

## 地表水中元素的 ICP-TOF-MS 法测定

### 1 实验部分

#### 1.1 方法概要

本文建立了地表水及其河水中多种元素同时分析的检测方法，水样经预处理后采用 ICP-TOF-MS 进行检测。样品由载气带入雾化系统进行雾化后，以气溶胶形式进入等离子体的轴向通道，在高温惰性气体中被充分的蒸发、解离、原子化和电离，转化成正离子经检测器检测，质谱仪根据离子的质荷比进行分离并定性定量分析。在一定浓度范围内，元素特征离子响应信号和浓度成正比。

#### 1.2 仪器与试剂

OptiMass 9500 型电感耦合等离子体飞行时间质谱仪，超纯水仪，分析天平，温控电热板，离心机，滤纸，聚四氟乙烯烧杯，容量瓶。

硝酸， $\rho=1.42$  g/ml，优级纯

盐酸， $\rho=1.19$  g/ml，优级纯

元素混合标准溶液（100mg/L），使用时采用 1% 硝酸水溶液稀释至所需浓度；高纯氩气，实验用水均为超纯水。

#### 1.3 仪器条件

表 1 仪器条件

Cal Curve Type	Linear Least Squares
Sample Introduction	Manual
SmartGate Ranges	( 13-22 ) , ( 29-45 ) , (77-84)
Acquisition Time	5
Replicates	3
Sample Intro Time	30
Sample Pump Speed	6
Flush Pump Speed	30
Flush Time	10

Rinse Time	10
Rinse Pump Speed	10
Torch X position (mm)	9
Torch Y position (mm)	0
Torch Z position (mm)	0
Gasbox nebulizer flow (l/min)	0.66
Gasbox plasma flow (l/min)	10
Gasbox auxiliary flow (l/min)	0.5
Generator set power (W)	1200
Skimmer (V)	-1500
Extraction (V)	-1400
Z1 (V)	-900
Y Mean (V)	-250
Y Deflection (V)	-2
Z Lens Mean (V)	-1000
Z Lens Deflection (V)	-30
Lens Body (V)	-160
Fill (V)	-30
Fill Bias (V)	0
Fill Grid (V)	-13
Pushout Grid (V)	-380
Pushout Plate (V)	690
Blanker (V)	150
Reflectron (V)	700
Multiplier Gain (V)	3100
Detector Time C0 Work (ns)	-825.226
Detector Time C1 Work	2013.48
Blanker Time C0 (ns)	158.339
Blanker Time C1	247.582

#### 1.4 标准溶液的配制

准确移取 1ml 100 $\mu$ g/mL 的混标母液于 25ml 容量瓶中，加入 250 $\mu$ L 硝酸，用水定容至刻度摇匀，即为 4 $\mu$ g/ml 的标准中间溶液；分别取适量多元素标准中间液（4 $\mu$ g/mL）于 50mL 容量瓶中，用 1% 硝酸溶液定容至刻度稀释至所需浓度摇匀备用。

#### 1.5 样品处理

##### 1.5.1 可溶性元素

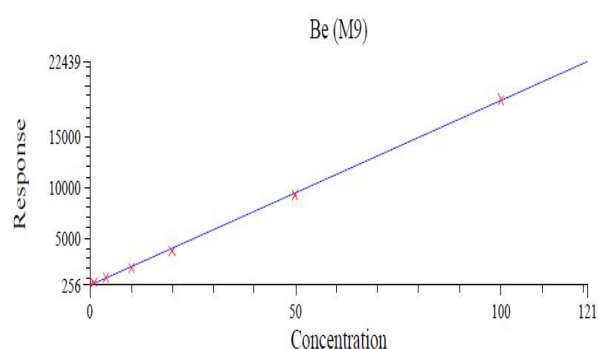
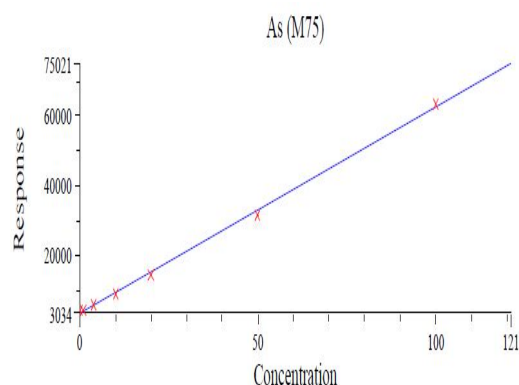
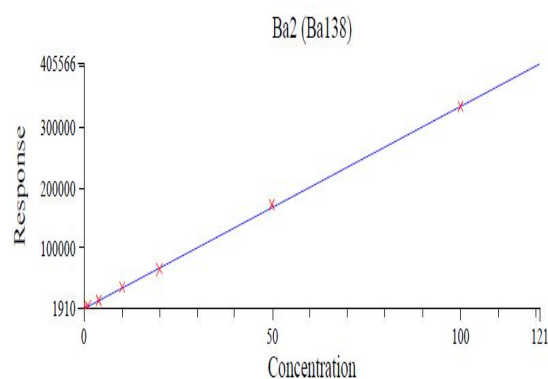
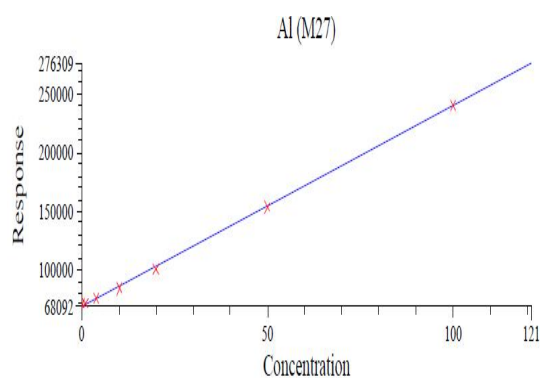
可溶性元素样品采集后立即用定量滤纸过滤，收集所需体积的滤液于聚四氟乙烯瓶中，加入适量硝酸（1:1）将酸度调节至  $\text{PH} < 2$ 。

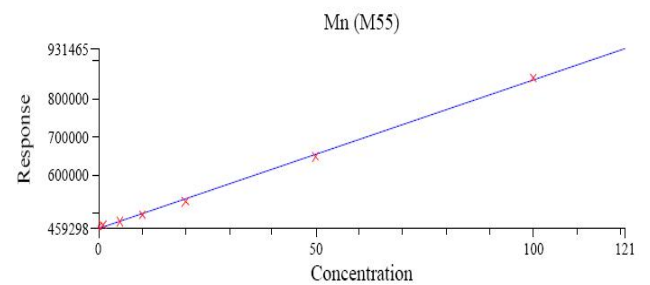
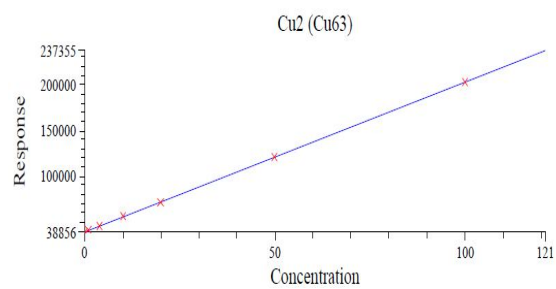
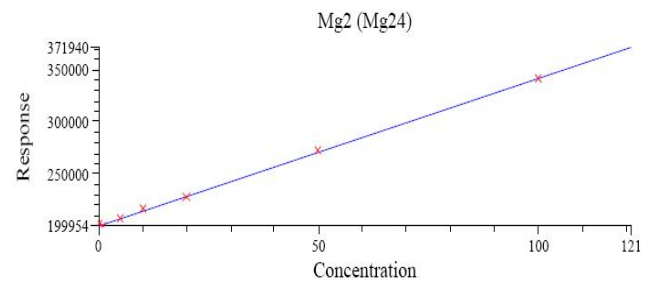
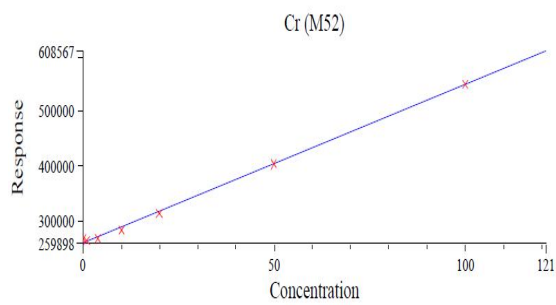
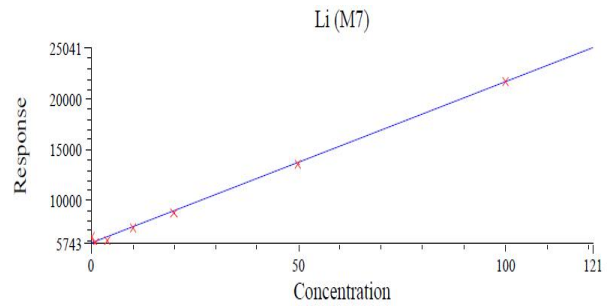
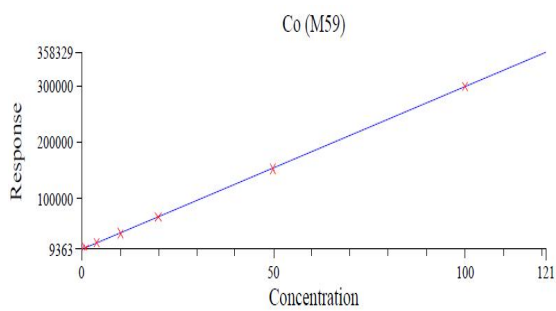
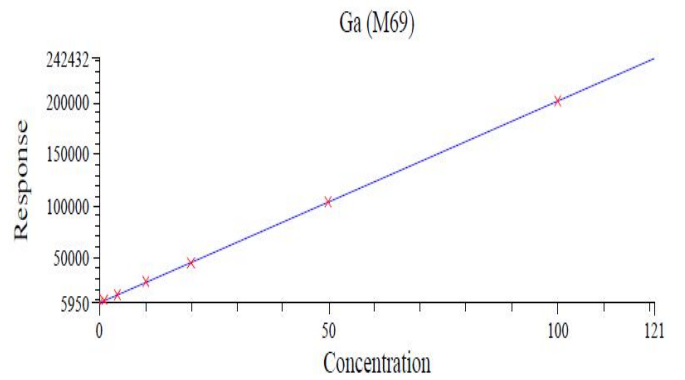
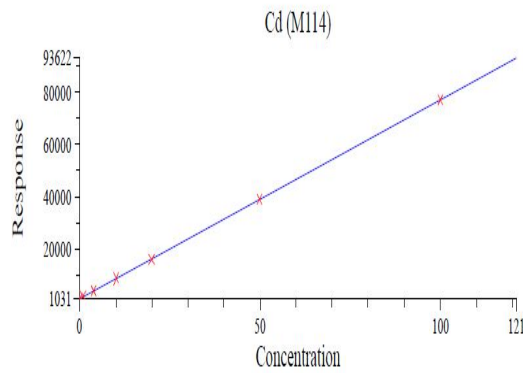
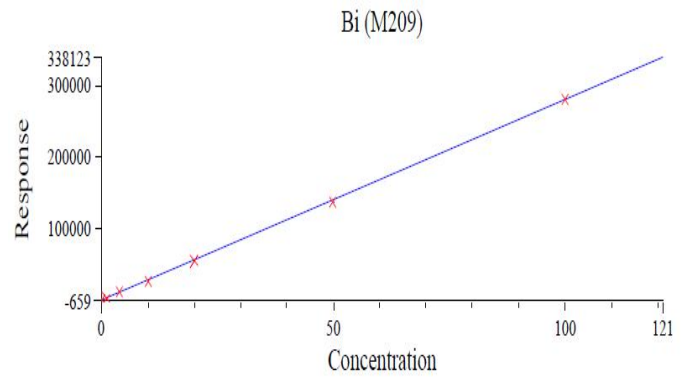
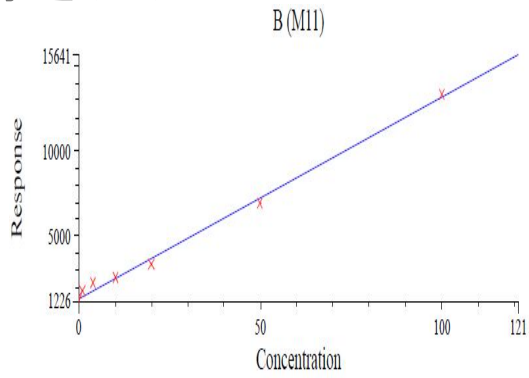
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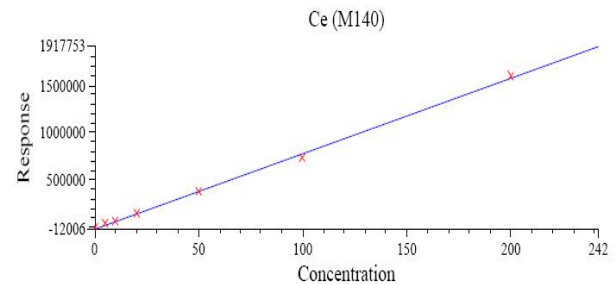
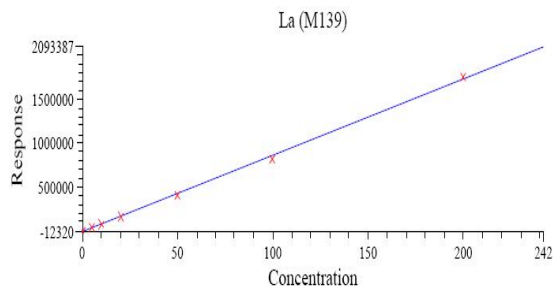
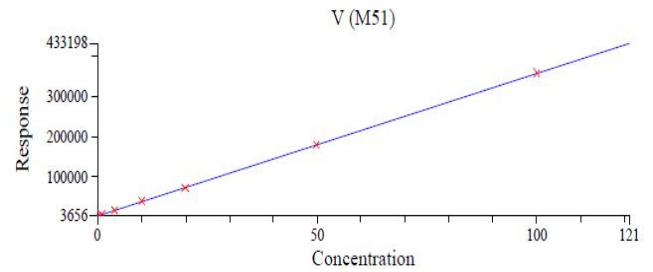
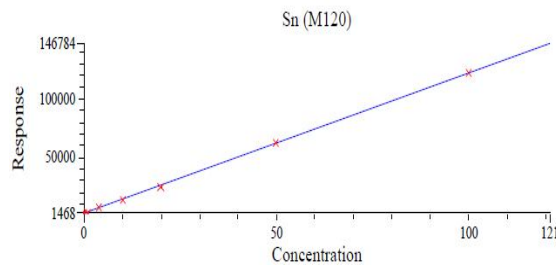
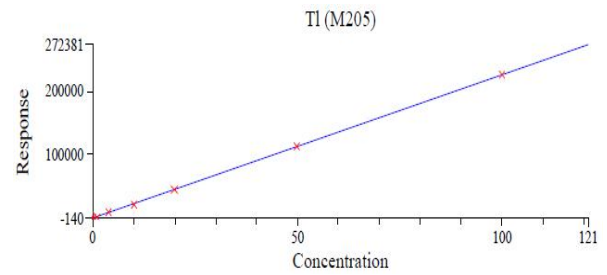
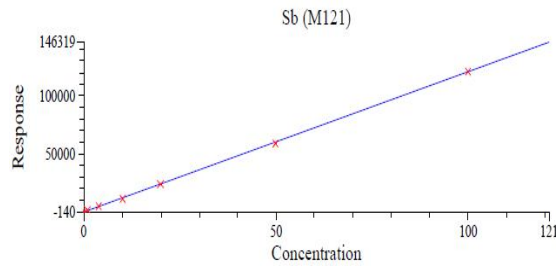
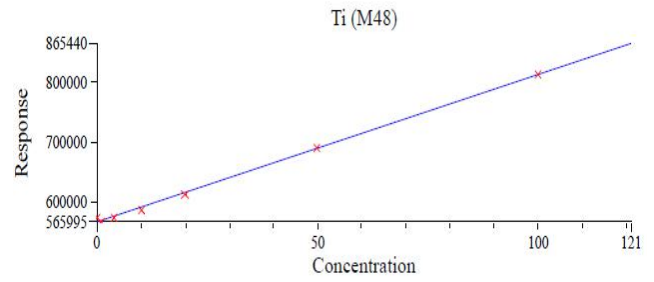
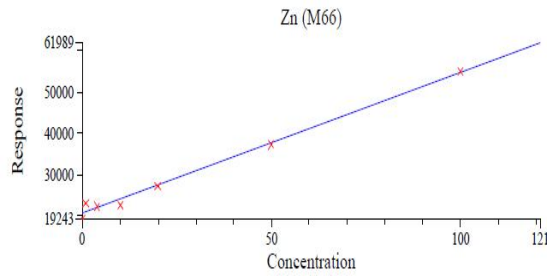
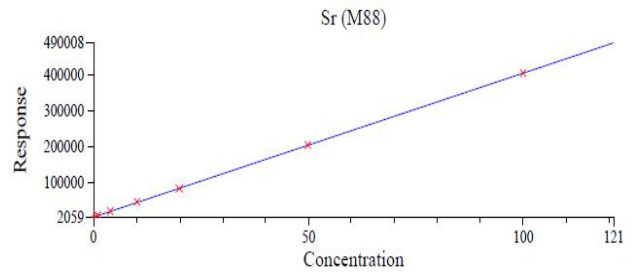
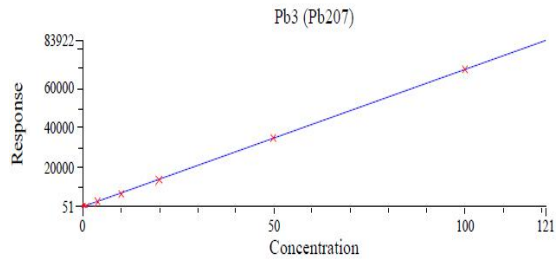
样品采集后加入适量硝酸（1:1）将酸度调节至  $\text{PH} < 2$ ，准确量取 100ml 摇匀后的样品于 250ml 聚四氟乙烯烧杯中，加入 2ml 硝酸溶液（1:1），1ml 盐酸溶液（1:1），摇匀，置于水浴锅中  $80^\circ\text{C}$  加热消解，静置过夜，用去离子水多次冲洗后转移至 100ml 容量瓶中定容，摇匀，然后取约 40ml 于离心试管中离心，取上清液上机测定。

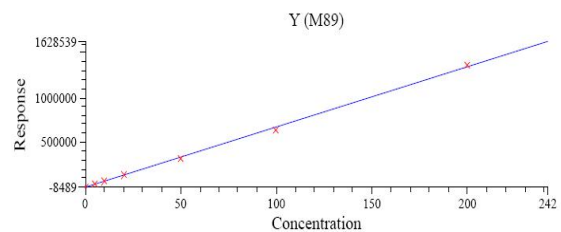
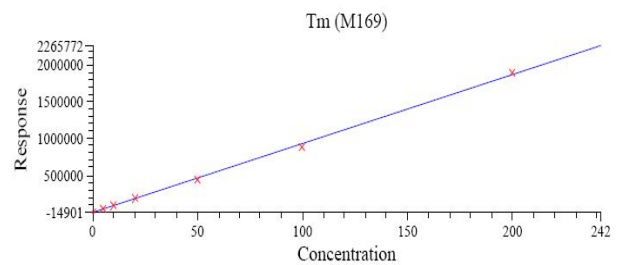
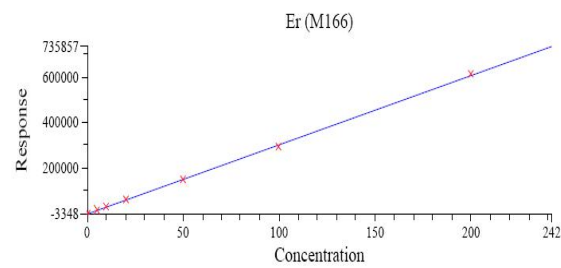
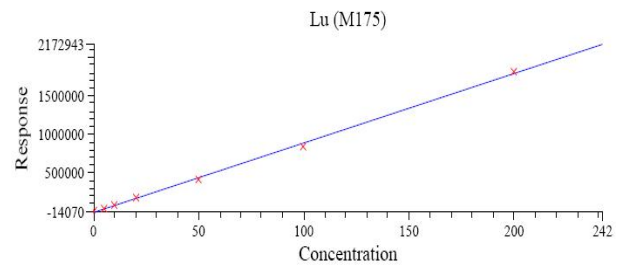
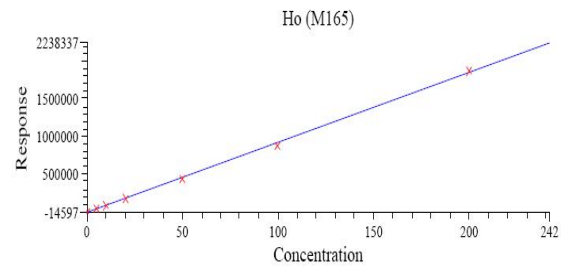
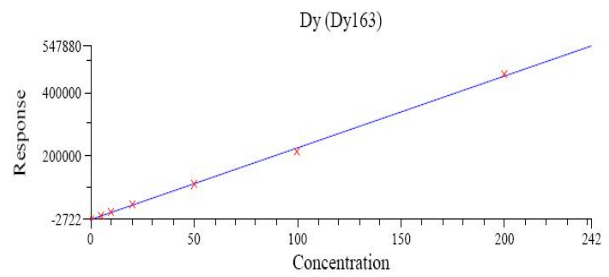
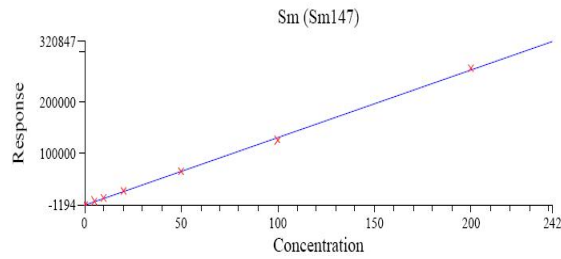
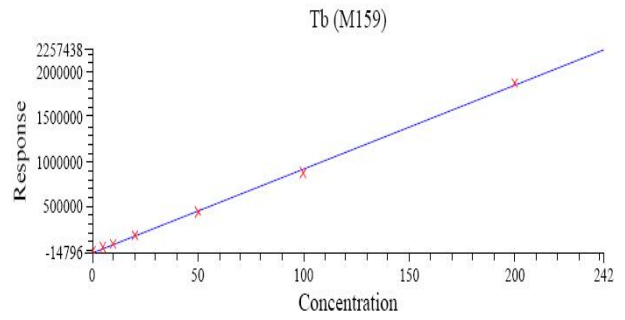
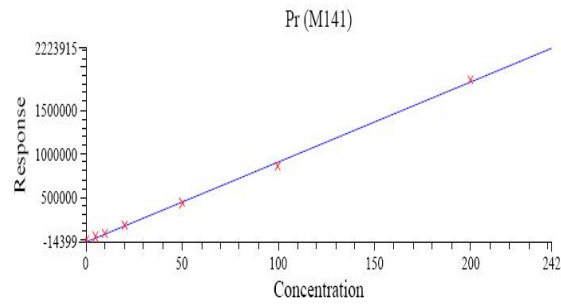
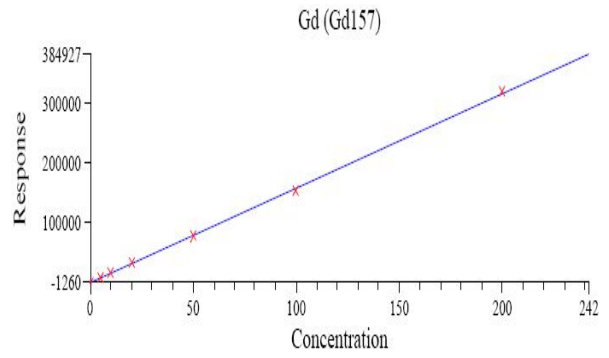
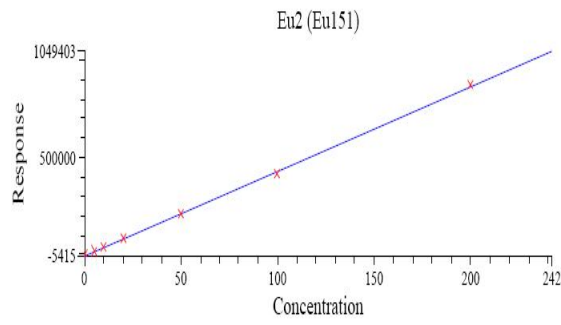
## 2 实验结果

### 2.1 标准曲线









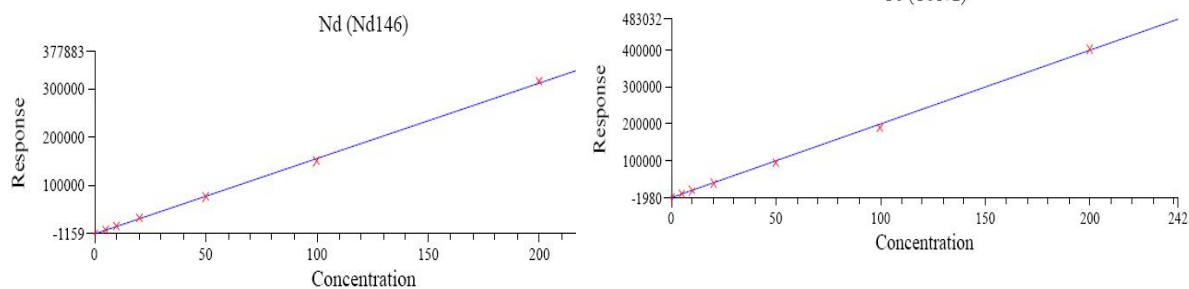


表 2 元素线性方程及相关系数

序号	元素	相关系数	线性方程	检测限 ng/mL
1	Al	0.9995	Conc = 0.00057953 * Resp - 39.2461	3.0
2	As	0.9986	Conc = 0.00167624 * Resp - 4.87032	0.60
3	B	0.9959	Conc = 0.00846692 * Resp - 11.5159	0.7
4	Ba	0.9995	Conc = 0.000298918 * Resp - 0.353772	0.20
5	Be	0.9996	Conc = 0.00543975 * Resp - 1.17896	0.16
6	Bi	0.9998	Conc = 0.000356178 * Resp + 0.450449	0.03
7	Cd	0.9999	Conc = 0.00130323 * Resp - 1.12866	0.08
8	Co	0.9999	Conc = 0.000345783 * Resp - 3.02182	0.16
9	Cr	0.9984	Conc = 0.000346054 * Resp - 89.7212	5.1
10	Cu	0.9998	Conc = 0.000607871 * Resp - 23.4029	0.13
11	Ga	0.9998	Conc = 0.00051025 * Resp - 2.82004	0.13
12	Li	0.9970	Conc = 0.00625128 * Resp - 35.6765	0.5
13	Mg	0.999	Conc = 0.000707465 * Resp - 142.134	1.7
14	Mn	0.9923	Conc = 0.000256266 * Resp - 117.702	0.12
15	Pb	0.9998	Conc = 0.00143868 * Resp + 0.143021	0.07
16	Sb	0.9997	Conc = 0.000823893 * Resp + 0.331256	0.16
17	Sn	0.9998	Conc = 0.000830376 * Resp - 1.00338	0.15

18	Sr	0.9999	Conc = 0.000247292 * Resp - 0.293286	0.13
19	Ti	0.9979	Conc = 0.000402919 * Resp - 227.831	0.6
20	Tl	0.9998	Conc = 0.000442767 * Resp + 0.278337	0.02
21	V	0.9999	Conc = 0.000280922 * Resp - 0.811622	0.23
22	Zn	0.9911	Conc = 0.00290493 * Resp - 59.1789	0.5
23	La	0.9990	Conc = 0.000114926 * Resp + 1.4159	0.04
24	Ce	0.9988	Conc = 0.000125404 * Resp + 1.50563	0.03
25	Pr	0.9989	Conc = 0.000108117 * Resp + 1.55677	0.01
26	Nd	0.9994	Conc = 0.000638452 * Resp + 0.740084	0.03
27	Sm	0.9992	Conc = 0.000751458 * Resp + 0.897189	0.02
28	Eu	0.9993	Conc = 0.000229423 * Resp + 1.24232	0.006
29	Gd	0.9995	Conc = 0.000626639 * Resp + 0.789725	0.03
30	Tb	0.9990	Conc = 0.000106503 * Resp + 1.57584	0.0009
31	Dy	0.9991	Conc = 0.000439519 * Resp + 1.19636	0.01
32	Ho	0.9990	Conc = 0.000107415 * Resp + 1.56795	0.006
33	Er	0.9993	Conc = 0.000327379 * Resp + 1.09618	0.02
34	Tm	0.9990	Conc = 0.000106109 * Resp + 1.58115	0.003
35	Yb	0.9993	Conc = 0.000498957 * Resp + 0.987788	0.02
36	Lu	0.9989	Conc = 0.000110653 * Resp + 1.55686	0.009
37	Y	0.9991	Conc = 0.000147829 * Resp + 1.25495	0.006

表 3 样品检测结果

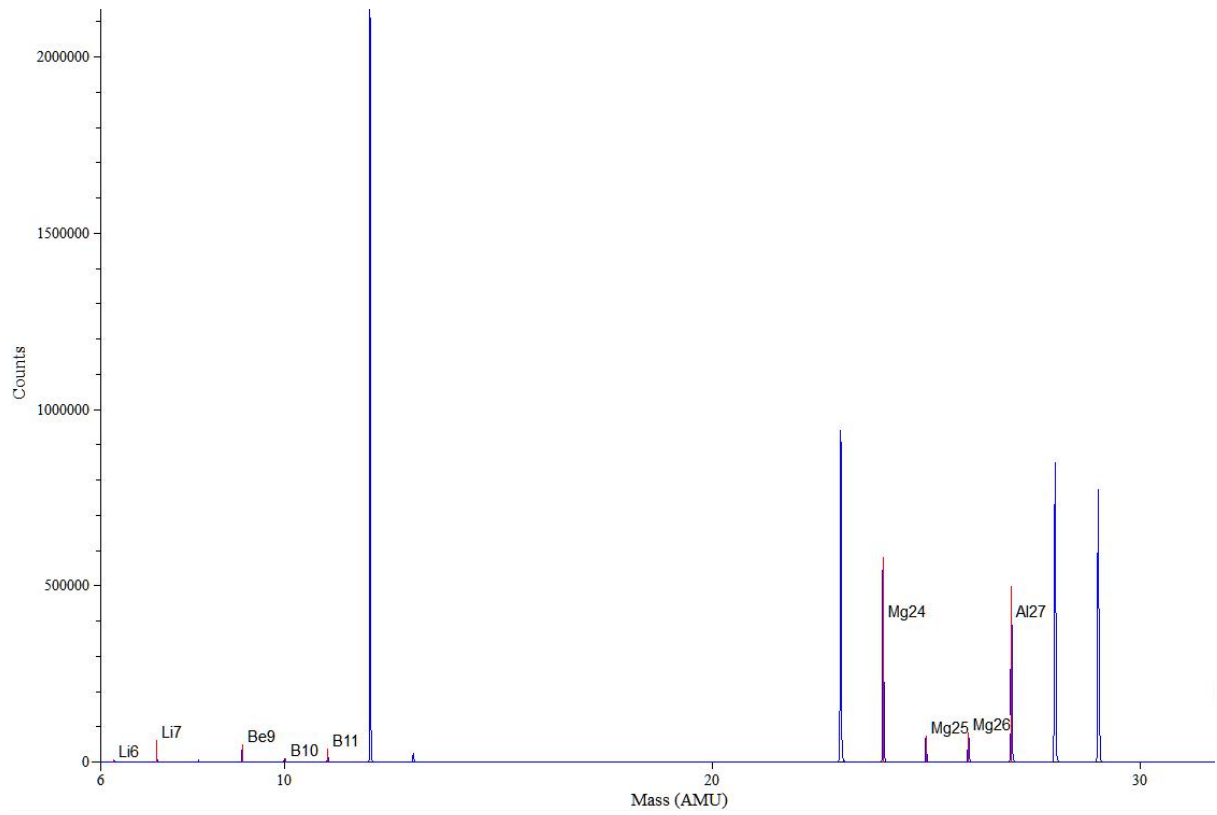
序号	元素	相关系数	可溶性元素		元素总量	
			山泉水 ng/mL	河水 ng/mL	山泉水 ng/mL	河水 ng/mL
1	Al	0.9995	4.1	24.0	5.8	185
2	As	0.9986	ND	ND	13.5	32.4



3	B	0.9959	18.8	127.3	18.9	136.3
4	Ba	0.9995	35.1	15.1	32.4	24.1
5	Be	0.9996	ND	ND	ND	ND
6	Bi	0.9998	ND	ND	ND	ND
7	Cd	0.9999	ND	ND	ND	ND
8	Co	0.9999	1.0	1.0	1.0	1.5
9	Cr	0.9984	10.5	ND	10.7	ND
10	Cu	0.9998	ND	ND	ND	ND
11	Ga	0.9998	ND	ND	4.4	2.1
12	Li	0.9970	ND	ND	ND	ND
13	Mg	0.999	10927	22146	10938	22250
14	Mn	0.9923	44.1	28.0	49.4	112
15	Pb	0.9998	0.1	0.13	0.3	0.8
16	Sb	0.9997	1.3	2.0	1.4	2.2
17	Sn	0.9998	ND	ND	ND	ND
18	Sr	0.9999	710	898	707	930
19	Ti	0.9979	3	0	24.2	27.1
20	Tl	0.9998	ND	ND	ND	ND
21	V	0.9999	ND	ND	410	411.8
22	Zn	0.9911	21.7	ND	30.1	ND
23	La	0.9990	0.3	0.1	0.4	0.36
24	Ce	0.9988	ND	ND	ND	0.5
25	Pr	0.9989	ND	ND	ND	ND
26	Nd	0.9994	ND	ND	ND	0.2
27	Sm	0.9992	ND	ND	ND	ND
28	Eu	0.9993	ND	ND	ND	ND
29	Gd	0.9995	ND	ND	ND	ND
30	Tb	0.9990	ND	ND	ND	ND
31	Dy	0.9991	ND	ND	ND	ND

32	Ho	0.9990	ND	ND	ND	ND
33	Er	0.9993	ND	ND	ND	ND
34	Tm	0.9990	ND	ND	ND	ND
35	Yb	0.9993	ND	ND	ND	ND
36	Lu	0.9989	ND	ND	ND	ND
37	Y	0.9991	1.0	1.4	1.1	1.59

注：ND 表示未检出。



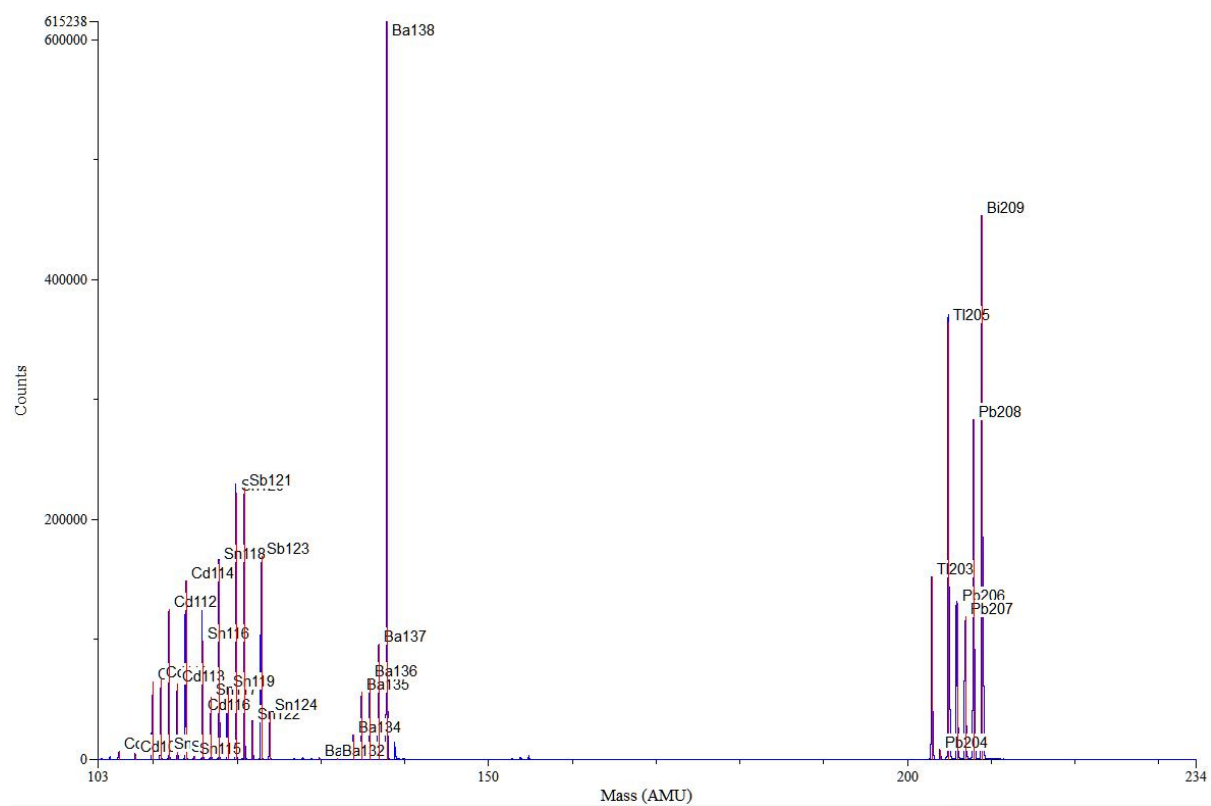
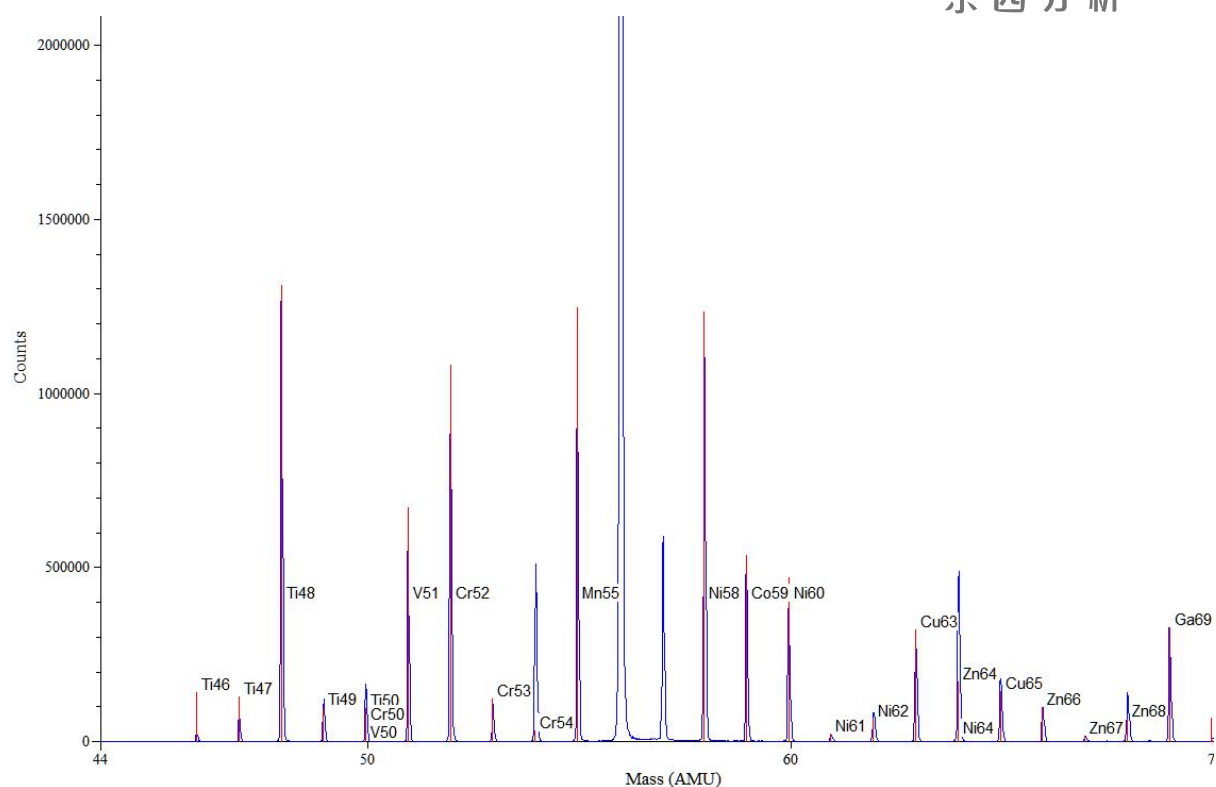


图 1 元素标样局部放大谱图