农业元素分析检测领域最新应用进展-

纳米颗粒

大数据分析

余晶晶

ICP-MS应用工程师

Agilent
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纳米颗粒

纳米颗粒物简介

来源

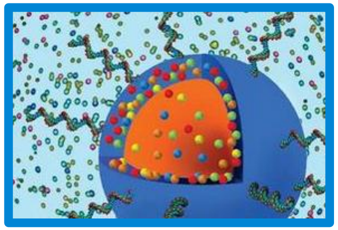
自然产生

风化，矿化，火山喷发，沙尘暴……

人类活动

排放到大气、水、土壤中

石化燃烧，机械磨损，金属冶炼和产品生产，机动车……



人工合成纳米材料 (ENPs)

根据需求而特别设计的纳米材料

碳纳米管，电子开关，药物…

纳米颗粒物简介

人工合成纳米材料 (ENPs)

- 日用消费品-防晒霜，化妆品…
- 食品添加剂和包装
- 药物和靶标
- 消毒纱布
- 半导体生产
- 超导材料
- 农药
- …







Many Methods for NP characterization

- **Imaging** methods (TEM, SEM, AFM)
- **Spectroscopic/optical** methods (UV-Vis, dynamic light scattering)
- **Hyphenated techniques** (Chromatographic (or other online) separation coupled with ICP-MS detection).

FFF-ICP-MS

CE -ICP-MS

HPLC-ICP-MS

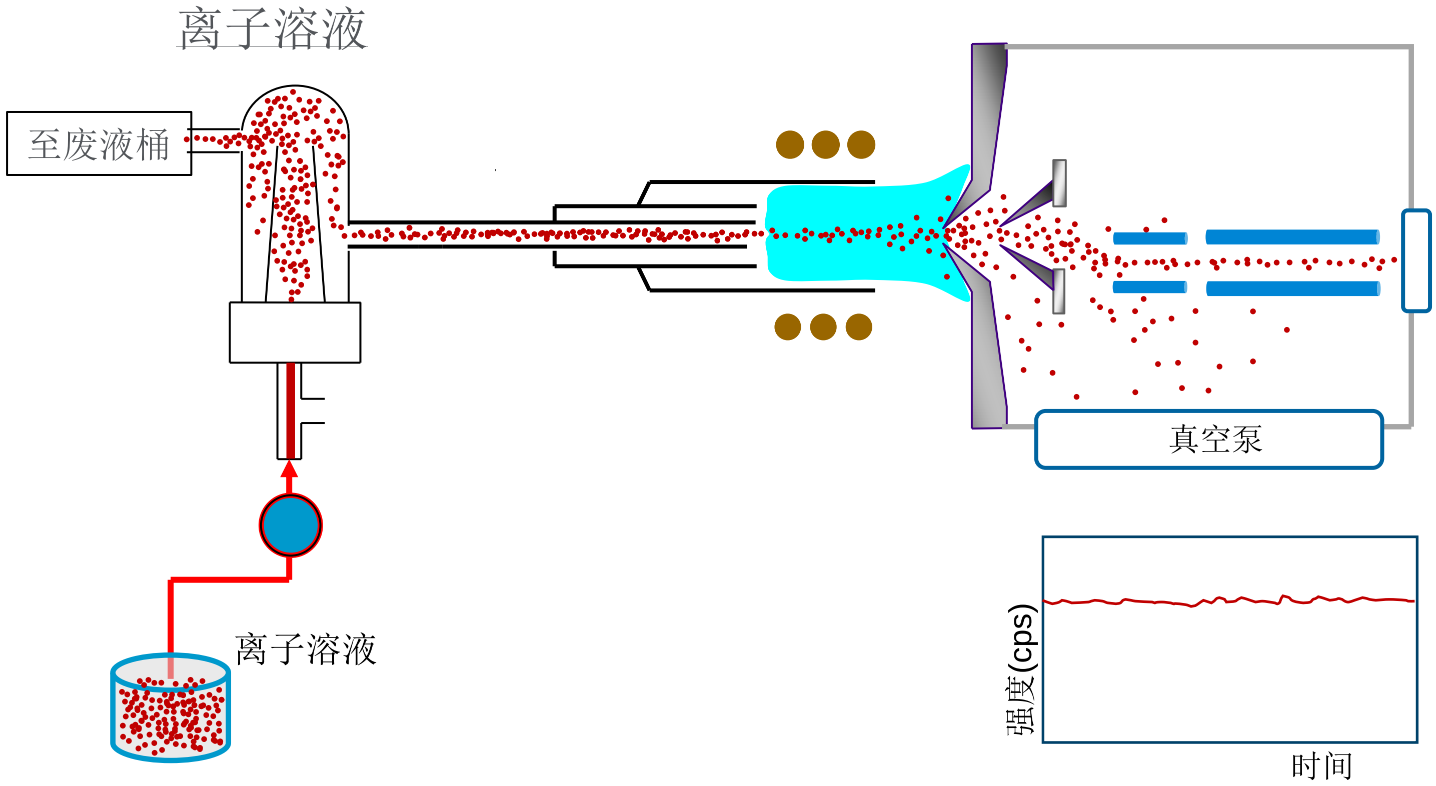
- **Single particle ICP-MS – today's topic**
  - Particle concentration – mass (μg/L)
  - Particle number (particles/L)
  - Particle size and size distribution
  - Particle composition

ICP-MS can perform all these measurements in a single analysis

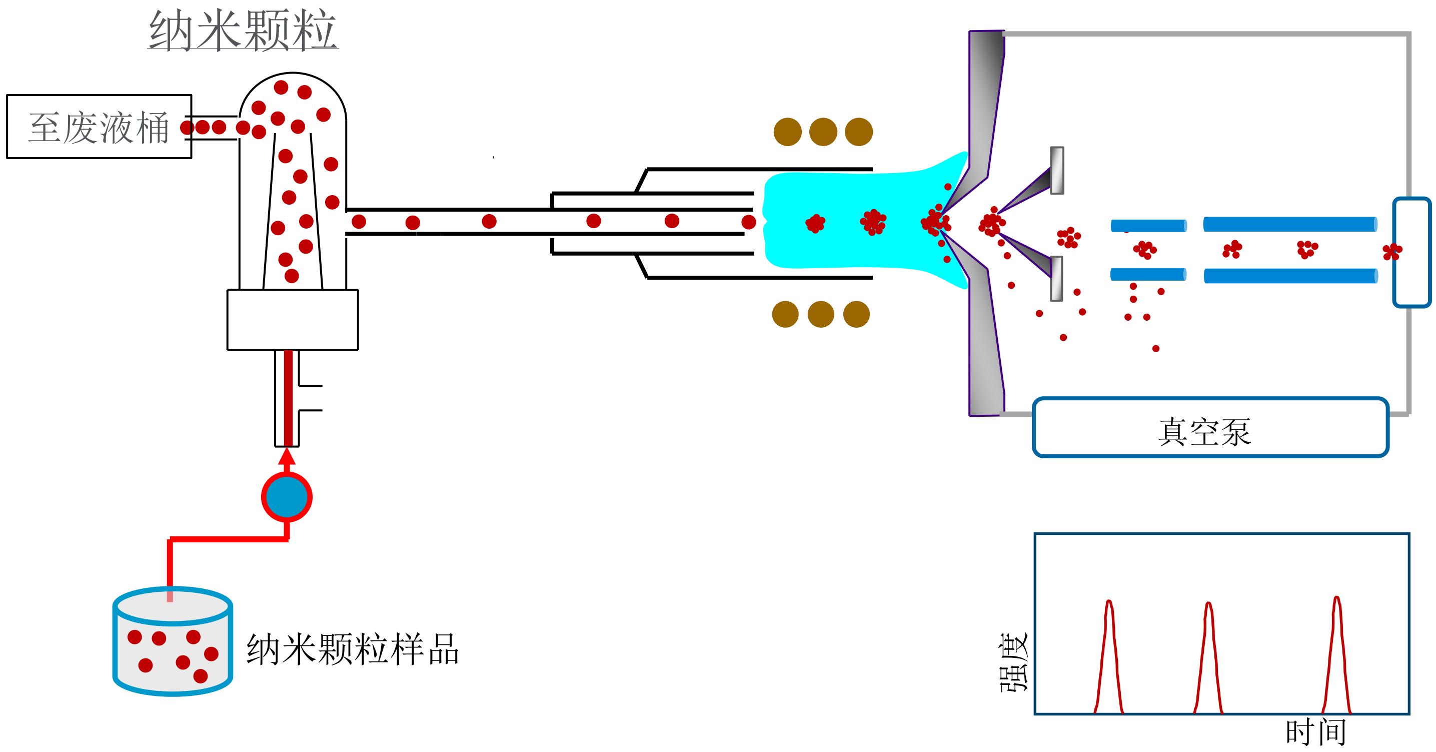
What is single particle (sp)-ICP-MS

何为单颗粒ICP-MS

常规 ICP-MS: 元素浓度及同位素比分析



单颗粒(sp)-ICP-MS: 纳米颗粒分析



Case： Detection of CuO nanoparticles in edible plants
案例：可食用植物中氧化铜纳米颗粒分析

In collaboration with:

Bren School of Environmental Science & Management
UNIVERSITY OF CALIFORNIA, SANTA BARBARA

J Nanopart Res (2018) 20: 101
https://doi.org/10.1007/s11051-018-4192-8

RESEARCH PAPER

Detection of nanoparticles in edible plant tissues exposed to nano-copper using single-particle ICP-MS

Arturo A. Keller · Yuxiong Huang · Jenny Nelson

- Rinse with DIW
- Spike 20-100 nm CuO NP
- Dry for 2 hours
- Rinse with DIW and collect
- Digest with Macerozyme R-10 (25 °C for 24 h)
- Dilute and analysis with sp-ICP-MS

[A.A. Keller, Y. Huang, and J. Nelson, Detection of nanoparticles in edible plant tissues exposed to nano-copper using single-particle ICP-MS, *J Nanopart Res*, **2018**, 20: 101]

5994-0214EN

Application Note
Food and Agriculture

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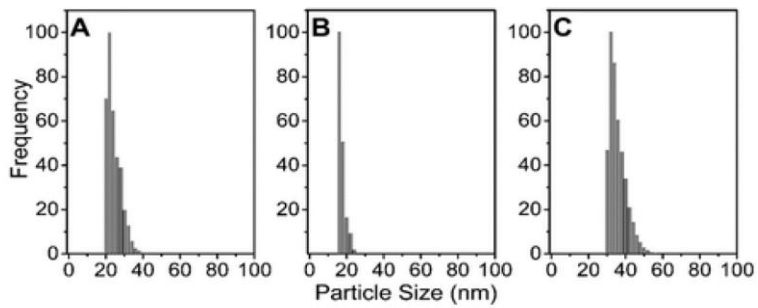
7900 ICP-MS parameters

Parameter	Value
RF power (W)	1550
Carrier gas flow rate (L/min)	0.67
Make-up gas flow rate (L/min)	0
Spray chamber temperature (°C)	2
Nebulizer pump (rps)	0.1
Sample depth (mm)	8.0
Oxide ratio (%)	1
Integration time (µs)	100
Acquisition time (s)	90
Mass monitored	^{63}Cu
ORS[4] cell mode	No gas

Quantifying Copper Nanoparticles on Plant Leaves using Single-Particle ICP-MS

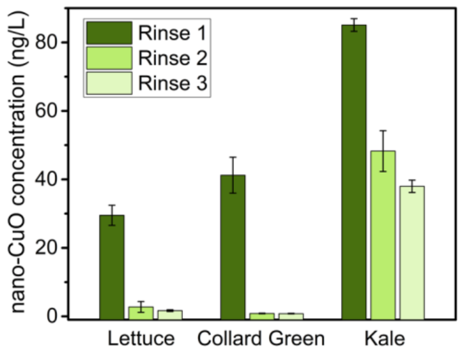
Investigating the adsorption and release of nano-pesticides on plants using the Agilent 7900 ICP-MS

Control samples – leaves not exposed to CuO NPs



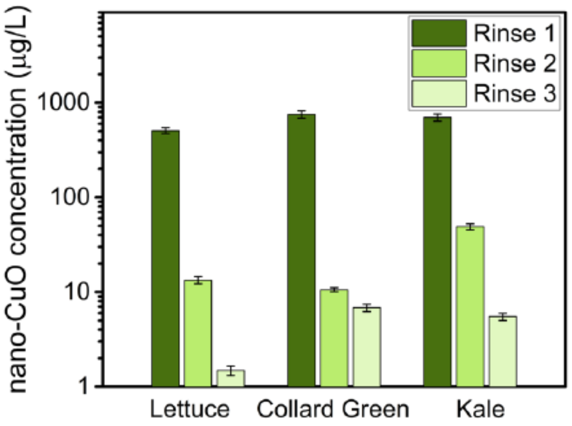
A green leaf lettuce, **B** collard green , **C** kale

Surface CuO NPs size distribution



Surface CuO NP concentration

Exposed samples – leaves exposed to CuO NPs



Surface CuO NP concentration

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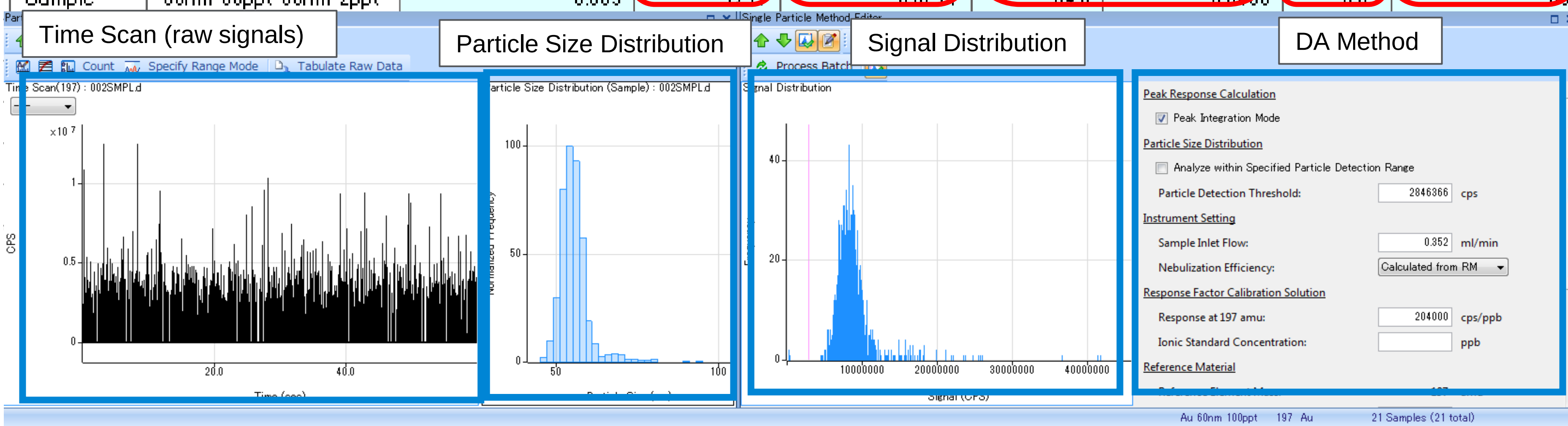
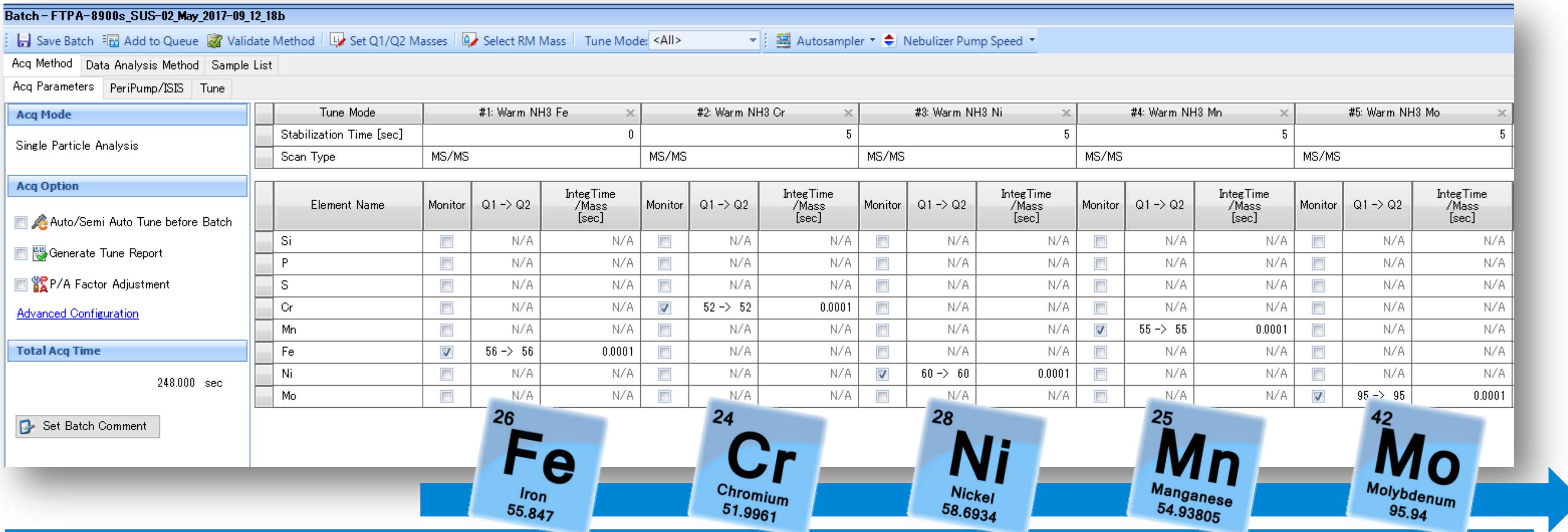
数据界面
-----纳米颗粒分析结果

- # of Particles
- Conc.(particles/L)
- Ionic Conc.(ng/L)
- Background Equivalent Diameter (nm)
- Particle size (nm)

		197 Au						
Type	Sample Name	Nebulization Efficiency	# of Particles	Conc. (particles/l)	Conc. (ng/l)	Ionic Conc. (ppb)	BED (nm)	Particle Size (nm)
Sample	EtOH10%							
RM	Au 60nm 100ppt	0.069	1377	5.6E+7	100.0	0.0469	5.65	55
Sample	Au 30nm 10ppt	0.069	988	4.0E+7	9.5	0.0133	3.77	27
Sample	Au 60nm 100ppt	0.069	1347	5.5E+7	103.2	0.0466	5.73	56
Sample	60nm 50ppt 30nm 5ppt	0.069	1116	4.6E+7	55.9	0.0362	5.26	53
Sample	60nm 80ppt 30nm 2ppt	0.069	1227	5.0E+7	84.3	0.0404	5.46	56
Sample	60nm 20ppt 30nm 8ppt	0.069	755	3.1E+7	25.3	0.0192	4.26	28
Sample	60nm 50ppt 30nm 5ppt	0.069	1115	4.6E+7	58.0	0.0337	5.14	54
Sample	60nm 80ppt 30nm 2ppt	0.069	1217	5.0E+7	84.0	[illegible]	5.59	[illegible]



强大的软件功能及数据处理能力



Tune Mode	#1: Warm NH3 Fe			#2: Warm NH3 Cr			#3: Warm NH3 Ni			#4: Warm NH3 Mn			#5: Warm NH3 Mo		
Stabilization Time [sec]			0			5			5			5			5
Scan Type	MS/MS			MS/MS			MS/MS			MS/MS			MS/MS		
Element Name	Monitor	Q1 -> Q2	IntegTime /Mass [sec]	Monitor	Q1 -> Q2	IntegTime /Mass [sec]	Monitor	Q1 -> Q2	IntegTime /Mass [sec]	Monitor	Q1 -> Q2	IntegTime /Mass [sec]	Monitor	Q1 -> Q2	IntegTime /Mass [sec]
Si	☐	N/A	N/A	☐	N/A	N/A	☐	N/A	N/A	☐	N/A	N/A	☐	N/A	N/A
P	☐	N/A	N/A	☐	N/A	N/A	☐	N/A	N/A	☐	N/A	N/A	☐	N/A	N/A
S	☐	N/A	N/A	☐	N/A	N/A	☐	N/A	N/A	☐	N/A	N/A	☐	N/A	N/A
Cr	☐	N/A	N/A	☑	52 -> 52	0.0001	☐	N/A	N/A	☐	N/A	N/A	☐	N/A	N/A
Mn	☐	N/A	N/A	☐	N/A	N/A	☐	N/A	N/A	☑	55 -> 55	0.0001	☐	N/A	N/A
Fe	☑	56 -> 56	0.0001	☐	N/A	N/A	☐	N/A	N/A	☐	N/A	N/A	☐	N/A	N/A
Ni	☐	N/A	N/A	☐	N/A	N/A	☑	60 -> 60	0.0001	☐	N/A	N/A	☐	N/A	N/A
Mo	☐	N/A	N/A	☐	N/A	N/A	☐	N/A	N/A	☐	N/A	N/A	☑	95 -> 95	0.0001

Single run collects multi-element sNP data and combines it into a single data batch table

- Save time
- Reduce the number of autosampler movements and sample contamination risk

大数据分析

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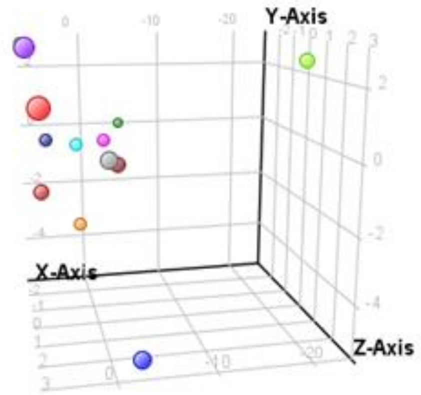
Agilent ICP-MS 应用于污染物示踪的工具

ICP-MS 定量分析与 MPP 同时使用



Food Profiling Can-Do in Food
轮廓分析在食品中的潜在应用

- 品种鉴定
- 产地判别
- 真伪鉴别
- 年份及采收季节判别
- 加工工艺质量控制
- ……

为什么用无机元素组分进行产地鉴定？

农产品吸收土壤和水中的金属，进而在其体内富集

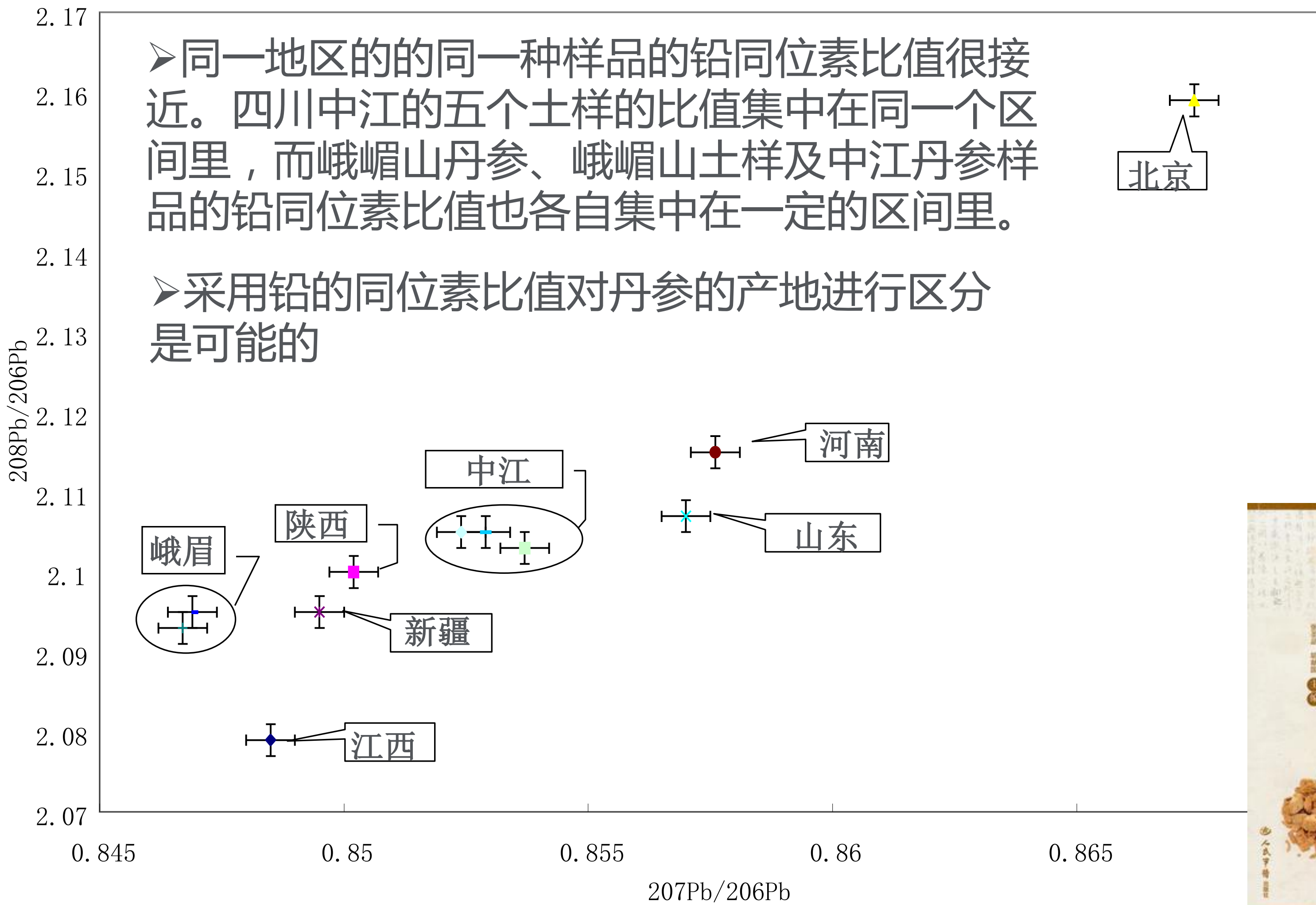
由于不同地区土壤和水中痕量元素含量不同，因此农产品中痕量金属的富集也会有差异

（一）应用ICP-MS判定中药丹参产地

各地区丹参样品的Pb同位素比值的比较

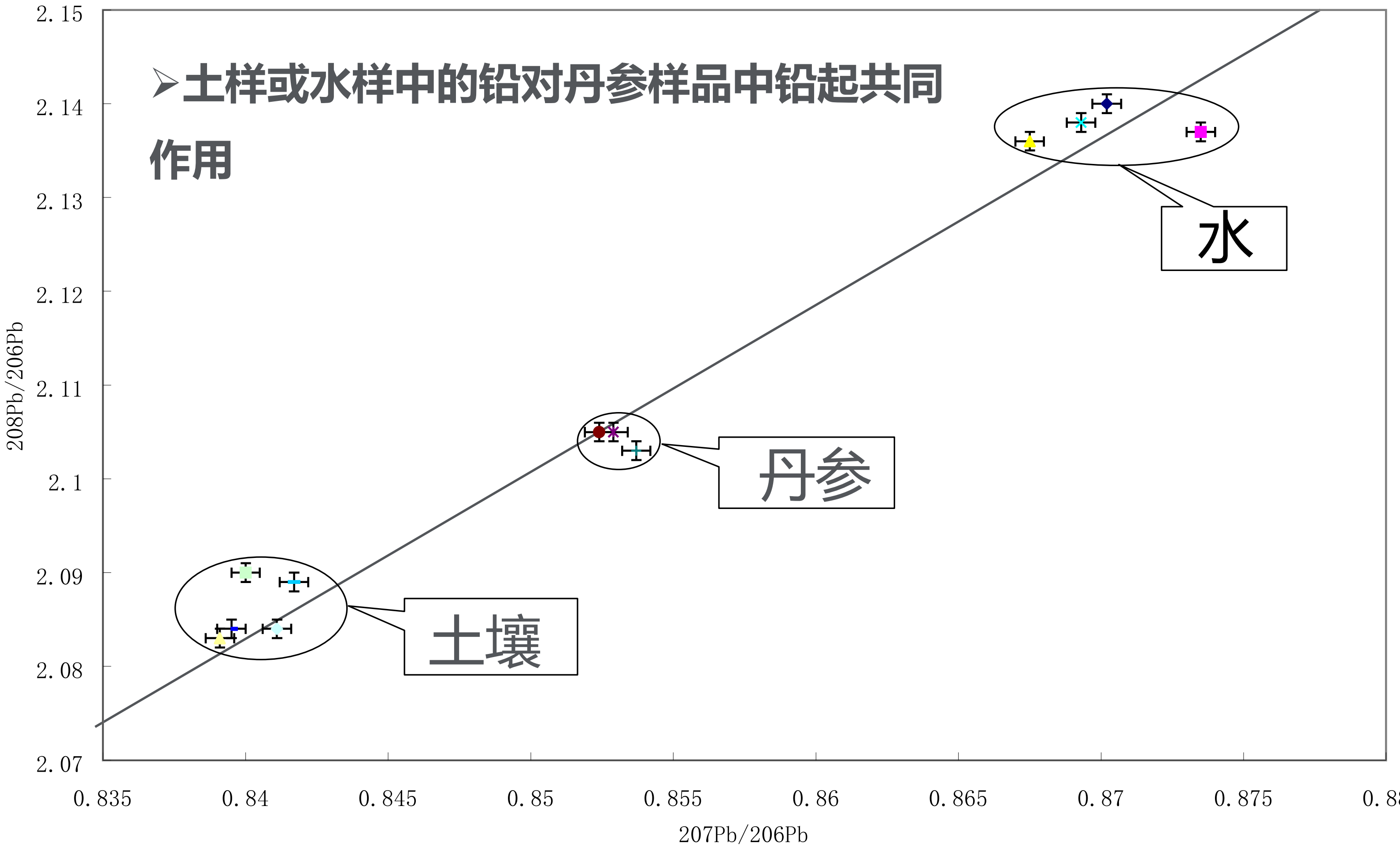
➢同一地区的的同一种样品的铅同位素比值很接近。四川中江的五个土样的比值集中在同一个区间里，而峨嵋山丹参、峨嵋山土样及中江丹参样品的铅同位素比值也各自集中在一定的区间里。

➢采用铅的同位素比值对丹参的产地进行区分是可能的



应用ICP-MS解析福建省水体和土质对植物的影响

同一地区（中江）采样的丹参、土壤和水样中的Pb 同位素比的比较



MPP软件应用--橄榄油产地判定

MPP: Mass Profiler Professional

Sample preparation

- 3g of Olive oil was weighed into 50 mL conical tubes, and diluted to 10g with a Premisolv diluent
- All samples were put in a mechanical shaker for 20 minutes
- Internal standard was “t-ed” in before the nebulizer (Sc and Y were used)

Country origin	n
USA (California)	2
Greece	14
Italy	6
Spain	7

50

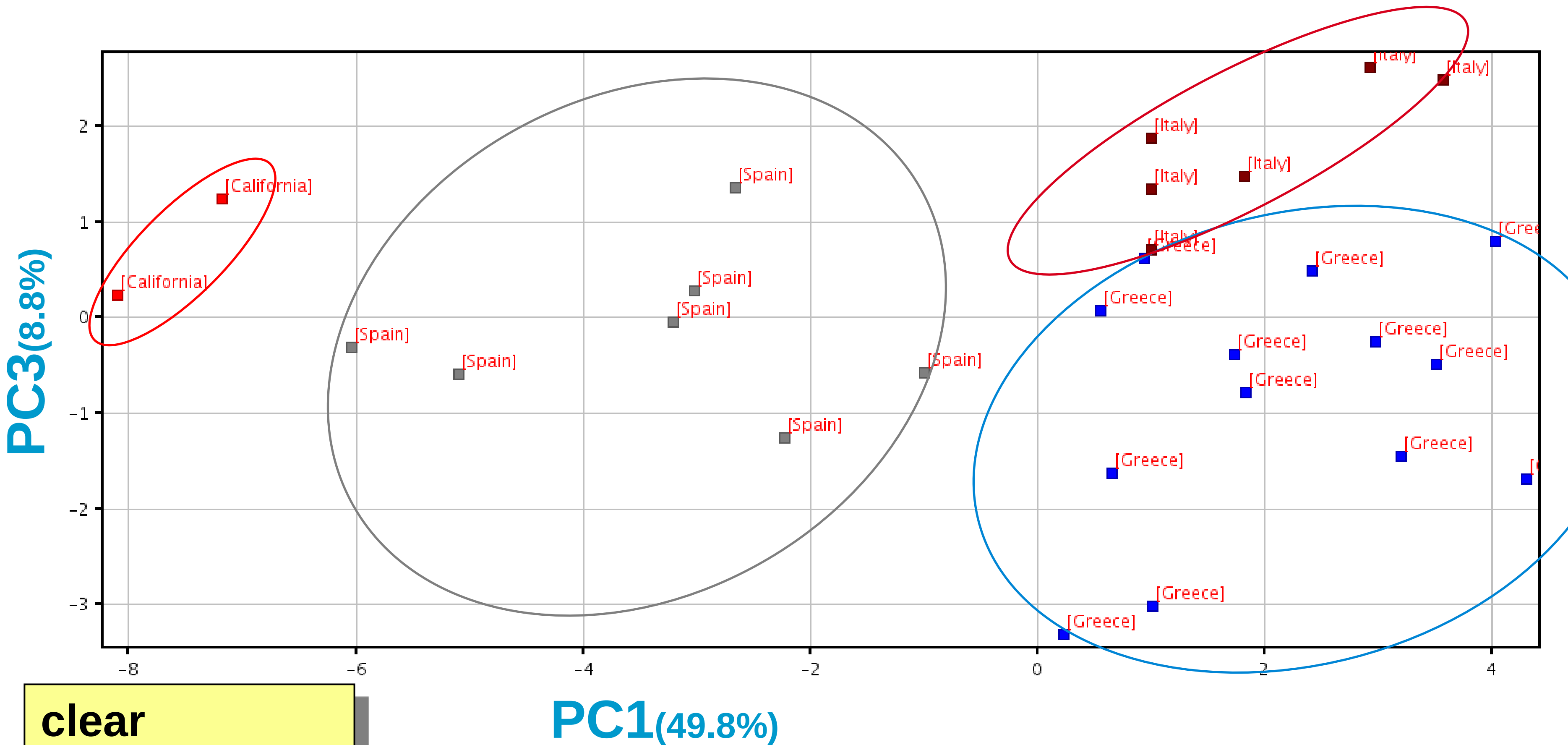
elements

Agilent ICP-MS System

Agilent 单一**He**模式测定**50**种元素；

良好的消干扰技术避免了假阳性结果

Filter function in MPP is very useful!



clear separation

The filters in MPP reduces the data analysis labor by extracting the elements with significant differences

中国蜂蜜种类鉴定 文献

----- 中国检验检疫科学研究院， 庞国芳院士实验室

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

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Chemometric Determination of the Botanical Origin for Chinese Honeys on the Basis of Mineral Elements Determined by ICP-MS

Hui Chen,[†,§] Chunlin Fan,[*,†] Qiaoying Chang,[†] Guofang Pang,[*,†,§] Xueyan Hu,[†] Meiling Lu,[#] and Wenwen Wang[#]

[†]Chinese Academy of Inspection and Quarantine, No. 3 Gaobeidian North Road, Chaoyang District, Beijing 100123, China

[§]College of Environmental and Chemical Engineering, Yanshan University, Qinhuangdao 066004, China

[#]Agilent Technologies (China) Company, Ltd., No. 3 Wang Jing Bei Lu, Chaoyang District, Beijing 100102, China

ABSTRACT: In this work, the potential of mineral elements and chemometric methods as a tool to classify Chinese honeys according to their botanical origin was examined. Twelve mineral elements (Na^{23}, Mg^{24}, P^{31}, K^{39}, Ca^{43}, Mn^{55}, Fe^{56}, Cu^{63}, Zn^{66}, Rb^{85}, Sr^{88}, and Ba^{137}) of 163 Chinese honey samples, including linden, vitex, rape, and acacia, collected from Heilongjiang, Beijing, Hebei, and Shaanxi, China, in 2013 were determined by the ICP-MS method. Principal component analysis (PCA) reduced 10 variables to four principal components and could explain 93.06% of the total variance. Partial least-squares discriminant analysis (PLS-DA) and back-propagation artificial neural network (BP-ANN) were explored to construct a classification model. By PLS-DA, the total correct classification rates for model training and cross-validation were 90.9 and 88.4%, respectively. By BP-ANN, the total correct classification rates for model training and cross-validation were 100 and 92.6%, respectively. The performance of BP-ANN was better than that of PLS-DA. The validation of the developed BP-ANN model was tested by the independent test set of 42 honey samples. Linden, vitex, and rape honey samples were predicted with an accuracy of 100%, whereas one acacia honey was predicted as rape honey with an accuracy of 92.3%. It is concluded that the profiles of mineral elements by ICP-MS with chemometric methods could be a potential and powerful tool for the classification of Chinese honey samples from different botanical origins.

KEYWORDS: *honey, mineral elements, ICP-MS, botanical origin, PCA, PLS-DA, BP-ANN*

采用 ICP-MS 和 Mass Profiler Professional 软件测定储存温度和包装类型对葡萄酒中痕量金属成分的影响

应用简报

食品安全

作者

Helene Hopfer 和 Susan E. Ebeler
葡萄栽培和酿酒系
加州大学戴维斯分校
美国

Jenny Nelson
安捷伦科技公司
5301 Stevens Creek Blvd.
加利福尼亚州圣克拉拉市
美国

摘要

本实验建立了一种采用 ICP-MS 测定葡萄酒中 20 多种痕量金属的方法，研究了包装以及储存条件对痕量金属成分的影响。实验发现 5 种痕量金属的检测限 (LOD) 介于 0.001 至 0.044 µg/L 之间，定量限 (LOQ) 介于 0.003 至 0.057 µg/L 之间，具体数据随包装和储存条件的不同会发生显著变化。葡萄酒中元素的含量随这两个变量而变化，其中包装类型（盒装式或带软木塞/螺旋盖的瓶装式）对金属成分的影响最大。

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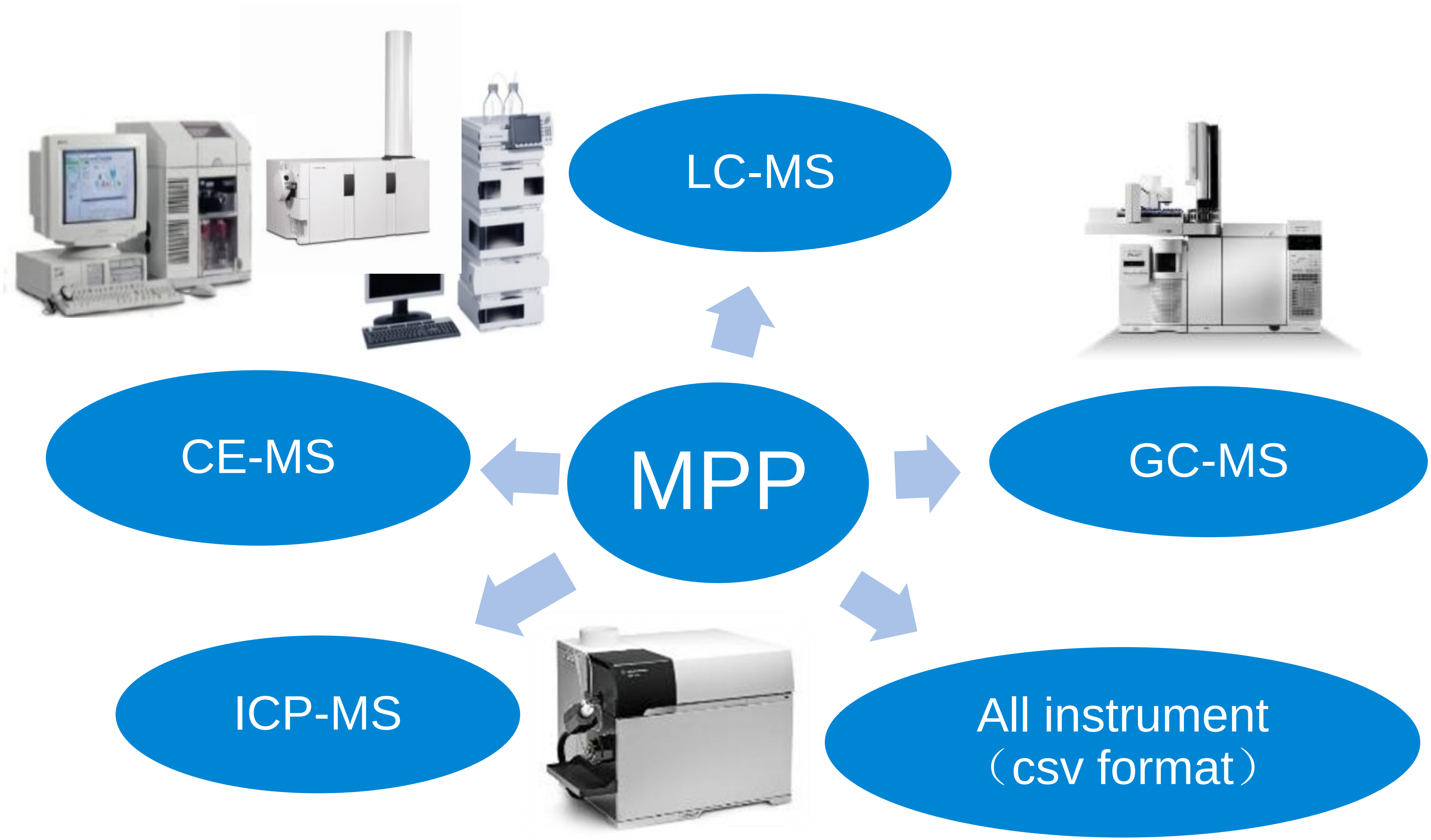
MPP 可用于Agilent 所有质谱



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