EDXRF APPLICATION NOTE
CHLORINE & ROHS ELEMENTS
IN POLYETHYLENE

#1033

SCOPE

This Application Note shows performance for the elemental analysis of Cl and elements regulated by RoHS in plastics. Analysis is shown for polyethylene. Empirical calibration summary and detection limits are shown and instrument repeatability is demonstrated.

BACKGROUND

The Restriction on Hazardous Substances initiative (RoHS) has been in force for several years. RoHS limits the allowable amounts of various toxic elements in plastics and consumer goods. The latest extension to the RoHS regulatory guidelines is the measurement and control of Total Halogens, with particular emphasis on the chlorine content. EDXRF is an accepted analysis technique for the screening and quantification of the hazardous element according to RoHS norms. To meet the industry challenge, Rigaku offers the NEX CG EDXRF analyzer using indirect excitation and polarization, giving QA/QC processes the means for fast and simple screening and analysis of materials that must conform to RoHS and similar directives.

INSTRUMENTATION

Model: Rigaku NEX CG

X-ray tube: 50 W Pd-anode

Detector: High performance SDD

Sample Type: Hot-pressed Pucks (32mm)

Environment: Helium Purge

Standard: 15-position Sample Tray (32mm)

Optional: 9-position Sample Spinner Tray

Analysis Times:

Cl application: Total Analysis Time = 300 sec (100 sec per analysis condition)

Multi-element: Total Analysis Time = 400 sec (100 sec per analysis condition)

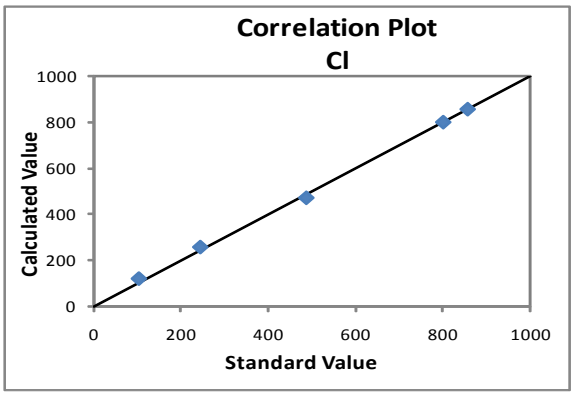
SAMPLE PREPARATION

Certified reference standards from ERM (European Reference Materials), MAT (Modern Analytical Techniques) and Thermo Scientific were used for this report. The standards were solid, homogeneous low density polyethylene pucks. No sample preparation was required, since flat, homogeneous samples that cover the instrument aperture require no sample preparation.

Cl CALIBRATION

Six reference standards were used for empirical calibration of Cl. The samples also contained unassayed amounts of the other elements. These elements were also measured and used to enable alpha corrections, which compensate for variations in X-ray matrix effects within the sample.

Element: Cl		RMS Dev: 17
Units: mg/kg		Correlation: 0.9991
Sample I.D.	Standard Value	Calculated Value
EC680k	102	122
CLPE-2018	243	259
CLPE-3018	486	472
EC681k	800	800
CLPE-4018	856	856



Cl REPEATABILITY

To demonstrate instrument precision, ten repeat analyses were performed with samples in static position using 300 sec analysis time.

Element: Cl	Units: mg/kg			
Sample ID	Standard Value	Average Value*	Std Dev	% Relative
EC680k	102	121	1	0.8
CLPE-2018	243	261	1	0.4
CLPE-3018	486	479	3	0.6
EC681k	800	799	7	0.8
CLPE-4018	856	851	4	0.5

* Average value reflects the calculated value from the calibration.

Cl DETECTION LIMITS

Cl lower detection limits were determined by analyzing 10 repeat analyses of the blank polyethylene puck to determine the standard deviation. The LLD (Lower Limit of Detection) is defined as three times the standard deviation.

Element	LLD	Count Time
Cl	1.2 mg/kg	100 sec
Cl	0.7 mg/kg	300 sec

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MULTI-ELEMENT CALIBRATIONS

Three of the certified standards were assayed for As, Br, Cd, Cl, Cr, Hg, Pb, S, Sb, Ba, and Se. A calibration was created for each element. Depending on the combination of elements in each standard, 1-, 2- or 3-point calibration curves were established for the particular element series. Multi-element analyses were performed with a total acquisition time of 400 sec per sample. All samples were measured against the calibrations to ensure effective recovery.

MULTI-ELEMENT REPEATABILITY

To demonstrate instrument precision, ten repeat analyses were performed with samples in static position using total analysis time of 400, 100 sec per analysis condition...

Element: As Units: mg/kg

Sample ID	Std Value	Avg Value*	Std Dev	% Relative
EC-680k	4.1	4.0	0.1	2.9
EC-681k	29.1	30.1	0.2	0.6
EN 71-3	50.0	50.5	0.2	0.3

Element: Hg Units: mg/kg

Sample ID	Std Value	Avg Value*	Std Dev	% Relative
EC-680k	4.6	3.5	0.3	7.4
EC-681k	23.7	26.1	0.9	3.3
EN 71-3	101.0	102.5	0.6	0.6

Element: Cr Units: mg/kg

Sample ID	Std Value	Avg Value*	Std Dev	% Relative
EC-680k	20.2	20.4	0.4	1.8
EC-681k	100.0	92.9	0.7	0.7
EN 71-3	102.0	102.0	0.4	0.3

Element: Pb Units: mg/kg

Sample ID	Std Value	Avg Value*	Std Dev	% Relative
EC-680k	13.6	15.9	0.4	2.23
EC-681k	98.0	94.9	0.6	0.6
EN 71-3	151.0	156.2	0.5	0.3

Element: Cd Units: mg/kg

Sample ID	Std Value	Avg Value*	Std Dev	% Relative
EC-680k	19.6	17.3	1.0	5.9
EC-681k	137.0	148.1	1.8	1.2
EN 71-3	290.0	297.7	4.2	1.4

Element: Br Units: mg/kg

Sample ID	Std Value	Avg Value*	Std Dev	% Relative
EC-680k	96.0	95.1	0.4	0.5
EC-681k	770.0	779.0	0.9	0.1

* Average value reflects the calculated value from the calibration.

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MULTI-ELEMENT REPEATABILITY *(cont.)*

Element: Ba Units: mg/kg				
Sample ID	**Std Value**	**Avg Value***	**Std Dev**	**% Relative**
EN 71-3	707.0	714.6	5.3	0.7

Element: S Units: mg/kg				
Sample ID	**Std Value**	**Avg Value***	**Std Dev**	**% Relative**
EC-680k	76.0	76.4	0.7	0.9
EC-681k	630.0	629.3	1.3	0.2

Element: Sb Units: mg/kg				
Sample ID	**Std Value**	**Avg Value***	**Std Dev**	**% Relative**
EC-680k	10.1	9.4	1.3	14.0
EC-681k	99.0	103.4	2.3	2.2
EN 71-3	96.0	122.6	2.2	1.8

Element: Se Units: mg/kg				
Sample ID	**Std Value**	**Avg Value***	**Std Dev**	**% Relative**
EN 71-3	204.0	204.5	0.5	0.2

* Average value reflects the calculated value from the calibration.

MULTI-ELEMENT DETECTION LIMITS

Multi-element lower detection limits were determined by analyzing 10 repeat analyses of the blank polyethylene puck to determine the standard deviation. The LLD (Lower Limit of Detection) is defined as three times the standard deviation and was obtained with 100 sec Condition Count Time for all elements.

Detection Limits Units: mg/kg	
Element	**LLD**
Cl	1.0
As	0.3
Br	0.2
Cd	1.2
Cr	0.2
Hg	0.8

Detection Limits Units: mg/kg	
Element	**LLD**
Pb	0.4
S	0.9
Sb	3.2
Ba	1.9
Se	1.3

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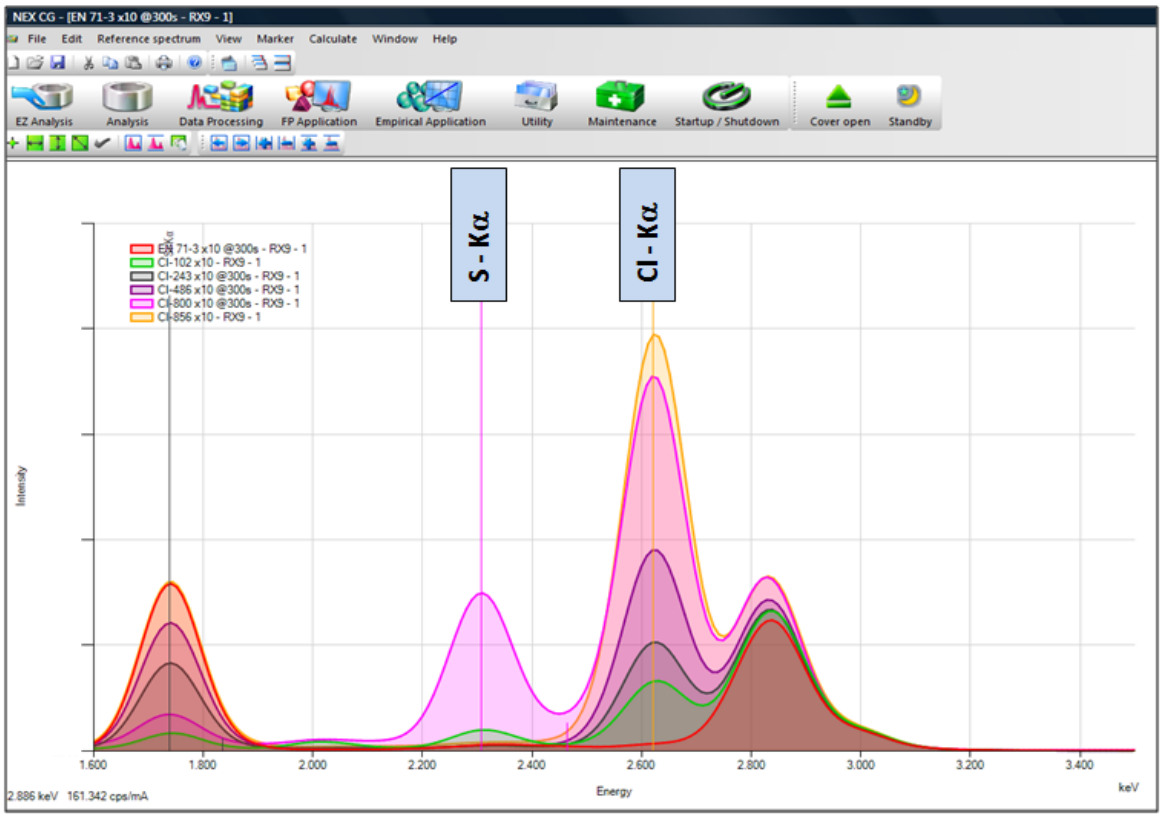
DISCUSSION

Review of spectral information shows that the Cl Kα peak is isolated and does not have any significant overlaps within the samples. This allows for accurate and repeatable results throughout the analysis range. An overlay of the spectrum from each sample is provided below:



CONCLUSION

The Rigaku NEX CG combines indirect excitation with secondary targets, polarization targets and a high performance SDD detector to yield the optimum performance in EDXRF instrumentation. The results shown here indicate the NEX CG is an excellent tool for the measurement of Cl and the RoHS elements in polyethylene. Similar performance can be expected in other non-PVC plastics. The NEX CG is wells-suited for QA checks of incoming material and QC of process control, as well as R&D of plastics formulations.

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