

第十五届PerkinElmer原子光谱用户会



ICPMS的干扰类型与消除技术

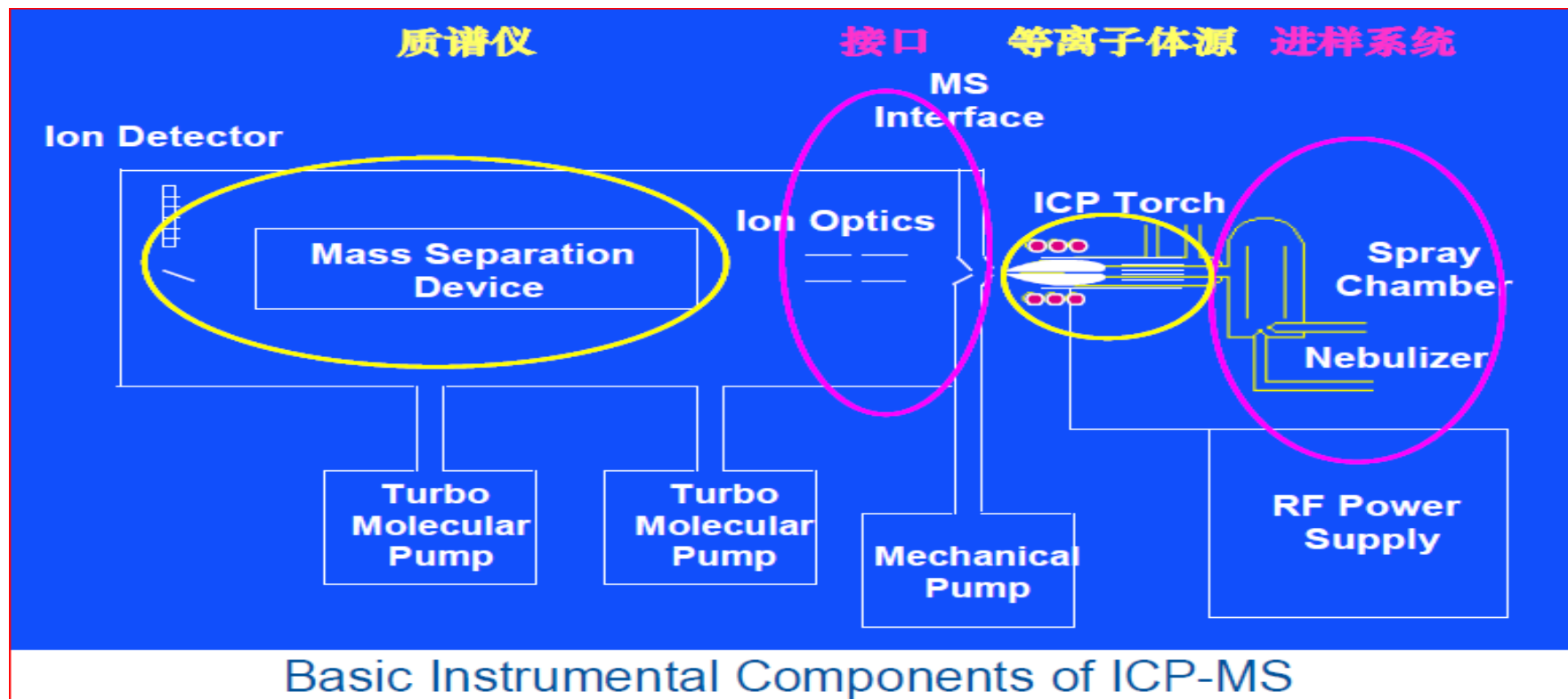
- 高光晔
- 2018-8-14

40
YEARS OF
MAKING
LIFE BETTER
IN CHINA

ARE YOU
IN?

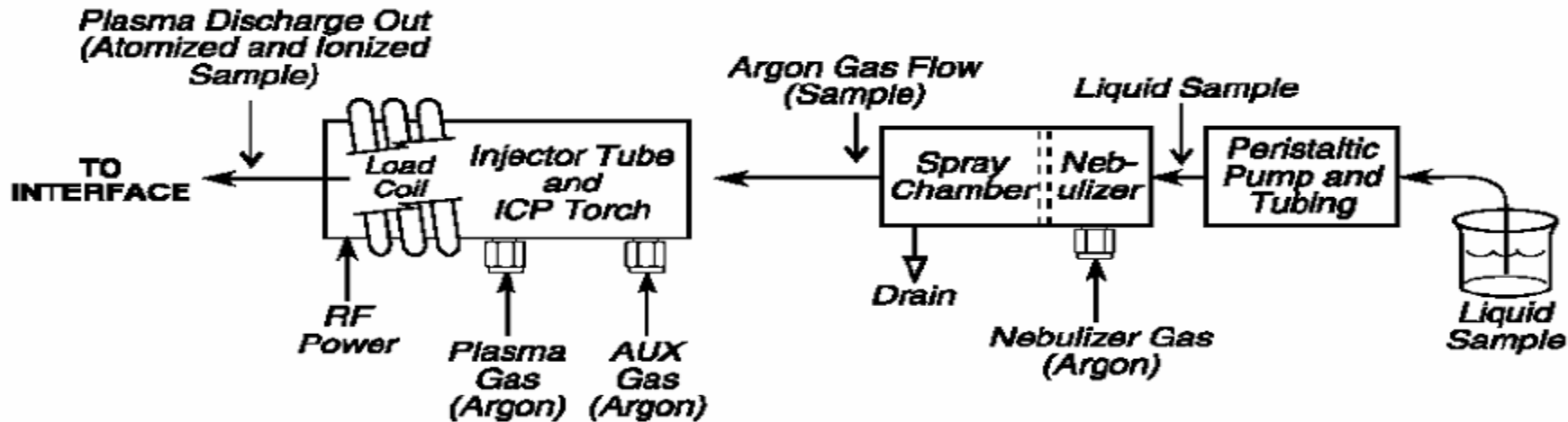


ICP-MS的仪器结构简图



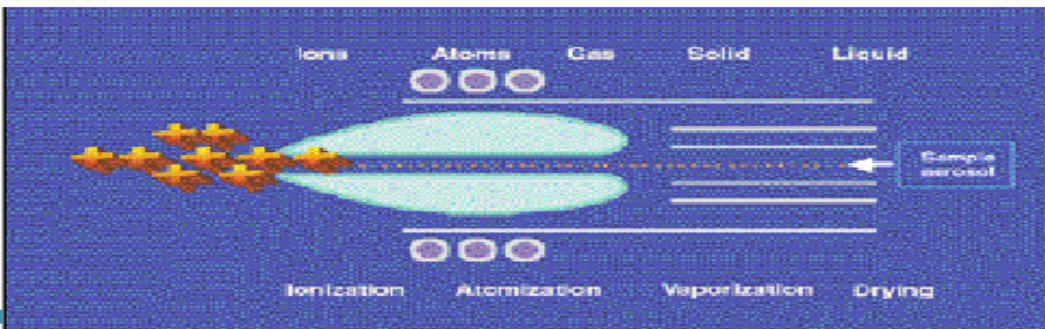
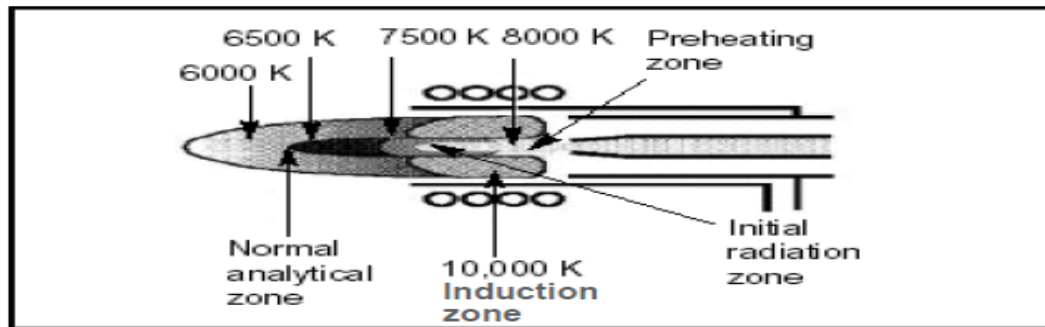
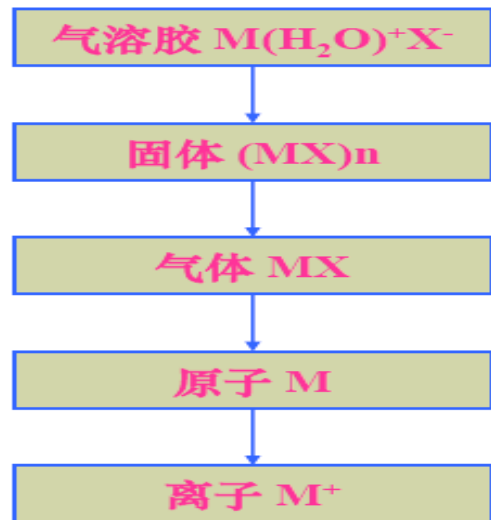
1、进样系统：溶液→气溶胶（进入ICP离子源）

样品进样系统是将待测样品转变成合适的形式，即雾化的电离状态从而进入仪器的接口区。简单地讲，样品进样系统的目的就是为将样品送入等离子体。下面的框图说明了样品在流经 ELAN 的样品进样区所经过的区域，包括以下几部分：蠕动泵、雾化器、雾室、ICP 炬管。



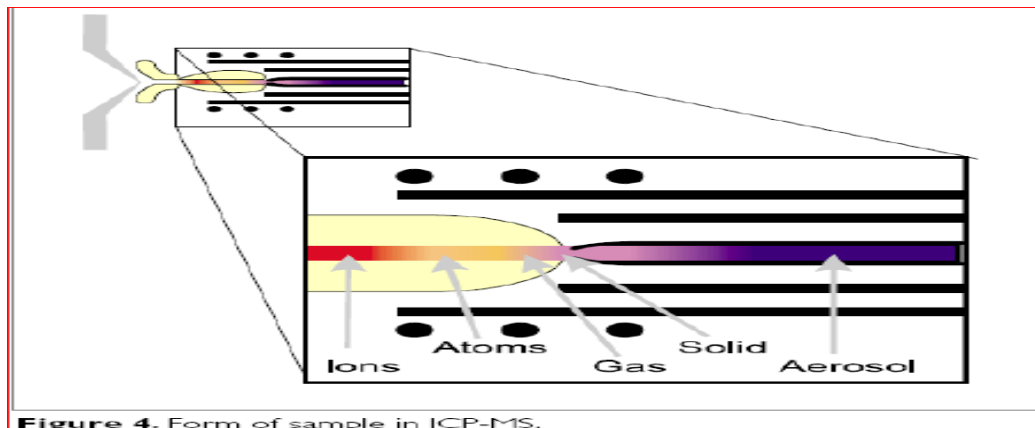
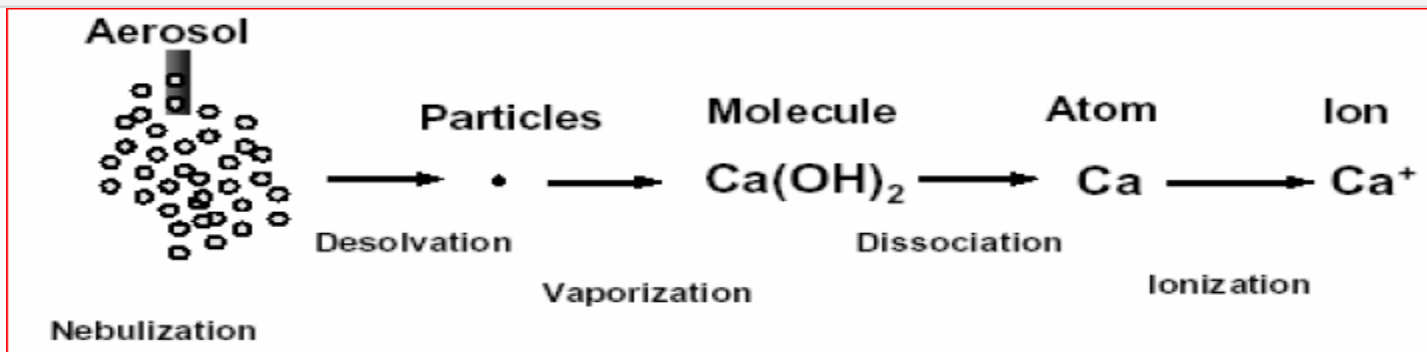
2、 ICP离子源：气溶胶→离子(去溶、气化、解离、电离)

(Times: <10ms)

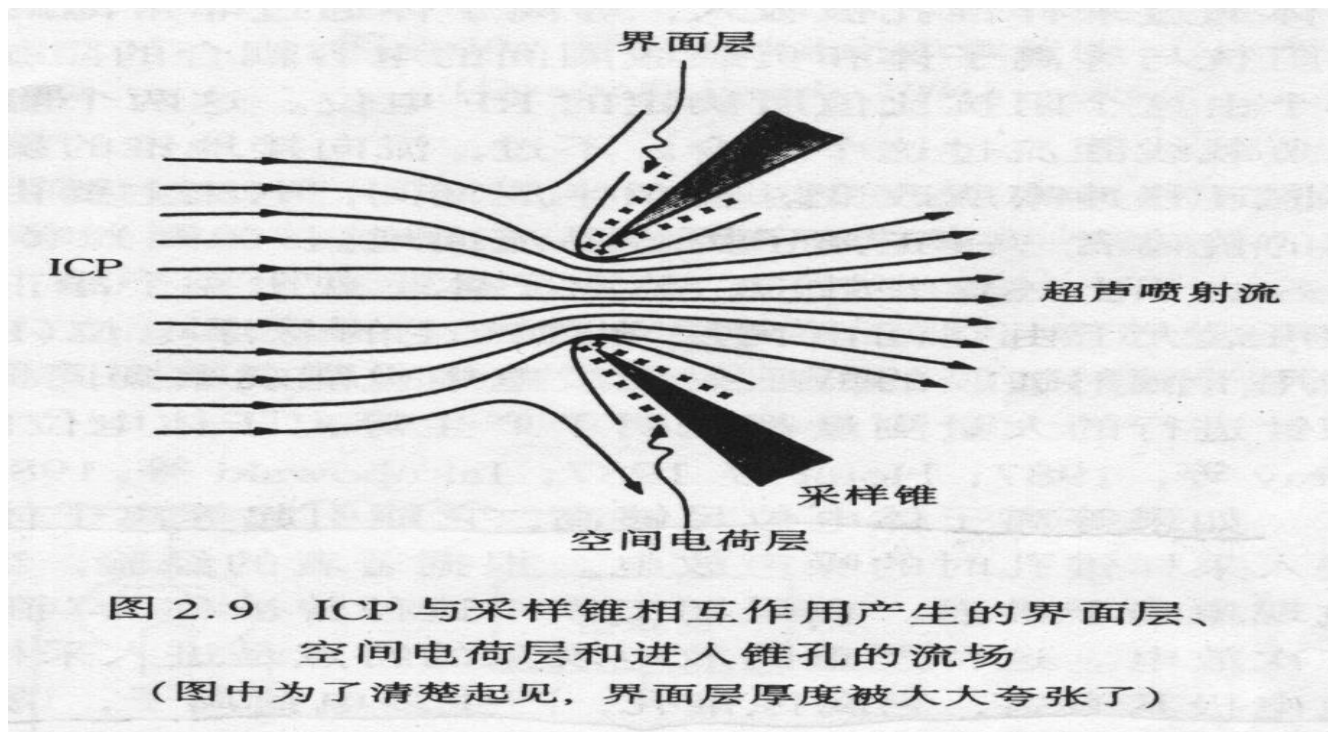


离子的形成过程（固态颗粒→ 分子→ 原子→ 离子）

离子化



3、接口：离子进入真空（界面层、等离子体电位与离子动能）



接口中离子与中性粒子、电子、光子分离并聚焦

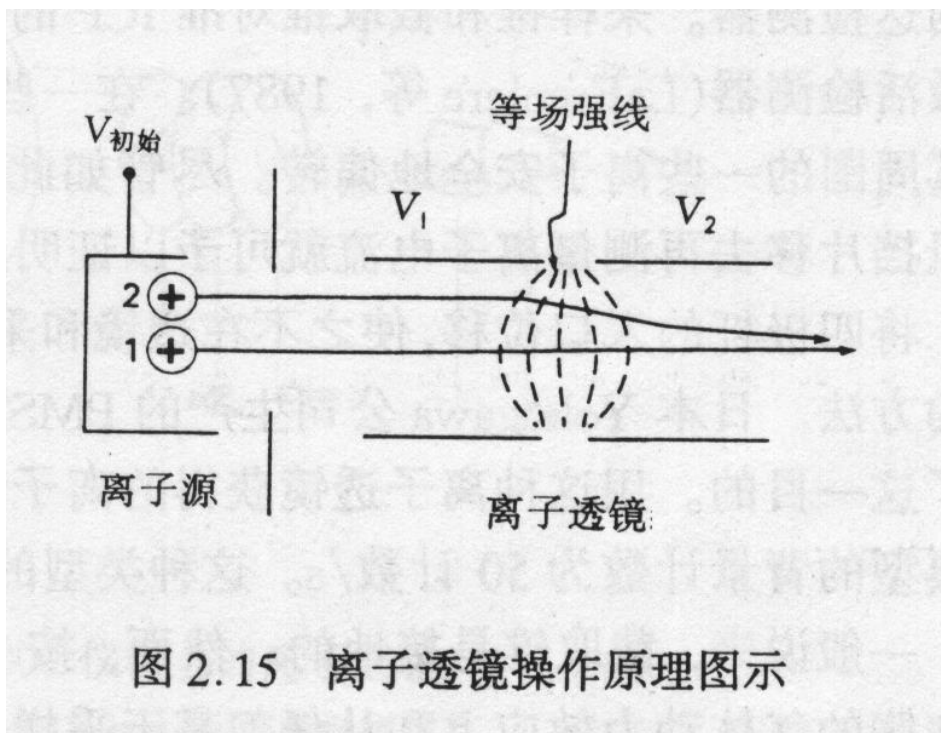
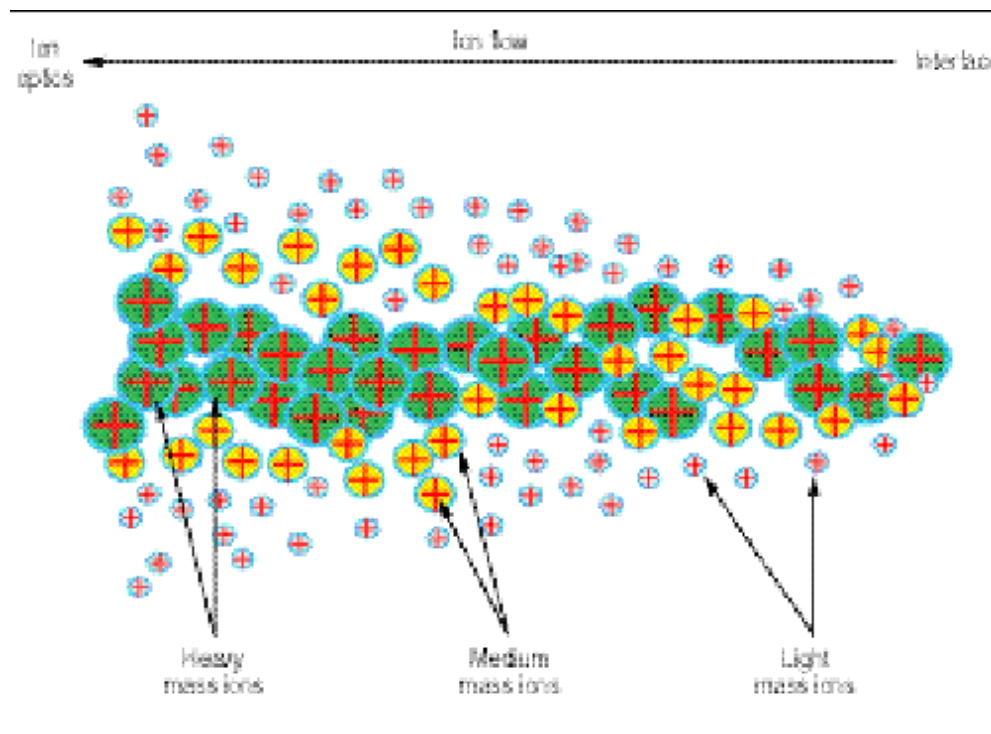
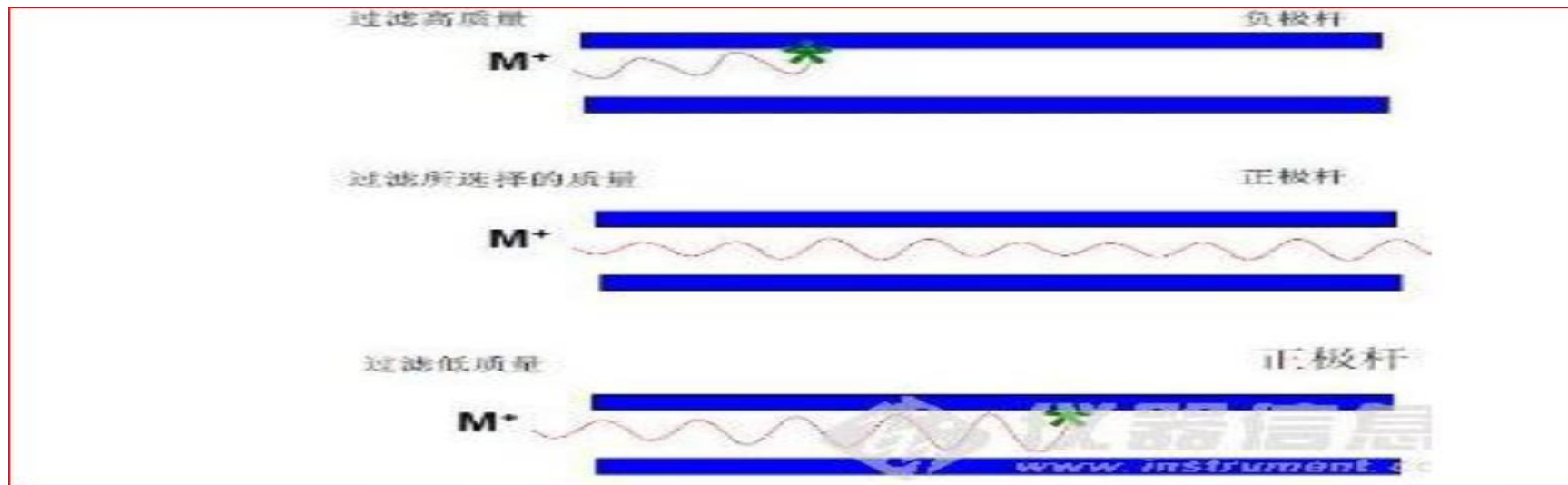


图 2.15 离子透镜操作原理图示

正离子聚焦导致的空间电荷效应与质量歧视



4、离子在四极杆中被按质荷比筛选



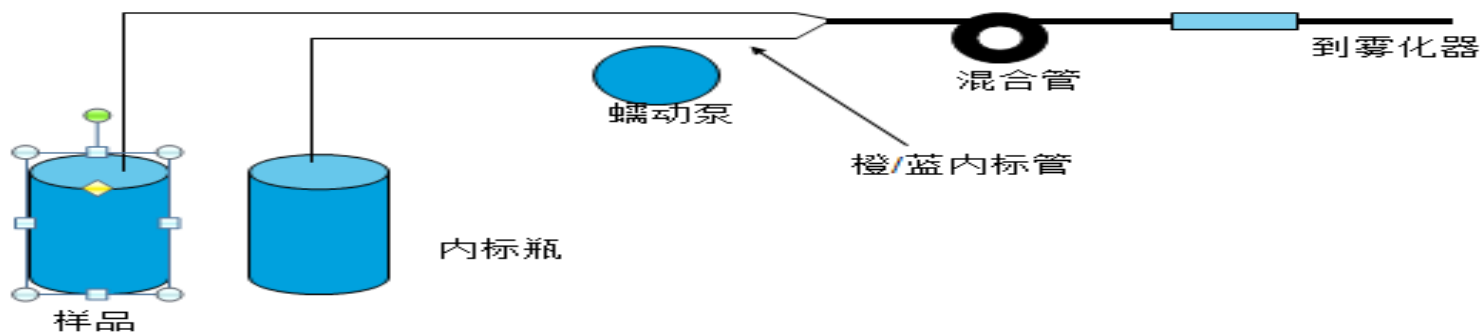
四极杆质谱仪是一个由四个平行的导电棒组成的质量过滤器，只有具有一定质荷比的离子才能在任意时刻及时通过质谱仪。质量不符合要求的离子与棒相碰撞或者离开棒之间的轨道，被泵抽出系统。

ICPMS的基体效应与质谱干扰

- 来自样品溶液或ICP中的其他物质可能在进样系统、ICP离子源、接口、四级杆质谱等环节对待测离子的测定结果产生影响，造成检测结果的失真。
- **进样系统：物理干扰。** 样品溶液因比重、粘度不同造成进样效率不同。
- **ICP离子源：化学与电离干扰。** 样品基体与待测组分形成稳定化合物，或基体组分电离影响ICP中的电子密度，影响待测组分的离子产率。
- **接口：空间电荷效应（质量歧视）。** 样品中基体组分电离形成的大量离子把待测离子推开导致待测离子传输效率变化。
- **四级杆：质谱干扰。** 相同质荷比的其他离子影响待测离子的测定。
- 其中前三项可以统称为非质谱干扰（**基体效应**）。

1、物理干扰的消除

- 稀释 (影响检出限)
- 使用蠕动泵管控制进样
- 内标校正



内标与样品以1到5倍比例混合

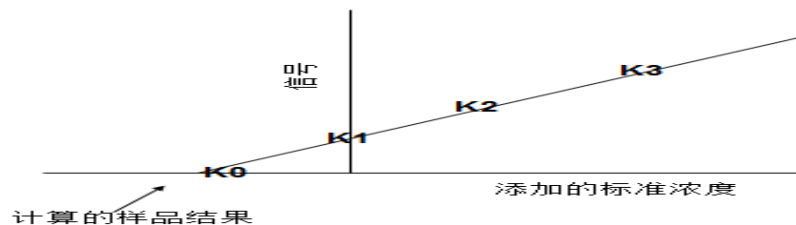
内标元素选择的要求

- 样品中不存在
- 在所有的样品溶液中准确加入内标，或者用内标混合管在线加入以确保准确而稳定的流量
- 内标离子（元素）与待测离子的质量数要相近，第一电离能相近。
- 常见内标：Re、Rh、Tb、Bi、In、Sc、Y、Ge等

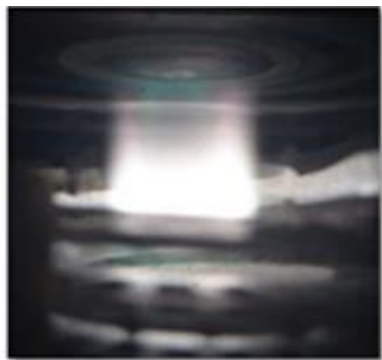


2、化学与电离干扰的消除

- 内标校正
- 标准加入法
- 增大ICP功率
- 引入基体改进气体

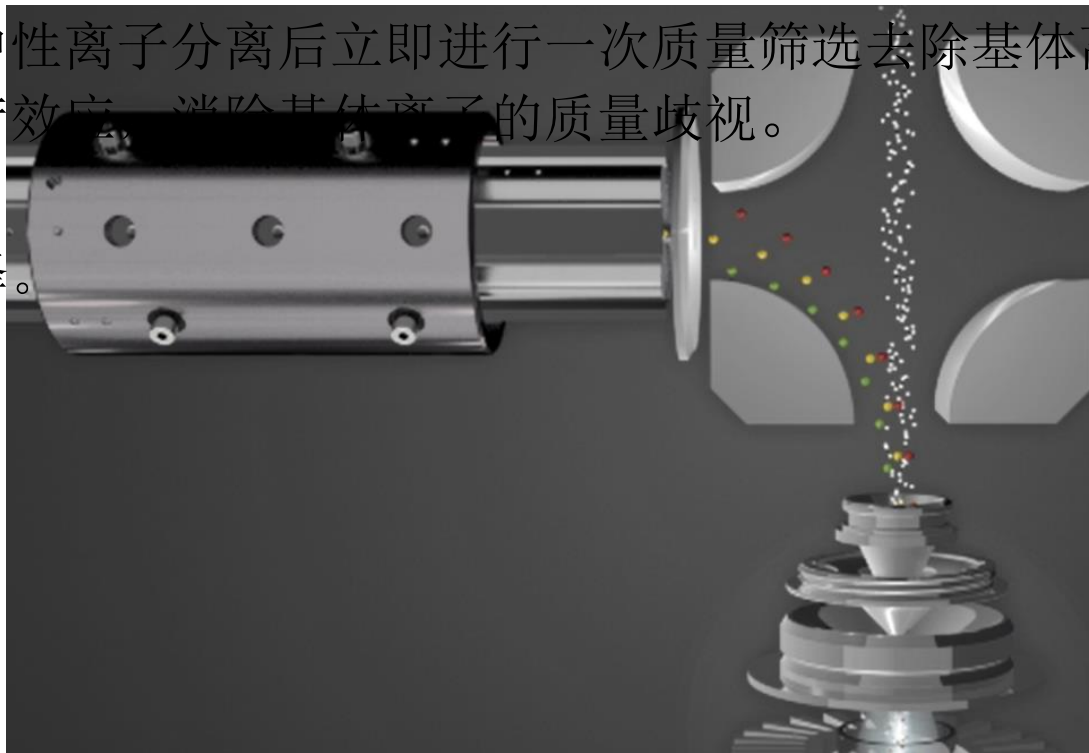


要求线性
所有的信号都是在分析中测得



3、基体离子质量歧视的处理

- 在离子与中性离子分离后立即进行一次质量筛选去除基体离子，可以降低空间电荷效应，消除基体离子的质量歧视。
- 基体匹配。
- 气溶胶稀释。



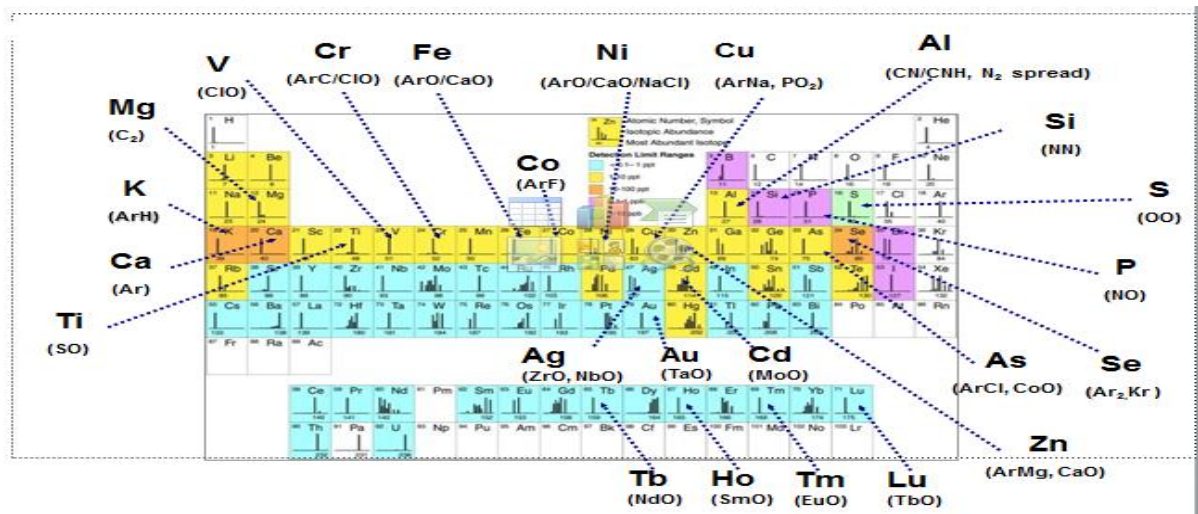
4、质谱干扰的消除

ICP-MS的质谱干扰可以分为：

同量异位素重叠干扰（多）：单原子单价离子

多原子离子干扰（最多）：多原子单价离子

双电荷离子干扰（较少）：单原子多价离子



质谱干扰的主要来源

1) 主体: Ar原子(>99.99%)

, SO, PO, CaO, Ca(OH), FeO, Fe(OH)

2) 未电离的样品基体: 这些成分会沉积在采样锥、截取锥、透镜、预四极杆、四极杆、检测器上(按先后顺序依次减少), 是实际样品分析时使仪器不稳定的主要因素, 也是仪器污染的主要因素;

3) 已电离的样品基体: ArO^+ , Ar^+ , ArH^+ , ArC^+ , ArCl^+ , ArAr^+ , (1、Ar基分子离子) CaO^+ , CaOH^+ , SO_n^+ , PO_n^+ , NOH^+ , ClO^+ …… (2、样品基体产生)

4) 的原子量相同, 是测定这些元素的主要干扰;

需要注意的是, 99.99%的样品及其基体停留在仪器内部或被排废消除; 因此, 加大进样量提高灵敏度的后果是同时加大仪器受污染速度。

来自基体的干扰

分子离子干扰-噪音的来源之一

主要的分子离子干扰来自于基体:

• 氦等离子体中的成分
(Ar, O, N, H)

• 基体成分
(Cl, S, C, Ca and Na)

• 常见的环境、食品、农业、
医学与其它样品的基体干扰

⁵¹ V	³⁵ Cl ¹⁶ O, ³⁷ Cl ¹⁴ N
⁵² Cr	³⁶ Ar ¹⁶ O, ⁴⁰ Ar ¹² C, ³⁵ Cl ¹⁶ OH, ³⁷ Cl ¹⁴ NH
⁵³ Cr	³⁶ Ar ¹⁶ OH, ⁴⁰ Ar ¹³ C, ³⁷ Cl ¹⁶ O, ³⁵ Cl ¹⁸ O, ⁴⁰ Ar ¹² CH
⁵⁴ Fe	⁴⁰ Ar ¹⁴ N, ⁴⁰ Ca ¹⁴ N
⁵⁵ Mn	³⁷ Cl ¹⁸ O, ²³ Na ³² S,
⁵⁶ Fe	⁴⁰ Ar ¹⁶ O, ⁴⁰ Ca ¹⁶ O
⁵⁷ Fe	⁴⁰ Ar ¹⁶ OH, ⁴⁰ Ca ¹⁶ OH
⁵⁸ Ni	⁴⁰ Ar ¹⁸ O, ⁴⁰ Ca ¹⁸ O, ²³ Na ³⁵ Cl
⁵⁹ Co	⁴⁰ Ar ¹⁸ OH, ⁴¹ K ¹⁸ O, ⁴³ Ca ¹⁶ O
⁶⁰ Ni	⁴⁴ Ca ¹⁶ O, ²³ Na ³⁷ Cl
⁶¹ Ni	⁴⁴ Ca ¹⁶ OH, ³⁸ Ar ²³ Na, ²³ Na ³⁷ ClH
⁶³ Cu	⁴⁰ Ar ²³ Na, ¹² C ¹⁶ O ³⁵ Cl, ¹² C ¹⁴ N ³⁷ Cl
⁶⁴ Zn	³² S ¹⁶ O ₂ , ³² S ₂ , ³⁶ Ar ¹² C ¹⁶ O, ³⁸ Ar ¹² C ¹⁴ N, ⁴⁸ Ca ¹⁶ O
⁶⁵ Cu	³² S ¹⁶ O ₂ H, ³² S ₂ H, ¹⁴ N ¹⁶ O ³⁵ Cl, ⁴⁰ Ar ²⁵ Mg, ⁴⁸ Ca ¹⁶ OH
⁶⁶ Zn	³⁴ S ¹⁶ O ₂ , ³² S ³⁴ S, ³³ S ₂ , ⁴⁸ Ca ¹⁸ O
⁶⁷ Zn	³² S ³⁴ SH, ³³ S ₂ H, ⁴⁸ Ca ¹⁸ OH, ¹⁴ N ¹⁶ O ³⁷ Cl, ¹⁶ O ₂ ³⁵ Cl
⁶⁸ Zn	³² S ¹⁸ O ₂ , ³⁴ S ₂
⁶⁹ Ga	³² S ¹⁸ O ₂ H, ³⁴ S ₂ H, ¹⁶ O ₂ ³⁷ Cl
⁷⁰ Zn	³⁴ S ¹⁸ O ₂ , ³⁵ Cl ₂
⁷¹ Ga	³⁴ S ¹⁸ O ₂ H
⁷² Ge	⁴⁰ Ar ³² S, ³⁵ Cl ³⁷ Cl, ⁴⁰ Ar ¹⁶ O ₂
⁷³ Ge	⁴⁰ Ar ³³ S, ³⁵ Cl ³⁷ ClH, ⁴⁰ Ar ¹⁶ O ₂ H
⁷⁴ Ge	⁴⁰ Ar ³⁴ S, ³⁷ Cl ₂
⁷⁵ As	⁴⁰ Ar ³⁴ SH, ⁴⁰ Ar ³⁵ Cl, ⁴⁰ Ca ³⁵ Cl
⁷⁷ Se	⁴⁰ Ar ³⁷ Cl, ⁴⁰ Ca ³⁷ Cl
⁷⁸ Se	⁴⁰ Ar ³⁸ Ar
⁸⁰ Se	⁴⁰ Ar ₂ , ⁴⁰ Ca ₂ , ⁴⁰ Ar ⁴⁰ Ca, ⁴⁰ Ar ³⁵ KH, ⁷⁹ BrH

常用试剂带入的干扰

➤	H₂O₂	---	Ar (Ca), ArH (K), ArO (Fe), O₃ (Ti)
➤	HF	---	ArF (Co)
➤	HCl	---	ClH₂ (K), ClO (V), ClOH (Cr), ClO₂ (Ga), ArCl (As, Se)
➤	H₂SO₄	---	SO, SOH (Ti, V, Cr), S₂, SO₂ (Zn)
➤	H₃PO₄	---	PO, POH (Ti), PO₂, PO₂H (Cu, Zn)
➤	Si matrix	---	SiO, SiF (Ti), SiO₂ (Cu, Zn)
➤	Photoresist	---	CC (Mg), CN (Al), ArC (Cr)

分析过程中常见的干扰

Analyte	mass	H2O	Cl	S	P	C	Na	Mg	Ca	K
Al						CN				
<i>As</i>	75		ArCl							
Ca	40	Ar								
Co	59								<u>CaO</u>	
Cr	52	ArC	<u>ClOH</u>	<u>SOH</u>		ArC				
Cu	63,65				<u>PO2</u>		ArNa	ArMg		
Fe	54, 56, 58	ArO, ArN							<u>CaO</u>	
Ga	69,71		ClO2							
Ge	72, 74			ArS						
K	39	ArH	<u>ClH2</u>							
Mg						CC				
Mn	55	ArOH, ArN								<u>KO</u>
Ni	58, 60								<u>CaO</u>	
<i>Se</i>	76, 77, 78, 80	ArAr	<u>ArCl</u>							
Ti	46, 47, 48, 49, 50	O3		SO, SN	PO, POH					
V	51		ClO	<u>SOH</u>						
<i>Zn</i>	64,66,68			<u>S2, SO2</u>	<u>PO2H</u>			ArMg	<u>CaO</u>	

红色斜体表示具有较高的离子能，无法在冷等离子体中分析。

棕色阴影的元素具有较高的氧化物结合能，无法在冷等离子体中分析。

绿色带下划线的干扰物无法在冷等离子体中除去

质谱干扰消除技术：化学分离与数学校正

（一）分离干扰元素

对于基体产生的质谱干扰，最常用的首选方法是除去基体。通常采取共沉淀过滤分离基体，色谱自动分离富集法等。比如，对于含有高氯化钠和氯化镁的海水中痕量元素分析，熔融法分析地质样品中稀土等痕量元素，以及高纯稀土化合物中的杂质分析，就经常采用分离富集的方法。分离富集法的最大缺点是容易带来试剂空白以及污染问题。

（二）数学校正法

数学校正法在实际分析中应用比较多。一般情况下，可以得到比较满意的结果。但如果遇到干扰元素浓度特别高，而分析元素很低的情况时，数学校正法误差较大，甚至无法应用。比如，测定 Cd 常用的同位素¹¹¹Cd 受到⁹⁴ZrOH⁺ 的干扰，虽然干扰系数很低，但由于地质样品中 Cd 含量一般很低（0.0x ~ 0. x μg/g），而 Zr 的含量通常很高（数百个 μg/g），所以如不加以校正，则造成 Cd 的测定结果严重偏高。选择¹¹⁴Cd 测定时，虽然也受到¹¹⁴Sn（0.65%）的同质异位素重叠干扰，但由于样品中 Sn 的含量一般较低（几个 μg/g），通过干扰公式扣除干扰后，可得到较为可靠的结果。而且¹¹⁴Cd 的丰度（28.7%）大于¹¹¹Cd（12.8%），有利于低含量 Cd 的测定。实际测定中最好同时测定¹¹¹Cd 和¹¹⁴Cd，分别扣除 Zr 和 Sn 的干扰后进行对比。¹¹⁵In 受到¹¹⁵Sn⁺（0.36%）的干扰也比较突出，必须进行干扰校正。

质谱干扰消除技术：碰撞与反应

◆ 等离子体,	Ar
◆ 水,	O、H
◆ 样品消解的试剂,	N、Cl、F、S、P
◆ 样品基体,	C、Na、Ca、Co、Nd、Sm等

干扰校正方法

干扰消除能力

校正公式

10^0

He气碰撞动能甄别 (KED)

10^2

H₂气碰撞动能甄别 (KED)

10^3

CH₄气还原反应质量甄别 (DBT)

10^6

NH₃气还原反应质量甄别 (DBT)

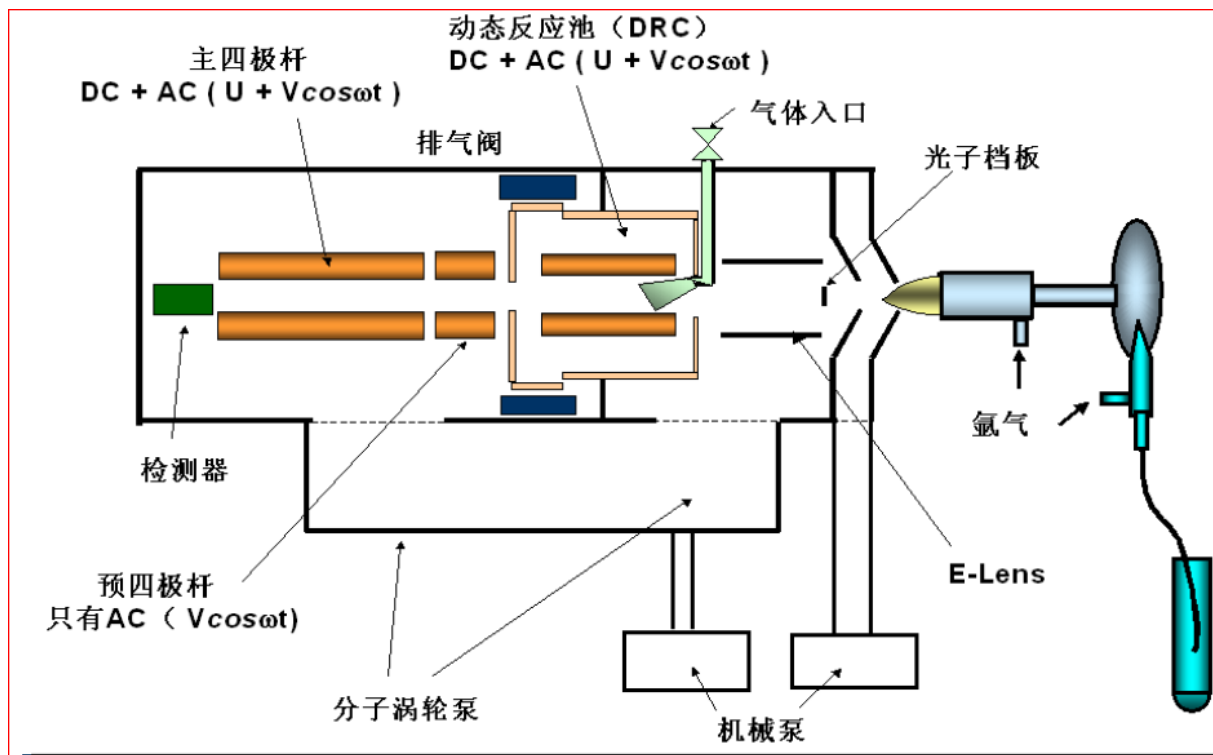
10^9

O₂气氧化反应质量甄别 (DBT)

10^9

所以，三种模式全部具备，才能完美解决我们将要遇到的问题。

质谱干扰消除技术：碰撞与反应



质谱干扰消除技术：碰撞与反应

The screenshot displays the SynGEM™ for ICP-MS Instrument Control Session software. The interface is divided into several sections:

- Top Bar:** Applications menu with icons for Control Diagnostics, SmartTune, Conditions Logbook, Method Sample Dataset, Reporter Realtime Interactive Calibration, Scheduler, and Review.
- Devices Panel:** Shows ICP-MS status with icons for ICP-MS, Pump, Autosampler, and PC3. Status indicators for Plasma (On), Vacuum (Ready), and Cone Access (Closed) are shown with green progress bars.
- System View:** A schematic diagram of the instrument showing the vacuum chamber and various components. The vacuum pressure is indicated as 3.29e-5 Torr. Below the schematic are icons for Ventilation, Power, Vacuum Pumps, Gases, RF Generator, and Cooling.
- System Status:** A table with columns for Item and Date/Time, currently empty.
- Diagnostics / Maintenance / Torch Position:** A table showing system parameters.

System	Subsystem	Component	Status	Override	Value
Analyzer	Detector	Analog Current IB	118 µAmps		
Analyzer	Detector	Analog Voltage IB	-1880 Volts		
Analyzer	Detector	Analog Voltage IB	-1882.56 Volts		
Analyzer	Detector	Discriminator Threshold	12 mVolts		
Analyzer	Detector	Gate Voltage IB	249.155 Volts		
Analyzer	Detector	Pulse Current IB	89 µAmps		
Analyzer	Detector	Pulse Voltage IB	1050 Volts		
Analyzer	Detector	Pulse Voltage IB	1051.51 Volts		

三种工作模式

干扰消除效果

气体	分子量	电离能 (eV)
NH ₃	17	10.16
O ₂	32	12.07
CH ₄	16	12.51
H ₂	2	15.43
Ar	40	15.76
He	4	24.59

BEST

Reaction Mode

使用条件:

可以消除 10^7 以上的干扰
与干扰的体积无关
必须用反应活性强的气体

反应气体:

还原性气体: CH₄、NH₃

氧化性气体: O₂、N₂O

甲烷氨气氦气反应四级杆

动态质量带宽调谐DBT干扰消除模式

BETTER

Collision Mode

使用条件:

干扰/分析物强度比<100

干扰/分析物体积比>1.5

碰撞气体:

氦气(He)、氢气(H₂)

氦气氢气碰撞

动能甄别KED干扰消除模式

GOOD

Standard Mode

使用条件:

干扰/分析物强度比<1

校正公式干扰消除模式

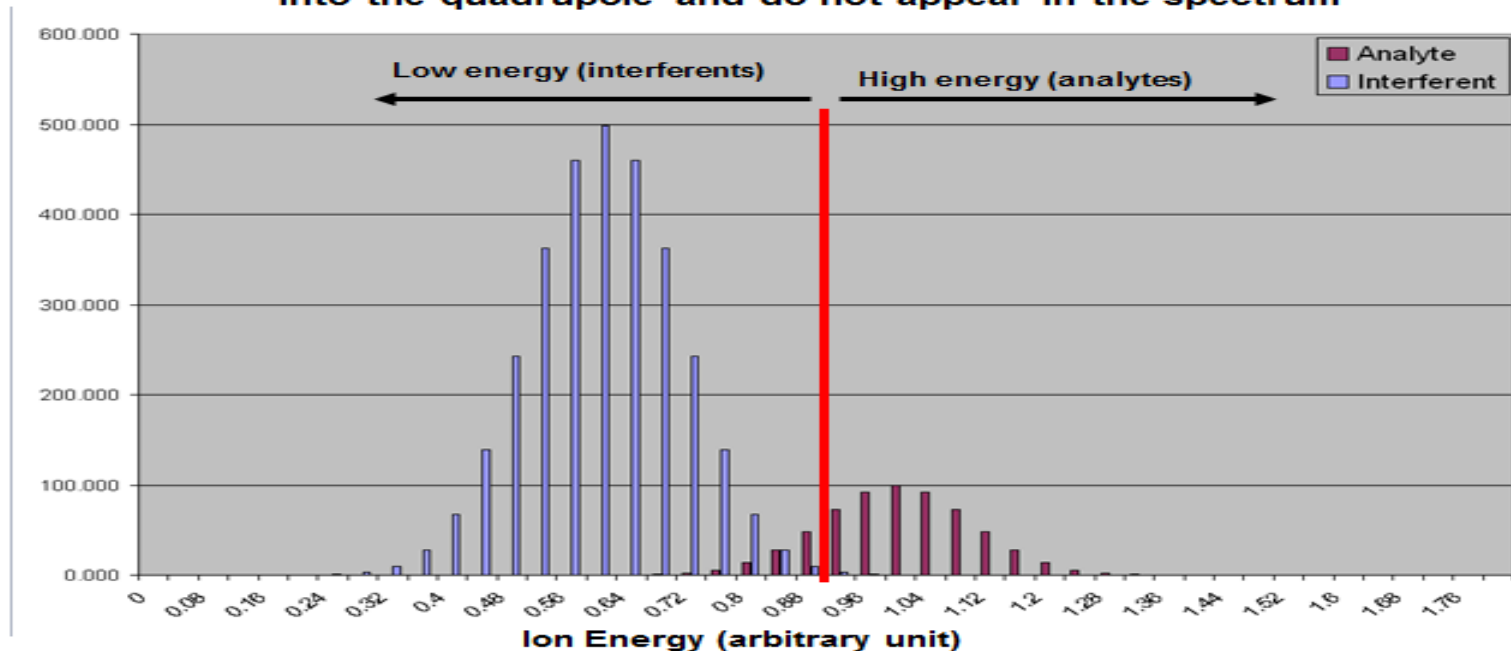
只有最适合的干扰消除方法，没有万能的消除所有干扰的方法

4.1 标准模式校正方程

Analyte	Symbol	Isotopes Monitored	Correction Equations
Aluminum	Al	27	
Antimony	Sb	121,123	$Sb\ 123 = Sb\ 123 - 0.127189 * Te\ 125$
Arsenic	As	75	$As\ 75 = As\ 75 - 3.127 * [ArCl\ 77 - (0.815 * Se\ 82)]$
Barium	Ba	135,137	
Beryllium	Be	9	
Cadmium	Cd	106,108,111,114	$Cd\ 111 = Cd\ 111 - 1.073 * [MoO\ 108 - (0.712 * Pd\ 106)]$ $Cd\ 114 = Cd\ 114 - 0.026826 * Sn\ 118$
Molybdenum	Mo	95,97,98	$Mo\ 98 = Mo\ 98 - 0.110588 * Ru\ 101$
Selenium	Se	77,82	$Se\ 82 = Se\ 82 - 1.008696 * Kr\ 83$
Thorium	Th	232	
Uranium	U	238	
Vanadium	V	51	$V\ 51 = V\ 51 - 3.127 * [ClO\ 53 - (0.113 * Cr\ 52)]$
Calcium	Ca	44	
Magnesium	Mg	24	
Sodium	Na	23	
Potassium	K	39	
Iron	Fe	54	$Fe\ 54 = Fe\ 54 - 0.028226 * Cr\ 52$

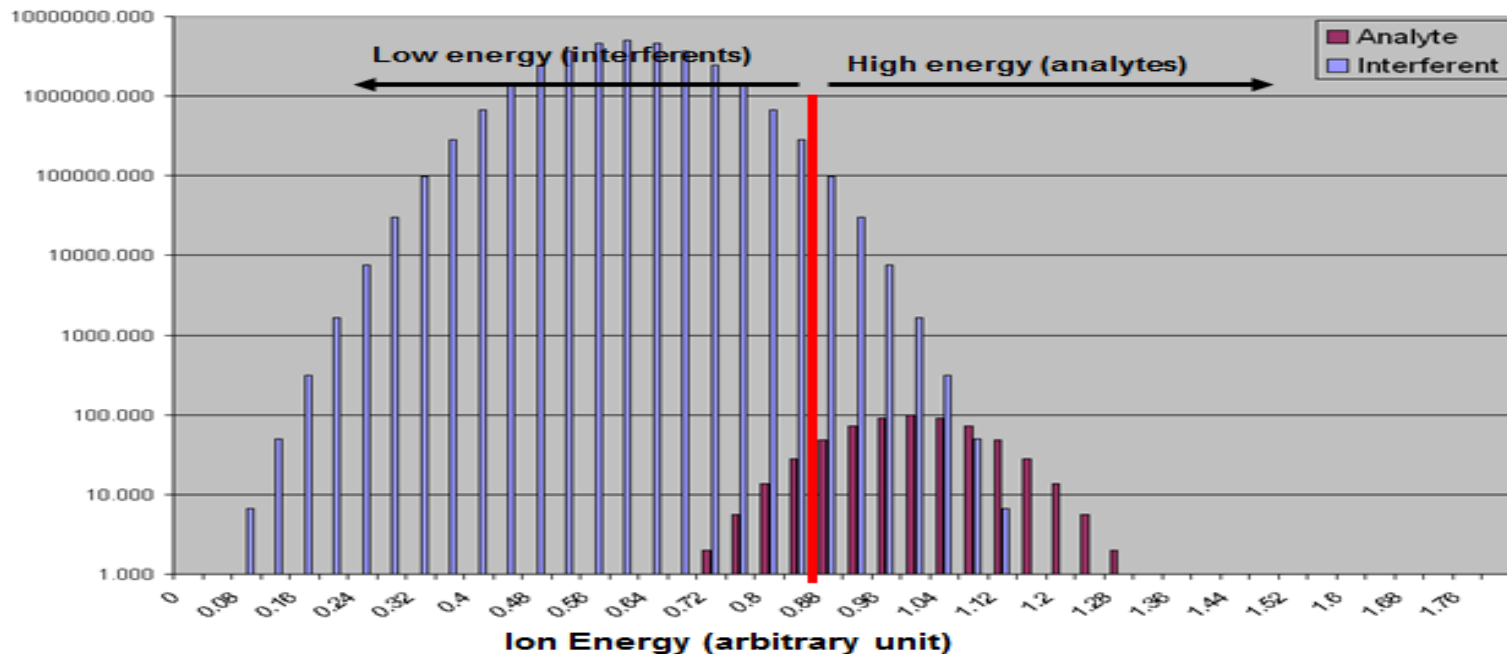
4.2 KED模式

After KED interferents have a lower energy than analytes and as such they do not pass into the quadrupole and do not appear in the spectrum



KED的局限性

For very high interferent to analyte ratios ($>10^4$), KED will fail to give any significant analytical advantage so for Ca, Fe, Se you need to use a reactive gas such as H₂ or NH₃



4.3 DRC模式

• DRC的应用

- 还原性反应:
 - $\text{CH}_4 + \text{ArCl}^+ \rightarrow \text{CH}_4^+ + \text{Ar} + \text{Cl}$
 - 包括 CH_4 , NH_3 , H_2 等
- 氧化性反应:
 - $\text{As}^+ + \text{O}_2 \rightarrow \text{AsO}^+ + \text{O}$
 - 包括 O_2 , N_2O 等

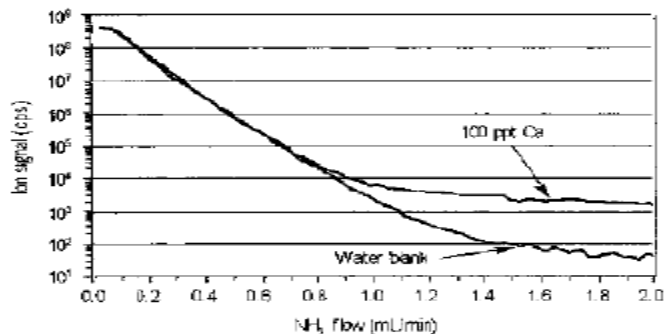


FIGURE 10.6 A reduction of 8 orders of magnitude in the $^{40}\text{Ar}^+$ background signal is achievable with the dynamic reaction cell—resulting in <0.5 ppt detection limit for $^{40}\text{Ca}^+$.

DRC模式强大能力 (Na、Mg、Al、K、Ca、V、Cr、Fe)

Table 4. Detection Limits, Background Equivalent Concentrations, and 10 ng/L Spike Recoveries in 20% HCl

Analyte	Mass	Detection Limits (ng/L)	BECs (ng/L)	10 ng/L Recoveries (%)
Li	7	0.01	0.01	99
Be	9	0.05	0.01	91
B	11	0.6	2.3	90
Na	23	0.09	0.4	99
Mg	24	0.03	0.08	99
Al	27	0.1	0.2	100
K	39	0.6	1.3	103
Ca	40	0.2	0.2	103
Ti	48	0.5	2.7	98
V	51	0.1	0.04	96
Cr	52	0.5	0.50	100
Mn	55	0.07	0.07	95
Fe	56	0.4	1.2	103
Co	59	0.1	0.02	94
Ni	60	0.2	0.3	100
Cu	63	1	2	101
Zn	64	0.7	3.3	102
Ga	71	0.09	0.06	97
Ge	74	2	0.50	92

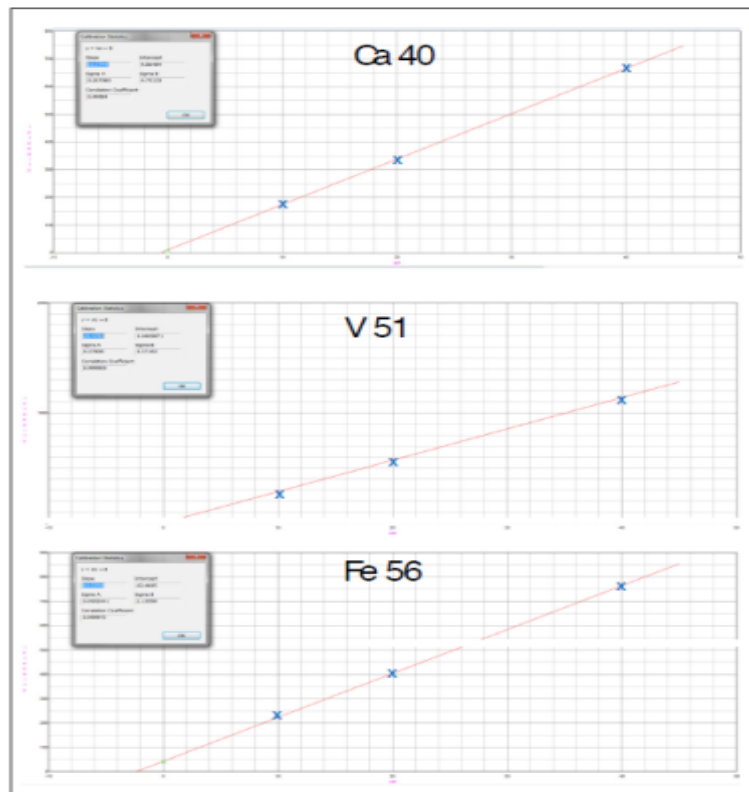


Figure 4. Calibration plots for 10, 20, 40 ng/L Ca, V, and Fe in 20% HCl.

DRC应用实例一：食品中元素分析

实例一 反应池条件（其中NH₃可以用CH₄代替，以下同）

DRC Conditions for Plant Materials

Table 1. Reaction Cell Conditions for the Analysis of Ling Zhi

Analyte	m/z	Reaction Gas	Gas Flow	RPq
V	51	---	---	0.25
Cd	114	---	---	0.25
Hg	202	---	---	0.25
Pb	208	---	---	0.25
As	75	NH ₃	0.25	0.25
Se	78	NH ₃	0.25	0.25

DRC应用实例一：食品中元素分析

分析测试NIST的桃树叶子里金属元素含量：

Analyte	Experimental ($\mu\text{g/g}$)	Certified ($\mu\text{g/g}$)
V	0.40	0.37 ± 0.03
Cd	0.025	0.026 ± 0.003
Hg	0.030	0.031 ± 0.007
Pb	0.80	0.87 ± 0.03
<i>As</i>	<i>0.06</i>	<i>0.06 ± 0.018</i>
As	0.13	0.06 ± 0.018
<i>Se</i>	<i>0.10</i>	<i>0.12 ± 0.009</i>
Se	0.62	0.12 ± 0.009

Italics = DRC Mode Normal = standard mode

高Ca基体测Ni的问题：

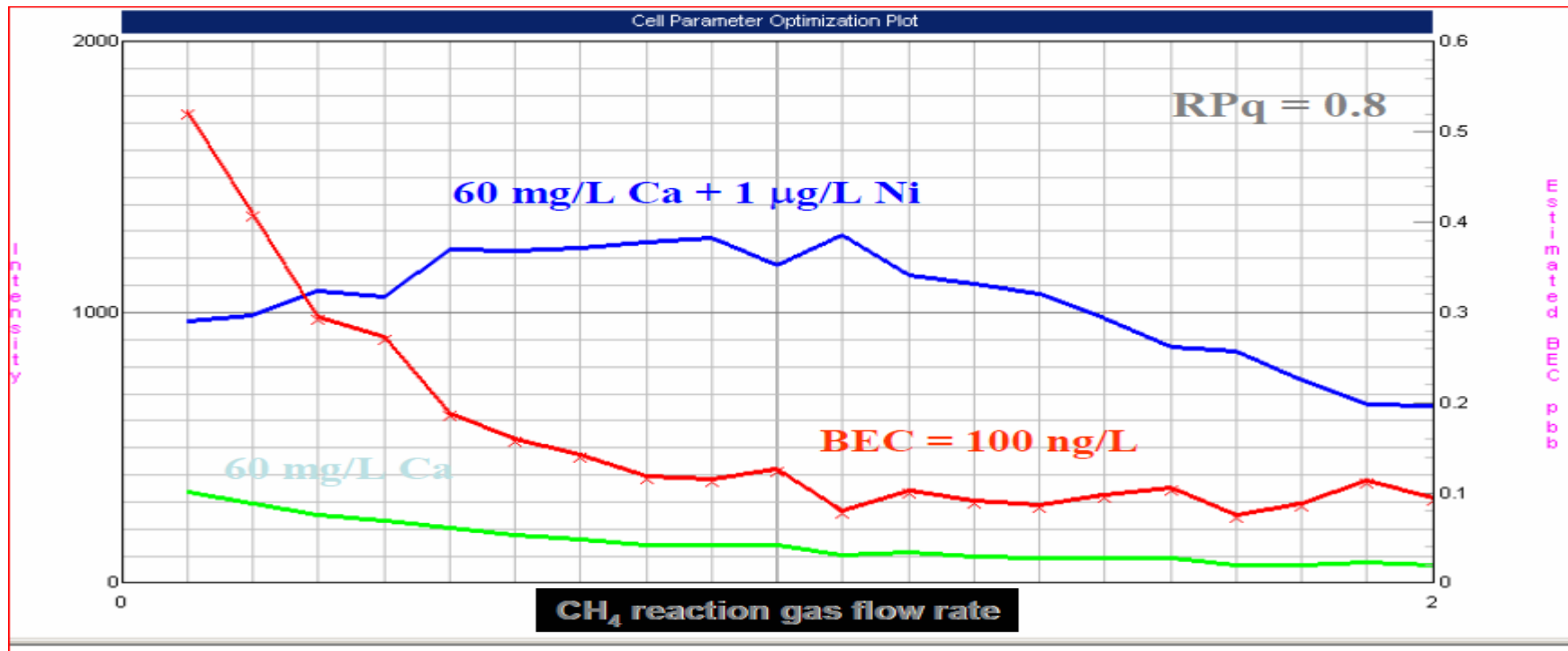
➤ The Problem

- **CaO⁺ formation on ⁶⁰Ni⁺**
- **Even though ⁵⁸Ni⁺ is free of CaO⁺, a minor isotope of Fe is present**
 - **⁵⁸Fe = 0.28%**
 - **Even though this is low, Fe is usually present at much higher amounts than Ni**

➤ The Solution

- **Eliminate the CaO⁺ interference using CH₄ as a reaction gas**

DRC应用实例二：高Ca基体测试Ni



DRC应用实例二：高Ca基体测试Ni

- **RF Power** **1500W**
- **Nebulizer** **Quartz Concentric**
- **Spray Chamber** **Quartz Cyclonic**
- **Sample Uptake** **0.5 mL/min**
- **CH₄ Flow** **1.5 mL/min**
- **RPq** **0.80**

Analysis of ^{60}Ni in a Calcium Matrix (units in $\mu\text{g/L}$)

Trial	50 mg/L Ca	50 mg/L Ca + 100 ng/L Ni	Recovery
1	0.101	0.219	118%
2	0.091	0.203	112%
3	0.083	0.192	109%

Mo基体测Cd的问题:

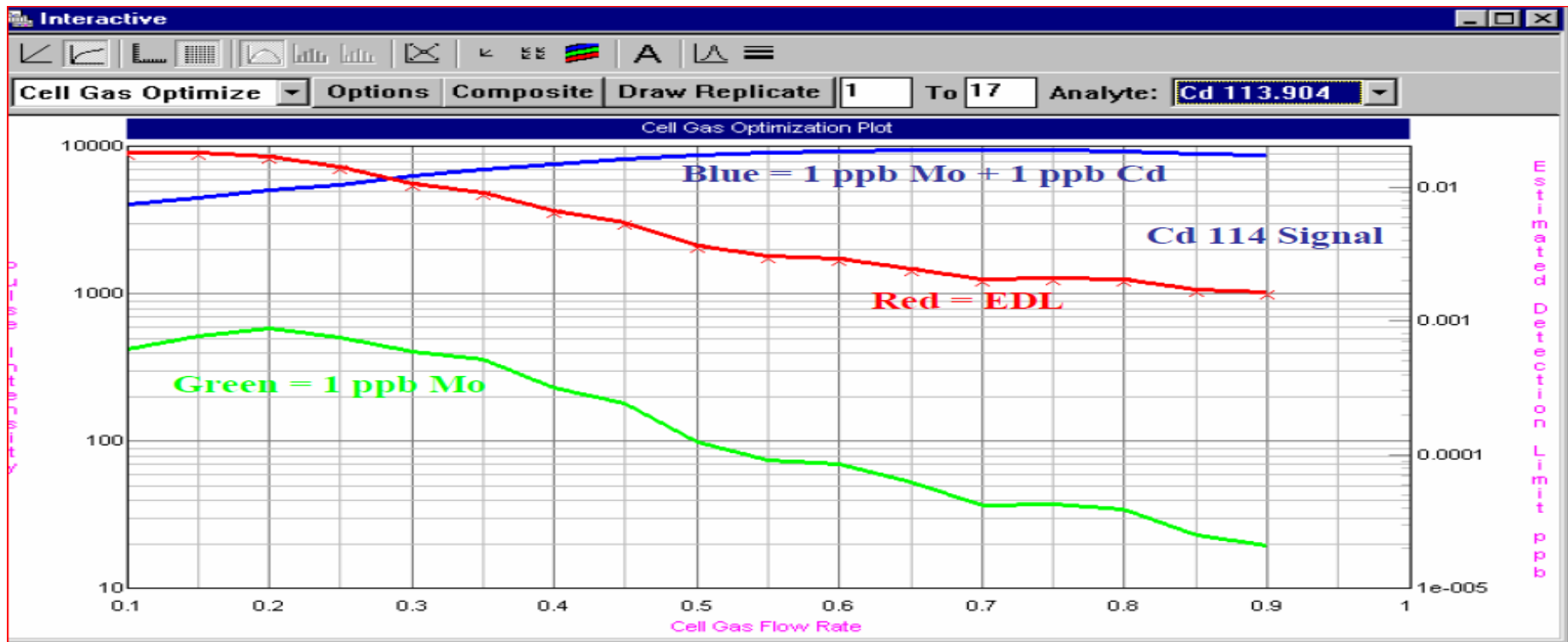
➤ The Problem

- MoO^+ on $^{114}\text{Cd}^+$

➤ The Solution

- Remove the interference using O_2 as reaction gas
 - MoO^+ reacts with O_2 , Cd does not

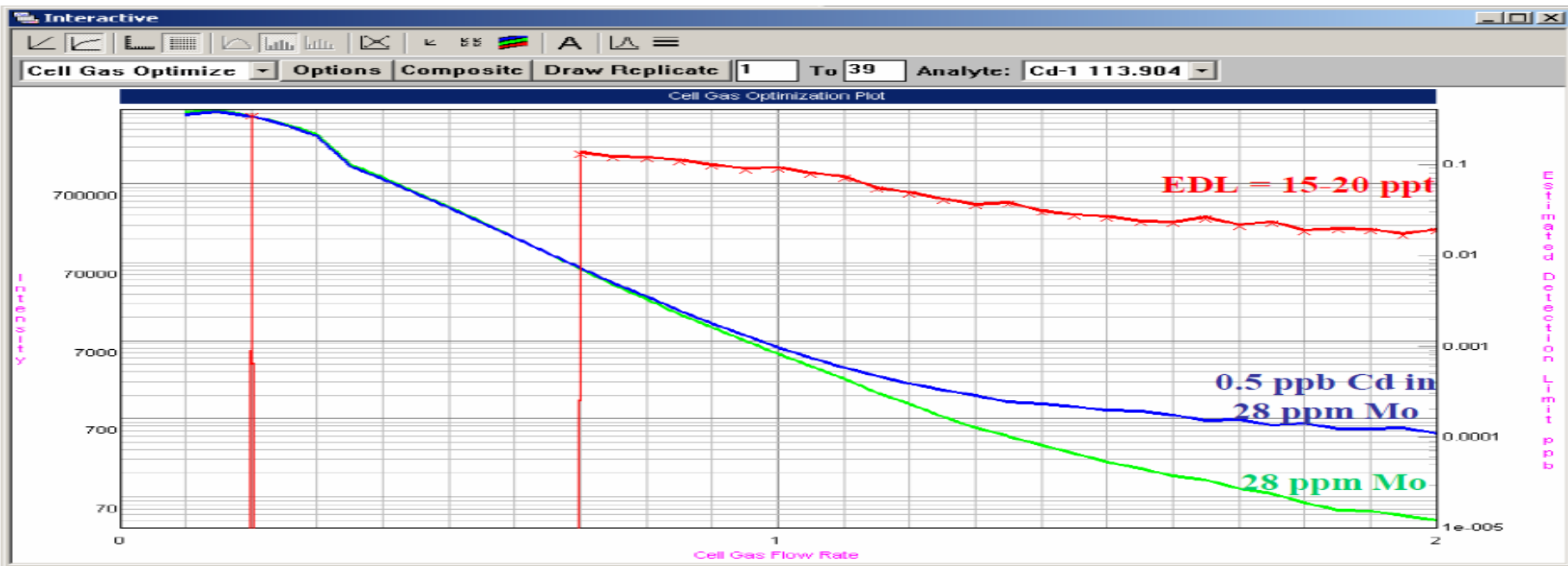
DRC应用实例三：高Mo基体测试Cd



DRC应用实例三：高Mo基体测试Cd

Matrix = 28 ppm Mo

Spike = 0.5 ppb Cd

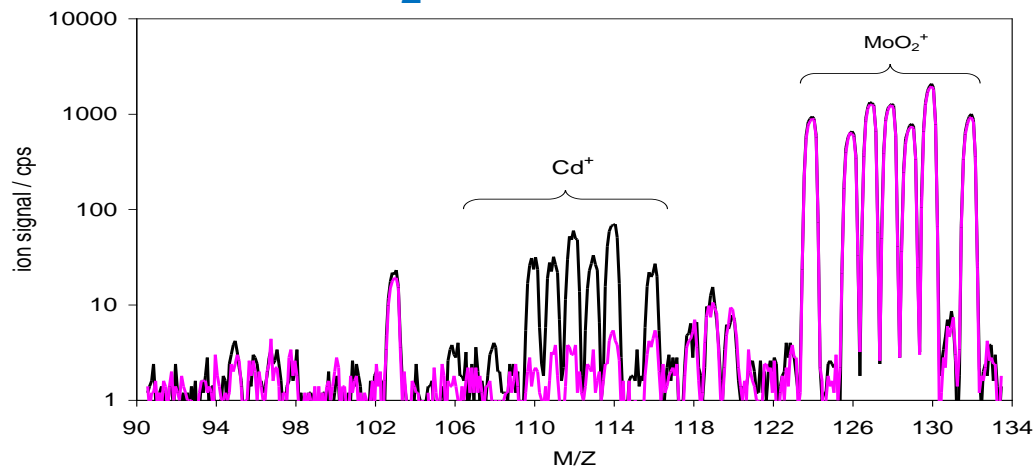


DRC应用实例三：高Mo基体测试Cd

Cd 105.9 Pd, SrO, ZrO, YO
 Cd 107.9 Pd, ZrO, MoO
 Cd 109.9 Pd, ZrO, MoO
 Cd 110.9 MoO
 Cd 111.9 Sn, ZrO, MoO
 Cd 112.9 In, MoO

样品编号	标准号	标样名称	Cd 111	Cd平均值	Cd标准值
GB-08-a	GBW07408	陕西洛川黄土	0.141	0.139	0.13±0.02
GB-08-b			0.138		
GB-10-a	GBW07424	松嫩平原	0.104	0.112	0.105±0.013
GB-10-b			0.119		
GB-13-a	GBW07427	华北平原	0.133	0.132	0.13±0.01
GB-13-b			0.131		
GB-14-a	GBW07428	四川盆地	0.215	0.216	0.20±0.02
GB-14-b			0.218		
GB-15-a	GBW07429	长江平原区	0.224	0.223	0.21±0.02
GB-15-b			0.222		
GB-16-a	GBW07430	珠江三角洲	0.268	0.265	0.25±0.02
GB-16-b			0.262		

利用O₂反应气转移干扰物



DRC应用实例三：高Mo基体测试Cd

Chemosphere 81 (2010) 1463–1468



Contents lists available at ScienceDirect

Chemosphere

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Direct determination of trace cadmium in environmental samples by dynamic reaction cell inductively coupled plasma mass spectrometry

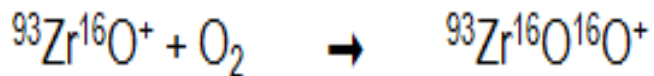
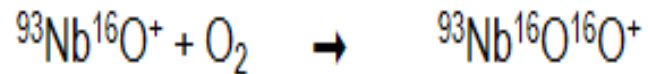
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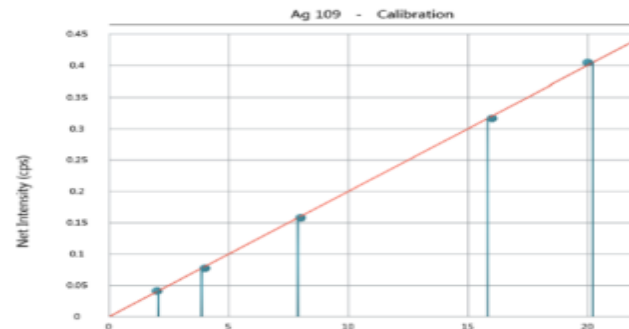
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^c Geological Survey Jiangsu Province, Nanjing 210018, PR China

土壤样品中测银 (Ag) O2模式



元素 样品名	Zr (ppm)	Nb (ppm)	Ag标准值 (ppm)	Ag检测值 (ppm)
Gss-8	229	15	0.060±0.009	0.055
Gss-13	257	14	0.067±0.006	0.063
Gss-15	272	19	0.15±0.02	0.158



Statistics

Eqn.: $y = 0.020x + 0.000$
 Cor.Coeff: 0.999925
 BEC: 0.033525 ppb
 DL: 0.001156 ppb

Concentration (ppb)

Calibration Table

	Net Intensity Ag 109 (cps)	Apparent Conc. Ag 109 (ppb)
Blank	451.174	
Cal. Std.1	0.041	2.050
Cal. Std.2	0.077	3.861
Cal. Std.3	0.158	7.890

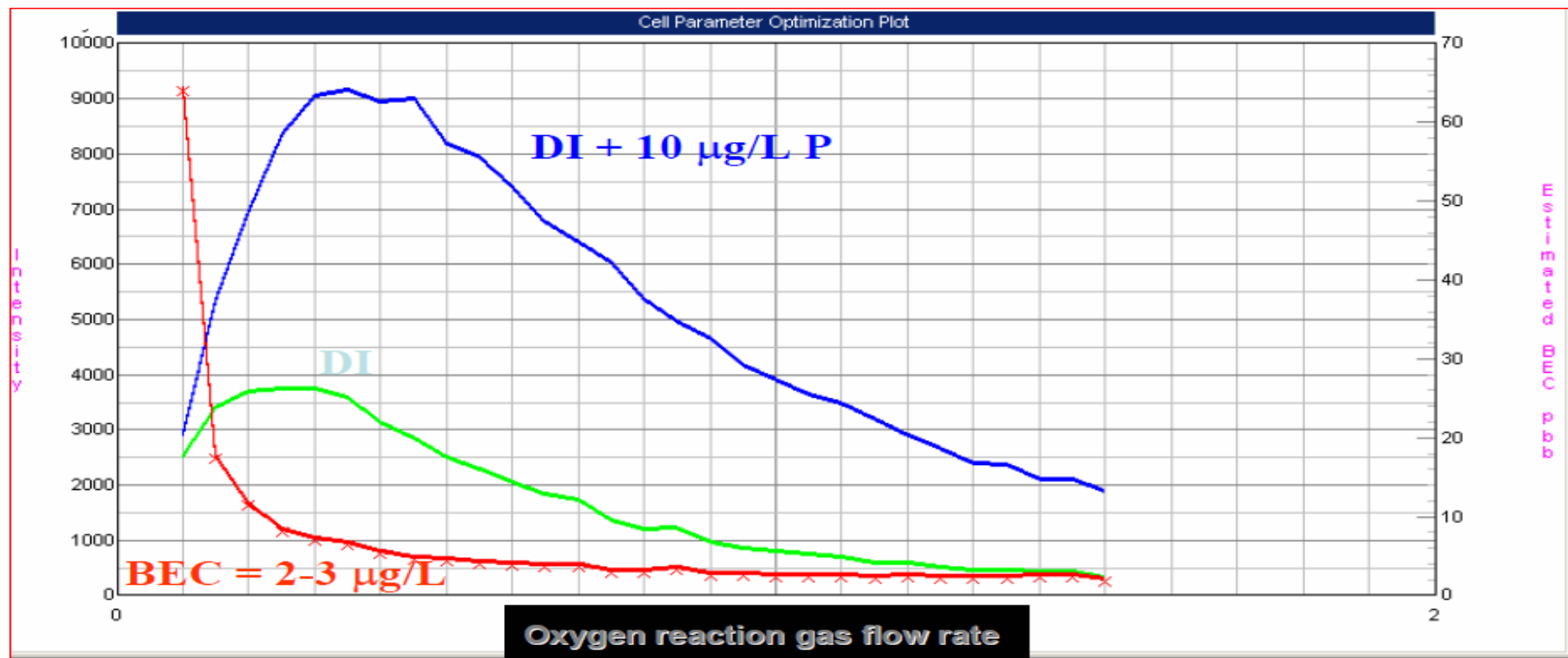
常规测S、P遇到问题:

- **P and S are difficult to determine by traditional quadrupole ICP-MS**
 - **Significant Interferences on the Major Isotopes**
 - **^{31}P** : $^{15}\text{N}^{16}\text{O}^+$, $^{14}\text{N}^{16}\text{O}^{1}\text{H}^+$
 - **^{32}S** : $^{16}\text{O}_2^+$
 - **High Ionization Potentials**
 - **P = 10.5 eV**
 - **S = 10.4 eV**
 - **Cold plasma cannot be used**

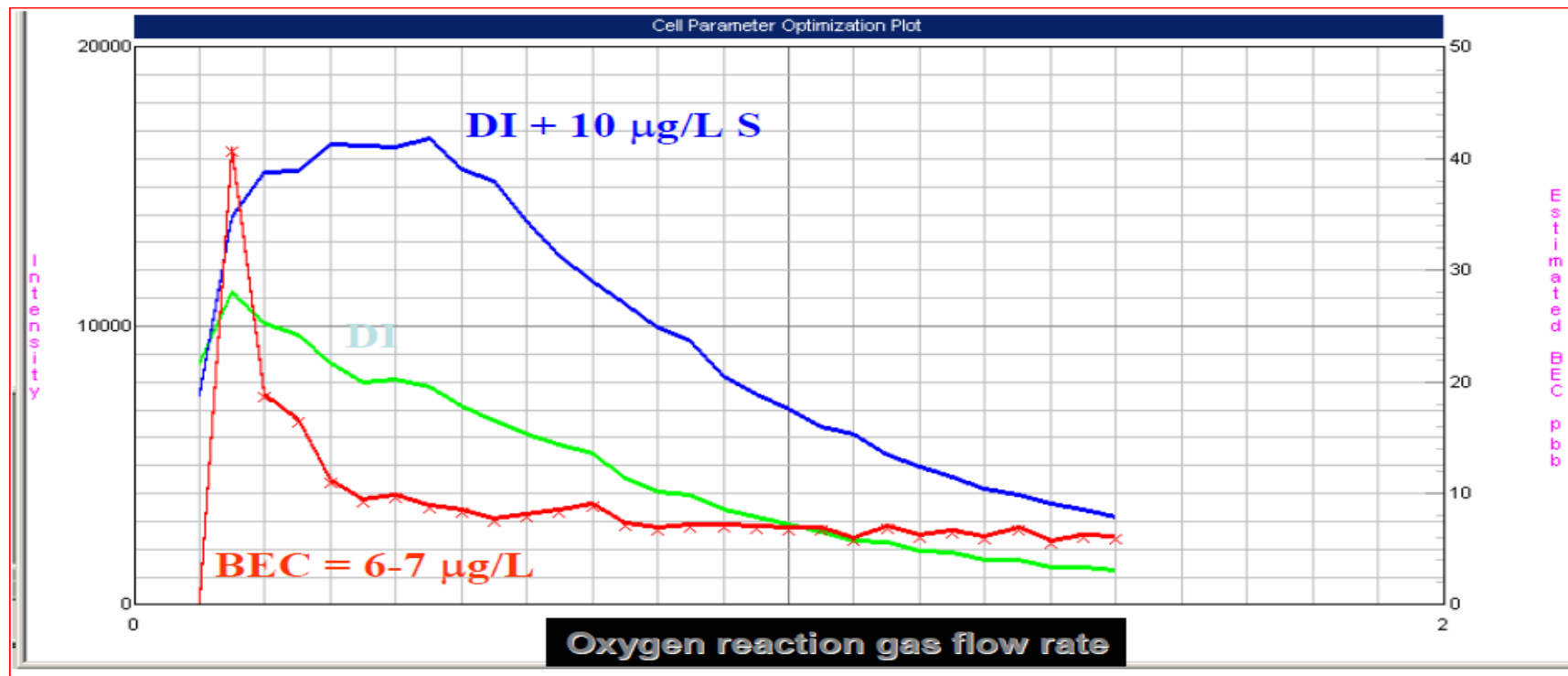
DRC应用实例四：S、P的测定

- **Can use controlled chemical reactions to move phosphorus and sulfur to new analytical masses away from the interferences**
- **React the analytes with oxygen and measure the products**
 - **PO⁺ (m/z 47)**
 - **SO⁺ (m/z 48)**
- **Reactions**
 - **P⁺ + O₂ → PO⁺ + O**
 - **S⁺ + O₂ → SO⁺ + O**

DRC应用实例四：S、P的测定



DRC应用实例四：S、P的测定



DRC应用实例四：S、P的测定



Spectrochimica Acta Part B 59 (2004) 1389–1394

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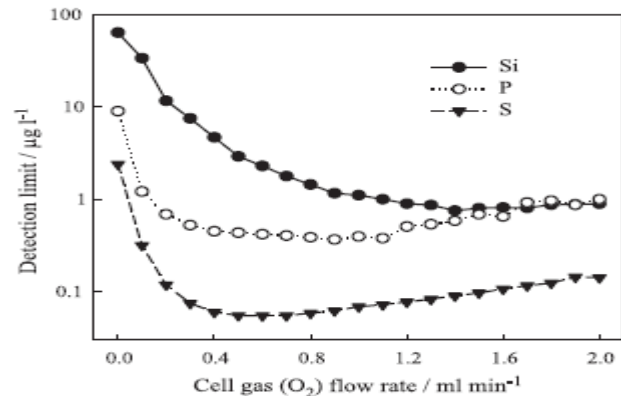
Determination of B, Si, P and S in steels by inductively coupled plasma quadrupole mass spectrometry with dynamic reaction cell

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Received 12 April 2004; accepted 1 June 2004

Available online 17 July 2004



综合应用：石油产品中痕量元素分析

Table 1. NexION 300D ICP-MS Instrumental Conditions.

Sample Uptake Rate	200 $\mu\text{L}/\text{min}$
Peristaltic Pump Tubing	Viton [®]
Nebulizer	Glass concentric
Spray Chamber	PC ³ LT with baffled glass cyclonic
Spray Chamber Temperature	-20 °C
O ₂ Flow	25 mL/min
Injector	0.85 mm quartz
RF Power	1600 W
Dwell Time	50 ms
Sweeps/Reading	20
Replicates	2
Modes	DRC (NH ₃) and Standard
Sample Run Time	1.7 min/sample

Table 2. Reaction Cell Conditions.

Element	Cell Gas	Gas Flow (mL/min)	RPq
Al 27	NH ₃	0.6	0.60
Cr 52	NH ₃	0.6	0.65
Fe 56	NH ₃	0.6	0.45

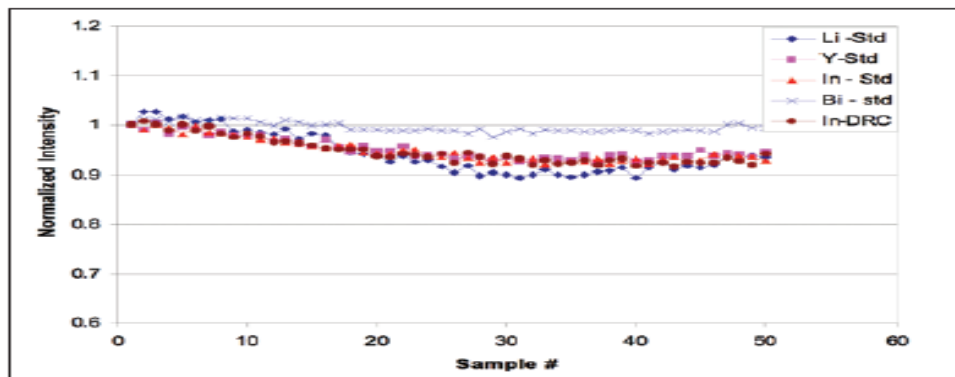


Figure 2. 2.5-hour stability of petroleum ether.

综合应用：石油产品中痕量元素分析

Table 3. Detection Limits in Naphtha Solvents (ng/g).

Element	Mass	Stoddard Solvent	Ligroin	Petroleum Ether
V	51	0.200	0.015	0.012
Mn	55	0.038	0.031	0.017
Ni	58	0.062	0.017	0.015
Cu	63	0.080	0.015	0.017
Se	82	0.150	0.051	0.043
Cd	114	0.036	0.031	0.017
Sn	120	0.084	0.025	0.012
Ba	138	0.067	0.022	0.018
Hg	202	0.170	0.022	0.015
Pb	208	0.044	0.017	0.017
Al*	27	0.017	0.048	0.025
Cr*	52	0.030	0.040	0.012
Fe*	56	0.025	0.024	0.017

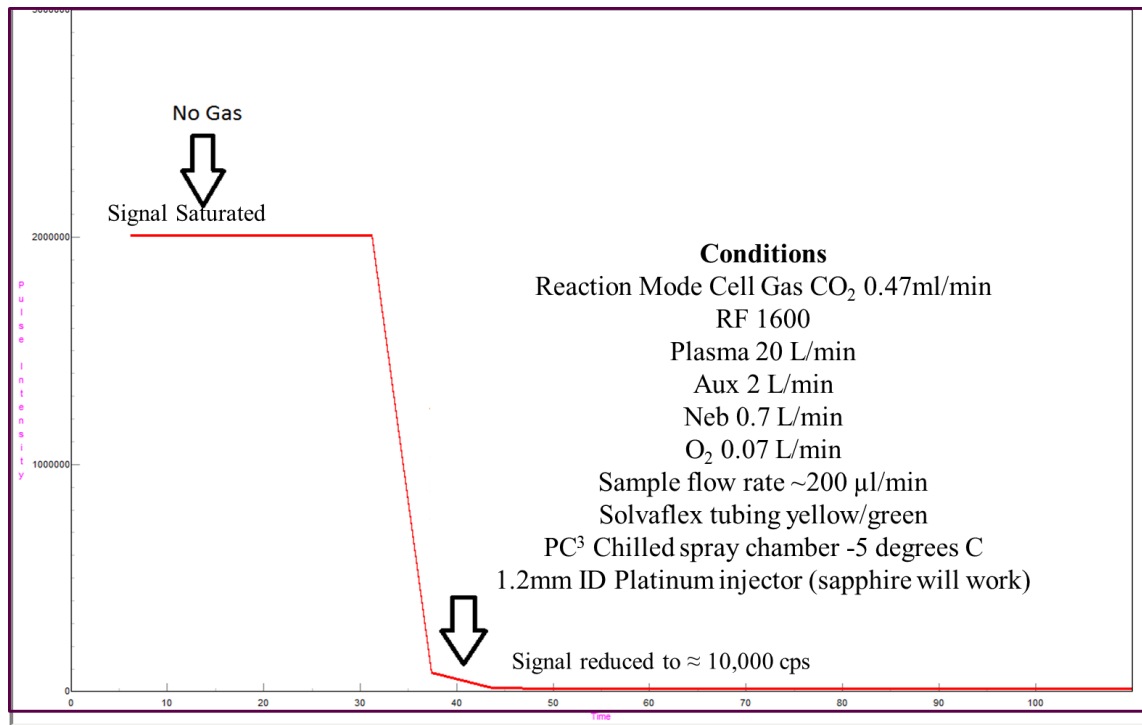
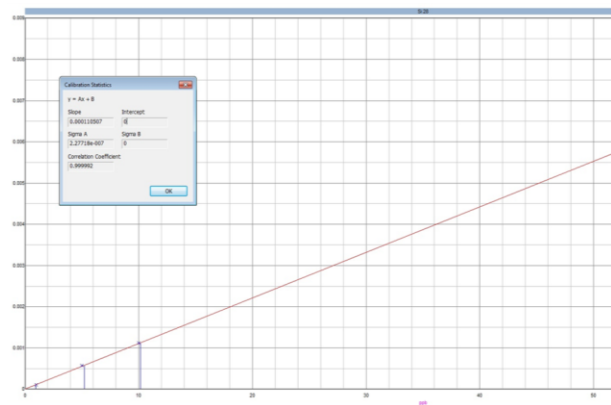
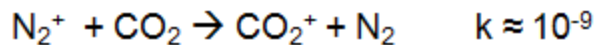
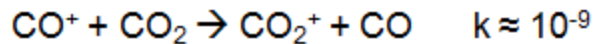
* = DRC mode

Table 4. Spike Recoveries in Petroleum Ether.

Element	Mass	Solvent (µg/L)	Spike (µg/L)	%Recovery
V	51	0.00	6.45	129
Mn	55	0.22	5.15	98.6
Ni	58	0.11	5.24	103
Cu	63	0.05	4.76	94.2
Se	82	0.00	5.41	108
Cd	114	0.10	5.35	105
Sn	120	0.01	5.63	112
Ba	138	0.01	4.74	94.6
Hg	202	0.02	5.28	105
Pb	208	0.03	4.81	95.6
Al*	27	0.21	6.15	123
Cr*	52	0.00	6.15	123
Fe*	56	0.05	6.54	130

* = DRC mode

综合应用：石油产品中痕量Si分析



综合应用：石油产品中痕量Si分析

- Run 10 ppb second source standard 7 times

Analysis	Result (ppb)
1	9.7
2	9.8
3	9.3
4	9.6
5	9.7
6	9.9
7	9.3

Statistics and MDL

Average = 9.6

Standard Deviation = 0.22

MDL = $0.22 * 3.707 = 0.80$ ppb

- Run 5 ppb second source standard

Analysis	Result (ppb)
1	4.5
2	5.4

- MDL < 1 ppb
- Ability to calibrate down to 1 ppb
- Ability to quantitatively measure low levels

- Dilute naphtha 20x in kerosene

- 20x dilution negates matrix differences among the samples
 - Allows use of external calibrations

Sample	Si (ppb)	Si Spike (ppb)	Result (ppb)	Recovery
Naphtha 1	4.70	10	14.2	97%
Naphtha 2	21.8	10	33.7	106%
Unifiner Charge	15.0	10	24.9	100%

- Accurate spike recoveries in three different sample types

综合应用：尿液中多元素分析

Table 1. Instrument conditions used for the analysis of UTAK® freeze-dried urine.

Parameter	Setting
Sample Introduction System	Baffled Cyclonic Spray Chamber with a Meinhard Low Flow nebulizer
Sample Uptake Rate	0.3 mL/min
Sampler and Skimmer Cones	Nickel
Forward Power	1500 watts
Nebulizer Gas Flow	0.8 L/min
Sweeps	20
Points per Peak	1
Replicates	3
Dwell Time	100 ms
Modes	Standard and DRC
Time to Change Modes	10 s
Internal Standards	Indium (¹¹⁵ In) for all elements except Yttrium (⁸⁹ Y) for ⁶⁶ Zn

Table 2. Reaction gases and gas flows used with the cell RPq values for the determination of As, Cr, Co, Cu, Mn, V in UTAK® normal and high level freeze-dried urine SRMs, using DRC mode.

Analyte (Mass)	Reaction Gas	Gas Flow (mL/min)	DRC Setting (RPq Value)
Arsenic Oxide (91)	Oxygen	0.7	0.65
Chromium (52)	Ammonia	0.7	0.75
Cobalt (59)	Ammonia	0.7	0.75
Copper (65)	Ammonia	0.7	0.75
Manganese (55)	Ammonia	0.7	0.75
Vanadium (51)	Ammonia	0.7	0.75

综合应用：尿液中多元素分析

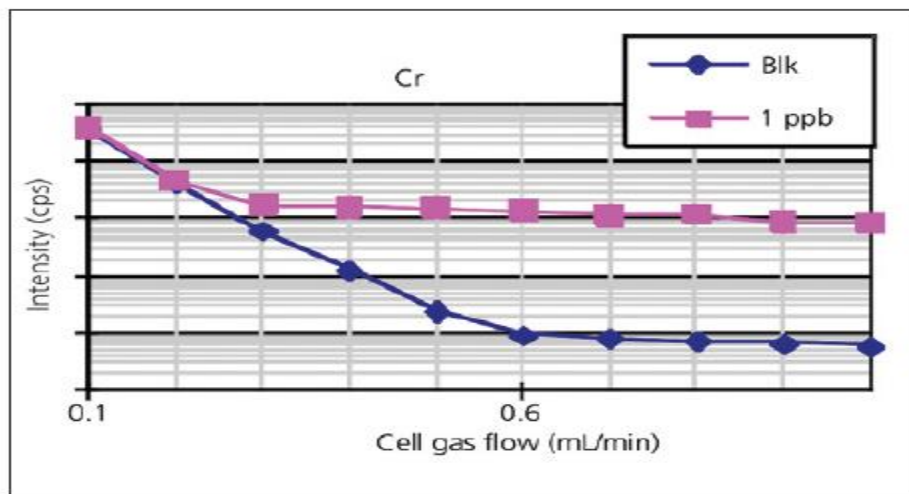
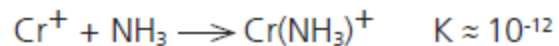
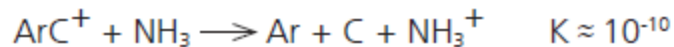
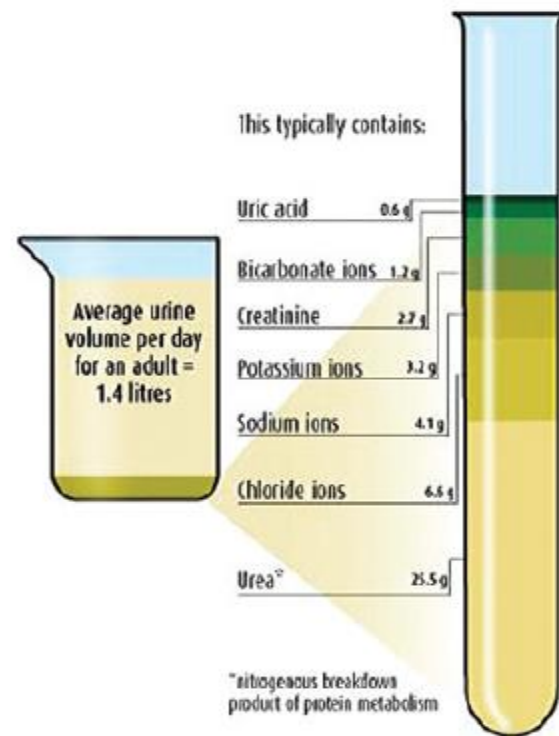


Figure 2. NH_3 Cell gas optimization of ^{52}Cr in the presence of $^{40}\text{Ar}^{12}\text{C}^+$ using reaction chemistry.



综合应用：尿液中多元素分析

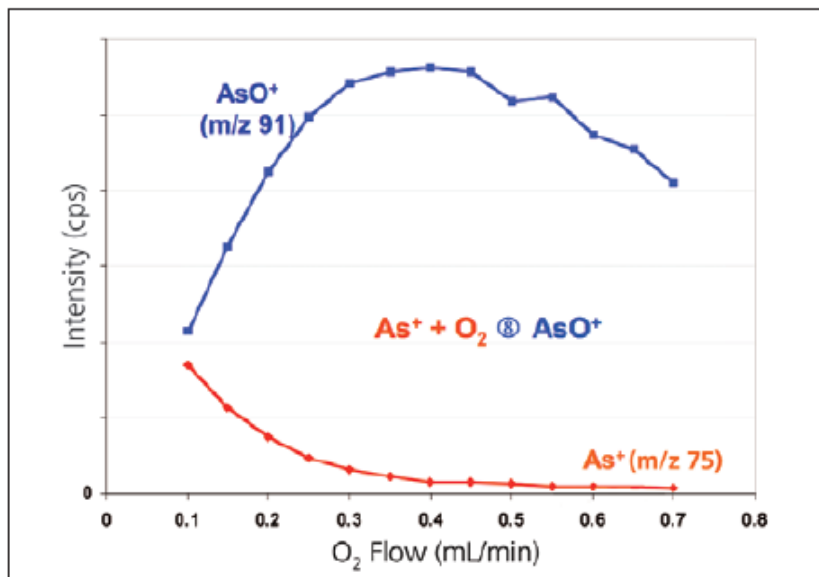


Figure 4. Optimization of the oxygen gas flow in the conversion of ⁷⁵As⁺ to ⁷⁵As¹⁶O⁺.

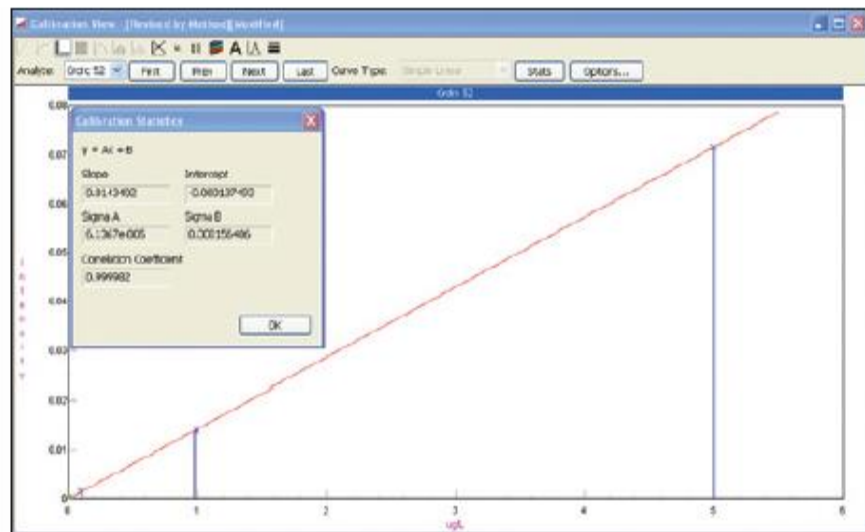


Figure 3. Calibration plot of 0.1, 1.0 and 5.0 µg/L of ⁵²Cr⁺ in urine.

综合应用：尿液中多元素分析

Table 3. Results for the normal-level UTAK® freeze-dried urine SRM.

Analyte (Mass)	Reported Value (µg/L)	Expected Range (µg/L)
*Arsenic as AsO (91)	9.2	8 to 11
*Chromium (52)	1.1	1.0 to 1.4
*Cobalt (59)	1.8	1.4 to 2.0
*Copper (65)	118	100 to 136
Lead (208)	0.56	0.5 to 0.7
*Manganese (55)	3.2	2.5 to 3.3
Molybdenum (98)	76	60 to 82
*Vanadium (51)	0.69	0.5 to 0.7
Zinc (66)	842	666 to 900

*denotes DRC mode

Table 4. Results for the high-level UTAK® freeze-dried urine SRM.

Analyte (Mass)	Reported Value (µg/L)	Expected Range (µg/L)
Aluminum (27)	35	32-44
*Arsenic as AsO (91)	99	88-116
Cadmium (114)	5.0	4.2-5.6
*Chromium (52)	7.6	6.3-8.5
*Copper (65)	171	143-193
Lead (208)	132	111-150
*Manganese (55)	3.9	3.0-4.0
Molybdenum (98)	98	75-101
*Vanadium (51)	10.8	9-12
Zinc (66)	1128	1112-1504

*denotes DRC mode

