UniQuant® 5

Ultra wide range metals analysis

Summary

X-Ray Spectrometers have been traditionally used for the routine analysis of a wide range of raw materials, intermediates and finished products in both the ferrous and non-ferrous metal industries. In particular, a number of alloys may have a very wide range of concentrations.

The conventional approach for wide-range alloy analysis is briefly discussed and compared with the UniQuant method.

Results obtained for a wide variety of alloys are presented and discussed.

The conventional method

The introduction, in the 1970ís, of mathematical models supported by regression analysis and interelement correction coefficients derived from theory resulted in highly accurate analysis, particularly for homogeneous samples.

This conventional approach enabled ultra-wide range metals analysis to become feasible if preceded by an extensive study using many standards to find or refine coefficients for interelement correction and for additional line overlap corrections.

Regression analysis as such can lead to unsuspected errors. For example, if calibration sample data are too much correlated, the resulting coefficients may have large errors that will show up if samples are analyzed with a composition not represented by the set of standards (even if each element is in the targeted range!).
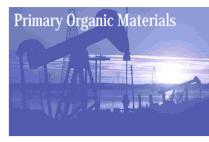
Also, regression analysis may attribute the effect of line overlap to an interelement effect and vice-versa. This implies that the user must be aware of such possibilities and have sufficient experience with multiple regression analysis.

Fortunately, once established, most coefficients can be used on other spectrometers with the same configuration resulting in fast calibration using a small set of standards. The latter are used to determine the instrument dependent coefficients, namely sensitivities (slopes), equivalent background at zero concentration. In addition the line overlap coefficients have to be checked since they are somewhat dependent on the calibration of goniometer angles.

The UniQuant method

Although UniQuant is primarily intended for use as a single program for any type of sample, it can also be used for a particular family of samples to achieve the highest possible accuracyís.

A major difference compared to the conventional method is that UniQuant depends far less on regression analysis. For example, line overlap coefficients are measured directly with samples of 100% of a particular element.

Regression coefficients for first and second order interelement corrections are not used, since UniQuant is based on the Fundamental Parameters method. As a result, regression analysis needs to be applied only for firming up the instrumental sensitivities, Kappas.

Primary Organic Materials

Primary Mineral Materials

Primary Metals

Components/Finished Products

Research

Waste Disposal & Environment

Unlike conventional methods, calibration data found with any family of samples can be used as a starting point for highly accurate analysis of another family of samples, for example an ultra-wide range of glass and bead samples. This is because instrumental sensitivities, Uni-Quantís Kappas, are in principle the same for any type of material e.g. alloys, glass, oil, polymers etc.

Analytical program

UniQuant prescribes the instrumental parameters (e.g. analyzing crystals and collimators) for about 100 analyte XRF lines. This set along with the measuring times constitutes the full analytical program for data collection. The standards listed in the next section were measured using the full analytical program with each line being measured for 4, 6 or 10 seconds as used by default. In other words, the analytical program has not been set up specifically for alloys.

Note:
A special analytical program for alloys would require a selection of some 30 XRF lines with increased measuring times for trace elements. Also, in specialized analytical programs, UniQuant allows the selection of more sensitive analyzing crystals and coarser collimators to increase intensities to a level limited only by resolution (line overlap) issues. In this case, for a given family of samples, there are fewer line overlaps and resolution can be allowed to be lower.

The sequential spectrometer used in this study was equipped with a high power Rhodium end window X-Ray tube.

Analysing crystals were LiF220, Ge111 and TlAP as normally prescribed by UniQuant.

Calibration

The spectrometer used had already been calibrated for universal applications i.e. for analysing any type of sample.
In order to maximise accuracies for an ultra-wide range of alloys, the universal calibration data were simply copied to a new data bank for the alloys and ì firmed upî using a small set of international standards.
The following 9 certified standards were used for this procedure;

Code	Description
BNRM_59C	Low alloy steel
BNRM_89E	Cr-Steel
BNRM_170	CoCrW Ni
BNRM_172	CoNiCrW
BNRM_181	CrMnNi
BNRM_198	NiCrCoMoTi
BNRM_625	NiCrMoFeNb
BNRM_510W	Bronze
BNRM_857C	Brass

In addition, to further extend the concentration ranges, an additional 12 samples of 100% of an element or oxide were used for Al, As2O3, Cd, Mn, Mo, Nb, Pb, Sn, Ti, V, W and Zr. The concentration ranges are shown in Table 1.

For each analytical XRF line, the sensitivity was determined by a weighted average of the Kappas found from the individual standards. In this procedure, the K-factor is minimized, being a measure for the accuracy over an entire range of concentrations.

Note:
The K-factor was introduced in XRF analysis by Willy K. de Jongh in 1967, the same pioneer responsible for the development of the UniQuant program.
The basis of the K-factor is the fact that analytical errors in chemistry and in XRF spectrometry are proportional to the square root of the concentration, except at very low concentrations where the errors are independent of the concentration. K-factors are calculated by UniQuant during calibration and are later used to estimate errors when analyzing unknown samples.

The Root Mean Square (RMS) deviations are formalized by

$$RMS = K \sqrt{\%C + \%EqBg}$$

where K is the K-factor and EqBg stands for equivalent background in weight% ranging from 0.02 to 0.2%.
K-factors of 0.008 to 0.050 represent high accuracy. Values higher then about 0.070 indicate low to poor accuracy.
The K-factors found from the standards used are shown in Table 1.

UniQuant®5

Table 1

Line	Range in wt% from	to	Kfactor
AlKa	0.005	100	0.023
AsKb	0.052	76	0.005
CdKa	58.74	100	0.046
CoKa	0.045	59	0.046
CrKa	1.02	30	0.031
CuKa	0.110	95	0.043
FeKa	0.018	86	0.019
MnKa	0.024	100	0.028
MoKa	0.031	100	0.017
MoLb	0.031	10	0.011
NbKa	0.013	100	0.008
NbLa	0.013	100	0.013
NiKa	0.130	61	0.023
P Ka	0.007	0.2	0.027
PbLb	0.008	100	0.017
PbLa	0.008	100	0.031
S Ka	0.020	0.1	0.017
SbKa	0.006	83	0.018
SiKa	0.016	34	0.028
SnKa	0.420	100	0.036
TiKa	0.008	100	0.034
V Ka	0.012	100	0.022
W Lb	0.036	100	0.056
W La	0.036	100	0.047
ZnKa	0.008	38	0.025
ZrKa	0.061	100	0.039
ZrLa	0.061	100	0.026

Results

The same standards used for calibration were treated as unknown samples. The calculated concentrations are shown in Table 2 together with the average values found in a round robin test by 15 laboratories using a variety of instrumental analysis techniques.

Tables 3 and 4 show the results in more detail for two of the samples.

Validity

It may be argued that always good results will be found for samples that themselves were used as standard. This would be perfectly true if many coefficients were determined by regression analysis, as is the case for the conventional method. Indeed, the method of multiple regression makes data fit regardless of their physical meaning. Then treating the same standards as unknown samples will always show good results.

With UniQuant however, only one coefficient per analytical equation is found by regression, namely Kappa.

All other coefficients, even those for line overlaps are determined independently on a physically sound basis.

Hence, it is perfectly correct to treat the 9 certified standards as unknown samples in order to demonstrate the performance of the UniQuant method.

A future unknown homogeneous sample with each element in the targeted concentration range will be correctly analyzed even if its composition is vastly different from any of the calibration standards used.

This is in contrast to the conventional method for which it is wise to check as many standards as possible to ensure that the set of regression coefficients are generally valid.

Conclusion

The UniQuant software and method is capable of providing highly accurate analysis of an ultra-wide range of alloys.

The calibration procedure used is simple and requires a small number of certified standards. Lower detection limits (LLDís) are good and if necessary can be made equivalent to conventional methods by adapting the instrumental parameters normally prescribed by UniQuant.

Table 2
Ultra-wide range of Alloys

Concentrations are in weight %.

BNRM	_59C	_89E	_170	_172	_181	_198	_625	_510W	_857C
El.	LowAlloy Steel	Cr-Steel	CoCr W Ni	CoNi CrW	CrMnNi	NiCrCo MoTi	NiCrMo FeNb	Bronze	Brass
Ni	0.15	0.370	2.29	24.28	8.34	53.64	59.99	0.0	0.13
	0.14	*0.372*	*2.27*	*24.53*	*8.27*	*53.94*	*60.16*	*(< 0.005)*	*?*
Fe	96.80	85.38	0.72	1.51	61.46	1.46	4.20	0	0.19
	96.84	*85.61*	*0.70*	*1.50*	*61.49*	*1.45*	*4.21*	*(< 0.003)*	*0.20*
Co	0.0	0.34	59.03	36.34	0.15	10.38	0.081	-	0.0013
		0.054	*59.12*	*36.28*	*0.15*	*10.26*	*0.089*	*-*	*-*
Cr	1.02	12.52	29.53	21.95	16.31	18.89	21.50	0.0003	0.0079
	1.01	*12.58*	*29.55*	*22.09*	*16.29*	*19.02*	*21.62*	*-*	*-*
W		0.0044	3.98	13.40	0.0339	0.12	0.0421	0.0374	0.0080
			3.89	*13.27*	*(0.036)*	*(0.13)*	*-*	*-*	*-*
Mo	0.15	0.031	0.79	0.35	0.24	9.81	8.23	0.0183	0.0019
	0.16	*0.031*	*0.81*	*0.34*	*0.24*	*9.76*	*8.24*	*-*	*-*
Nb		0.014	0.017	0.013	0.0256	0.051	3.47	0.0029	0
			0.017	*0.013*	*0.024*	*0.050*	*3.45*	*-*	*-*
Mn	0.89	0.43	1.50	0.95	8.58	0.0202	0.19	< 0.002	0.002
	0.89	*0.45*	*1.54*	*0.96*	*8.53*	*0.024*	*0.21*	*0.0023*	*0.038*
Cu	0.11	0.14	0.0083	0.0394	0.40	0.0618	0.38	94.70	60.32
	0.11	*0.15*	*0.004*	*< 0.002*	*0.39*	*(0.026)*	*0.31*	*94.49*	*60.19*
Zn				0.0162		0.0178	0.0161	0.031?	37.99
							-	*(< 0.008)*	*0.006*
Sn	0.0095	0.0022	0.0008		0.008	0.006	0.0063	4.91	0.43
		0.003			*0.007*		*-*	*4.77*	*0.42*
Sb	0.0041				0.002	0	0	0	0.0056
							-	*(< 0.005)*	*0.006*
Pb						0.024	0	0.009	0.62
							-	*0.008*	*0.63*
Ti		0.0010	0.0054	0.030	0.0118	3.39	0.31	0.0001	0.0009
			0.0033				*0.32*	*-*	*-*
V	0.0028	0.066	0.0055	0.003	0.074	0.019	0.016	0.0015	0.0003
		0.067	*(0.004)*		*0.075*	*0.012*	*-*	*-*	*-*
Si	0.21	0.35	0.59	0.42	4.02	0.053	0.27	0.016	0.0231
	0.21	*0.36*	*0.62*	*0.47*	*4.10*	*0.053*	*0.28*	*0.016*	*0.023*
Al	0.039	< 0.006	0.17	0.10	0.045	1.56	0.20	< 0.004	0.19
	0.032	*0.005*			*0.058*	*?*	*0.21*	*0.039*	*0.21*
P	0.010	0.016	0.0038	0.007	0.031	0.008	0.013	0.19	< 0.008
	0.011	*0.015*	*0.0081*	*(0.002)*	*0.028*	*0.012*	*0.015*	*0.18*	*0.007*
S	0.067	0.028	< 0.008	< 0.009	0.030	0.010	0.019	< 0.009	0.007
	0.056	*0.020*	*(< 0.004)*	*< 0.001*	*0.024*	*0.012*	*(0.024)*	*(< 0.002)*	*-*
As								< 0.012	< 0.015
								< 0.005)	*0.015*
									(< 0.010)
SumC	99.0	100.1	100.6	100.1	100.5	100.9	101.1	99.8	101.2

SumC = Sum of concentrations before normalisation to 100%

Bold: UniQuant results
Italic: Average of 15 laboratories

UniQuant®**5**

Table 3

Standard BNRM_170 treated as unknown sample
All values are in weigt%

	XRF+UniQuant 5		Fifteen laboratories		
	[%]	StdErr	Min.	Average	Max.
Co	59.03	0.24	58.44	59.12	59.48
Cr	29.53	0.14	29.15	29.55	30.33
W	3.98	0.10	3.80	3.89	3.99
Ni	2.29	0.03	2.23	2.27	2.30
Mn	1.50	0.03	1.51	1.54	0.83
Mo	0.79	0.02	0.79	0.81	0.83
Fe	0.72	0.02	0.69	0.70	0.72
Si	0.59	0.02	0.56	0.62	0.65
Nb	0.017	0.001	0.016	0.017	0.020
V	0.0055	0.001		(0.004)	
P	0.0038	0.0009	0.0073	0.0081	0.0092
Ti	0.0054	0.0008	0.0020	0.0033	0.0059
Cu	0.0083	0.003	0.001	0.004	0.009
S	< 0.008			(< 0.004)	
C	1.18	fix		1.18	

Additionally by UniQuant:

Al	0.19	0.03
Mg	0.012	0.001
La	0.008	0.002
Cd	0.004	0.001

Table 4

Standard BNRM_625 treated as unknown sample
All values are in weigt%

	XRF+UniQuant 5		Fifteen laboratories		
	[%]	StdErr	Min.	Average	Max.
Ni	59.99	0.105	9.91	60.16	61.16
Cr	21.50	0.13	21.35	21.62	22.22
Mo	8.23	0.05	8.12	8.24	8.37
Fe	4.20	0.05	4.14	4.21	4.26
Nb	3.47	0.02	3.31	3.45	3.86
Cu	0.38	0.03	0.26	0.31	0.34
Ti	0.31	0.01	0.31	0.32	0.33
Si	0.27	0.02	0.24	0.28	0.31
Mn	0.19	0.02	0.20	0.21	0.21
Al	0.20	0.03	0.16	0.21	0.24
Co	0.081	0.003	0.084	0.089	0.096
S	0.019	0.008		(0.024)	
P	0.013	0.006	0.013	0.015	0.017
C	0.03	fix		0.03	

Additionally by UniQuant:

As	0.73	0.02
Tl	0.044	0.006
V	0.017	0.001
Cd	0.005	0.002

StdErr= Standard error, a practical value derived from equivalent
background and line overlaps, K-factor and counting error.
±1 StdErr gives 70 to 90% confidence interval.

UniQuant® 5

UniQuant Æ is a registered trademark of

Omega Data Systems BV

St. Servaasweg 20

5614 CB Eindhoven

The Netherlands

E-mail: ods@uniquant.com

Web Site: www.uniquant.com