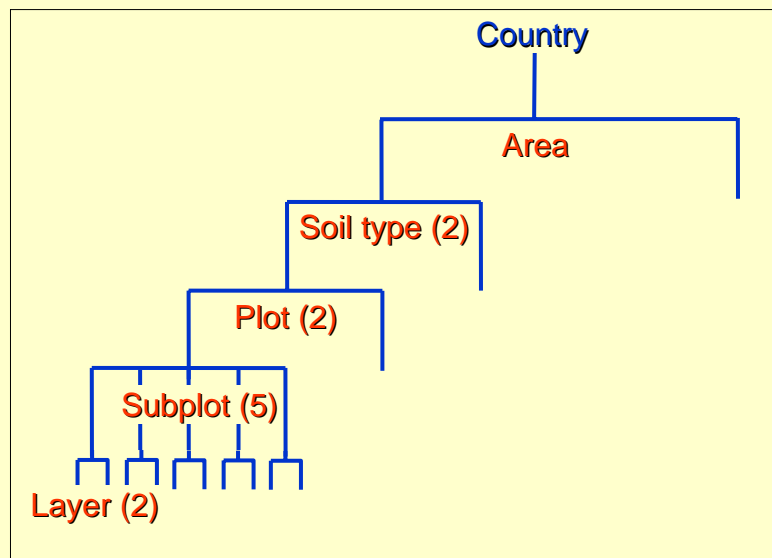


## Quality Assurance/ Quality Control (QA/QC) in Monitoring Soil

- **Statistical Model**
- **Statistical procedures for estimation of precision and improvement of data**

## Effective factors for data

- **Selection of “areas”**
- **Selection of “soil types”**
- **Establishment of “plots”**
- **Establishment of “subplots”**
- **Collection from the fixed “layer”  
(probably, effect of horizon)**
- **Analysis error in “repeatability”,  
“within-laboratory reproducibility”,  
and “reproducibility” condition.**



Variability of each stage in the multi-stage sampling would be estimated.

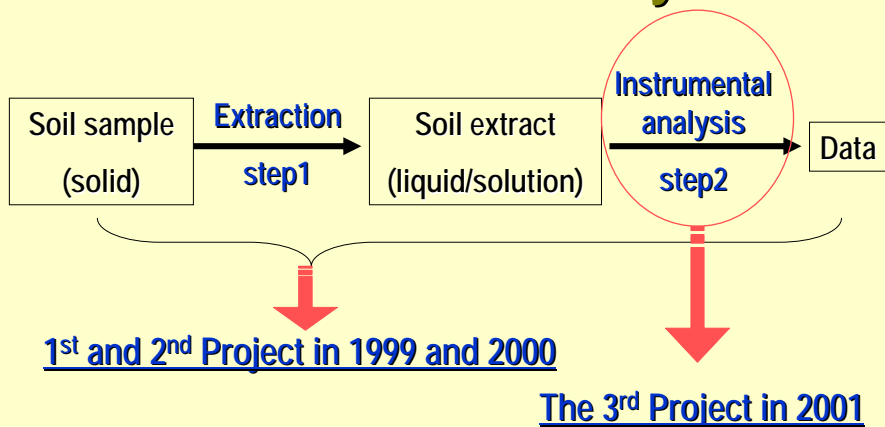
### Estimation of analytical quality

- Repeatability
- Reproducibility-within-laboratory
- Reproducibility

The collaboration of laboratories is necessary.

→ The 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup>, 4<sup>th</sup> inter-laboratory comparison project on soil

## QA/QC on Soil analysis



Which step is the major factor ?

Precision of each step should be evaluated.

## Dispatched Soil Extract Sample (1<sup>st</sup> – 3<sup>rd</sup> Projects)

### 1<sup>st</sup> and 2<sup>nd</sup> Projects in 1999 and 2000 (soil samples)

- No.991: Acrisols
- No.992: Gleysols
- No.001: Cambisols
- No.002: Andosols (used for the 3<sup>rd</sup> Project)

### 3<sup>rd</sup> Project in 2001 (soil extract samples)

- No. 011: Soil extract by  $\text{CH}_3\text{COONH}_4$  solution
- No. 012: Soil extract by KCl solution

## Procedures of analysis in the participating laboratories

- **Triplicate analysis:** Analyze three times under the same condition (repeatability condition)
- **Repeat analysis:** Analyze twice under the within-laboratory reproducibility condition
- **Calculation of soil content:** According to the equations shown in the instruction, the values were converted to the soil contents.
- **Reporting:** Concentration of extract, (calculated) Soil content, information on analytical condition

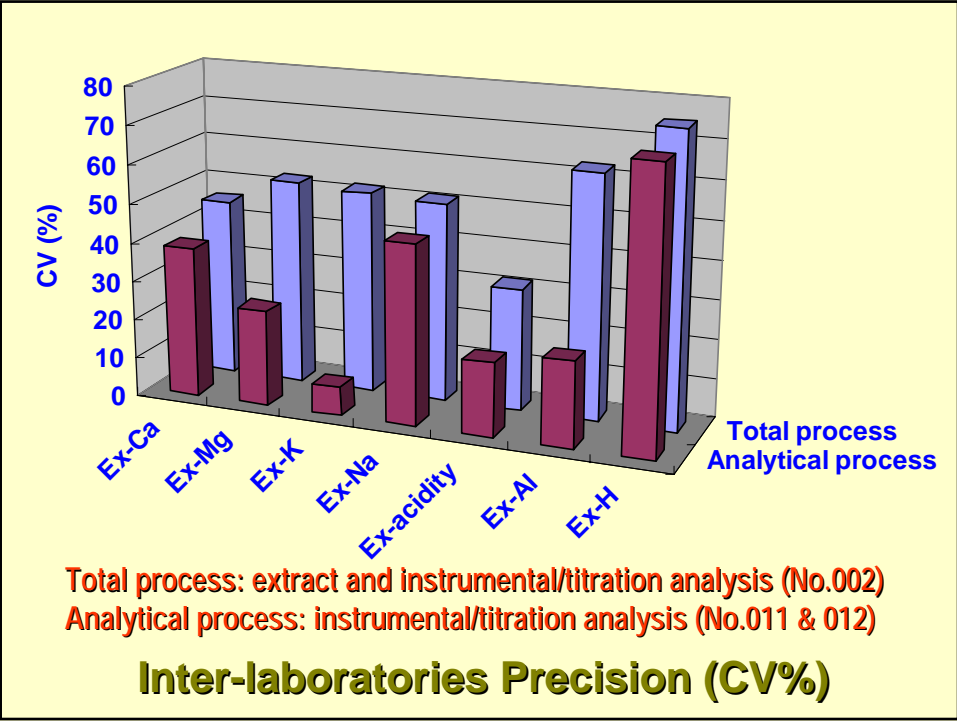
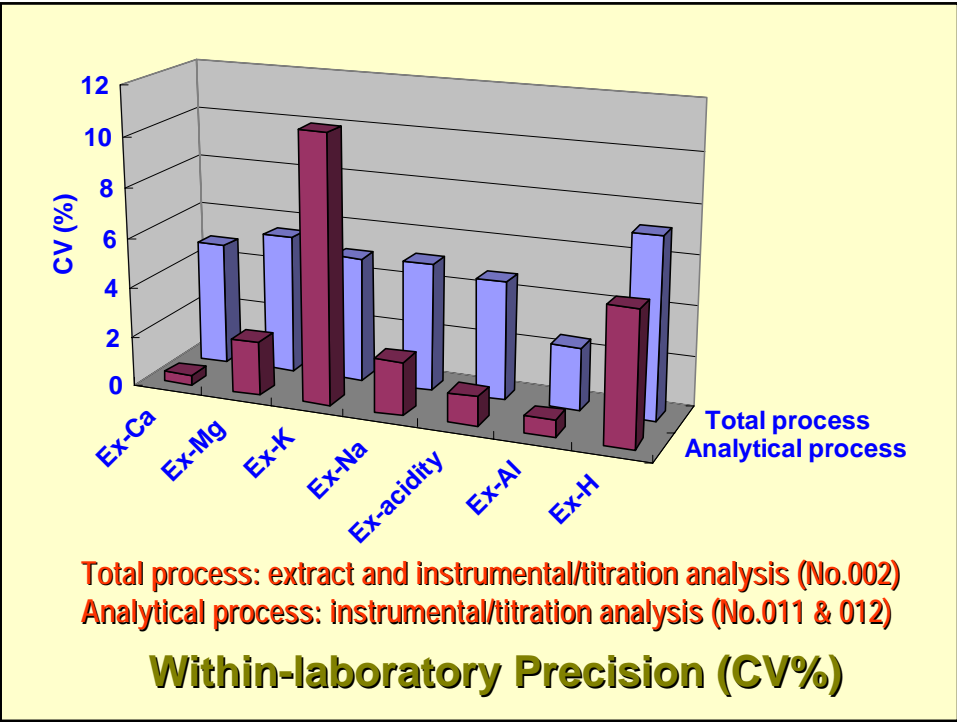
## Statistical analysis

1. Verification of data  
by Cochran and Grubbs methods
2. ANOVA and Estimated precision

$$S_T = S_R + S_{RW} + S_r$$

Based on the above equation, **Inter-laboratories variance**, **Within-laboratory-reproducibility variance**, and **Repeatability variance** were calculated, and then the precisions were estimated.

3. Calculation of permissible tolerance



## Result of the 3<sup>rd</sup> Project-1 Analytical instruments

**Table. Analytical instrument**

Lab.	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-Acidity	Ex-Al
ch01	AAS	AAS	AAS	AAS	Titration	Titration
ch02	AAS	AAS	AAS	AAS	Titration	Titration
ch03	AAS	AAS	AAS	AAS	Titration	Titration
ch04	AAS	AAS	FEP	FEP	Titration	ICP-AES
id01	AAS	AAS	AAS	AAS	Titration	AAS
id02	AAS	AAS	FEP	FEP	Titration	AAS
jp01	AAS	AAS	FEP	FEP	Titration	Titration
my01	AAS/ICP-AES <sup>*1</sup>	AAS/ICP-AES <sup>*1</sup>	AAS/ICP-AES <sup>*1</sup>	AAS/ICP-AES <sup>*1</sup>	Titration	ICP-AES
mn01	-	-	-	-	Titration	Titration
ph01	AAS/AAS <sup>*2</sup>	AAS/AAS <sup>*2</sup>	AAS/AAS <sup>*2</sup>	AAS/AAS <sup>*2</sup>	Titration	-
ph02	AAS	AAS	FEP	AAS	Titration	Titration
kr01	AAS	AAS	AAS	AAS	Titration	Titration
ru01	AAS	AAS	FEP	FEP	Titration	Titration
ru02	AAS	AAS	FEP	FEP	Titration	Others (photometry)
th01	AAS	AAS	AAS	AAS	Titration	Titration
vn01	Titration	Calculation <sup>*3</sup>	FEP	FEP	Titration	Titration

Note: AAS, Atomic absorption Spectrometry; FEP, Flame (emission) photometry; ICP-AES, Inductively Coupled Plasma Atomic Emission Spectroscopy. \*1. The 1st and 2nd analyses were carried out by different instruments, AAS and ICP-AES, respectively. \*2. The 1st and 2nd analyses were carried out by different makes of AAS. \*3. Calculation from Ca and hardness

**Ex-K: by AAS, 0.08 (0.00) cmol(+)/kg  
by FEP, 0.12 (0.03) cmol(+)/kg**

## Result of the 3<sup>rd</sup> Project-2 Effect of La, Sr, or Cs solution

**Table. Effect of La, Sr, or Cs solution**

La, Sr, or Cs	Ex-Ca	Ex-Mg	Ex-K	Ex-Na
Not added	0.66 (0.13)	0.09 (0.02)	0.12 (0.03)	0.07 (0.01)
Added	0.73 (0.13)	0.11 (0.02)	0.08 (0.01)*	0.05 (0.02)**

**Note: Value in parenthesis shows 95% confidence interval.**

**\*, Significant difference by ANOVA,  $P < 0.05$ . \*\*,  $P < 0.01$ .**

Effect of La or Sr was suggested  
(but not statistically).

Effect of Cs and/or  
instruments (FEP)?

## Result of the 3<sup>rd</sup> Project-3 Preparation method of standard solution

APPENDIX 3.1. Results of Ex-base cations in ADORC

Date	Instrument	Methods	Ex-Ca	Ex-Mg	Ex-K	Ex-Na
			cmol(+)/kg			
23-Mar	AAS	Calibration curve <sup>*1</sup>	<b>0.76 (0.01)</b>	0.10 (0.00)	0.09 (0.00)	0.07 (0.00)
25-Mar	AAS	Calibration curve <sup>*1</sup>	<b>0.76 (0.01)</b>	0.10 (0.00)	0.09 (0.00)	0.07 (0.00)
		Standard addition <sup>*2</sup>	<b>0.93 (0.02)</b>	0.12 -	0.10 -	0.09 -
19-Sep	ICP-AES	Calibration curve <sup>*3</sup>	<b>0.90 (0.03)</b>	0.11 (0.00)	0.10 (0.00)	0.08 (0.00)
29-Sep	ICP-AES	Calibration curve <sup>*3</sup>	<b>0.86 (0.01)</b>	0.10 (0.01)	0.10 (0.00)	0.07 (0.00)
Total average			0.84	0.11	0.10	0.08

Note: \*1. HCl was also added for stability of ionization. \*2. Sample was used for preparation of standard solution. \*3. Ammonium acetate was used for preparation of standard solution. \*4. Ex-Ca was diluted by five times.

↓

**Standard addition method is preferable for canceling effect of matrix and other constituent ions. Preparation of standard solutions using extractant may also be effective.**

### Possible factors

for improvement of inter-laboratories precision

**Effect of analytical process on total precision was relatively large.**

- Instrument for Ex-K and Na  
Possibility of standardization of instruments should be discussed: **FEP or AAS ?**
- 2. **Addition of La or Sr (Cs?) solution for AAS analysis**
- 3. **Preparation of standard solution**  
e.g. **Standard solution prepared by extractant**