

PM 大气颗粒物分析操作流程 SOP

■ 参考标准

HJ 830-2017 《环境空气 颗粒物中无机元素的测定 波长色散 X 射线荧光光谱法》

■ 适应范围

本方法适用于利用滤膜采集的环境空气和无组织排放颗粒物中的：Na、Mg、Al、Si、P、S、Cl、K、Ca、Sc、Ti、V、Cr、Mn、Fe、Co、Ni、Cu、Zn、As、Se、Sr、Br、Cd、Ba、Pb、Sn、Sb 等 28 个元素的测定。也适用于经方法验证能够达到准确度和精密度要求的其他无机元素。

■ 方法原理

X 射线管产生的初级 X 射线照射到平整、均匀的颗粒物样品表面时，被测元素发射出特征的荧光 X 射线，经晶体分光后，探测器在所选择特征波长相对应的 2θ 角处测得 X 射线荧光强度。采用薄样品分析技术，当颗粒物负载量在一定范围内时，X 射线荧光强度与被测元素含量（附着量）成正比。

■ 仪器及辅助设备

XRF-1800 波长色散 X 射线荧光光谱仪

环境采样器

可以确保有效直径的切刀

■ 标准样品

滤膜标样现在主要由美国 MICROMATTER™ 公司生产的单元素标样，国内有少量的单元素或几个元素的标样。也可以使用有准确定值的其他薄膜标准样品。

标样形状见图，尺寸应选有效直径大于 30 mm 的标准片，涂敷面分为正向和反向。岛津 X 射线仪器选择 B 型环（涂敷在外侧）。



标准样品的附着量一般有： $0.5 \sim 2 \mu\text{g}/\text{cm}^2$ 、 $3 \sim 8 \mu\text{g}/\text{cm}^2$ 、 $15 \sim 25 \mu\text{g}/\text{cm}^2$ 、 $40 \sim 60 \mu\text{g}/\text{cm}^2$ 多个规格。按照工作曲线的基本要求，一般不少于 3 点（含空白点）。不建议选用高点。

■ 方法的建立步骤

6.1 检查仪器环境，确认各状态正常。进行 PHD 检查确认

6.2 建立分析条件：命名程序

6.3 打开程序，依序设定下面各项。

6.3.1 元素条件选择和设定

Group Condition: [Quantitative][PM-Test-STD]

File Help

Group Condition

- Quantitative Information
 - Element Information
 - Measurement Condition
 - Calibration Curve
 - Sensitivity Coefficient
 - BG/Intensity Calculati
 - Overlap Correction
 - Internal Standard
 - Result Format
 - L/H Decision
 - Additional Calculation
 - Sensitivity Coefficient
 - Meas. Condition List
- Standard Sample
 - Standard Sample
 - Standardization
 - Drift Check
 - Master Curve
 - Blank Sample

Group Measurement Condition

Aperture: 30 Atmosphere: Vac.

Spin Slow Evac./Air Pu

Rotation: 0 Vacuum Stabiliz

Pressure to: 30 Pa

Optimization

Online Output

Quant: Calculat

Output: Print File

Display: Cond. Intern. Each Quant.

Matching (No Value)

Information of a Sample

Sample Form: Bulk Film Filter Pap

Compound Form: Metal Oxide Reference System: default

Elements Included

Layer Structure:

1	Layer1	Pb	Ba	Sr	Br	Se	As	Sb	Sn	Cd	Zn
		Cu	Ni	Co	Fe	Mn	Cr	V	Ti	So	Ca
		K	Cl	S	P	Si	Al	Mg	Na		

Group Condition

- Quantitative Information
 - Element Information
 - Measurement Condition
 - Calibration Curve
 - Sensitivity Coefficient
 - BG/Intensity Calculati
 - Overlap Correction
 - Internal Standard
 - Result Format
 - L/H Decision
 - Additional Calculation
 - Sensitivity Coefficient
 - Meas. Condition List
- Standard Sample
 - Standard Sample
 - Standardization
 - Drift Check
 - Master Curve
 - Blank Sample

Layer	Info	Analyte	Fixed.Val.	Unit	Proc.-Calc.	Line	Ms	BG	Ds	Bo	Ov
1	Layer1			mg/cm2	Total		x	x	x	x	x
1	Elem. Pb			ug/cm2	Quant-EC PbLb1		o	x	x	x	x
1	Elem. Ba			ug/cm2	Quant-EC BaLa		o	x	x	x	x
1	Elem. Sr			ug/cm2	Quant-EC SrKa		o	x	x	x	x
1	Elem. Br			ug/cm2	Quant-EC BrKa		o	x	x	x	x
1	Elem. Se			ug/cm2	Quant-EC SeKa		o	x	x	x	x
1	Elem. As			ug/cm2	Quant-EC AsKa		o	x	x	x	x

Element Information

[Layer 1] Layer Info.

Compound Name:

Unit:

Proc.-Calc.

Quant. Correct Fix Flux Balance Total

Type of Quantification

FP BG-FP Calibration Cu

Fixed Value

Fix: 0.0000

Input: Fixed

Bg Analysis:

Prev Next

6.3.2 谱线的选择和确认

Group Condition

- Quantitative Information
 - Element Information
 - Measurement Condition
 - Calibration Curve
 - Sensitivity Coefficient
 - BG/Intensity Calculati
 - Overlap Correction
 - Internal Standard
 - Result Format
 - L/H Decision
 - Additional Calculation
 - Sensitivity Coefficient
 - Meas. Condition List
- Standard Sample
 - Standard Sample
 - Standardization
 - Drift Check
 - Master Curve
 - Blank Sample

Layer	Info	Analyte	Fixed.Val.	Unit	Proc.-Calc.	Line	Ms	BG	Ds	Bo	Ov
1	Layer1			mg/cm2	Total		x	x	x	x	x
1	Elem. Pb			ug/cm2	Quant-EC PbLb1		o	x	x	x	x
1	Elem. Ba			ug/cm2	Quant-EC BaLa		o	x	x	x	x
1	Elem. Sr			ug/cm2	Quant-EC SrKa		o	x	x	x	x
1	Elem. Br			ug/cm2	Quant-EC BrKa		o	x	x	x	x
1	Elem. Se			ug/cm2	Quant-EC SeKa		o	x	x	x	x
1	Elem. As			ug/cm2	Quant-EC AsKa		o	x	x	x	x

Element Information

[Layer 1] Elem. Info.

Compound Name:

Unit:

Proc.-Calc.

Quant. Correct Fix Flux Balance Total

Type of Quantification

FP BG-FP Calibration Cu

Line:

Fixed Value

Fix: 0.0000

Input: Fixed

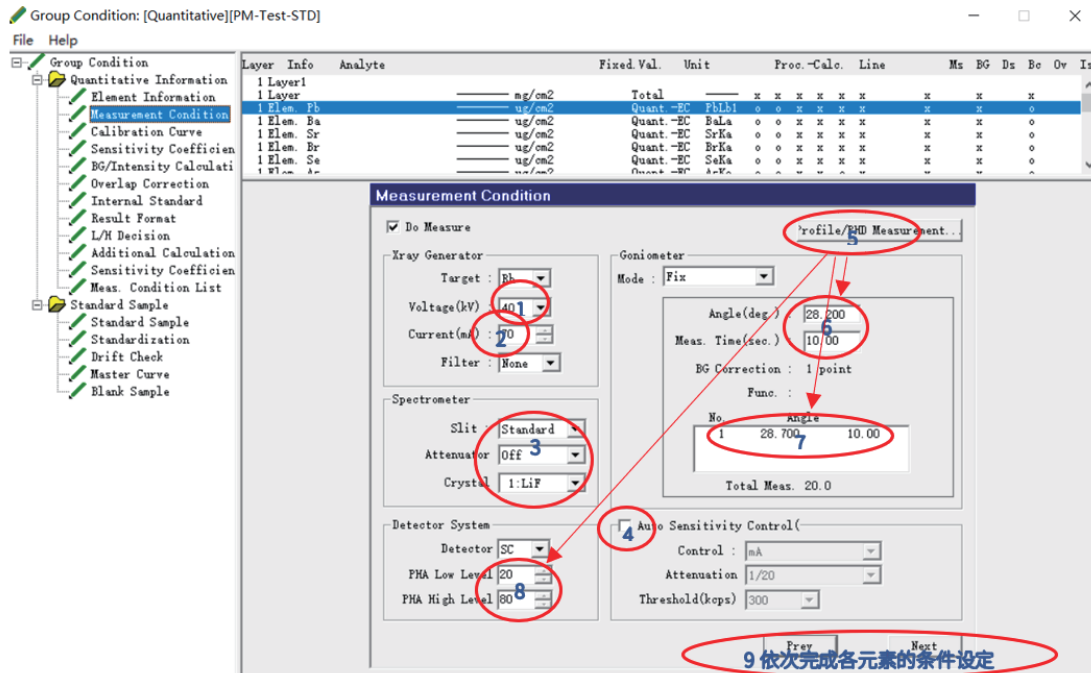
Bg Analysis:

Prev Next

选择谱线请参考下表：个别元素非默认条件

1 Elem. Pb	_____ ug/cm2	Quant.-EC	PbLb1
1 Elem. Ba	_____ ug/cm2	Quant.-EC	BaLa
1 Elem. Sr	_____ ug/cm2	Quant.-EC	SrKa
1 Elem. Br	_____ ug/cm2	Quant.-EC	BrKa
1 Elem. Se	_____ ug/cm2	Quant.-EC	SeKa
1 Elem. As	_____ ug/cm2	Quant.-EC	AsKa
1 Elem. Sb	_____ ug/cm2	Quant.-EC	SbLb1
1 Elem. Sn	_____ ug/cm2	Quant.-EC	SnLa
1 Elem. Cd	_____ ug/cm2	Quant.-EC	CdLa
1 Elem. Zn	_____ ug/cm2	Quant.-EC	ZnKa
1 Elem. Cu	_____ ug/cm2	Quant.-EC	CuKa
1 Elem. Ni	_____ ug/cm2	Quant.-EC	NiKa
1 Elem. Co	_____ ug/cm2	Quant.-EC	CoKa
1 Elem. Fe	_____ ug/cm2	Quant.-EC	FeKa
1 Elem. Mn	_____ ug/cm2	Quant.-EC	MnKa
1 Elem. Cr	_____ ug/cm2	Quant.-EC	CrKa
1 Elem. V	_____ ug/cm2	Quant.-EC	V Ka
1 Elem. Ti	_____ ug/cm2	Quant.-EC	TiKa
1 Elem. Sc	_____ ug/cm2	Quant.-EC	ScKa
1 Elem. Ca	_____ ug/cm2	Quant.-EC	CaKa
1 Elem. K	_____ ug/cm2	Quant.-EC	K Ka
1 Elem. Cl	_____ ug/cm2	Quant.-EC	ClKa
1 Elem. S	_____ ug/cm2	Quant.-EC	S Ka
1 Elem. P	_____ ug/cm2	Quant.-EC	P Ka
1 Elem. Si	_____ ug/cm2	Quant.-EC	SiKa
1 Elem. Al	_____ ug/cm2	Quant.-EC	AlKa
1 Elem. Mg	_____ ug/cm2	Quant.-EC	MgKa
1 Elem. Na	_____ ug/cm2	Quant.-EC	NaKa

6.4 测量条件——确认



Group Condition: [Quantitative][PM-Test-STD]

File Help

Group Condition

- Quantitative Information
- Element Information
- Measurement Condition
- Calibration Curve
- Sensitivity Coefficient
- BG/Intensity Calculati
- Overlap Correction
- Internal Standard
- Result Format
- L/H Decision
- Additional Calculation
- Sensitivity Coefficient
- Meas. Condition List
- Standard Sample
- Standard Sample
- Standardization
- Drift Check
- Master Curve
- Blank Sample

Layer	Info	Analyte	Fixed.Val.	Unit	Proc.-Calc.	Line	Ms	BG	Ds	Be	Ov	Is
1 Layer1												
1 Layer												
1 Elem. Pb				mg/cm2	Total		x	x	x	x	x	x
1 Elem. Ba				ug/cm2	Quant.-EC	PbLb1	o	o	x	x	x	o
1 Elem. Sr				ug/cm2	Quant.-EC	SrKa	o	o	x	x	x	o
1 Elem. Br				ug/cm2	Quant.-EC	BrKa	o	o	x	x	x	o
1 Elem. Se				ug/cm2	Quant.-EC	SeKa	o	o	x	x	x	o

Measurement Condition

Do Measure

X-ray Generator: Target: Pb, Voltage (kV): 40, Current (mA): 70, Filter: None

Goniometer: Mode: Fix, Angle(deg): 28.200, Meas. Time(sec): 10.00, BG Correction: 1 point, Func.: No. Angle

No.	Angle
1	28.700 7 10.00

Total Meas. 20.0

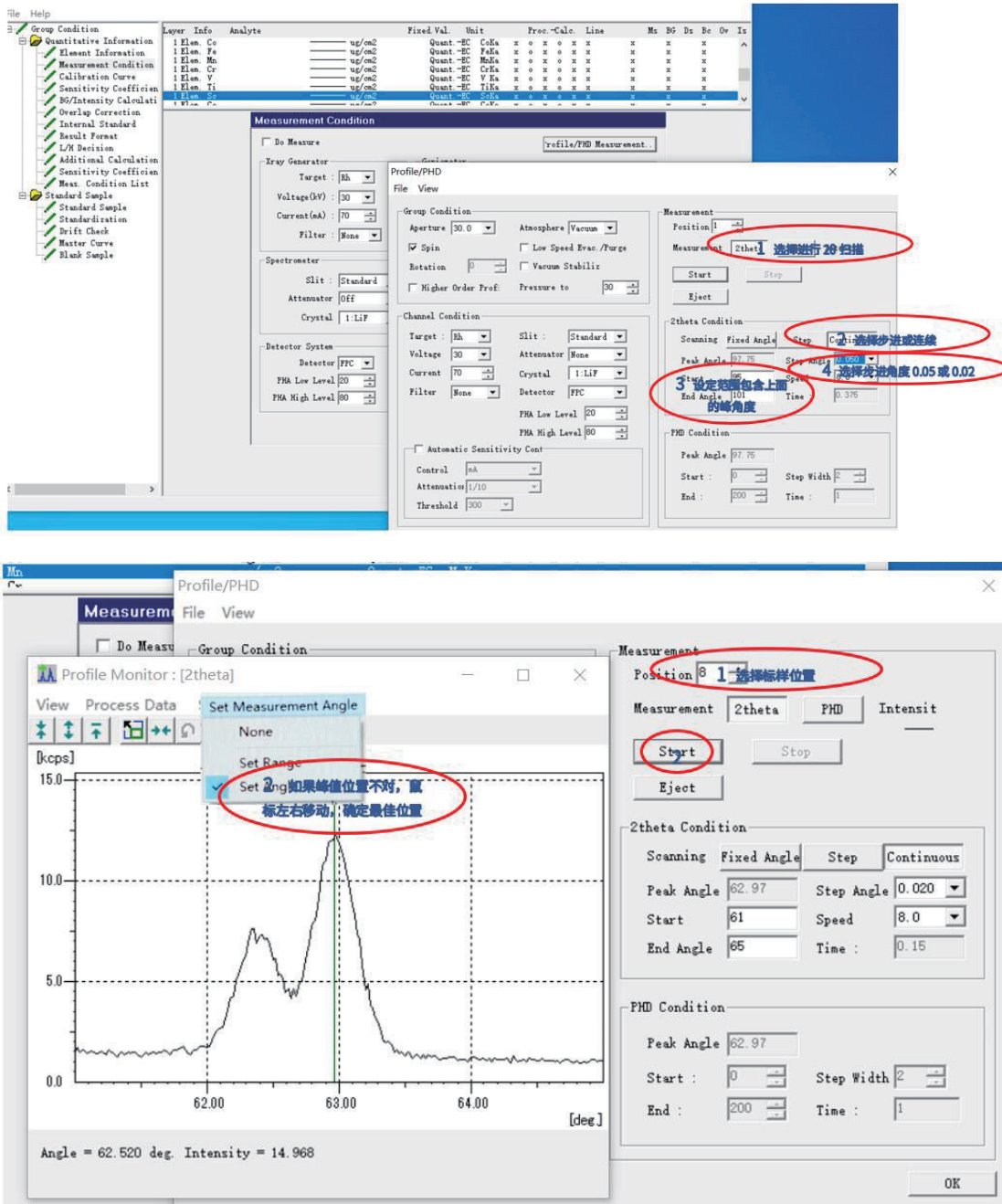
Spectrometer: Slit: Standard, Attenuator: Off, Crystal: 1:LiF

Detector System: Detector: SC, PHA Low Level: 20, PHA High Level: 80

Auto Sensitivity Control: Control: mA, Attenuation: 1/20, Threshold(kcps): 300

9 依次完成各元素的条件设定

6.5 分析角度的确认



The image displays two screenshots from the Shimadzu software interface, illustrating the process of confirming the analysis angle.

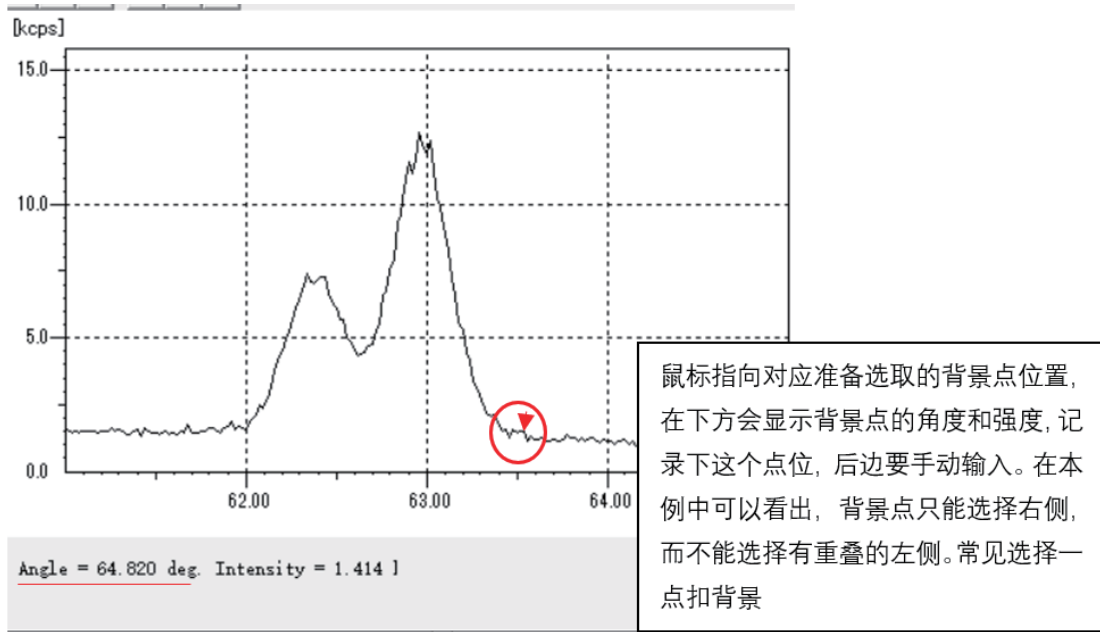
Top Screenshot: Measurement Condition Dialog

- Measurement:** Position 1, Measurement 2theta. *1 选择进行 2θ 扫描*
- 2theta Condition:** Scanning Fixed Angle, Step Continuous, Peak Angle 62.97, Start 61, End Angle 65. *2 选择少步或连续*
- 3 设定范围包含上面峰的角度** (Set range to include the peak angle above)
- 4 选择步长角度 0.05 或 0.02** (Select step angle 0.05 or 0.02)

Bottom Screenshot: Profile Monitor and Measurement Dialog

- Profile Monitor:** Shows a graph of intensity [kcps] vs. angle [deg]. A peak is visible at approximately 62.5 degrees. A context menu is open over the peak with options: None, Set Range, and Set Ang. *Set Ang 如果峰值位置不对, 鼠标左右移动, 确定最佳位置*
- Measurement Dialog:** Position 8, Measurement 2theta, PHD, Intensit. *1 选择标样位置*
- Start Button:** Circled in red, indicating the start of the measurement.
- 2theta Condition:** Scanning Fixed Angle, Step Continuous, Peak Angle 62.97, Step Angle 0.020, Start 61, Speed 8.0, End Angle 65, Time 0.15.
- PHD Condition:** Peak Angle 62.97, Start 0, Step Width 2, End 200, Time 1.

6.6 背景点的确认



6.7 背景点设定：

Group Condition: [Quantitative][PM-Test-STD]

File Help

Layer Info	Analyte	Fixed Val.	Unit	Proc.-Calc.	Line	Ms	B
1 Layer1							
1 Layer		Total		x x x x x x x		x	x
1 Elem. Pb		Quant-EC	PbLb1	o o x x x x x		x	x
1 Elem. Ba		Quant-EC	BaLa	o o x x x x x		x	x
1 Elem. Sr		Quant-EC	SrKa	o o x x x x x		x	x
1 Elem. Br		Quant-EC	BrKa	o o x x x x x		x	x
1 Elem. Se		Quant-EC	SeKa	o o x x x x x		x	x
1 Fl... A-		Quant-EC	A-Ka	o o x x x x x		x	x

BG/Intensity Calculation

BG Correction

Main Peak
Angle : 28.200
Meas. Time 10.0

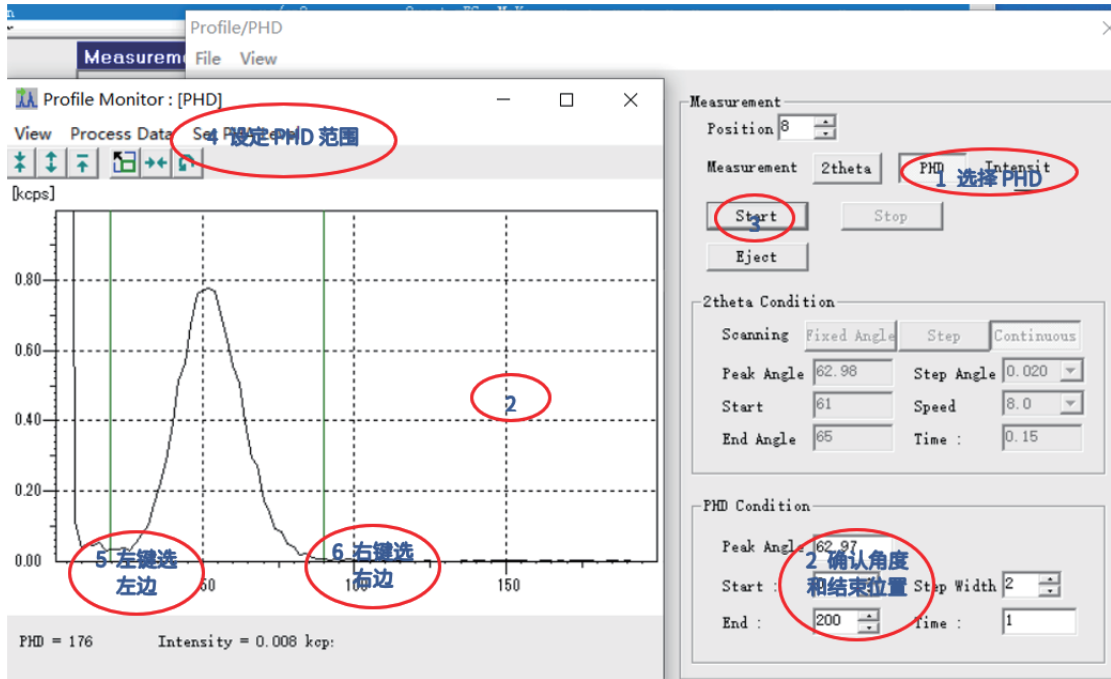
BG Point :

Angle(2thet)	Meas. Time
1 28.200	10.0
2	
3	
4	
5	

BG Calculation
BG Func: 1 Point
Coeff: 1.0000

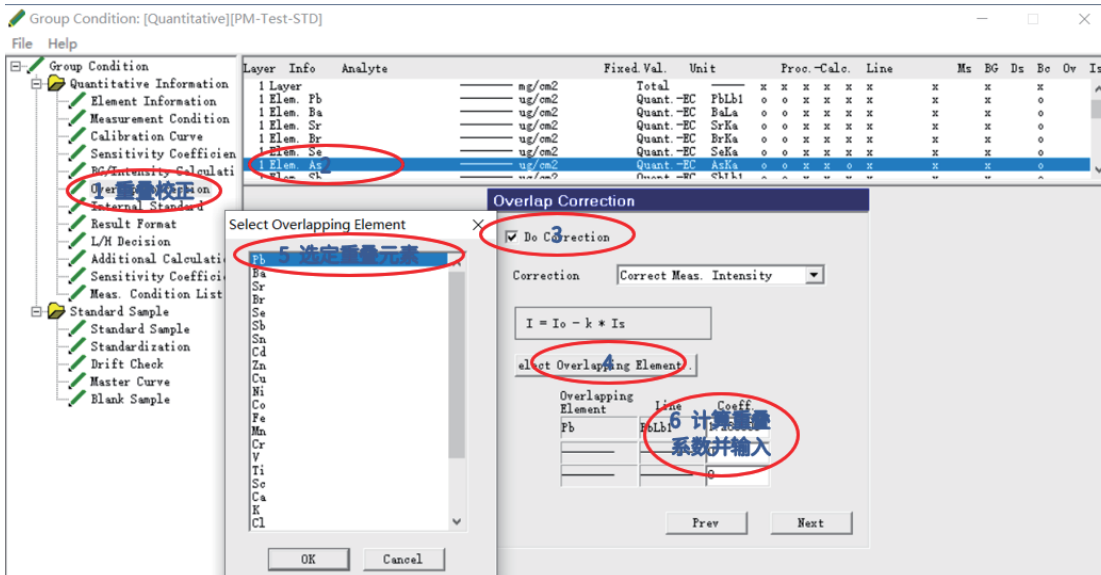
Intensity Calculation
Method :
Calculation :
Fitting : Angle Range[26.000 - 30.000]
Analyzed Peak :
Main Peak 57.52 deg
1 :
2 :
3 :
4 :
Fitting Condition
Func. :
Method :
BG :

6.8 PHD 的确定



做完后退出样品：EJECT。依次做完每一个元素。

6.9 Pb 对 As 重叠校正的处理：



重叠校正系数算法参看标准。

6.10 标准样品的设定及标样含量的输入：

Group Condition: [Quantitative][PM-Test-STD]

File Help

Group Condition

- Quantitative Information
 - Element Information
 - Measurement Condition
 - Calibration Curve
 - Sensitivity Coefficient
 - BG/Intensity Calculati
 - Overlap Correction
 - Internal Standard
 - Result Format
 - L/H Decision
 - Additional Calculation
 - Sensitivity Coefficient
- Standard Sample
 - Standard Sample
 - Standardization
 - Drift Check
 - Master Curve
 - Blank Sample

Standard Sample

Standard: Blank

Info	Compound Name	Std. Value	Unit	Proc. -Calc	Line	Measured		Theoretical	
						Net	BG	Net	BG
1 : Lay		0.0000	mg/cm2	Total		0.00000	0.00000	0	0
1 : Ele:Pb		0.0000	ug/cm2	Quant.-EC	PbLb1	0.20121	3.43579	0	0
1 : Ele:Ba		0.0000	ug/cm2	Quant.-EC	BaLa	0.00390	0.06620	0	0
1 : Ele:Sr		0.0000	ug/cm2	Quant.-EC	SrKa	0.42695	4.84199	0	0
1 : Ele:Br		0.0000	ug/cm2	Quant.-EC	BrKa	0.00000	0.00000	0	0
1 : Ele:Se		0.0000	ug/cm2	Quant.-EC	SeKa	0.15696	2.25033	0	0
1 : Ele:As		0.0000	ug/cm2	Quant.-EC	AsKa	0.00000	2.01072	0	0
1 : Ele:Sb		0.0000	ug/cm2	Quant.-EC	SbLb1	0.00000	0.36905	0	0
1 : Ele:Sn		0.0000	ug/cm2	Quant.-EC	SnLa	0.00000	0.29483	0	0
1 : Ele:Cd		0.0000	ug/cm2	Quant.-EC	CdLa	0.00427	0.02720	0	0

Standard Sample Name Input

Standard Value Input

Change Display

Rows: Sample / Cols: Ele / Rows: Element / Cols: Sa

	As	Sb	Sn	Cd	Zn
41463	0	0	0	0	17.19
41464	4.3	0	0	0	0
41465	35.8	0	0	0	0
41466	0	0	0	0	0
41467	0	0	0	0	0
41468	0	0	0	3.26	0
41469	0	0	0	29.47	0
41470	0	0	6.25	0	0
41471	0	0	49.2	0	0
41472	0	6.53	0	0	0

Number of samples = 71

为了延长标样的使用时间，可以考虑每次分析仅仅选择相应元素和相应标样，这样可以大大缩短分析时间，全部完成后再组合到一起使用。注意标样空白和试样空白的不同，不能公用。

6.11 测试标样：

Select Group

[Analysis] : [Ready]

File Edit View Test Measurement Help

Sample Name... Process Data...

Schedule of Analysis

No	Sample Name	Purpose of Measurement
1	[Instrument Setup]Shutdown	
1	Keeps Xray	
2	[Quantitative]PM-test1	-F-
1	Blank	Std.--Intensity
2	33964	Std.--Intensity
3	33951	Std.--Intensity
4	33953	Std.--Intensity
5	33952	Std.--Intensity
6	33946	Std.--Intensity
7	33949	Std.--Intensity
8	33950	Std.--Intensity

Sample Registration

Analysis Instrument Setup PH

Analytical Group: Easy Analysis...

[Quantitative]PM-test1

Detail Settings

Repeat: Pause:

Sample

Sample Name	Position
Blank	1
33964	2
33951	3
33953	4
33952	5
33946	6
33949	7
33950	8
33961	1
33948	2

Select Analytical Group

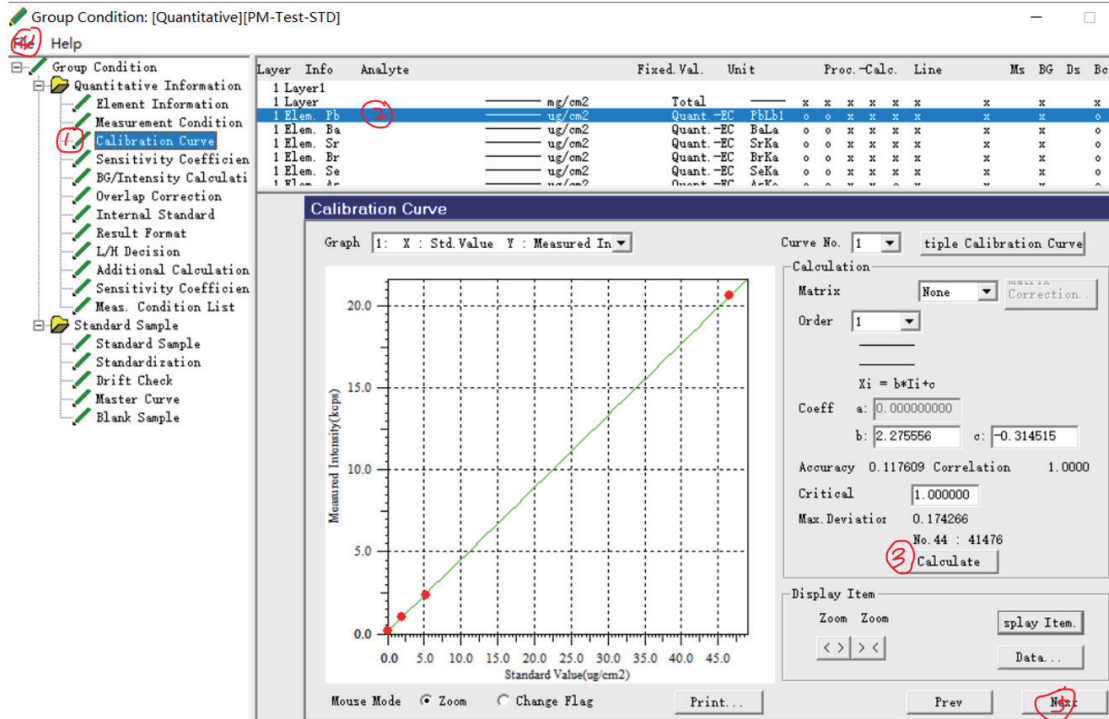
Easy Analysis Qual-Quant. Quantitative

Group Name	Date	Comment
薄膜吸附量-过零点-Pb	2020/11/11 11:11:51	Comment
薄膜吸附量-3mm	2019/03/15 17:15:22	Comment
薄膜吸附量-新-过零点	2019/03/15 12:15:28	Comment
薄膜吸附量-新1	2017/12/18 15:35:44	Comment
薄膜吸附量-guangxi2	2017/06/23 10:03:36	special for NaCl
薄膜吸附量-CaPbTi	2016/05/17 16:13:44	Comment
薄膜吸附量-guangxi1	2016/05/16 16:03:30	Comment
normal el@ant-SY	2016/04/18 16:06:08	Comment
PM-test1	2016/04/18 10:19:30	Comment
薄膜吸附量-加膜	2016/03/30 08:03:02	Comment
薄膜吸附量	2015/12/22 10:16:34	Comment

Purpose of Measurement

Standard Intensity Registration Coefficient Renewal

6.12 绘制曲线



Group Condition: [Quantitative][PM-Test-STD]

Layer	Info	Analyte	Fixed Val.	Unit	Proc.	Calc.	Line	Ms	BG	Ds	Bo
1	Layer1			Total	x	x	x	x	x	x	x
1	Elem.	Pb		ug/cm2	Quant.-EC	PbLb1	o	o	x	x	x
1	Elem.	Ba		ug/cm2	Quant.-EC	BaLa	o	o	x	x	x
1	Elem.	Sr		ug/cm2	Quant.-EC	SrKa	o	o	x	x	x
1	Elem.	Br		ug/cm2	Quant.-EC	BrKa	o	o	x	x	x
1	Elem.	Se		ug/cm2	Quant.-EC	SeKa	o	o	x	x	x
1	Elem.	As		ug/cm2	Quant.-EC	AsKa	o	o	x	x	x

Calibration Curve

Graph 1: X : Std Value Y : Measured In

Curve No. 1 Multiple Calibration Curve

Calculation

Matrix: None

Order: 1

$Y_i = b \cdot X_i + c$

Coeff: a: 0.000000000, b: 2.275556, c: -0.314515

Accuracy: 0.117609, Correlation: 1.0000

Critical: 1.000000

Max. Deviation: 0.174266

No. 44 : 41476

Calculate

Display Item: Zoom, Zoom, Display Item, Data...

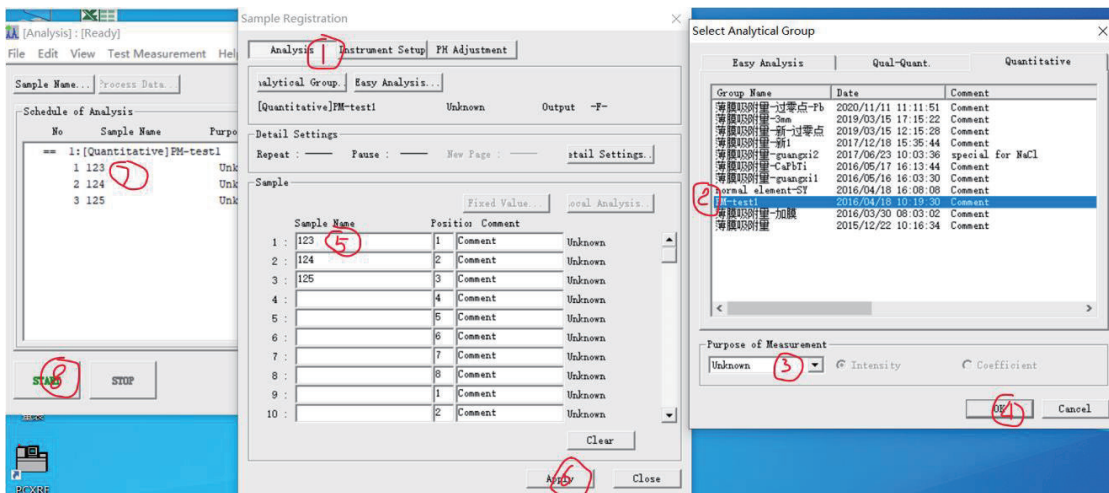
Mouse Mode: Zoom Change Flag

Print... Prev Next

依次完成各元素的工作曲线制作。最后总检查，保存完整曲线。及时将建好的分析条件备份到非本机妥善位置。

6.13 样品分析：注意每一批样品要带相同批次的空白。

制备好的样品放入样品盒中，放置在相应位置上。按以下步骤设定并分析。



Sample Registration

Analysis Instrument Setup PM Adjustment

Analytical Group: Easy Analysis...

[Quantitative]PM-test1 Unknown Output -F-

Repeat: ___ Pause: ___ New Page: ___ Detail Settings...

Sample Name	Position	Comment	Fixed Value	Special Analysis
1: 123	1	Comment	Unknown	
2: 124	2	Comment	Unknown	
3: 125	3	Comment	Unknown	
4:	4	Comment	Unknown	
5:	5	Comment	Unknown	
6:	6	Comment	Unknown	
7:	7	Comment	Unknown	
8:	8	Comment	Unknown	
9:	1	Comment	Unknown	
10:	2	Comment	Unknown	

Clear Apply Close

Select Analytical Group

Easy Analysis Qual-Quant. Quantitative

Group Name	Date	Comment
薄层吸附-过零点-Pb	2020/11/11 11:11:51	Comment
薄层吸附-3m	2019/03/15 17:15:22	Comment
薄层吸附-新-过零点	2019/03/15 12:15:28	Comment
薄层吸附-新1	2017/12/18 15:35:44	Comment
薄层吸附-新-guangpi2	2017/06/23 10:03:36	special for NaCl
薄层吸附-新-CaPb1	2016/05/17 16:19:44	Comment
薄层吸附-新-guangpi1	2016/05/16 16:03:30	Comment
Normal element-SY	2016/04/18 16:08:08	Comment
薄层吸附-新-加膜	2016/03/30 09:03:02	Comment
薄层吸附-新	2015/12/22 10:16:34	Comment

Purpose of Measurement: Unknown Intensity Coefficient

Cancel

■ 质量控制

根据标准要求，定期不定期进行质控检查。确保分析结果的正常。

质控样可以选择含量合适的单元素标准滤膜、复合多元素滤膜。也可以考虑选择元素强度合适的均匀稳定的其它标物。以建立曲线时的测得值作为参考含量进行管控。质控范围参照标准，检查中误差超出范围应重新校准或重新建立校准曲线。

岛津应用云

