EDXRF APPLICATION NOTE

ROHS RAPID SCREENING BY BENCHTOP XRF

THE EMPIRICAL METHOD

#1238

INTRODUCTION

The measurement of Cr, Hg, Pb, Br and Cd in polyethylene (PE) by XRF rapid screening using the empirical method is discussed.

RoHS RAPID SCREENING BY XRF

The Restriction on Hazardous Substances (RoHS) has been in effect for several years and regulates the maximum allowable levels of Cr, Hg, Pb, Br, Cd and Cl in consumer goods, particularly in plastics and polymers. XRF is used in the RoHS and RoHS 2 protocols as a tool for rapid screening to quickly determine the presence of hazardous materials regulated by RoHS, mainly the elements Cr, Hg, Pb, Br and Cd. (Cl is also included in the regulated elements; see also Rigaku Application Note #1169). In the rapid screening protocols, tight accuracy is not required by the XRF screening tool. Exact levels controlled and screening ranges may vary slightly within the global regions adopting RoHS and similar protocols. A typical scheme is given here for rapid screening by XRF given maximum allowable limits of 1000 ppm each for Cr, Hg, Pb and Br and 100 ppm for Cd. When a result falls within the Inconclusive range, the sample is measured by ICP to confirm the elemental concentrations.

	XRF Measurement Result by rapid screening		
Element	**PASS Range (ppm)**	**INCONCLUSIVE Range (ppm)**	**FAIL Range (ppm)**
Cr	0-600	600-1200	>1200
Hg	0-600	600-1200	>1200
Pb	0-600	600-1200	>1200
Br	0-600	600-1200	>1200
Cd	0-75	75-150	>150

INSTRUMENTATION

Model: NEX QC VS

Excitation: Direct with filters

Collimators: 14mm, 8mm, 3mm

Camera: CMOS

X-ray tube: 4 W Ag-anode

Detector: Semiconductor

Atmosphere: Air

Applied Rigaku Technologies, Inc. ▪ 9825 Spectrum Drive, Bldg. 4, Suite 475 ▪ Austin, TX 78717 USA
www.RigakuEDXRF.com ▪ info@RigakuEDXRF.com ▪ (+1) 512-225-1796

NEX QC Accessories

Film: Mylar film was used.

Atmosphere: The NEX QC can be configured with optional helium purge. For RoHS rapid screening, an air atmosphere is suitable and helium is not required.

Window Rings: The 25mm diameter flat window ring was used. Other window rings include 10mm aperture flat, for small samples. Single position window rings are available for 32mm or 40mm sample cups. NEX QC can also be configured with optional 6-position 32mm autosampler, or a 5-position autosampler for 40mm diameter samples.

SAMPLE PRESENTATION & ANALYSIS METHODOLOGY

For the screening of incoming raw materials and during the manufacturing process of PE and other plastics, samples are typically granules, solid form after a melt poured into an XRF sample cup, or cold-pressed or hot-pressed pucks. Alternately, granules can be made into a fine powder using cryogenic mill (freezer mill). Whether in XRF sample cup or as pucks, samples lie flat and cover the measurement area and spot size determined by the particular collimator in use. Final products that fit inside the analysis chamber can also be tested, given the sample covers the 14mm, 8mm or 3mm spot size dictated by the collimator.

Samples below approximately 6mm in height may not be infinitely thick for all elements present, especially the higher energy elements like Br and Cd. When measuring a sample that is not infinitely thick to the fluorescent X-rays of all of the elements, several “aliquots” of the sample are stacked until the total sample is infinitely thick, >6mm in height.

Two measurement Conditions we used to generate the data shown.

Filter	Elements	Condition Measurement Time
A	Cr, Hg, Pb, Br	90 sec
B	Cd	90 sec

ASTM F2617-08e

ASTM committee F produces standards for declarable substances. In September, 2008, ASTM published standard test method F2617 Identification and Quantification of Chromium, Bromine, Cadmium, Mercury, and Lead in Polymeric Material Using Energy Dispersive X-ray Spectrometry. ASTM F2617 offers a standard measurement protocol, which is used in the following sections of this Application Note. ASTM F2617 Sec. 10 discusses Specimen Preparation, and Sec. 12.2 describes the empirical calibration technique.

This ASTM method can be purchased from the ASTM web site http://www.astm.org/Standards/F2617.htm.

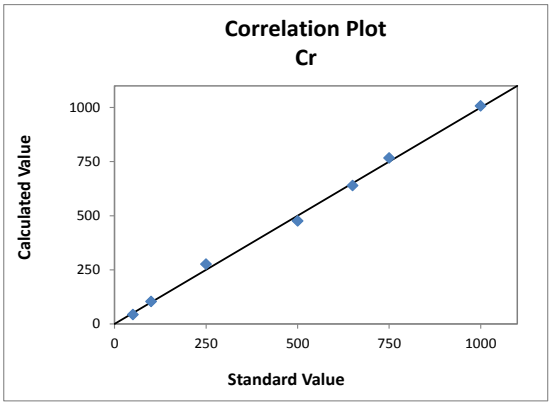
Applied Rigaku Technologies, Inc. ▪ 9825 Spectrum Drive, Bldg. 4, Suite 475 ▪ Austin, TX 78717 USA
www.RigakuEDXRF.com ▪ info@RigakuEDXRF.com ▪ (+1) 512-225-1796

EXAMPLE CALIBRATIONS

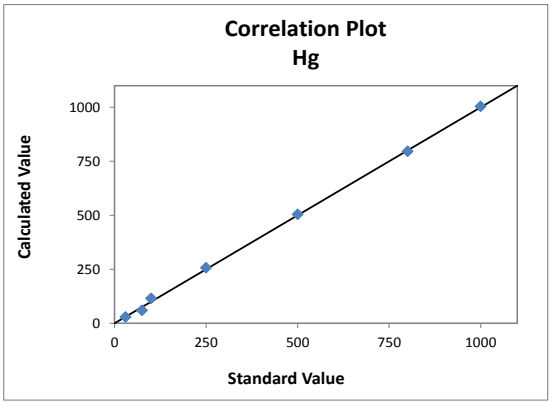
The following shows typical empirical calibrations in PE suitable for rapid screening using a set of 8 calibration standards provided by the group that made the set used for the ASTM F2617 inter-laboratory study. The calibrations were performed using the standard configuration in air environment and a total analysis time of 180 sec. Each sample was prepared as PE melt poured into a 32mm XRF sample and allowed to cool. Each sample was approximately 14mm in height. The calibrations shown below are an example of empirical calibration, and each fit has at least 3 degrees of freedom. The results shown here for the 14mm collimator are applicable to the standard NEX QC configuration, as well.

14mm collimator

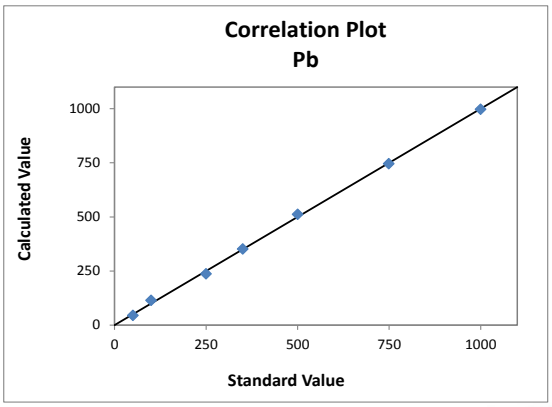
Element: Cr		Std Error of Est: 24
Units: ppm		Correlation: 0.99863
Sample I.D.	Standard Value	Calculated Value
STD 1	50	42
STD 2	750	766
STD 3	1250	1245
STD 4	1000	1007
STD 5	650	638
STD 6	250	275
STD 7	500	475
STD 8	100	102



Element: Hg		Std Error of Est: 14
Units: ppm		Correlation: 0.99962
Sample I.D.	Standard Value	Calculated Value
STD 1	100	114
STD 2	75	59
STD 3	500	503
STD 4	250	256
STD 5	801	795
STD 6	1000	1003
STD 7	30	28
STD 8	1200	1199



Element: Pb		Std Error of Est: 14
Units: ppm		Correlation: 0.99957
Sample I.D.	Standard Value	Calculated Value
STD 1	1000	997
STD 2	250	236
STD 3	50	44
STD 4	1250	1252
STD 5	749	745
STD 6	100	113
STD 7	500	511
STD 8	350	351

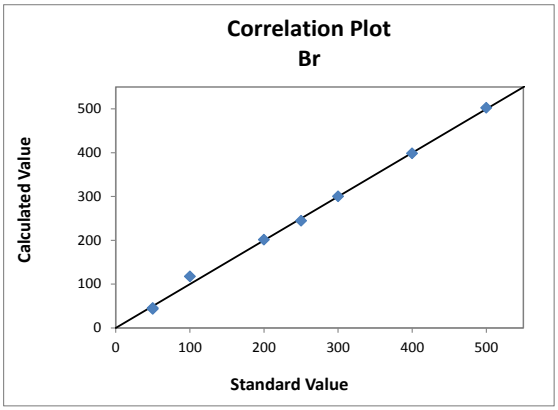


Applied Rigaku Technologies, Inc. ▪ 9825 Spectrum Drive, Bldg. 4, Suite 475 ▪ Austin, TX 78717 USA
www.RigakuEDXRF.com ▪ info@RigakuEDXRF.com ▪ (+1) 512-225-1796

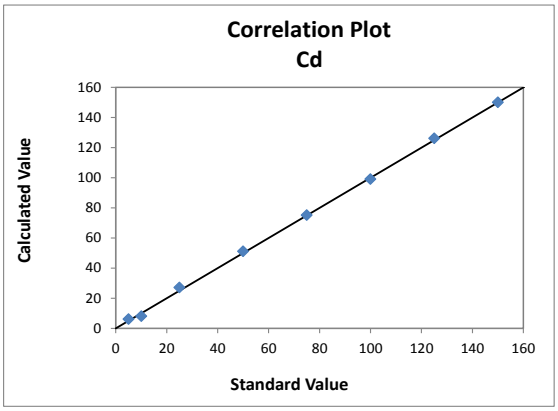
EXAMPLE CALIBRATIONS (*continued*)

14mm collimator

Element: Br		Std Error of Est: 12
Units: ppm		Correlation: 0.99790
Sample I.D.	Standard Value	Calculated Value
STD 1	50	45
STD 2	400	398
STD 3	100	117
STD 4	250	244
STD 5	500	502
STD 6	200	201
STD 7	300	300
STD 8	50	43



Element: Cd		Std Error of Est: 3
Units: ppm		Correlation: 0.99902
Sample I.D.	Standard Value	Calculated Value
STD 1	25	27
STD 2	100	99
STD 3	125	126
STD 4	75	75
STD 5	10	8
STD 6	5	6
STD 7	50	51
STD 8	150	150



Applied Rigaku Technologies, Inc. ▪ 9825 Spectrum Drive, Bldg. 4, Suite 475 ▪ Austin, TX 78717 USA
www.RigakuEDXRF.com ▪ info@RigakuEDXRF.com ▪ (+1) 512-225-1796

EXAMPLE CALIBRATIONS (*continued*)

Collimators: 8mm and 3mm

Comparable calibration is achieved using the 8mm collimator or the 3mm collimators, and a total analysis time of 180 sec.

Element	Concentration Range	RMS Deviation 8mm	R^2 Correlation 8mm	RMS Deviation 3mm	R^2 Correlation
Cr	50 – 1250 ppm	24 ppm	0.99879	27	0.99839
Hg	75 – 1200 ppm	16 ppm	0.99939	17	0.99969
Pb	50 – 1250 ppm	16 ppm	0.99943	17	0.99935
Br	50 – 500 ppm	13 ppm	0.99741	13	0.99802
Cd	5 – 150 ppm	4 ppm	0.99963	6	0.99479

RECOVERY

To demonstrate calibration recovery, STD8 was chosen for analysis. The sample was measured once using each collimator and using a total analysis time of 180 sec per analysis.

Element	Assay (ppm)	NEX QC 14mm (ppm)	NEX QC 8mm (ppm)	NEX QC 3mm (ppm)
Cr	500	504	497	488
Hg	30	27	23	27
Pb	500	509	512	522
Br	300	305	307	303
Cd	50	51	51	53

DETECTION LIMITS

To determine the Lower Limit of Detection (LLD) using the empirical method, ten repeat analyses of a blank PE sample were measured and the standard deviation calculated. The LLD is then defined as three times the standard deviation. Total analysis time of 180 sec was used.

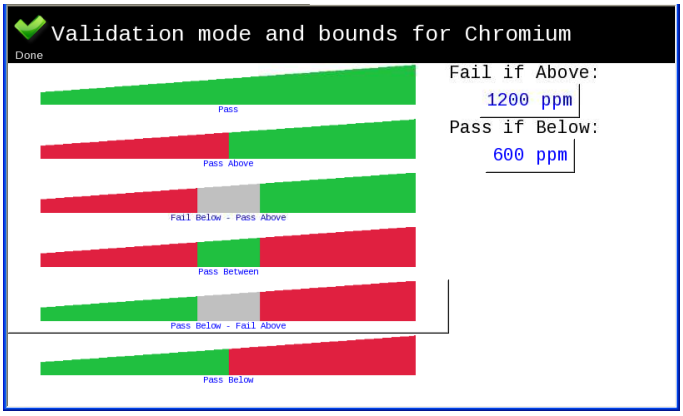
NEX QC	Cr	Hg	Pb	Br	Cd
Standard Configuration	12 ppm	1.5 ppm	0.9 ppm	0.5 ppm	3.9 ppm
VS using 8mm collimator	15 ppm	2.0 ppm	1.0 ppm	0.7 ppm	4.1 ppm
VS using 3mm collimator	16 ppm	3.0 ppm	1.0 ppm	0.9 ppm	7.5 ppm

Applied Rigaku Technologies, Inc. ▪ 9825 Spectrum Drive, Bldg. 4, Suite 475 ▪ Austin, TX 78717 USA
www.RigakuEDXRF.com ▪ info@RigakuEDXRF.com ▪ (+1) 512-225-1796

NEX QC FEATURES

Customizable Report Fields and Validation

NEX QC allows the user the ability to create customized fields for a measurement report. The example here shows report fields setup for the manufacturing plant name, the sample batch number, and the operator ID. The NEX QC also has 6 pre-configured Validation schemes. For RoHS rapid screening, the Pass-Inconclusive-Fail scheme is used. As with reports, the user can easily define the names given to each segment of a Validation scheme, and also can easily define the bounds that trigger Pass, Inconclusive and Fail responses.



Validation Setup Screen
Showing user defined bounds for Cr.

Sample Report Tickets
Customizable Report Fields

VALIDATION

Inconclusive: This sample to be taken to ICP for verification

Fail: This sample fails due to high Pb content

Sample ID: 72#9428428
Timestamp: 15:27:10 2012-06-11
Instrument: NEX QC S/N QC1003
Product: RoHS PE
Plant: Austin
Batch: 17b
Operator: Day Shift
Total Acquisition Time: 180 sec

ID	QC	Result
Chromium	Inconclusive	767 ppm
Bromine	Pass	399 ppm
Cadmium	Inconclusive	95 ppm
Mercury	Pass	57 ppm
Lead	Pass	241 ppm

Quality Check: Inconclusive

Sample ID: 72#9428745
Timestamp: 15:32:29 2012-06-11
Instrument: NEX QC S/N QC1003
Product: RoHS PE
Plant: Austin
Batch: 17b
Operator: Day Shift
Total Acquisition Time: 180 sec

ID	QC	Result
Chromium	Inconclusive	1020 ppm
Bromine	Pass	246 ppm
Cadmium	Inconclusive	74 ppm
Mercury	Pass	262 ppm
Lead	Fail	1273 ppm

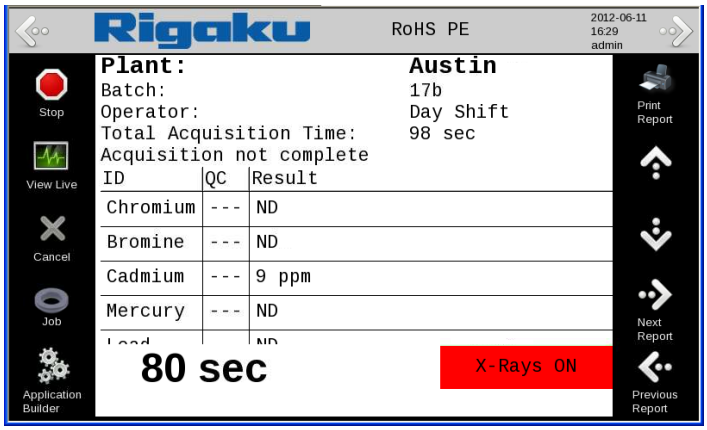
Quality Check: Fail

Applied Rigaku Technologies, Inc. ▪ 9825 Spectrum Drive, Bldg. 4, Suite 475 ▪ Austin, TX 78717 USA
www.RigakuEDXRF.com ▪ info@RigakuEDXRF.com ▪ (+1) 512-225-1796

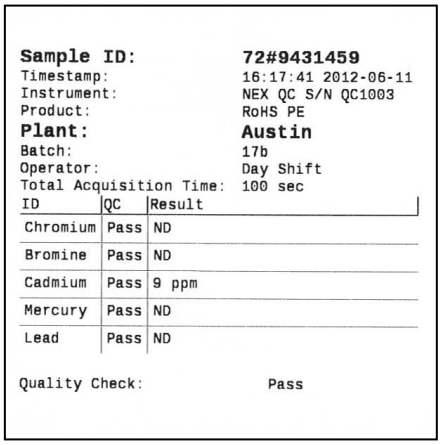
NEX QC FEATURES (*continued*)

Live Report Update

NEX QC can be set to display the concentration results live every 2 seconds during analysis of the final Condition measurement time. In this way the operator can stop the measurement when acceptable performance is observed, without waiting for the entire analysis time to complete. When Stop is pressed, the measurement halts and the concentrations are reported. Pressing Cancel terminates the measurement without a report of concentration.



Main Measurement Screen
Stop is pressed with 80 sec remaining.



Report Ticket
Showing the analysis results after Stop was pressed.

USB and Network Logging, Method Import/Export

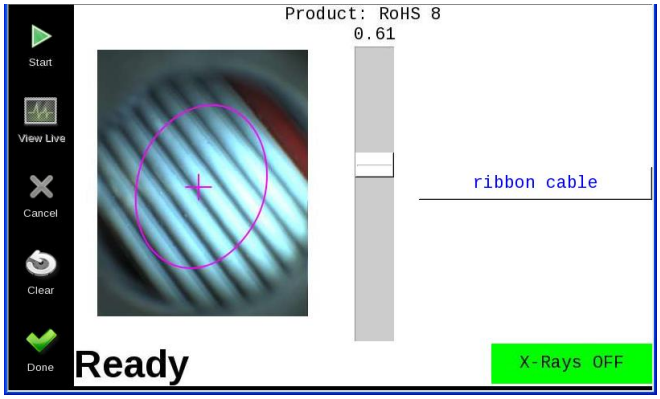
Each measurement of an unknown sample can be logged to a spreadsheet on a USB flash drive inserted in the back of the analyzer, or to a network folder via the NEX QC Ethernet port. Results as shown on a report ticket given by the onboard thermal printer can also be printed as PDF to the flash drive or a network folder. Using the flash drive or networking, NEX QC also allows for easy Import and Export of an analysis method for quick transfer to another analyzer or for safely storing on another computer.

Applied Rigaku Technologies, Inc. ▪ 9825 Spectrum Drive, Bldg. 4, Suite 475 ▪ Austin, TX 78717 USA
www.RigakuEDXRF.com ▪ info@RigakuEDXRF.com ▪ (+1) 512-225-1796

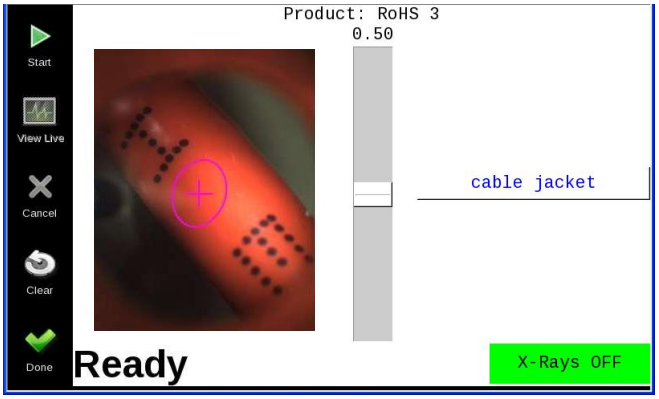
NEX QC FEATURES (*continued*)

Camera View

For positioning of smaller samples, the camera reticle is displayed showing the spot size of the collimator. The examples below show using the camera to position various cable samples.



8mm collimator used to measure 12mm wide ribbon cable.



3mm collimator used to measure 5mm wide cable jacket.

Sample ID: ribbon cable
Timestamp: 12:58:00 2012-06-13
Instrument: NEX QC S/N QC1011
Product: RoHS 8
Total Acquisition Time: 180 sec

ID	QC	Result
Chromium	Pass	130.6 ppm
Mercury	Pass	ND
Lead	Pass	ND
Bromine	Pass	ND
Cadmium	Pass	4.7 ppm

Check: Pass

Sample ID: cable jacket
Timestamp: 13:15:06 2012-06-13
Instrument: NEX QC S/N QC1011
Product: RoHS 3
Total Acquisition Time: 180 sec

ID	QC	Result
Chromium	Pass	10.4 ppm
Mercury	Pass	ND
Lead	Pass	ND
Bromine	Pass	ND
Cadmium	Pass	ND

Check: Pass

CONCLUSION

The Rigaku NEX QC gives the user a reliable and rugged low-cost tool for measuring the toxic metals in PE and similar polymers for screening incoming raw materials and during the production process. For an example of the Cl analysis and performance using simpler 1-, 2- or 3-point calibrations for Cr, Hg, Pb, Br and Cd, see also Rigaku Application Note #1169.

Applied Rigaku Technologies, Inc. ▪ 9825 Spectrum Drive, Bldg. 4, Suite 475 ▪ Austin, TX 78717 USA
www.RigakuEDXRF.com ▪ info@RigakuEDXRF.com ▪ (+1) 512-225-1796