

0.1%的精密度是如何实现的— 实时内标法的原理和应用



Avio 500的关键特点

- Truly simultaneous

- 全谱全读UDA

- Syngistix软件：
data viewer

- 符合RoHS要求！



- 专利的平板等离子体技术

- 垂直炬管 双向观测

- 专利的等离子体切割
PlasmaShear

- 全彩色等离子体摄像头
PlasmaCam

- 4通道12滚柱
蠕动泵

- SCD检测器

- 高性能的光学系统

- 干扰校正：MSF和IEC

Avio 500的关键特点



• 多快好省准

- 多快?
- 多省?
- 多准?

多快好省准

1秒钟把元素周期表测遍!

The image shows a software interface for a spectrometer. The main window is titled "Method Editor : Untitled" and has tabs for Spectrometer, Sampler, Process, Calibration, Checks, QC, and Options. The "Spectral settings" section includes "Purge gas flow" (set to "None"), "Spectral profiling" (set to "None"), and "Resolution" (set to "Fixed"). The "Read parameters" section includes "Time (sec)" (set to "Manual") and "Replicates" (set to "999").

A "Periodic Table" dialog box is open, showing a grid of elements. The element "Plutonium (Pu)" is selected, and the "Active row in Method Editor" is set to "77". Below the table are buttons for "Enter in Method" and "λ Table".

A "Set Manual Integration" dialog box is also open, showing a table of integration parameters:

F'n	Analyte	Integration Time (sec)	Read Time (sec)
68	Dy	0.001	0.001
	Ho	0.001	0.001
	Er	0.001	0.001
	Tm	0.001	0.001
	Yb	0.001	0.001
	Lu	0.001	0.001
	Hf	0.001	0.001
	Ta	0.001	0.001
	W	0.001	0.001
	Re	0.001	0.001
	Os	0.001	0.001
	Ir	0.001	0.001
	Pt	0.001	0.001
	Au	0.001	0.001
	Hg	0.001	0.001
	Tl	0.001	0.001
	Pb	0.001	0.001
	Bi	0.001	0.001
	Po	0.001	0.001
	At	0.001	0.001
	Rn	0.001	0.001

A "Read Time Column Fill" dialog box is also open, showing input fields for "0.001" sec and "0.001" sec. Below the fields is a note: "The read time divided by the integration time must be a whole number less than 65536." Buttons for "OK" and "Cancel" are at the bottom.

多快好省准

≥ 50% reduction in total Argon use



← 21 L/min, COMPETITOR A

← 18 L/min, COMPETITOR B

← 9 L/min, AVIO 500

半价运行!



多快好省准

ISO/CD 11494

Jewellery — Determination of platinum in platinum jewellery alloys — ICP-OES method using yttrium as internal standard element

ISO/CD 11495

1 Scope

This International Standard describes a method for the determination of platinum in platinum jewellery alloys, preferably within the range of fineness specified in ISO 9202, by means of inductively coupled plasma optical emission spectrometry (ICP-OES).

The preferred palladium content of the alloys lies between 500 ‰ (parts per thousand) and 950 ‰ palladium.

NOTE

This method can be used to analyse other contents of platinum.



Jewellery — Determination of palladium in palladium jewellery alloys — ICP-OES method using yttrium as internal standard element

1 Scope

This International Standard describes a method for the determination of palladium in palladium jewellery alloys, preferably within the range of fineness specified in ISO 9202, by means of inductively coupled plasma optical emission spectrometry (ICP-OES).

The preferred palladium content of the alloys lies between 500 ‰ (parts per thousand) and 950 ‰ palladium.

NOTE This method can be used to analyse other contents of palladium.

RSD < 0.1%!

0.02%
RSD

ISO和INIST要求:

电感耦合等离子体原子发射光谱法测定 NiCu 合金中铝钛铁硅

王丹,孙莹

(中国科学院金属研究所, 辽宁沈阳 110016)

摘要: 采用盐酸、硝酸及氢氟酸溶解样品, 采用基体匹配法配制标准溶液消除基体效应的影响, 选择 Al 396.152 nm、Ti 337.280 nm、Fe 238.204 nm、Si 251.611 nm 为分析线, 使用电感耦合等离子体原子发射光谱法 (ICP-AES) 测定 NiCu 合金中的铝硅铁钛。Al、Ti 的质量分数在 0.005%-1.0% 范围内, Fe、Si 的质量分数在 0.10%-8.0% 范围内, 各元素质量分数与对应的发射强度呈线性, 校准曲线线性相关系数不小于 0.9996; 方法中各元素检出限为 0.0002%-0.0010%; 测定结果的相对标准偏差为 0.49%-3.0%; 加标回收率为 90.0%-105%。方法简单、快速, 结果令人满意。

关键词: 电感耦合等离子体原子发射光谱法 (ICP-AES); NiCu 合金; 铝; 钛; 铁; 硅

高温合金中高含量钨的测定

郭莉莉 马洪波

(中国科学院金属研究所 110016)

摘要: 介绍了用电感耦合等离子体发射光谱法 (ICP-AES) 测定高温合金中高含量 W 的分析方法。从试样的溶解、基体干扰、谱线选择和酸度控制等方面进行了实验。选择谱线 207.911 nm 为 W 的分析线, 基体匹配法配制标准曲线, 选择仪器最佳工作条件, 可以准确快速地测定高温合金中较高含量的 W。用该方法测定标准样品中 W 含量, 所得值与所给值相符。

关键词: 高温合金; 钨; ICP-AES

标准样品	W 含量标准值 (%)	W 含量测定值 (%)	RSD
1#	9.91	9.90	0.37
2#	15.04	15.06	1.56

电感耦合等离子体光谱法测定银铜焊料中铜和锌元素含量

陈妮绒 彭骛 杨晓琴 王路

中国航发贵州红林动力控制科技有限公司

控制样品中铜和锌的含量均为 25%，检测五次，检测情况如下：

表 2 控制样品的测定值

元素	标准值%	测定值%	平均值%	RSD/%
铜	25.0	25.10, 25.24, 24.86, 25.15, 24.98	25.07	0.59
锌	25.0	25.02, 25.21, 24.78, 24.86, 25.14	25.00	0.73

2.5 样品分析

按照此试样方法对 2 批样品（17-5-22； 17-11-18）进行分析，平行测定 6 次，测试结果如表 3。

表 3 试样的测定值

编号	Cu (%)	Zn (%)
17-5-22	29.7	25.2
17-11-18	30.2	25.8

电镀镉钛合金镀层中钛含量测定方法

陈妮绒 彭戩 王路 杨晓琴

中国航发贵州红林动力控制科技有限公司

摘要：本文通过 ICP 测定电镀合金镀层中钛含量，用硝酸铵褪镀层，用硝酸硫酸溶解镀层，然后上机测定。此方法操作简便，准确度高。相对标准误差 RSD 小于 5%。

关键词：电感耦合等离子发射光谱仪 电镀镉钛

表 4 标准样品

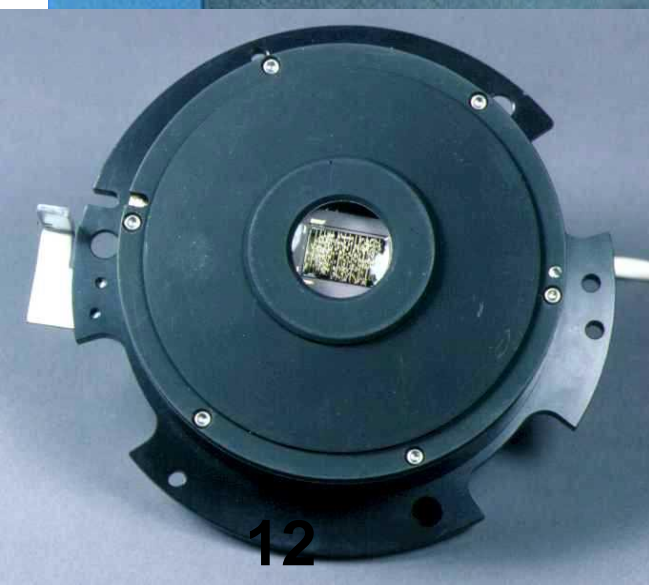
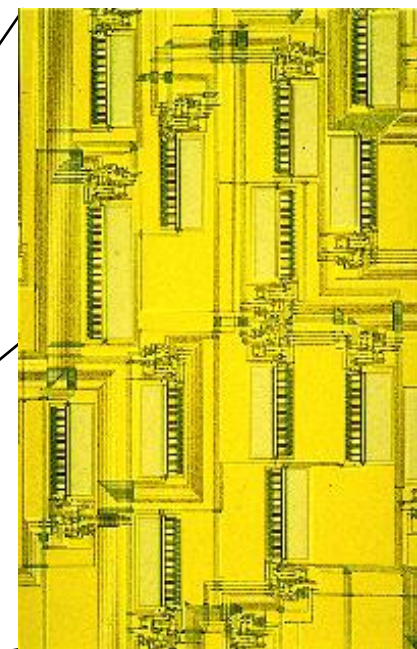
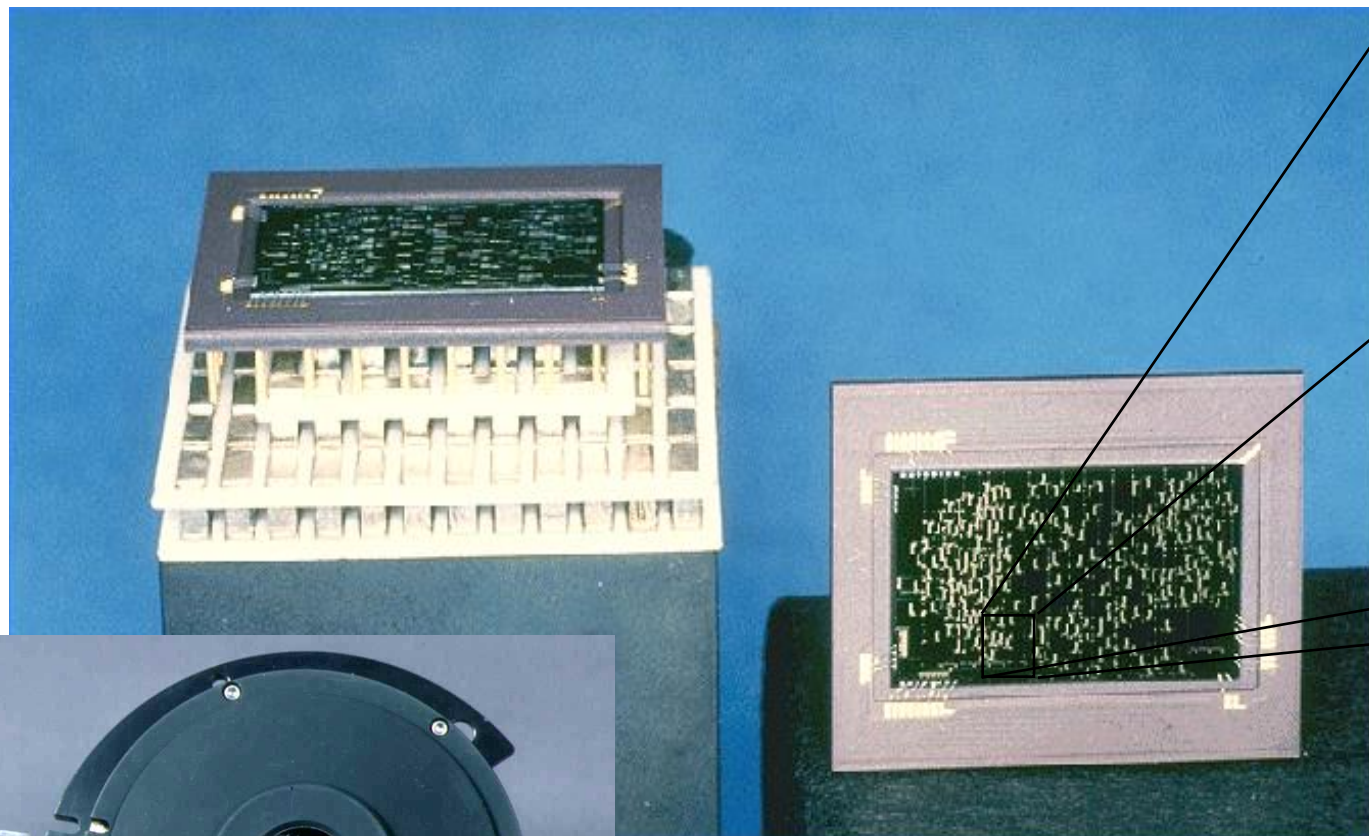
元素	标准值%	测定值%	平均值 %	RSD%
钛	0.20%	0.21 0.21 0.19 0.21 0.20	0.202	4.4
钛	0.50%	0.52 0.48 0.52 0.51 0.49	0.504	3.6
钛	0.70%	0.71 0.69 0.68 0.72 0.69	0.698	2.4

从上边的实验数据可以看出，RSD 值小于 5%，此方法可靠，可以满足试验要求。

Oh!
Why?

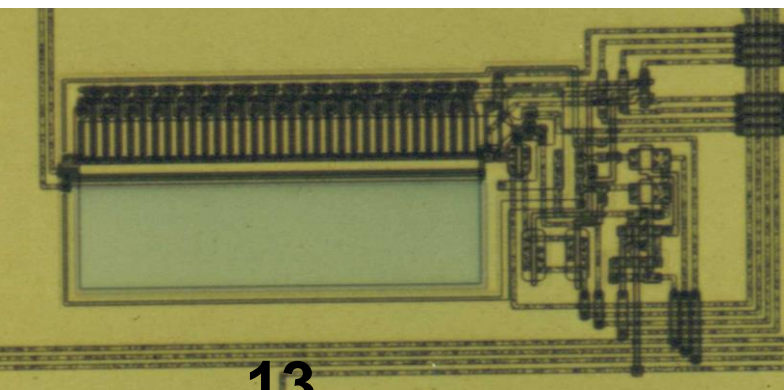
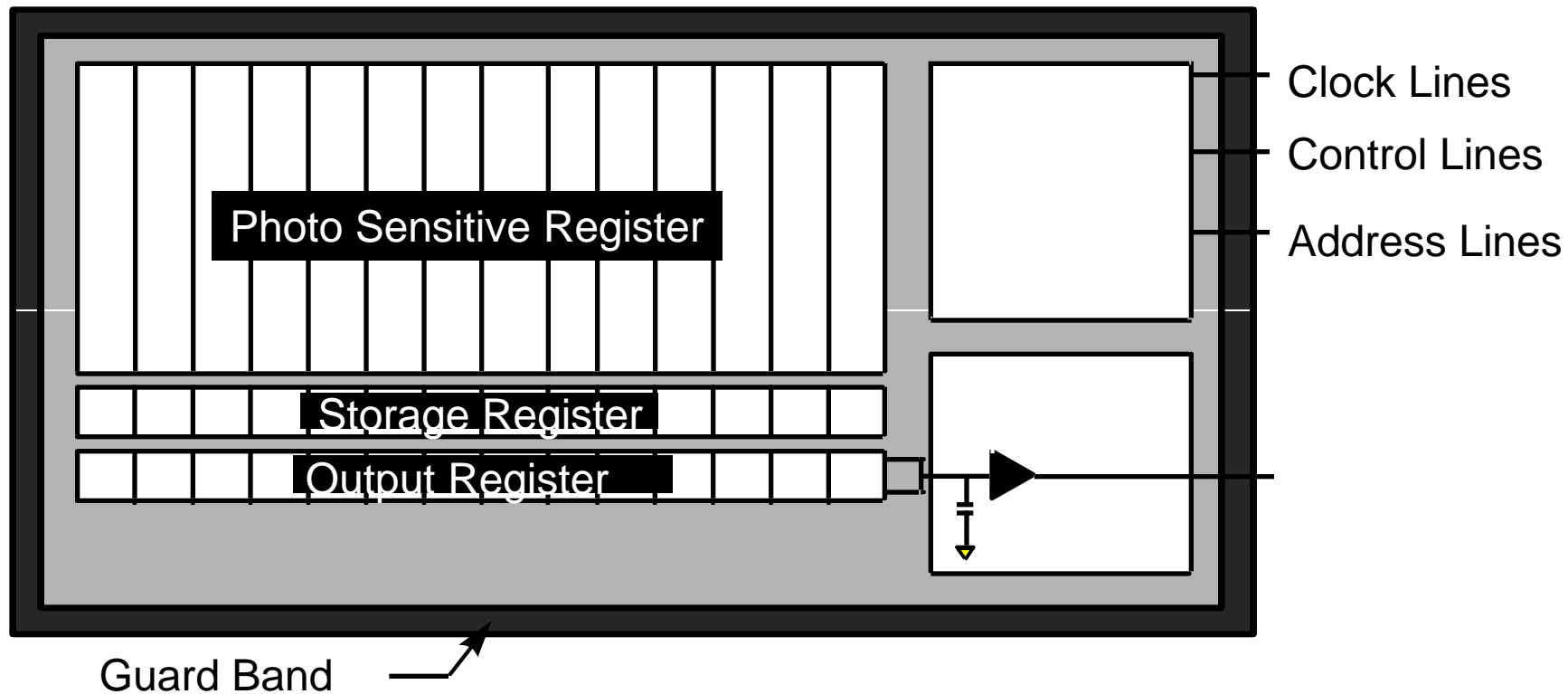


Segmented-array Charge-coupled Device Detector (SCD)



500:1

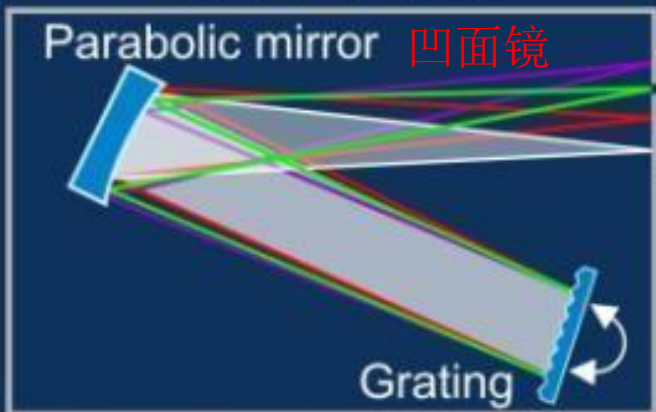
Segmented-array Charge-coupled Device Detector (SCD)



500:1

PinAAcle 900为什么有实时双光束，而其它公司的产品没有？

单色器 Monochromator



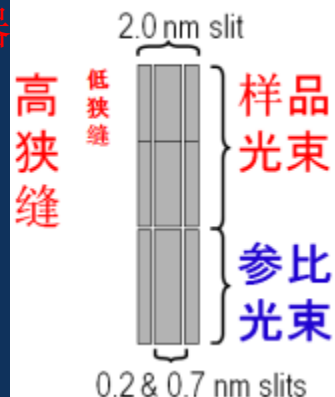
Exit slit/ detector 出射狭缝/固态检测器

出射狭缝/固态检测器

Entrance slit 入射狭缝

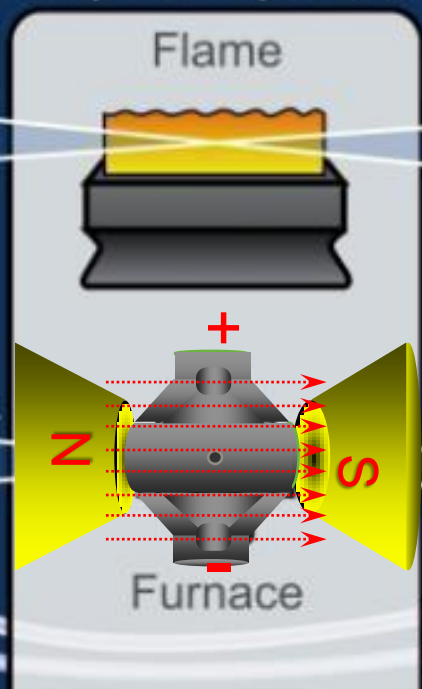


CCD检测器功能区域分布图



1800线大面积光栅

样品仓 Sample compartment



氘灯

Deuterium lamp

加样

可移动光源反光镜

Movable source mirror

原子化

Fiber coupler

光纤耦合器

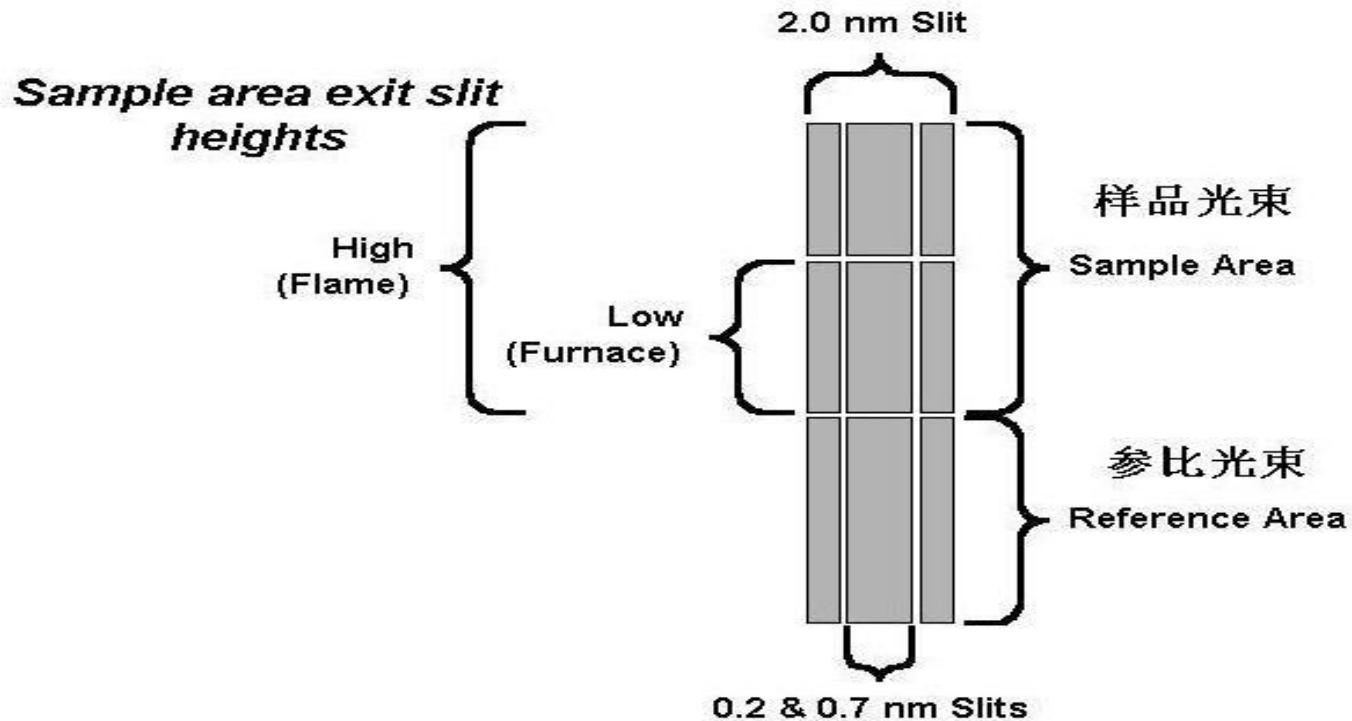
8灯位

8 lamp positions

EDL

HCL

Sample area exit slit widths



稳定性更好 — 完全克服了因灯发射强度改变而引起仪器的零点漂移。

提高仪器的测定精度和准确度

在仪器每一个读数周期内（如10毫秒），交替检测仅用半个周期测定样品（5毫秒），而同时检测用整个周期测定样品（10毫秒）。同时检测延长了样品光束和参比光束的测量时间，提高了仪器的测定精度和准确度。

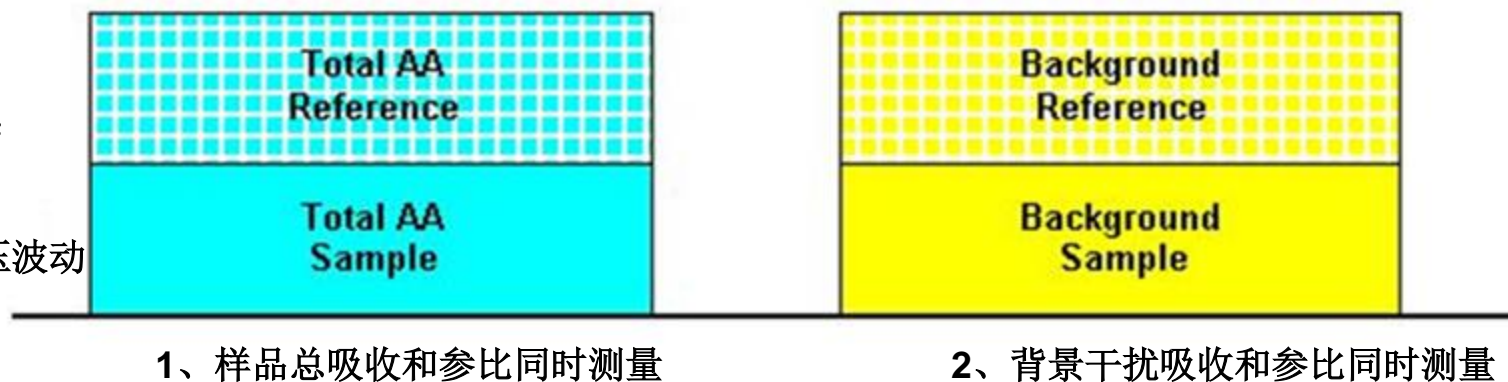
一般的AAS厂家：
只有一个PMT，
交替双光束

无法校正瞬间电压波动

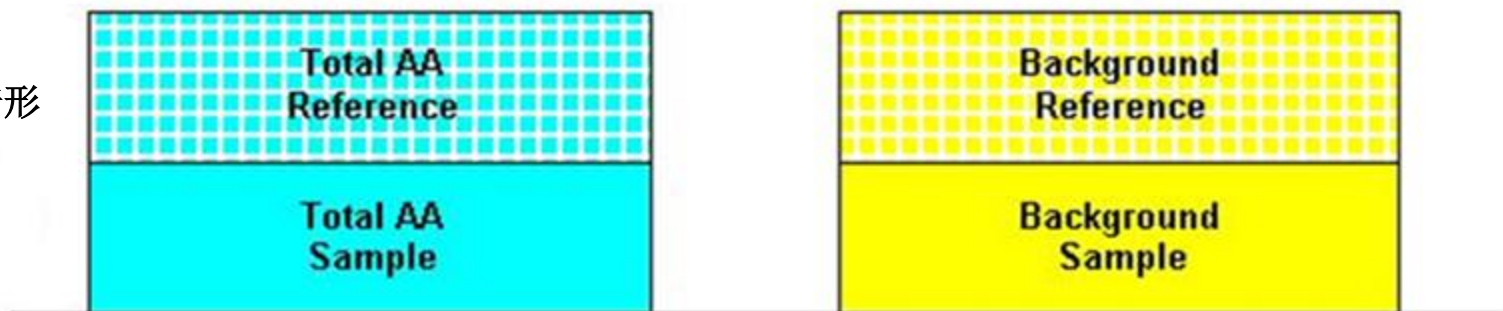


PerkinElmer：
9区域CCD，
实时双光束

实时校正瞬间电压波动



使用氘灯时的情形

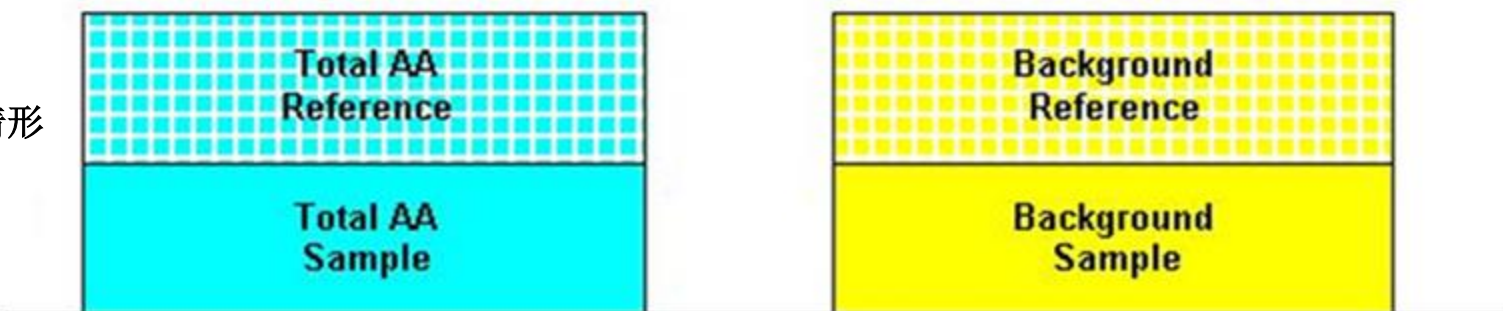


1、元素灯开，氘灯灭，
测量**总吸收**与参比吸收的比值

3、元素灯灭，氘灯开，测量背景吸收
测量**背景吸收**与参比吸收的比值

两个比值之间再进行差减，求得净吸收

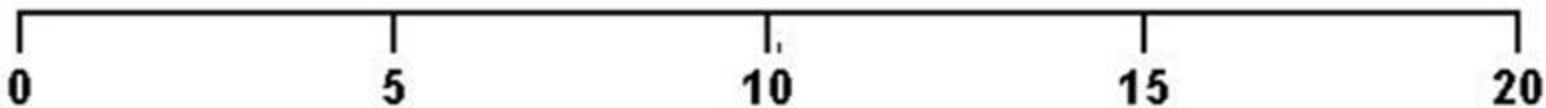
使用塞曼时的情形



1、元素灯开，磁场关，
测量**总吸收**与参比吸收的比值

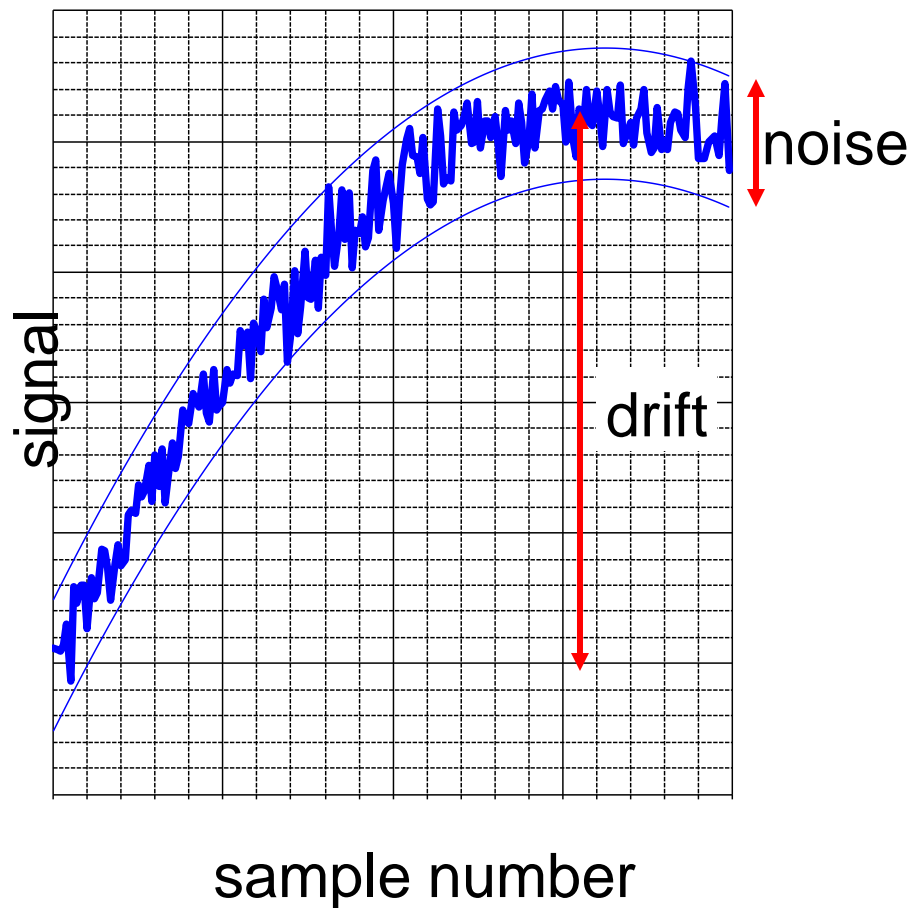
3、元素灯开，磁场开，相当于待测元素消失
测量**背景吸收**与参比吸收的比值

之间再进行差减，求得净吸收



信号 = 漂移 + 噪声

- 噪声是短期的
- 漂移是长期的



Drift is major
source of
uncertainty

Drift Correction

$$S_{measured} = S_{truth} + \varepsilon_{drift} + \varepsilon_{noise}$$

- separate variables to estimate drift as $f(t)$
 - use grand mean for sample to estimate S_{truth}
 - create time series of deviations from mean
 - use *ALL* standards and samples
 - this is our estimate of $(\varepsilon_{drift} + \varepsilon_{noise})!$
 - use relative deviations for multiplicative drift, absolute deviations for additive drift
 - fit smooth function to these deviations
 - this is our estimate of $\varepsilon_{drift}!$

内标：交替双光束，从10% → 1%

Spectrochimica Acta, Vol. 38B, No. 9, pp. 1227-1253, 1983.
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© 1983, Pergamon Press Ltd.

Improved performance using internal standardization in inductively-coupled plasma emission spectroscopy

S. A. MYERS and D. H. TRACY

Perkin-Elmer Corporation, Main Avenue, Norwalk, CT 06856, U.S.A.

(Received 30 June 1982, in revised form 25 February 1983)

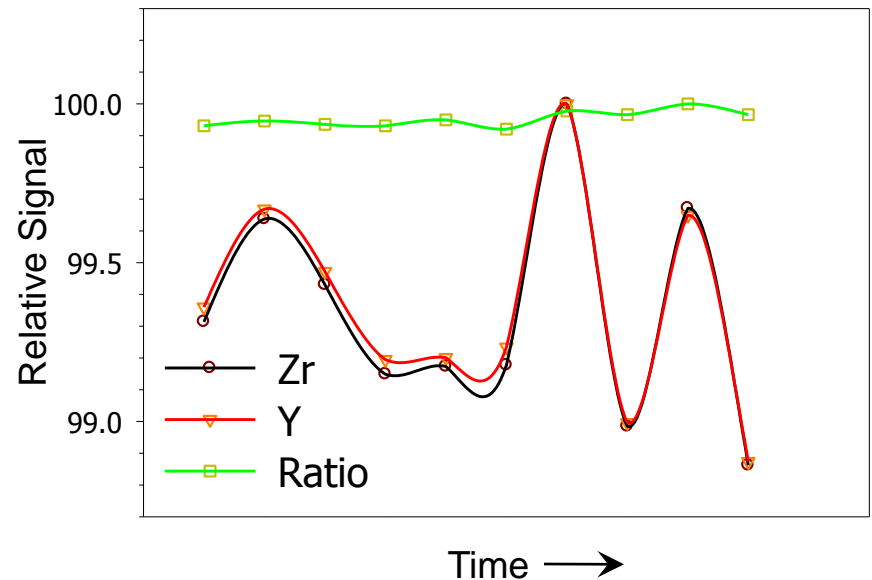
Abstract—Significantly improved performance in ICP emission spectroscopy is possible using internal standardization given the proper choice of operating conditions. A dual monochromator detection system was used to study the correlation between two emission signals recorded simultaneously as several ICP parameters were varied. The behavior of the signal formed by dividing the analyte and reference signals was also measured.

The noise behavior of twenty analytically important elements was compared to that of a manganese ion line used as the internal standard for a single, compromise choice of ICP operating parameters (RF power = 1250 W, carrier gas flow rate = 0.7 or 0.9 l/min, and viewing height = 20 mm). The elements differed widely in excitation and ionization energies. Sample concentrations were chosen so that the analyte emission signals were sufficiently intense that the noise and drift contributions due to plasma background and shot noise could be ignored. Under these conditions very good signal correlation ($r \geq 0.95$) and similar noise proportionality factors were observed leading to noise reductions of $\geq 10 \times$ after signal division in almost every instance. After signal division the noise, defined as the relative standard deviation of the emission signal, (time constant = 1.0 s, $n = 20$) was less than 0.1%. The closely similar noise behavior is attributed to sample density fluctuations arising from corresponding fluctuations of the sample aerosol density. Good correlation is also observed between fluctuations in the plasma background simultaneously detected at two widely separated wavelengths when appropriate steps are taken to reduce shot noise.

At carrier gas flow rates above 1.0 l/min and at viewing heights below 15 mm or above 20 mm, the signal correlation is reduced or absent, yielding little or no improvement using internal standardization.

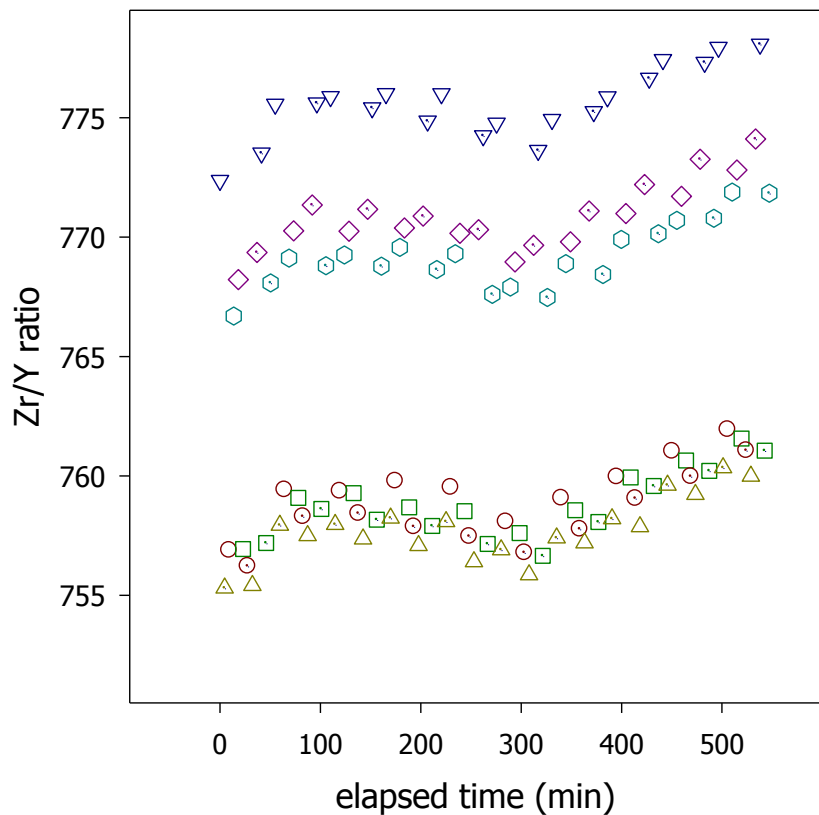
The use of internal standardization leads to other improvements in analytical performance in addition to noise reduction. Drift is reduced, and nebulizer performance is improved in that it is less sensitive to variations in liquid sample uptake rate, or nebulizer instabilities associated with high solids content sample introduction. The divided signal takes much less time to reach equilibrium following introduction of a new sample.

- precision enhancement
 - matched internal standard
 - can be ~20x improvement

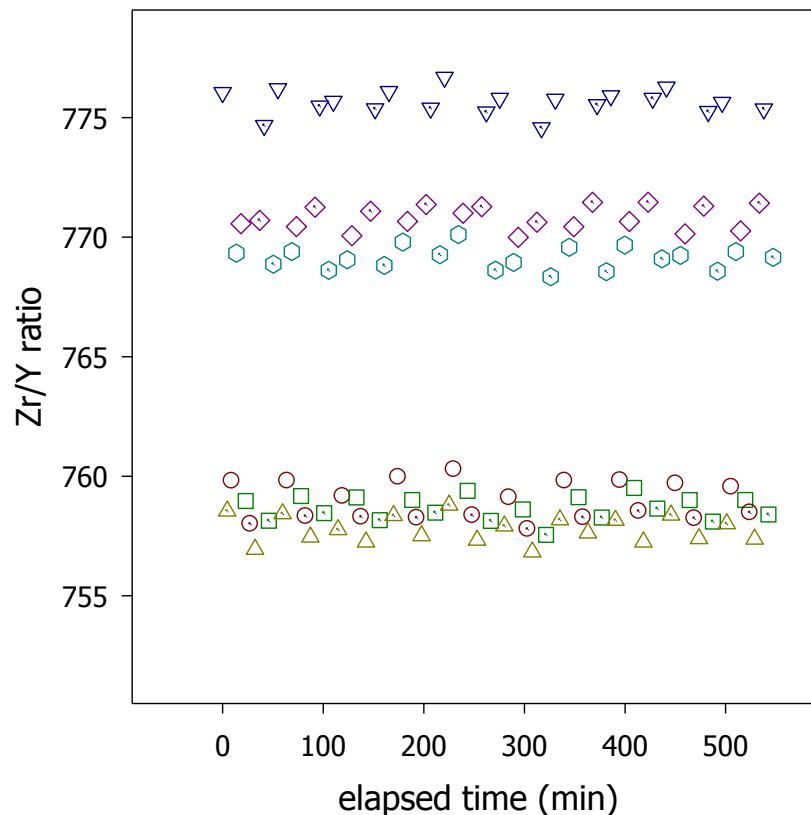


Drift Corrected Results

Data after correction for dilution

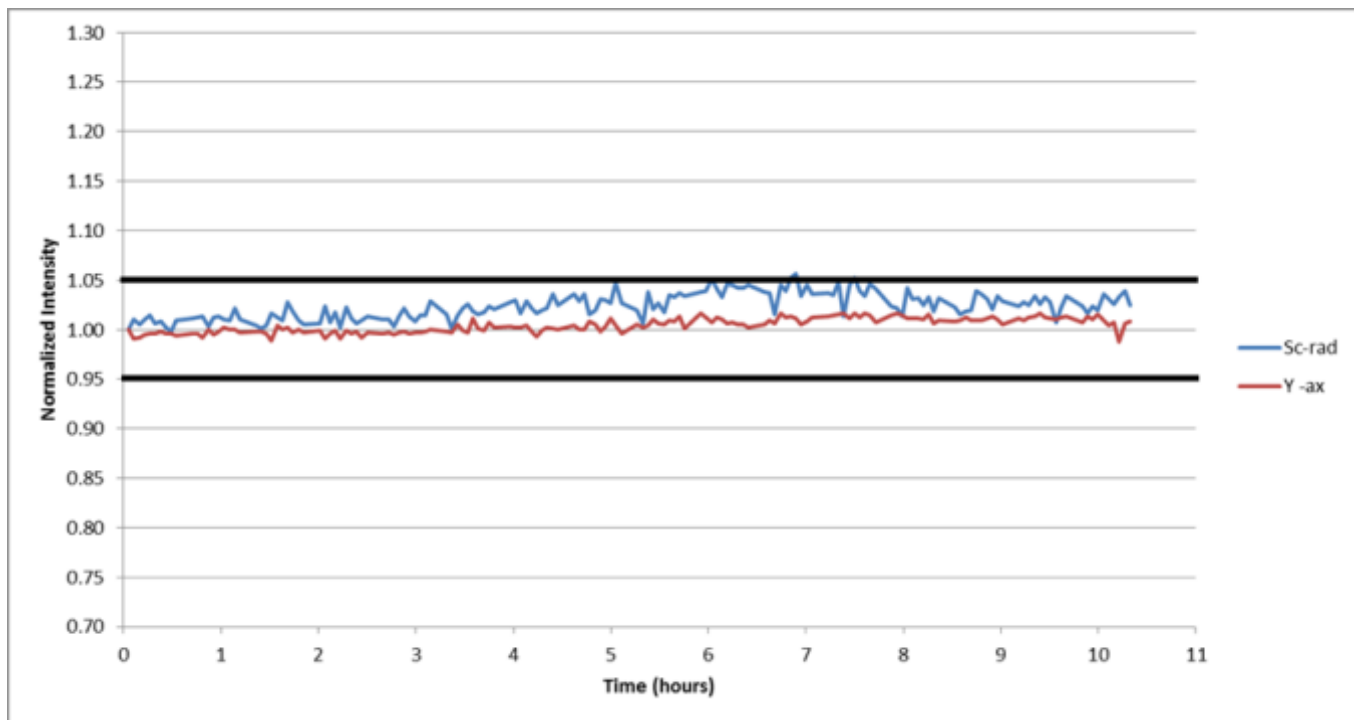


Drift and dilution corrected data



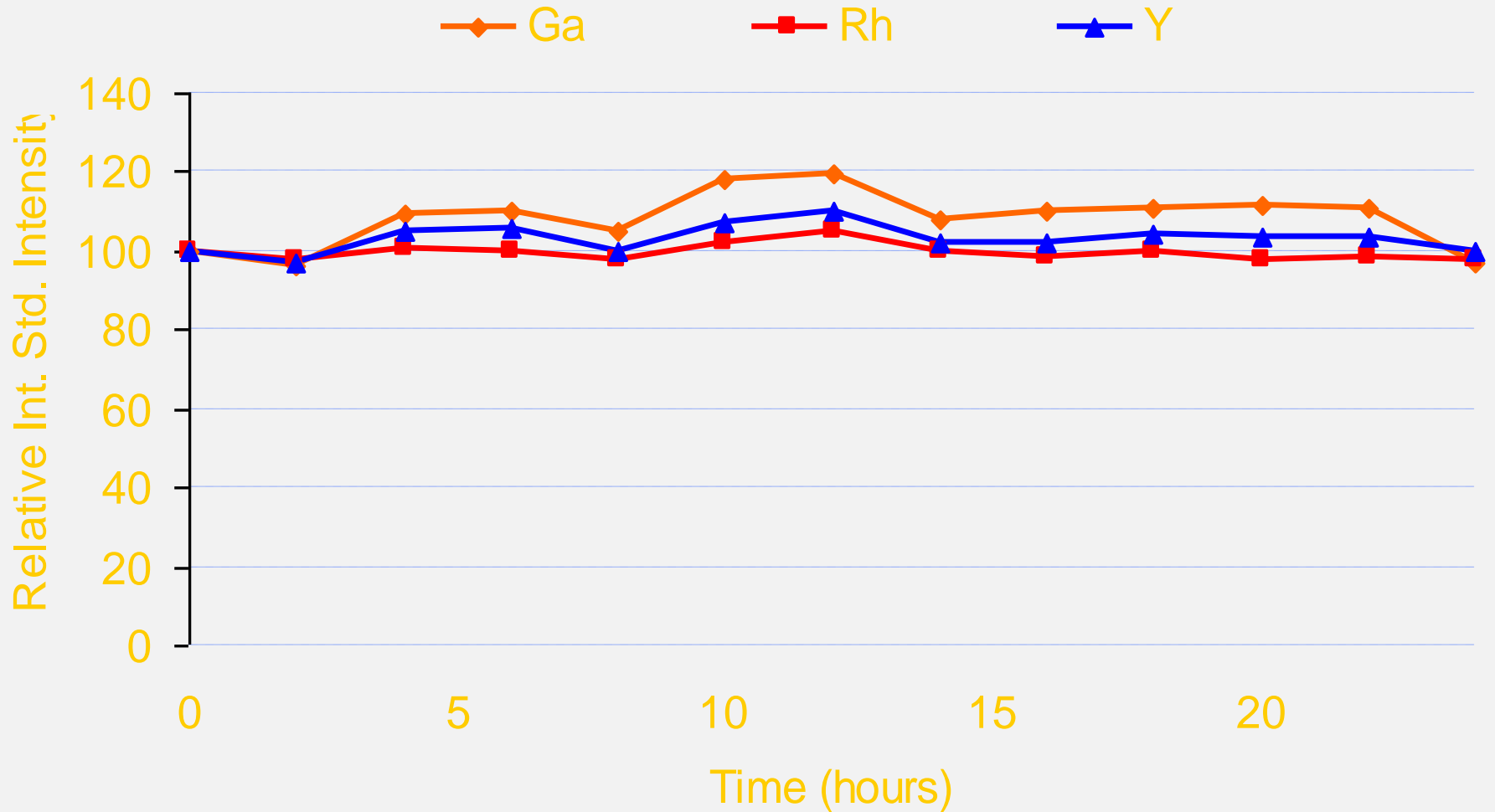
Results: Stability

- Monitor internal standards to check for instrument drift
 - Sc in radial mode, Y in axial mode



Variations of 5% over 10 hours

Stability During Analysis



Efficient Drift Correction

- What does an experiment look like?
 - 5 samples, 5 replicate measurements

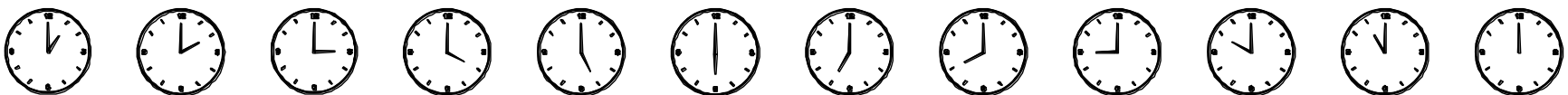
Experiment design for traditional drift correction



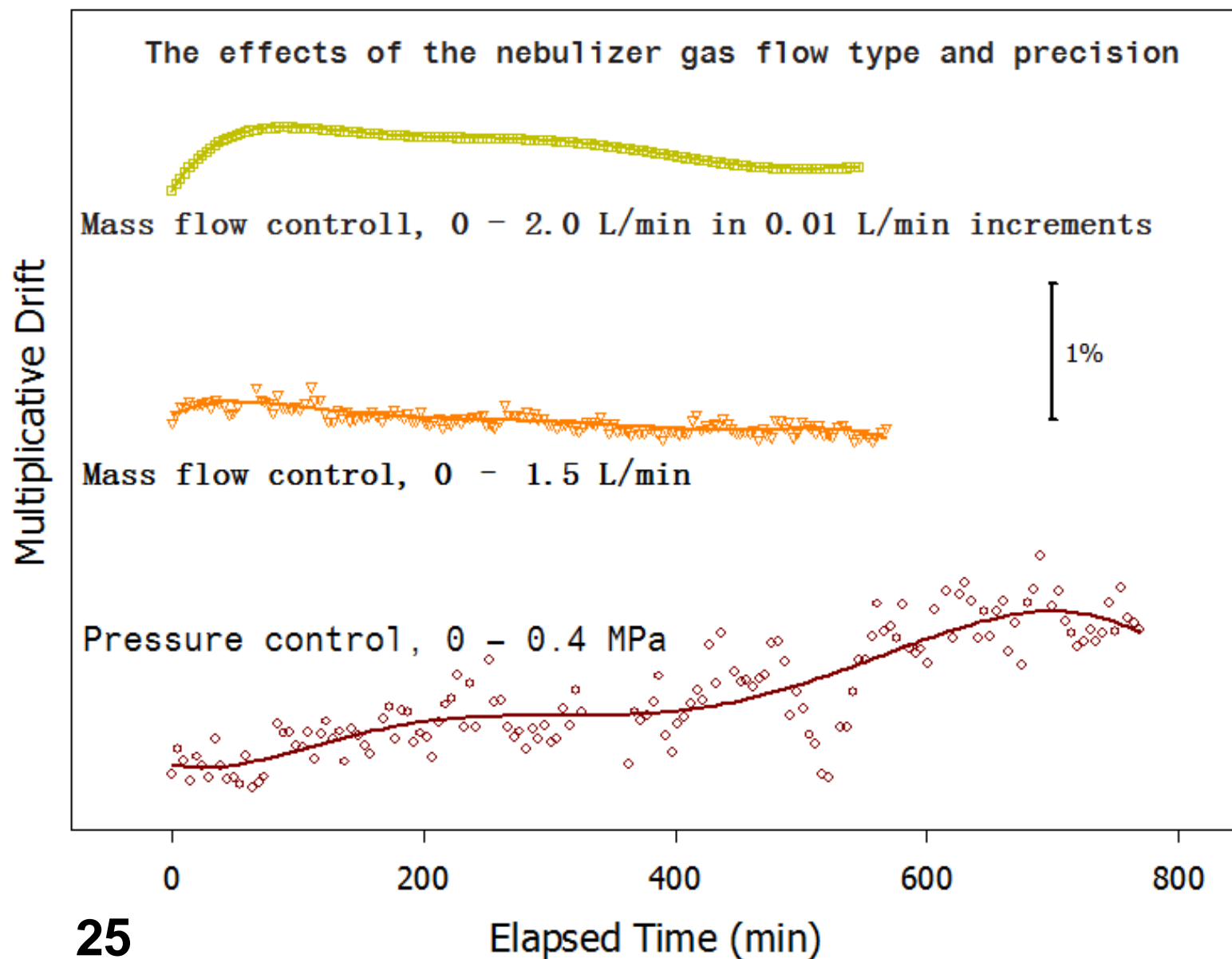
Experiment design for efficient drift correction



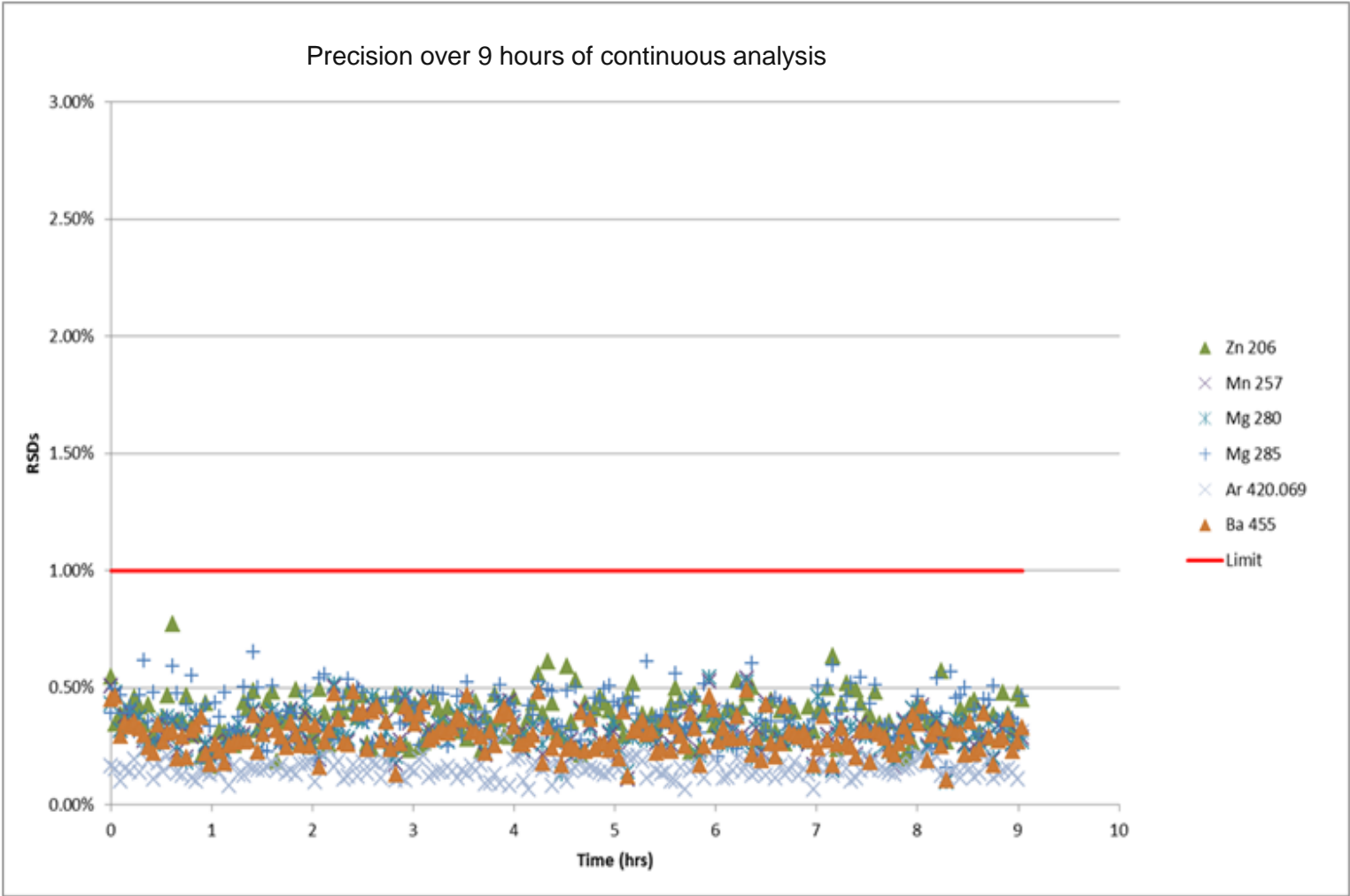
- Standard
- Sample 1
- Sample 2
- Sample 3
- Sample 4
- Sample 5



如何从1% → 0.1% ?



Avio 500 Performance: Unsurpassed stability



Meinhard Type K1 and standard baffled cyclonic spray chamber

9-hour stability run results in <1% RSD

噪音来自蠕动泵、雾化气、电压波动、温度波动。。。

Make a simple Argon diagnostic method and monitor the RSD.
Run a 2v/v% nitric acid solution with four different conditions:

1. Pump on and nebulizer on
2. Pump on and nebulizer off
3. Pump off and nebulizer on
4. Pump off and nebulizer off



A	B	C	D	E	F	G	H	I
Exp_5 Ar-diagnose test								
Plasma power:	1350		Nebulizer type:	CF	resolution	normal		
Nebulizer flow:	0.85		Nebulizer tubing:	B/B	profiling	no		
Auxiliary flow:	0.2		Injector diameter:	2.0 mm	Replicates	10		
Plasma flow:	15		Peak Algorithm:	Area				
Pump speed:	1.5		Points per peak:	3	torch position	-3		
methode:	Exp 5		Results file:	Exp_5				
Read parameters	min 1	max 5						
test	Ar 420.069 % RSD							
pump on neb on	0.28							
pump on neb uit	0.18							
pump off neb on	0.14							
pump off neb out	0.03							

Biggest contribution is the PERISTALTIC PUMP!!

Step 1. Method

- Add at least 3 wavelengths for each analyte (if possible)
- Same for the internal standard(s)

把大象装冰箱，分几步？

The screenshot shows the 'Method Editor' window for 'Pt950Ru'. The 'Define elements' section contains a table with the following data:

	Symbol	Wavelength (nm)	Name	Function
1	Be	313.042	Be 313.042 Ax	Int. Std.
2	Be	313.042	Be 313.042 Rad	Int. Std.
3	Be	313.107	Be 313.107 Ax	Int. Std.
4	Be	313.107	Be 313.107 Rad	Int. Std.
5	Pt	193.700	Pt 193.700 Rad	Analyte
6	Pt	204.937	Pt 204.937 Rad	Analyte
7	Pt	214.423	Pt 214.423 Rad	Analyte
8	Pt	265.945	Pt 265.945 Ax	Analyte
9	Pt	265.945	Pt 265.945 Rad	Analyte
10	Ru	240.272	Ru 240.272 Ax	Analyte
11	Ru	279.535	Ru 279.535 Ax	Analyte
12	Ru	349.894	Ru 349.894 Ax	Analyte
13	Sc	361.383	Sc 361.383 Ax	Int. Std.
14	Sc	361.383	Sc 361.383 Rad	Int. Std.
15	Y	371.029	Y 371.029 Ax	Int. Std.
16	Y	371.029	Y 371.029 Rad	Int. Std.
17	Yb	289.138	Yb 289.138 Ax	Int. Std.
18	Yb	289.138	Yb 289.138 Rad	Int. Std.
19				

Elements and wavelengths can be selected by clicking on one of the buttons to the right

Buttons: Periodic table, Wavelength table

Right sidebar: Define Elements, Settings, Spectral Windows

Step 1a. Method

- Resolution: Normal
- Integration Time: Auto Min 5 – Max 5
- Replicates 5

Method Editor : Pt950Ru Baffled

Spectrometer | Sampler | Process | Calibration | Checks | QC | Options

Spectral settings

Purge gas flow Normal High

Spectral profiling No Yes

Resolution Fixed Normal Variable Set...

Read parameters

Time (sec) Auto Min 5 Max 5 Manual Set...

Delay time 70 sec

Replicates 5

Define Eler
Settings
Spectral Windows

Step 1b. Method

- Calibration with 1 standard (highest, why?*), because we are only interested in the timing parameters
- Use Auto Integration Report

*Answer: If you use the lowest standard, then the highest standard can become saturated if the final reading times are manual inserted in the reading parameters (step 4b).

Method Editor : Pt950Ru Baffled

Spectrometer | Sampler | Process | Calibration | Checks | QC | Options

Include in results and printed log

Headers

- Analytical header
- Method header
 - Short
 - Expanded
- Sample header
- Start each sample on a new page

Sample data items

- Replicate Data
- Means and Statistics
- Auto Integration Report
- Display over calibration message

150 %

Summary items

- Analysis list
- Matrix test reports
- Calibration summary
- Detailed calibration summary

Save with results

- Spectral Data
- Universal Data Acquisition
 - Radial
 - Axial

Remarks

Step 2. Analysis

- Run the blank and standard and open the timing parameters from the Results page

Results			
Sequence No.: 1	Autosampler Location:		
Sample ID: Stand High	Date Collected: 12/18/2014 10:08:54 AM		
Analyst:	Data Type: Reprocessed on 12/30/2014 2:41:03 PM		
Logged In Analyst (Original) : ICP1	Initial Sample Vol:		
Initial Sample Wt: 1 g	Sample Prep Vol: 100 mL		
Dilution:			
Wash Time:			

Auto-Integration Report			
Analyte	Integration Time (s)	Number of Integrations	Read Time (s)
Be 313.042 Ax	0.010	1000	10.000
Be 313.042 Rad	0.100	100	10.000
Be 313.107 Ax	0.010	1000	10.000
Be 313.107 Rad	0.100	100	10.000
Sc 361.383 Ax	0.010	1000	10.000
Sc 361.383 Rad	0.500	20	10.000
Y 371.029 Ax	0.010	1000	10.000
Y 371.029 Rad	0.500	20	10.000
Yb 289.138 Ax	0.100	100	10.000
Yb 289.138 Rad	0.500	20	10.000
Pt 193.700 Rad	0.500	20	10.000
Pt 204.937 Rad	0.500	20	10.000
Pt 214.423 Rad	0.500	20	10.000
Pt 265.945 Ax	0.010	1000	10.000
Pt 265.945 Rad	0.100	100	10.000
Ru 240.272 Ax	0.100	100	10.000
Ru 279.535 Ax	0.100	100	10.000
Ru 349.894 Ax	0.100	100	10.000

Step 3. Evaluation

- Try to find the same Integration Times for all analytes and find a similar or corresponding Internal Standard for each analyte.
- Note: You can always change the concentration of the Internal Standard!

Results

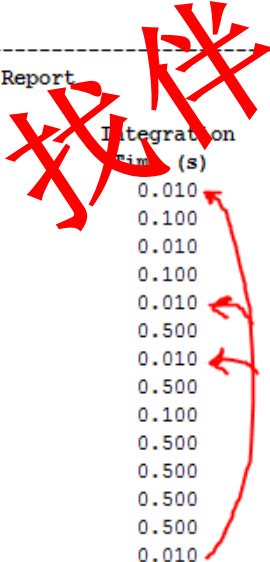
Sequence No.: 1
Sample ID: Stand High
Analyst:
Logged In Analyst (Original) : ICP1
Initial Sample Wt: 1 g
Dilution:
Wash Time:

Autosampler Location:
Date Collected: 12/18/2014 10:08:54 AM
Data Type: Reprocessed on 12/30/2014 2:41:03 PM

Initial Sample Vol:
Sample Prep Vol: 100 mL

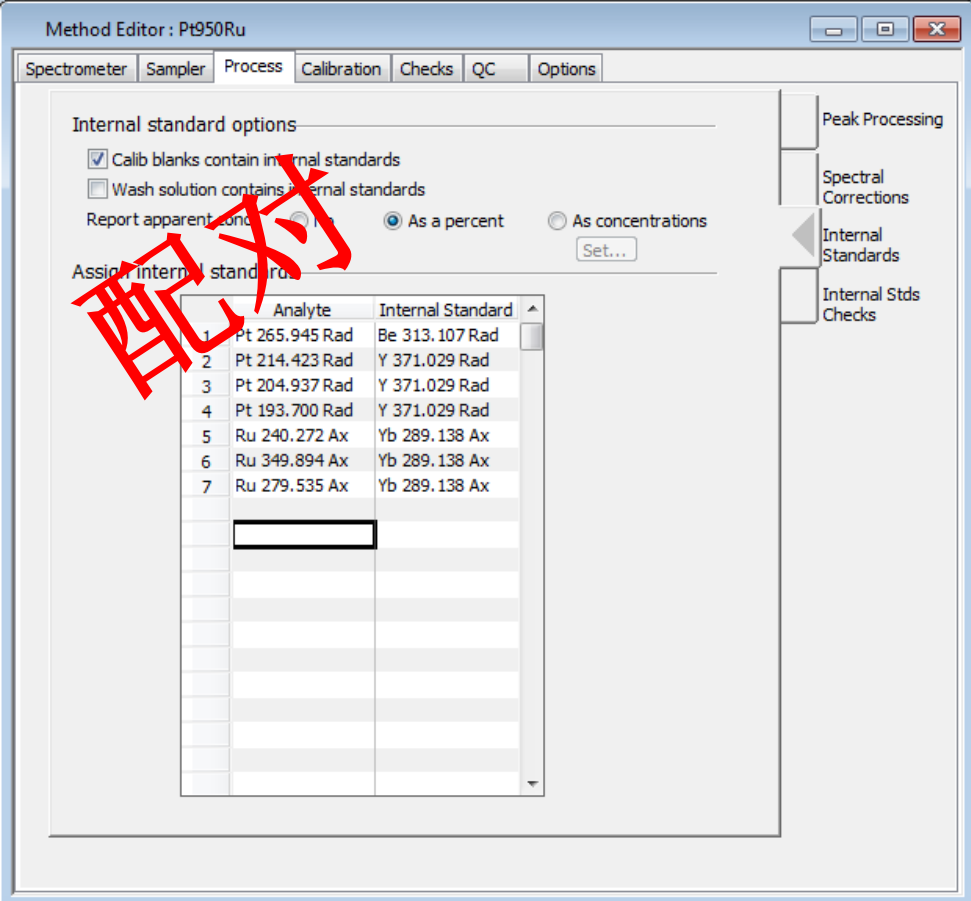
Auto-Integration Report

Analyte	Integration Time (s)	Number of Integrations	Read Time (s)
Be 313.042 Ax	0.010	1000	10.000
Be 313.042 Rad	0.100	100	10.000
Be 313.107 Ax	0.010	1000	10.000
Be 313.107 Rad	0.100	100	10.000
Sc 361.383 Ax	0.010	1000	10.000
Sc 361.383 Rad	0.500	20	10.000
Y 371.029 Ax	0.010	1000	10.000
Y 371.029 Rad	0.500	20	10.000
Yb 289.138 Ax	0.100	100	10.000
Yb 289.138 Rad	0.500	20	10.000
Pt 193.700 Rad	0.500	20	10.000
Pt 204.937 Rad	0.500	20	10.000
Pt 214.423 Rad	0.500	20	10.000
Pt 265.945 Ax	0.010	1000	10.000
Pt 265.945 Rad	0.100	100	10.000
Ru 240.272 Ax	0.100	100	10.000
Ru 279.535 Ax	0.100	100	10.000
Ru 349.894 Ax	0.100	100	10.000



Step 4a. Method, Assign Internal Standards

- Assign for each analyte the internal standard as obtained in Step 3.



The screenshot displays the 'Method Editor: Pt950Ru' software interface. The 'Internal standard options' section includes the following settings:

- Calib blanks contain internal standards
- Wash solution contains internal standards
- Report apparent concentration: As a concentration, As a percent, As concentrations

The 'Assign internal standards' table is shown below:

	Analyte	Internal Standard
1	Pt 265.945 Rad	Be 313.107 Rad
2	Pt 214.423 Rad	Y 371.029 Rad
3	Pt 204.937 Rad	Y 371.029 Rad
4	Pt 193.700 Rad	Y 371.029 Rad
5	Ru 240.272 Ax	Yb 289.138 Ax
6	Ru 349.894 Ax	Yb 289.138 Ax
7	Ru 279.535 Ax	Yb 289.138 Ax

A large red watermark '配内' is overlaid on the table.

Step 4b. Method, Read Parameters

- Change the Read Parameters to Manual and fill in exactly the same timing parameters as obtained IN STEP 3.

The screenshot shows the 'Method Editor : Pt950Ru' window with the 'Options' tab selected. The 'Spectral settings' section includes radio buttons for Purge gas flow (Normal selected), Spectral profiling (No selected), and Resolution (Fixed selected, Normal dropdown). The 'Read parameters' section has radio buttons for Time (sec) (Auto selected, Manual selected), a delay time of 70 sec, and 5 replicates. A 'Set Manual Integration' dialog box is open, showing a table with 14 rows of analyte data.

	F'n	Analyte	Integration Time (sec)	Read Time (sec)
1	A	Pt 265.945 Rad	0.100	10.000
2	A	Pt 214.423 Rad	0.500	10.000
3	A	Pt 204.937 Rad	0.500	10.000
4	A	Pt 193.700 Rad	0.500	10.000
5	A	Ru 240.272 Ax	0.100	10.000
6	A	Ru 349.894 Ax	0.100	10.000
7	A	Ru 279.535 Ax	0.100	10.000
8	IS	Be 313.107 Ax	0.100	10.000
9	IS	Be 313.042 Ax	0.100	10.000
10	IS	Be 313.107 Rad	0.100	10.000
11	IS	Be 313.042 Rad	0.100	10.000
12	IS	Y 371.029 Ax	0.100	10.000
13	IS	Y 371.029 Rad	0.500	10.000
14	IS	Yb 289.138 Ax	0.500	10.000

Step 4c. Method bracketing

- Prepare Standards in the expected working range
- Use Lin, Bracketing

Method Editor : Pt950Ru

Spectrometer | Sampler | Process | Calibration | Checks | QC | Options

Calibration units and standard concentrations

	Analyte	Calib Units	Std1	Std2	Std3
1	Pt 265.945 Rad	mg/L	200	250	300
2	Pt 214.423 Rad	mg/L	200	250	300
3	Pt 204.937 Rad	mg/L	200	250	300
4	Pt 193.700 Rad	mg/L	200	250	300
5	Ru 240.272 Ax	mg/L	5	10	15
6	Ru 349.894 Ax	mg/L	5	10	15
7	Ru 279.535 Ax	mg/L	5	10	15

Define Standards
Calib Units and Concentrations
Blank Usage
Equations and Sample Units
Initial Calibration

Method Editor : Pt950Ru

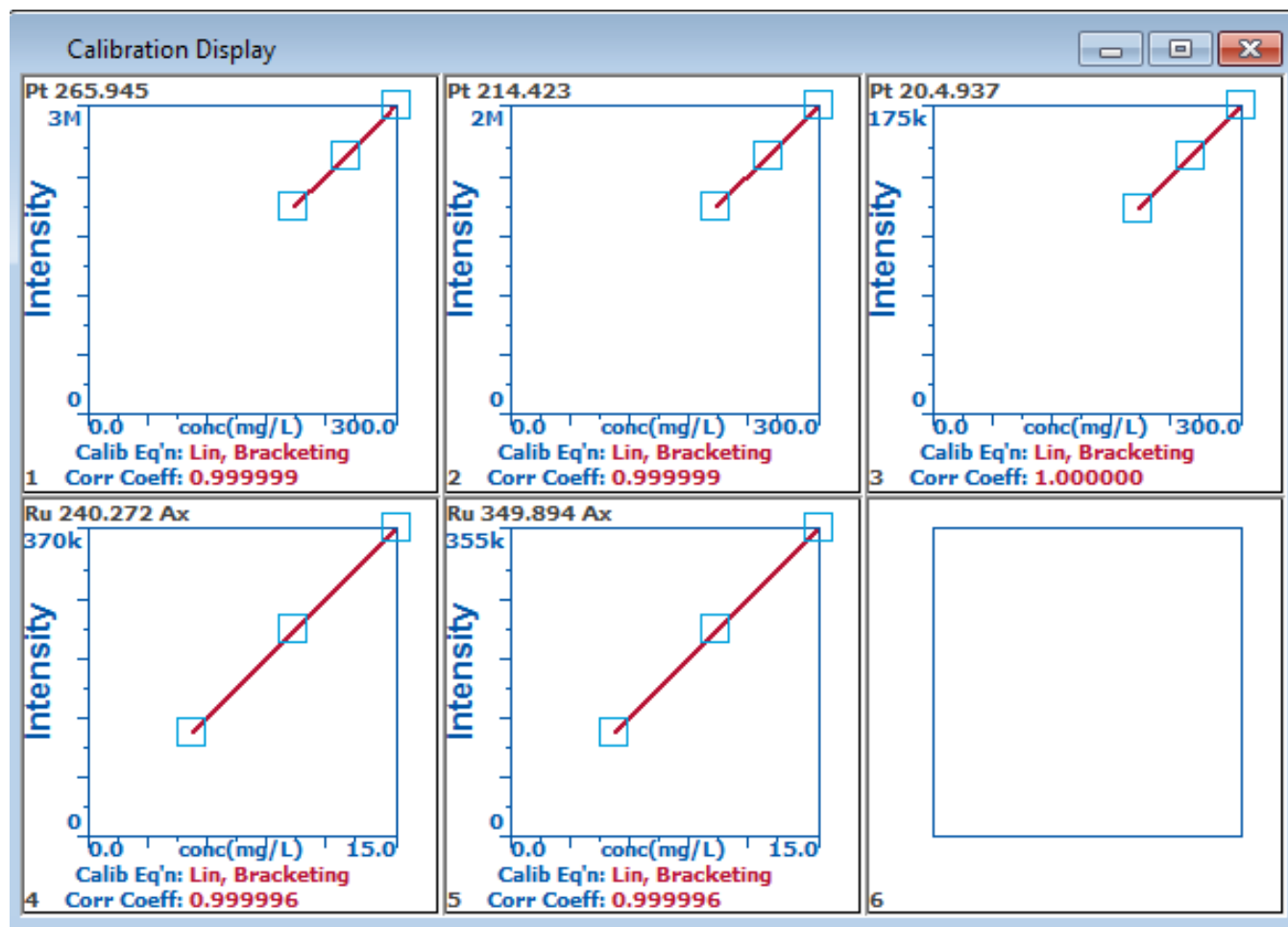
Spectrometer | Sampler | Process | Calibration | Checks | QC | Options

Calibration equations and sample units

	F'n	Analyte	Calibration Equation	Sample Units	Max. Dec. Places	Max. Signif. Figs
1	A	Pt 265.945 Rad	Lin, Bracketing	mg/L	3	4
2	A	Pt 214.423 Rad	Lin, Bracketing	mg/L	3	4
3	A	Pt 204.937 Rad	Lin, Bracketing	mg/L	3	4
4	A	Pt 193.700 Rad	Lin, Bracketing	mg/L	3	4
5	A	Ru 240.272 Ax	Lin, Bracketing	mg/L	3	4
6	A	Ru 349.894 Ax	Lin, Bracketing	mg/L	3	4
7	A	Ru 279.535 Ax	Lin, Bracketing	mg/L	3	4
8	IS	Be 313.107 Ax	n/a	mg/L	3	4
9	IS	Be 313.042 Ax	n/a	mg/L	3	4
10	IS	Be 313.107 Rad	n/a	mg/L	3	4
11	IS	Be 313.042 Rad	n/a	mg/L	3	4
12	IS	Y 371.029 Ax	n/a	mg/L	3	4
13	IS	Y 371.029 Rad	n/a	mg/L	3	4
14	IS	Yb 289.138 Ax	n/a	mg/L	3	4
15	IS	Yb 289.138 Rad	n/a	mg/L	3	4
16	IS	Sc 361.383 Ax	n/a	mg/L	3	4
17	IS	Sc 361.383 Rad	n/a	mg/L	3	4

Define Standards
Calib Units and Concentrations
Blank Usage
Equations and Sample Units
Initial Calibration
Multiline Calibration

Linear Bracketing



Full Compliance with ISO11494, 11495, etc.

Step 5. Analysis, Run all.....That's all

Sequence No.: 3
Sample ID: Std2
Analyst:
Logged In Analyst (Original) : ICP1
Initial Sample Wt:
Dilution:
Wash Time:

Autosampler Location: 3
Date Collected: 12/18/2014 2:02:20 PM
Data Type: Reprocessed on 12/30/2014 3:08:56 PM
Initial Sample Vol:
Sample Prep Vol:

Mean Data: Std2

Analyte	Mean Corrected Intensity	Std.Dev.	RSD	Conc.	Units
Be 313.107 Ax	2119890.3	7221.66	0.34%	98.67	%
Be 313.042 Ax	4285765.2	14410.54	0.34%	98.72	%
Y 371.029 Ax	1337847.3	3817.57	0.29%	98.38	%
Yb 289.138 Ax	154247.0	448.19	0.29%	98.23	%
Sc 361.383 Ax	1485809.9	4170.77	0.28%	98.30	%
Pt 265.945†	2529182.3	818.69	0.03%	[250]	mg/L
Pt 214.423†	1699057.0	632.78	0.04%	[250]	mg/L
Pt 20.4.937†	145684.1	63.67	0.04%	[250]	mg/L
Ru 240.272 Axt	247572.0	177.19	0.07%	[10]	mg/L
Ru 349.894 Axt	236982.8	20.39	0.01%	[10]	mg/L

内标

分析物

标准溶液

- NIST produces and certifies 70 Spectrometric Solution SRMs
 - 1000's sold annually for calibration of ICP, AAS
 - typically 10 mg/g
 - **~0.3% uncertainty**
- transfer standards used for calibration



High Performance ICP-OES, NIST

Anal. Chem. 2001, 73, 4821–4829

Single-Element Solution Comparisons with a High-Performance Inductively Coupled Plasma Optical Emission Spectrometric Method

Marc L. Salit,* Gregory C. Turk, Abigail P. Lindstrom, Therese A. Butler, Charles M. Beck II, and Bruce Norman

Chemical Science and Technology Laboratory, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, Maryland 20899-8391

A solution-based inductively coupled plasma optical emission spectrometric (ICP-OES) method is described for elemental analysis with relative expanded uncertainties on the order of 0.1% relative. The single-element determinations of 64 different elements are presented, with aggregate performance results for the method and parameters for the determination of each element. The performance observed is superior to that previously reported for ICP-OES, resulting from a suite of technical strategies that exploit the strengths of contemporary spectrometers, address measurement and sample handling noise sources, and permit rugged operation with small uncertainty. Taken together, these strategies constitute *high-performance* ICP-OES.

Instructions:

http://www.nist.gov/mml/csd/inorganic/upload/SRM-3100_Version-1-2-Instructions.pdf

Spreadsheet:

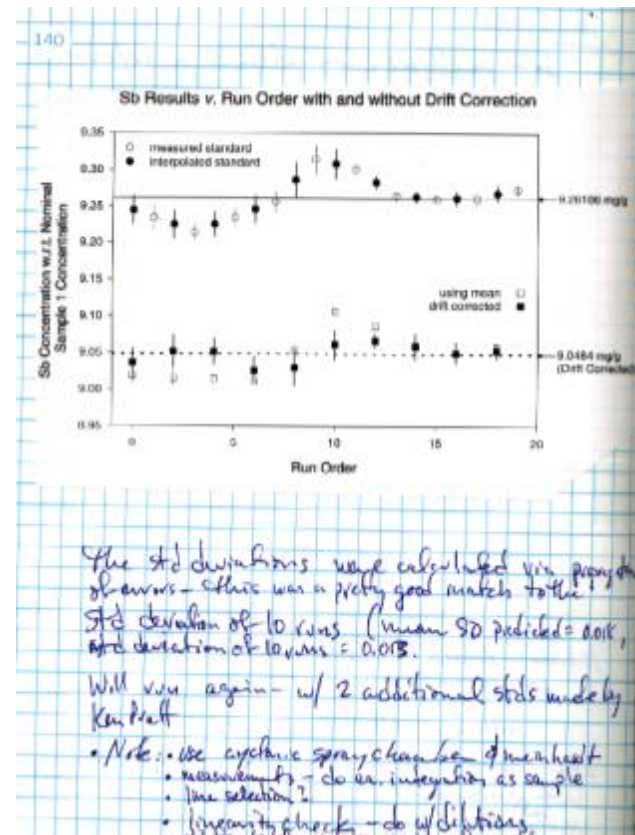
http://www.nist.gov/mml/csd/inorganic/upload/SRM-3100_Traceability-Tool-Version-1-2.xls

Sample Data:

http://www.nist.gov/mml/csd/inorganic/upload/SRM-3100_Example-Data-Set-for-Traceability-Tool-Version-1-2.xls

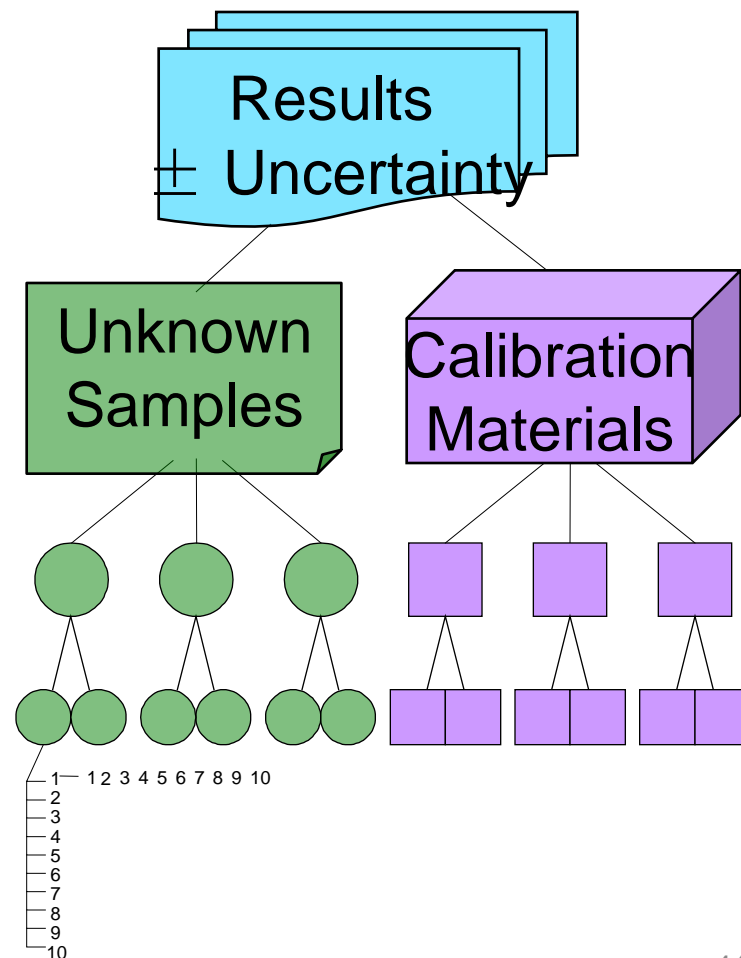
Sb comparison

- first experiment
 - using “conventional” drift correction
 - standard, sample, standard, sample, standard, sample...
 - obvious narrowing of distribution
 - **0.05% standard error of “unknown”**



Experiment Design

- captures variability from...
 - standard materials and preparation
 - solution homogeneity
 - solution-to-solution prep
- robust
 - at least 3x sampling
 - duplicate preparation
 - independent chemists
 - calibrants, SRM, analysis

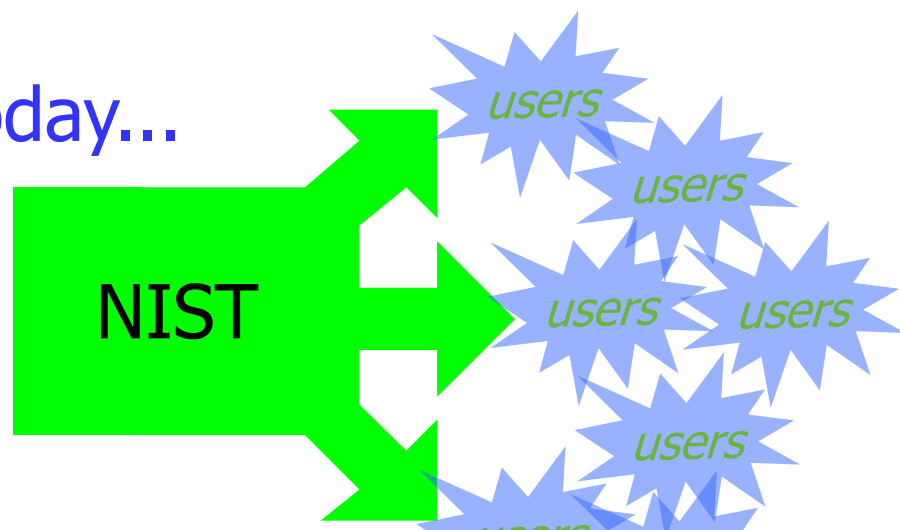


Future of Spectroscopy Solution SRMs

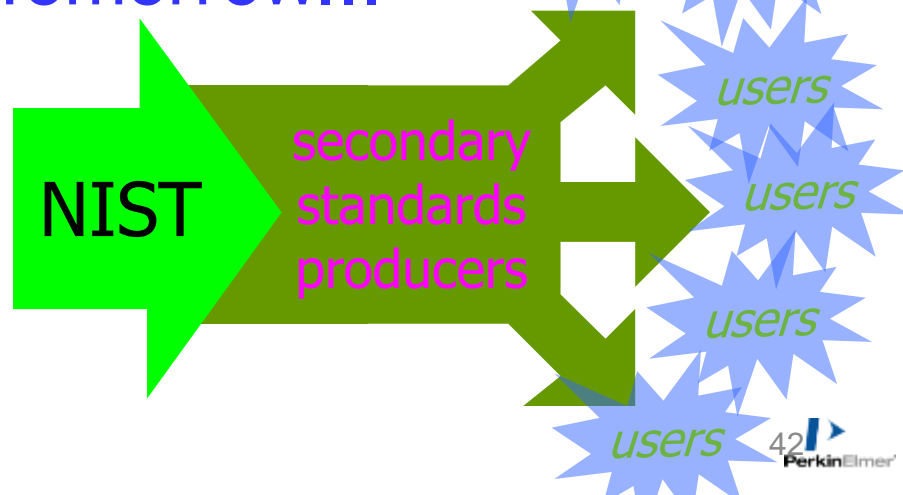
- Goals

- ensure accurate solutions available
 - through *traceability*, not through *production*!
- NIST focus
 - enable traceability
 - accuracy of solutions
 - 1^o materials
 - stability of materials
 - gravimetric aliquots

Today...

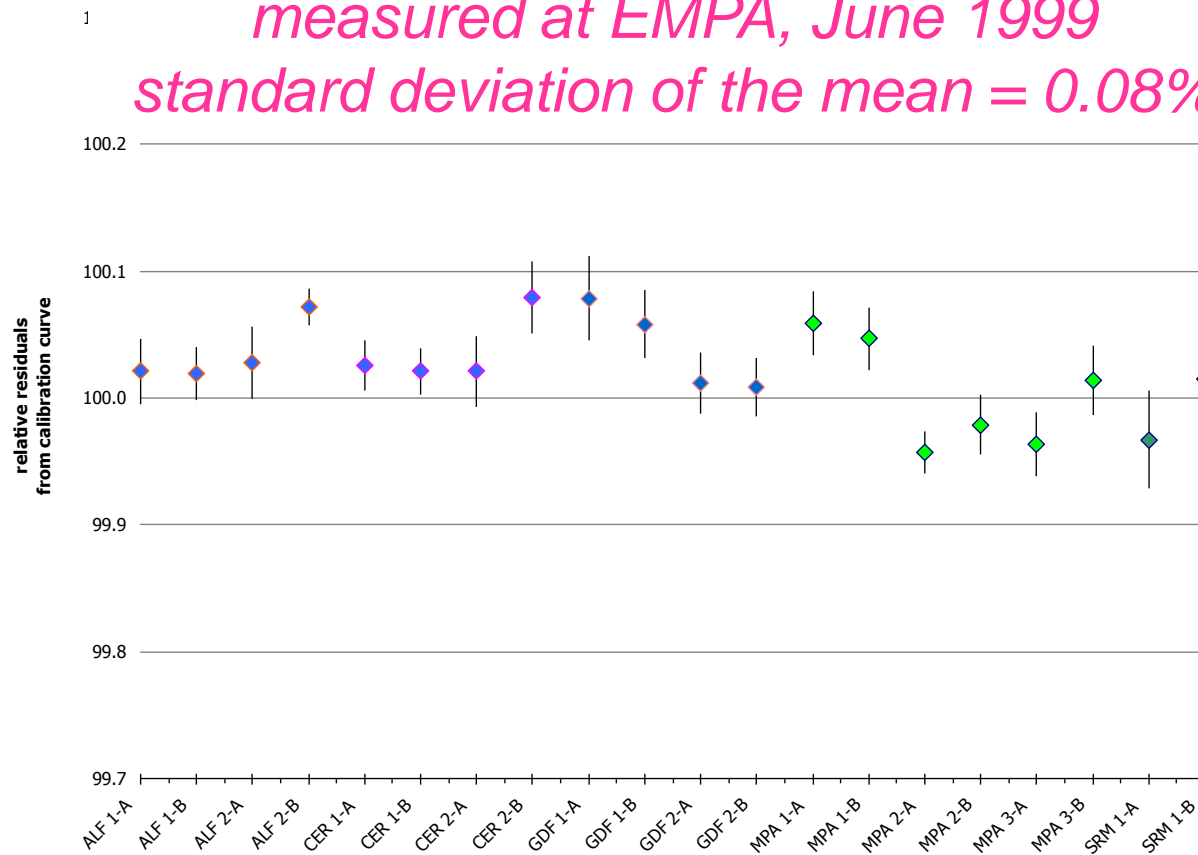


Tomorrow...



US — Swiss Zn residuals

measured at EMPA, June 1999
standard deviation of the mean = 0.08%



标准物质

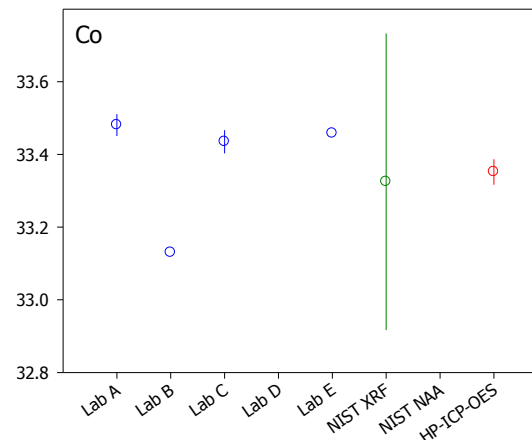
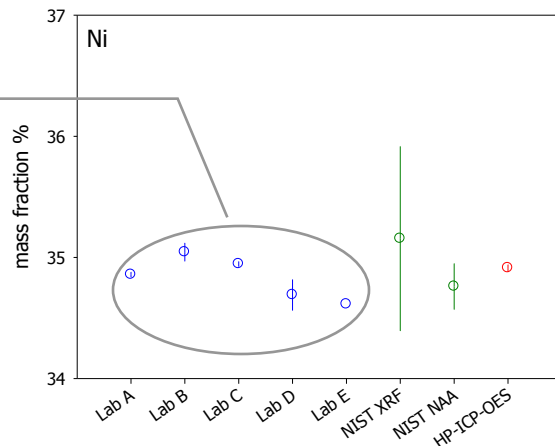
“Real” Samples?

- HP-ICP-OES is 1^o for simple, dilute solutions...
 - is it 1^o for “real” samples?
- MP35N high temperature alloy
 - 30% Ni, 30% Co, 20% Cr, 10% Mo

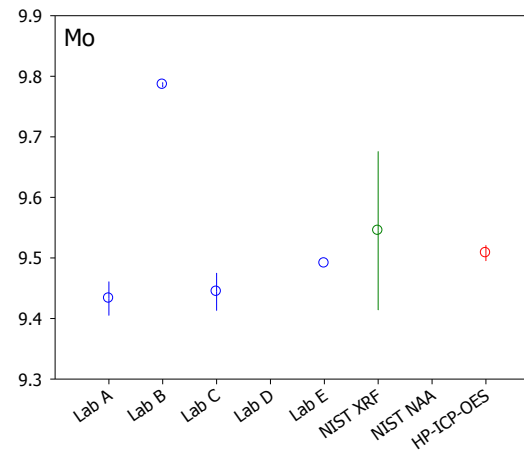
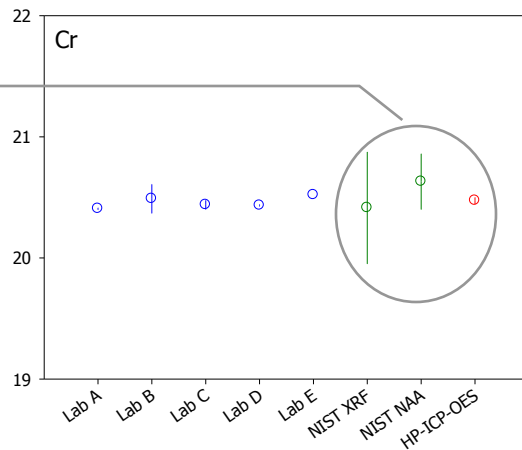


HP-ICP-OES Results Compared

error bars
are std. dev.



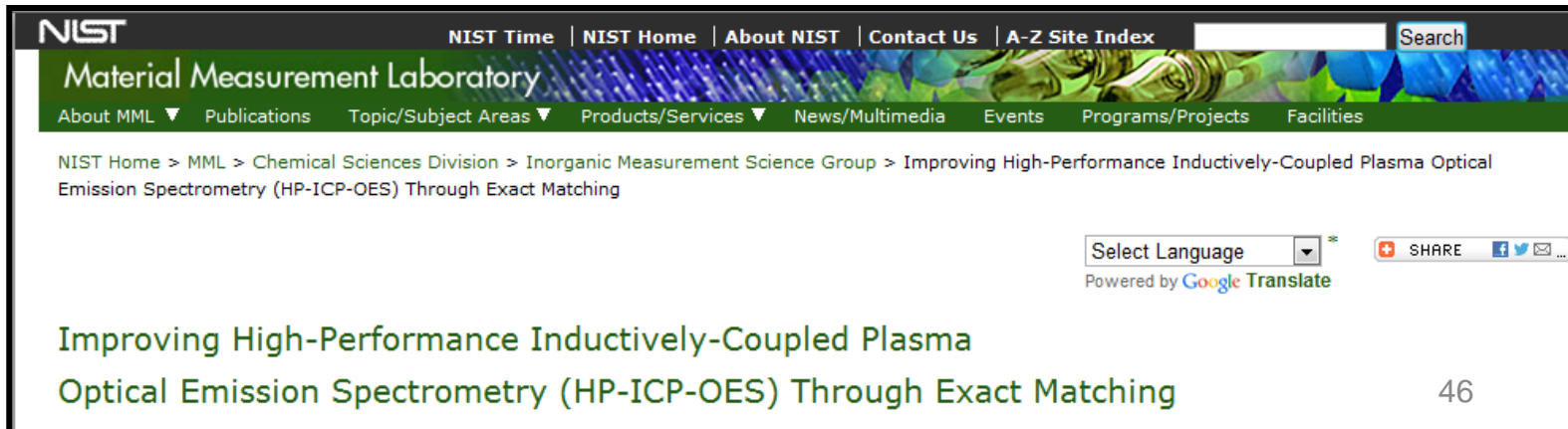
error bars are
exp. uncert.



贵金属

- **The Customer Request**
 - Demonstrate that the Optima is capable of analyzing high accurate and precise determinations of PMGs
- **The Elements**
 - Au, Pt, Pd, Rh, Ir, Ag, Ru
 - e.g. ISO 11494 & 11495
- **The Problem**
 - Analytical Precision Relatively Poor : 0.20 - 0.40%
- **Problem can be partly overcome by using High Performance ICP-OES, as proposed by NIST, but this method is time-consuming.**

See also:



The screenshot shows the NIST Material Measurement Laboratory website. The header includes the NIST logo and navigation links: NIST Time, NIST Home, About NIST, Contact Us, and A-Z Site Index. A search bar is located in the top right corner. Below the header is a green navigation bar with links for About MML, Publications, Topic/Subject Areas, Products/Services, News/Multimedia, Events, Programs/Projects, and Facilities. The main content area displays the breadcrumb path: NIST Home > MML > Chemical Sciences Division > Inorganic Measurement Science Group > Improving High-Performance Inductively-Coupled Plasma Optical Emission Spectrometry (HP-ICP-OES) Through Exact Matching. A language selection dropdown menu is set to "Select Language" with a "Powered by Google Translate" notice below it. To the right of the language menu are social media sharing icons for Facebook, Twitter, and Email, along with a "SHARE" button. The page title is "Improving High-Performance Inductively-Coupled Plasma Optical Emission Spectrometry (HP-ICP-OES) Through Exact Matching".

A closer look at e.g. ISO 11494 and 11495

3.1
bracketing
running of standards and samples in the following sequence: low standard – sample – high standard –
sample – low standard – sample – high standard – sample – low standard – sample – high standard

The RSD of m_{Pd} shall not exceed 0,30 %.

Method is derived from NIST. High Performance Inductively
Coupled Plasma Optical Emission Spectroscopy

Anal. Chem. 2001, 73, 4821–4829

Single-Element Solution Comparisons with a High-Performance Inductively Coupled Plasma Optical Emission Spectrometric Method

**Marc L. Salit,* Gregory C. Turk, Abigail P. Lindstrom, Therese A. Butler, Charles M. Beck II, and
Bruce Norman**

*Chemical Science and Technology Laboratory, National Institute of Standards and Technology,
100 Bureau Drive, Gaithersburg, Maryland 20899-8391*

磷肥

4.3.5 分析结果的表述

有效五氧化二磷(P_2O_5)含量 w_1 以质量分数(%)表示,按式(1)计算:

$$w_1 = \frac{(m_1 - m_2) \times 0.03207}{m_{01} \times \frac{V_{01}}{250}} \times 100$$
$$= \frac{(m_1 - m_2) \times 801.75}{m_{01} V_{01}} \dots\dots\dots(1)$$

式中:

m_1 ——测定时所得磷钼酸喹啉沉淀质量,单位为克(g);

m_2 ——空白试验时,所得磷钼酸喹啉沉淀质量,单位为克(g);

0.03207——磷钼酸喹啉质量换算为五氧化二磷质量的系数;

m_{01} ——试料的质量,单位为克(g);

V_{01} ——所取试样溶液的体积,单位为毫升(mL);

250——试样溶液总体积,单位为毫升(mL)。

取平行测定结果的算术平均值为测定结果。

4.3.6 允许差

平行测定结果的绝对差值不大于0.20%。

不同实验室测定结果的绝对差值不大于0.30%。



A Drift Correction Procedure

Marc L. Salit* and Gregory C. Turk

Chemical Science and Technology Laboratory, Analytical Chemistry Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8391

CONCLUSIONS

The drift correction approach presented here is effective in reducing the uncertainty of the results of a comparison of solutions with ICP-OES. The procedure is simple and should prove to be generally useful in any analytical methodology where the precision of the results is detrimentally effected by system drift. We have demonstrated that this procedure permits the use of ICP-OES at a level of precision that was previously expected only from the classical methods—titrimetry and gravimetry—or from isotope dilution measurements.

(11) Cleveland, W. S. *J. Am. Stat. Assoc.* **1979**, *74*, 829-836.

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quantitatively different from that previously reported for ICP-OES results. Different chemical information becomes available with this ability to discriminate between solutions of very similar composition—an improvement in *concentration resolution*. Additionally, at this level of uncertainty, uncertainty is dominated by effects other than spectroscopic measurement (e.g., sample handling and preparation).

Measurements are performed using unmodified commercially available equipment and are significantly less costly than classical analysis. The opportunity to achieve results of the quality expected of classical analysis with instrumental efficiency enables new analytical applications. In contrast to classical analysis, instrumental automation permits the analysis of multiple samples with little incremental cost per sample. Similar to classical analysis, this method is suitable for determination of “major” and “minor”

Avio 500的关键特点



• 多快好省准

- 多快?
- 多省?
- 多准?

差异化在哪里？

- LC, Liquid Chromatography
- HPLC, High Performance Liquid Chromatography
- ICP, Inductively Coupled Plasma Optical Emission Spectrometry
- HPICP, High Performance Inductively Coupled Plasma
- 不是我们自己吹的，而是NIST命名的！
- 特征：测量不确定度 $\leq 0.1\%$ ，HPICP比ICP好10倍！
- 价格：HPICP仅仅是ICP的两倍！

