X荧光分析实验

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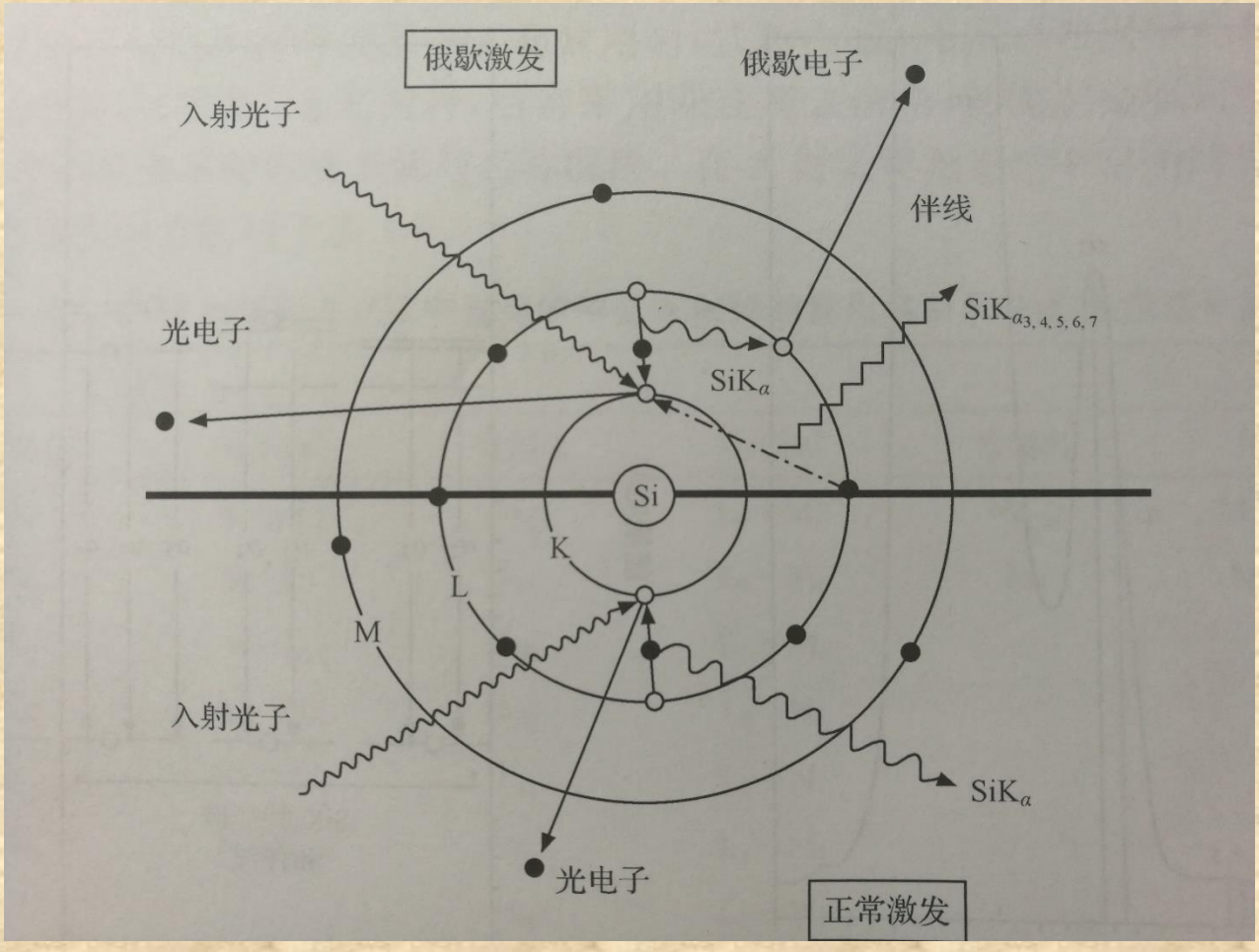
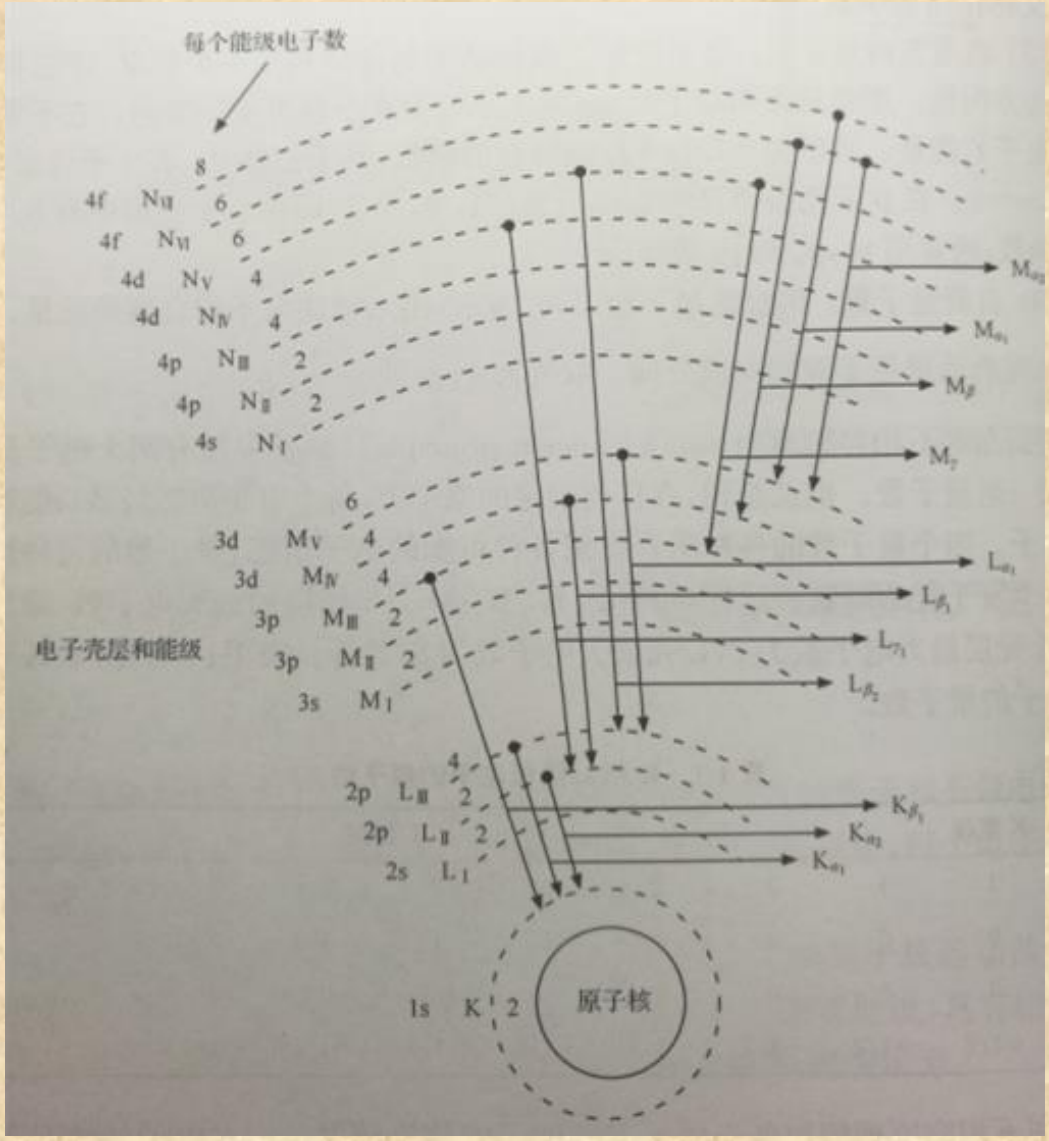
X射线荧光

- 能量大于轨道电子结合能的X射线光子，逐出内层电子形成空穴
- 高能态向低能态跃迁——选择定则
- 辐射跃迁——X射线荧光
- 非辐射跃迁——俄歇电子

产生X射线荧光与俄歇电子过程示意图



K、L、M系X射线特征谱线示意图



荧光产额与原子序数关系图

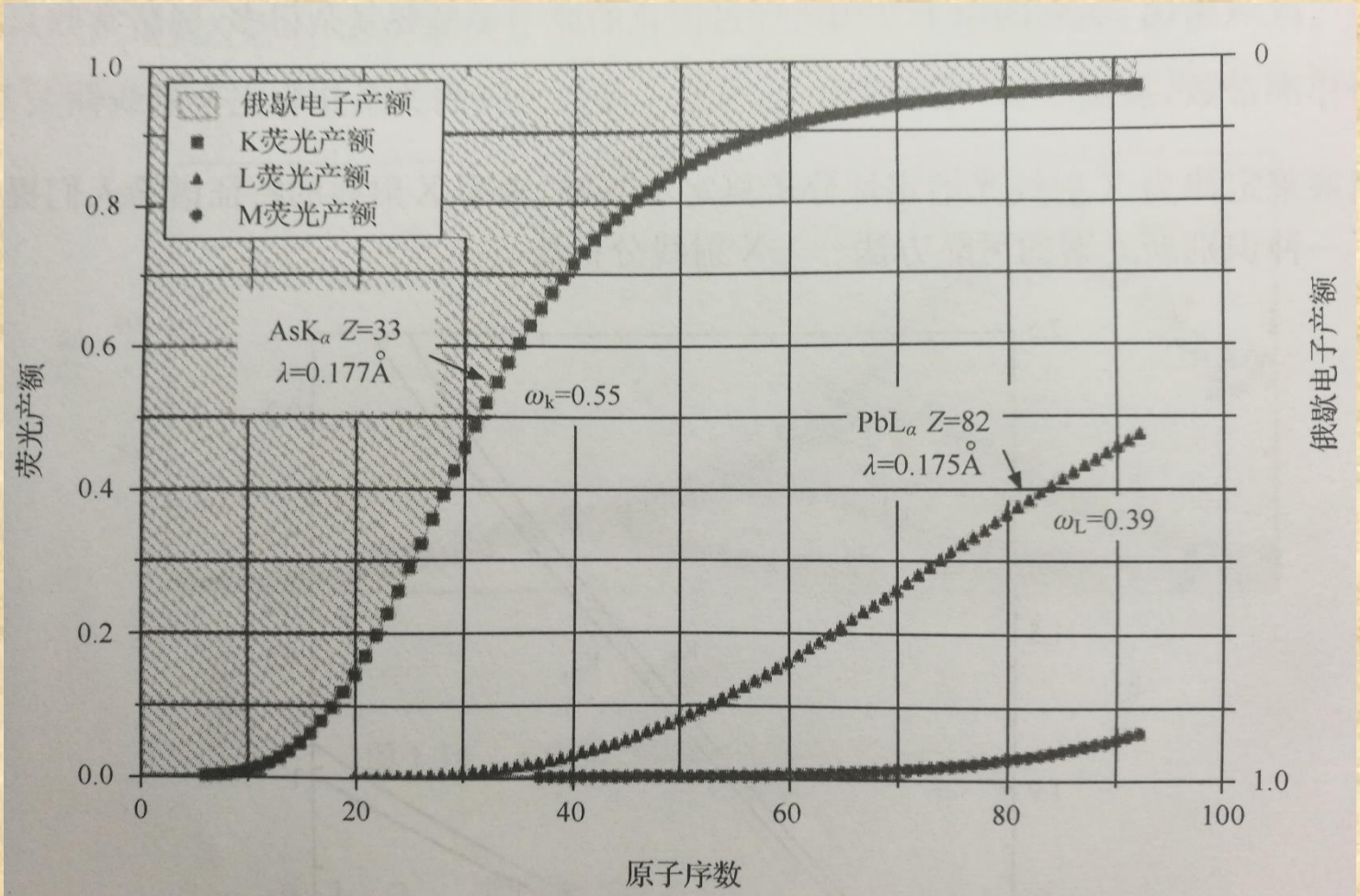


图 1-18　荧光产额与原子序数关系图[15]

莫塞莱定律

- 同一线系特征X射线谱的频率平方根与原子序数成正比

$$\sqrt{\nu} = Q(Z - \sigma)$$

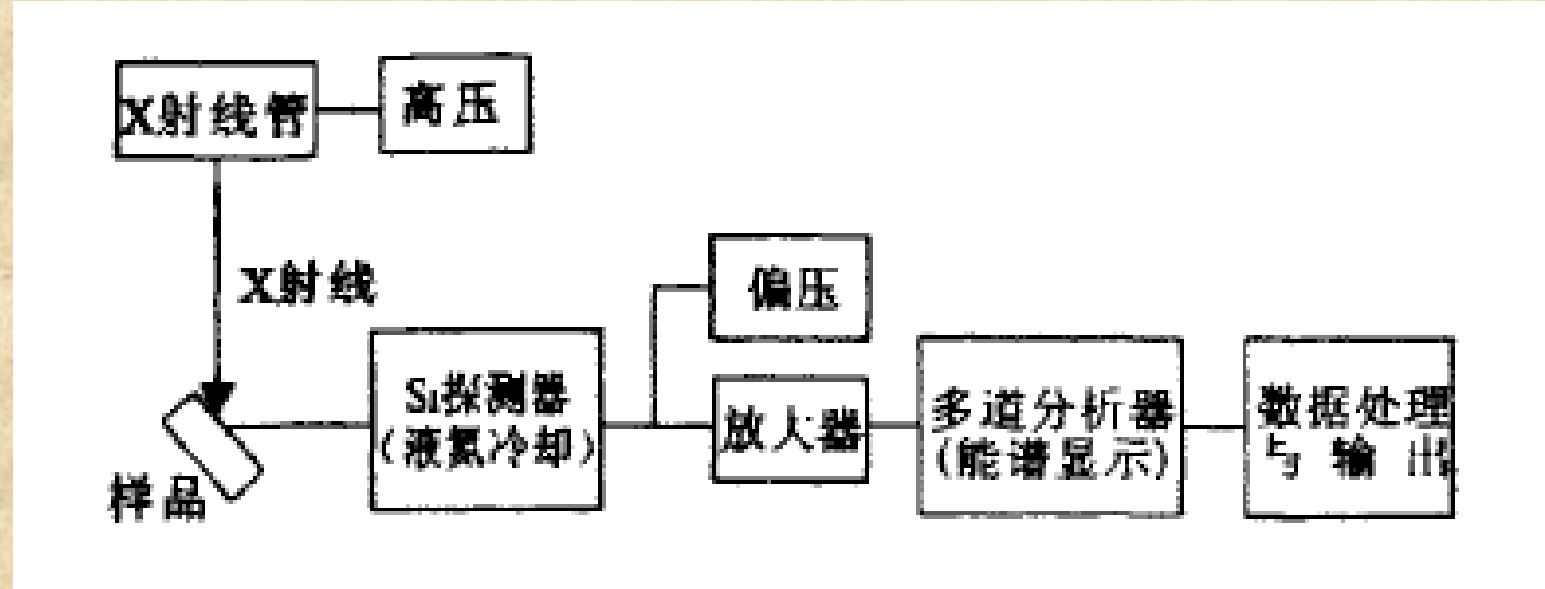
- 屏蔽常数σ看作准常数
- 为X射线光谱分析奠定了基础，X射线特征谱为人们提供了识别新元素的可靠方法

RoHS标准

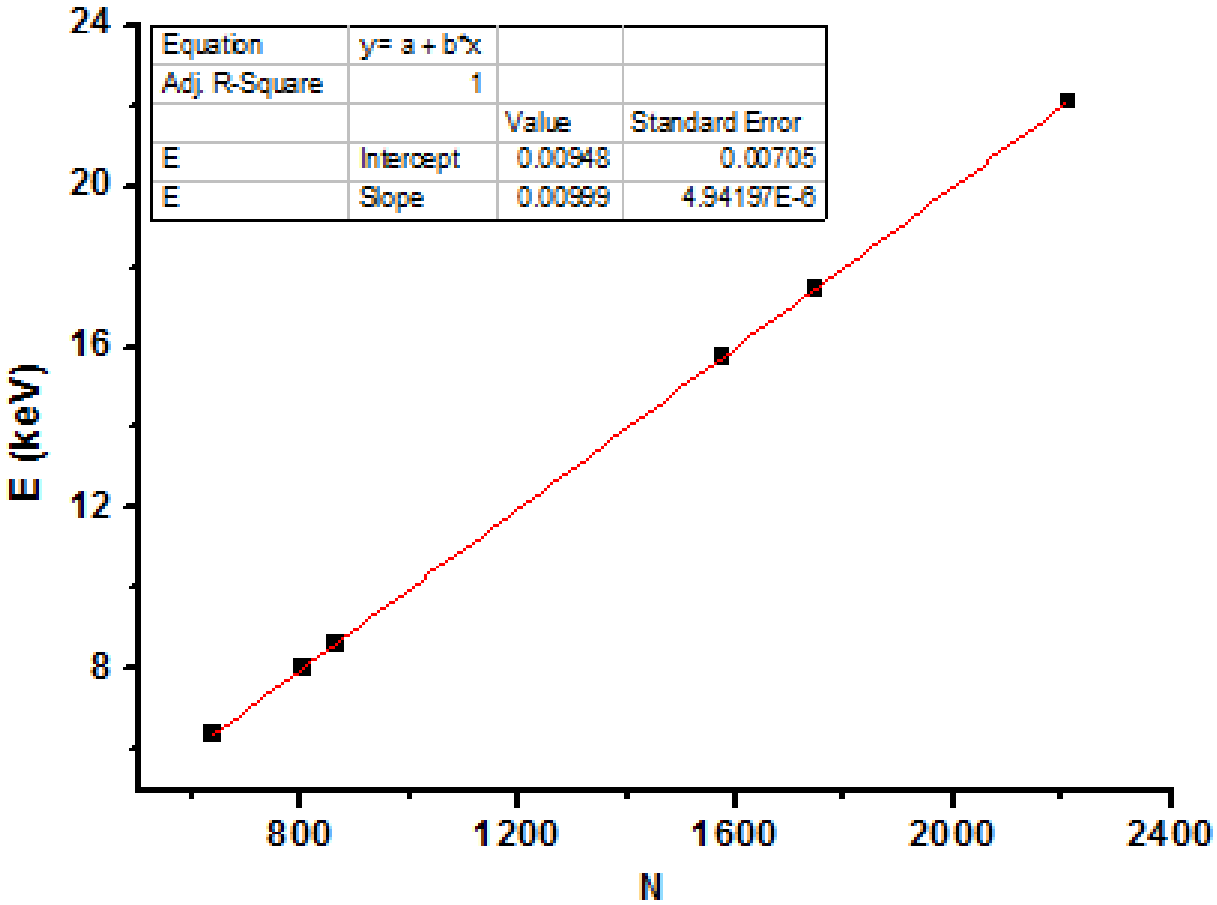
- 《电气、电子设备中限制使用某些有害物质的指令》
- 铅（Pb）：1000mg/kg
- 镉（Cd）：100mg/kg
- 汞（Hg）：1000mg/kg
- 六价铬（Cr^{6+}）：1000mg/kg
- 多溴联苯：1000mg/kg
- 多溴联苯醚：1000mg/kg

EDXRF（能量色散型X射线荧光光谱仪）

EDXRF光谱仪示意图



仪器定标


Equation
y= a + b*x
Adj. R-Square
1
Value
Standard Error
E
Intercept
0.00948
0.00705
E
Slope
0.00999
4.94197E-6
E (keV)
24
20
16
12
8
800
1200
1600
2000
2400
N

实验内容

Part1：

单质测量

定标荧光分析光谱

验证莫塞莱定律

测量荧光产额

Part2：

EDXRF物质分析

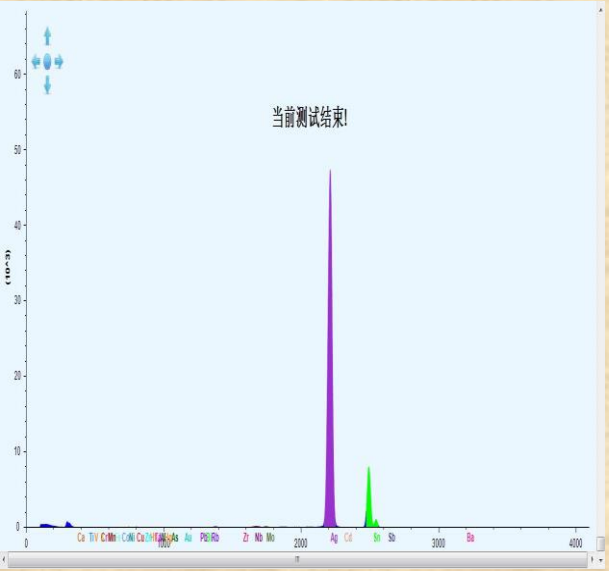
RoHS有害物质分析

Part3：

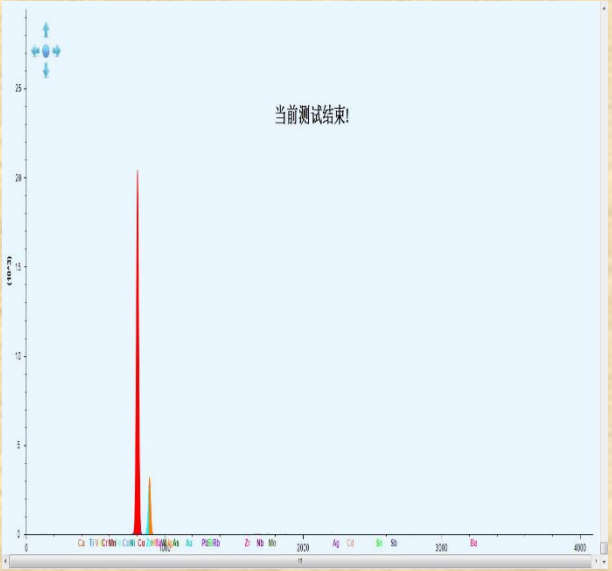
样品条件探究

二级荧光现象探究

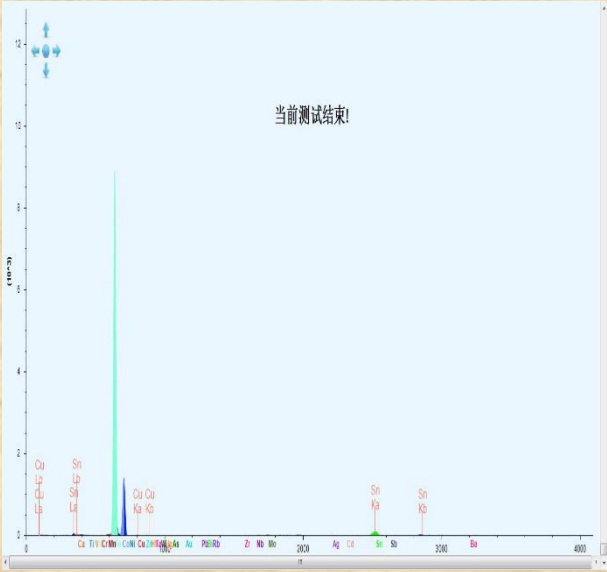
单质测量



Ag

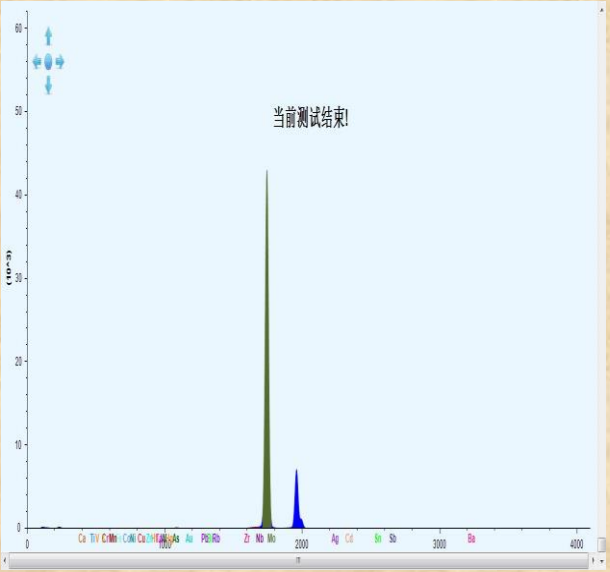


Cu

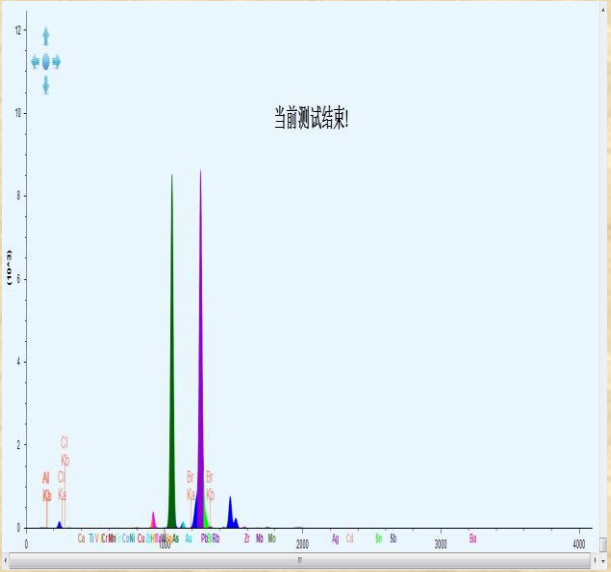


Fe

单质测量

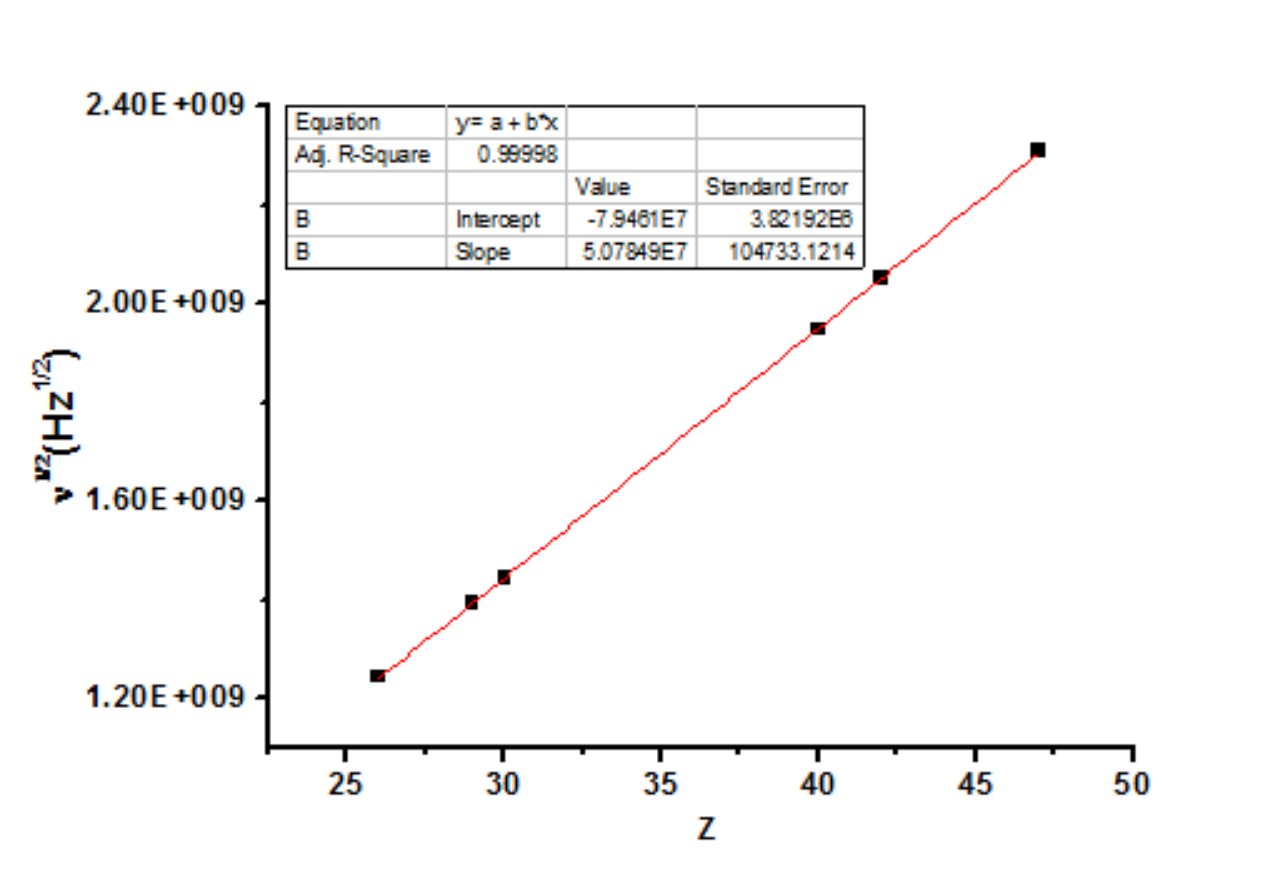


Mo



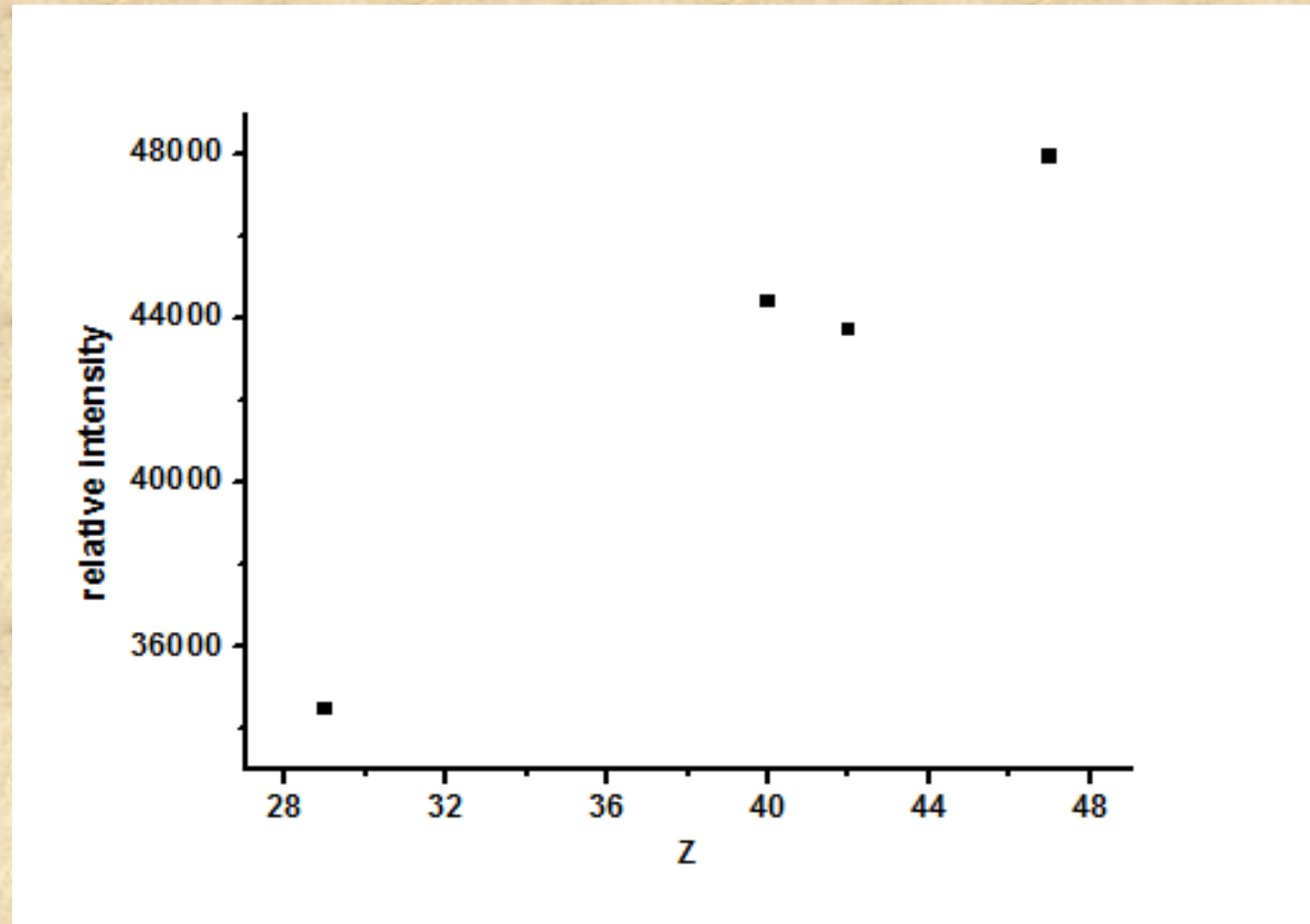
Pb

验证莫塞莱定律



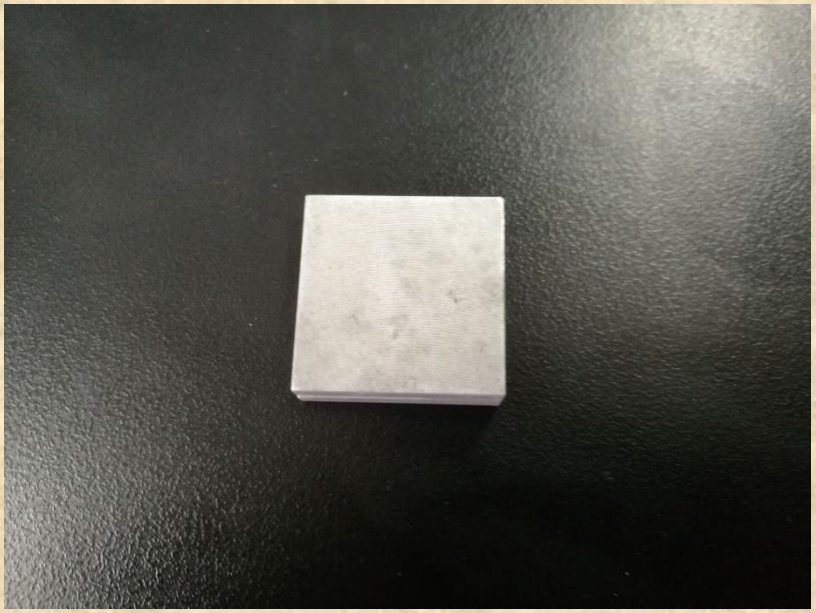
屏蔽常数$\sigma = 1.564 \pm 0.003$

验证荧光产额曲线


48000
44000
40000
36000
relative intensity
28
32
36
40
44
48
Z

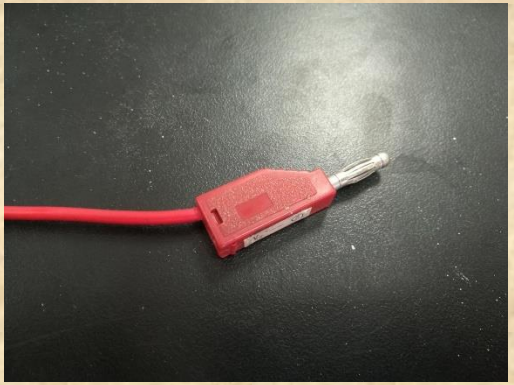
EDXRF分析

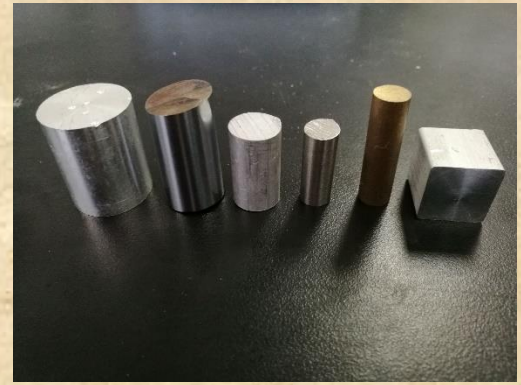
样品：



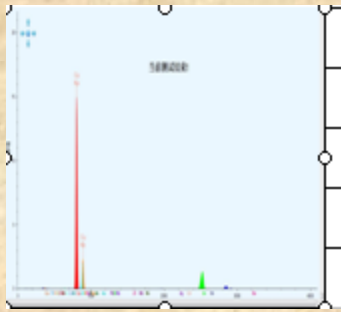
EDXRF分析

样品：



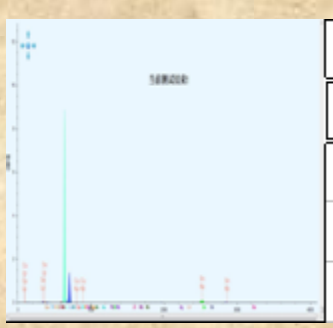


EDXRF分析



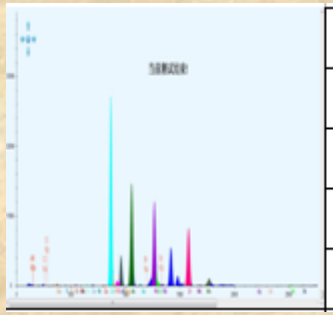
	强度	含量（%）
Ca(%)	5.33667	0.00000
Fe(%)	5.06516	0.00990
Cu(%)	1058.54458	12.26187
Sn(%)	181.63000	0.35610

五角钱硬币



Fe(%)	594.51135	9.76423
Sn(%)	12.09333	0.00000

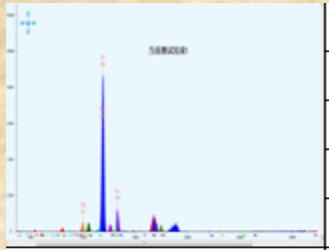
铁盖子



Zn(%)	191.61880	1.83771
Zr(%)	75.15866	0.04256
Pb(%)	104.45349	0.70437
Ba(%)	8.11667	0.00000
Bi(%)	9.20000	0.01447

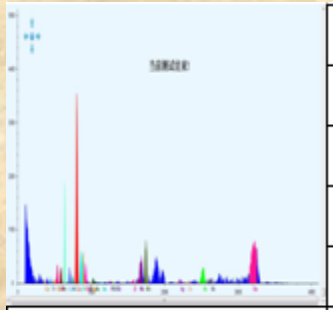
老师喝水杯盖

EDXRF分析



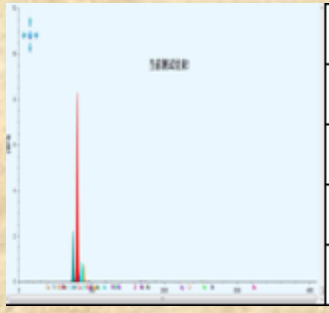
	强度	含量（%）
Cu(%)	1.48962	0.03395
As(%)	1.01480	0.00000
Nb(%)	4.94258	0.00041
Mo(%)	3.06583	0.00465
Pb(%)	3.19505	0.00152
Rb(%)	9.21127	0.00530
Bi(%)	1.91667	0.00272
Hg(%)	1.91000	0.51188

未知塑料



Fe(%)	12.36327	0.16042
Cu(%)	23.84504	0.16984
Zn(%)	4.07091	0.03486
Nb(%)	3.57308	0.00028
Mo(%)	8.14653	0.01324
Ba(%)	5.80333	0.00000

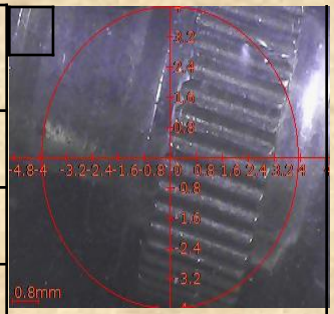
未知金属柱1号



Ni(%)	153.61486	1.89475
Cu(%)	579.37990	5.39611
Zn(%)	62.31358	0.59461
Nb(%)	1.54976	0.00011
Mo(%)	2.44331	0.00359

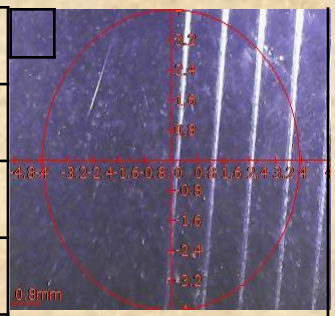
圆接头

RoHS分析

样品名称 Sample Name	yuanjietou				
测量时间 Test Time	200(s)	管压 Voltage	45(KV)		
操作员 Operator	User	管流 Current	700(μA)		
测量日期 Test Date	2017/5/31 星期三 12:50:33	工作曲线 WorkCurve	BRASS-ZINC		
仪器型号 Mode		供应商 Supplier			
元素 Element	强度 Intensity	含量(ppm) Content(ppm)	误差(ppm) Error(ppm)	限定标准 Limits	判定 Results
Cr(ppm)	0.00187	330.57	17.52	1000	Pass
Cd(ppm)	0.00093	13.37	1.65	100	Pass
Hg(ppm)	0.00000	ND	0.00	1000	Pass
Pb(ppm)	0.00374	749.81	68.45	1000	Pass

RoHS分析

样品名称 Sample Name	zhijiadao				
测量时间 Test Time	200(s)	管压 Voltage	45(KV)		
操作员 Operator	User	管流 Current	700(μA)		
测量日期 Test Date	2017/5/31 星期三 13:01:02	工作曲线 WorkCurve	Fe		
仪器型号 Mode		供应商 Supplier			
元素 Element	强度 Intensity	含量(ppm) Content(ppm)	误差(ppm) Error(ppm)	限定标准 Limits	判定 Results
Cr(ppm)	0.04118	8444.06	135.89	1000	TBD
Cd(ppm)	0.00000	ND	0.00	100	Pass
Hg(ppm)	0.00057	ND	0.00	1000	Pass
Pb(ppm)	0.00087	2.54	0.31	1000	Pass

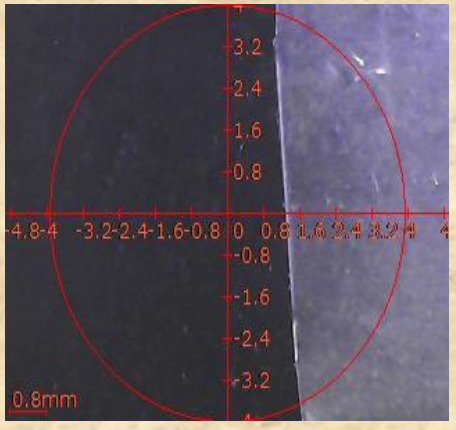


样品条件探究

实验思路

- 水平面积 → X光呈散射角打在样品上，面积影响着反射x光的强度。
- 样品厚度 → X光可以穿过薄样品，而且与元素吸收能力相关。样品选取x射线饱和厚度才能保证条件统一。
- 样品高度 → 待测物体为二级x光漫反射光源，物体高度不同导致反射进入接收器x光子数不同。

水平面积

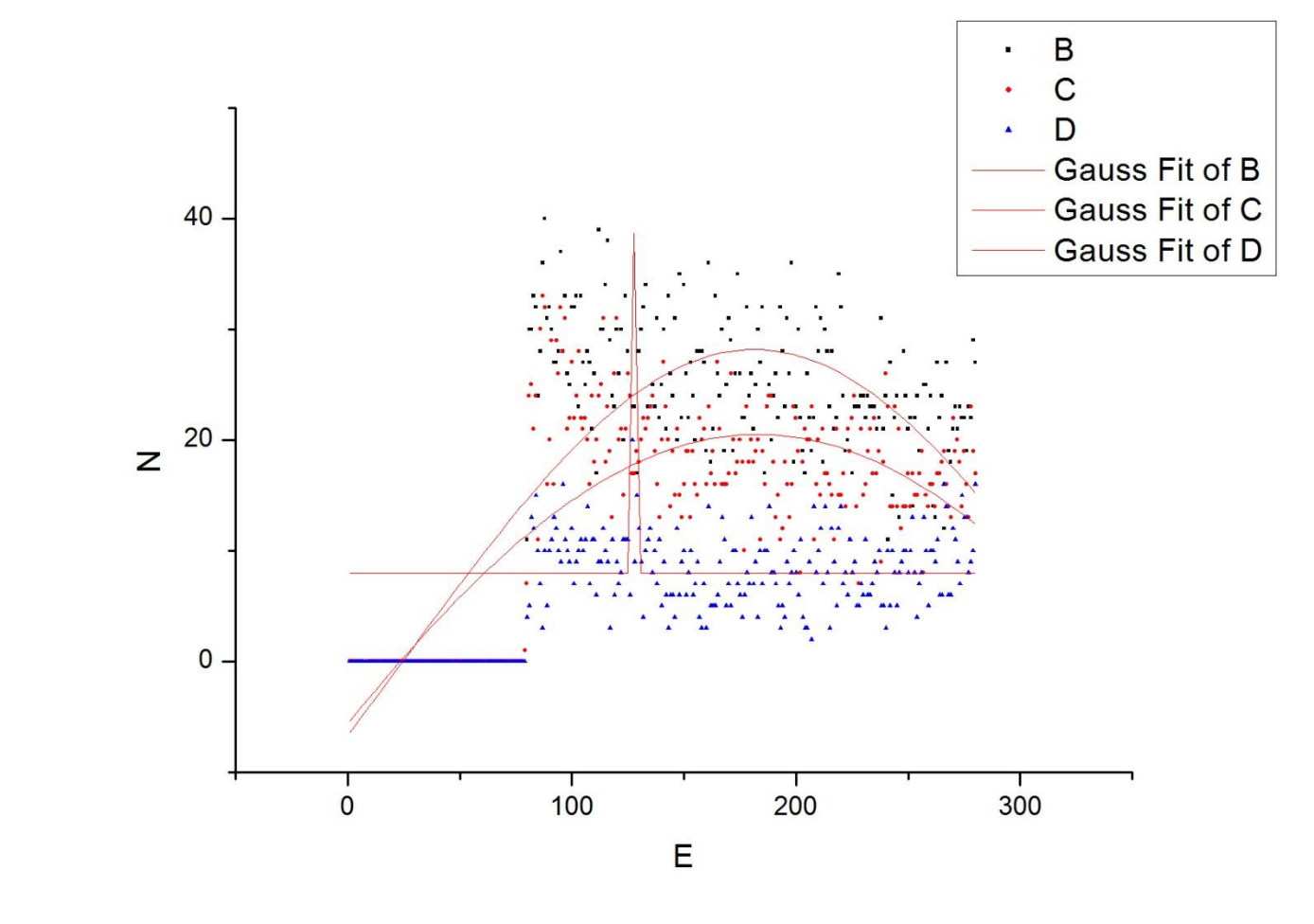


Cr含量平均值：

91059.71ppm

143571.74ppm

样品厚度

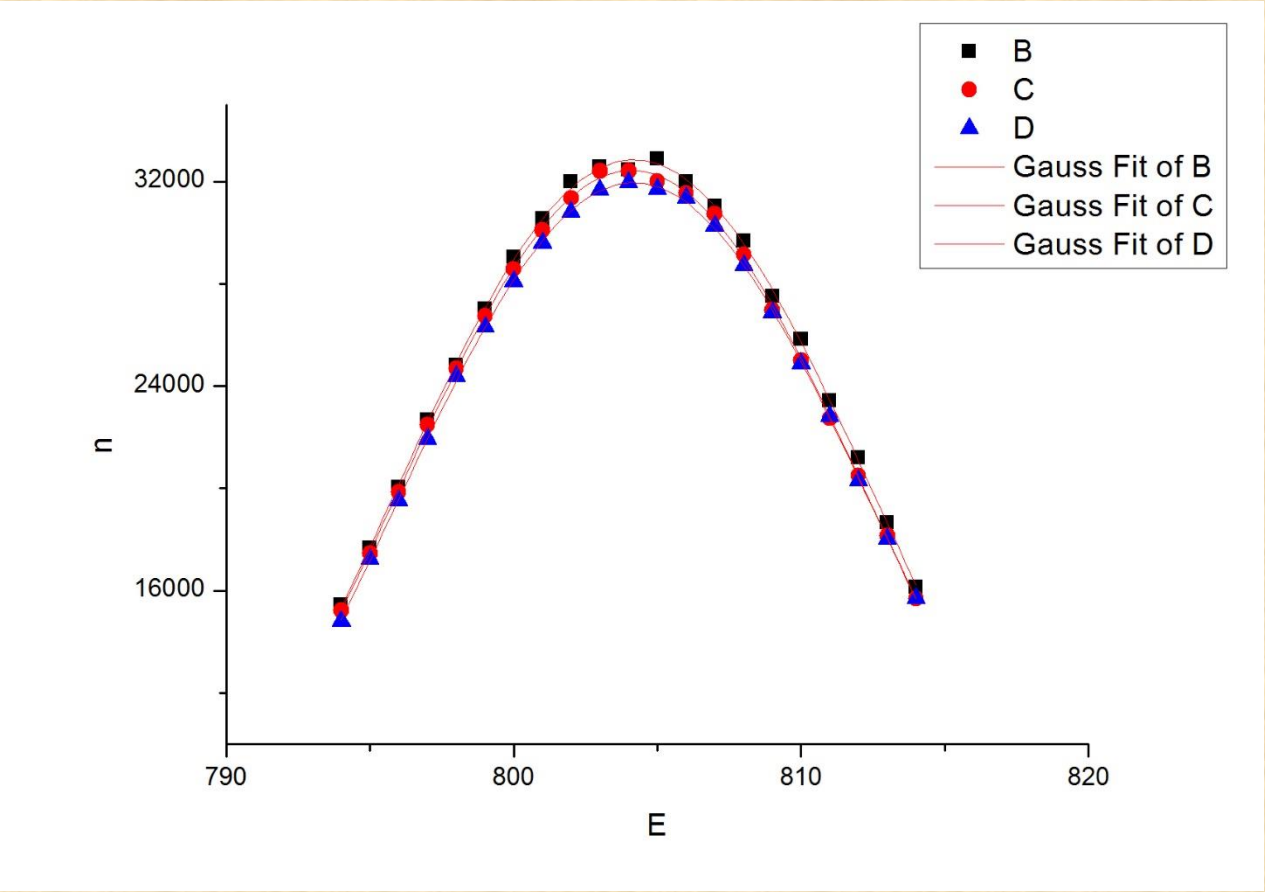


B：三片铝片

C：二片铝片

D：一片铝片

样品高度



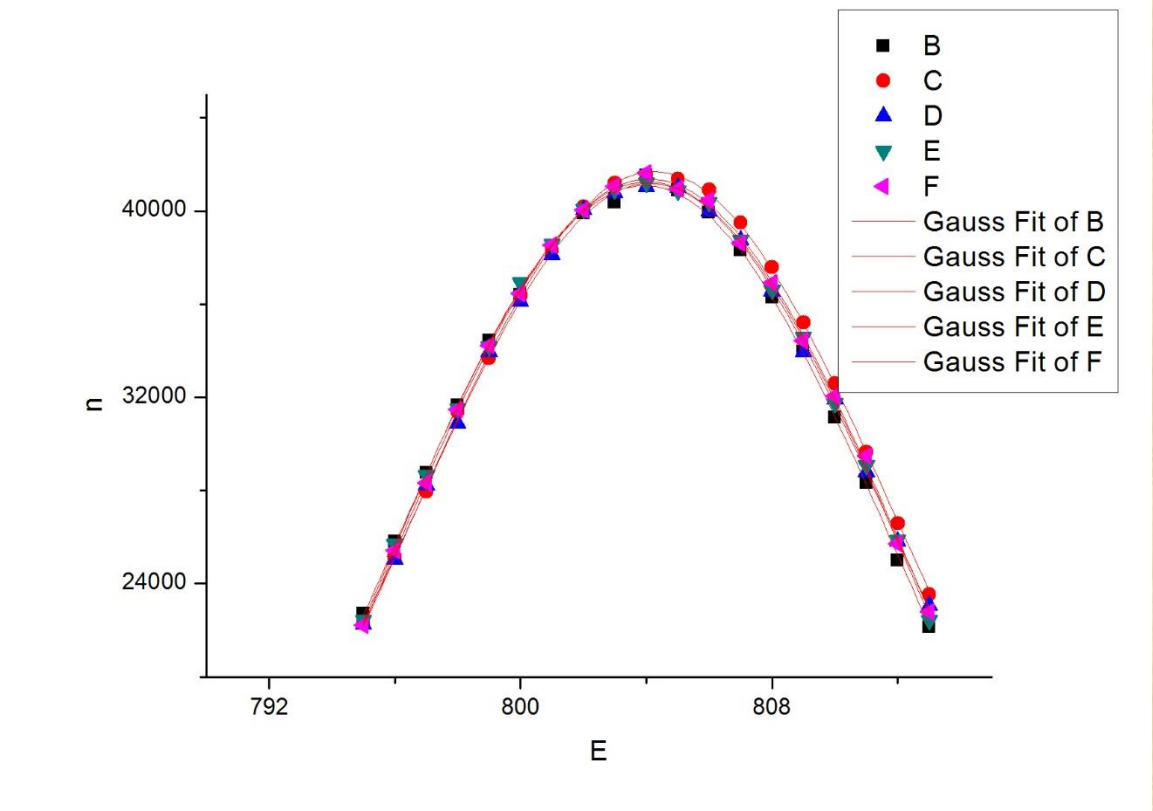
B：加一个铅片

C：加两个铅片

D：加三个铅片

样品台是一片塑料膜，铅片相当于重物，加在样品后面使得样品下沉，从而改变了空间位置。其中B是最接近原位置的。

二级荧光

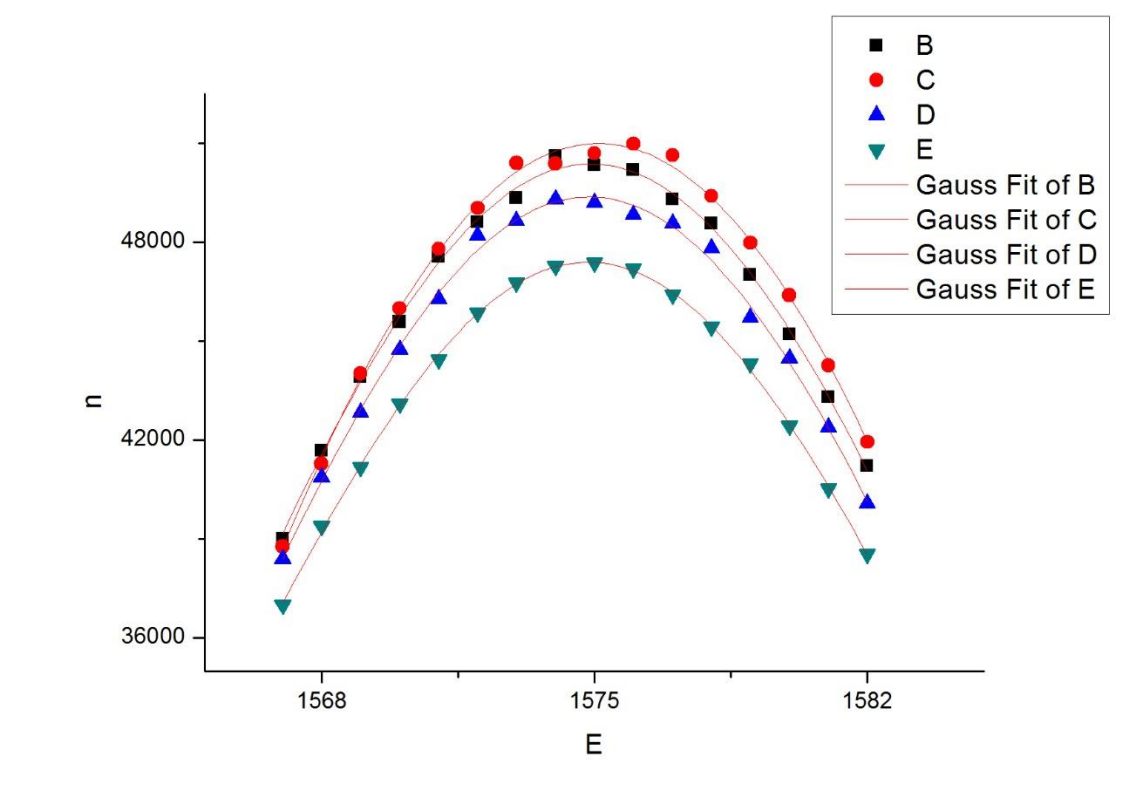


B、C、D：只放一片Cu

E、F：Cu上放一片铅片

每条谱线正负误差在100计数以内，属于测量误差，这组实验认为Pb没有让Cu产生二级荧光

二级荧光



B、C：只放一片Zr

D、E：Zr上放一片铅片

图中明显看到加上铅片谱线出现**反常**的降低

谢谢！