Application Note EDXRF3197

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Application Note EDXRF 3197: Additives in Polymers

Scope

This application note demonstrates the use of EDXRF to measure additives in petroleum-based polymers and polyvinyl chloride (PVC) using the Rigaku NEX QC+ QuantEZ.

Background

Petroleum-based petrochemical polymers such as polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET, PETE), and polyvinyl chloride (PVC) often contain compound additives that help achieve specific properties desired in the polymer. These additives include lubricants, plasticizers, stabilizers, anti-block, impact modifiers, and flame retardants and typically include elements such as Mg, Al, Si, P, Cl, Ca, Ti, Zn, Br, and Sb. During the production process, the elemental composition must be measured to ensure that the polymer formulations meet targeted specifications. To maintain proper quality control during production, test samples are made, and the trace elements are measured.

Energy dispersive X-ray fluorescence (EDXRF) offers a fast, non-destructive method for performing elemental analysis in various sample forms. Applied Rigaku Technologies provides a full line of benchtop EDXRF analyzers, such as the NEX QC+ QuantEZ. They are well-suited for quality control applications throughout the polymer manufacturing process due to their intuitive software interface, innovative design, and powerful analytical performance. Rigaku EDXRF systems make an excellent tool for quality control checks at several places along the polymer production process.

Methodology

Empirical best-fit regression calibration, Fundamental Parameters (FP) screening, and FP with Matching Library are demonstrated.

Additives in PP

Calibration by empirical best-fit regression

Because all elements are at trace levels, X-ray absorption/enhancement effects are negligible and can be ignored for process quality control. Each calibration standard can include all elements dispersed independently, or a series of single-element standards can be used to make calibrations. A series of single-element standards were used in this demonstration, with the calibration results summarized here.

Element	Number of standards	Concentration range
Al	3	76 – 230 ppm
Si	5	0.018 – 0.097 mass%
P	4	36 – 92 ppm
Cl	5	24 – 103 ppm
Ca	4	38 – 188 ppm
Ti	2	3.7 – 9.2 ppm

Repeatability (precision)

Typical precision is shown here. Ten repeat analyses of each middle concentration sample were performed with the sample in a static position using a total analysis time of 600 sec per analysis.

Element	Units	Known value	Average result	Std. deviation	% Relative
Al	ppm	109	114	11	10%
Si	mass%	0.0597	0.0584	0.0010	1.7%
P	ppm	51	55.2	2.4	4.7%
Cl	ppm	54	52.0	0.7	1.3%
Ca	ppm	74	73.8	1.1	1.5%
Ti	ppm	3.7	3.8	0.3	8.1%

Additives in PVC

Calibration by FP with Matching Library

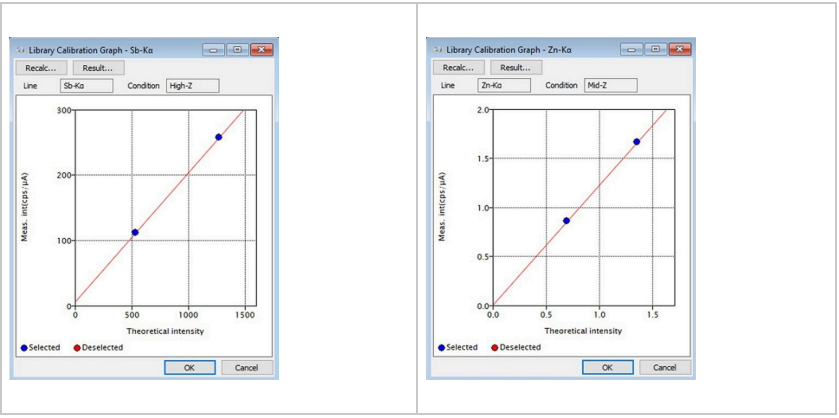
Rigaku RPF-SQX FP software estimates elemental concentration based on XRF theory Fundamental Parameters (FP). Rigaku Profile Fitting automatically deconvolutes spectral peaks and models the sample matrix using fundamental XRF equations to provide semi-quantitative measurements of elemental concentrations without the need for any known standards.

FP accuracy is optimized by creating Matching Libraries using well-assayed, matrix-matched type standards. Matching Libraries can be easily created by the user and are used in conjunction with the standard FP library in the modeling of a sample matrix and calculation of concentration results. This allows for a quantitative measurement of elemental concentrations without needing a large suite of known assayed calibration standards.

For this demonstration analyzing PVC, the default Polymer template was used as the basis for the analysis of the PVC plaques. Cl was analyzed as an element to give Cl content, and polyethylene was set as the default matrix balance component (unmeasurable portion of the sample) to represent the remaining C_2H_3 part of PVC.

A 2-point Matching Library was used to optimize FP using two PCV samples with accurate known assay numbers for each element.

A Matching Library adjusts FP theory to match the actual material and referee numbers.



Example: Matching Libraries for Sb and Zn in PVC

Results — FP with Matching Library

Sample ID: PVC Sample 1 Units: Mass%			
Component	**Known value**	**Result**	**Stat. error**
Mg	0.510	0.485	0.0016
Al	1.48	1.36	0.0045
Si	1.30	1.20	0.0026
Cl	30.60	30.95	0.0113
Ca	4.02	4.12	0.0196
Fe	n/a	0.0160	0.0004
Zn	0.0300	0.0310	0.0002
Sr	n/a	0.0020	<0.0001
Sb	0.499	0.508	0.0008
Pb	n/a	0.0007	<0.0001

Polyethylene	Balance	61.32	Balance

Sample ID: PVC Sample 2 Units: Mass%			
Component	**Known value**	**Result**	**Stat. error**
Mg	0.180	0.177	0.0024
Al	1.33	1.41	0.0046
Si	1.31	1.38	0.0027
Cl	30.90	29.54	0.0100
Ca	3.96	4.58	0.0209
Fe	n/a	0.0173	0.0004
Zn	0.0100	0.0098	0.0001
Sr	n/a	0.0021	<0.0001
Sb	2.00	2.12	0.0019
Pb	n/a	0.0021	0.0001
Polyethylene	Balance	60.7675	Balance

n/a means no Matching Library was used, results are semi-quant screening for informational purposes

Flame retardants in polymer additive beads and finished polymer sheets

Demonstrated here are the analyses of flame-retardant additives as beads and a finished polymer sheet containing flame retardants by FP semi-quant screening.

Sample ID: Additive Units: Mass%		
Component	**Quant EZ value**	**Stat. error**
Br	3.85	0.0021
Sb	1.94	0.0023
Si	0.524	0.0017
Ti	0.0383	0.0012
Ni	0.0140	0.0002
PE	93.64	Balance

Sample ID: Finished Film Units: Mass%		
Component	**Quant EZ value**	**Stat. error**
Br	0.423	0.0005
Sb	0.200	0.0015
Si	0.134	0.0009
Ti	0.580	0.0020
Ni	0.0008	0.0001
PE	98.86	Balance

Conclusion

EDXRF provides a rapid, non-destructive means of semi-quantitative measurement for screening and identification, as well as elemental quantification of metals, solids, powder, pellets, thin films, and liquids. Various methods of calibration and measurement give the user flexibility to develop calibrations and methodology to best suit the needs of their quality control programs. The NEX QC+ QuantEZ is powerful yet simple and intuitive software that gives the quality control lab and at-line technicians a fast means of making QC checks along the production process line in the manufacturing of polymers.

Related products

NEX QC II Series

Compact, intuitive benchtop EDXRF for everyday elemental testing