理化分析中心实验室
部分大型仪器介绍

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稳定性同位素质谱仪MAT253功能及原理

一、稳定性同位素质谱仪-MAT253

- D/H同位素比
- $^{18}O/^{16}O$同位素比
- $^{15}N/^{14}N$同位素比
- $^{13}C/^{12}C$同位素比

美国热电出品

一、Finnigan MAT 253

- 质谱仪工作原理
- 仪器构件及其功能

稳定同位素比例质谱仪工作原理

- 质谱是按照原子（分子）质量的顺序排列的图谱，利用光谱法、核感应法或微波吸收法都可以构成试验装置，进行质谱研究
- 质谱仪（**mass spectrometer**）是基于电磁学原理设计而成的仪器，它只能对带电粒子起分离作用，所以要求将被研究的原子（分子）转变成离子，而仪器所获得的信息则是离子的质量**m**与电荷**e**之比——**m/e**。
- 近百年来，人们利用质谱仪进行了原子量测定、同位素分离与分析、有机物结构分析和其它科学实验，形成质谱法，在现代分离、分析研究领域中占有重要地位。

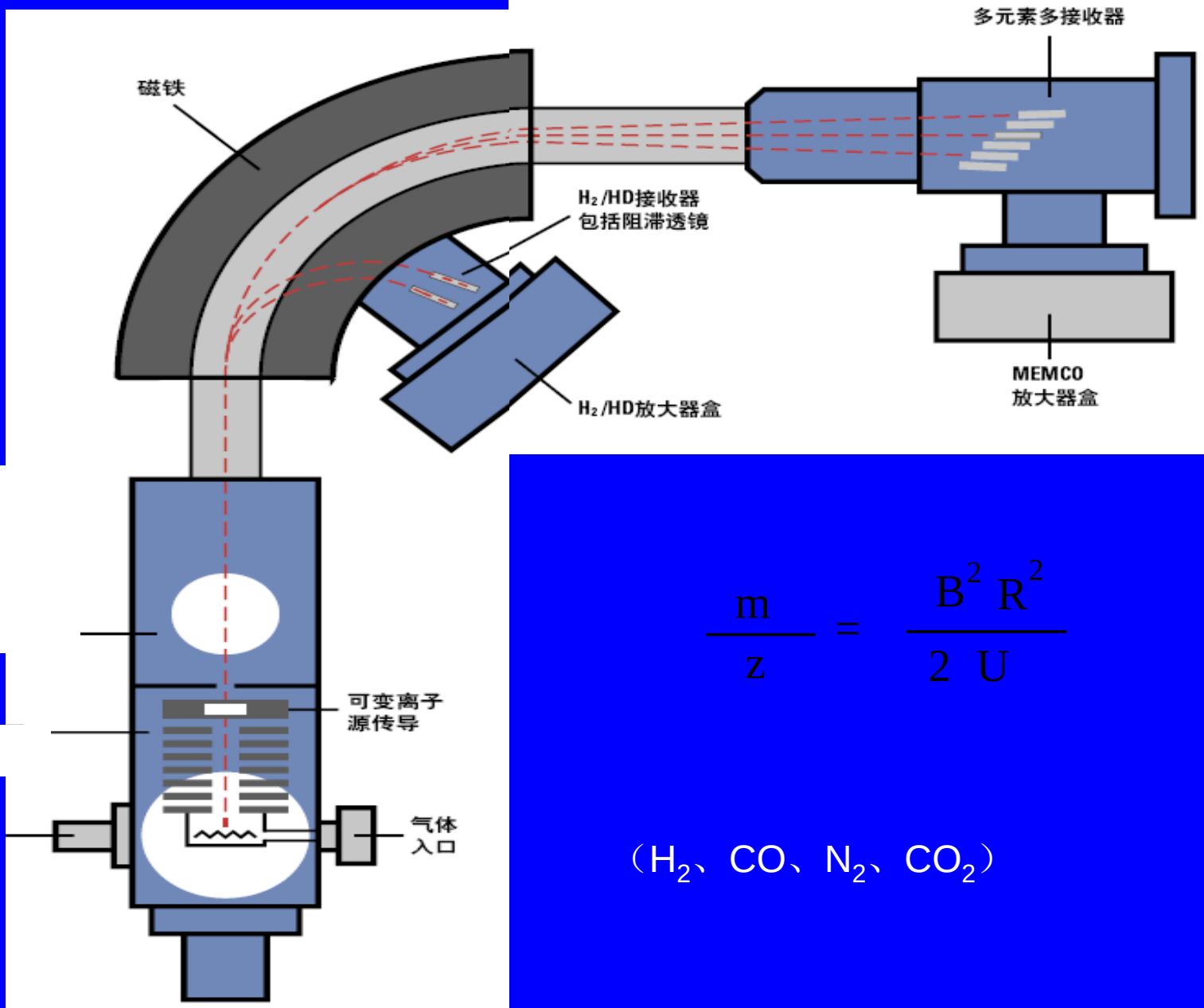
一、Finnigan MAT 253

- 质谱仪工作原理
- 仪器构件及其功能
  - MAT253主机
  - CONFLLO多功能接口
  - TC-EA分析仪
  - FLASH-EA分析仪

MAT253质谱仪主机

德国Finnigan公司生产

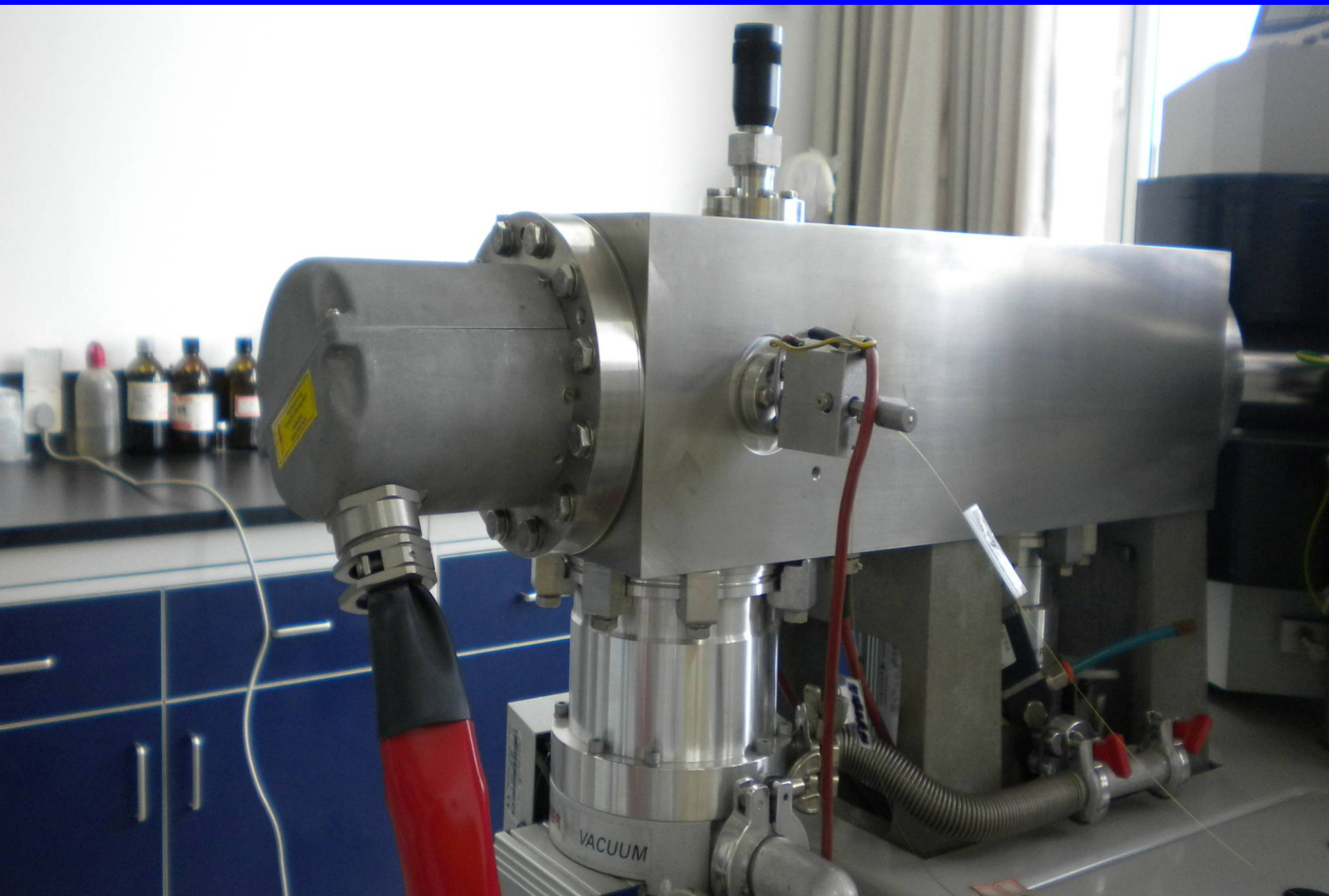
质谱仪内部核心系统



$$\frac{m}{z} = \frac{B^2 R^2}{2U}$$

（H_2、CO、N_2、CO_2）

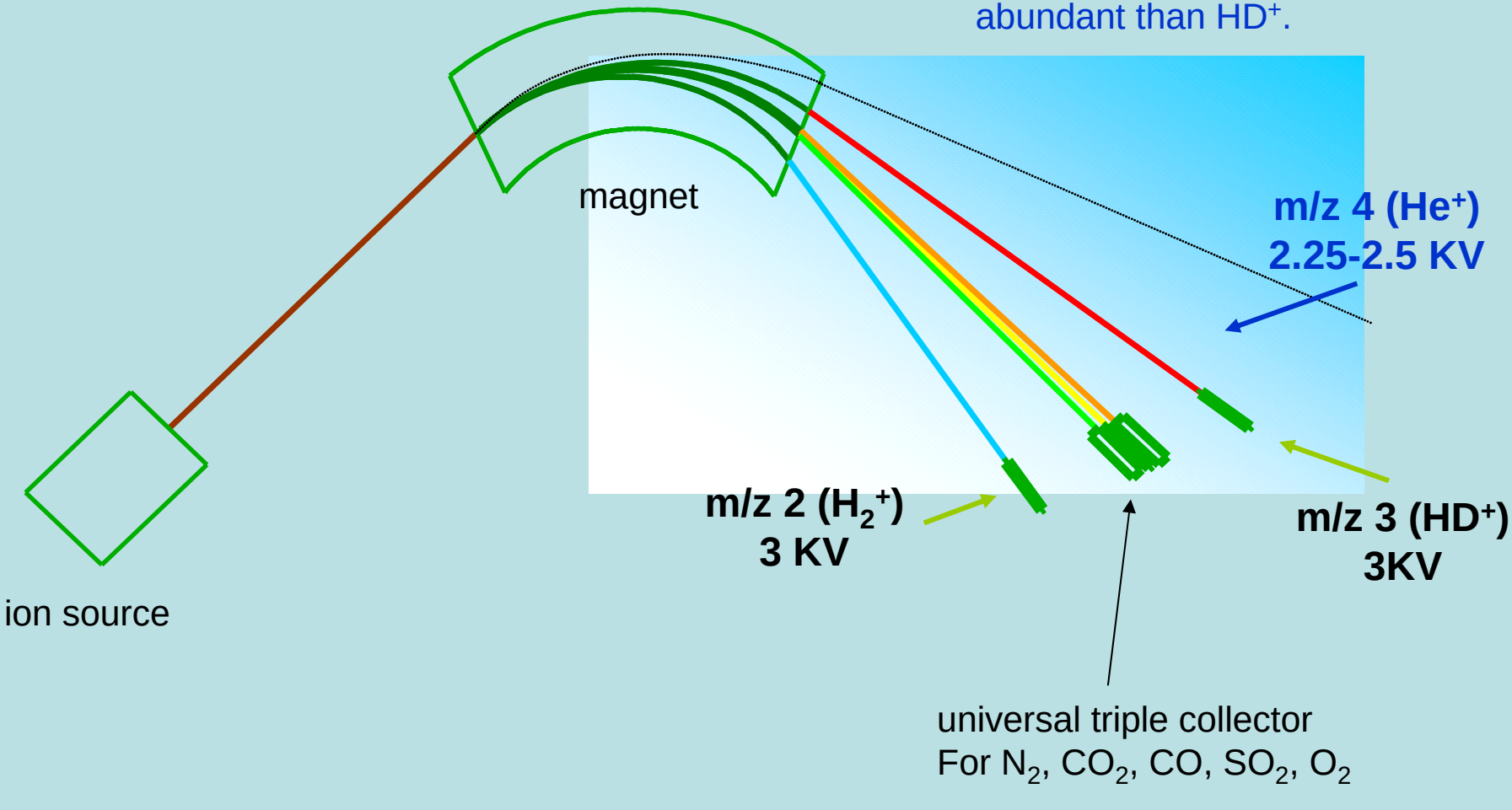
离子源发生器



同位素测定原理-磁场偏转

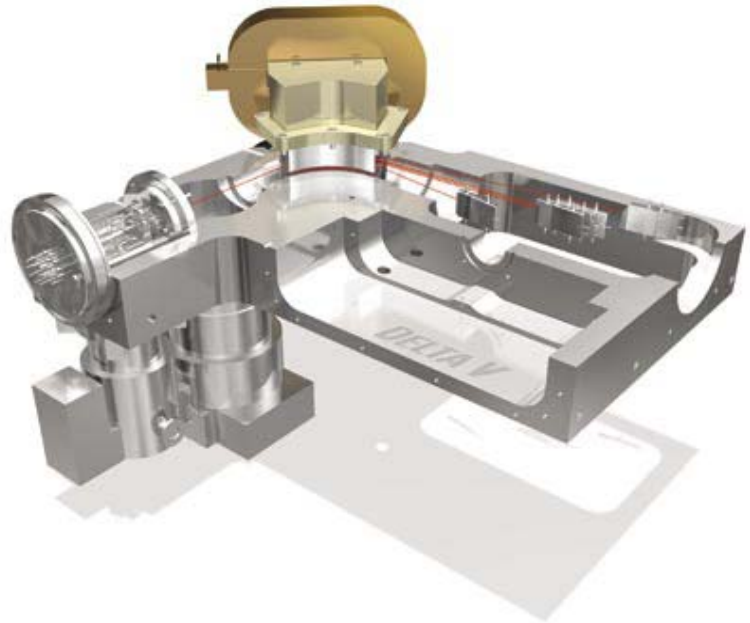
$$\frac{m}{z} = \frac{B^2 R^2}{2U}$$

Under continuous flow conditions $^4He^+$ is about 10^7 times more abundant than HD^+.

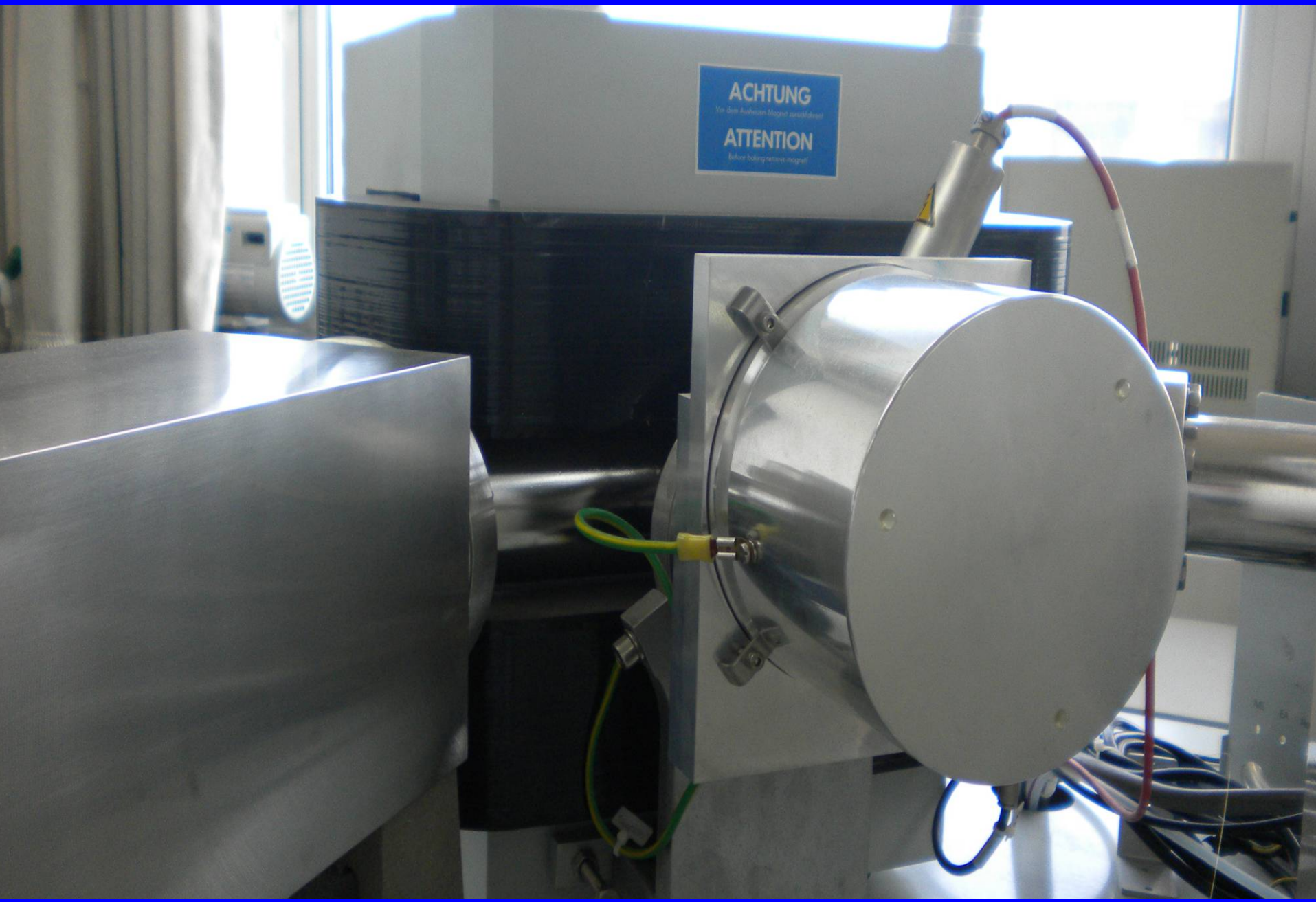


接收器

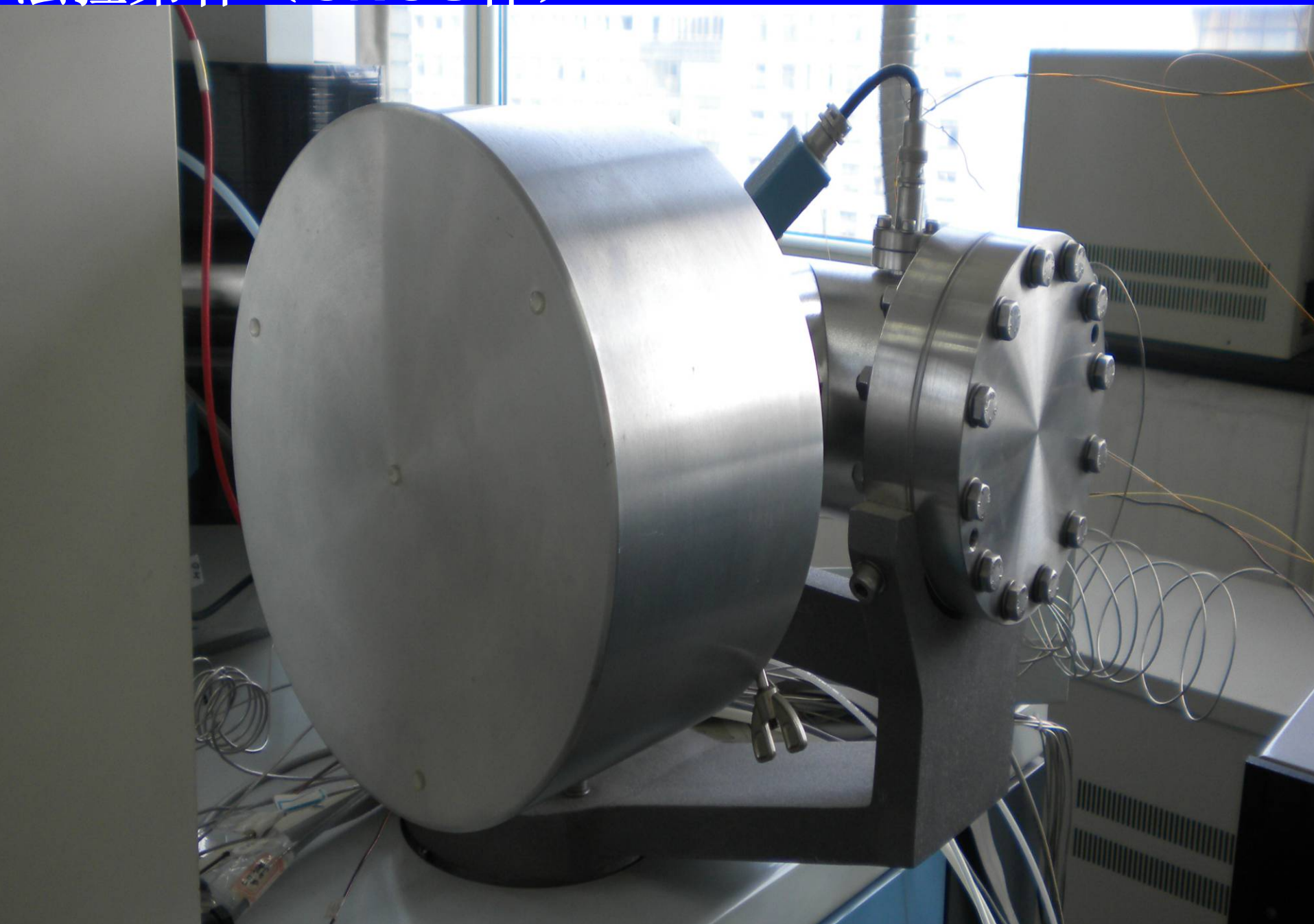
- 用于C、N、O、S、Si、Ar、Kr、和 Xe的接收器位于全偏转半径的焦点平 面上。
- 使用深的、单独屏蔽的法拉第杯以抑制二次电子。最多可配置8个独立的杯，具体取决于应用要求。每个 杯的数据可被同时采集。
- D/H接收器位于小的偏转半径上。m/z 3(DH)的杯配备了阻滞透镜。这使得 Finnigan MAT 253可以测量大量He存在下，连续流中的D/H比。
- 放大器的动态线性范围为50V，每个通道可计算机切换的增益，通过切换反馈电阻得以实现。此 新设计使得宽范围比值摆动的测量得以实现，如：浓缩或富集的样品。



法拉第杯（氢杯）



法拉第杯（CNOS杯）



系统控制：各部分有机的连接

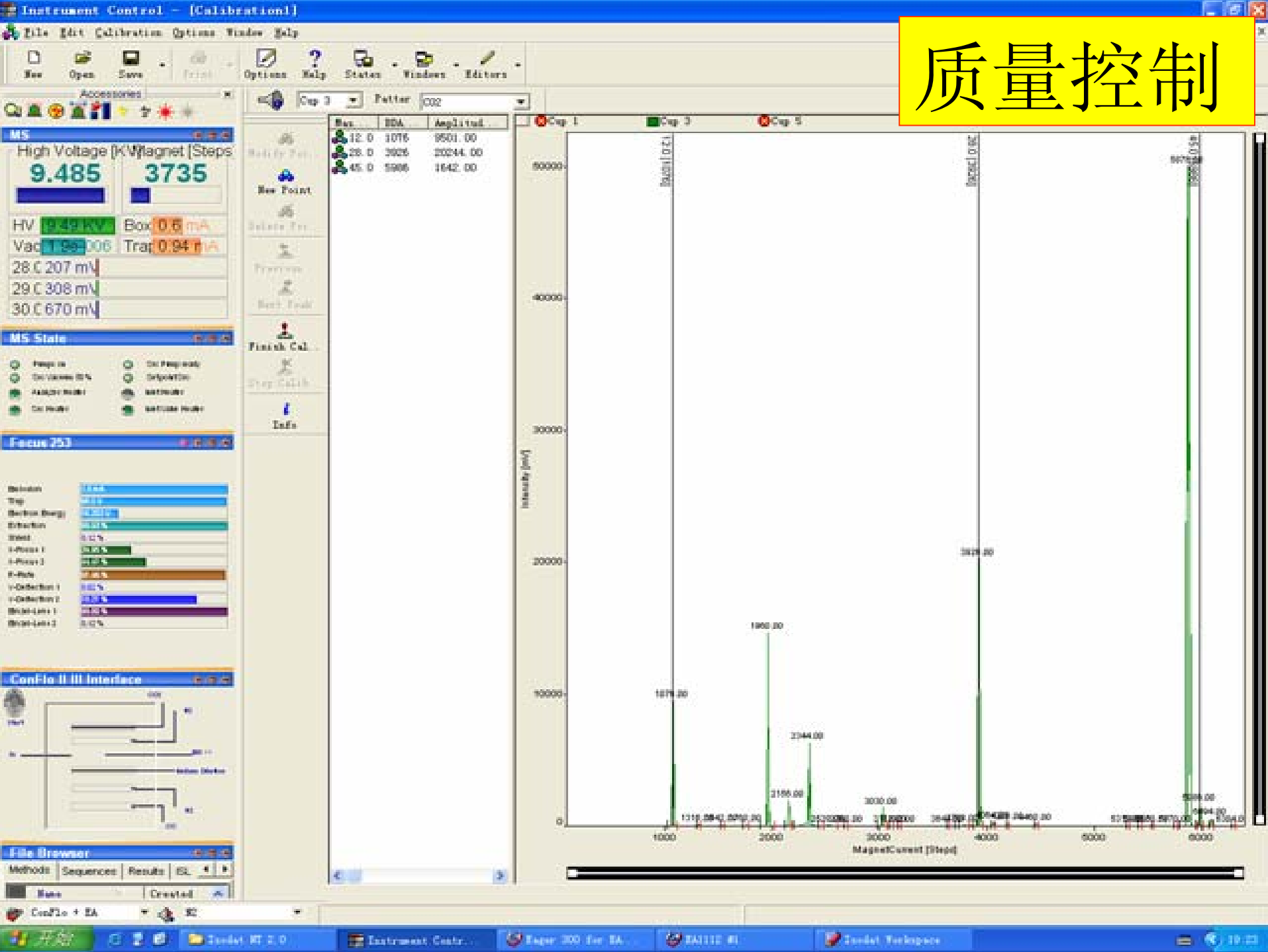
所有的质谱仪的状态均由软件控制，包括

- 离子的产生
- 质量的分离
- 离子的检测

- 离子源控制允许手动调谐、自动调谐并可存储和提取离子源参数。系统配置很容易被限定。不同配置象征不同的分析设定可被存储和提取。最多支持八个数据采集通道同时进行。

应用软件智能化


Intuitive Method Creation
Clearly Structured Sequence
Comprehensive Display of Results
Powerful Acquisition Launcher
Flexible & Powerful
Straightforward & Easy


质量控制
Instrument Control - [Calibration1]
File Edit Calibration Options Window Help
New Open Save Print Options Help States Windows Editors
Accessories
MS
High Voltage [kV] Magnet [Steps]
9.485
3735
HV 9.49 KV Box 0.6 mA
Vac 1.9E-006 Trap 0.94 mA
28 C 207 mV
29 C 308 mV
30 C 670 mV
MS State
Focus 253
ConFlo II III Interface
File Browser
Methods Sequences Results ISL
Name Created
Cup 3 Putter CO2
Run RDA Amplitud
12.0 1076 9501.00
28.0 3026 20244.00
45.0 5906 1642.00
New Point
Finish Cal
Info
Cup 1 Cup 3 Cup 5
50000
40000
30000
20000
10000
0
Intensity [mV]
1879.00
1960.00
2344.00
2155.00
3000.00
3829.00
1000
2000
3000
4000
5000
6000
MagnetCurrent [Steps]
ConFlo + EA
开始
Isodat NT 2.0
Instrument Contr...
Eager 300 for EA...
EA3112 #1
Isodat Workspace

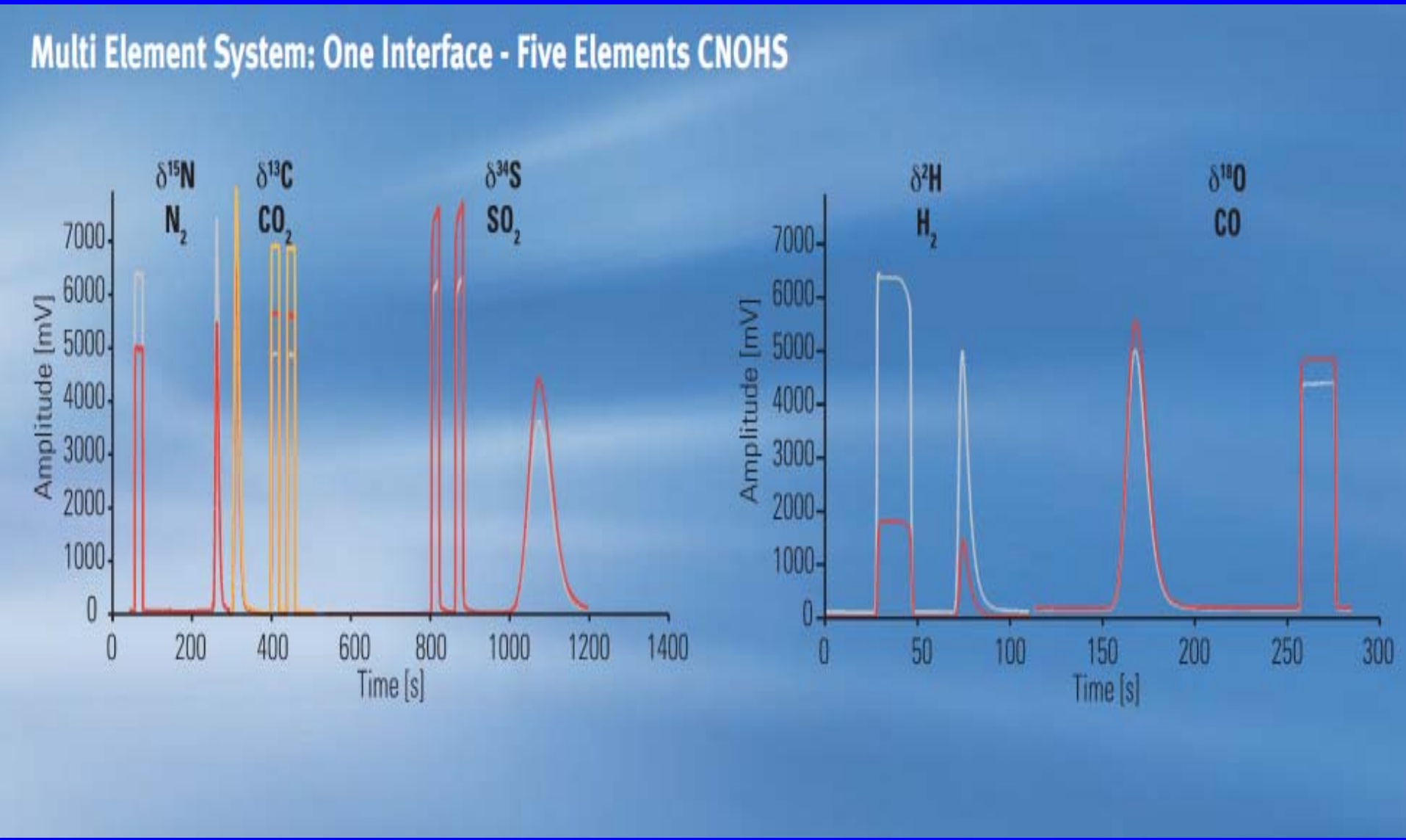
系统性能：

分析性能

气体	精度(‰)	
	内精度 (2σ mean)	外精度* (1σ)
CO_2 [C]	0.005 0.03	0.01 0.1
CO_2 [O]	0.01 0.02	0.03 0.05
N_2	0.008 0.05	0.01 0.1
SO_2	0.006	0.01
SF_6	0.006	0.01
H_2	0.1	0.4

* 使用内置多通阀的10次测定

可测定单元素及双元素


Multi Element System: One Interface - Five Elements CNOHS
δ15N
N2
δ13C
CO2
δ34S
SO2
δ2H
H2
δ18O
CO
Amplitude [mV]
Time [s]
0
1000
2000
3000
4000
5000
6000
7000
0
200
400
600
800
1000
1200
1400
50
100
150
200
250
300

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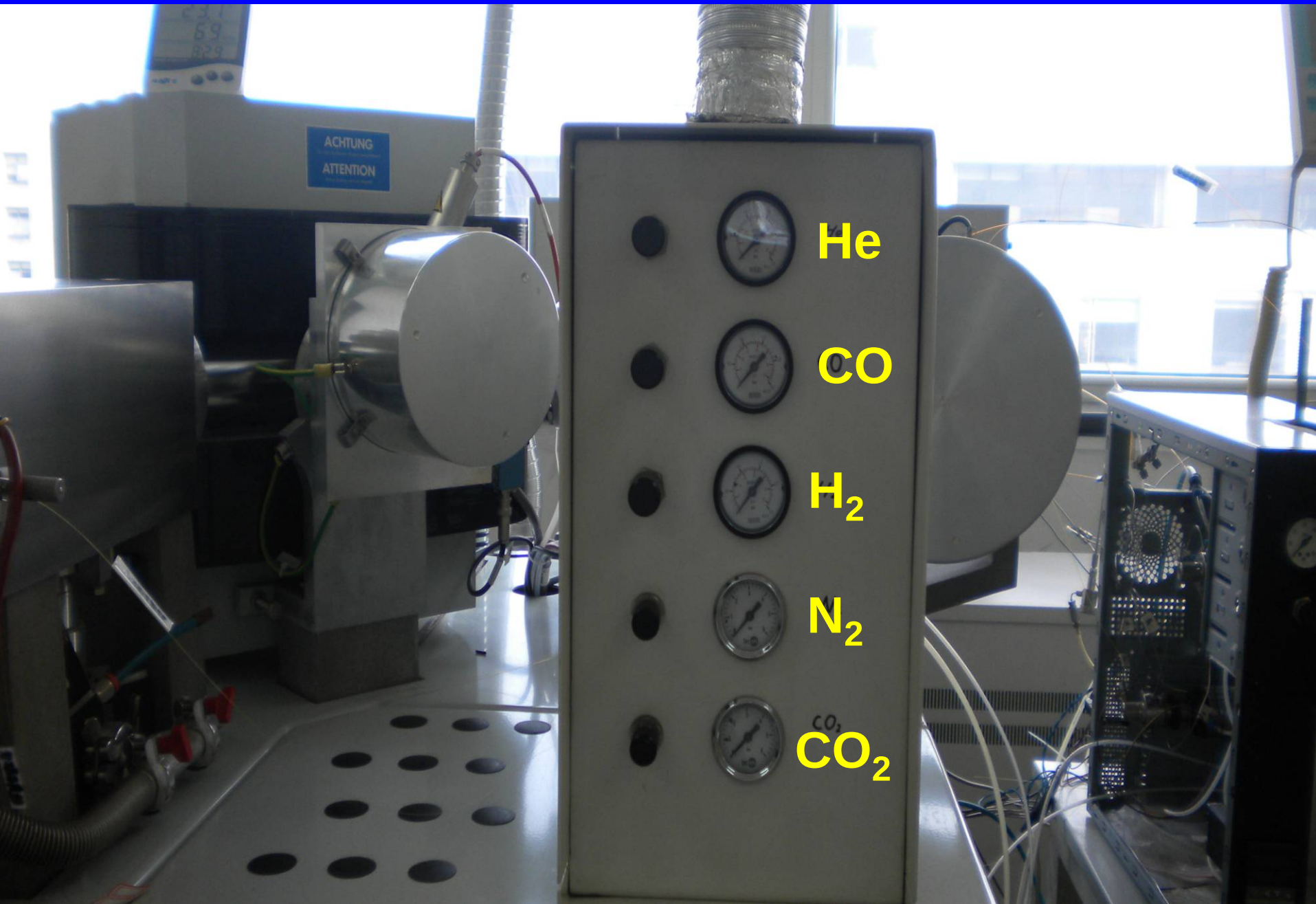
CONFLO-多功能接口



特点

新型ConFlo IV的特点:

- 更高的样品通量和更短的待机时间
- 利用3个前处理装置进行连续的全自动分析
- 软件控制Trace GC和Flash EA的待机和启动

- smartEA™模式: 根据参考气体的强度自动检出和调节样品气体
- 根据EA 的TCD检出信号，具有计算机控制的样品气体自动稀释机制

- 同时有效的五路参考气体
- 在同一批样品中完成CNOHS五种同位素比的分析和参照
- 参考气体的消费量最低

- 计算机控制的参考气体强度
- 线性、稳定性和H_3^+因子的自动测定
- 监视和自我诊断的集成系统

Instrument | Time Events | Component Names | Evaluation@H2 | Peak Detection@H2 | Printout@H2

Time [s]	Start Sampler	Elemental Anal.	Dilution	Reference 1	Reference 2	Switch Gas	Cov Close	Cov Left	Cov
0	●		●						
30	●								
60	●								

在软件上方便设置

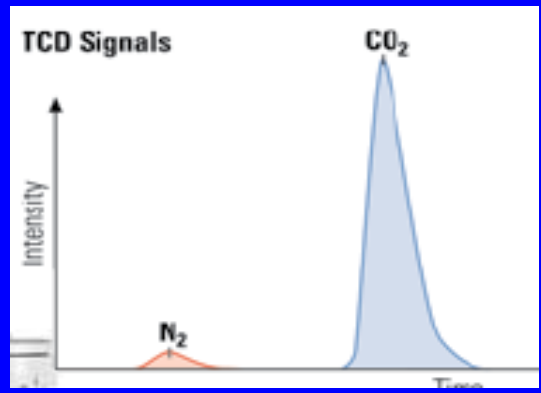
Acquisition Start: Immediately

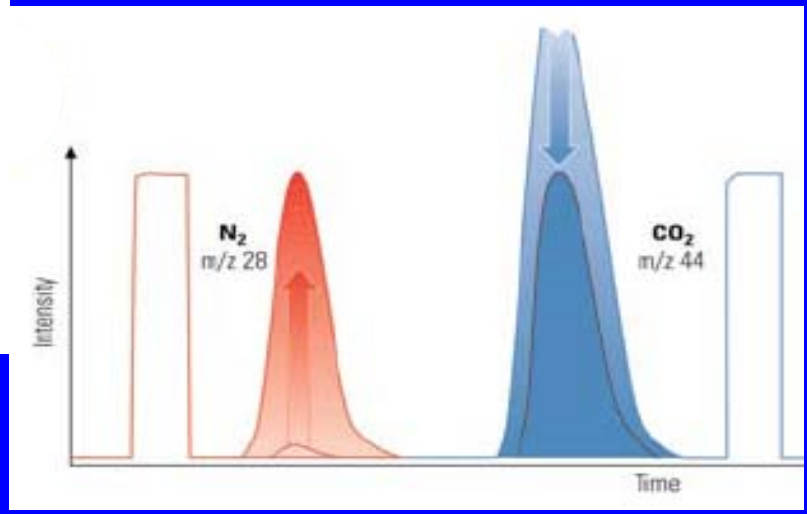
Acquisition End Time [s]: 290

可以自动稀释样品的含量比例

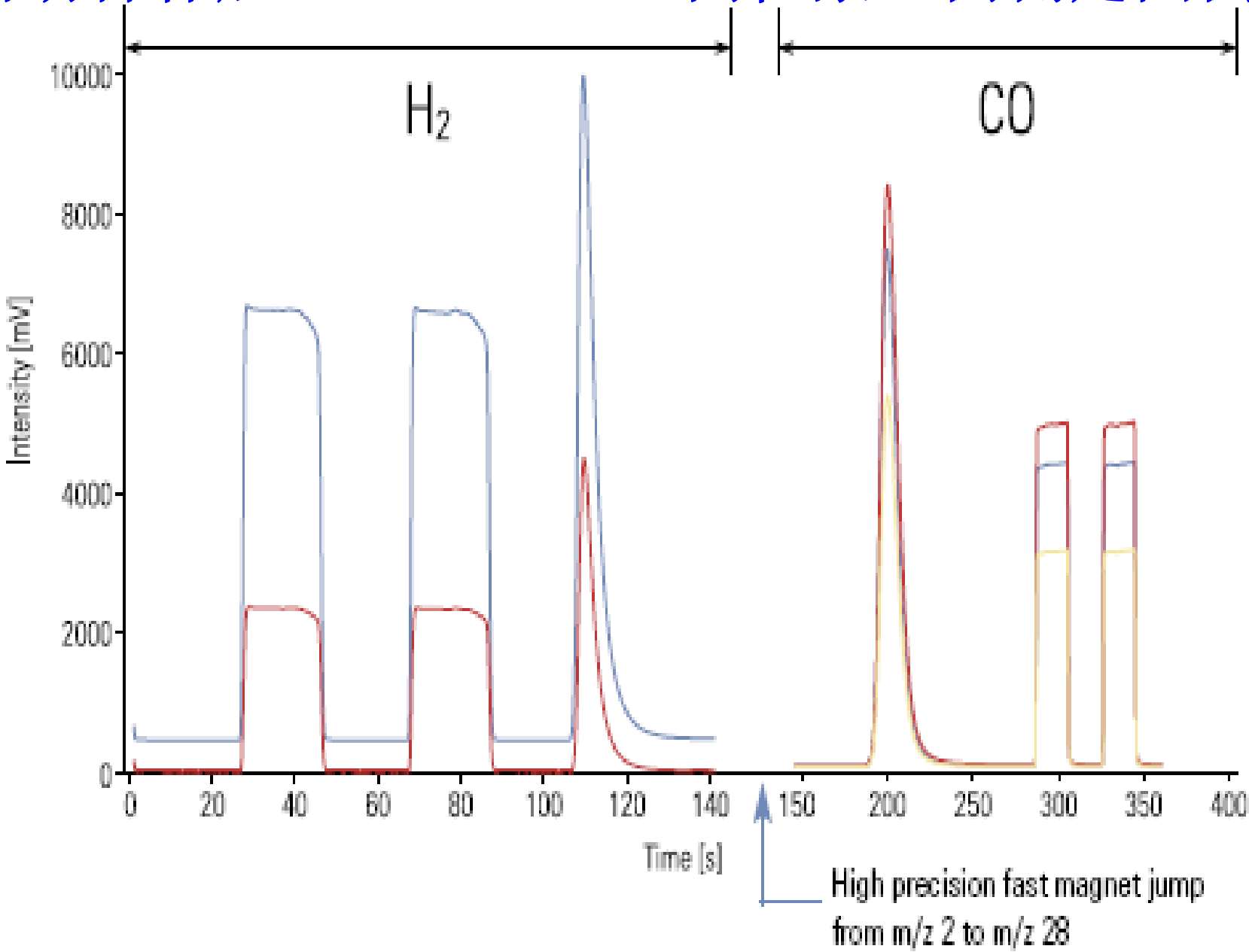
自动稀释

因为在自然界C/N/S和H/O的相对含量变化极大，也因为不同元素的离子化效率非常不同，连续流样品前处理导致信号强度变化范围极宽。ConFlo IV 在设计上通过使用氦气稀释的专利技术可以操纵宽幅可变的线性范围*。稀释在开口分流管中实施，是样品气体进入离子源前的最后一个端点，排除了任何可能的同位素效应。





自动稀释后D/H、$^{16}O/^{18}O$ 同位素比例测定图例



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MAT-253-TC-EA仪器

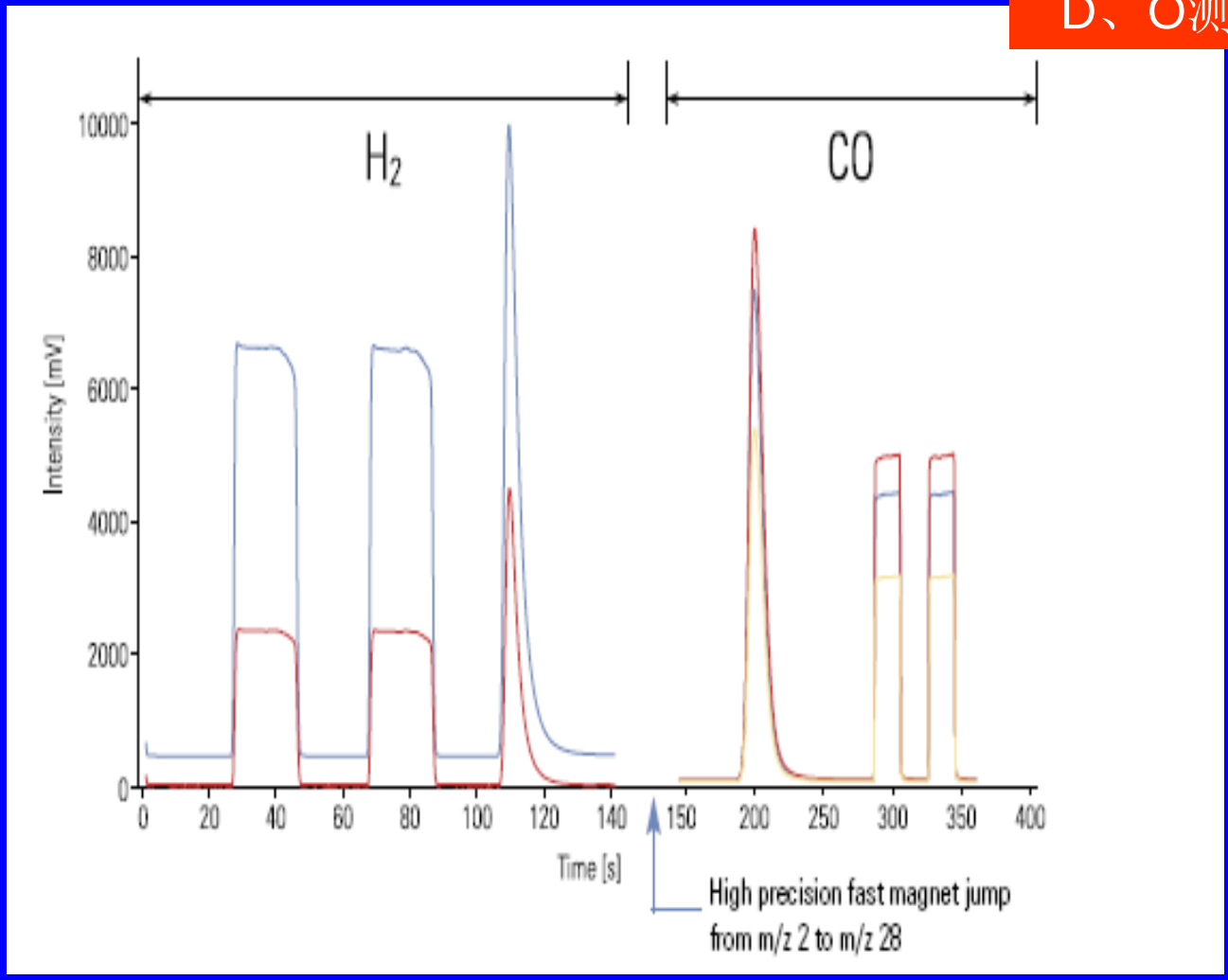
MAT253-TC-EA

TC-EA 仪器功能：测定水样及固体样品

- **D/H**同位素比值
- **^{16}O /^{18}O**同位素比值

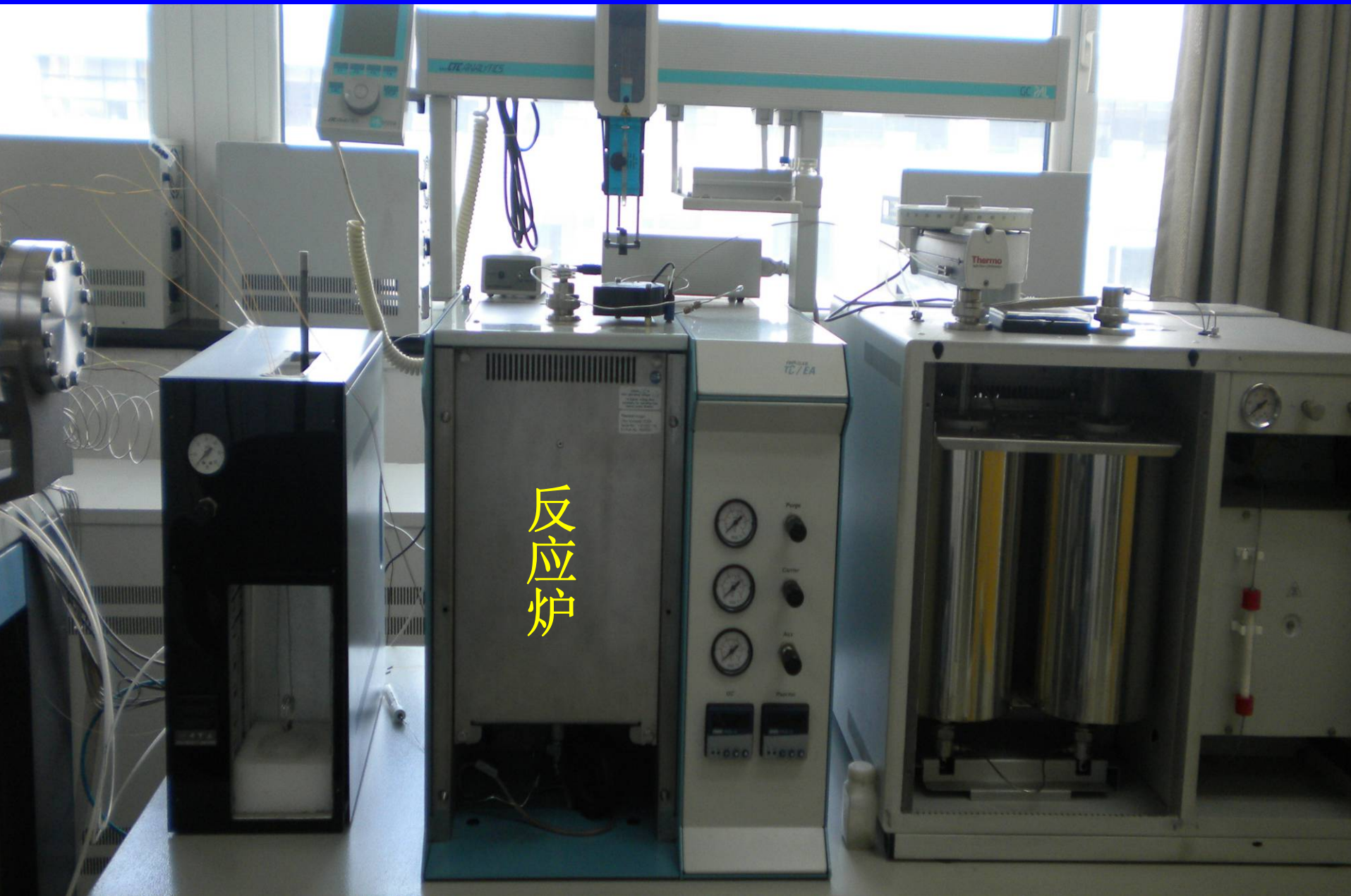
TC-EA测定水、固体D/H、$^{16}O/^{18}O$同位素比值

D、O测定

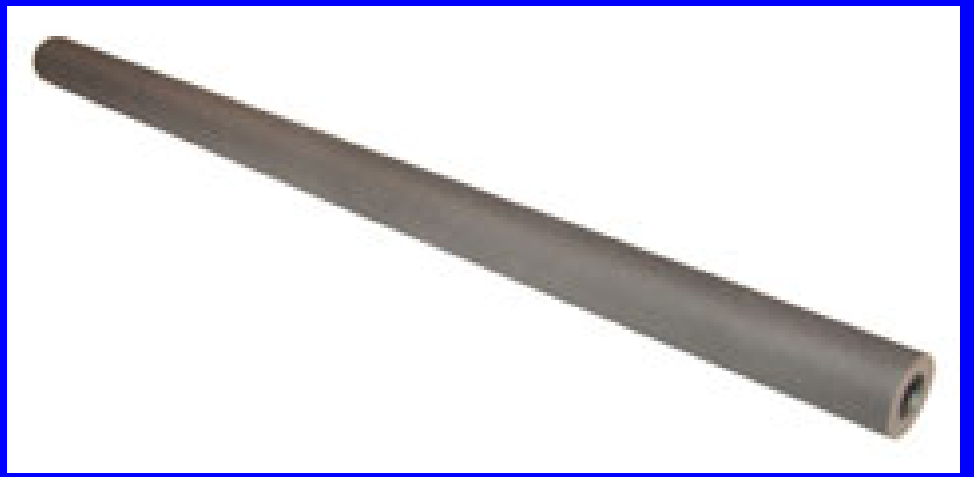


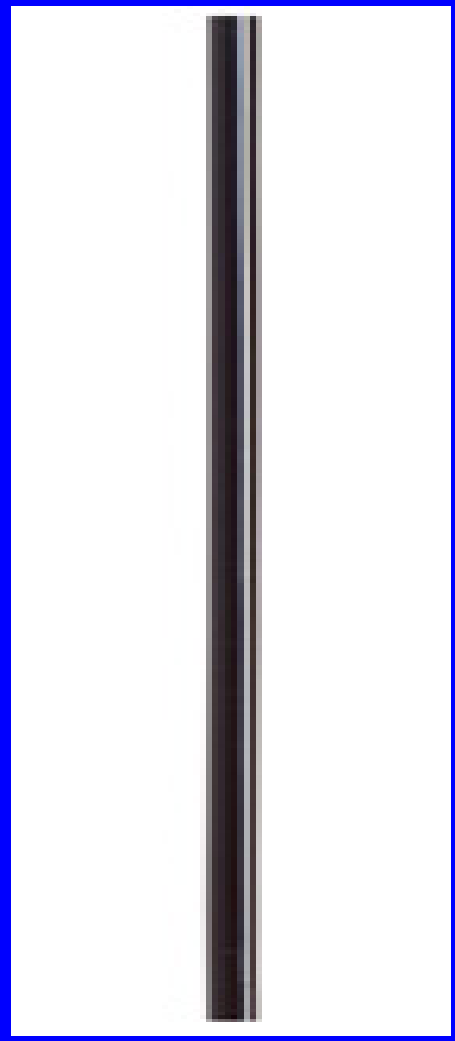

CTC自动进样器
Thermo
TC / EA
FlashEA
Thermo
Thermo
TC-EA

仪器内部结构

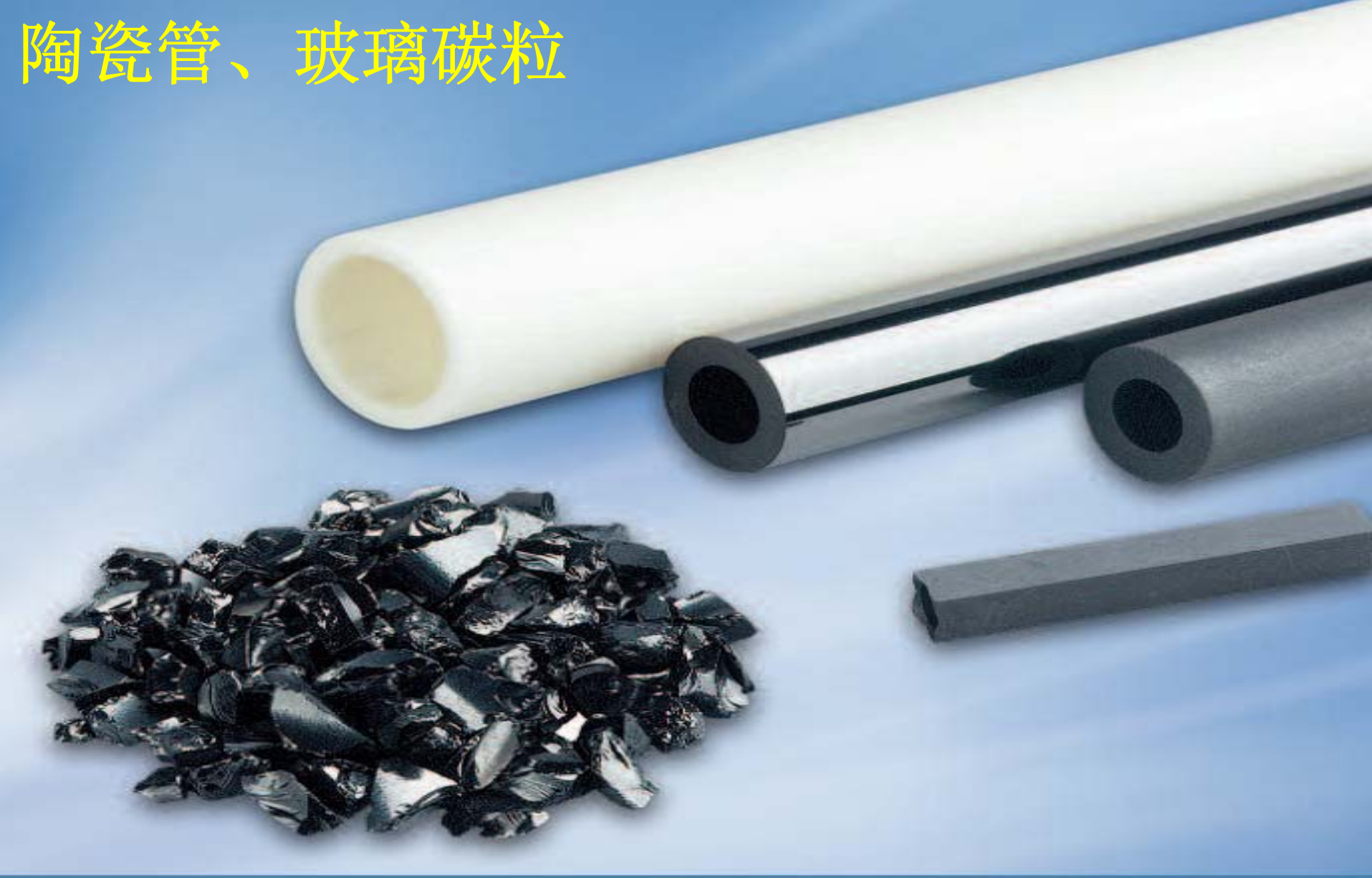


反应原理：玻璃碳管、高温裂解



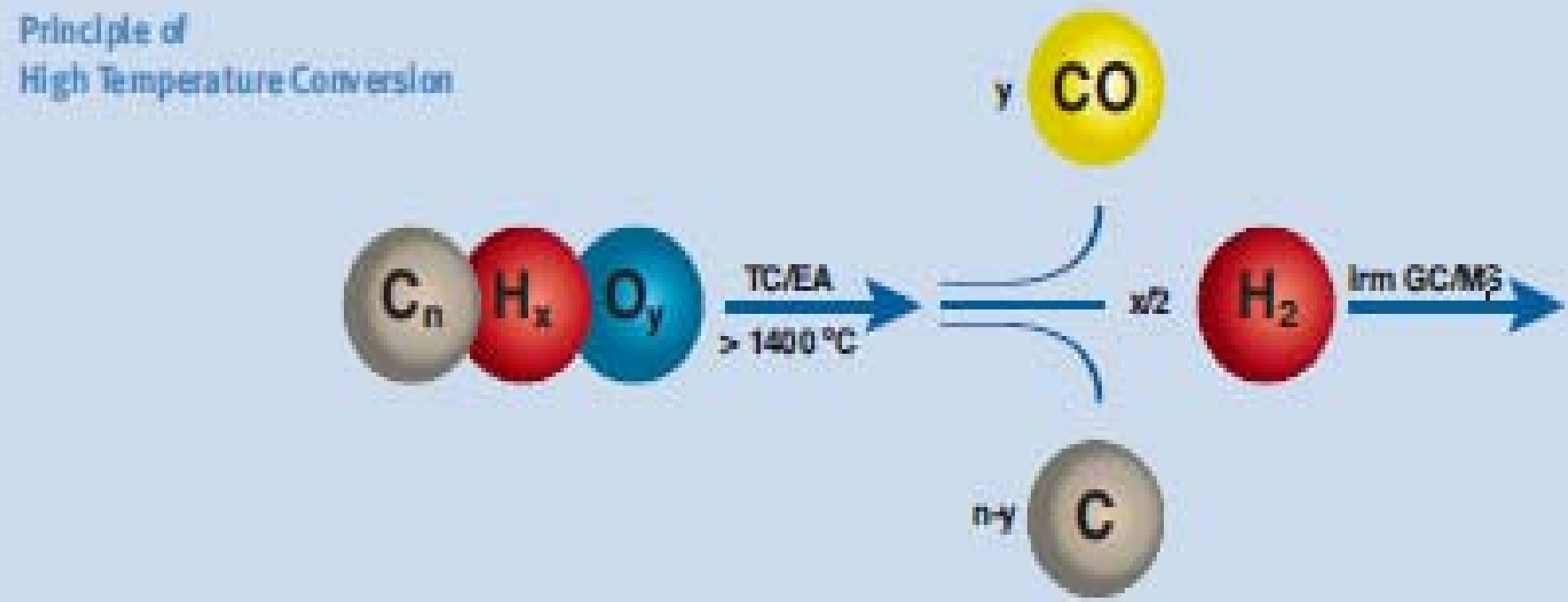


陶瓷管、玻璃碳粒



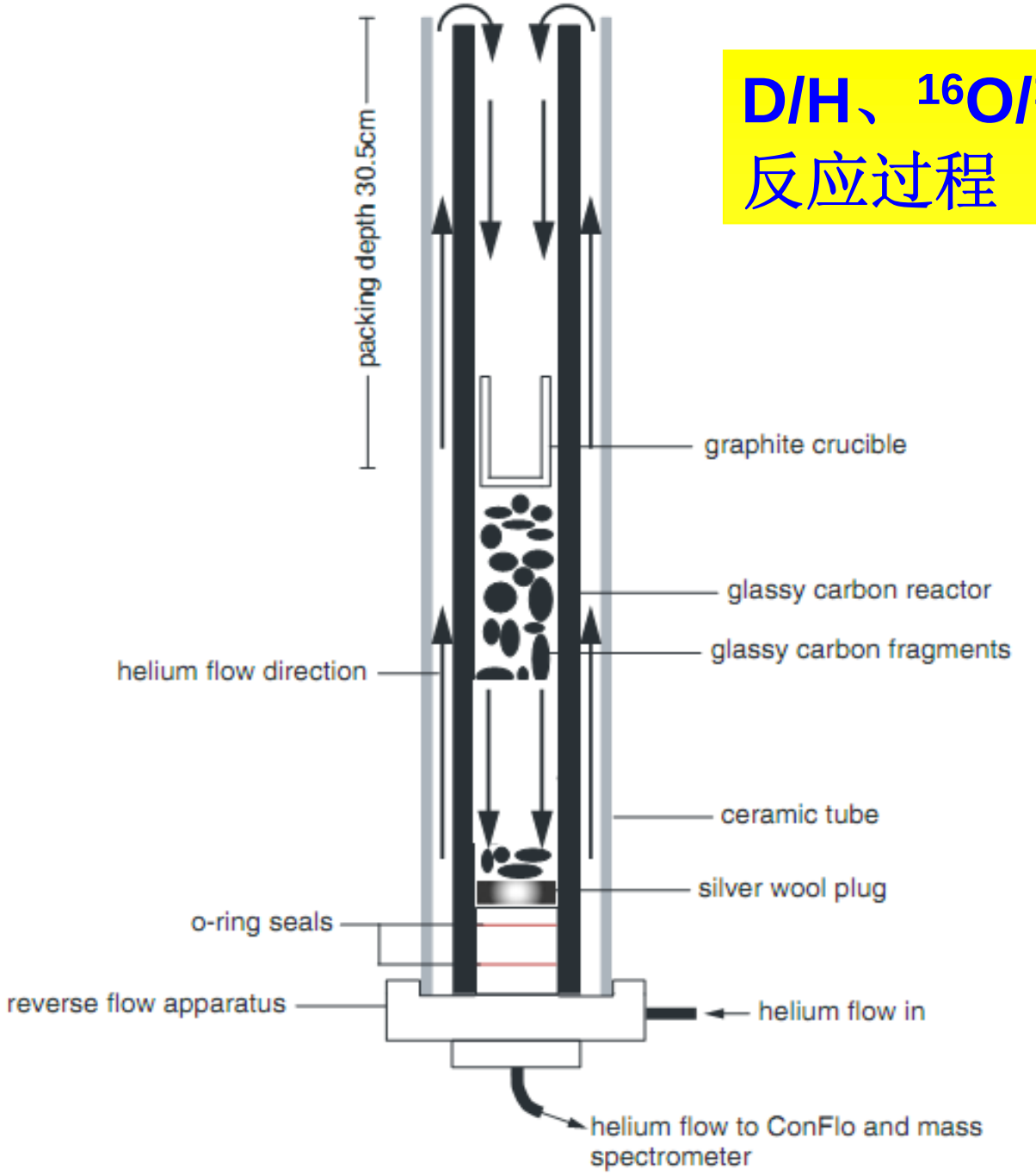
High Temperature Conversion Elemental Analyzer

D/H、$^{16}O/^{18}O$同位素反应原理



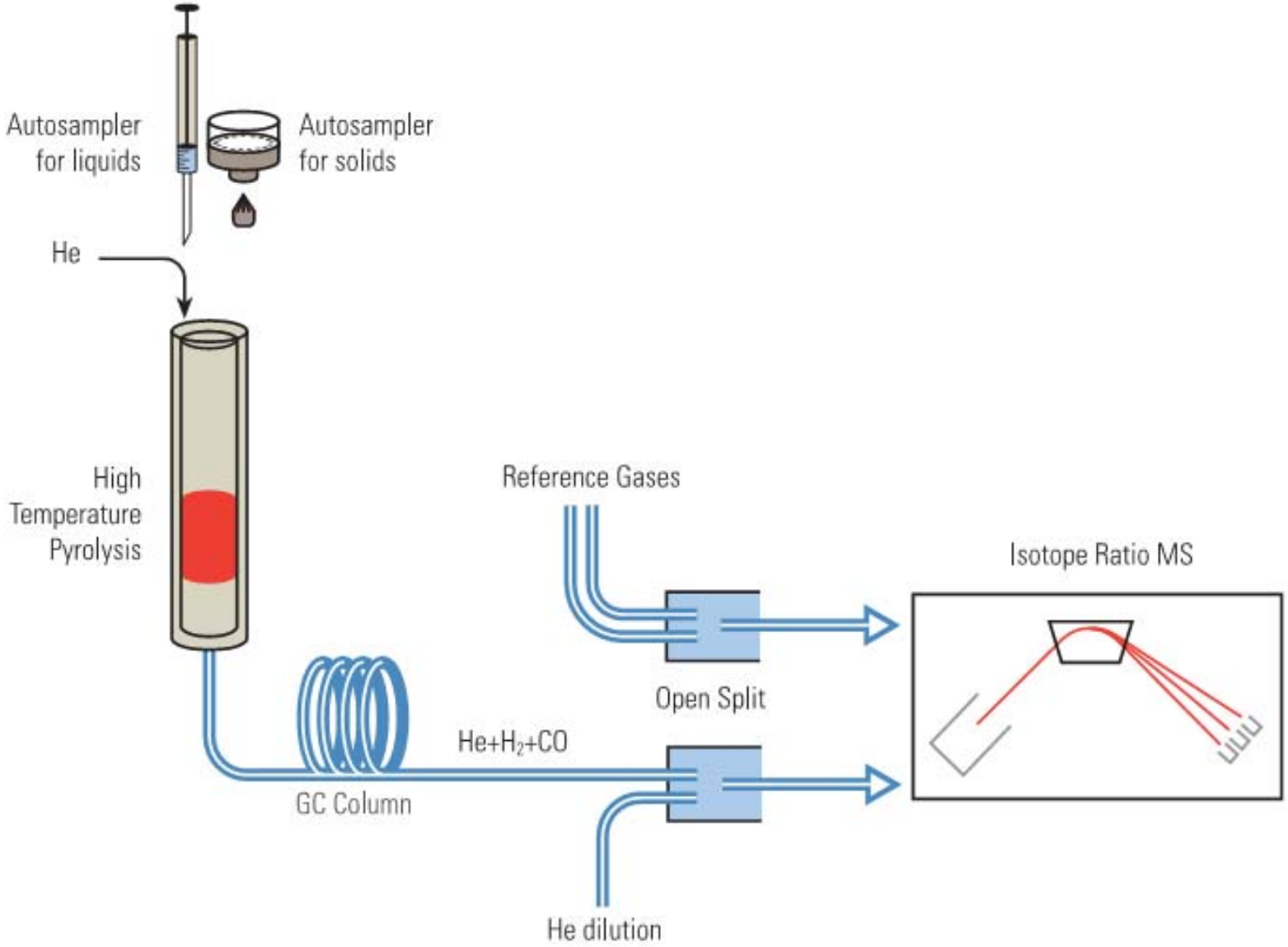
高温裂解

D/H、$^{16}O/^{18}O$测定反应过程



to scale) of the 'reverse-plumbed' TC/EA reactor showing the flow of He carrier gas. The purpose of t

TC-EA测定D/H、$^{16}O/^{18}O$过程示意图



TC-EA操作步骤（测定D/H、$^{18}O/^{16}O$同位素比）

(1) 制备样品

(2) 编辑sequence进样序列，选择方法

(3) 上机测试样品

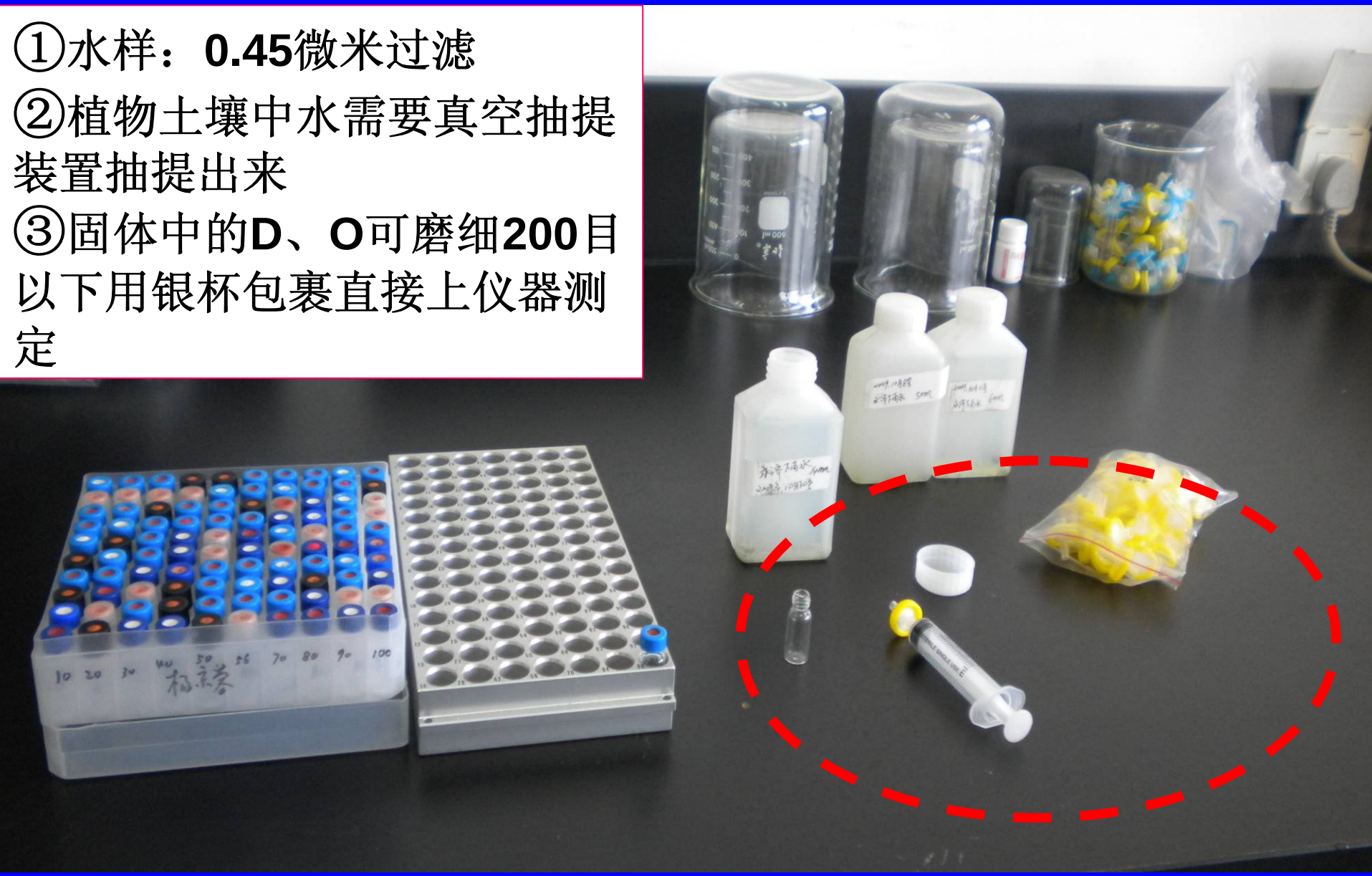
(4) 处理数据

样品制备

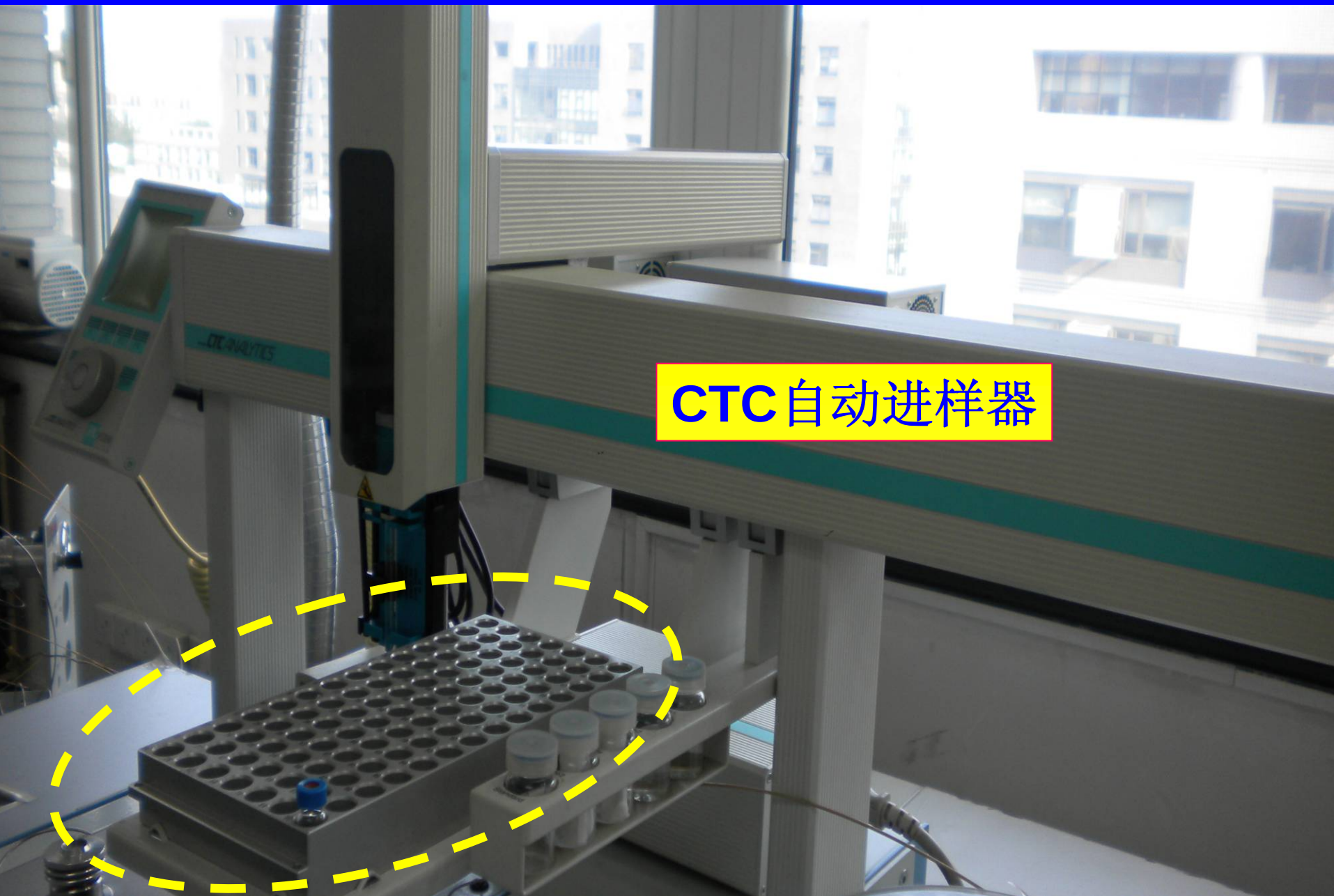
①水样：0.45微米过滤

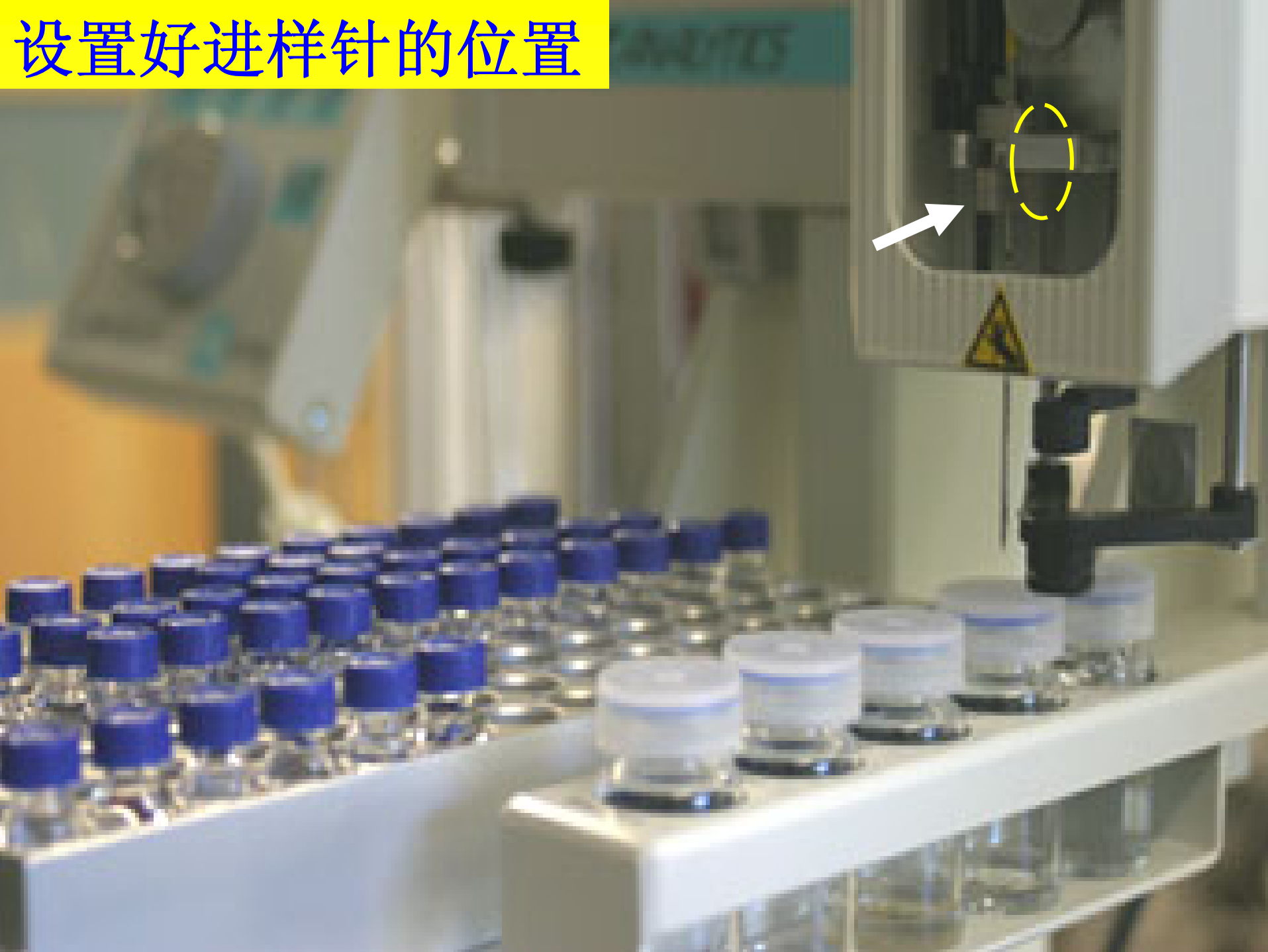
②植物土壤中水需要真空抽提装置抽提出来

③固体中的D、O可磨细200目以下用银杯包裹直接上仪器测定



摆放样品到自动进样器上




设置好进样针的位置

上机操作软件

HD-CO liquid-short.met

Instrument | Time Events | Component Names | Evaluation@H2 | Peak Detection@H2 | Printout@H2 | Evaluation@CO | Peak Detection@CO | Printout@CO

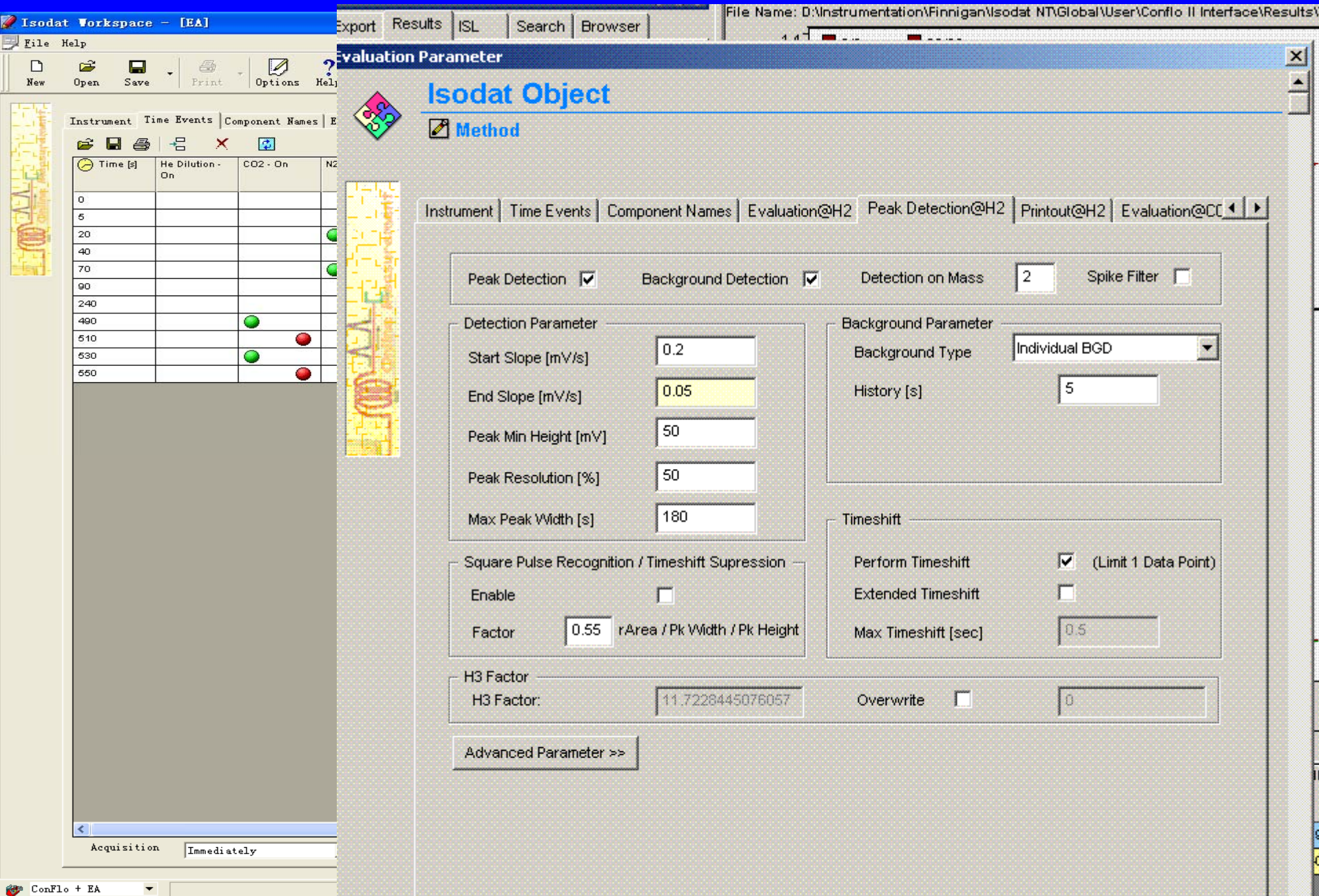
Time [s]	Start Sampler	Elemental Anal.	Dilution	Reference 1	Reference 2	Switch Gas	Cov Close	Cov Left	Cov
0	●		●						
10				●					
40				●					
146						CO			
265					●				
295					●				

建立方法

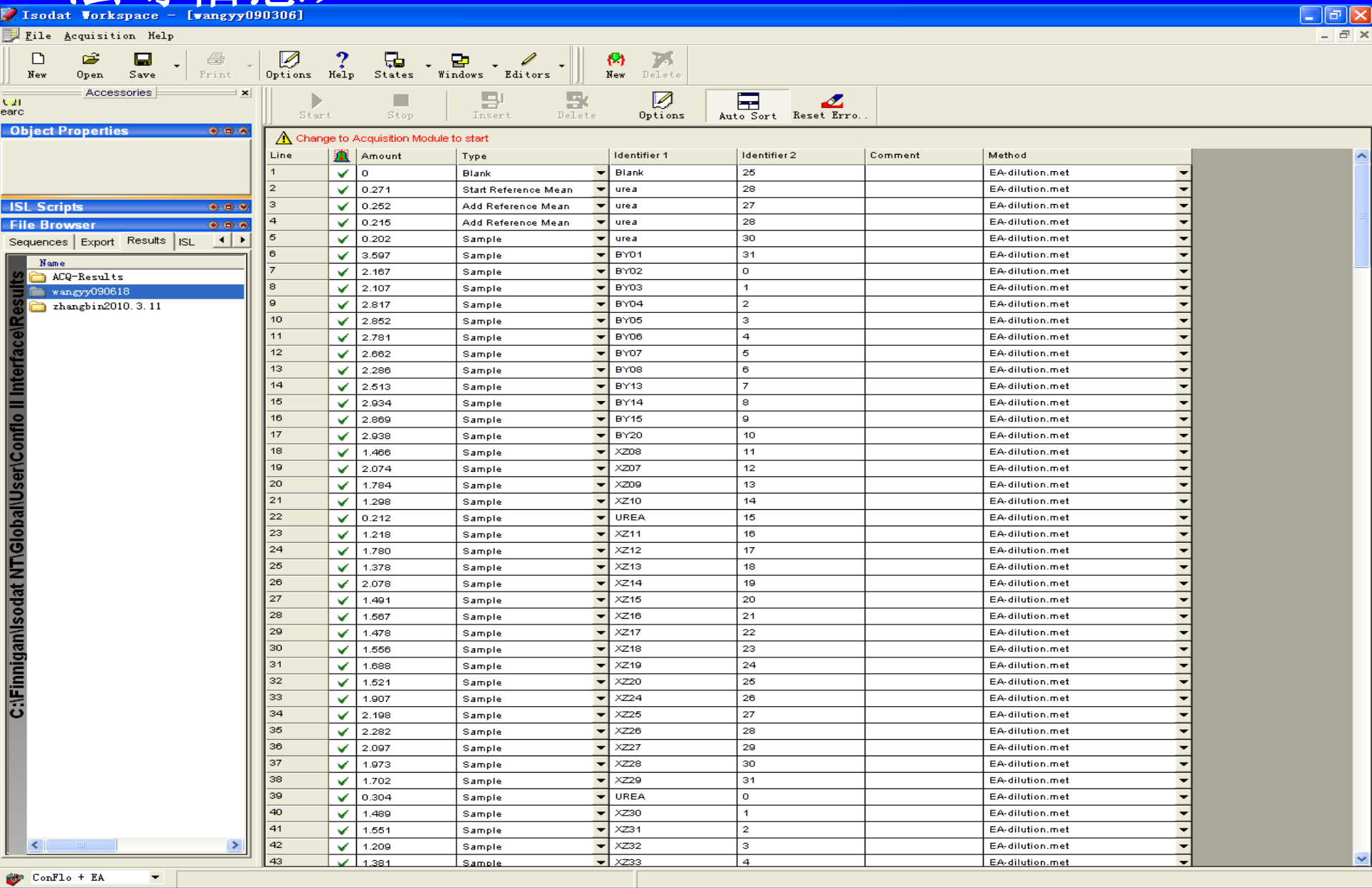
Acquisition Start: Immediately

Acquisition End Time [s]: 315

调用、选择方法


Isodat Workspace - [EA]
File Help
New
Open
Save
Print
Options
Instrument
Time Events
Component Names
Time [s]
He Dilution - On
CO2 - On
Acquisition
Immediately
ConFlo + EA
Export
Results
ISL
Search
Browser
File Name: D:\Instrumentation\Finnigan\Isodat NT\Global\User\Conflo II Interface\Results\
Evaluation Parameter
Isodat Object
Method
Instrument
Time Events
Component Names
Evaluation@H2
Peak Detection@H2
Printout@H2
Peak Detection
Background Detection
Detection on Mass
2
Spike Filter
Detection Parameter
Start Slope [mV/s]
0.2
End Slope [mV/s]
0.05
Peak Min Height [mV]
50
Peak Resolution [%]
50
Max Peak Width [s]
180
Square Pulse Recognition / Timeshift Supression
Enable
Factor
0.55
rArea / Pk Width / Pk Height
Background Parameter
Background Type
Individual BGD
History [s]
5
Timeshift
Perform Timeshift
(Limit 1 Data Point)
Extended Timeshift
Max Timeshift [sec]
0.5
H3 Factor
H3 Factor:
11.7228445076057
Overwrite
0
Advanced Parameter >>

上机编辑进样序列表（样品名称、质量、调用方法等信息）

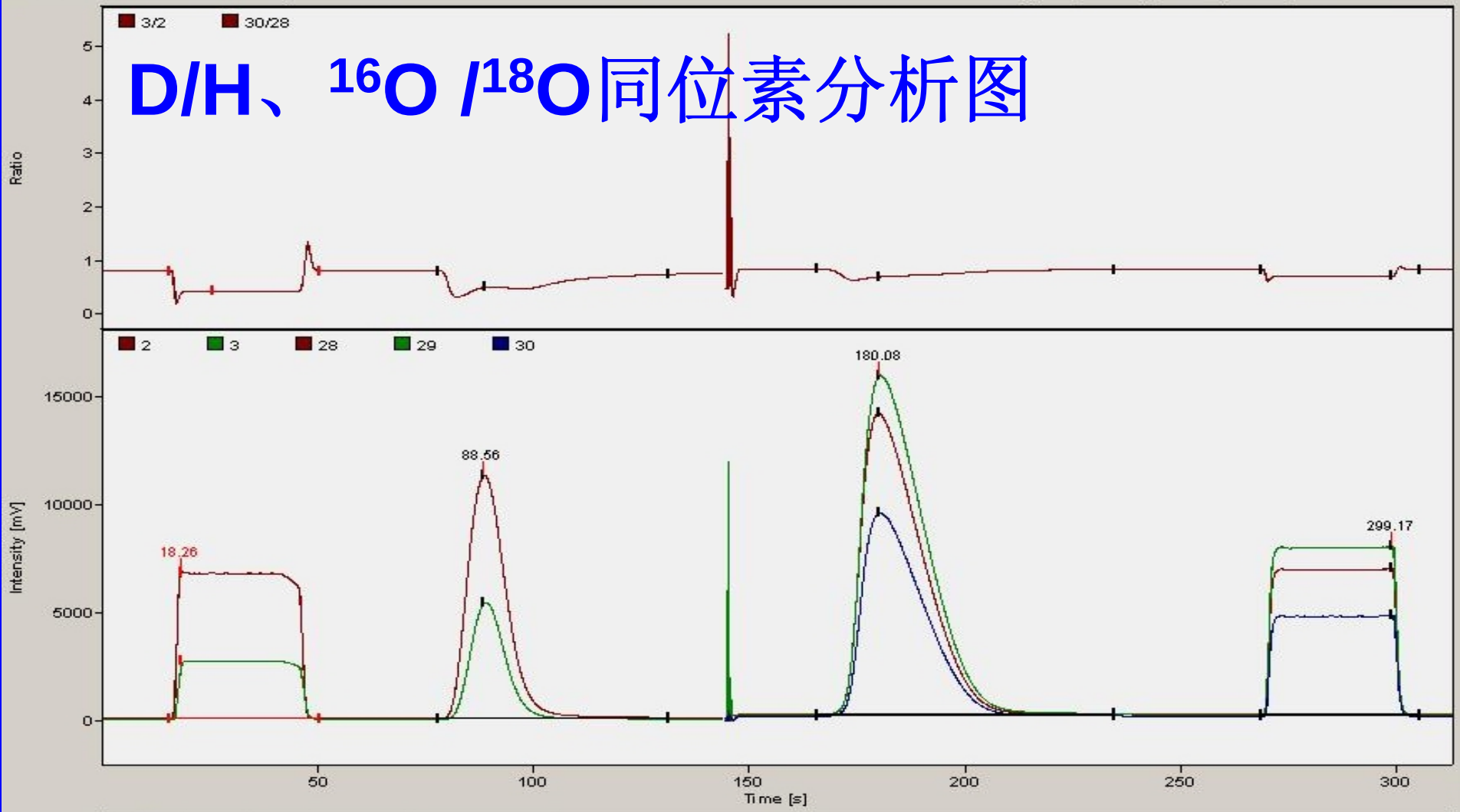


Line	Amount	Type	Identifier 1	Identifier 2	Comment	Method
1	0	Blank	Blank	25		EA-dilution.met
2	0.271	Start Reference Mean	urea	28		EA-dilution.met
3	0.252	Add Reference Mean	urea	27		EA-dilution.met
4	0.215	Add Reference Mean	urea	28		EA-dilution.met
5	0.202	Sample	urea	30		EA-dilution.met
6	3.597	Sample	BY01	31		EA-dilution.met
7	2.167	Sample	BY02	0		EA-dilution.met
8	2.107	Sample	BY03	1		EA-dilution.met
9	2.817	Sample	BY04	2		EA-dilution.met
10	2.852	Sample	BY05	3		EA-dilution.met
11	2.781	Sample	BY06	4		EA-dilution.met
12	2.662	Sample	BY07	5		EA-dilution.met
13	2.286	Sample	BY08	6		EA-dilution.met
14	2.513	Sample	BY13	7		EA-dilution.met
15	2.934	Sample	BY14	8		EA-dilution.met
16	2.869	Sample	BY15	9		EA-dilution.met
17	2.938	Sample	BY20	10		EA-dilution.met
18	1.466	Sample	XZ08	11		EA-dilution.met
19	2.074	Sample	XZ07	12		EA-dilution.met
20	1.784	Sample	XZ09	13		EA-dilution.met
21	1.298	Sample	XZ10	14		EA-dilution.met
22	0.212	Sample	UREA	15		EA-dilution.met
23	1.218	Sample	XZ11	16		EA-dilution.met
24	1.780	Sample	XZ12	17		EA-dilution.met
25	1.378	Sample	XZ13	18		EA-dilution.met
26	2.078	Sample	XZ14	19		EA-dilution.met
27	1.491	Sample	XZ15	20		EA-dilution.met
28	1.567	Sample	XZ16	21		EA-dilution.met
29	1.478	Sample	XZ17	22		EA-dilution.met
30	1.556	Sample	XZ18	23		EA-dilution.met
31	1.688	Sample	XZ19	24		EA-dilution.met
32	1.521	Sample	XZ20	25		EA-dilution.met
33	1.907	Sample	XZ24	26		EA-dilution.met
34	2.198	Sample	XZ25	27		EA-dilution.met
35	2.282	Sample	XZ26	28		EA-dilution.met
36	2.097	Sample	XZ27	29		EA-dilution.met
37	1.973	Sample	XZ28	30		EA-dilution.met
38	1.702	Sample	XZ29	31		EA-dilution.met
39	0.304	Sample	UREA	0		EA-dilution.met
40	1.489	Sample	XZ30	1		EA-dilution.met
41	1.551	Sample	XZ31	2		EA-dilution.met
42	1.209	Sample	XZ32	3		EA-dilution.met
43	1.381	Sample	XZ33	4		EA-dilution.met

Line		Type	AS Sample	AS Method	Identifier 1	Identifier 2	Method
386		Sample	55	>Internal No 8	050105	clear memory	TC-EA\needle flush-new.met
387	✓	Sample	55	>Internal No 7	050105		TC-EA\HD-CO liquid-short.met
388	✓	Sample	55	>Internal No 7	050105		TC-EA\HD-CO liquid-short.met
389	✓	Sample	55	>Internal No 7	050105		TC-EA\HD-CO liquid-short.met
390	✓	Sample	55	>Internal No 7	050105		TC-EA\HD-CO liquid-short.met
391		Sample	1	>Internal No 8	PNZ	clear memory	TC-EA\needle flush-new.met
392	✓	Sample	1	>Internal No 7	PNZ		TC-EA\HD-CO liquid-short.met
393	✓	Sample	1	>Internal No 7	PNZ		TC-EA\HD-CO liquid-short.met
394	✓	Sample	1	>Internal No 7	PNZ		TC-EA\HD-CO liquid-short.met
395	✓	Sample	1	>Internal No 7	PNZ		TC-EA\HD-CO liquid-short.met
396		Sample	2	>Internal No 8	ANT	clear memory	TC-EA\needle flush-new.met
397	✓	Sample	2	>Internal No 7	ANT		TC-EA\HD-CO liquid-short.met
398	✓	Sample	2	>Internal No 7	ANT		TC-EA\HD-CO liquid-short.met
399	✓	Sample	2	>Internal No 7	ANT		TC-EA\HD-CO liquid-short.met
400	✓	Sample	2	>Internal No 7	ANT		TC-EA\HD-CO liquid-short.met
401		Sample	46	>Internal No 8	050106	clear memory	TC-EA\needle flush-new.met
402	✓	Sample	46	>Internal No 7	050106	replicate	TC-EA\HD-CO liquid-short.met
403	✓	Sample	46	>Internal No 7	050106	replicate	TC-EA\HD-CO liquid-short.met
404	✓	Sample	46	>Internal No 7	050106	replicate	TC-EA\HD-CO liquid-short.met
405	✓	Sample	46	>Internal No 7	050106	replicate	TC-EA\HD-CO liquid-short.met

File Name: D:\Instrumentation\Finnigan\Isodat NT\Global\User\Conflo II Interface\Results\TC-EA\Michaud\20060808 coal test\23_DAS_no coal_12480__060808_200348.cf

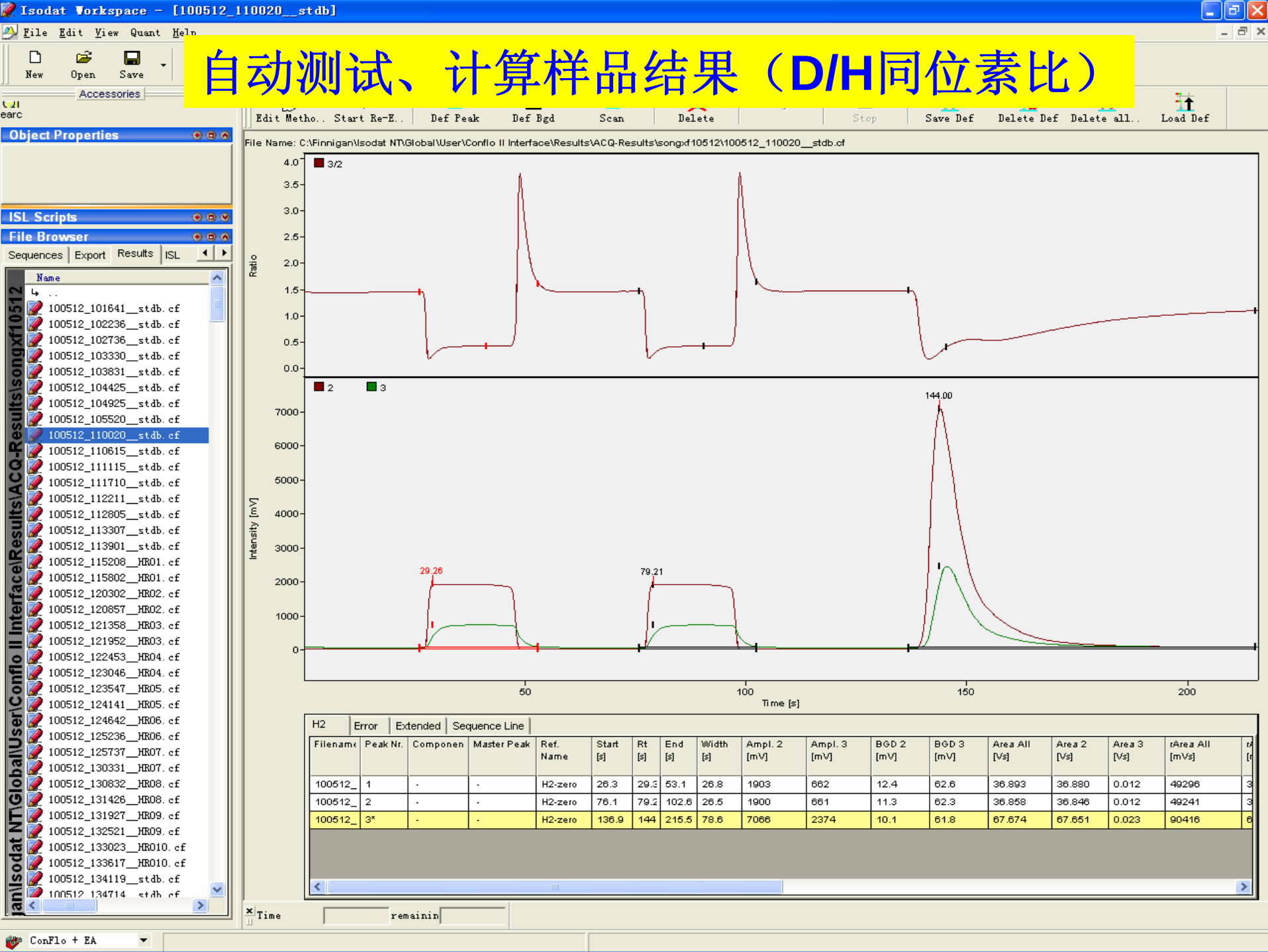
D/H、^{16}O /^{18}O同位素分析图



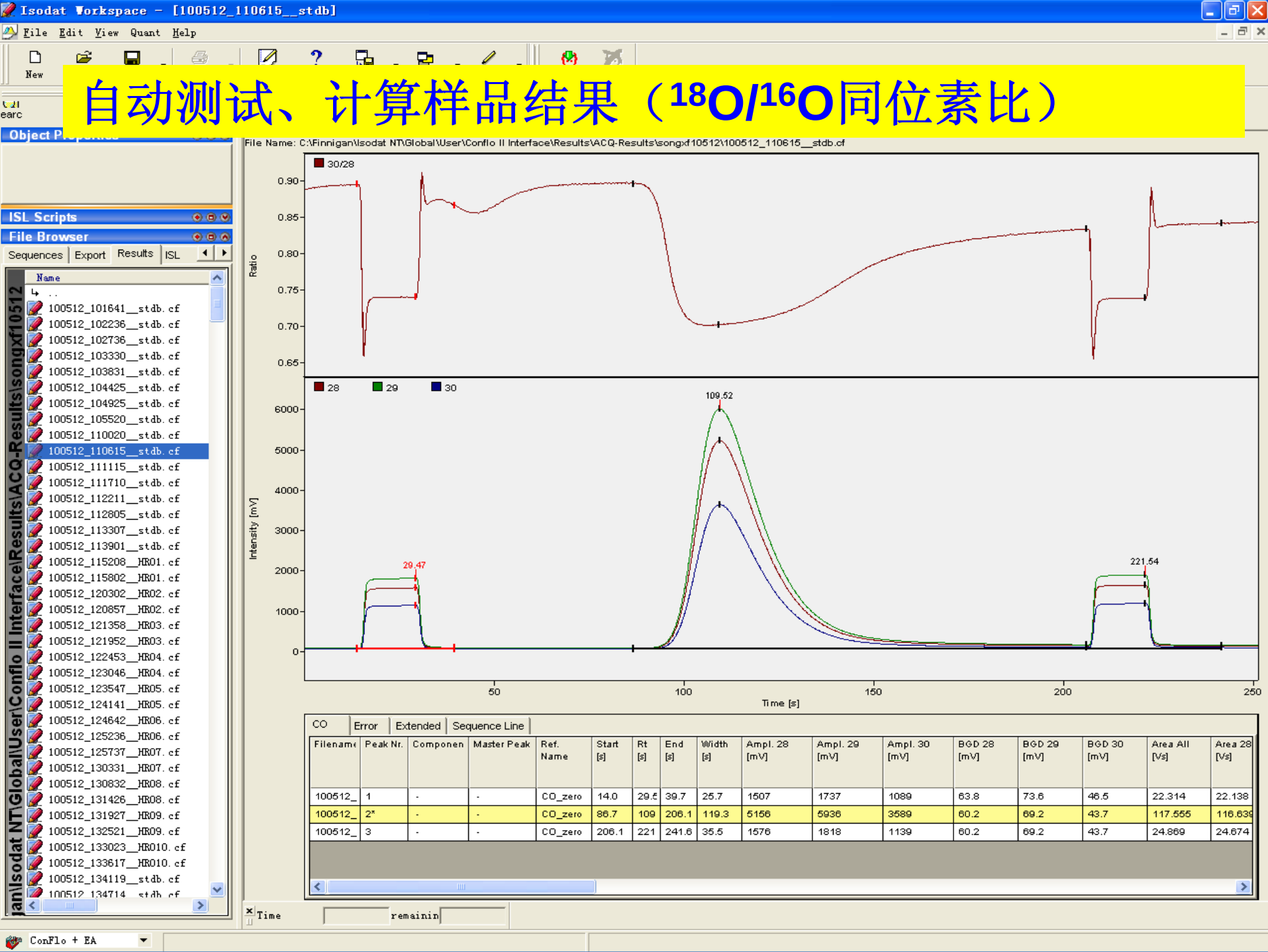
H2 | CO | Error | Extended | Sequence Line

Peak Nr.	Start [s]	Rt [s]	End [s]	Width [s]	Ampl. 2 [mV]	Area All [Vs]	Amt% [%]	R 2H/1H	d 2H/1H [per mil] vs. VSMOW	AT% 2H/1H [%]
1*	15.8	18.3	50.5	34.7	6788	194.047	-	0.000155750	0.0000	0.015573
2	77.8	88.6	131.3	53.4	11228	116.191	-	0.000166825	71.1129	0.016680

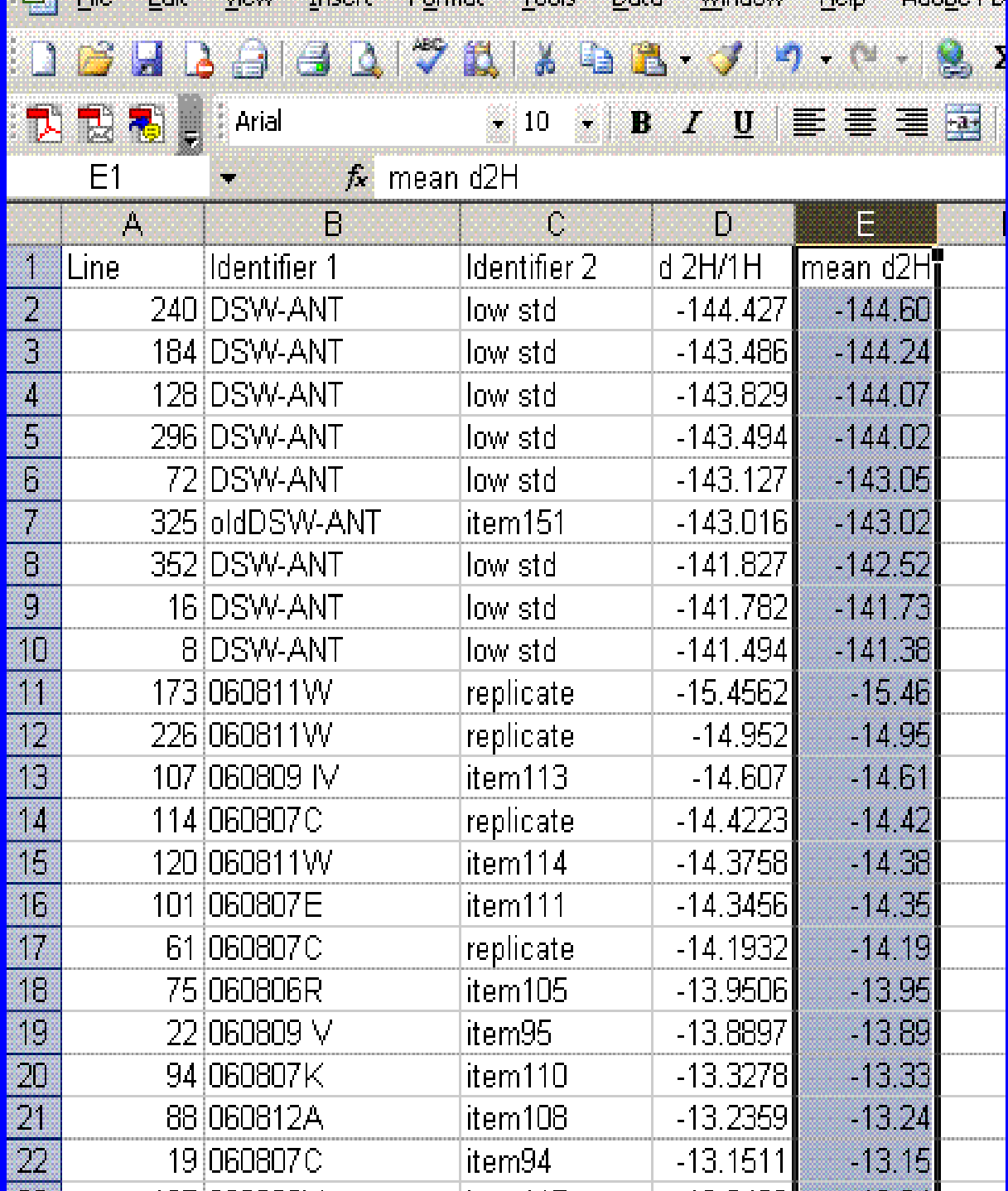
自动测试、计算样品结果（D/H同位素比）



自动测试、计算样品结果（$^{18}O/^{16}O$同位素比）



数据导出



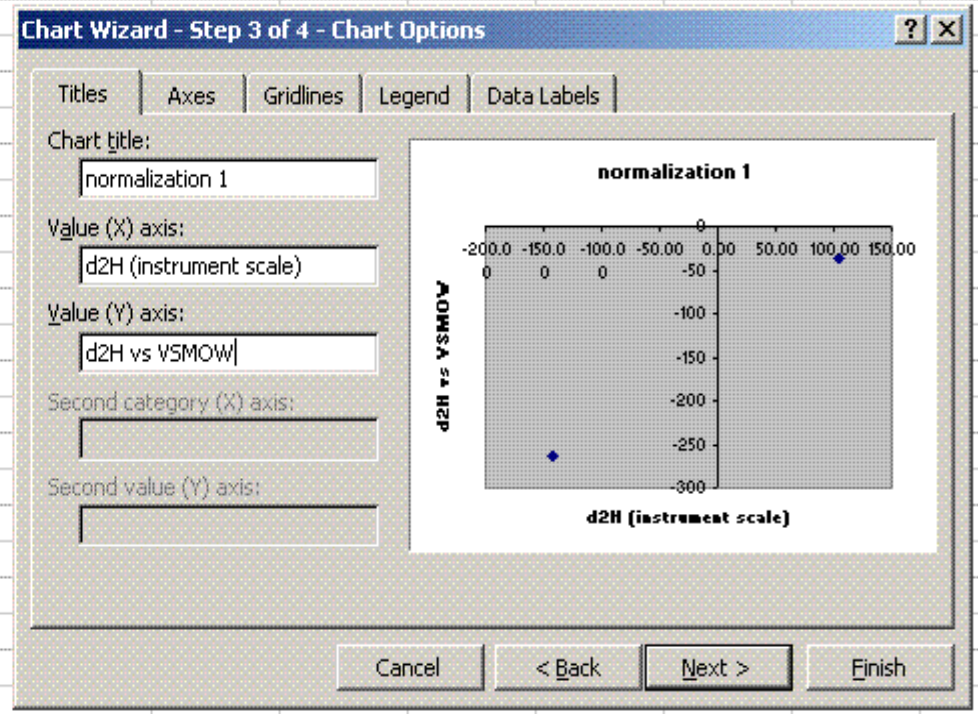
Arial 10 B I U

E1 fx mean d2H

	A	B	C	D	E
1	Line	Identifier 1	Identifier 2	d 2H/1H	mean d2H
2	240	DSW-ANT	low std	-144.427	-144.60
3	184	DSW-ANT	low std	-143.486	-144.24
4	128	DSW-ANT	low std	-143.829	-144.07
5	296	DSW-ANT	low std	-143.494	-144.02
6	72	DSW-ANT	low std	-143.127	-143.05
7	325	oldDSW-ANT	item151	-143.016	-143.02
8	352	DSW-ANT	low std	-141.827	-142.52
9	16	DSW-ANT	low std	-141.782	-141.73
10	8	DSW-ANT	low std	-141.494	-141.38
11	173	060811W	replicate	-15.4562	-15.46
12	226	060811W	replicate	-14.952	-14.95
13	107	060809 IV	item113	-14.607	-14.61
14	114	060807C	replicate	-14.4223	-14.42
15	120	060811W	item114	-14.3758	-14.38
16	101	060807E	item111	-14.3456	-14.35
17	61	060807C	replicate	-14.1932	-14.19
18	75	060806R	item105	-13.9506	-13.95
19	22	060809 V	item95	-13.8897	-13.89
20	94	060807K	item110	-13.3278	-13.33
21	88	060812A	item108	-13.2359	-13.24
22	19	060807C	item94	-13.1511	-13.15

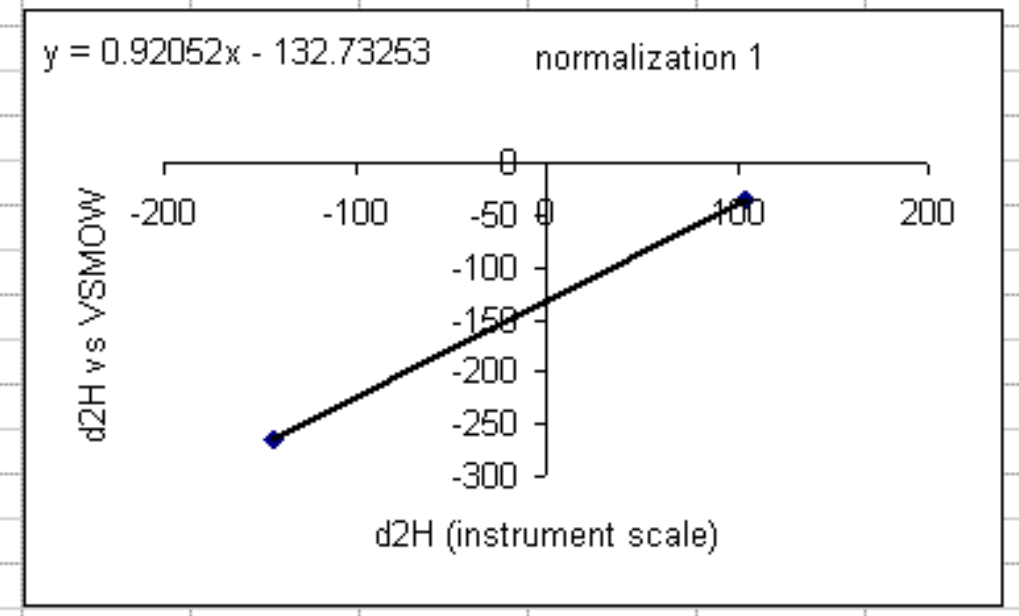
数据分析

	A	B	C	D	E	F	G	H	I	J	K	L	M
1	Line	Identifier 1	Identifier 2	mean d2H	known d2H	d2H vs VSMOW							
2	4	PNZ	high std	105.28	-36.3								
3	8	DSW-ANT	low std	-141.38	-263.5								
4	12	PNZ	high std	105.39	-36.3								
5	16	DSW-ANT	low std	-141.73	-263.5								
6	19	060807C	item94	-13.15									
7	22	060809 V	item95	-13.89									
8	25	060809 IX	item96	-11.95									
9	29	MSW	mid std	27.35	-107.7								
10	32	060812H	item97	-7.42									
11	35	060807J	item98	-11.15									
12	38	JRH060811D	item99	-12.08									
13	42	DAS	mid std	73.95	-63.7								
14	45	JRH060806L	item100	-9.83									
15	48	060807B	item101	-12.63									
16	51	060810 XIX	item102	4.13									
17	55	DMSW	mid std	-4.27	-136.7								
18	58	060810 XX	item103	4.11									
19	61	060807C	replicate	-14.19									
20	64	060805X	item104	16.76									
21	68	PNZ	high std	103.59	-36.3								
22	72	DSW-ANT	low std	-143.05	-263.5								
23	75	060806R	item105	-13.95									
24	78	060811 VI	item106	-3.02									
25	81	060811 IV	item107	-6.03									
26	85	MSW	mid std	25.28	-107.7								
27	88	060812A	item108	-13.24									



结果计算

D	E	F	G	H	I	J	K	L	M
mean d2H	known d2H	d2H vs VSMOW							
105.28	-36.3								
-141.38	-263.5								
105.39	-36.3								
-141.73	-263.5								
-13.15									
-13.89									
-11.95									
27.35	-107.7								
-7.42									
-11.15									
-12.08									
73.95	-63.7								
-9.83									
-12.63									
4.13									
-4.27	-136.7								
4.11									
-14.19									
16.76									
103.59	-36.3								
-143.05	-263.5								



一、Finnigan MAT 253

- 质谱仪工作原理
- 仪器构件及其功能
  - MAT253主机
  - CONFLLO多功能接口
  - TC-EA分析仪
  - FLASH-EA分析仪

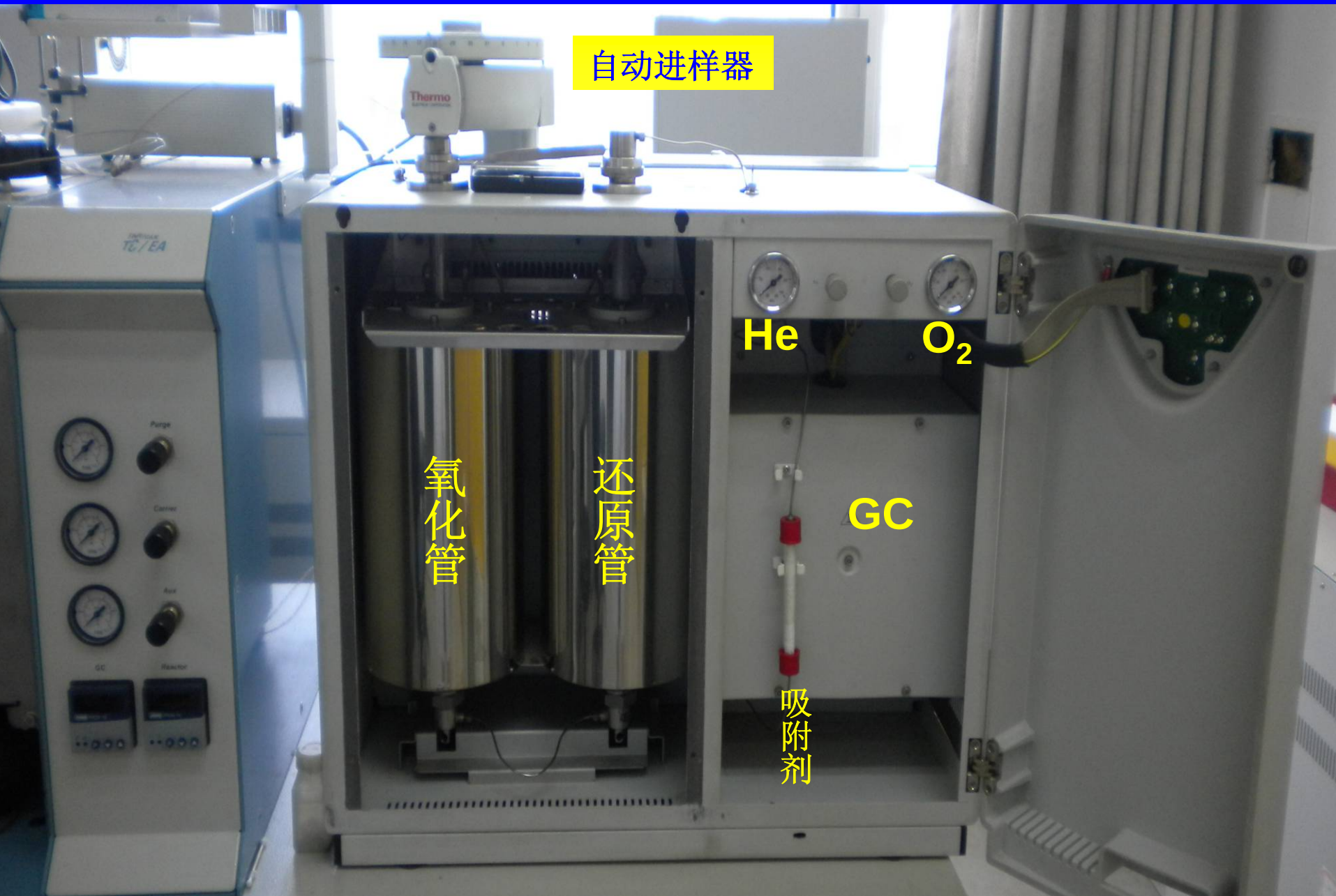

Thermo
TC / EA
FlashEA
1112 Series
Thermo
Thermo
FLASH-EA

MAT253-FLASH-EA

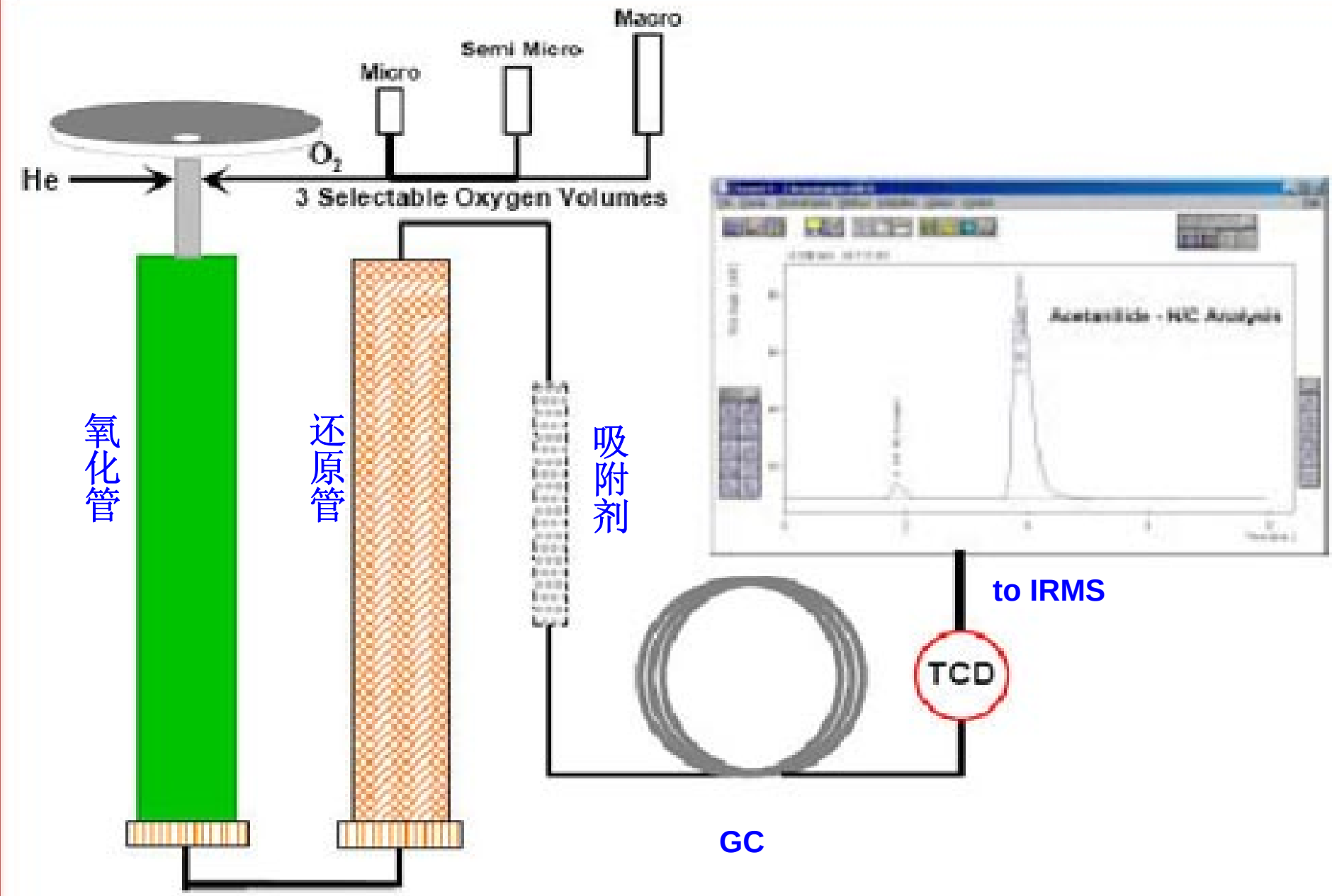
FLASH-EA仪器用于测定土壤及植物：

- **$^{15}N/^{14}N$同位素比值**
- **$^{13}C/^{12}C$同位素比值**

FLASH-EA内部结构



FLASH-EA反应原理示图示



样品制备

$^{15}N/^{14}N$ 、$^{13}C/^{12}C$同位素测定

①土壤过**2mm**土壤筛；

②植物用蒸馏水清洗；

③植物和土壤样品置于**60°C**烘干至恒重；

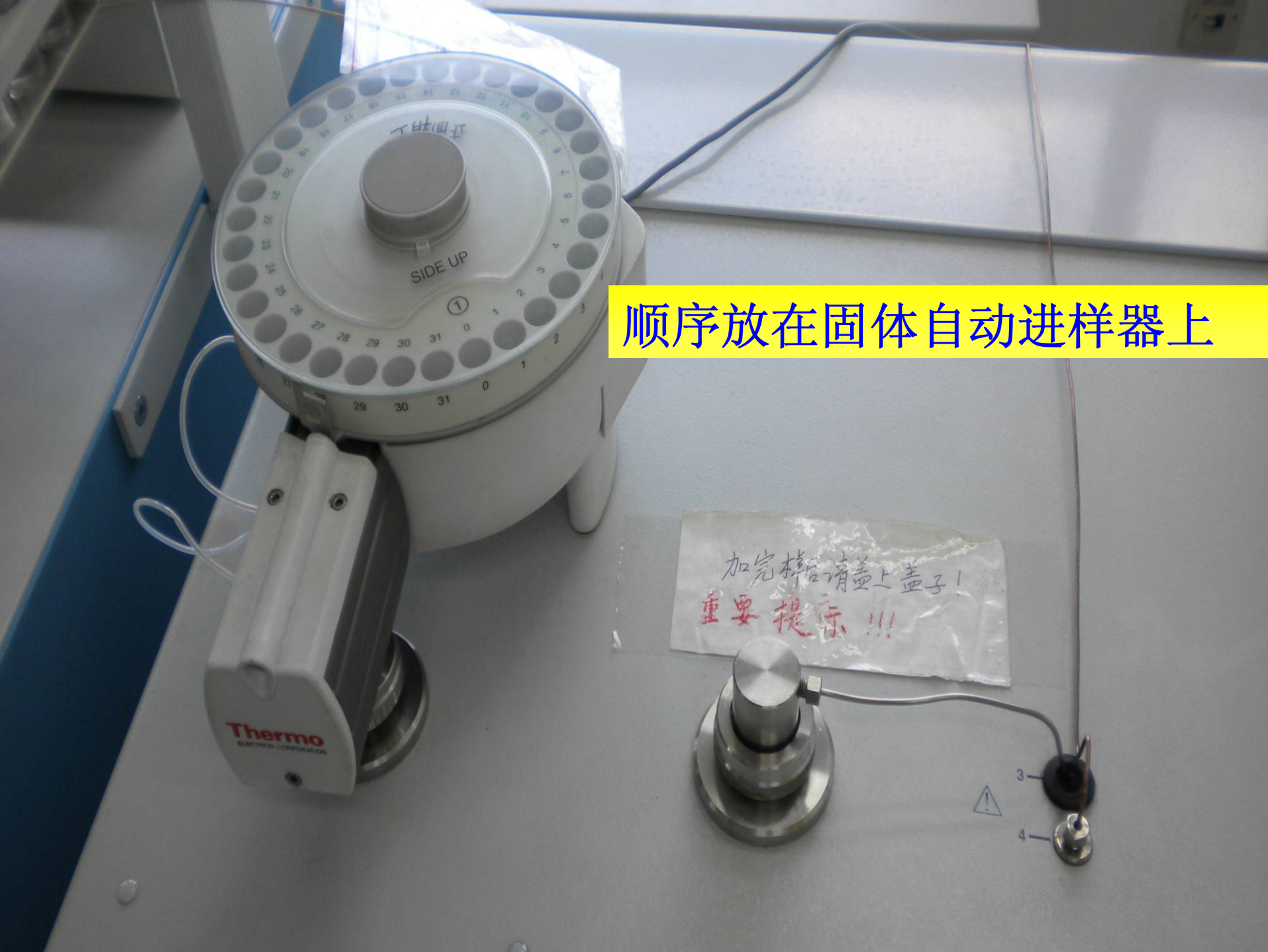
④研磨至**200**目以下；

⑤用锡杯天平称重、包裹上仪器测定

精密天平

百万分之一分析天平（感量：1微克）

称量、包裹样品



顺序放在固体自动进样器上

$^{15}N/^{14}N$ 、$^{13}C/^{12}C$同位素测定软件

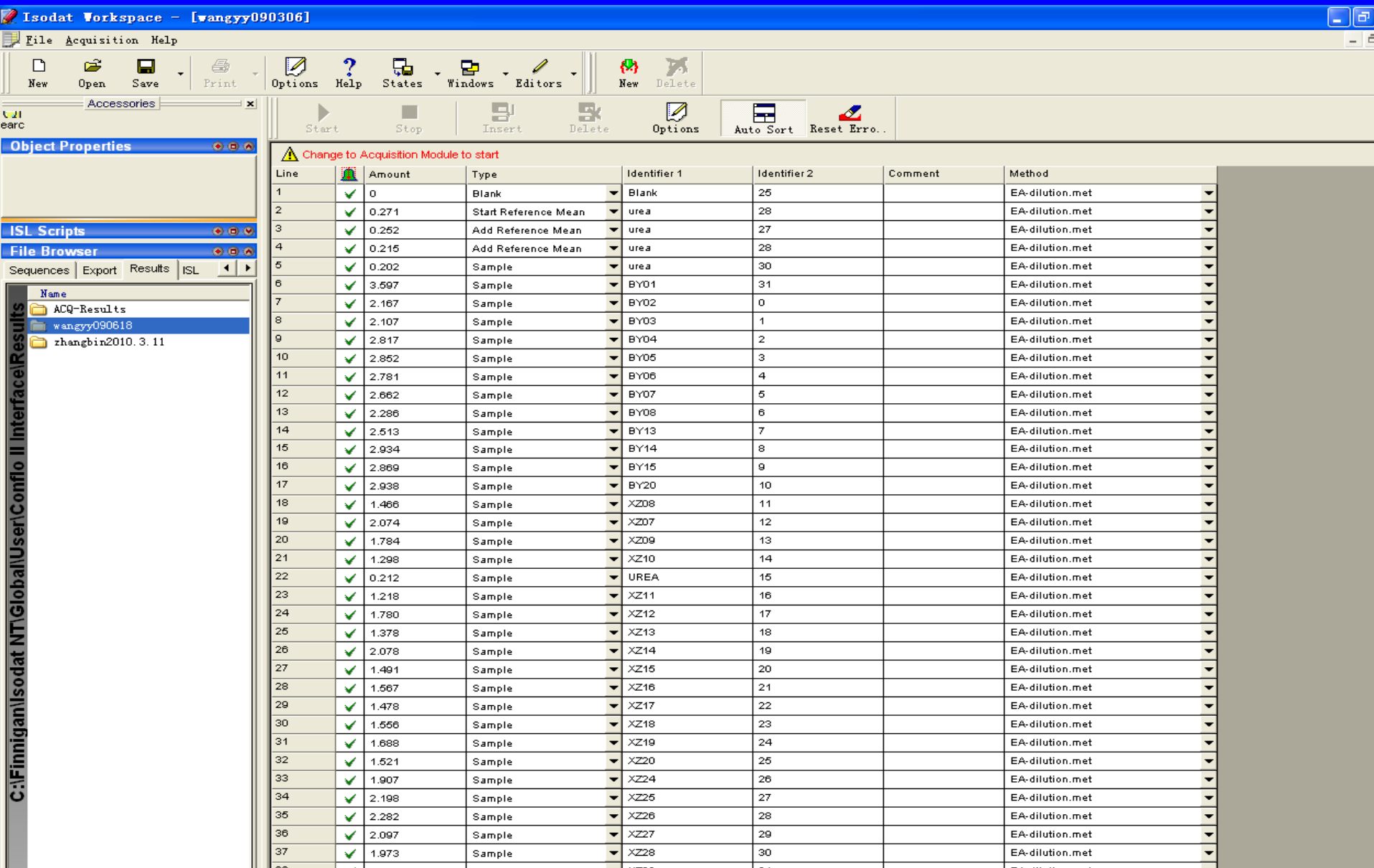
1. 在**acquisition**界面
2. 新建、编辑**sequence:**：输入样品质量、样品号、洞号等，检查正确后保存。
3. 放样品：依次将样品按号码从小到大小心夹入洞中，第一个样品为正对着圆圈的样品。每**32**个样品放一盘。注意勿将样品掉入其他洞中。然后盖好盖子（注意正面朝上），仔细检查正确。

$^{15}N/^{14}N$、$^{13}C/^{12}C$同位素测定软件

4. 在**sequence:**中选中将要开始的样品（正对着圆圈的样品）下拉至这一盘的最后一个样品（不要多选），点击**start**。则开始测定。测定过程中不能打开盖子。样品测试过程尽量不要经常翻开前面测过的样品，容易造成计算机死机。

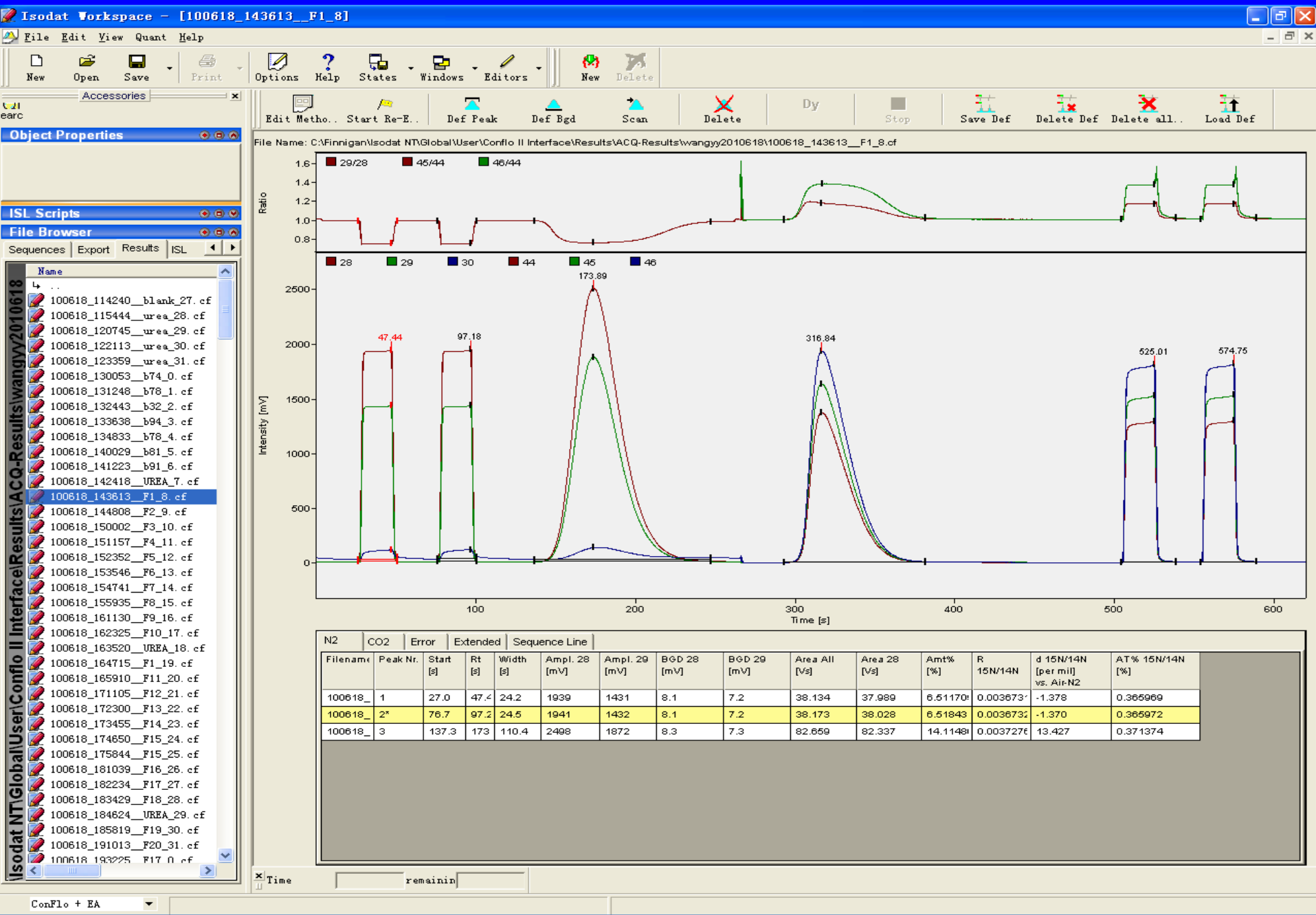
5. 如果要在中间停止，点击正在测定样品视窗上的**stop**，在“完成本样品”前打“√”，则仪器在测定完当前样品后自动停止下面样品实验。重新开始时要重新选定将要开始的下面的样品行。

编辑进样序列表（样品名称、质量信息、方法选定、开始实验）

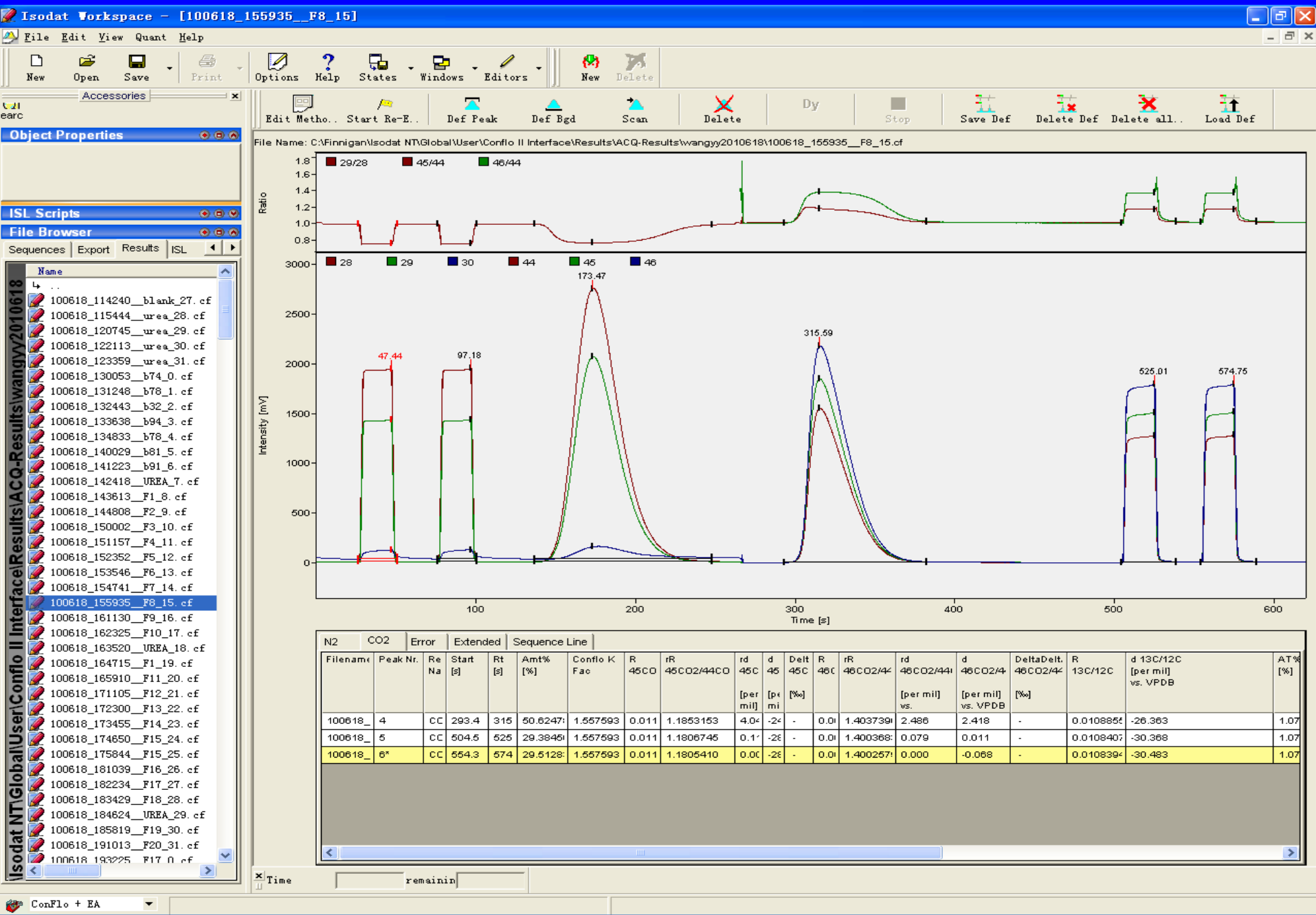


Line	Amount	Type	Identifier 1	Identifier 2	Comment	Method
1	0	Blank	Blank	25		EA-dilution.met
2	0.271	Start Reference Mean	urea	28		EA-dilution.met
3	0.252	Add Reference Mean	urea	27		EA-dilution.met
4	0.215	Add Reference Mean	urea	28		EA-dilution.met
5	0.202	Sample	urea	30		EA-dilution.met
6	3.597	Sample	BY01	31		EA-dilution.met
7	2.167	Sample	BY02	0		EA-dilution.met
8	2.107	Sample	BY03	1		EA-dilution.met
9	2.817	Sample	BY04	2		EA-dilution.met
10	2.852	Sample	BY05	3		EA-dilution.met
11	2.781	Sample	BY06	4		EA-dilution.met
12	2.662	Sample	BY07	5		EA-dilution.met
13	2.286	Sample	BY08	6		EA-dilution.met
14	2.513	Sample	BY13	7		EA-dilution.met
15	2.934	Sample	BY14	8		EA-dilution.met
16	2.869	Sample	BY15	9		EA-dilution.met
17	2.938	Sample	BY20	10		EA-dilution.met
18	1.466	Sample	XZ08	11		EA-dilution.met
19	2.074	Sample	XZ07	12		EA-dilution.met
20	1.784	Sample	XZ09	13		EA-dilution.met
21	1.298	Sample	XZ10	14		EA-dilution.met
22	0.212	Sample	UREA	15		EA-dilution.met
23	1.218	Sample	XZ11	16		EA-dilution.met
24	1.780	Sample	XZ12	17		EA-dilution.met
25	1.378	Sample	XZ13	18		EA-dilution.met
26	2.078	Sample	XZ14	19		EA-dilution.met
27	1.491	Sample	XZ15	20		EA-dilution.met
28	1.567	Sample	XZ16	21		EA-dilution.met
29	1.478	Sample	XZ17	22		EA-dilution.met
30	1.556	Sample	XZ18	23		EA-dilution.met
31	1.688	Sample	XZ19	24		EA-dilution.met
32	1.521	Sample	XZ20	25		EA-dilution.met
33	1.907	Sample	XZ24	26		EA-dilution.met
34	2.198	Sample	XZ25	27		EA-dilution.met
35	2.282	Sample	XZ26	28		EA-dilution.met
36	2.097	Sample	XZ27	29		EA-dilution.met
37	1.973	Sample	XZ28	30		EA-dilution.met

样品测定图例（ $^{15}N/^{14}N$同位素比）



样品测定图例（ $^{13}C/^{12}C$同位素比）



自动计算输出结果

Sample No.	称重 (mg)	Peak	Amt%	d 15N/14N	AT% 15N/14N	d 13C/12C	AT% 13C/12C
urea	0.271	1	54.619	-1.836	0.365		
urea	0.271	2	54.666	-1.598	0.365		
urea	0.271	3	46.685	-1.418	0.365		
urea	0.271	4	19.430			-43.051	1.058
urea	0.271	5	23.561			-30.662	1.072
urea	0.271	6	23.268			-30.897	1.071
A1	2.225	1	4.220	-1.866	0.365		
A1	2.225	2	4.224	-1.598	0.365		
A1	2.225	3	1.681	-1.348	0.365		
A1	2.225	4	47.092			-29.109	1.073
A1	2.225	5	17.095			-30.85	1.071
A1	2.225	6	17.183			-30.897	1.071