北京大学
PEKING UNIVERSITY

PANDA X

Ultra-low radionuclide concentration measurement lab in School of Physics and High Energy Physics Centre, PKU*

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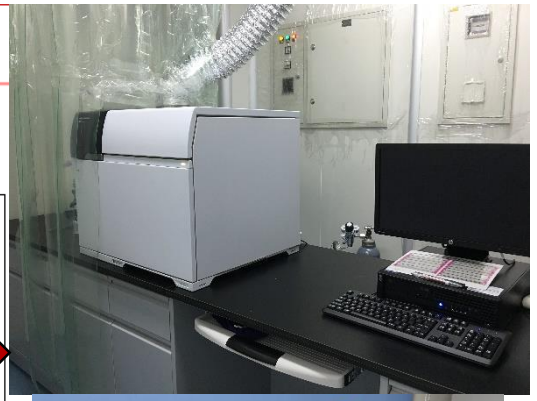
中国物理学会高能物理分会第十二届全国粒子物理学术会议, August 24, 2016

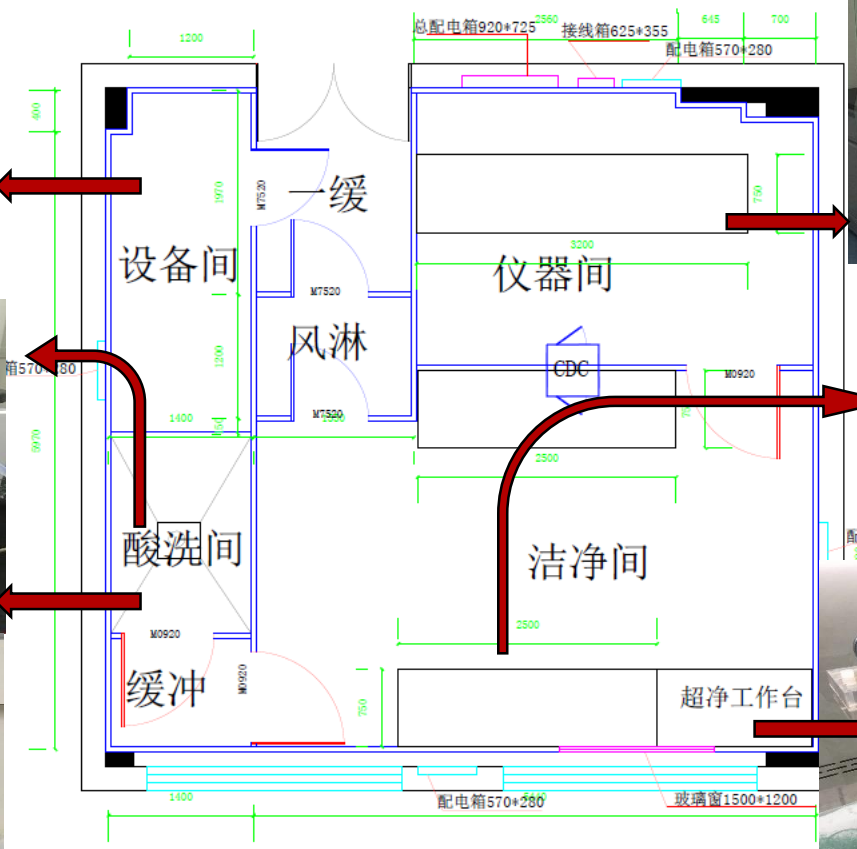
*Supported by Pandax Group

Outline

1. Brief introduction to Trace Analysis Lab
2. ICP-MS & Sample Preparation System
3. Several Exploratory Experiments

Schematic Diagram for the lab





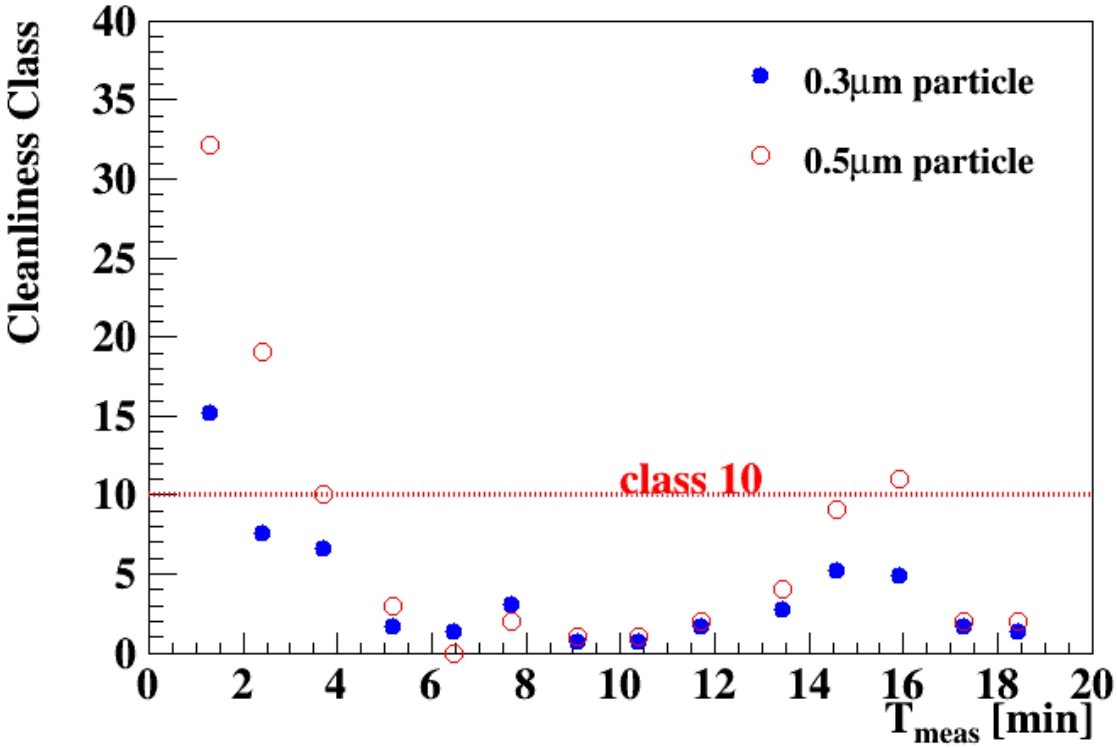
ISO 14644-1 cleanroom standards

Cleanrooms are classified according to the counts and size of particles permitted per volume of air.

Class	maximum particles/m^3						FED STD 209E equivalent
	≥0.1 µm	≥0.2 µm	≥0.3 µm	≥0.5 µm	≥1 µm	≥5 µm	
ISO 1	10	2.37	1.02	0.35	0.083	0.0029	
ISO 2	100	23.7	10.2	3.5	0.83	0.029	
ISO 3	1,000	237	102	35	8.3	0.29	Class 1
ISO 4	10,000	2,370	1,020	352	83	2.9	Class 10
ISO 5	**100,000**	**23,700**	**10,200**	**3,520**	**832**	**29**	**Class 100**
ISO 6	1.0×10^6	237,000	102,000	35,200	8,320	293	Class 1,000
ISO 7	1.0×10^7	2.37×10^6	1,020,000	352,000	83,200	2,930	Class 10,000
ISO 8	1.0×10^8	2.37×10^7	1.02×10^7	3,520,000	832,000	29,300	Class 100,000
ISO 9	1.0×10^9	2.37×10^8	1.02×10^8	35,200,000	8,320,000	293,000	Room air

https://en.wikipedia.org/wiki/Cleanroom

Cleanliness Measurement in Sample Preparation Room (Apr. 16,2016)



Cleanliness in Chemical Hood(Mar. 7, 2016)

Time(minutes)	Class (0.3μm)	Class (0.5μm)	Class (1.0μm)
0	104.6	200.8	344.0
1.45	27.4	70.3	85.0
2.90	10.4	21.1	21.3
4.35	3.8	5.0	12.7
5.80	2.8	1.0	0.0
7.25	6.2	11.1	4.2
8.70	4.9	8.0	4.2
10.15	2.1	4.0	8.5
11.60	2.1	4.0	4.2
13.05	4.2	2.0	0.0
14.50	4.5	7.0	8.5
15.95	5.2	6.0	0.0
17.40	4.2	6.0	8.5

Cleanliness Measurement in Super Clean Bench (Apr.26,2016)

ROOM:02
LOCATION: 01/01
CYCLE: 001/001
DATE:2016-04-26
TIME: 10:21:01
PERIOD: 120Sec
VOLUME:1m³

SIZE	CUMU
0.3㎛	18
0.5㎛	0
1.0㎛	0
3.0㎛	0
5.0㎛	0
10.㎛	0

LOCATION: 01/01
CYCLE: 003/001
DATE:2016-04-26
TIME: 10:25:45
PERIOD: 120Sec
VOLUME:1m³

SIZE	CUMU
0.3㎛	18
0.5㎛	0
1.0㎛	0
3.0㎛	0
5.0㎛	0
10.㎛	0

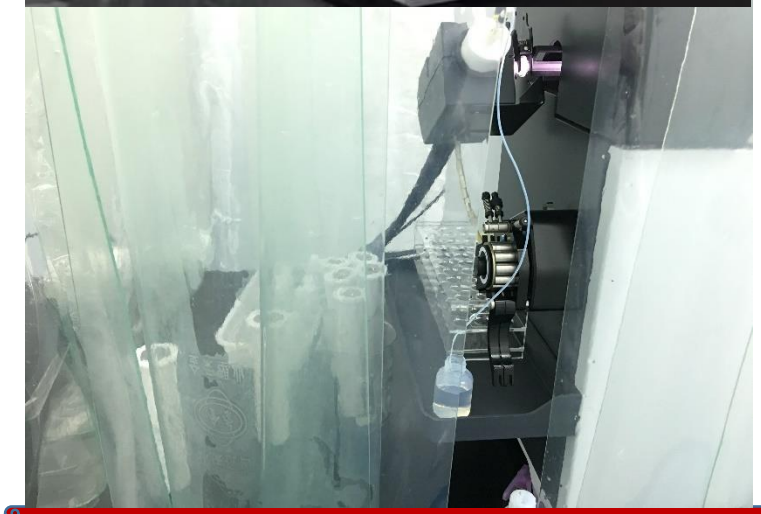
ROOM:02
LOCATION: 01/01
CYCLE: 002/001
DATE:2016-04-26
TIME: 10:23:23
PERIOD: 120Sec
VOLUME:1m³

SIZE	CUMU
0.3㎛	0
0.5㎛	0
1.0㎛	0
3.0㎛	0
5.0㎛	0
10.㎛	0

ROOM:02
LOCATION: 01/01
CYCLE: 004/001
DATE:2016-04-26
TIME: 10:28:07
PERIOD: 120Sec
VOLUME:1m³

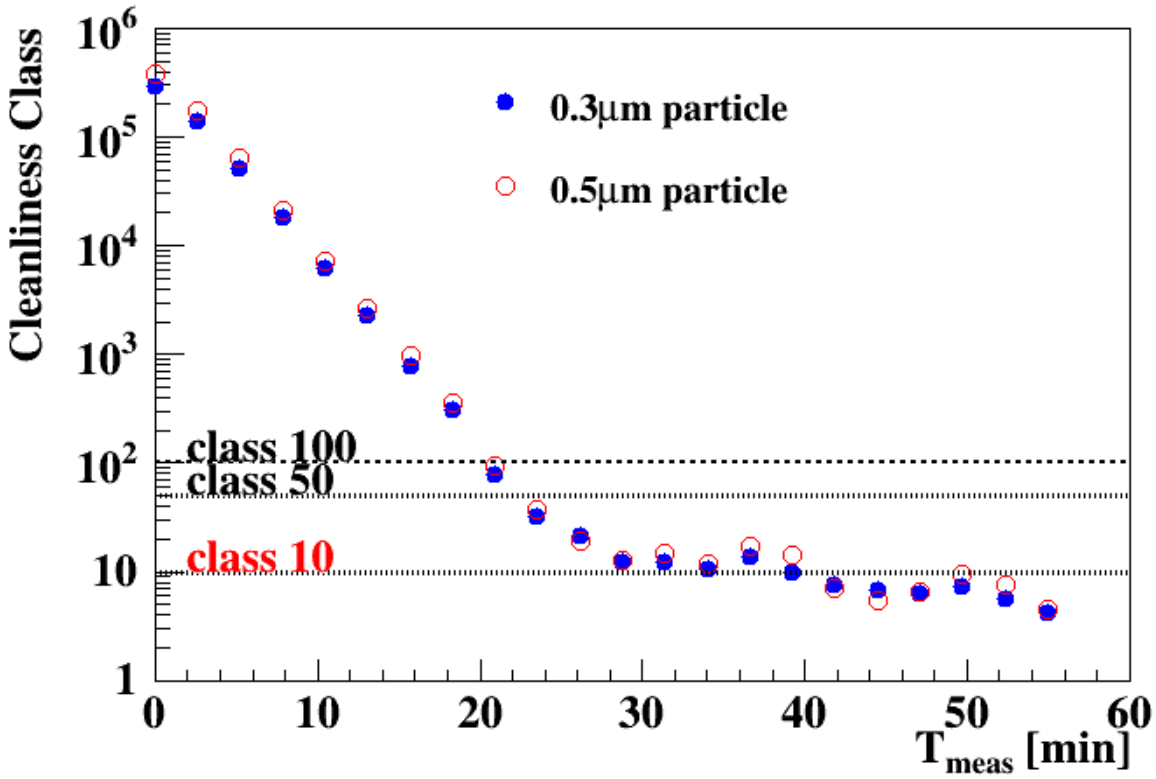
SIZE	CUMU
0.3㎛	0
0.5㎛	0
1.0㎛	0
3.0㎛	0
5.0㎛	0
10.㎛	0

Cleanliness Measurement in the Injection Port of ICP-MS



Time(minutes)	Class (0.3μm)	Class (0.5μm)	Class (1.0μm)
0	0. 0	0. 0	0. 0
1. 45	0. 0	0. 0	0. 0
2. 9	0. 0	0. 0	0. 0
4. 35	0. 3	0. 0	0. 0

Cleanliness Measurement in buffer area (May 8, 2016)



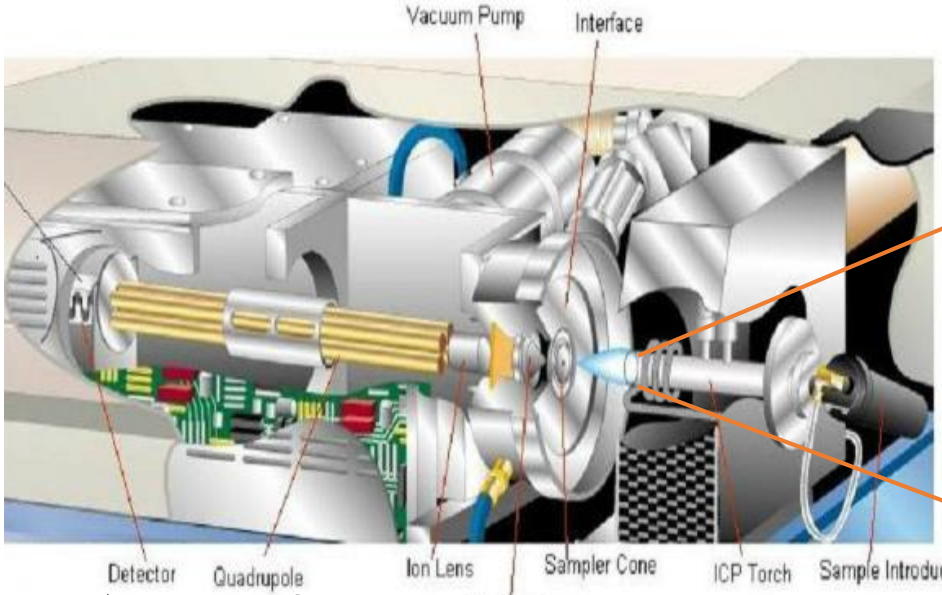
Outline

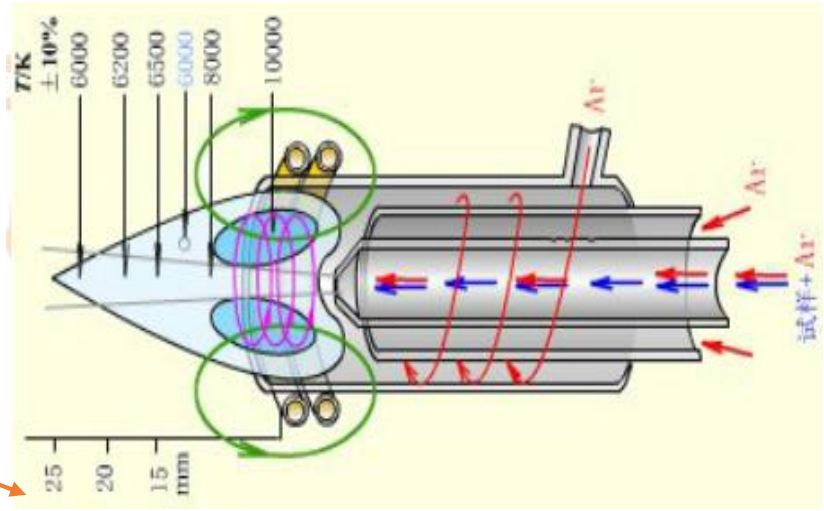
1. Brief introduction to Trace Analysis Lab

2. **ICP-MS & Sample Preparation System**

3. Several Exploratory Experiments

ICP-MS





- High frequency current excites alternating electromagnetic field
- Argon gas was ionized by high voltage electric spark, the ions of Argon are collided each other to product inductive current and heat the gas into plasma
- Sample molecules break apart, and then the constituent atoms ionize.
- Ions are separated on the basis of their mass-charge ratio in quadrupole and a detector receives an ion signal proportional to the concentration

ICP-MS (Agilent 7900)

Agilent Technologies

承 诺 书

致：北京大学实验室与设备管理部

关于贵方设备采购项目：北京大学物理学院“电感耦合等离子体质谱仪”招标采购项目（第 2015【022】号），我方作出以下承诺：

（1） 设备到货后，U238 灵敏度（按照斜率计算）能达到 1000Mcps/ppm，同时，检出限可以达到 5ppq；

（2） 如果设备到货验收时达不到第一条所述指标（即 U238 灵敏度（按照斜率计算）达到 1000Mcps/ppm 同时检出限可以达到 5ppq），免费即时更换能达到指标的新仪器一台，或者退货赔偿用户损失 5 万元人民币；

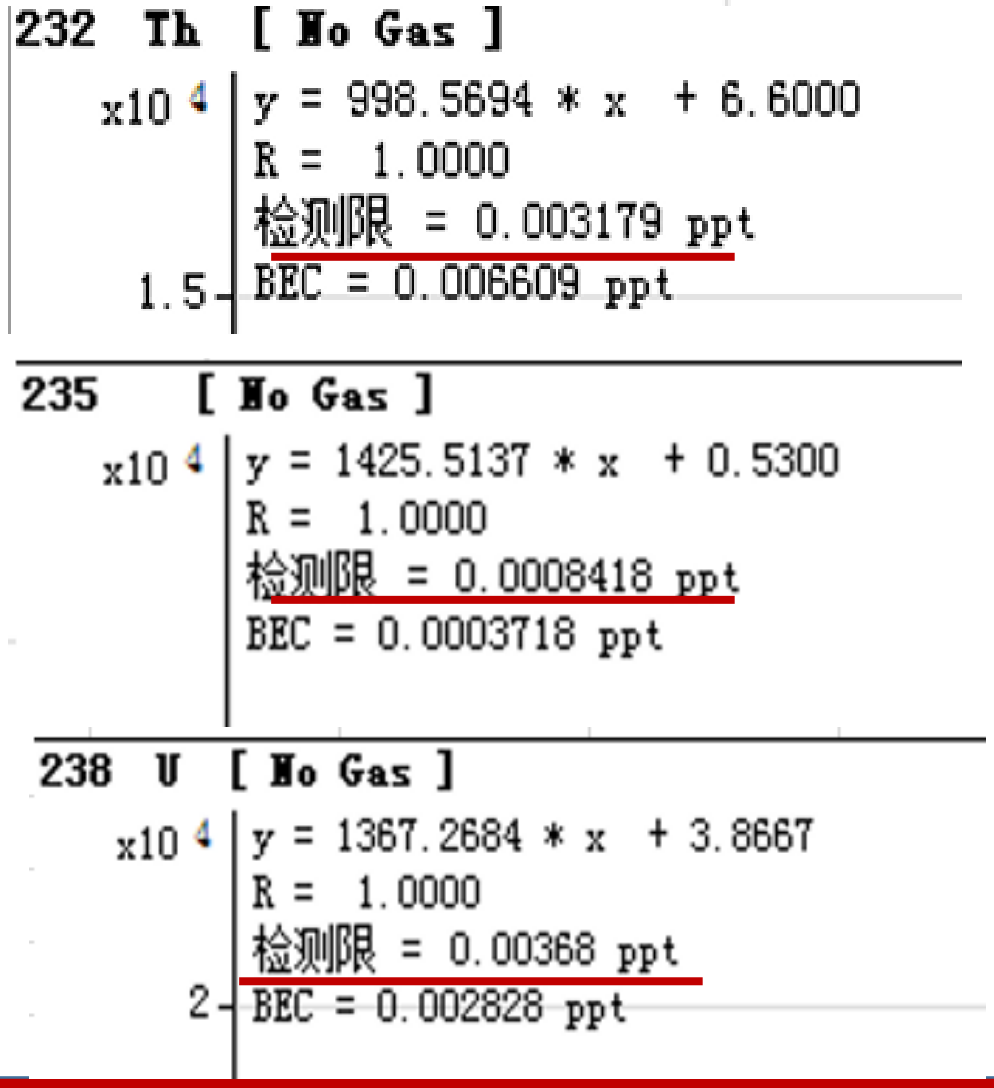
此承诺。

Agilent Technologies Singapore (Sales) Pte Ltd.

2015 年 7 月 21 日

CHEONG Chiang Huo, David
Director, Business Operations
South Asia Pacific and Korea Regional Sales Operations
For and on behalf of
AGILENT TECHNOLOGIES SINGAPORE (SALES) PTE LTD

ICP-MS (Agilent 7900)



Sample Preparation

1. Preparation of Reagents

Savillex DST-1000

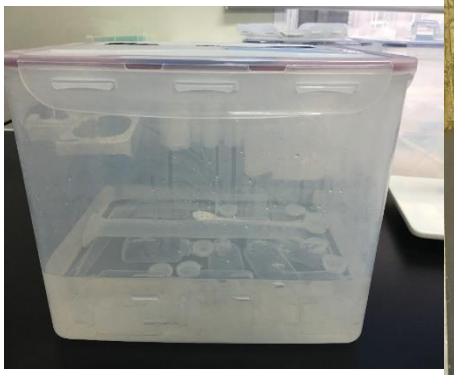
➢ Experimental water：
18.2MΩ·cm Milli-Q water

Th & U in HNO_3 and HCl

Sample	232 Th CPS (RSD)	235 U CPS (RSD)	238 U CPS (RSD)
5% HNO_3	6.6 (16.035)	0.53 (75.472)	3.867 (43.378)
0.1 M HCl	3.733 (24.157)	-0.47 (0)	0.933 (53.927)

Sample Preparation

2. Preparation of Labware and Sample



weighting error :0.02mg

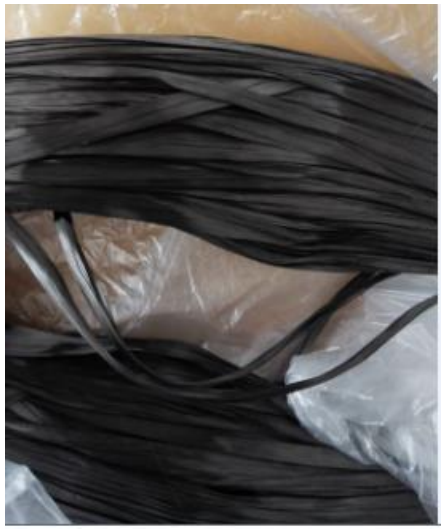
- Before using, all vials, comtainers and lids were **soaked in HNO_3** at least for three days
- After proper leach with 18.2MΩ.cm Milli-Q deionized water, the labware required were cleaned **by ultrasonic cleaner in UPW** for at least ten minutes
- At last , **triply rinse with 18.2MΩ.cm Milli-Q deionized water**, blow dry and set aside

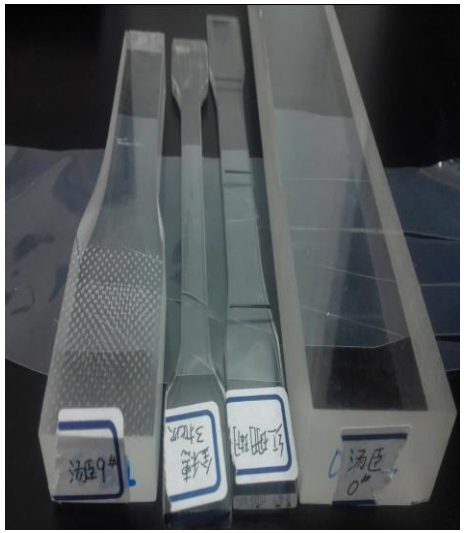
Sample Preparation

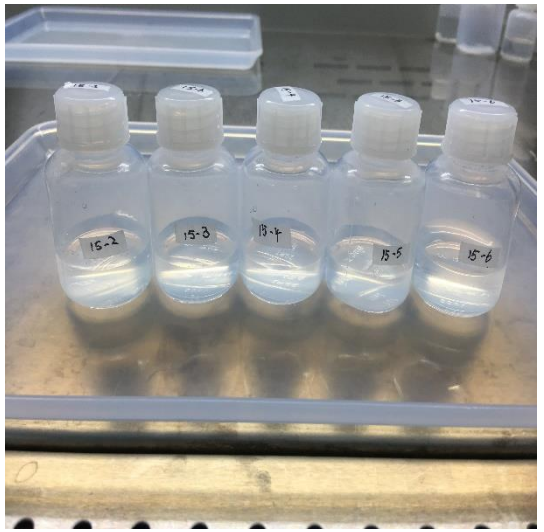
3. Sample digestion (analytikjena TOPwave)

Material	TFM®, PEEK, quartz, aluminium oxide				
	Volume	Max. pressure	Max. temperature	max. sample weight (organic)	Min. fill volume (acid)
CX 100	100 ml	100 bar (1450 psi)	230 °C (446 °F)	< 1000 mg	> 7 ml

Microwave System for Pressure Digestion
(analytikjena TOPwave)







select as favourite (0..12): 5

	temperature	pressure	ramp	time	power
1	90	80	5	10	60
2	120	80	5	10	80
3	220	80	10	30	80
4	50	80	5	5	0
5	50	80	5	0	0

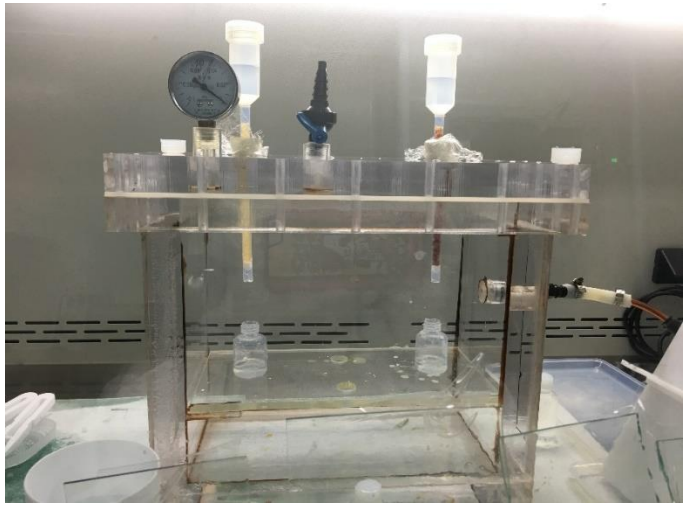
int	p-band	total time	vessel	magT
1	20	85	8	120

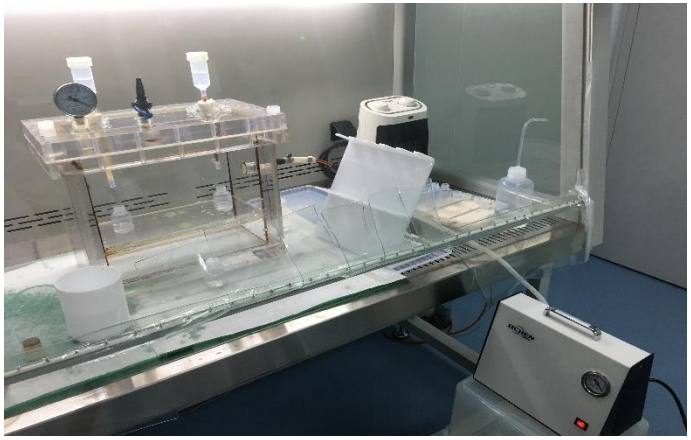
	T	p	ramp	time	power
1	110	80	20	5	50
2	170	80	15	5	90
3	200	80	15	15	90
4	230	80	5	20	90
5	50	0	1	1	0

int	p-band	total time	vessel	mag temp.
20	20	102	8	120

Sample Preparation

4. Separation & Preconcentration





Anion exchange resin :

Bio-Rad Corp AG 1×4, 100–200

Separation:

$$2R\text{-}NO_3^- + UO_2(NO_3)_4^{2-} \leftrightarrows R_2\text{-}UO_2(NO_3)_4^{2-} + 2NO_3^-$$

$$2R\text{-}NO_3^- + Th(NO_3)_6^{2-} \leftrightarrows R_2\text{-}Th(NO_3)_6^{2-} + 2NO_3^-$$

Concentration:

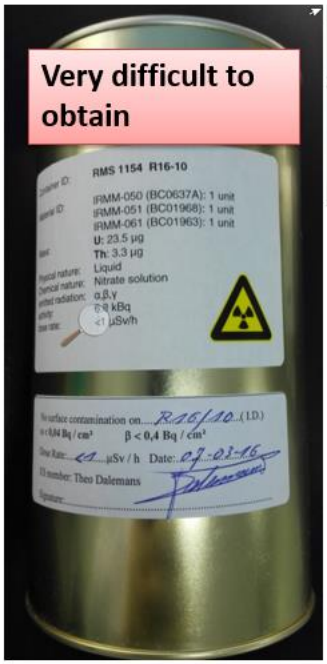
$$R_2\text{-}UO_2(NO_3)_4^{2-} + 2Cl^- \leftrightarrows 2R\text{-}Cl^- + UO_2^{2+} + 4NO_3^-$$

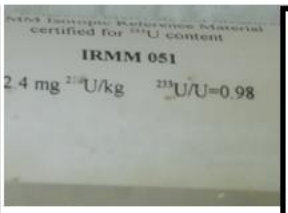
$$R_2\text{-}Th(NO_3)_6^{2-} + 6Cl^- \leftrightarrows 2R\text{-}Cl^- + ThCl_{4(aq)} + 6NO_3^-$$

Quantitative Analysis

1. a linear external calibration
2. the recovery of standard addition

$$\text{Recovery} = \frac{A_{tracer}}{C_{tracer}} \times 100\%$$





mass fraction (·100)	
$m(^{233}U)/m(U)$	98.020 1(58)
$m(^{234}U)/m(U)$	0.918 3(02)
$m(^{235}U)/m(U)$	0.216 0(56)
$m(^{236}U)/m(U)$	0.024 4(03)
$m(^{238}U)/m(U)$	0.821 2(20)

2.3539(42)ppm ^{233}U

mass fraction (·100)	
$m(^{234}U)/m(U)$	0.035 9(02)
$m(^{235}U)/m(U)$	99.941 4(18)
$m(^{236}U)/m(U)$	0.009 6(10)
$m(^{238}U)/m(U)$	0.013 1(03)

0.9999(25)ppm ^{235}U

mass fraction (·100)	
$m(^{230}Th)/m(Th)$	99.849(50)
$m(^{232}Th)/m(Th)$	0.151(50)

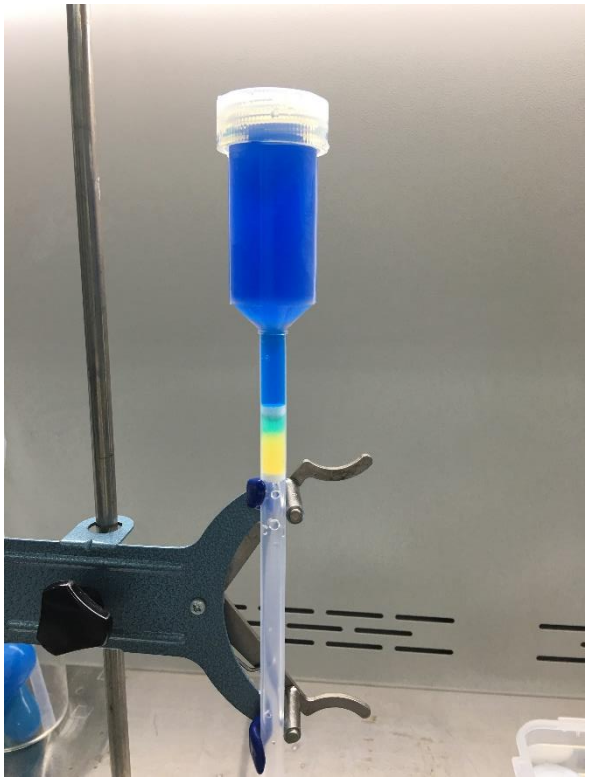
0.5691(42)ppm ^{230}Th

Outline

1. Brief introduction to Trace Analysis Lab
2. ICP-MS & Sample Preparation System
3. **Several Exploratory Experiments**

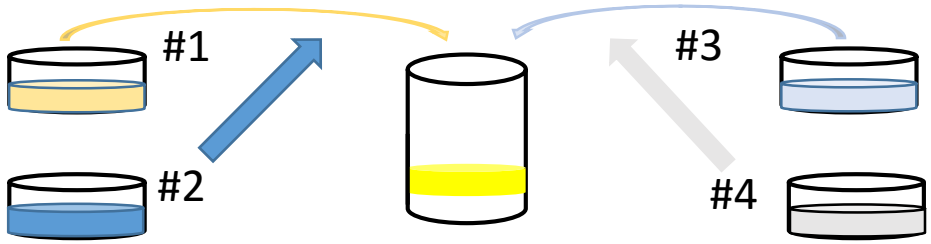
Experimental Section

1. Cu



flow rate ： 0.05ml/min

Pre-cleaning:



#1： 2 ml 8M HNO_3 #2: 2ml UPW

#3: 2ml HCl (37%) #4： 8ml 0.1 M HCl

Concentration：

$$2R\text{-}NO_3^- + UO_2(NO_3)_4^{2-} \leftrightarrows R_2\text{-}UO_2(NO_3)_4^{2-} + 2NO_3^-$$

$$2R\text{-}NO_3^- + Th(NO_3)_6^{2-} \leftrightarrows R_2\text{-}Th(NO_3)_6^{2-} + 2NO_3^-$$

$$R_2\text{-}UO_2(NO_3)_4^{2-} + 2Cl^- \leftrightarrows 2R\text{-}Cl^- + UO_2^{2+} + 4NO_3^-$$

$$R_2\text{-}Th(NO_3)_6^{2-} + 6Cl^- \leftrightarrows 2R\text{-}Cl^- + ThCl_{4(aq)} + 6NO_3^-$$

8M HNO_3 → Sample loaded → 8 M HNO_3 → 0.1 M HCl

Results and discussion

Initial Cu sample (g)： 9.05589
Surface preparation (g)： 6.26617
Amount of digestion (g)： 6.26617

1.1 20160615

$$\text{Recovery} = \frac{A_{tracer}}{C_{tracer}} \times 100\%$$

Tracer_^{235}U (pg)	Tracer_^{235}U_ICP-MS (pg)	Recovery
621.136	1.1922(0.0155)	0.1919%
^{232}Th_ana (pg)	Tot-in-Cu (pg)	Concentration(pg/g)
5.9547(0.1664)	2933.7286	~~468.1853(0.1664)~~
^{238}U_ana (pg)	Tot-in-Cu (pg)	Concentration(pg/g)
1.1966(0.0058)	560.5987	89.4643(0.0058)

Experimental Section

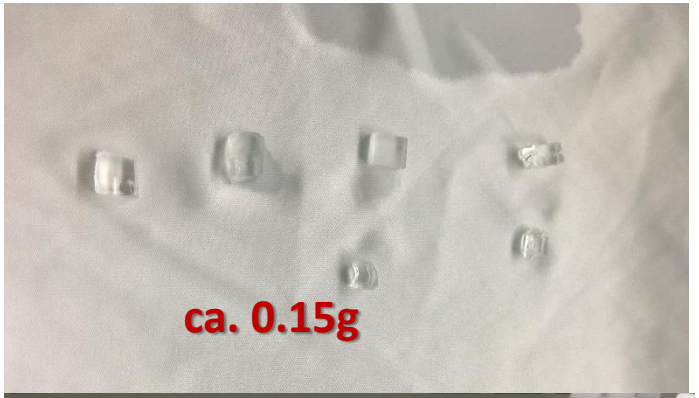
2. A comparison of two composite resins

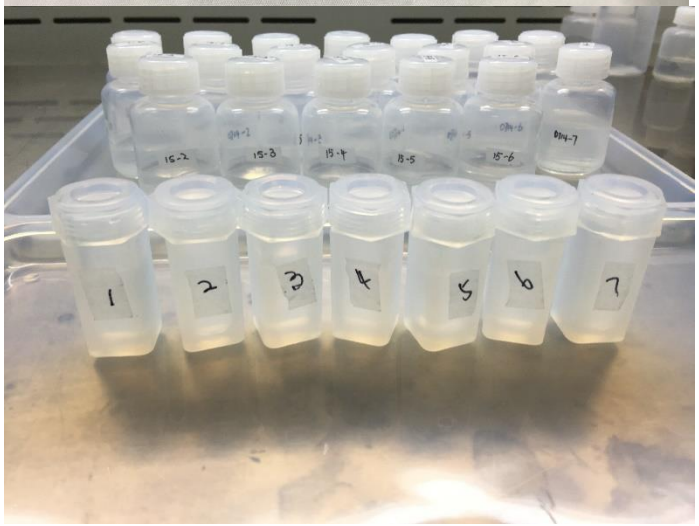
ca. 9ml
flow rate ： 1 ml/min

Sample	232 Th CPS (RSD)	235 U CPS (RSD)	238 U CPS (RSD)
Watson water	1 (20)	-0.27 (-128.300)	1.733 (24.019)
Watson water resin-I	0.867 (13.323)	-0.27 (-74.074)	-0.067 (-346.410)
Watson water resin-D	0.733 (56.773)	-0.403 (-28.629)	0.133 (312.250)
Spiked solution ca. 0.3 pg/g	343.607 (0.717)	503.673 (1.949)	424.01 (2.795)
Spiked solution resin-I	2.067 (29.565)	-0.27 (-128.300)	2.133 (48.109)
Spiked solution resin-D	2.533 (31.906)	-0.137 (-223.540)	1.133 (100.345)

Experimental Section

3. Acrylic





the problems :

- Efficient cutting method
- The total chemical blank
- Fast cleaning for high pressure digestion tank

Summary

1. Quickly and convenient cleaning technology for all the vials, containers and lids

2. The recovery of standard addition

3. Minimize the total chemical blank:
   - ✓vessels, reagent, specification operation

4. Seek optimal experimental scheme and equipment

Still need learn more about trace analysis!

Thanks

Any suggestion or question will be thankful!

袁 影
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