Application Note WDXRF1102

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XRF1102 - Standardless FP analysis of plant, animal and food samples applying correction by scattering line

Introduction

X-ray fluorescence (XRF) analysis has been widely used for quality or production control in a variety of industries because of its simple sample preparation and high precision/repeatability.

Current XRF spectrometers are also capable of analyzing non-routine samples owing to the standardless FP analysis function using fundamental parameter (FP) technology. Progress in the FP method has improved the accuracy of standardless FP analysis in XRF.

For the FP quantification calculation, information about all the elements contained in a sample is required. When analysis samples contain elements that cannot be measured, it is necessary to define a balance component.

Organic compounds are the main components in plant, animal and food samples. Since it is difficult to accurately analyze the major elements of organics (i.e., C, H, O and N) by XRF, an organic compound is set as the balance component in standardless FP analysis of these materials. However, since only a single compound can be set as the balance component, the chemical composition of the organic compounds must be different from that of the balance component, which causes analysis error.

Furthermore, for tube-below systems such as ZSX Primus IVi, polymer film is placed under the analysis sample during measurement to avoid contamination or damage to the spectrometer caused by falling samples. Since the film absorbs fluorescent X-rays from the sample, fluorine or lighter elements cannot be analyzed.

Rigaku's standardless FP analysis program "SQX" has an optional function in which scattering X-ray lines (Rh-Kα Compton and Thomson) derived from the X-ray tube are used in the FP method of the SQX calculation to estimate the influence of components that cannot be analyzed in SQX, e.g. H, B, C, N and O. This option, the SQX Scatter FP Method, is effective for samples whose balance component is difficult to set, such as plant or animal samples, waste oil or plastic, sludge, and soil.

This application note demonstrates analysis results from plant, animal and food samples by standardless FP analysis with the SQX Scatter FP Method.

Sample and sample preparation

Twenty-four CRMs (certified reference materials) of plant, animal and food were chosen. Table 1 shows the list of the CRMs analyzed in this report.

Each CRM, in powder form, was pre-dried and pressed without a ring or cup at 100 kN using a cylinder-type pressing die with the inner diameter 32 mm. The pressed powder disk was placed in a sample holder with 6 μm polypropylene film under the disk.

Table 1: CRMs analyzed in this report.

Supplier*)	Sample code	Material
NIST	SRM1577b	Bovine liver
NRC	DOLT-2	Dogfish liver
NRC	DORM-2	Dogfish muscle
NRC	TORT2	Lobster hepatopancreas
JRC	BCR-062	Olive leaves
JRC	BCR-100	Beech leaves
JRC	BCR-101	Spruce needles
JRC	BCR-129	Hay powder
JRC	BCR-281	Rye grass
JRC	BCR-482	Lichen powder
NIES	CRM No.7	Tea leaves
NIM	GBW07603	Bush branches and leaves
NIM	GBW07604	Poplar leaves
NIM	GBW08501	Peach leaves
NIST	SRM1515	Apple leaves powder
NIST	SRM1570a	Spinch leaves
NIST	SRM1572	Citrus leaves powder
NIST	SRM1573a	tomato leaves powder
NIST	SRM8412	Corn stalk (zea mays)
JRC	BCR-151	Milk powder
NIES	CRM No.3	Chlorella
NIST	SRM1549	Non-fat milk powder
NIST	SRM1567a	Wheat flour
NMIJ	7405-a	Seaweed (Hijiki)

* • NIST : National Institute of Standards and Technology
• NRC : National Research Council of Canada
• JRC : European Commission's Joint Research Centre
• NIES : National Institute for Environmental Studies, Japan

- NIM : National Institute of Metrology, China
- NMIJ : National Metrology Institute of Japan

SQX Scatter FP Method

The "SQX Scatter FP Method" program has been improved. Since the scattered X-ray lines used in this program are measured with LiF(200), one of the standard crystals, it is not necessary to add LiF(220), which was required in the previous version of the SQX Scatter FP Method. Additionally, a measurement area 30 mm in diameter (in addition to 20 mm in diameter, available in the previous version) has become available for the SQX Scatter FP Method.

To apply the SQX Scatter FP Method, pressed powder disks of samples to be analyzed are weighed and their diameter and height (thickness) are measured. After measurement, the weight, diameter (or area) and height are entered into the software. Since the program estimates contents of elements that cannot be measured, it is not necessary to set a balance component. The FP calculation of this program considers the thickness of the specimen. When the pressed disk is thinner than the infinite thickness of elements contained in the sample, special procedures are not required.

This program is effective for not only organic-based material but also oxide samples that contain LOI components.

Instrument and measurement

The new SQX Scatter FP Method is available with the ZSX Primus IVi, a new tube-below sequential wavelength dispersive X-ray fluorescence (WDXRF) spectrometer, and the ZSX Primus IV, a tube-above sequential WDXRF spectrometer.

Measurement for this application note was carried out using the ZSX Primus IVi. The SQX Scatter FP Method was applied to all the CRMs listed in Table 1.

Analysis results

Table 2 shows analysis results of Na – Ca by the SQX Scatter FP Method together with the certified values of the CRMs.

Table 2: Analysis results by the standardless FP analysis with SQX Scatter FP Method. (unit: mass%)

Supplier & code		**Material**	**Na**		**Mg**		**Al**		**Si**	
			Std.	**XRF**	**Std.**	**XRF**	**Std.**	**XRF**	**Std.**	**XRF**
NIST	SRM1577b	Bovine liver	0.242	0.240	0.0601	0.056	(0.0003)	0.0026	-	0.0049
NRC	DOLT-2	Dogfish liver	-	0.615	0.0800	0.078	0.0025	0.0033	-	0.0090
NRC	DORM-2	Dogfish muscle	0.4946	0.383	0.1024	0.082	0.0011	0.0030	-	0.0057
NRC	TORT2	Lobster hepatopancreas	-	1.16	0.1184	0.092	0.003	0.0074	-	0.012
JRC	BCR-062	Olive leaves	-	0.017	-	0.108	0.0450	0.048	-	0.141
JRC	BCR-100	Beech leaves	-	0.023	0.088	0.105	0.0435	0.049	-	1.260
JRC	BCR-101	Spruce needles	-	n.d.	0.0619	0.049	-	0.017	-	0.307

JRC	BCR-129	Hay powder	-	0.362	0.145	0.141	-	0.014	-	0.155
JRC	BCR-281	Rye grass	-	0.368	-	0.146	-	0.015	-	0.144
JRC	BCR-482	Lichen powder	-	n.d.	0.0578	0.034	0.1103	0.081	-	0.183
NIES	CRM No.7	Tea leaves	-	n.d.	0.153	0.157	0.076	0.079	-	0.023
NIM	GBW07603	Bush branches & leaves	1.96	2.03	0.48	0.511	0.20	0.205	0.60	0.440
NIM	GBW07604	Poplar leaves	0.020	0.019	0.65	0.714	0.104	0.116	0.71	0.736
NIM	GBW08501	Peach leaves	-	0.024	0.47	0.493	-	0.087	-	0.244
NIST	SRM1515	Apple leaves powder	0.0024	n.d.	0.2710	0.239	0.0285	0.032	-	0.057
NIST	SRM1570a	Spinch leaves	1.821	1.98	(0.9)	0.837	0.0310	0.028	(0.1137)	0.103
NIST	SRM1572	Citrus leaves powder	0.0160	0.016	0.58	0.524	0.0092	0.014	-	0.118
NIST	SRM1573a	Tomato leaves powder	0.0136	n.d.	(1.2)	0.970	0.0598	0.051	(0.23)	0.214
NIST	SRM8412	Corn stalk (zea mays)	(0.0028)	n.d.	0.160	0.149	-	0.0076	-	0.236
JRC	BCR-151	Milk powder	-	0.405	-	0.112	-	0.0035	-	0.0056
NIES	CRM No.3	Chlorella	-	n.d.	0.33	0.375	-	0.012	-	0.028
NIST	SRM1549	Non-fat milk powder	0.497	0.369	0.120	0.086	(0.0002)	0.0029	(<0.0050)	0.0033
NIST	SRM1567a	Wheat flour	0.0006	n.d.	0.040	0.042	0.0006	0.0021	-	0.0077
NMIJ	7405-a	Seaweed (Hijiki)	1.62	1.53	0.679	0.625	0.0147	0.018	-	0.079

Supplier & code		**P**		**S**		**Cl**		**K**		**Ca**	
		Std.	**XRF**	**Std.**	**XRF**	**Std.**	**XRF**	**Std.**	**XRF**	**Std.**	**XRF**
NIST	SRM1577b	1.10	0.980	0.785	0.661	0.278	0.271	0.994	0.890	0.0116	0.017
NRC	DOLT-2	0.77	0.682	-	0.912	-	0.642	0.8	0.679	0.046	0.039
NRC	DORM-2	1.01	0.711	0.79	0.631	-	0.560	1.44	1.22	0.049	0.032
NRC	TORT2	1.0	0.781	1.04	0.820	-	1.57	0.81	0.707	0.33	0.256
JRC	BCR-062	-	0.110	0.1600	0.146	0.0700	0.079	-	0.595	-	2.00
JRC	BCR-100	0.155	0.176	0.269	0.316	0.149	0.185	0.99	1.18	0.530	0.594
JRC	BCR-101	0.1690	0.145	0.1700	0.152	0.0688	0.061	-	0.725	0.4280	0.365
JRC	BCR-129	0.236	0.219	0.316	0.304	-	0.970	3.38	3.15	0.640	0.599
JRC	BCR-281	-	0.226	-	0.314	-	0.967	-	3.16	-	0.635

JRC	BCR-482	0.069	0.043	0.2166	0.127	-	0.224	0.39	0.267	0.2624	0.149
NIES	CRM No.7	0.38	0.353	-	0.252	-	0.082	1.91	1.99	0.319	0.305
NIM	GBW07603	0.100	0.102	0.73	0.709	(1.92)	2.07	0.92	1.08	1.68	1.76
NIM	GBW07604	0.168	0.175	0.35	0.398	(0.23)	0.257	1.38	1.61	1.81	1.96
NIM	GBW08501	-	0.286	-	0.233	-	0.067	2.17	2.47	-	1.57
NIST	SRM1515	0.1593	0.140	(0.180)	0.166	0.0582	0.050	1.61	1.54	1.53	1.39
NIST	SRM1570a	0.5187	0.504	(0.5)	0.501	-	0.673	2.900	3.09	1.526	1.48
NIST	SRM1572	0.13	0.125	0.407	0.399	(0.0414)	0.040	1.82	1.87	3.15	2.88
NIST	SRM1573a	0.2161	0.186	(0.96)	0.831	(0.66)	0.600	2.6760	2.44	5.0450	4.35
NIST	SRM8412	-	0.059	-	0.068	0.244	0.264	1.735	1.84	0.216	0.217
JRC	BCR-151	-	0.983	-	0.342	0.97	0.961	-	1.76	-	1.23
NIES	CRM No.3	(1.7)	1.44	-	0.783	-	0.023	1.24	1.11	0.49	0.423
NIST	SRM1549	1.06	0.776	0.351	0.264	1.09	0.863	1.69	1.34	1.30	0.994
NIST	SRM1567a	0.134	0.131	0.165	0.156	(0.0565)	0.055	0.133	0.124	0.0191	0.018
NMIJ	7405-a	0.101	0.094	-	1.36	-	2.02	4.75	4.81	1.52	1.51

Std. : standard (certified) value
( ) : information value
XRF : analysis value
- : no certified value provided
n.d. : not detected

To demonstrate how the results match the certified values, the analysis values by the SQX Scatter FP and the certified values of the CRMs are plotted in Figure 1, where there is a good correlation between these values, as demonstrated by a correlation factor of 0.98. Since analysis results of light elements, in particular, are significantly influenced by the setting of immeasurable elements (oxygen or lighter elements), incorrect setting of the balance component causes large errors in the light element results.

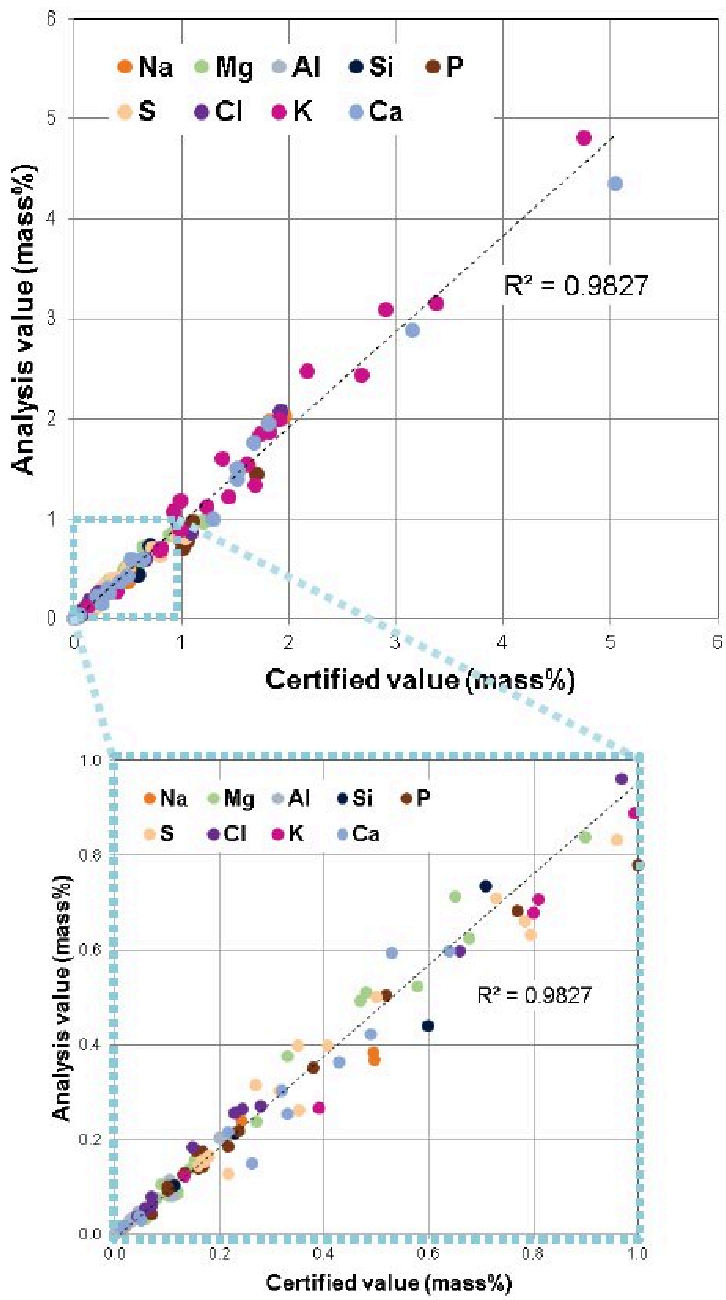

Figure 1: XRF analysis results by the SQX Scatter FP with the certified values of the CRMs used. The lower plot is a magnified plot for 1 mass% or lower concentration.

The SQX Scatter FP Method automatically corrects for influences by immeasurable elements of oxygen or lighter elements.

Conclusion

The SQX Scatter FP Method, an optional function in Rigaku's standardless FP analysis program "SQX", estimates the influence of components that cannot be analyzed in SQX, e.g. H, B, C, N and O.

The analysis results demonstrated using ZSX Primus IVi in this application report prove that the SQX Scatter FP Method is effective for samples whose main component cannot be measured or defined as a balance component, such as animal, plant and food.

Related products

ZSX Primus IV*i*

High-power, tube-below, sequential WDXRF spectrometer wi th new ZSX Guidance expert system software