农药产品分析的质量控制

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1 农药产品质量检测与判定

- 原药含量分析
- 制剂含量分析
- 杂质分析

原药产品质量的指标规定（**FAO** 规格）

- According the FAO Manual[i], the active ingredient content of technical materials should be expressed as:
- "The [ISO common name] content shall be declared (not less than ...g/kg) and, when determined, the *mean* measured *content shall not be lower than* the declared content."

制剂产品质量规定（ FAO规格）

- The active ingredient content of technical concentrates and formulated pesticides should be expressed as:
- “The [ISO common name] content shall be declared (g/kg or g/l at 20 ± 2° C,) and, when determined, the *mean measured content shall not differ from* that declared by more than the following *tolerances*:”

Table 1. Tolerance limits for active ingredients of pesticide products

Declared content in g/kg or g/l at 20±2°C	Tolerance
up to 25	± 15% of the declared content for homogeneous formulations (EC, SC, SL, etc.), **or** ± 25% for heterogeneous formulations (GR, WG, etc.)
above 25 up to 100	± 10% of the declared content
above 100 up to 250	± 6% of the declared content
above 250 up to 500	± 5% of the declared content
above 500	± 25 g/kg or g/l
Note In each range the upper limit is included	

Where the formulation contains more than one active ingredient, specifications must be provided for all active ingredients present.

- As the tolerances for pesticide product generally correspond to the 95% confidence level,
- thus standard deviation of the variability of active ingredient content, S_T, can be derived from the tolerance intervals (T) specified for the mean measured content of the product: $S_T = T/1.96$,

- T： tolerance intervals， a.i. 可变化范围
- S_T：a.i.可变性标准偏差

$$S_{\overline{m}} = \sqrt{S_T^2 - S_{\overline{C}}^2}$$

$$S_{\overline{C}} = \frac{S_{Ra}}{\sqrt{n}}$$

Table 2. Tolerance intervals and performance characteristics of CIPAC methods for some pesticide formulations

Active ingredient	Formu-lation	± Tolerance %	± Tolerance g/kg	Content, g/kg	r	R	S_R g/kg	CV_r%	$S_R/\sqrt{2}$	$S_{\bar{m}}$ g/kg
Glyphosate	SG		25	731	9 to 11	11 to 14	3.92-5.00	0.54	2.70-3.53	12.26
			25	874	8	14	5.00	0.33	3.53	12.59
Flusilazole	WG	6	*11.82*[a]	197	7	16	5.71	1.27	4.04	4.48
	EC	5	*12.85*	257	12	16	5.71	1.67	4.04	5.16
			0	396	16	25	8.93	1.44	6.31	7.89
Methomyl	WP	6	*14.64*	244	9	14	5.00	1.32	3.54	6.58
	UL	5	*14.9*	298		8	2.86		2.02	7.33
Metsulfuron-methyl	WG	6	*12.72*	212	6 to 9	6 to 9	2.14-3.21	1.52	1.52-2.28	6.08
		5	*30.35*	607	15 to 19	19 to 20	7.14	1.12	5.05	14.64
Profenofos	EC	5	*22.4*	448	8	15	5.36	0.64	3.79	10.78
		5	*17.6*	352	9	23	8.21	0.91	5.81	6.85
Propineb	WP		25	700	10	29	10.36	0.51	7.32	10.44
Quinclorac	WP	5	25	500	23	26	9.29	1.64	6.57	10.94
	WG		25	762	26	42	15.00	1.22	10.61	7.08
	SC	6	*13.14*	219	12	18	6.43	1.96	4.55	4.93
Triazophos	EC	5	*21.65*	433	12	12	4.29	0.99	3.03	10.62
			25	570	12	24	8.57	0.75	6.06	11.22

within laboratory Sra ≤ 1.5 CIPAC Sr
: (Sra ~ Sr).

$$S_L = \sqrt{S_{Sp}^2 + S_A^2}$$

建立新的可信范围？

$$S_{R\bar{a}} = \sqrt{\frac{S_{ra}^2}{2} + \frac{S_r^2}{2}}$$

$$S_T^{'} = \sqrt{S_{R\bar{a}}^2 + S_{\bar{m}}^2}$$

$$T = 2S_T^{'}$$

获得较窄范围 S_T 的可能性

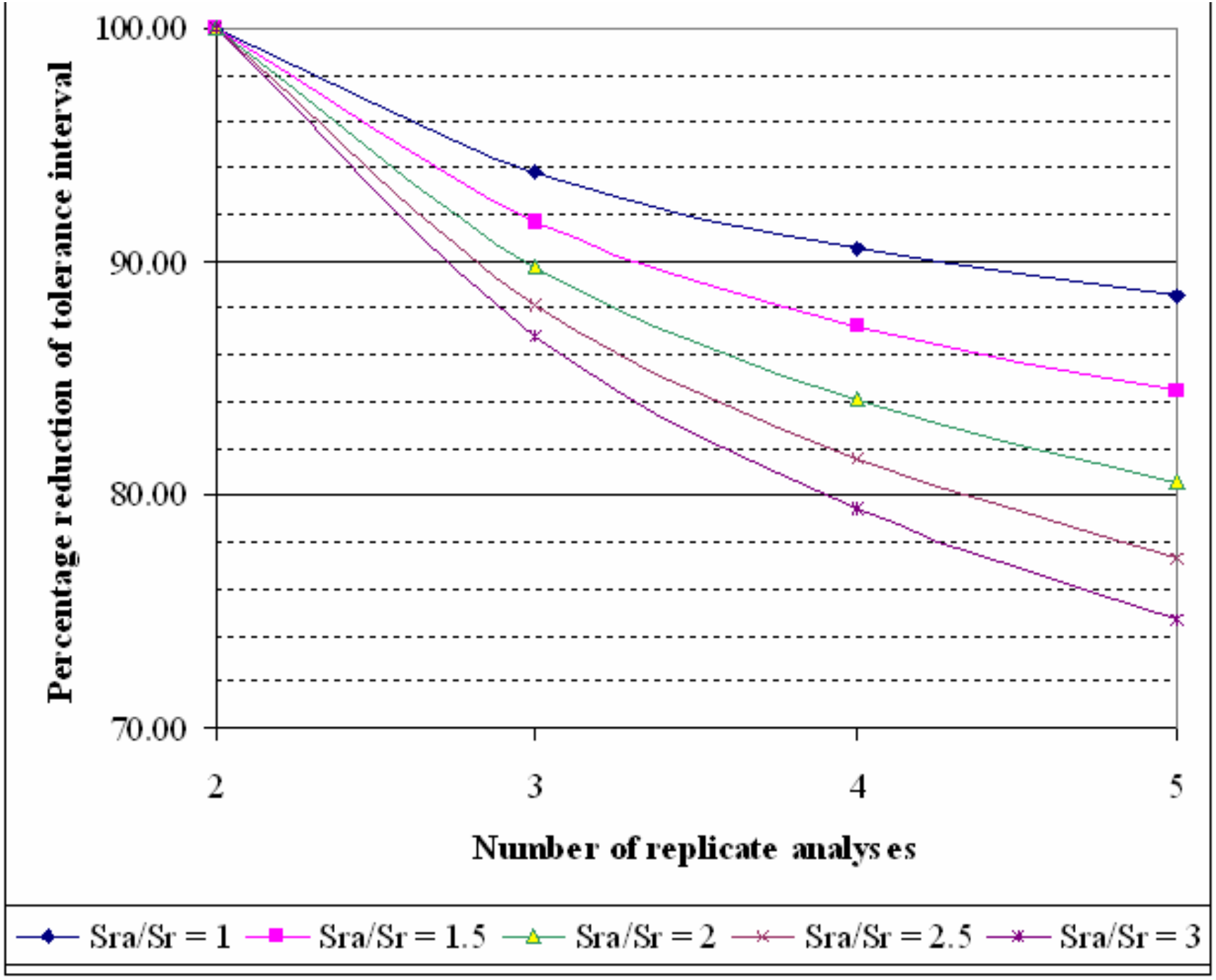
Table 3. $S_{R\bar{a}}$ values calculated for various S_{ra} and n assuming S_r =1

	S_{Ra} values				
n	S_{ra} = 1	S_{ra} =1.5	S_{ra}=2	S_{ra} = 2.5	S_{ra} = 3
2	1.00	1.27	1.58	1.90	2.24
3	0.91	1.12	1.35	1.61	1.87
4	0.87	1.03	1.22	1.44	1.66
5	0.84	0.97	1.14	1.32	1.52

增加分析的重复次数？

增加分析方法的精密度？

$$S_{R\bar{a}} = \sqrt{\frac{S_{ra}^2}{2} + \frac{S_r^2}{2}}$$


100.00
90.00
80.00
70.00
Percentage reduction of tolerance interval
2
3
4
5
Number of replicate analyses
Sra/Sr = 1
Sra/Sr = 1.5
Sra/Sr = 2
Sra/Sr = 2.5
Sra/Sr = 3

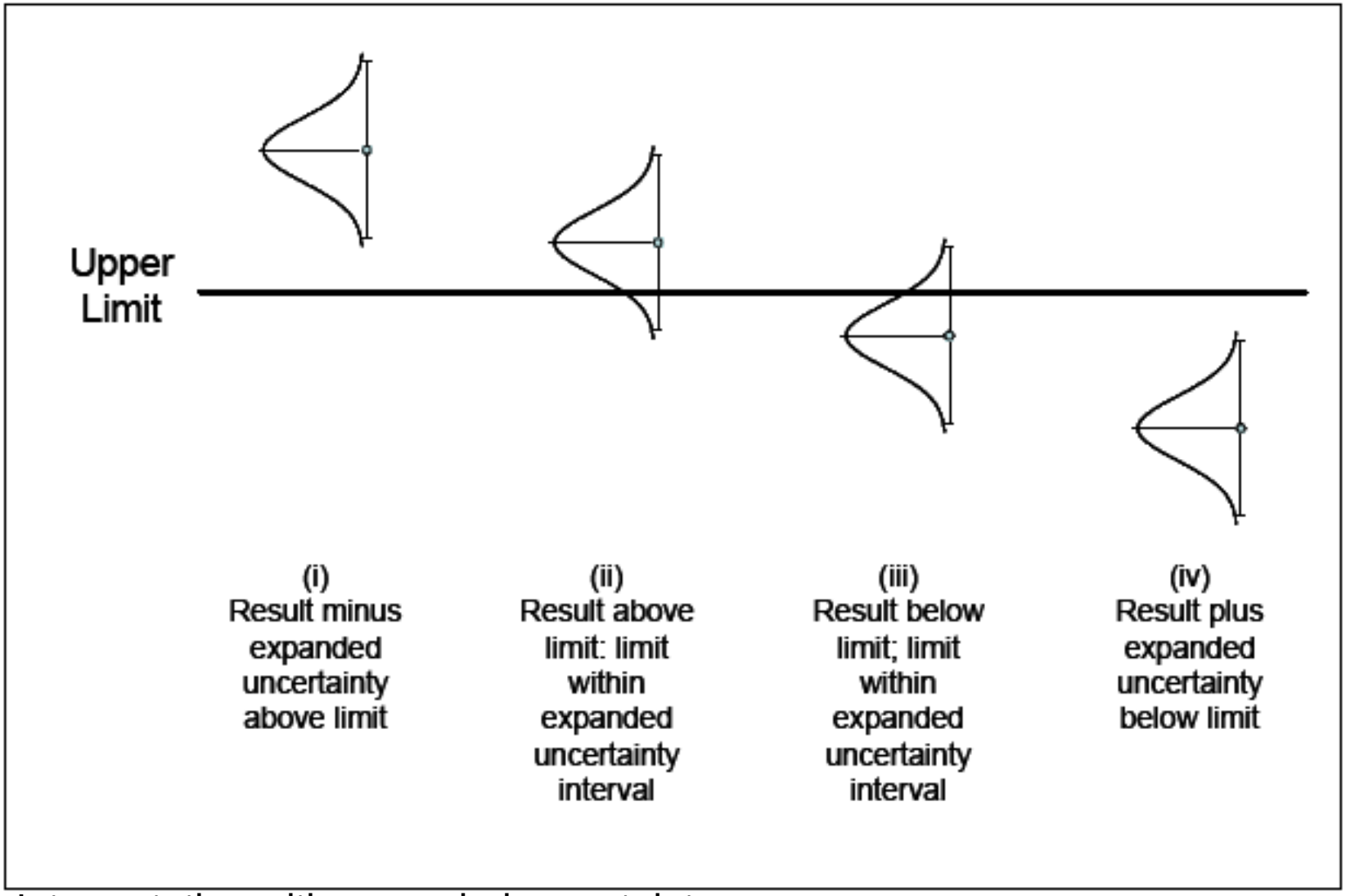
原药产品分析：
有效成分的最低值

- **Testing the minimum active ingredient content of technical active ingredient**

- The mean a.i. content should not be significantly lower than the declared content.

Uncertainty and compliance limits

Figure 1 Assessment of Compliance with an Upper Limit



Interpretation with expanded uncertainty

- The FAO Specification declares the minimum a.i. content, e.g. 950 g/kg. The mean a.i. content should not be significantly lower than the declared content.

$$\mu \leq \bar{x} + \frac{ts}{\sqrt{n}}$$

Testing the minimum active ingredient content of technical active ingredient

$$q_{\bar{x},\mu} = \frac{\left|\bar{x} - \mu\right|}{X_n - X_1}$$

X < U 时

Table A9a. Significance limits ($q_{\bar{x},\mu}$) for the differences between the mean of a sample and a hypothetical mean

Significance limits[2] for the difference between the mean of a sample and a hypothetical mean μ

Test quotient: $\frac{|\bar{x} - \mu|}{x_N - x_1}$

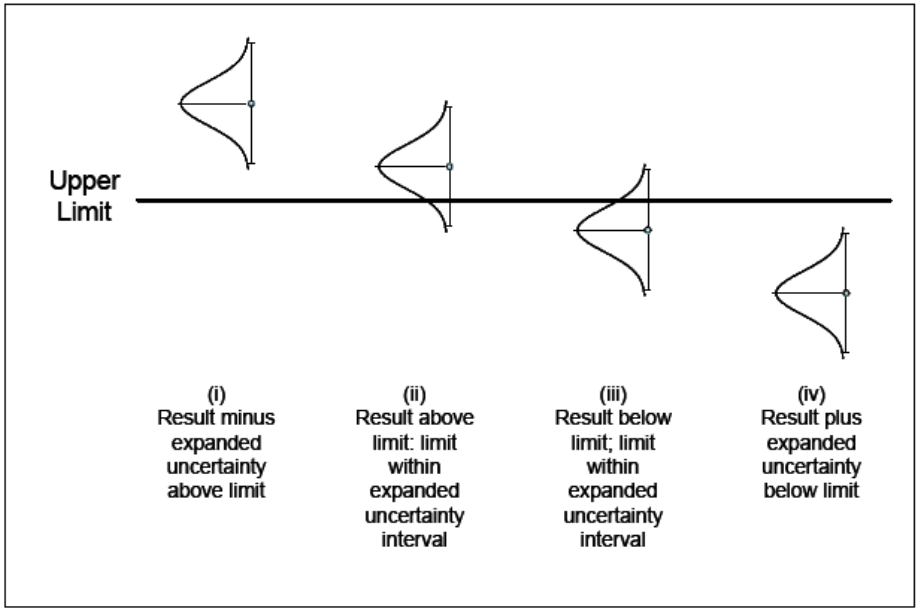
x_N is the highest, x_1 the lowest value of a sample of size N

2α	0,10	0,05	0,02	0,01	0,002	0,001
N						
2	3,157	6,353	15,910	31,828	159,16	318,31
3	0,885	1,304	2,111	3,008	6,77	9,58
4	0,529	0,717	1,023	1,316	2,29	2,85
5	0,388	0,507	0,685	0,843	1,32	1,58
6	0,312	0,399	0,523	0,628	0,92	1,07
7	0,263	0,333	0,429	0,507	0,71	0,82
8	0,230	0,288	0,366	0,429	0,59	0,67
9	0,205	0,255	0,322	0,374	0,50	0,57
10	0,186	0,230	0,288	0,333	0,44	0,50
11	0,170	0,210	0,262	0,302	0,40	0,44
12	0,158	0,194	0,241	0,277	0,36	0,40
13	0,147	0,181	0,224	0,256	0,33	0,37
14	0,138	0,170	0,209	0,239	0,31	0,34
15	0,131	0,160	0,197	0,224	0,29	0,32
16	0,124	0,151	0,186	0,212	0,27	0,30
17	0,118	0,144	0,177	0,201	0,26	0,28
18	0,113	0,137	0,168	0,191	0,24	0,26
19	0,108	0,131	0,161	0,182	0,23	0,25
20	0,104	0,126	0,154	0,175	0,22	0,24

Impurity tests

- if the measured impurity is significantly exceeds the specified limit or not.

Figure 1 Assessment of Compliance with an Upper Limit



$$m \leq \bar{x} - \frac{ts}{\sqrt{n}}$$

2 产品质量分析的重要要素

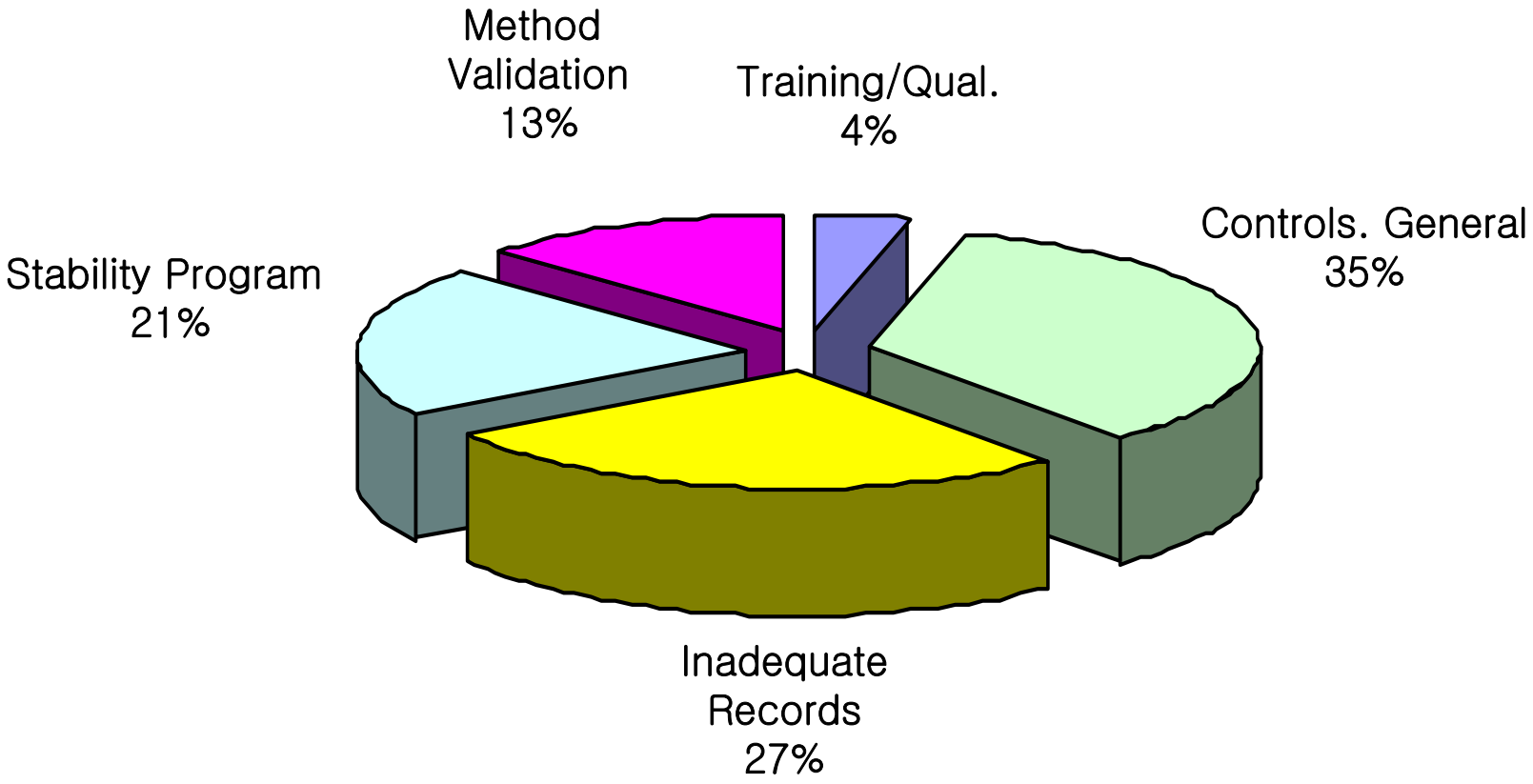
- 可靠的分析方法： CIPAC、AOAC、 国标、行业标准、经过验证的企业标准、权威文献报道的方法

- 可靠的分析实验室质量控制手段： 内部质量控制IQC； 外部质量控制

- 公认的原则： 采用标准分析方法；开发并验证用于质量控制的分析方法、使用实验室熟练掌握的分析方法

FDA 实验室检查中发现的一些问题:
Laboratory System

2002: 212 Inspections (US)



* Reference: Albinus D' Sa, FDA, CDER Office of Compliance, from AAPS, Nov. 2002 presentation.

测量值的组成

- **Observed value**:

  xi = m + B + e

- where
- ***M:*** *平均值*
- ***B*** is bias ;
- ***e*** is 随机误差;
- μ is 真值; often not known

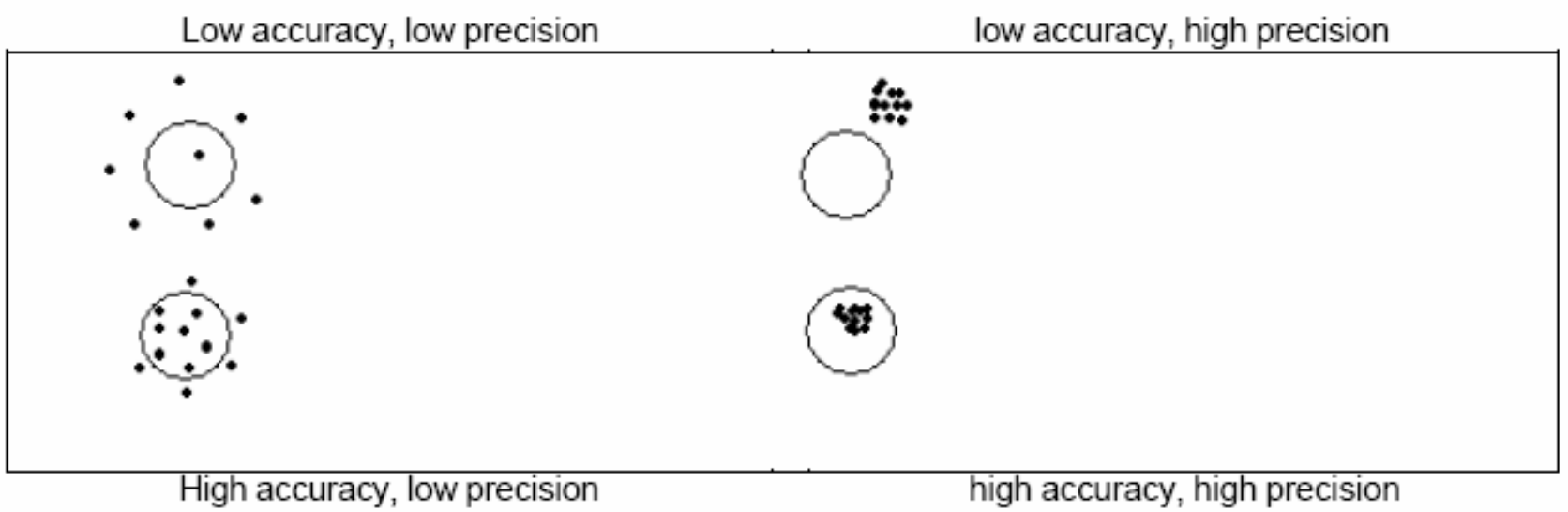
单个实验室内部的误差来源

1- 每个分析测试员之间的差异,

2- 仪器之间的差异,

3- 实验试剂与消耗品之间的差异,

4- 一定时间内以上1、2、3的差异,



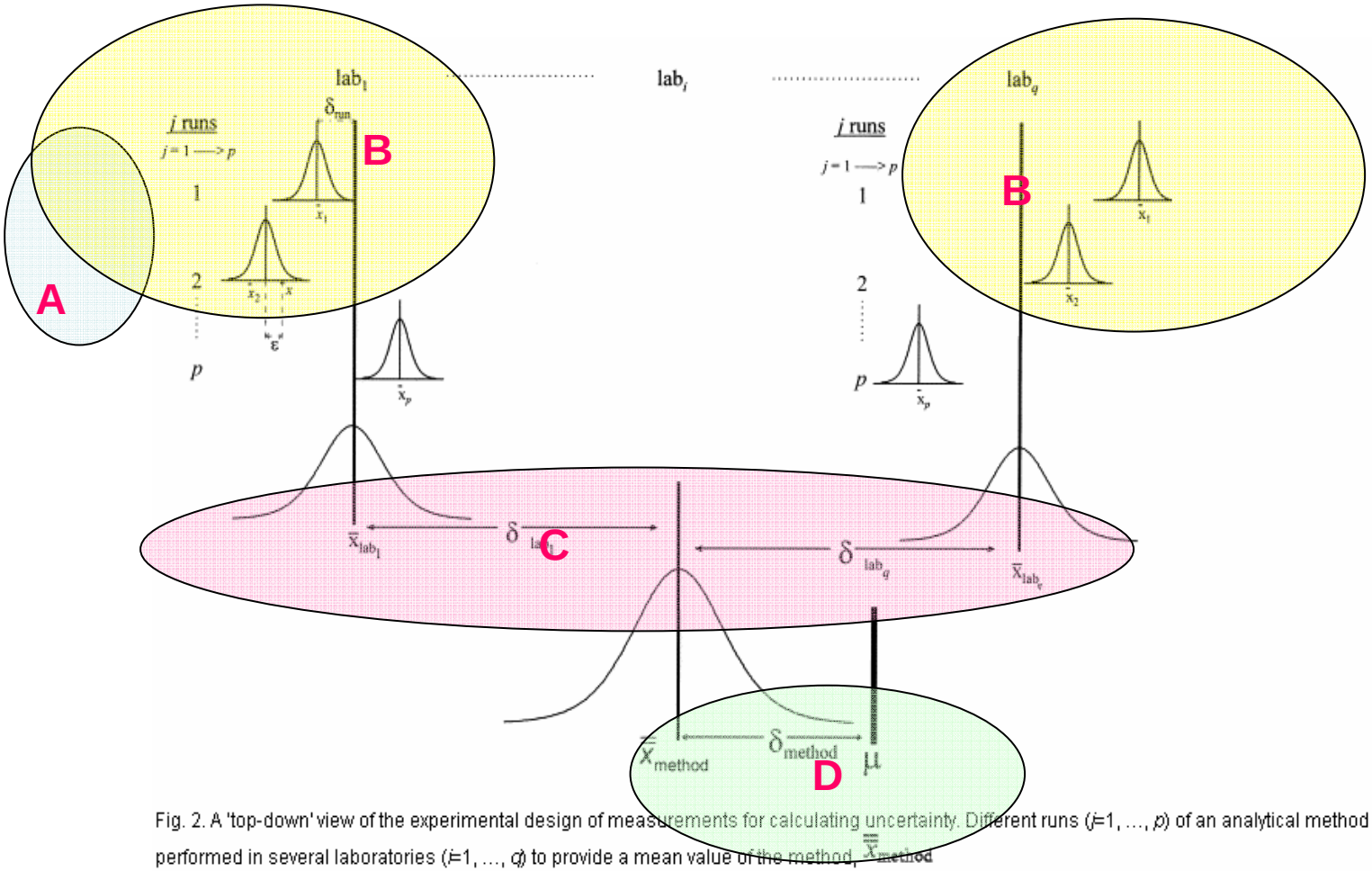


Fig. 2. A 'top-down' view of the experimental design of measurements for calculating uncertainty. Different runs (j=1, …, p) of an analytical method are performed in several laboratories (i=1, …, q) to provide a mean value of the method, $\bar{\bar{x}}_{method}$

. The random error of individual results, ε, the run bias, δ_{run}, the laboratory bias, δ_{lab}, and the method bias, δ_{method}, are shown.

A: Sr; B: run bias; C: lab bias; D: method bias

测量不确定度的来源

在实际分析工作中，不确定度典型的来源包括：

1）对样品的定义不完整或不完善；

2）分析的方法不理想；

3）取样的代表性不够；

4）对分析过程中环境影响的认识或控制不完善；

5）对仪器的读数存在偏差；

6）分析仪器计量性能（灵敏度、分辨力、稳定性等）上的局限性；

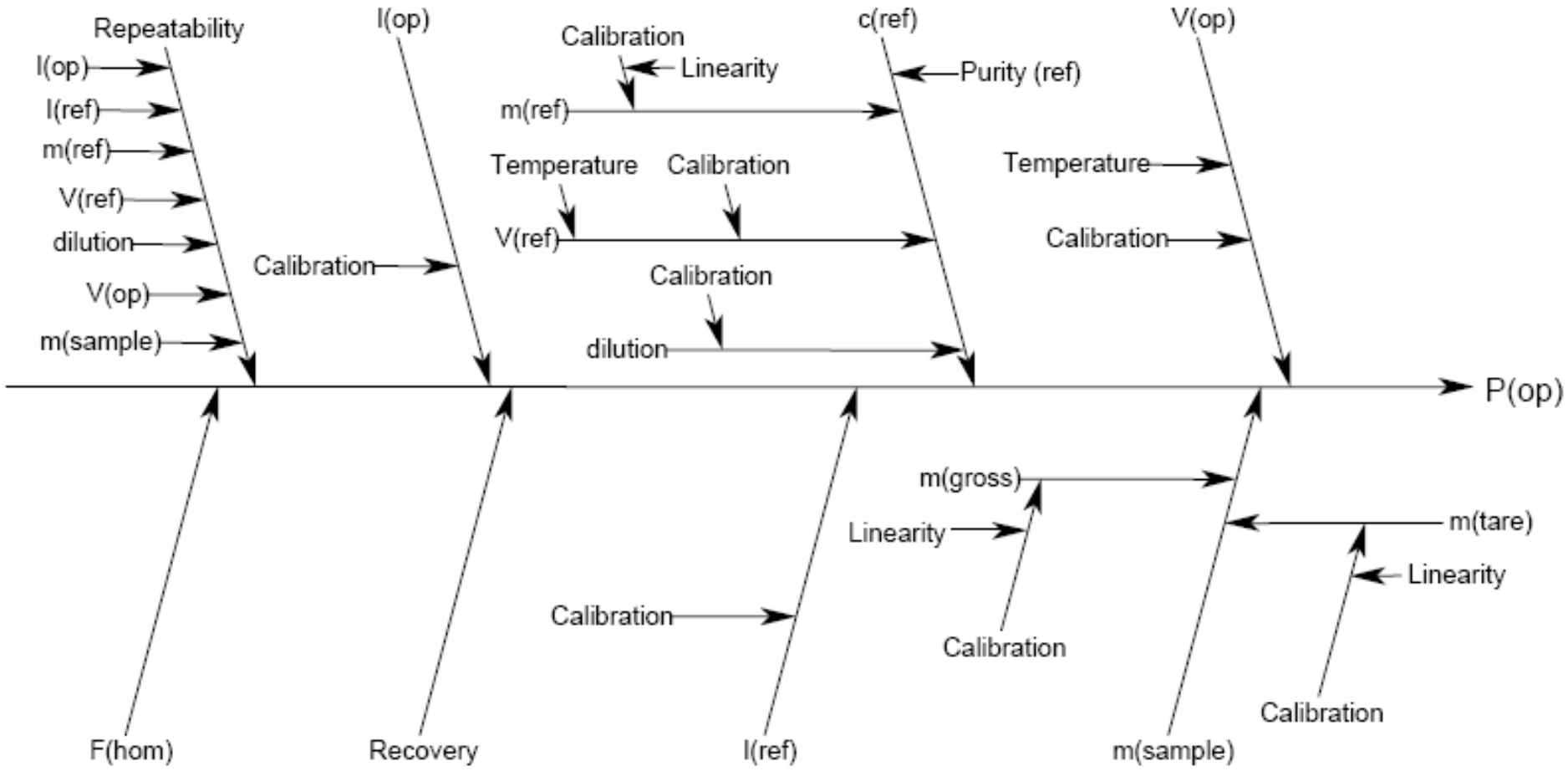
7）标准物质的标准值不准确；

8）引进的数据或其他参量的不确定度；

9）与分析方法和分析程序有关的近似性和假定性；

10）在表面上看来完全相同的条件下，分析时重复观测值的变化等。

Figure A4.2: Uncertainty sources in pesticide analysis



结果精密度的表述

- X = Average(Xi) +(-) t * Sigma * / Squareroot(n)
- n＝测定次数； Sigma：方法的重复性； t：一定容错概率下包含因子； Xi：平均值

不确定度计算： 例

PART 2 – PROPOSED EXTENSION OF CAC-GL 59-2006:

PRACTICAL AND SIMPLIFIED MU ESTIMATION BASED ON TOP-DOWN APPROACHES

Underlying principles, formulas and statistics for PT based estimation of MU

Within-laboratory reproducibility standard deviation is combined with estimates of the method and laboratory bias using PT data:

$$U' = k * u' = \sqrt{u'(R_W)^2 + u'(bias)^2}$$

where:

$$u'(bias) = \sqrt{RMS'_{bias}{}^2 + u'(C_{ref})^2}$$

and:

$$RMS'_{bias} = \sqrt{\frac{\sum (bias'_i)^2}{m}}$$

and:

$$u'(C_{ref}) = \frac{\sum_i \frac{S'_{Ri}}{\sqrt{n_i}}}{m}$$

不确定表述实例

Table A4.4: Uncertainties in pesticide analysis

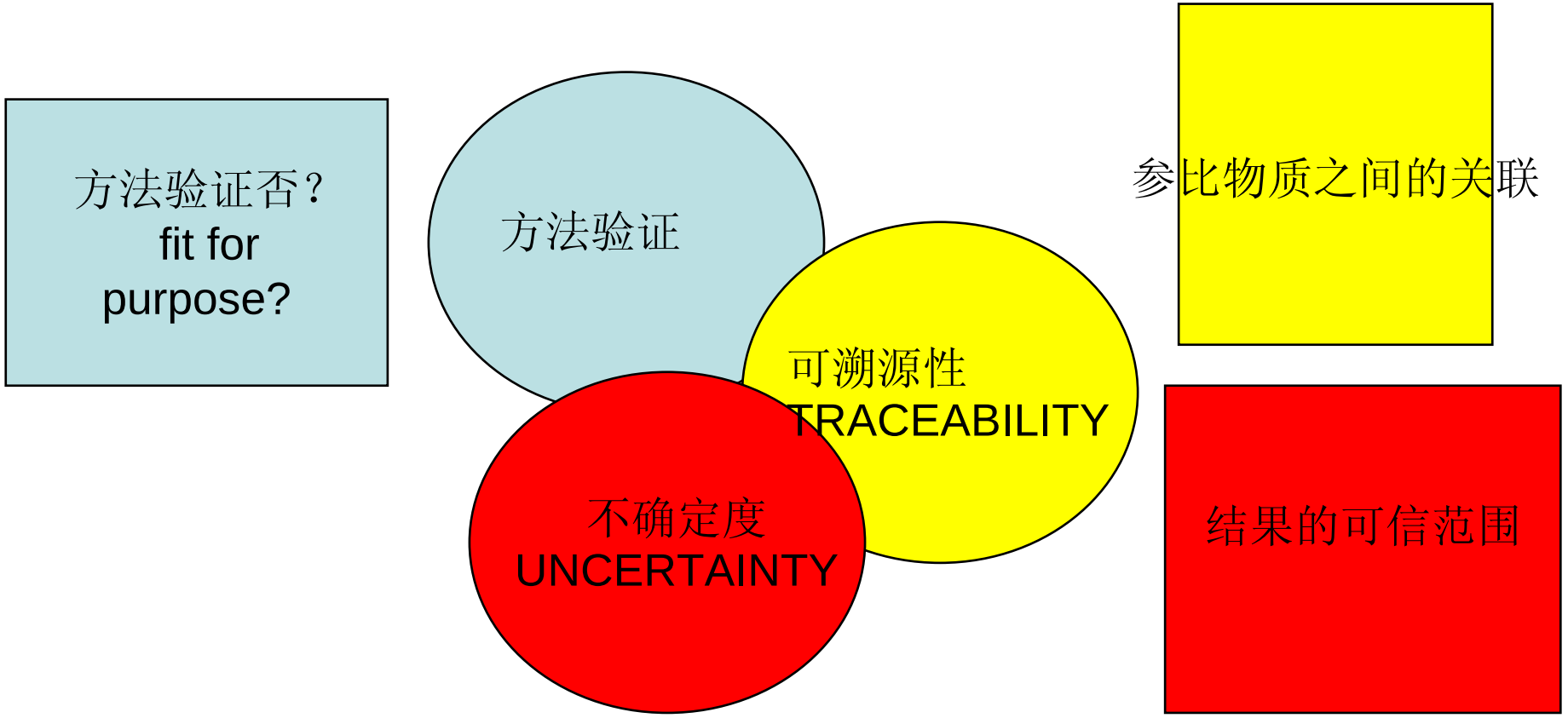
Description	Value x	Standard uncertainty $u(x)$	Relative standard uncertainty $u(x)$	Remark
Repeatability(1)	1.0	0.27	0.27	Duplicate tests of different types of samples
Bias (*Rec*) (2)	0.9	0.043	0.048	Spiked samples
Other sources (3) (Homogeneity)	1.0	0.2	0.2	Estimations founded on model assumptions
P_{op}	--	--	0.34	Relative standard uncertainty

$$\frac{u_c(P_{op})}{P_{op}} = \sqrt{0.27^2 + 0.048^2 + 0.2^2} = 0.34$$

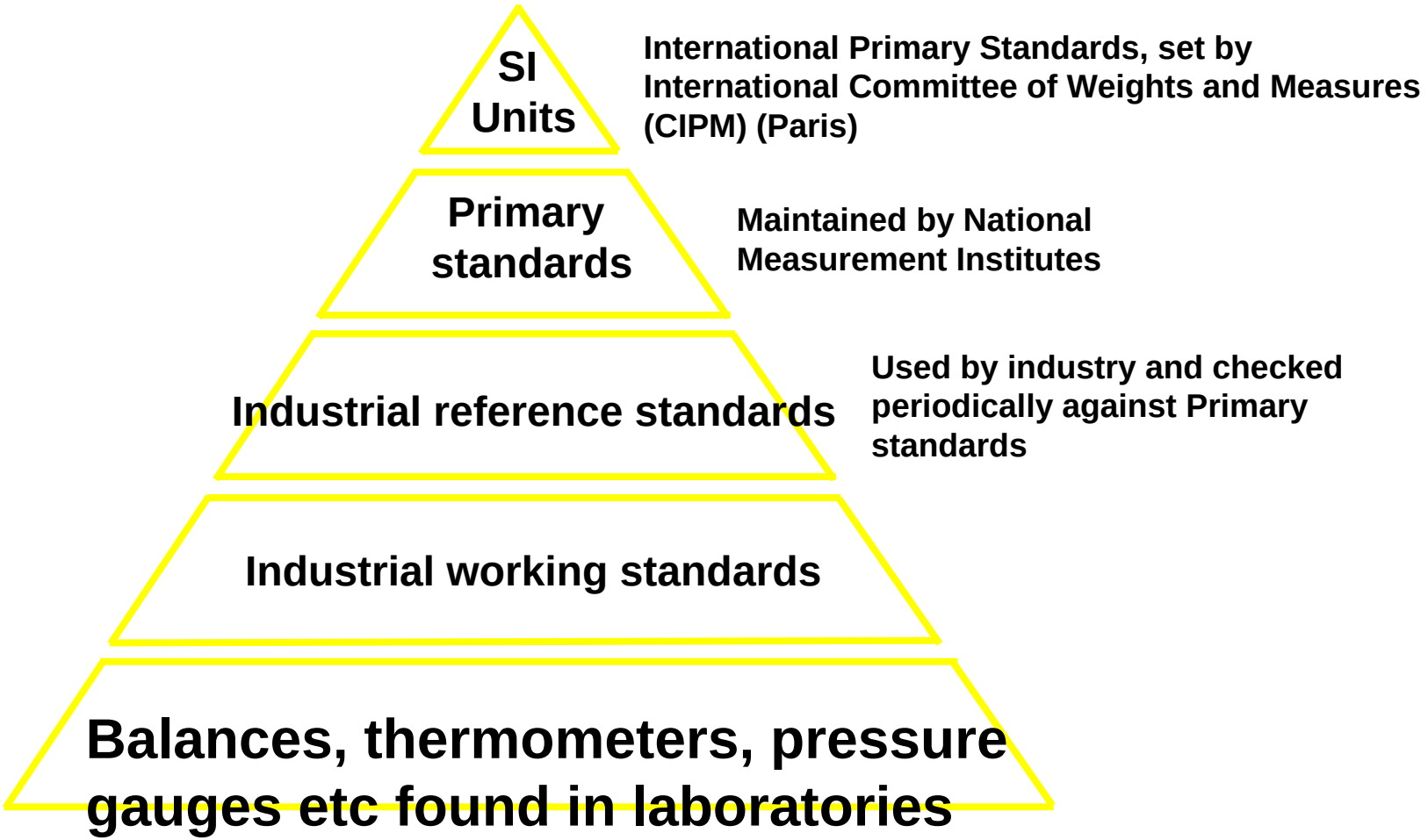
$$\Rightarrow u_c(P_{op}) = 0.34 \times P_{op}$$

分析中的三个重要因素

3 inter-linking parameters in analysis



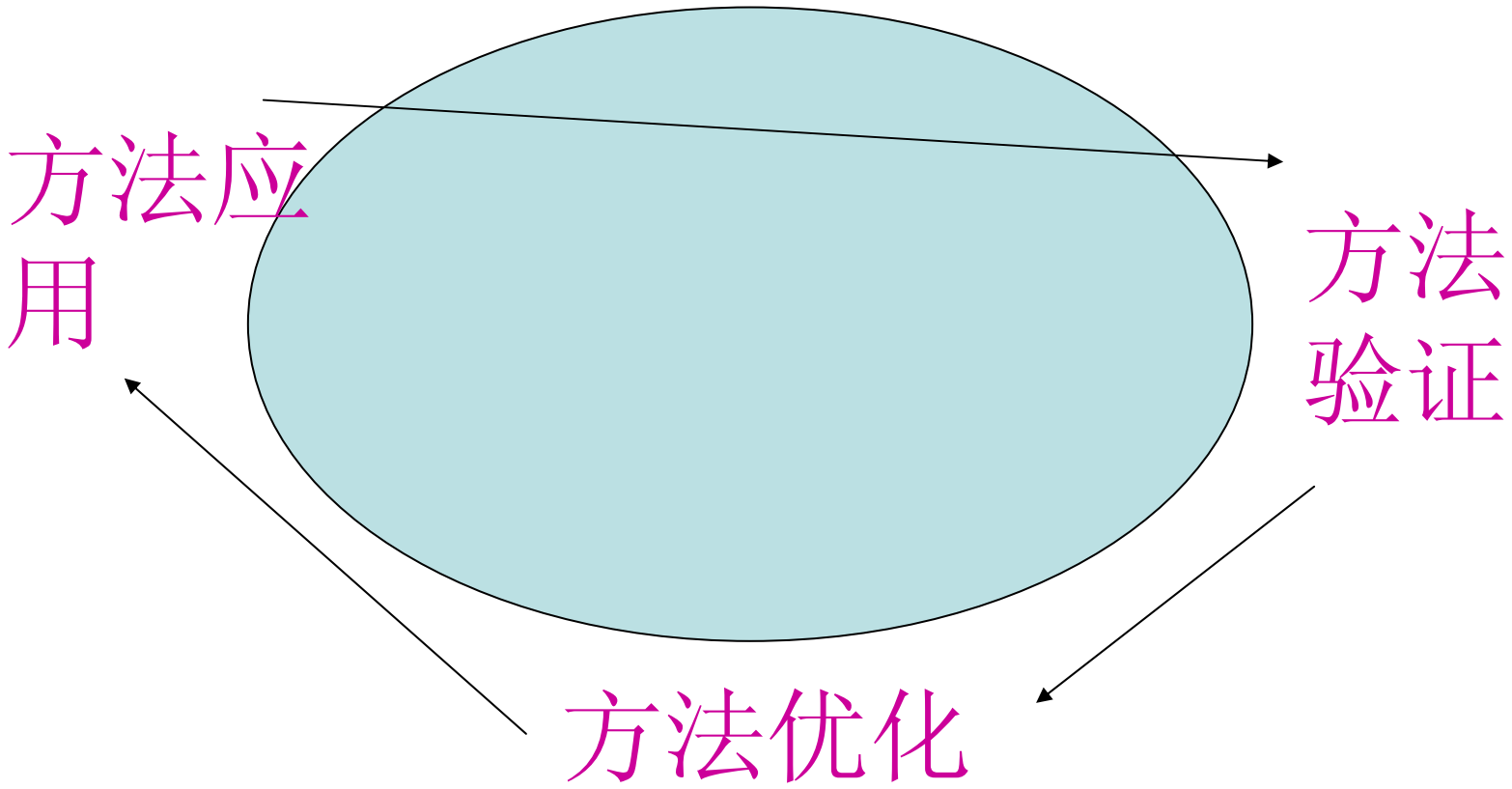
可溯源性通过一系列的比较来实现



何时进行方法验证

新方法开发	F[1,2,3]
现有方法的适应（新的基质等）	F[1,2,]F or P[3]
标准方法的改良	P or F[1]
质量控制显示分析方法有偏离	P or F[1]
不同实验室之间方法交换	P[1] or E[2]
仪器、操作人员改变	P[1]
新的试剂与配件	P[1]
已验证方法长时间未采用	P[2]
实验室管理或相关的改变	P[2]
新的协作研究方法	P[2]
经过验证但未经协作研究验证	P + E[2]
文献报道、有方法的特征参数	P + E[2]
文献报道、无方法的特征参数	F[1,2,3]

F: full validation; E: extensive validation; P: partial validation;


方法应用
方法验证
方法优化

The definitions used in the requirements for extension of CIPAC analytical methods to other formulation types

- *Concentration range*. The range of concentrations from the highest concentration of the analyte in a collaborative trial to 50 % of the lowest concentration.

- *Minor change*. e.g. the change of the procedure for the preparation of the sample solution without any further dilution of sample and calibration solutions. The change may be required by the physical nature of the formulation or by interference from formulation components.

- *Major change*. A change of the basic principles of the method e.g. change of chromatographic conditions etc.

农药分析方法验证的内容（1）

准确性 Accuracy：与真值的偏离程度

线性范围 Linearity: 分析的可靠范围（定量分析的基础）

精确性 Precision: 结果之间的接近程度

重要的参考： CIPAC 分析方法指南

农药分析方法验证的内容（2）

灵敏度 Sensitivity: 不同浓度样本的响应大小

特异性 Specificity: 分析物定性的考察

添加回收率Recovery: 测定样本中分析物全部的能力

重现性 Reproducibility

稳定性 Stability 分析方法各步骤中分析物稳定性

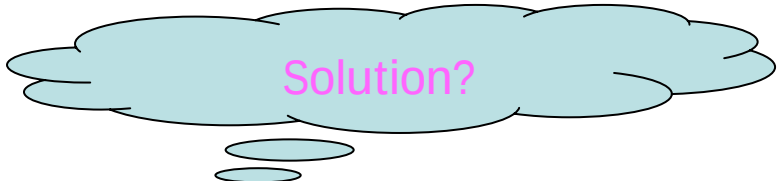
抗干扰能力

分析范围

	Quantification and analysis of a.i. in technical material	Quantification and analysis of significant impurities (>0.08 % and substances of toxicological concern below this level) in technical material	Qualitative analysis of low level impurities (<0.08 %) in technical material	Quantification and analysis of a.i. in a matrix (formulation)		Quantification and analysis of a.i. in drinking water (0.1 $\mu g\ l^{-1}$)
				High Concentration (≥1 %w/w)	Low Concentration (≤1 %w/w)	
Accuracy	✓	✓	x	✓	✓	✓
Repeatability	✓	✓	x	✓	✓	✓
Reproducibility	Where the method is to be used in other laboratories reproducibility should be addressed					
Specificity	✓	✓	✓	✓	✓	✓
LOD	x	x	✓	x	✓	✓
LOQ	x	x	x	x	✓	✓
Linearity	✓	✓	x	✓	x	✓
Range	x	✓	x	✓	✓	✓
Robustness	Robustness should be addressed as part of the method development					

Deviation from the AOAC-CIPAC procedure

- Regulatory laboratories are forced to deviate from the CIPAC procedure if they have to analyze a number of different pesticide products. as they cannot change columns and eluents after each product or on daily basis due to cost and time restrictions.
- deviation: at the determination step? sample preparation? extraction can be carried out according to the CIPAC or AOAC procedure ; use of large amount of very expensive analytical standards?



Application of CIPAC method:

- Blank formulation or no interference proof are necessary when apply with new formulations.

- no interface proof by different columns etc.

The use of "multi pesticide analytical methods"

Q: 双柱验证－定量分析的例子

- 假设采取内标法测定某杂质，**(CVra = 1.5%).** 对同一个提取液的含量分别进行3次测定。

- **CPSIL8CB 0.535 mg/ml ：**
- **CPSIL5CB 0.562 mg/ml.**

- Q：两次的结果是否有差异？ －> 是否色谱柱中有干扰物？

$$t = \frac{\left|\bar{x}_1 - \bar{x}_2\right|}{s_p \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}}$$

$$s_p^2 = \frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}$$

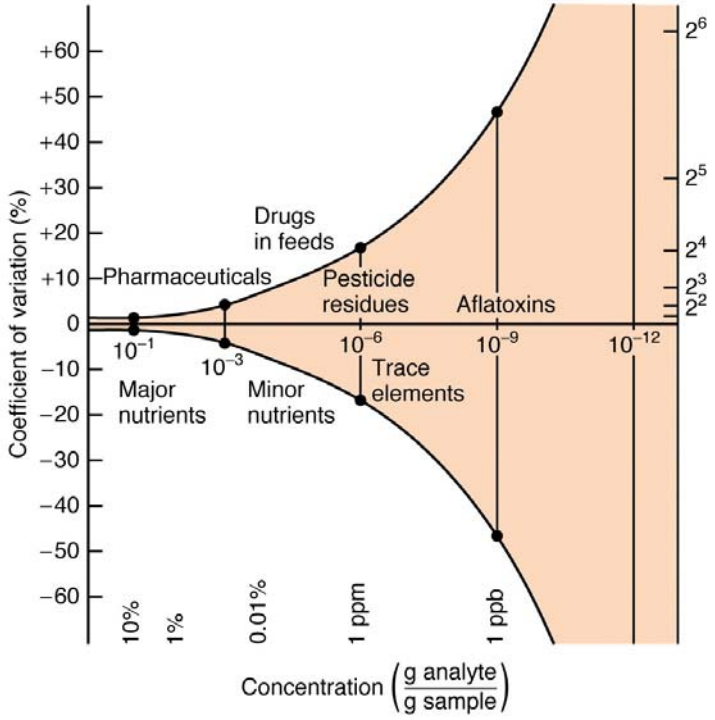
- The calculated t value is 4.018,
- $t2\alpha=0.05$, $\nu=4$ = 2.776

- The difference is significant (5.9238%). The results indicate the possibility of impurity.

Method Validation for the active substance

- 特异性：干扰物< 3% area
- 线性： ＋ — 20%：r>0.99： 3×2 or 1*5level
- *Accuracy: 回收率, 需要测定干扰物质影响和方法精密度。*
- *重复性： 至少5个重复， 符合改良的*Horwitz 方程。

- % Analyte Proposed acceptable F
- (Horwitz value x 0.67) %
- RSDR = 2(1-0.5 logC)
- 100 1.34 ; 50 1.49
- 20 1.71; 10 1.90
- 5 2.10; 2 2.41
- 1 2.68; 0.25 3.30



Method Validation for relevant impurities

- 特异性： 证明在有效成分、或者其它杂质存在时可以检出某一杂质
- 线性范围
- 准确性： 回收率
- 精密度
- LOQ

不同含量下 回收率要求

Guideline confidence intervals for % mean recovery from preparations, based on consultation with Industry, are as follows.

% active (nominal)	mean % recovery	% impurities(nominal)	mean % recovery
>10	98-102	>1	90-110
1-10	97-103	0.1-1	80-120
<1	95-105	<0.1	75-125
0.01-0.1	90-110		
<0.01	80-120		

实验室质量控制

实验室内质控

- 自我控制
- 发现随机误差和新出现的系统误差
- 评价分析质量的稳定性
- 是分析的基础、必需、常规

实验室间质控

- 外部质控
- 发现系统误差和实验室间数据的可比性
- 评价实验室的测试系统和分析能力
- 有效的校核是参加与标准实验室的比对

外部质量控制手段

- 初步实验室间研究： 由两个或多个实验室参加， 评价一种方法， 确定其是否具备条件作为协作研究的对象。

- 实验室间检测能力测试 Performance Test：

  分析经仔细制备的均匀样本， 以证实和考核实验室或分析人员的试验水平。

CNAS—GL02

能力验证结果的统计处理和能力评价指南

Guidance on Statistic Treatment of Proficiency Testing Results and Performance Evaluation

International Advisory Committee

Ecaterina Andronescu	Politehnica University, Bucharest, Romania (www.pub.ro)
Paul De Bièvre	National Committee on Chemistry, The Royal Academies, Belgium (www.Soringerlink.com); (www.accuel.elsmar.com)
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The Second International Proficiency Testing Conference

PTconf

The Second Announcement

Sibiu, România

(15)16th – 18th September, 2009

国际能力验证要求

- 国际指南**ISO/IEC**指南**43**：**1997**。正在由**ISO/CASCO-WG28**进行修订，修订后将变更为国际标准，代号为**ISO/IEC17043**，预计在**2010**年发布；
- **ISO13528**的发布。该标准经过多年的准备和讨论，于**2005**年发布实施。为能力验证提供统计上的支持。**ISO/IEC 17011**：**2004**《合格评定-认可机构通用要求》（**GB/T27011-*2005***）
- **ISO/IEC** 指南**43**《利用实验室间比对的能力验证》（**GB/T15483**，**IDT**）
- **ISO13528**：**2005**《利用实验室间比对的能力验证中的统计方法》
- **ISO/IEC 17025**：**2005**《检测和校准实验室能力的通用要求》（**GB/T27025-2008**）
- **ISO15189**：**2003**《医学实验室-质量和能力的专用要求》

实验室内部控制手段

- 方法验证中采用已知 repeatability σ_r and reproducibility σ_R .
- 及时监测 accuracy, σ_r and σ_R parameters
- 统计学原理和手段.
- 有力工具之一:

统计控制图 The control charts

单一样本的测试 - I

- 一定时间内结果稳定性? ————》 统计控制图

- 如果试验结果不能提供充足数据建立统计控制图：
  - 平行分析次数
  - 添加回收、线性关系

单一样本的测试 - II

- 建立 CD值：critical difference.

- CR＝f * σ * sqrt(2).

  – f (CR factor) depends on the probability level to be associated with the critical difference and on the shape of the distribution.

单一样本的测试 - III

- the repeatability limit $r=2.8\ \sigma_r$
- the reproducibility limit $R=2.8\ \sigma_R$.

For R and r, the probability level is 95% and we assume an approximately normal distribution.

  - Under these conditions, *f* is 1,96 and *f* sqrt2 is 2,77 (we use a rounded value of 2,8).

附 录 B
（资料性附录）
9种磺酰脲类除草剂精密度数据

表B 9种磺酰脲类除草剂精密度数据

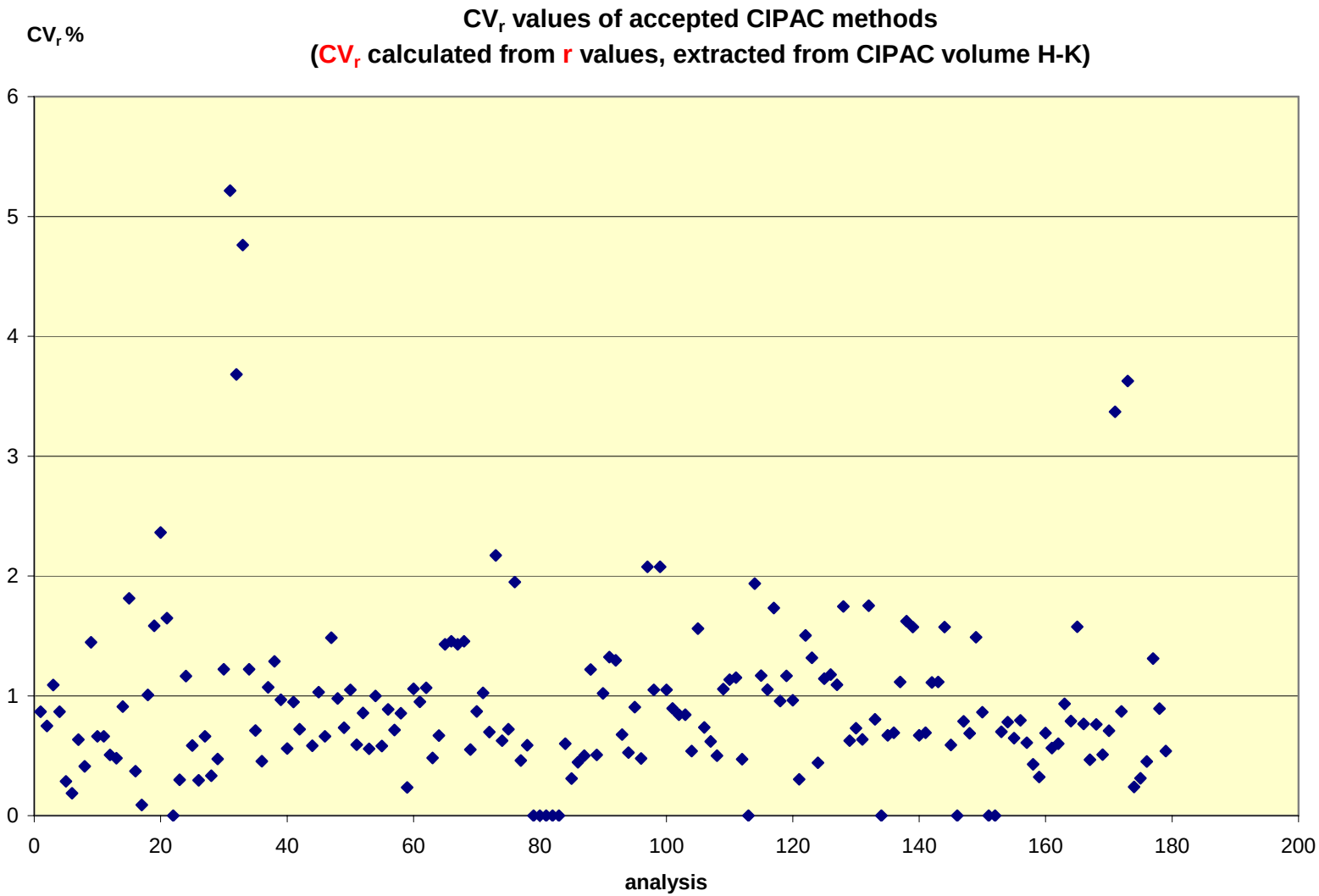
序号	农药名称	添加水平 mg/kg	重复性限 r	再现性限 R	添加水平 mg/kg	重复性限 r	再现性限 R
1	烟嘧磺隆	0.01	0.001 1	0.001 9	1	0.06	0.11
2	噻吩磺隆	0.01	0.000 9	0.001 2	1	0.10	0.15
3	甲磺隆	0.01	0.000 8	0.001 8	1	0.08	0.14
4	甲嘧磺隆	0.01	0.000 5	0.001 4	1	0.12	0.17
5	氯磺隆	0.01	0.001 1	0.001 1	1	0.12	0.14
6	胺苯磺隆	0.01	0.001 0	0.001 6	1	0.09	0.13

where:

f_i = response factor
f = average response factor
H_s = area of sulfotep peak in the calibration solution
H_w = area of sulfotep peak in the sample solution
I_r = area of internal standard peak in the calibration solution
I_q = area of internal standard peak in the sample solution
q = mass of internal standard in the sample solution
r = mass of internal standard in the calibration solution
s = mass of sulfotep in the calibration solution (g)
w_a = mass of the intact smoke tin (g)
w_b = mass of the empty smoke tin (g)
P = purity of sulfotep reference substance (g/kg)

Repeatability r = 11 g/kg at 172 g/kg active ingredient content (small tins)
= 3 g/kg at 178 g/kg active ingredient content (large tins)

Reproducibility R = 28 g/kg at 172 g/kg active ingredient content (small tins)
= 10 g/kg at 178 g/kg active ingredient content (large tins)


CVr values of accepted CIPAC methods
(CVr calculated from r values, extracted from CIPAC volume H-K)
CVr %
6
5
4
3
2
1
0
0
20
40
60
80
100
120
140
160
180
200
analysis

What is the within laboratory repeatability (Sr) of the method?

It is the average of the variations obtained by all analysts:

Pooled standard deviation

$$S_p = \sqrt{\frac{(s_1^2 x\, df_1) + (s_2^2 x\, df_2) + \ldots + (s_n^2 x\, df_n)}{df_1 + df_2 + \ldots + df_n}}$$

$$df_p = df_1 + df_2 + \ldots + df_n$$

The $df = \nu$ of each set of measurement in this case is 5-1=4. The $\nu_p = 8*4=32$!

$S_p = S_r = 0.02718$

What is the within laboratory reproducibility (SR) of the method?

$$s = \left\{ \frac{\sum_i \left(x_i - \bar{x}\right)^2}{n-1} \right\}^{\frac{1}{2}}$$

- The within laboratory reproducibility of the method is the SD of all measurements calculated with eq. 2.5: SR= 0.02632

- Note: Sr ≤ SR!

实验室内部两组结果的比较研究

- group 1 ⟶ n_1 results giving a mean of y_1
- group 2 ⟶ n_2 results giving a mean of y_2
- the SD of (y_1- y_2) is:

$$\sigma = \sqrt{\sigma_r^2 \left(\frac{1}{n_1} + \frac{1}{n_2} \right)}$$

- and the critical difference for |y_1- y_2| at 95% probability level is:

$$CD = 2.8\sigma_r \sqrt{\frac{1}{2n_1} + \frac{1}{2n_2}}$$

两个实验室间对同一样本分析结果的比较:

- lab. 1 ⟶ n_1 results giving a mean of y_1
- lab. 2 ⟶ n_2 results giving a mean of y_2
- under repeatability conditions, the SD (y_1-y_2) is: $\sigma = \sqrt{\sigma_L^2 + \frac{1}{n_1}\sigma_r^2 + \sigma_L^2 + \frac{1}{n_2}\sigma_r^2}$

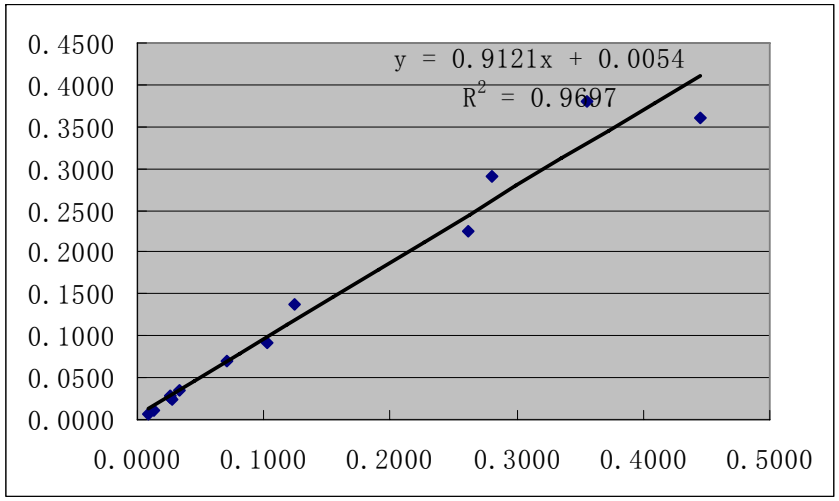
- and the critical difference for $|y_1-y_2|$ is:

$$CD = \sqrt{(2.8\sigma_R)^2 + (2.8\sigma_r)^2\left(1 - \frac{1}{2n_1} - \frac{1}{2n_2}\right)}$$

方法 A与B的比较研究

	Method A			Method B or reference method			
	Replicate 1	Replicate 2	Average	Replicate 1	Replicate 2	Average	Difference
87	0.532	0.545	0.5385	0.518	0.524	0.521	0.0175
88	0.52	0.53	0.525	0.538	0.523	0.5305	-0.0055
89	0.535	0.531	0.533	0.527	0.519	0.523	0.01
90	0.517	0.526	0.5215	0.513	0.531	0.522	-0.0005
91	0.529	0.523	0.526	0.521	0.528	0.5245	0.0015

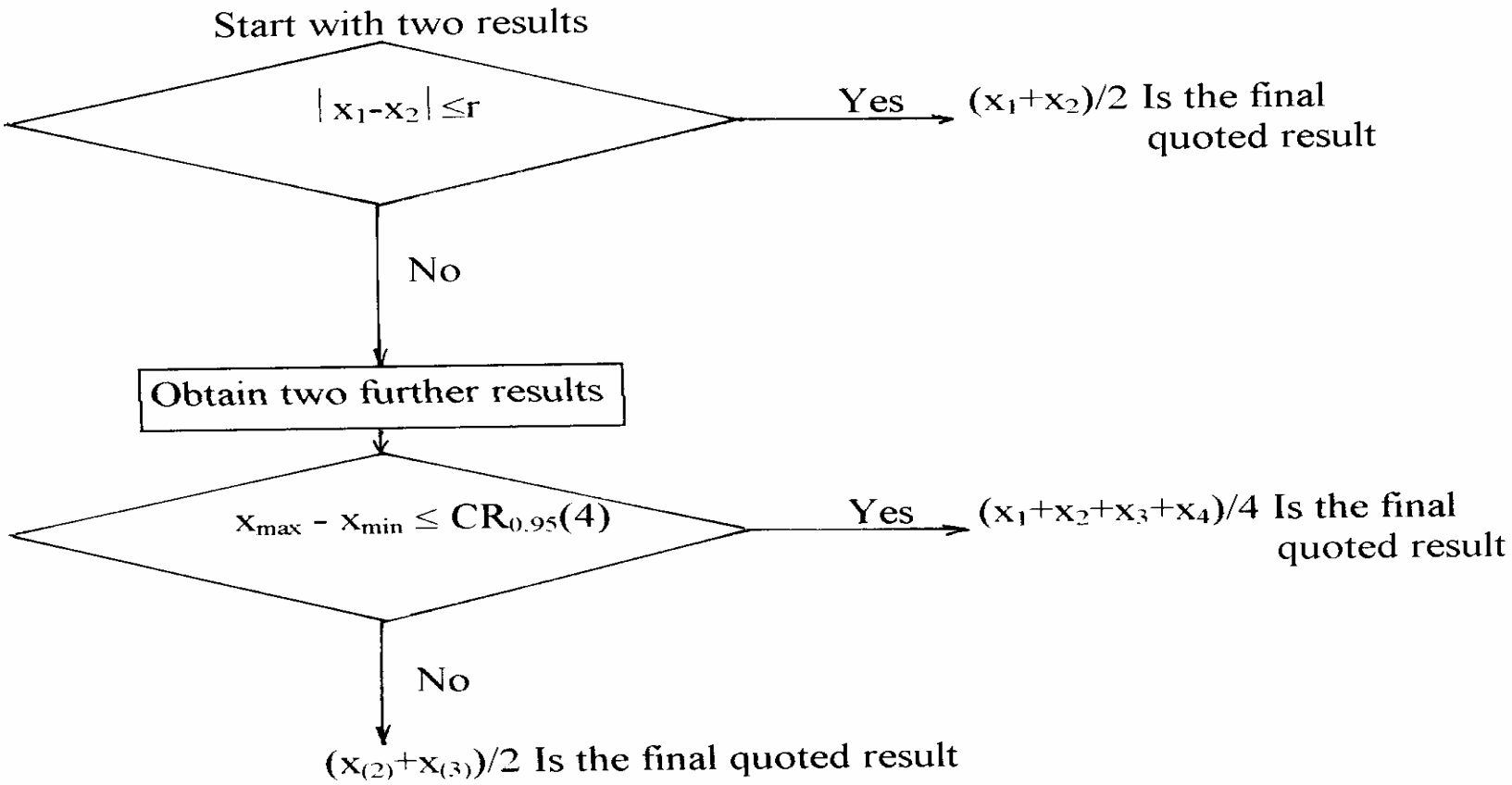
s_{Ara}	0.007447	Average	0.0046
		SD_{dif}	0.009127
		t_{calc}=	1.126991
		t_{crit}=	2.776



	Lab 1	Lab 2	R_1-R_2
1	0.0266	0.0259	0.0007
2	0.0256	0.0279	-0.0023
3	0.0710	0.0709	0.0001
4	0.0334	0.0352	-0.0018
5	0.0087	0.0062	0.0025
6	0.0123	0.0118	0.0005
7	0.0269	0.0249	0.0020
8	0.2810	0.2910	-0.0100
9	0.3550	0.3800	-0.0250
10	0.2610	0.2240	0.0370
11	0.1030	0.0920	0.0110
12	0.1240	0.1370	-0.0130
13	0.4450	0.3610	0.0840

测试结果的评价与表达

- σ_r and σ_R of the measurement method are known.



Where

$x_{(2)}$ is the second smallest result

$x_{(3)}$ is the third smallest result

例： 分析结果的有效性与表示

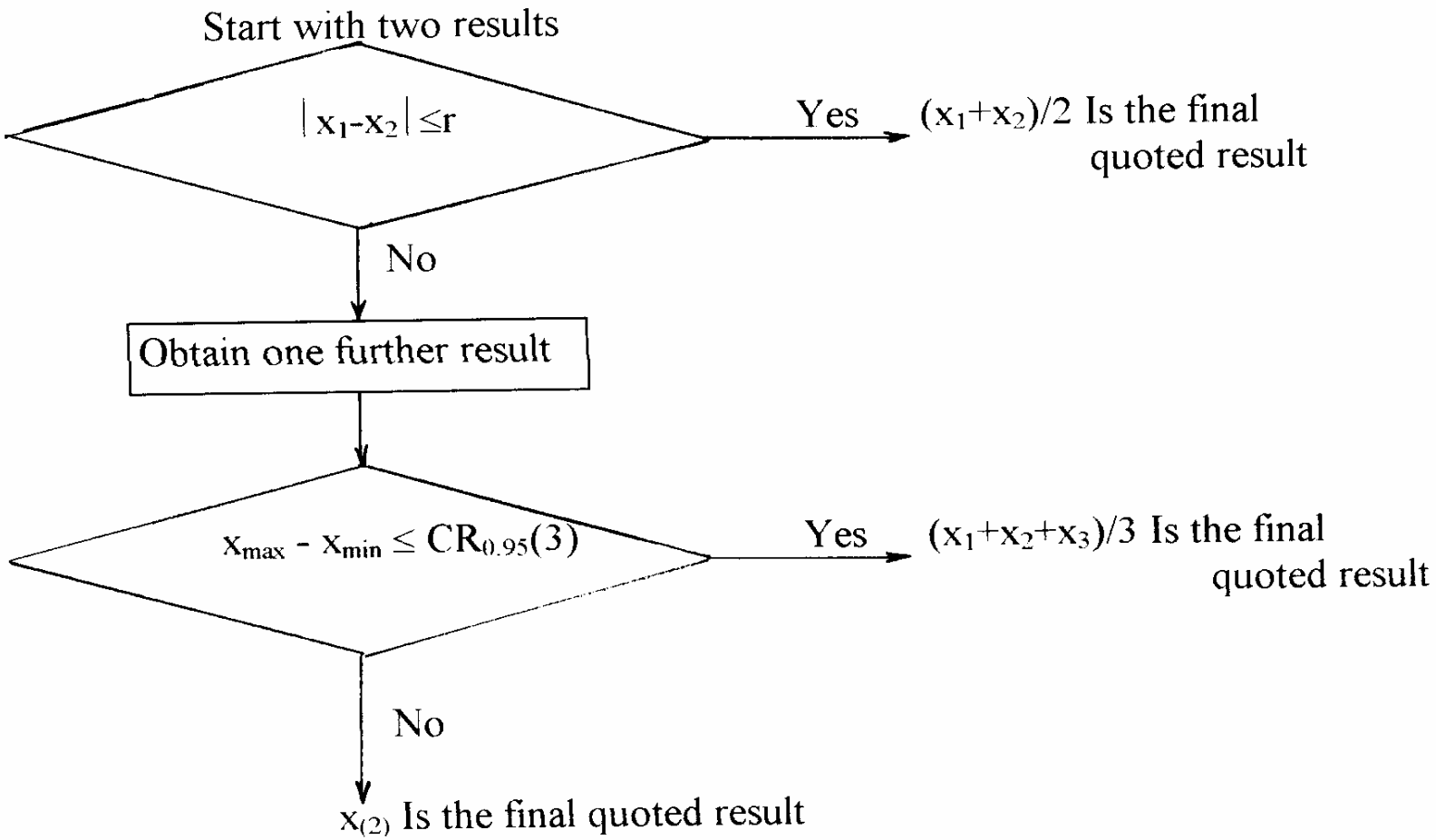
- 乐果乳油分析 (CIPAC E p.69).

- r = 7 g/kg at 463 g/kg a.i. content.
- R = 20 g/kg at 463 g/kg a.i. content (18 results)

- We obtain 2 test results: x_1= 451 and x_2= 457 g/kg
- $|x_1-x_2|$= 6 < r, so the final quoted result is

(451 +457)/2 = 454 g/kg.

当测定费时、花费较大时结果的评价



Where

$x_{(2)}$ is the second smallest result

例： 分析结果的有效性与表示（续）

- 又例如： x_1= 453 and x_2=468 g/kg
- $|x_1-x_2|$= 15 > r. We shall obtain 2 further results.
- x_3= 460 and x_4= 450 g/kg,
  - the $CR_{0.95(4)} = f(4)\ \sigma_r$.
  - $r = 2.8\sigma_r$, σ_r = r/2.8 = 7/2.8 = 2.5 g/kg
- *f*(4) = 3.6, therefore $CR_{0.95(4)} = 3.6*2.5 = 9$

- We calculate $x_{max} - x_{min}$ = 468 -450 = 18 > 9
- In this case the median （中值） of the 4 results is reported as the final quoted result. 450, 453, 460, 468,
- so x = (453 + 460)/2 = 456 g/kg .

- 如果$x_{max} - x_{min} < CR$, 则结果应表示为四次测定的平均值。

分析同一样本的重复性考察

- 对同一样本的三个部位分析结果应符合:

  Cmax-Cmin< 3.31*r/2.8

每两个重复分析间至少满足：

Amax—Amin≤3.64*CV*Xmean

分析同一样本的三个部位的考察

RATIO of AS/IS	Content	Average	SD	CV
1.12616	39.35703	39.28324	0.10436	0.26565
1.12193	39.20945			
1.10382	38.39576	38.31078	0.12017	0.31366
1.09893	38.22581			
1.11266	38.75563	38.59627	0.22537	0.58391
1.10351	38.43691			
		Cmax-Cmin:	0.97245	
		3.31*r/2.8:	1.773214	
		r=1.5		

Summary of most commonly used QC activities

- Analysis of reagent blank
- Analysis of blank samples
- Duplicate analysis
- System suitability tests （SST）
- Spike or Recovery samples
- Efficient use of control charts
- Blind samples
- Participation in collaborative studies, proficiency tests

SOP of QA QC：
File：4391.pdf

Effective Date: 1/15/2009
Revision Date: 1/15/2009
Revision Author: A. Niculescu
GC-001-2.10

Quality Assurance/Quality Control in the GC Pesticides Laboratory

1. SCOPE AND APPLICATION

1.1. This SOP details the Quality Assurance (QA) and Quality Control (QC) procedures for the GC-Pesticides Work Group.

1.2. Quality Assurance consists of all of the practices undertaken in a laboratory to insure the data generated are as accurate and precise as possible. It includes not only quality control measures, but can be as specific as the cleaning of glassware and preparation of standards. This SOP will concentrate on Quality Control measurements that are used to measure and track the Quality Assurance in the GC Pesticides lab. It will touch briefly on some general guidelines for QA. Refer to the individual preparation or analysis SOPs for more specific details on QA.

1.3. Most of these QA/QC practices described are common throughout the Chemistry Section.

问题与交流讨论

- Email: panc@cau.edu.cn

Science net 博客：http://www.sciencenet.cn/blog/canpingp2222.htm