	0.4238	0.0889	0.0099	0.0200	90	0.0164	0.0097	14	77.72
Run 3	0.803	0.0560	0.0563	3.742	5.976	11.045	0.1091	0.4229	0.0881	0.0103	0.0186	90	0.0189	0.0171	17	77.67
Run 4	0.802	0.0559	0.0530	3.731	5.968	11.035	0.1091	0.4227	0.0879	0.0095	0.0231	91	0.0180	0.0122	15	77.70
Run 5	0.802	0.0566	0.0545	3.734	5.986	11.024	0.1106	0.4222	0.0881	0.0103	0.0210	89	0.0159	0.0124	14	77.69
Run 6	0.805	0.0543	0.0533	3.735	5.985	11.017	0.1098	0.4234	0.0883	0.0105	0.0202	88	0.0176	0.0173	17	77.69
Run 7	0.805	0.0556	0.0540	3.730	5.988	11.034	0.1108	0.4241	0.088	0.0090	0.0214	90	0.0158	0.0182	17	77.68
Run 8	0.802	0.0550	0.0560	3.735	5.980	11.030	0.1107	0.4241	0.0876	0.0107	0.0212	89	0.0161	0.0187	17	77.68
Run 9	0.803	0.0575	0.0561	3.742	5.981	11.050	0.1119	0.4232	0.0882	0.0102	0.0208	90	0.0159	0.0192	17	77.65
Run 10	0.805	0.0551	0.0550	3.733	5.967	11.026	0.1118	0.4227	0.088	0.0079	0.0207	88	0.0173	0.0109	16	77.70
Run 11	0.801	0.0554	0.0539	3.733	5.979	11.029	0.1118	0.4235	0.0881	0.0109	0.0196	87	0.0159	0.0132	14	77.69
Average	**0.803**	**0.0558**	**0.0546**	**3.7356**	**5.979**	**11.03**	**0.1102**	**0.4233**	**0.0882**	**0.0101**	**0.0206**	**89**	**0.0168**	**0.015**	**16**	**77.68**
Std Dev	0.002	0.0009	0.0012	0.004	0.007	0.012	0.0014	0.0006	0.0004	0.0011	0.0011	1.1	0.001	0.003	1.3	0.020

Table 3d: Short term precision test over one hour and a half using the goniometer – brass sample.

	Zn	Ni	Al	Si	Mn	S	As	Cu
	20 s	20 s	20 s	20 s	20 s	20 s	20 s	Diff
	%	ppm	%	%	%	%	%	%
Run 1	40.41	19	0.0190	0.0395	0.0027	0.0012	0.0148	59.54
Run 2	40.33	19	0.0191	0.0399	0.0028	0.0013	0.0147	59.62
Run 3	40.46	19	0.0205	0.0395	0.0027	0.0013	0.0153	59.48
Run 4	40.31	16	0.0180	0.0414	0.0027	0.0011	0.0161	59.64
Run 5	40.45	18	0.0196	0.0410	0.0027	0.0013	0.0147	59.50
Run 6	40.40	20	0.0189	0.0411	0.0030	0.0012	0.0147	59.55
Run 7	40.29	19	0.0184	0.0424	0.0030	0.0012	0.013	59.66
Run 8	40.50	20	0.0182	0.0418	0.0025	0.0013	0.0127	59.45
Run 9	40.29	19	0.0184	0.0431	0.0027	0.0012	0.017	59.65
Run 10	40.35	19	0.0195	0.0434	0.0027	0.0011	0.0122	59.60
Run 11	40.39	16	0.0192	0.0432	0.0028	0.0013	0.0161	59.56
Average	**40.38**	**19**	**0.019**	**0.0415**	**0.0027**	**0.0012**	**0.0147**	**59.57**
Std Dev	0.072	1.3	0.00072	0.0015	0.0001	8E-05	0.0015	0.071

Table 3c: Short term precision test over one hour and a half using the goniometer – cupro-aluminum sample.

	Zn	Sn	Pb	Ni	Fe	Al	Si	P	S	Cd	Bi	Sb	As	Ag	Te	Cu
	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	Diff
	GON	GON	GON	GON	GON	GON	GON	GON	GON	GON	GON	GON	GON	GON	GON	FOR
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Run 1	0.903	15.32	0.249	0.0546	0.0668	0.081	0.088	0.033	0.0252	0.034	0.010	0.447	0.029	0.028	0.072	82.64
Run 2	0.898	15.32	0.252	0.0546	0.0674	0.080	0.089	0.035	0.0259	0.036	0.009	0.444	0.028	0.030	0.072	82.64
Run 3	0.901	15.31	0.255	0.0547	0.0671	0.082	0.087	0.034	0.0257	0.038	0.010	0.445	0.030	0.029	0.071	82.64
Run 4	0.901	15.34	0.254	0.0554	0.0669	0.083	0.089	0.033	0.0256	0.035	0.011	0.449	0.029	0.031	0.073	82.61
Run 5	0.903	15.37	0.256	0.0550	0.0672	0.082	0.090	0.034	0.0256	0.037	0.011	0.445	0.027	0.029	0.073	82.57
Run 6	0.905	15.34	0.253	0.0550	0.0673	0.082	0.089	0.034	0.0258	0.035	0.010	0.446	0.028	0.027	0.072	82.61
Run 7	0.899	15.34	0.250	0.0549	0.0672	0.081	0.090	0.034	0.0256	0.037	0.010	0.448	0.031	0.028	0.072	82.61
Run 8	0.905	15.36	0.253	0.0550	0.0669	0.082	0.090	0.034	0.0257	0.038	0.010	0.447	0.029	0.030	0.074	82.58
Run 9	0.906	15.35	0.252	0.0549	0.0673	0.081	0.091	0.033	0.0253	0.038	0.010	0.447	0.027	0.028	0.072	82.61
Run 10	0.903	15.36	0.253	0.0552	0.0667	0.083	0.091	0.033	0.0256	0.039	0.010	0.449	0.029	0.028	0.073	82.58
Run 11	0.908	15.34	0.249	0.0550	0.0670	0.082	0.090	0.034	0.0262	0.034	0.011	0.445	0.031	0.028	0.072	82.61
	0.903	**15.34**	**0.252**	**0.0549**	**0.0671**	**0.082**	**0.089**	**0.034**	**0.0256**	**0.037**	**0.010**	**0.447**	**0.029**	**0.029**	**0.072**	**82.61**
	0.003	0.0194	0.002	0.0002	0.0002	0.001	0.001	0.001	0.0003	0.002	0.001	0.002	0.0015	0.001	8E-04	0.03

These results show the excellent repeatability that the innovative goniometer fitted in the ARL X900 spectrometer provided for all types of copper alloys, e.g. brass, bronze, cupro-aluminum, and cupro-nickel. Given the 20-second measuring time per element, each test of 11 runs lasts for about 80 minutes. For some elements, the 20-second per element counting time could be reduced due to the excellent precision achieved. If the precision is not sufficient for a given element, the counting time can be increased, or a fixed monochromator channel can be fitted for that element to get best precision and fast response time.

Conclusion

Analysis of all sorts of copper alloys can be performed with ease using the ARL X900 Simultaneous-Sequential XRF Spectrometer. The performance of the Moiré fringe goniometer is such that it can be used for analysis of all the elements when the required response time is in the range of 5 to 8 minutes.

Alternatively, several fixed monochromator channels can be fitted to the configuration to speed up the analysis. Measurements on the goniometer are done while the fixed channels are measuring. The goniometer can be fitted to the configuration to speed up the analysis. In that case, the Measurements on the goniometer are done while the fixed channels are measuring. The goniometer can be used as a backup in case of failure of any of the fixed channels.

Appropriate calibrations for copper alloys can be delivered turnkey from the Thermo Fisher Scientific factory. In this case, the spectrometer's commissioning time is reduced to a minimum.

The precision is excellent in these matrix types for routine or R&D analysis, especially when the new high-counting fixed channel monochromator is used for elements like Cu, Zn and Ni.

Furthermore, operation is made easy through the state-of-the-art Thermo Scientific™ OXSAS™ X-Ray Fluorescence Analysis Software that operates with the latest Microsoft Windows® package.

Thermo Fisher Scientific's extensive experience in metals analysis is backed by an installed base of over 2,000 XRF spectrometers worldwide. The ARL X900 spectrometer is the answer to your metallurgical analysis needs, whether for incoming material control, metal QC, or production analysis. Operating 24/7, the ARL X900 spectrometer delivers dependable performance year after year.

The high performance of the ARL X900 spectrometer will meet your analytical needs today and in the future.