

## X-ray fluorescence

## Analysis of copper alloys with the ARL X900 XRF Spectrometer

### Keywords

ARL X900, X-ray fluorescence, XRF, WDXRF, copper, brass, bronze



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

### Goal

Describe the analytical performance of Thermo Scientific™ ARL™ X900 Series Spectrometer for copper alloys analysis using fixed channels and the Moiré fringe goniometer.

### 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 of 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) used for marine applications, car radiators and fittings.

### Brass

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  $\alpha$ -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.

## Bronze alloys

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.
- **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 accommodate up to 24 fixed monochromator channels alongside the goniometer or up to 32 fixed monochromator channels when no goniometer is fitted. New high counting fixed channel monochromators using an SCX detector are available to further improve the precision of analysis, especially for elements like Cu, Zn and Ni.

Our unique proprietary Moiré fringe goniometer ensures speed, flexibility and reliability of analysis thanks to the clever 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.

The ARL X900 XRF spectrometer can be calibrated using commercially available certified reference materials (CRM) or well analyzed samples from the user. Calibrations can be delivered from the factory, hence reducing the commissioning time at the customer's site.

It should be stressed that an XRF spectrometer is a very accurate comparator, but 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 which must be identical for CRMs and for routine samples as well.

This application note only includes data obtained mostly on fixed channels and on some goniometer channels. For more results using goniometer channels please refer to [AN41426](#).

## Typical performance in copper alloys samples

Table 1 gives a summary of limits of detection (LoD) determined by repeat analysis of a blank sample (pure copper) using 40 seconds and 100 seconds counting time per element on fixed channel monochromators at high power (4200W). The limits of detection are calculated as 3 times the standard deviation of 21 repeatability runs.

Forty seconds is the selected counting time for fixed channels used in the copper industry, permitting a final result in just over one minute. A hundred seconds counting time is often used to express limits of detection in X-ray fluorescence technique as a point of comparison.

**Table 1. Typical limits of detection in copper matrix for fixed channels at 40s and 100s counting time.**

Element	Line	Channel type	Detector	LoD (ppm)	
				40 s	100 s
Al	Kα	fixed channel	Gas sealed	5	3.2
Co	Kα	fixed channel	Scintillation	1.2	0.8
Cr	Kα	fixed channel	Gas sealed	5	3.2
Fe	Kα	fixed channel	Scintillation	2.4	1.5
Mn	Kα	fixed channel	Scintillation	2.4	1.5
Ni	Kα	fixed channel	SCX	5.1	3.2
P	Kα	fixed channel	Gas sealed	12.2	7.7
Pb	Lβ	fixed channel	Scintillation	7.5	4.7
S	Kα	fixed channel	Gas sealed	1.6	1.0
Si	Kα	fixed channel	Gas sealed	4	2.5
Sn	Kα	fixed channel	Scintillation	7	4.4
Zn	Kα	fixed channel	Scintillation	4	2.5

The values listed in the general table are calculated from the following formulas:

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

where Q = counts per second per 1 % element

B = background equivalent concentration

T = time of analysis in seconds

P = the percentage concentration at which the sigma value is calculated.

The limits of detection are determined using low alloy copper samples. In practice, these values should agree with values measured practically using the mathematical derivation of standard deviation (1sigma).

$$1\text{sigma} = \pm \sqrt{\frac{\sum(X-\bar{X})^2}{n-1}}$$

where

X = the individual readings

$\bar{X}$  = 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 1.5.

## Typical precision tests

The stability of an instrument reflects the precision that can be obtained. A short-term repeatability test consisting of eleven runs on a low alloy chill cast copper sample was performed. At each run, a counting time of 40 seconds is used for all elements on fixed channels and 20 seconds for the two elements on goniometer. This means that the total counting time per run is 40 seconds.

**Table 2a. Short term precision test using fixed channels and goniometer for Cd and As at 3500W – low alloy copper.**

Element	Zn	Sn	Pb	Ni	Fe	Al	Si	Mn	S	Cr	Co	Cd	As	Cu
Type	Fixed	Fixed	Fixed	Fixed	Fixed	Fixed	Fixed	Fixed	Fixed	Fixed	Fixed	GON	GON	by
Counting time (s)	40	40	40	40	40	40	40	40	40	40	40	20	20	diff
Unit	%	%	ppm	%	%	ppm	%	ppm	ppm	%	%	%	%	%
Run 1	0.0480	0.0608	16	0.0623	0.0109	40	0.0353	12	18	0.0550	0.0211	0.0337	0.0451	99.619
Run 2	0.0478	0.0605	17	0.0623	0.0107	44	0.0362	12	19	0.0548	0.0211	0.0311	0.0450	99.621
Run 3	0.0479	0.0603	12	0.0623	0.0108	39	0.0368	12	22	0.0549	0.0212	0.0327	0.0417	99.623
Run 4	0.0482	0.0609	17	0.0622	0.0108	47	0.0374	13	22	0.0548	0.0210	0.0319	0.0422	99.621
Run 5	0.0481	0.0606	15	0.0621	0.0109	47	0.0379	14	24	0.0550	0.0210	0.0297	0.0439	99.621
Run 6	0.0477	0.0604	13	0.0619	0.0107	49	0.0381	14	24	0.0547	0.0211	0.0319	0.0433	99.620
Run 7	0.0477	0.0603	9	0.0623	0.0109	42	0.0383	13	25	0.0553	0.0211	0.0318	0.0440	99.619
Run 8	0.0480	0.0608	10	0.0624	0.0107	40	0.0393	12	26	0.0549	0.0210	0.0355	0.0433	99.615
Run 9	0.0479	0.0602	12	0.0623	0.0109	47	0.0393	14	27	0.0551	0.0211	0.0329	0.0430	99.617
Run 10	0.0477	0.0604	11	0.0621	0.0107	45	0.0396	13	27	0.0551	0.0211	0.0317	0.0445	99.618
Run 11	0.0479	0.0605	12	0.0623	0.0107	41	0.0402	14	27	0.0548	0.0211	0.0311	0.0415	99.621
Average	<b>0.0479</b>	<b>0.0605</b>	<b>13</b>	<b>0.0622</b>	<b>0.0108</b>	<b>44</b>	<b>0.0380</b>	<b>13</b>	<b>24</b>	<b>0.0549</b>	<b>0.0211</b>	<b>0.0322</b>	<b>0.0434</b>	<b>99.620</b>
Std Dev	0.0002	0.0002	3	0.0001	0.0001	4	0.0015	1	3	0.0002	0.0001	0.0015	0.0013	0.0021

A short-term repeatability test consisting of eleven runs on a bronze sample was performed. At each run, a counting time of 40 seconds is used for all elements on fixed channels and 20 seconds for the elements on goniometer. This means that the total counting time per run is 160 seconds.

**Table 2b. Short term precision test using fixed channels on 9 elements and goniometer for 8 elements at 3500W – bronze.**

Element	Zn	Sn	Pb	Ni	Fe	Al	Si	P	S	Cd	Bi	Sb	As Kb	Ag	Se	Te	Zr	Cu
Type	Fixed	Fixed	Fixed	Fixed	Fixed	Fixed	Fixed	Fixed	Fixed	GON	GON	GON	GON	GON	GON	GON	GON	by
counting time (s)	40	40	40	40	40	40	40	40	40	20	20	20	20	20	20	20	20	Diff
Unit	%	%	%	%	%	%	%	%	%	%	ppm	%	%	%	ppm	%	ppm	%
Run 1	0.8905	15.383	0.3648	0.0524	0.0586	0.0789	0.0657	0.0269	0.0216	0.0380	92	0.4414	0.0307	0.0294	15	0.0730	54	82.429
Run 2	0.8889	15.374	0.3678	0.0525	0.0586	0.0789	0.0651	0.0265	0.0217	0.0354	89	0.4406	0.0330	0.0275	16	0.0678	55	82.446
Run 3	0.8907	15.374	0.3654	0.0524	0.0587	0.0788	0.0654	0.0272	0.0218	0.0363	91	0.4428	0.0320	0.0279	21	0.0712	57	82.438
Run 4	0.8915	15.383	0.3656	0.0523	0.0589	0.0789	0.0660	0.0270	0.0216	0.0383	94	0.4440	0.0316	0.0274	14	0.0702	57	82.427
Run 5	0.8908	15.372	0.3646	0.0524	0.0587	0.0789	0.0653	0.0257	0.0218	0.0377	91	0.4446	0.0321	0.0289	19	0.0712	59	82.439
Run 6	0.8902	15.369	0.3637	0.0522	0.0587	0.0795	0.0650	0.0269	0.0218	0.0357	97	0.4410	0.0293	0.0282	14	0.0704	54	82.452
Run 7	0.8918	15.356	0.3662	0.0522	0.0584	0.0785	0.0655	0.0263	0.0221	0.0347	95	0.4437	0.0326	0.0287	17	0.0723	54	82.454
Run 8	0.8916	15.383	0.3650	0.0524	0.0585	0.0783	0.0659	0.0261	0.0223	0.0403	88	0.4427	0.0328	0.0306	18	0.0699	53	82.425
Run 9	0.8906	15.376	0.3658	0.0524	0.0587	0.0777	0.0657	0.0270	0.0221	0.0369	91	0.4438	0.0323	0.0275	20	0.0713	56	82.436
Run 10	0.8904	15.379	0.3645	0.0525	0.0584	0.0791	0.0654	0.0276	0.0221	0.0365	94	0.4456	0.0322	0.0290	17	0.0705	53	82.431
Run 11	0.8903	15.374	0.3672	0.0526	0.0587	0.0795	0.0658	0.0292	0.0223	0.0339	02	0.4457	0.0321	0.0287	18	0.0692	56	82.434
Average	<b>0.8907</b>	<b>15.375</b>	<b>0.3655</b>	<b>0.0524</b>	<b>0.0586</b>	<b>0.0788</b>	<b>0.0655</b>	<b>0.0269</b>	<b>0.0219</b>	<b>0.0367</b>	<b>93</b>	<b>0.4433</b>	<b>0.0319</b>	<b>0.0285</b>	<b>17</b>	<b>0.0706</b>	<b>55</b>	<b>82.437</b>
Std Dev	0.0008	0.008	0.0012	0.0001	0.0002	0.0005	0.0003	0.0009	0.0003	0.0018	4	0.0017	0.0011	0.0010	<b>2.3</b>	<b>0.0014</b>	<b>2</b>	<b>0.010</b>

A short-term repeatability test consisting of eleven runs on a cupro-nickel sample was performed. At each run, a counting time of 40 seconds is used for all elements on fixed channels and 20 seconds for the two elements on goniometer. This means that the total counting time per run is 40 seconds. A power level of 3500W is used for this test. Due to their low fluorescence yield, both As and Te would benefit from longer counting time or being fitted as fixed channels depending on the response time needed.

**Table 2c. Short term precision test using fixed channels on 9 elements and goniometer for 2 elements at 3500W – cupro-nickel**

Element	Sn	Pb	Ni	Fe	Al	Si	Mn	Cr	Co	As Kb	Te	Cu
Type	Fixed	Fixed	Fixed	Fixed	Fixed	Fixed	Fixed	Fixed	Fixed	GON	GON	by
counting time (s)	40	40	40	40	40	40	40	40	40	20	20	diff
Unit	ppm	ppm	%	%	ppm	%	%	ppm	%	ppm	%	%
Run 1	34	53	20.028	0.9914	41	0.4822	0.7995	19	0.0683	55	66	77.604
Run 2	39	50	20.029	0.9917	38	0.4844	0.7996	18	0.0683	22	53	77.605
Run 3	28	49	20.023	0.9913	40	0.4832	0.7999	24	0.0682	19	49	77.613
Run 4	32	50	20.016	0.9912	36	0.4847	0.7994	18	0.0683	31	48	77.619
Run 5	35	52	20.022	0.9911	36	0.4851	0.7995	21	0.0680	32	54	77.612
Run 6	29	53	20.019	0.9912	36	0.4855	0.7994	22	0.0682	25	51	77.616
Run 7	32	51	20.019	0.9903	39	0.4845	0.7992	22	0.0680	29	44	77.618
Run 8	31	52	20.014	0.9918	32	0.4837	0.7997	22	0.0683	42	69	77.618
Run 9	29	51	20.012	0.9906	31	0.4837	0.7998	24	0.0683	26	41	77.625
Run 10	26	49	20.008	0.9914	32	0.4834	0.8001	18	0.0683	34	49	77.628
Run 11	33	51	20.010	0.9925	32	0.4833	0.8003	25	0.0683	48	70	77.620
<b>Average</b>	<b>32</b>	<b>51</b>	<b>20.018</b>	<b>0.9913</b>	<b>36</b>	<b>0.4840</b>	<b>0.7996</b>	<b>21</b>	<b>0.0682</b>	<b>33</b>	<b>54</b>	<b>77.616</b>
<b>Std Dev</b>	4	1.4	0.007	0.0006	4	0.0010	0.0003	3	0.0001	11	10	0.0072

A short-term repeatability test consisting of eleven runs on a brass sample was performed. At each run, a counting time of 40 seconds is used for all elements on fixed channels and 20 seconds for the three elements on goniometer. This means that the total counting time per run is 60 seconds. Due to their low fluorescence yield, elements Bi, As and Ag would benefit from longer counting time or being fitted as fixed channels depending on the response time needed. In case of need, the Bäkerud special method would provide better precision on Cu and Zn (please check separate dedicated application note).

**Table 2d. Short term precision test using fixed channels on 9 elements and goniometer for 3 elements at 3500W – brass**

Element	Zn	Pb	Ni	Al	Mn	S	Bi	As	Ag	Cu
Type	Fixed	Fixed	Fixed	Fixed	Fixed	Fixed	GON	GON	GON	by
counting time (s)	40	40	40	40	40	40	20	20	20	diff
Unit	%	ppm	ppm	%	ppm	ppm	ppm	ppm	ppm	%
Run 1	40.195	28	34	0.0161	51	9	5	76	7	59.767
Run 2	40.195	23	34	0.0164	51	8	5	50	2	59.770
Run 3	40.192	28	34	0.0159	52	9	5	59	1	59.772
Run 4	40.200	28	35	0.0166	50	9	3	59	10	59.762
Run 5	40.183	27	34	0.0168	52	9	15	55	14	59.778
Run 6	40.178	25	35	0.0162	51	10	2	50	17	59.785
Run 7	40.168	24	35	0.0165	51	10	6	61	1	59.795
Run 8	40.186	24	34	0.0166	50	9	4	51	4	59.779
Run 9	40.180	29	34	0.0168	51	9	12	45	9	59.782
Run 10	40.166	24	35	0.0165	51	10	1	50	15	59.797
Run 11	40.166	26	35	0.0159	51	9	8	63	2	59.796
<b>Average</b>	<b>40.183</b>	<b>26</b>	<b>34</b>	<b>0.0164</b>	<b>51</b>	<b>9</b>	<b>6</b>	<b>56</b>	<b>7</b>	<b>59.780</b>
<b>Std Dev</b>	0.012	2	0.5	0.00033	0.6	0.5	4	9	6	0.012

A short-term repeatability test consisting of eleven runs on a brass sample was performed. At each run, a counting time of 40 seconds is used for all elements on fixed channels and 20 seconds for the three elements on goniometer. This means that the total counting time per run is 60 seconds.

**Table 2e. Short term precision test using fixed channels on 9 elements and goniometer for 3 elements at 3500W – brass.**

Element	Zn	Sn	Pb	Ni	Fe	Al	Si	Mn	P	S	Cr	Bi	Sb	As Kb	Cu
Type	Fixed	Fixed	Fixed	Fixed	Fixed	Fixed	Fixed	Fixed	Fixed	Fixed	Fixed	GON	GON	GON	by
counting time (s)	40	40	40	40	40	40	40	40	40	40	40	20	20	20	Diff
Unit	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Run 1	14.529	0.1850	0.1618	0.1907	0.1056	0.2228	0.1490	0.1621	0.1335	0.1262	0.0028	0.1853	0.1821	0.1301	<b>83.529</b>
Run 2	14.536	0.1855	0.1616	0.1908	0.1059	0.2213	0.1490	0.1618	0.1324	0.1262	0.0031	0.1850	0.1827	0.1310	<b>83.521</b>
Run 3	14.532	0.1851	0.1620	0.1905	0.1057	0.2216	0.1492	0.1620	0.1321	0.1263	0.0032	0.1854	0.1832	0.1279	<b>83.529</b>
Run 4	14.530	0.1856	0.1616	0.1904	0.1056	0.2238	0.1497	0.1620	0.1298	0.1262	0.0032	0.1853	0.1830	0.1306	<b>83.527</b>
Run 5	14.527	0.1854	0.1613	0.1909	0.1057	0.2243	0.1501	0.1620	0.1298	0.1263	0.0037	0.1866	0.1838	0.1277	<b>83.529</b>
Run 6	14.523	0.1847	0.1620	0.1905	0.1055	0.2230	0.1499	0.1619	0.1304	0.1265	0.0034	0.1852	0.1818	0.1310	<b>83.534</b>
Run 7	14.527	0.1852	0.1624	0.1909	0.1054	0.2224	0.1500	0.1618	0.1317	0.1265	0.0033	0.1861	0.1808	0.1307	<b>83.528</b>
Run 8	14.537	0.1852	0.1616	0.1905	0.1055	0.2224	0.1493	0.1619	0.1315	0.1263	0.0035	0.1850	0.1789	0.1306	<b>83.525</b>
Run 9	14.524	0.1850	0.1615	0.1909	0.1054	0.2239	0.1502	0.1620	0.1322	0.1267	0.0029	0.1832	0.1809	0.1279	<b>83.537</b>
Run 10	14.529	0.1853	0.1615	0.1908	0.1057	0.2217	0.1501	0.1616	0.1323	0.1262	0.0030	0.1849	0.1780	0.1286	<b>83.534</b>
Run 11	14.537	0.1857	0.1615	0.1904	0.1057	0.2220	0.1498	0.1622	0.1330	0.1264	0.0028	0.1858	0.1827	0.1298	<b>83.520</b>
Average	<b>14.530</b>	<b>0.1852</b>	<b>0.1617</b>	<b>0.1906</b>	<b>0.1056</b>	<b>0.2227</b>	<b>0.1497</b>	<b>0.1619</b>	<b>0.1317</b>	<b>0.1263</b>	<b>0.0032</b>	<b>0.1853</b>	<b>0.1816</b>	<b>0.1296</b>	<b>83.529</b>
Std Dev	0.0050	0.0003	0.00032	0.00022	0.00015	0.0010	0.00047	0.00015	0.0012	0.00015	0.00028	0.00084	0.0018	0.0014	<b>0.0053</b>

## 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 any elements that are not fitted as fixed channels. The analysis on the goniometer is done while the fixed channels are measuring. In addition, it 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 commissioning time of the spectrometer 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 innovative Thermo Scientific™ OXSAS™ Software that operates with the latest Microsoft Windows® package.

Thermo Fisher Scientific's long experience in metals analysis comes from an installed base of over 2,000 XRF spectrometers worldwide. The ARL X900 spectrometer is the answer to your metallurgical analysis needs, whether they involve incoming material control, metal QC, or production analysis. Working 24 hours a day and 7 days a week, the ARL X900 spectrometer delivers dependable performance year after year.

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

 Learn more at [thermofisher.com/arlX900xrf](https://thermofisher.com/arlX900xrf)