

**Convention on Long-Range Transboundary Air Pollution  
International co-operative Programme on Assessment and  
Monitoring of Air Pollution Effects on Forests  
and  
European Union Scheme  
On the Protection of Forests against Atmospheric Pollution**

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**ICP-Forests**

**4<sup>th</sup> Needle/Leaf Interlaboratory Test 1999/2000**

**Results**

- Prepared by:** North Rhine-Westphalia  
State Environment Agency (LUA)  
Wallneyer Str. 6 / D-45133 Essen
- Author:** Dr. Ulrich Bartels  
assisted by  
Ursula Busch, Hans Joachim Fermer (LUA).
- In co-operation with:** Austrian Federal Forest Research Centre, Vienna  
The Finnish Forest Research Institute, Parkano  
Bundesministerium f. Ernährung, Landwirtschaft  
und Forsten, Bonn

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# ICP-Forests 4th Needle/Leaf Interlaboratory Test 1999/2000

## Results

(December 1st, 2000)

by

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### O. Summary

52 Laboratories from 29 European countries took part in the 4<sup>th</sup> ICP Needle/Leaf Interlaboratory Test 1999/2000.

In comparison to the 3<sup>rd</sup> test, the results show a distinct improvement of analysis quality at European laboratories working on the issue of forestry analysis. This improvement results, apart from a growing awareness of the problems of quality management, especially from the increased use of elemental analyzers and multi-element spectrometers. These more and more replace classic analytical methods.

Still the elements sodium and lead are as problematic as before.

The evaluation of the applied methods indicates for some elements tendencies that should be taken into consideration in the revised manual:

**Nitrogen:**

Analysis by Kjeldal methods results in distinctly lower values than analysis by elemental analyzers. This was to be expected in theory but had not shown so clearly in former ring tests. In future, elemental analyzers are to be used with preference.

**Sulphur:**

The combination of HNO<sub>3</sub> pressure digestion with ICP results in very homogenous results close to the overall lab mean and therefore has advantages over classic BaCl<sub>2</sub> - methods.

**Metals (in general):**

The 4<sup>th</sup> ringtest basically confirms the formerly detected tendency that closed digestion systems (HNO<sub>3</sub> pressure digestion prior to HNO<sub>3</sub> microwave digestion) produce greater comparability of the results than digestion in open systems. The combination with ICP is the most favourable method.

**Aluminium:**

Only a minority of laboratories have kept to the instructions given in the manual and used HF for digestion. Whereas the results from the few laboratories that used both variants (with and without HF) were clearly higher when using HF, the differences disappeared when looking at the overall results. Seemingly digestion and/or determination are so faulty that the differences between the methods applied within one laboratory disappear among all participants.

Because of that methodology has to be discussed again. But if the majority of the laboratories are not prepared to keep to the manual, aluminium should be cancelled from the list of "optional elements".

**It is suggested to reduce the selection of recommended methods in favour of automatic methods.**

**Sensible would be:**

- 1. C-N-S - elemental analyzers (for C, N, S)**
- 2. HNO<sub>3</sub> - digestion in closed systems (pressure bomb or microwave digestion) combined with ICP-OES-MS (for S, P, Ca, etc)**
- 3. X-ray - spectroscopy: This has not proved to be as successful as the before mentioned methods because of higher determination limits but should be maintained and developed for a quick, automatic and non-destructive multi element method of analysis. (for S, etc.)**

**It is suggested to carry out a ringtest with these methods exclusively.**

## 1.1 Introduction

ICP-Forests of UN-ECE in collaboration with EU initialised a programme for intensive and continuous monitoring of forest ecosystems for Europe in order to realise a better understanding of air pollution processes. An important task in this field is the needle/leaf-analysis of trees, because they serve as bioindicators for nutrition state and damages.

Necessary is the harmonising and the improvement of analytical techniques. A high and comparable laboratory standard in all countries is indispensable for a European-wide survey of forest state. Important steps on this way have been the edition of the „Manual on methods and criteria for harmonised sampling, assessment, monitoring and analysis of the effects of air pollution on forests“ (UN-ECE, Hamburg and Prague 1994) and the performance of the first European needle/leaf interlaboratory test on two certified standards (BCR 100-beech leaves and BCR 101 - spruce needles) with 24 laboratories from 21 countries, organised by France in 1993.

The intensive discussion of ICP-expert panel in As 1994 ended with the recommendation of a second test with 4 unknown samples (spruce, pine, oak) during the running level-II monitoring programme. It was organised by Germany in 1995/96 and subsequently discussed on expert panels in Vienna 1997 (BARTELS 1996, STEFAN et al. 1997). The expert panel in Vienna therefore decided on a complete repetition and authorised the Landesumweltamt North-Rhine-Westfalia (LUA) to organise another interlaboratory test on foliage every two years. The 3<sup>rd</sup> interlaboratory study with 5 unknown samples (spruce, pine, oak, beech) and its consequences for the analytical quality management (BARTELS 1998) were intensively discussed in Bonn 1999 and ended with a revision of Part IV “Sampling and analysis of needles and leaves” of the above mentioned manual.

These results of the 4<sup>th</sup> test will be commented on in the following text.

## 1.2 Material

In October 1999 the LUA sent dried plant powder of the following five samples to more than 50 European laboratories:

1. Spruce needles (Austria)
2. Spruce needles (Norway)
3. Pine needles (Germany)
4. Beech leaves (Slovakia)\*

All materials were foremost ground with a Retsch-centrifugal-mill (sieve 0.25 mm, Cr-Ni steel) and homogenised by the LUA-laboratory by shaking over head for 24 hours before dispatch.

I have to thank **Alfred Fürst** (Vienna, A), **Svein Solberg** (As, N), **Lutz Genßler** (Recklinghausen, D) and their co-workers for sampling and my co-workers **Hans-Joachim Fermer** for preparing the samples and **Ursula Busch** for various help in preparing the data processing and text translation.

\* **Sample 4** was – unknown to the participants – identical with **sample 5** ('beech Slovenia') of the 3<sup>rd</sup> interlaboratory test. The real sample 'beech leaves Slovakia' prepared by **Branka Mankowska** (Zvolen) will be used in the 5<sup>th</sup> test 2001/2002.

### 1.3 Participant countries

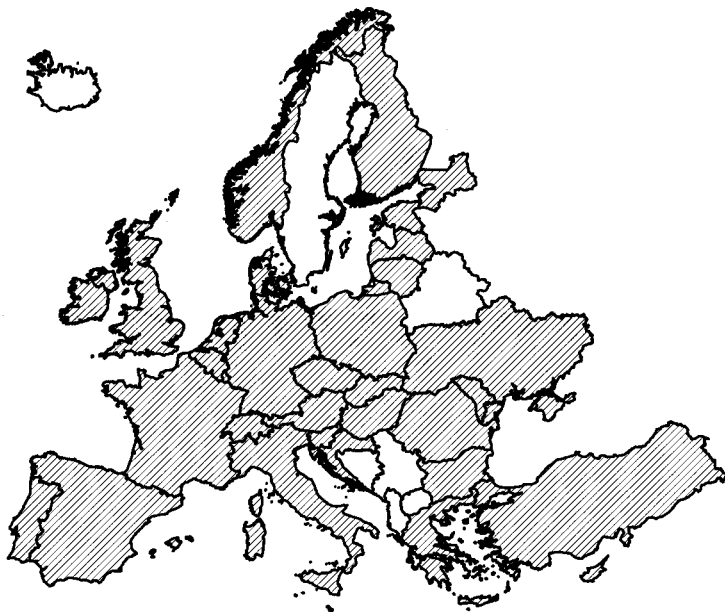
52 laboratories from 29 countries joined in this test (1<sup>st</sup> test: 24/21; 2<sup>nd</sup> test: 39/25; 3<sup>rd</sup> test 51/29).

**Figure 1** gives an overview of the participant countries. Because of diverse problems we got no results from Belarus. From Sweden we got no response.

The code numbers of the laboratories are mostly the same as in the last interlaboratory test to make it easy to compare the two runs. An 'a' or a 'b' after the number means the same laboratory or country, but another data set using other methods.

ICP - Forests 4 th. Needle and Leaf Interlaboratory Test 1999/2000

 Participating countries



FBVA-FFCC / JLeitner

**Figure 1:** Europe map of participant countries

## 1.4 Task

The laboratories were asked to analyse the following elements with three replicates before February 15, 2000 :

<i>a) mandatory elements</i>	<i>b) optional elements</i>	<i>c) additional elements</i>
<i>Nitrogen</i>	<i>Sodium</i>	
<i>Sulphur</i>	<i>Zinc</i>	
<i>Phosphorus</i>	<i>Manganese</i>	
<i>Magnesium</i>	<i>Iron</i>	<i>no limitation</i>
<i>Calcium</i>	<i>Copper</i>	
<i>Potassium</i>	<i>Lead</i>	
	<i>Aluminium</i>	
	<i>Boron</i>	
	<i>Cadmium</i>	
	<i>Carbon</i>	

The samples - moisture content was about 5% - were to be dried at 80 °Celsius prior to analysis. Anyhow all results had to be reported as by dry matter (105 °C). With a few exceptions all laboratories analysed the complete list of mandatory elements and most of the optional elements. An overview is given in **Table 1**.

All laboratories were given the opportunity to recheck their data.

## 2. Data Evaluation

### 2.1 Method of data calculation

A computer programme (RING 4.0, author: Dr. Steffen Uhlig, Berlin) was used to calculate the ring test data. The evaluation was carried out for all mandatory elements and all optional elements. All other elements with only a few data bases are given in **pp 4-1** without further comments. These data are very useful to characterise the samples.

The evaluation is presented in the same way as in the past for the 2nd ring test and calculated on the basis of modern „robust statistics“. The procedure is given by LISCHER in the ‘Schweizer Lebensmittelbuch’ (‘Swiss food handbook’, chapter 60A). Its advantage is that it works without elimination of outliers and its complete absence of any manipulations by the ring-test leader. It is based on a monofactoral variance analysis but requires no assumptions on the distribution of the measurement deviations. The disadvantage is the black box character of the used iterative calculations. They are normally not understandable for most chemists without deeper knowledge of statistic methods. Some foundations are cited and translated from chapter 60 A, Schweizer Lebensmittelbuch:

**Table 1.:** Participant laboratories and elements they analysed

Nr.	N	S	P	Ca	Mg	K		Na	Zn	Mn	Fe	Cu	Pb	Al	B	Cd	C
1	X	X	X	X	X	X			X	X	X						
2	X	X	X	X	X	X		X	X	X	X	X	X	X	X		
3	X	X	X	X	X	X			X	X	X						
3a	X																
4		X	X	X	X	X		X	X	X	X	X	X	X		X	
4a	X	X	X	X	X	X		X	X	X	X	X	X	X	X		
4b	X	X		X	X	X		X	X	X	X	X	X		X	X	X
5	X	X	X	X	X	X		X	X	X	X	X					
6	X	X	X	X	X	X			X	X	X	X		X	X		X
7	X	X	X	X	X	X		X	X	X	X	X			X		
8	X	X	X	X	X	X		X	X	X	X	X	X	X	X		
8a	X																
9	X	X	X	X	X	X		X	X	X	X	X	X	X		X	
10	X	X	X	X	X	X			X	X	X	X			X		
11	X	X	X	X	X	X			X	X	X	X		X			
12	X	X	X	X	X	X		X	X	X	X	X	X	X	X		X
13	X	X															
14	X	X	X	X	X	X		X	X	X	X	X		X	X		
15	X	X	X	X	X	X											X
16	X	X	X	X	X	X		X	X	X	X	X		X			
17	X	X	X	X	X	X			X	X	X	X	X	X	X		
18	X	X	X	X	X	X		X	X	X	X	X	X	X	X		
19	X	X	X	X	X	X											
20	X	X	X	X	X	X					X						
21	X	X	X	X	X	X		X	X	X	X	X		X	X		
22																	
23	X	X	X	X	X	X		X	X	X	X	X		X	X		
24	X	X	X	X	X	X		X	X	X	X	X	X		X	X	
25	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	
26	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X
27			X	X	X	X		X	X	X	X	X					
28	X	X	X	X	X	X		X	X	X	X	X			X		
29	X	X	X	X	X	X			X	X	X	X			X		
30	X	X	X	X	X	X			X	X	X						
31																	
32																	
33																	
33a									X			X	X			X	
34																	
35	X		X	X	X	X		X	X	X	X	X	X			X	
36	X	X	X	X	X	X		X	X	X	X	X	X		X	X	X
37	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	
38	X	X	X	X	X	X		X	X	X	X	X	X	X	X		
38a		X	X	X	X	X		X	X	X	X	X					
39	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X
40	X		X	X	X	X		X		X	X	X					
41	X	X	X	X	X	X		X	X	X	X	X	X	X		X	X
42	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X
43	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	
44	X	X	X	X	X	X		X	X	X	X	X	X	X		X	X
44a		X	X	X	X	X		X	X	X	X	X	X	X		X	
45	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X
46	X	X	X	X	X	X		X	X	X	X		X	X			X
47	X	X	X	X	X	X		X	X	X	X	X	X	X		X	X
48	X	X	X	X	X	X			X	X	X	X		X			X
49	X		X	X	X	X			X	X	X	X		X			X
50	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	
51		X	X	X	X	X				X	X						
52	X	X	X	X	X	X			X	X	X	X		X			X
53	X	X	X	X	X	X		X		X	X			X			X

*„In order to find out whether or not chemical-analytical or physical methods of determination provide comparable results not only when repeated in the same laboratory but also in different laboratories, it is necessary to carry out joint studies (interlaboratory experiments). In ISO 5725, very detailed information is given on how such interlaboratory experiments are to be carried out and evaluated. A central factor in judging such a measuring method are the quantities of repeatability and reproducibility, or more precisely, repeatability standard deviation and reproducibility standard deviation. In order to prevent these quantities being distorted by the results of isolated non-representative laboratories, the ISO norm 5725 suggests conducting outlier tests before the final evaluation. Robust statistical methods allow us to circumvent outlier tests.*

*The important thing about these robust methods is that a different measure is used for variability than empirical variance. There are different reasons that suggest such a method. On the one hand, no systematic error should be committed with data that have exactly normal distribution. Yet this is not the case for the ISO norm (and with other methods using outlier tests). If such a test operates with a probability for error of 5%, then in one case out of twenty on average one laboratory will be eliminated, even if its results are completely correct. Since several such tests are carried out in an interlaboratory experiment, these probabilities for error accumulate. Rejection measurement values with large residues (difference between estimated and measured quantities) results in the variance components systematically coming out too small and in methods being considered more precise than they actually are.*

*On the other hand, results deviating too strongly from the great majority should not be weighted or should only be weighted with a very little weight so that final result is not distorted.*

...

*In general, the characteristic quantities calculated according to different methods do not deviate strongly from one another. Still, the robust method is preferable to the ISO norm. The absence of systematic error is important, as well as the fact that subjective decisions by the interlaboratory experiment leaders become superfluous. The problematic outlier tests can also be dispensed with. By contrast, the robust method permits a constant transition between accepting and completely rejecting doubtful measurement values.“*

For further information please see the ‘Schweizer Lebensmittelbuch’ or the more specialised literature listed in chapter 2.5 (HAMPEL 1980, HAMPEL 1987, LISCHER 1987, ROCKE 1983).

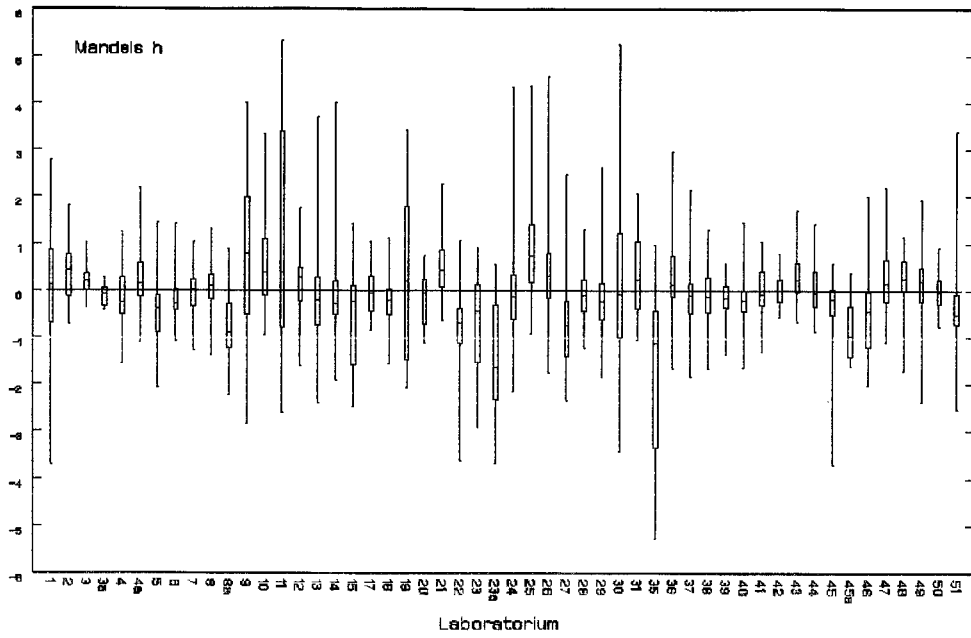
The complete data are presented on **pages 2-1** and following. If single values have an enclosed ‘a’, ‘b’, or ‘ab’ their data are automatically ‘trimmed’ (the original German term is ‘gestutzt’) by the iteration process, but, as explained in the above citation, not eliminated. Only the data with values lower than the determination limits were not included in evaluation.

## **2.2 Comparability with the 3<sup>rd</sup> interlaboratory test 1997/98**

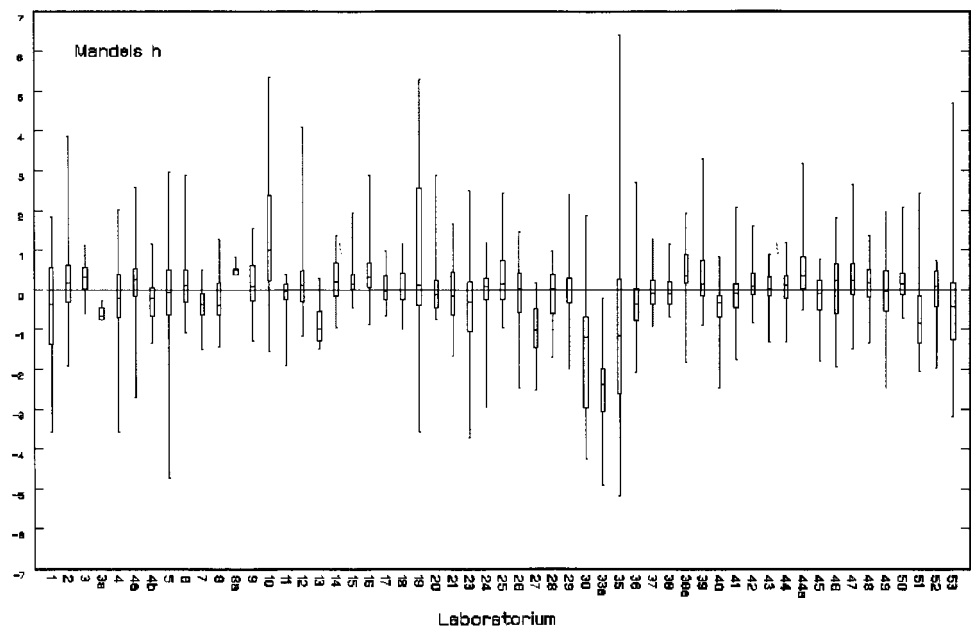
**Figure 2** compares the 3<sup>rd</sup> to the 4<sup>th</sup> ring test the so-called Mandel's h plot over all samples and elements. It demonstrates whether the laboratory trends towards higher or lower values than the mean of all laboratories and likewise extremes. 50% of all values are to be found within the rectangular box. One can see, that in the 4<sup>th</sup> ringtest there are not so many extremes as in the 3<sup>rd</sup> one.

**Figure 3** compares the interlab variances of 3<sup>rd</sup> and 4<sup>th</sup> ringtest according to all elements. The variances (%) are in the same range for most elements, but much higher for sodium and lower for lead and noteworthy better for cadmium. This will be discussed in chapter 3.

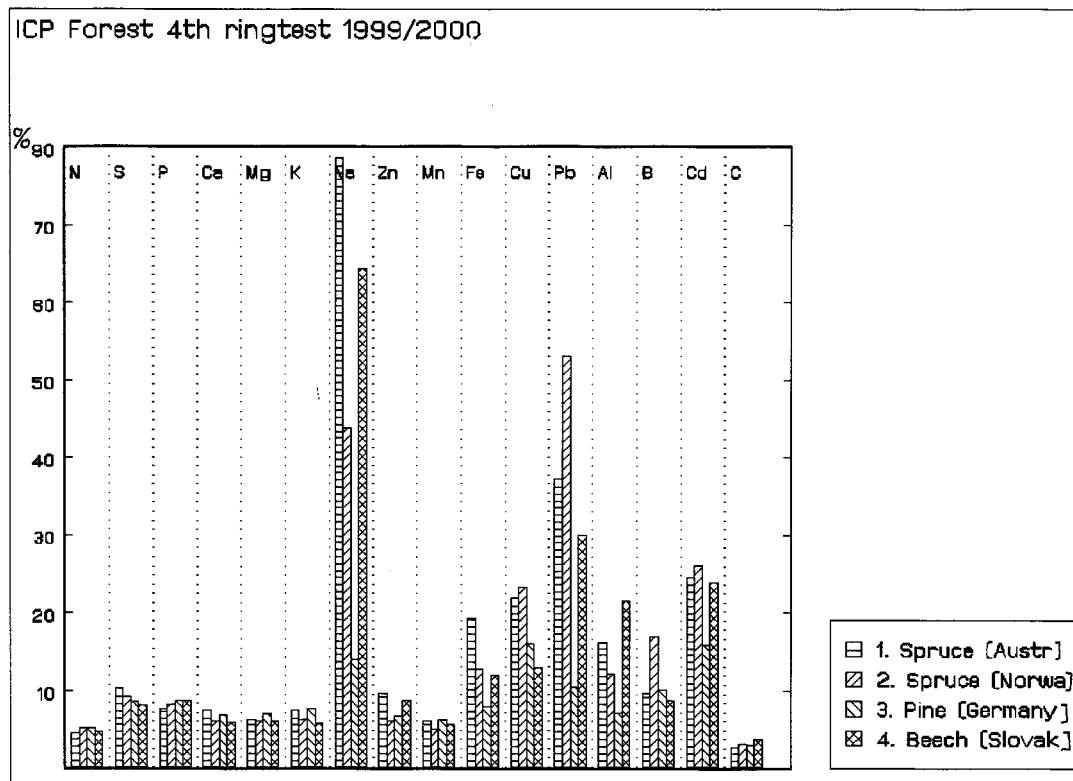
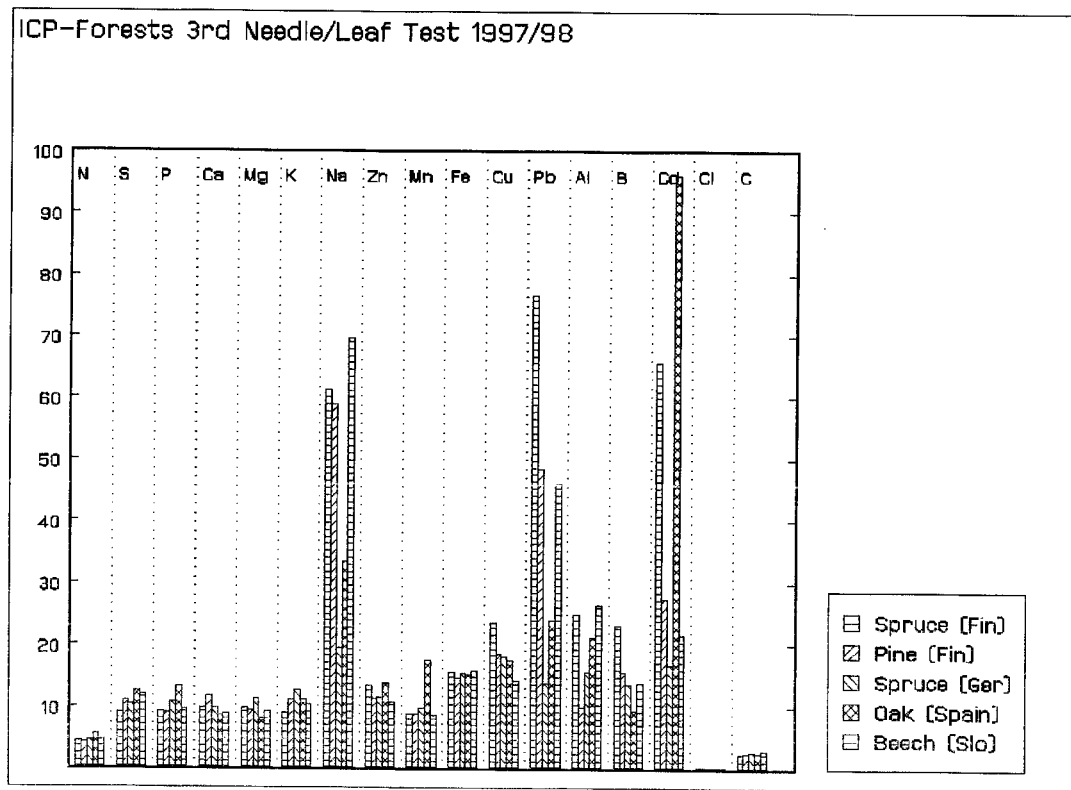
### ICP-Forests 3rd Needle/Leaf Test 1997/98



### ICP Forest 4th ringtest 1999/2000



**Figure 2:** Comprehensive comparison of Mandels h plot (3<sup>rd</sup> and 4<sup>th</sup> ring test)



**Figure 3:** Comprehensive comparison of interlab variances (3<sup>rd</sup> and 4<sup>th</sup> ringtest)

As mentioned before, sample 5 (beech, Slovenia) of the 3<sup>rd</sup> test and sample 4 (“beech Slovakia”) have been identical. The following **Table 2** gives a comparison of element means of 3<sup>rd</sup> and 4<sup>th</sup> interlaboratory study.

For almost all elements we find a surprisingly high harmony among the means. It proves a very good comparability between 3<sup>rd</sup> and 4<sup>th</sup> ringtest.

It is an important conclusion that on principle the 4<sup>th</sup> interlaboratory needle/leaf test 1999/2000 is fully comparable with the study of 1997/98.

**Table 2:** Mean comparison of sample 5 (3<sup>rd</sup> ring test) and sample 4 (4<sup>th</sup> ring test) (*n* = number of data sets)

Element	3 <sup>rd</sup> test 97/98 sample 5		4 <sup>th</sup> test 99/00 sample 4	
	Robust Stat.	<i>N</i>	Robust Stat.	<i>N</i>
<b>Nitrogen</b> (mg/g)	<b>20.02</b>	45	<b>20.14</b>	49
<b>Sulphur</b> (mg/g)	<b>1.87</b>	46	<b>1.82</b>	46
<b>Phosphorus</b> (mg/g)	<b>1.16</b>	50	<b>1.21</b>	49
<b>Calcium</b> (mg/g)	<b>7.25</b>	49	<b>7.10</b>	49
<b>Magnesium</b> (mg/g)	<b>1.02</b>	49	<b>1.00</b>	49
<b>Potassium</b> (mg/g)	<b>6.80</b>	50	<b>6.87</b>	49
<b>Sodium</b> (µg/g)	<b>30.55</b>	37	<b>32.47</b>	33
<b>Zinc</b> (µg/g)	<b>27.54</b>	45	<b>27.95</b>	45
<b>Manganese</b> (µg/g)	<b>1328.00</b>	45	<b>1313.00</b>	48
<b>Iron</b> (µg/g)	<b>70.29</b>	45	<b>71.03</b>	49
<b>Copper</b> (µg/g)	<b>5.88</b>	38	<b>5.82</b>	42
<b>Lead</b> (µg/g)	<b>0.96</b>	21	<b>0.69</b>	19
<b>Aluminium</b> (µg/g)	<b>60.04</b>	33	<b>65.13</b>	30
<b>Boron</b> (µg/g)	<b>17.52</b>	23	<b>16.58</b>	26
<b>Cadmium</b> (ng/g)	<b>200.7</b>	13	<b>177.4</b>	16
<b>Carbon</b> (%)	<b>48.99</b>	17	<b>49.03</b>	15

## 2.3 Data Evaluation

The agreements of As (1994) and Vienna (1997) say that the ring tests should be evaluated on the basis of fixed limits. **Table 3** presents an overview of the percentage of non-tolerable values, based on the original data given on pp 2-1.

**Table 3:** Percentage of non tolerable values; comparison of 2<sup>nd</sup>, 3<sup>rd</sup> and 4<sup>th</sup> ring test

		2 <sup>nd</sup> Labtest 1995/96		3 <sup>rd</sup> Labtest 1997/98		4 <sup>th</sup> Labtest 1999/00	
Element	Tolerable deviation from mean (±%)	Non tolerable (%)	<i>n</i>	non tolerable (%)	<i>n</i>	non tolerable (%)	<i>n</i>
<b>Nitrogen</b>	15* / 10**	<b>2.7</b>	148	<b>4.4</b>	225	<b>6.6</b>	196
<b>Sulphur</b>	20	<b>25.8</b>	132	<b>14.3</b>	230	<b>9.8</b>	184
<b>Phosphorus</b>	15	<b>6.8</b>	148	<b>19.6</b>	250	<b>7.1</b>	196
<b>Calcium</b>	15	<b>9.6</b>	156	<b>16.3</b>	245	<b>6.6</b>	196
<b>Magnesium</b>	15	<b>12.2</b>	156	<b>16.7</b>	245	<b>5.1</b>	196
<b>Potassium</b>	15	<b>7.7</b>	156	<b>20.4</b>	250	<b>6.6</b>	196
<hr/>							
<b>Sodium</b>	30	<b>61.0</b>	84	<b>46.6</b>	178	<b>43.4</b>	136
<b>Zinc</b>	20	<b>18.9</b>	132	<b>16.9</b>	225	<b>12.0</b>	183
<b>Manganese</b>	20	<b>3.6</b>	139	<b>10.9</b>	229	<b>4.2</b>	192
<b>Iron</b>	20	<b>20.6</b>	136	<b>23.7</b>	224	<b>17.9</b>	196
<b>Copper</b>	30	<b>20.7</b>	116	<b>16.2</b>	191	<b>20</b>	165
<b>Lead</b>	30	<b>53.0</b>	66	<b>42.4</b>	99	<b>32.1</b>	78
<b>Aluminium</b>	20	<b>32.3</b>	99	<b>31.1</b>	164	<b>16.1</b>	124
<b>Boron</b>	20	<b>33.9</b>	56	<b>18.2</b>	115	<b>18.4</b>	103
<b>Cadmium</b>	30	<b>48</b>	25	<b>39.0</b>	77	<b>16.9</b>	65
<b>Carbon</b>	10* / 5**	<b>0</b>	24	<b>0</b>	85	<b>3.3</b>	60

\* 2<sup>nd</sup> and 3<sup>rd</sup> Labtest, \*\* 4<sup>th</sup> Labtest

The percentage of results out of the given tolerable limits decreases for all elements, especially for all mandatory elements. Even for Nitrogen and Carbon, where the limits became much stronger, we do not notice any significant deterioration.

**Table 4** gives a short survey about the laboratories with 'values out of tolerance'. But this is not the place to censure single laboratories. Each laboratory is appealed to criticise itself and to improve its own methods, equipment and the training of staff.

**Table 4: Values out of tolerance (< = too low; > = to high)**

Nr.	N	S	P	Ca	Mg	K	Na	Zn	Mn	Fe	Cu	Pb	Al	B	Cd	C
1	<<<<	><	.	<<<	.	.		<<	.	.	<<<					
2	.	.	.	.	.	.	<<	.	.	.	><<	.	<<	.		
3	.	.	.	.	.	.		.	.	.						
3a	.															
4	.	.	.	.	.	.	.	.	.	>>	>>>>	>	<<		.	
4a	.	.	.	.	>	.	<	.	.	>	.	>>	<	.	.	
4b	.	.		<	.	.	<<	.	.	.	.	<		.	.	.
5	.	<	<>	<	.	.	<<	<	.	.	>>					
6	.	.	.	.	.	.	<	.	.	.	>		.	>		.
7	.	.	.	.	.	.	.	.	.	.	.			.		
8	.	.	.	.	.	.	>>>	.	.	.	.	.	.	>		
8a	.															
9	.	.	.	.	.	.	.	.	.	<	.	>	.		.	
10	.	>>>>	>	.	.	.		>	.	>	>>>>			>		
11	.	.	.	.	.	.		.	.	.	.		.			
12	.	.	.	.	.	.	.	.	.	.	.	>>	>>>	>>>		.
13	.	.														
14	.	.	.	.	.	.	>>	.	.	.	>		.	.		
15	.	>	.	.	.	.							<			.
16	.	.	.	.	.	>	.	.	.	.	.		<			
17	.	.	.	.	.	.							.	.		
18	.	.	.	.	.	.	<<	.	.	.	.	.	.	.		
19	>>	>><	<<	.	.	.										
20	.	.	.	.	.	.				>>						
21	.	.	.	.	.	.	.	>	.	<<	.		.	<<		
22																
23	.	>	.	.	.	.	.	<<<	.	<	.		<	<<<<		
24	.	.	.	.	.	.	<<	.	.	.	.	>		<	<	
25	.	.	.	.	.	>>	>>>	.	.	>	.	.	.	.	.	
26	.	.	.	.	.	<<	>>>	.	.	<<	.	>>>	<	>	.	.
27			.	<	<	<<<	<<	.	.	<<<	.					
28	.	.	.	.	<	.	<<	.	.	<	.			.		
29	.	.	.	.	.	.		.	.	<	>			.		
30	<<<<	<<<	<	<<<	<<<<	<<<<	<	>	<<<<	<						
31																
32																
33																
33a								<<<<			<<<	<<<<			<<	
34																
35	.		.	<	<<	<	>>>	<<<	<<<<	<<>	<<	.			><	
36	.	.	.	.	.	.	>>>	<	.	>	>	.		.	>	.
37	.	.	>	.	.	.	<<	.	.	.	.	<	.	.	.	
38	.	.	.	.	.	.	<<	.	.	.	.	.	.	.	.	
38a		.	.	.	>	.	>>>	.	.	<<<	>>>					
39	.	.	.	.	.	.	>>>	.	.	>	.	<	.	.	.	.
40	.		<<	.	.	.	.	.	.	<	.					
41	.	.	.	.	.	.	>	.	.	.	.	.	>		<<	.
42	.	.	.	.	.	.	<<	.	.	.	.	<	.	.	.	>
43	.	.	.	.	.	.	.	.	.	.	.	<<<	>	.	.	
44	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
44a		.	.	.	.	.	>>>	.	.	.	.	.	>>>		.	
45	.	.	.	.	.	.	<	.	.	.	.	.	.	<<<	.	.
46	>	>	<<	<<	.	.	.	.	.	.	.	.	.	.		.
47	.	.	.	.	.	.	<<<	.	.	.	>>	>	.		>>>	.
48	>>	.	.	.	.	.		.	.	.	.					.
49	.	.	.	.	.	.		<<	.	.	>>>		<			>
50	.	.	.	.	.	.	<<	.	.	.	.	>>>	.	.	.	
51		<	<	.	.	<		.	.	<<>						
52	.	.	.	.	.	.		<<	.	.	<<<		.			.
53	>>>>	.	<<	.	.	.	<<<	.	.	>			<<>			.

**Table 5** demonstrates that numerous values out of tolerance depend on element contents in the foliar samples. In most cases lower element contents cause higher numbers of intolerable values.

Element contents (mean) and percentage of values out of tolerance (%)					
Elem./Sample		1 Spruce (A)	2 Spruce (N)	3 Pine (D)	4 Beech (SK)
<b>N</b>	mg/g	13,26	11,3	21,84	20,14
	%	6,1	8,2	6,1	6,1
<b>S</b>	mg/g	0,99	1,27	1,52	1,82
	%	10,9	8,7	6,5	13
<b>P</b>	mg/g	1,95	2,19	1,32	1,21
	%	8,2	10,2	6,1	4,1
<b>Ca</b>	mg/g	4,11	11,32	3,28	7,1
	%	6,1	2	12,2	6,1
<b>Mg</b>	mg/g	1,3	0,86	0,53	1
	%	4,1	2	12,2	2
<b>K</b>	mg/g	3,7	7,65	4,78	6,87
	%	8,2	4,1	8,2	6,1
<b>Na</b>	µg/g	24,16	50,75	411,6	32,47
	%	71	40	5,4	63,6
<b>Zn</b>	µg/g	21,9	100,4	60,45	27,95
	%	17,4	8,7	6,5	15,6
<b>Mn</b>	µg/g	1519	1007	826	1313
	%	4,2	4,2	4,2	4,2
<b>Fe</b>	µg/g	136	57,88	195,9	71,03
	%	26,5	24,5	6,1	14,3
<b>Cu</b>	µg/g	3,44	3,03	4,34	5,82
	%	24,4	24,4	17,1	14,3
<b>Pb</b>	µg/g	0,53	0,43	5,23	0,69
	%	41,2	61,1	8,3	26,3
<b>Al</b>	µg/g	83,82	135,5	263,4	65,13
	%	13,3	9,4	6,3	36,7
<b>B</b>	µg/g	21,5	11,44	20,07	16,58
	%	16	26,9	15,4	15,4
<b>Cd</b>	ng/g	120,5	93,73	537,7	177,4
	%	25	13,3	5,6	25
<b>C</b>	%	51,27	49,51	51,77	49,03
	%	0	6,7	0	6,7

### 3. Evaluation by analysis methods

This part will discuss in detail the problems of used pretreatment and measurement methods. The evaluation by methods is based on the following informations for each element:

a) Elementspecific code index according to the used methods on pp1-21.

As against the 3<sup>rd</sup> ringtest the code has been supplemented in a way that it is extendable and more generally applicable. Furthermore that renders it possible to integrate any future development.

b) Original laboratory data with graphic presentation on pp 2-1

The graph shows the plus/minus deviations of methods for each element from mean based on the robust evaluated data (annex) and arranged by ascending pretreatment methods. Each column represents one of the 4 samples. The broken lines define the tolerable limits (see table 3).

„PN“ means pretreatment method, „DN“ means determination method

c) Presentations of data arranged acc. method codes on pp 3-1

For these graphs the same explanations are valid as for the graphs of the original data pp 2-1.

It will be tried to gain important results from this ringtest for each element by comparing graphs for each digestion and determination method. Methods that lead to the best comparable results and help to further optimise and, if possible, concentrate/condense the manual will be highlighted.

#### 3.1 Nitrogen (pp 2-1, 3-1)

The result of the ringtest can be stated as remarkably positive. This applies even more as the determination tolerance had been reduced from  $\pm 15\%$  in the 3<sup>rd</sup> ringtest to  $\pm 10\%$ .

Only two laboratories (19, 35) clearly overstep the limits, not so much because of reasons concerning the apparatus but more so due to mishandling or wrong calibration of the elemental analyzers.

It is remarkable that classic wet chemical analysing methods result in means below the average mean, and those from elemental analyzers lie above it. It was to be expected in theory that Kjeldal digestion is not able to digest the sample matrix completely, but was not so clear from the 3<sup>rd</sup> ringtest.

In the medium term it should be aspired to give up Kjeldal digestion whenever possible to optimise the comparability of nitrogen determination.

As concerning elemental analyzers, measurement by LECO-CNS analyser (P1-D17.1) achieve the best results.

### **3.2 Sulphur** (pp 2-6, 3-3)

As against earlier ringtests the determination of sulphur has improved considerably. Almost each laboratory stayed inside the tolerance limit of  $\pm 20\%$ . Only the means from three laboratories (10, 19, 30) show big deviations, using various methods.

In tendency, those laboratories that use a combination of  $\text{HNO}_3$ -digestion followed by ICP-determination are the closest to the overall mean.

Classic  $\text{BaCl}_2$  - methods seems to be rather risky. They demand a more thorough handling and sufficient experience.

It is recommended that in the medium term all laboratories should focus on using elemental analyzers or the combination of  $\text{HNO}_3$  digestion/ICP.

Furthermore, X-ray methods have proved feasible.

### **3.3 Phosphorus** (pp 2-11, 3-5, 3-6)

A few laboratories (5, 10, 19, 53) apparently have great difficulty in determining phosphorus. This may be due to internal problems because the participants applied different methods. Generally all wet digestions using  $\text{HNO}_3$  followed by determination by ICP lead to very good results.

Results achieved by X-ray-spectroscopy are acceptable.

Classic methods using dry ashing and colometric determination with (Vanadium)-

Molybdenum blue lead to results within the allowed limits of  $\pm 15\%$ , yet faults occur more frequently.

### **3.4 Calcium** (pp 2-16, 3-7, 3-8)

Two laboratories (10, 35) found extremely deviating results for calcium. Single outliers were found among data from a few other laboratories.

The best results can be obtained from the combination of  $\text{HNO}_3$  digestion with ICP determination. This will be the chosen method in the future. Pressure digestion should be preferred to digestion in open systems and microwave digestion.

The use of flame AAS often leads to lower or higher results.

Results from X-ray spectroscopy are good.

### **3.5 Magnesium** (pp 2-21, 3-9, 3-10)

Results for magnesium are altogether very good. Only one laboratory (30) found extremely low values in all four samples. Few laboratories have come up with one single outlier.

As with calcium, the best results are obtained from combined  $\text{HNO}_3$  digestion with ICP. This will be the chosen method for magnesium as well.

Application of flame AAS more often leads to lower results.

Results from energy disperse X-ray-spectroscopy are good, those from wavelength disperse are faulty in some cases.

### **3.6 Potassium** (pp 2-26, 3-11, 3-12)

Results for potassium are rather good. One laboratory (30) finds definitely too little in all 4 samples.

Eight laboratories show single outliers or range close to the tolerated limit of  $\pm 15\%$ .

Pressure digestion in combination with ICP leads to the best results and should be preferred in future. Yet results obtained by flame AAS or classic flame photometry are fairly acceptable.

Results from X-ray spectroscopy are good.

### **3.7 Sodium** (pp 2-31, 3-13, 3-14)

Sodium is the element with the highest percentage of outliers by far that has not improved significantly since the 3<sup>rd</sup> ringtest.

Especially samples containing low amounts of sodium  $< 100 \mu\text{g/g}$  (samples 1, 2, 4) are problematic and show 40 – 70% of values lying outside the generously limited range of  $\pm 30\%$ .

On the contrary, sample 3 with  $> 400 \mu\text{g/g}$  shows only 5.4% outliers. The reason for this is not the poor sensitivity of spectrometers but the ubiquity of the element in laboratories and measurement equipment which causes a high risk of blind values. On the basis of the data given it seems to be an urgent demand to work exclusively with closed systems, either with pressure digestion or microwave ovens. Moreover, measurement by ICP is favourable against flame AAS.

To limit the risk of blind values only glass-free instruments are to be used.

### **3.8 Zinc** (pp 2-36, 3-15, 3-16)

Zinc is one of the heavy metals which analysis causes the least problems. The number of values below the tolerance limit of  $\pm 20\%$  is with 12% even lower than in the 3<sup>rd</sup> ringtest. Very few laboratories (23, 33a, 35) delivered values well below the lower limit.

Open acidic digestion should be avoided. Digestion with HNO<sub>3</sub> in closed pressure or microwave systems is recommended.

ICP-OES and X-ray fluorescence spectrometry have proved advantageous against flame AAS.

### **3.9 Manganese** (pp 2-41, 3-17, 3-18)

Of all metals, manganese shows the lowest number of values outside the limits of  $\pm 20\%$ . Only two laboratories (30, 35) find too little in all 4 samples, applying open acid digestion followed by flame AAS.

For the future, pressure or microwave digestion in combination with ICP, as well as X-ray fluorescence spectroscopy, are recommendable.

### 3.10 Iron (pp 2-46, 3-19, 3-20)

Iron analysis has improved slightly against the 3<sup>rd</sup> ringtest. Nevertheless, the number of values beyond the limits of  $\pm 20\%$  is still too high. The number of outliers decreases with higher values of iron ( $> 100 \mu\text{g/g}$ ). Similar to sodium the ubiquity of iron in all laboratory equipment plays an important role. Another possible source of faulty results could lie in the inhomogeneity of the samples caused by metal abrasion from grinding.

Graphic evaluation according to digestion methods indicates risks with open acid digestion. Simple pressure digestion with  $\text{HNO}_3$  followed by ICP is recommended, microwave digestion would be the second choice.

X-ray fluorescence analysis proved to be not so feasible.

### 3.11 Copper (pp 2-51, 3-21, 3-22)

The quantity of 20% non-tolerable results is slightly higher than in the 3<sup>rd</sup> ringtest. A number of laboratories show clearly deviating results (2, 4, 10, 33a, 35, 38a, 52). A look at the graphic evaluation reveals that microwave digestion seems to have advantages over pressure digestion and open acid digestion. Self-made purest water can contain copper from copper pipes and cause false results. Contamination can stem from contact of digestion acids with metal parts in the pressure system as well.

Good results can be obtained from ICP and graphite tube AAS.

For such low concentrations X-ray fluorescence is less recommendable because it reaches its determination limits.

### 3.12 Lead (pp 2-56, 3-23, 3-24)

Apart from sodium, lead is the element with the highest percentage of values outside the tolerance limits of  $\pm 30\%$ . However, there is an obvious correlation to the concentration, as shown in chart 5. There are relatively few outliers for sample 3 with a high concentration of more than  $5 \mu\text{g/g}$  lead. At the same time, lead is an element that has been analysed by less than half of the laboratories altogether. The decrease of the sensitive but slow graphite tube AAS in laboratory routine is to be taken seriously, as well as the insufficient use of methods with a comparable sensitivity, like ICP-MS.

Because of the incomplete participation the present data do not state a clear hint to recommendable methods, neither to digestion nor determination techniques.

For the future, digestion in closed systems (pressure or microwave digestion) followed by ICP- OES with USN or ICP-MS seem to be more recommendable.

X-ray fluorescent spectroscopy is not suitable for concentrations of  $<1 \mu\text{g/g}$  pb.

### 3.13 Aluminium (pp 2-61, 3-25, 3-26)

The ring test for aluminium cannot be evaluated because only 4 out of 31 laboratories have kept to the manual which requires digestion using HF. Two laboratories have analysed the samples by x-ray spectroscopy. All the other data sets are contradictory to the instructions given in the ringtest.

It is well-known that without the use of HF, aluminium which is combined with silica in plants cannot be dissolved completely which causes a considerable risk of low findings. That

has clearly been proved by laboratory 44. Data set 44 shows the results obtained without the use of HF against data set 44a with HF. The latter is 10 –50 % higher for all samples! It is recommended to delete aluminium from the list of "optional elements", because even after the 4<sup>th</sup> ringtest only a small number of laboratories keep to the ICP-manual.

### **3.14 Boron** (pp 2-66, 3-27, 3-28)

Boron has been determined by about half of the laboratories, of which three delivered strongly deviating results.

According to the evaluation of the methods, in particular pressure digestion with HNO<sub>3</sub> followed by ICP-OES seems to be the future method.

The use of borosilica glass has to be avoided by all means.

### **3.15 Cadmium** (pp 2-71, 3-29, 3-30)

The toxic heavy metal cadmium has been added later to the list of "optional elements" and determined by only a third of the laboratories. Compared to the results for sodium, lead and copper, the overall result has to be considered very positive. Only nearly 17% of the results lie outside the tolerance range of  $\pm 30\%$ . Like with lead, the error (fault) rate decreases drastically with the increase of the concentration (sample 3). Only one laboratory (47) delivered too high values for all samples. Apart from that single outliers dominate. No particular digestion method is to be stated as being clearly of advantage. It is remarkable that results from graphite tube AAS tend to be rather lower than the overall mean, results from ICP rather higher.

### **3.16 Carbon** (pp 2-76, 3-31, 3-32)

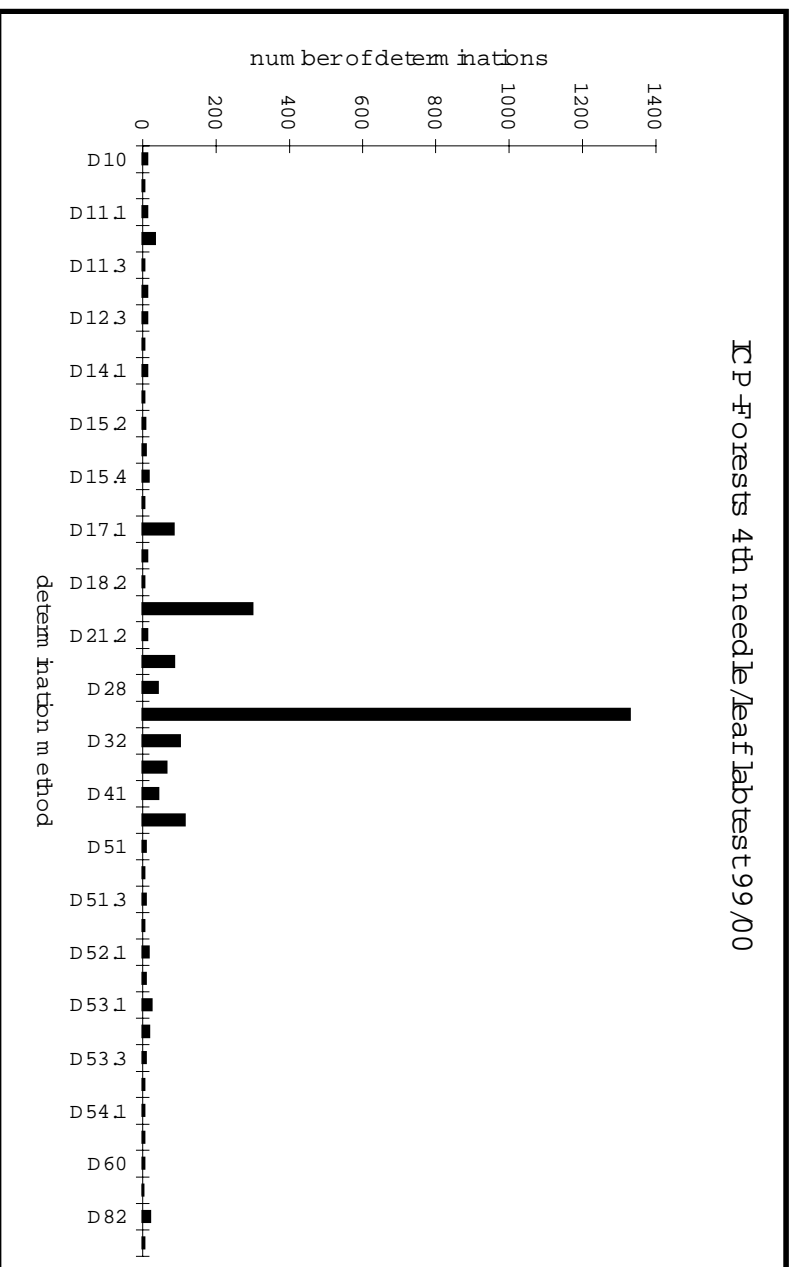
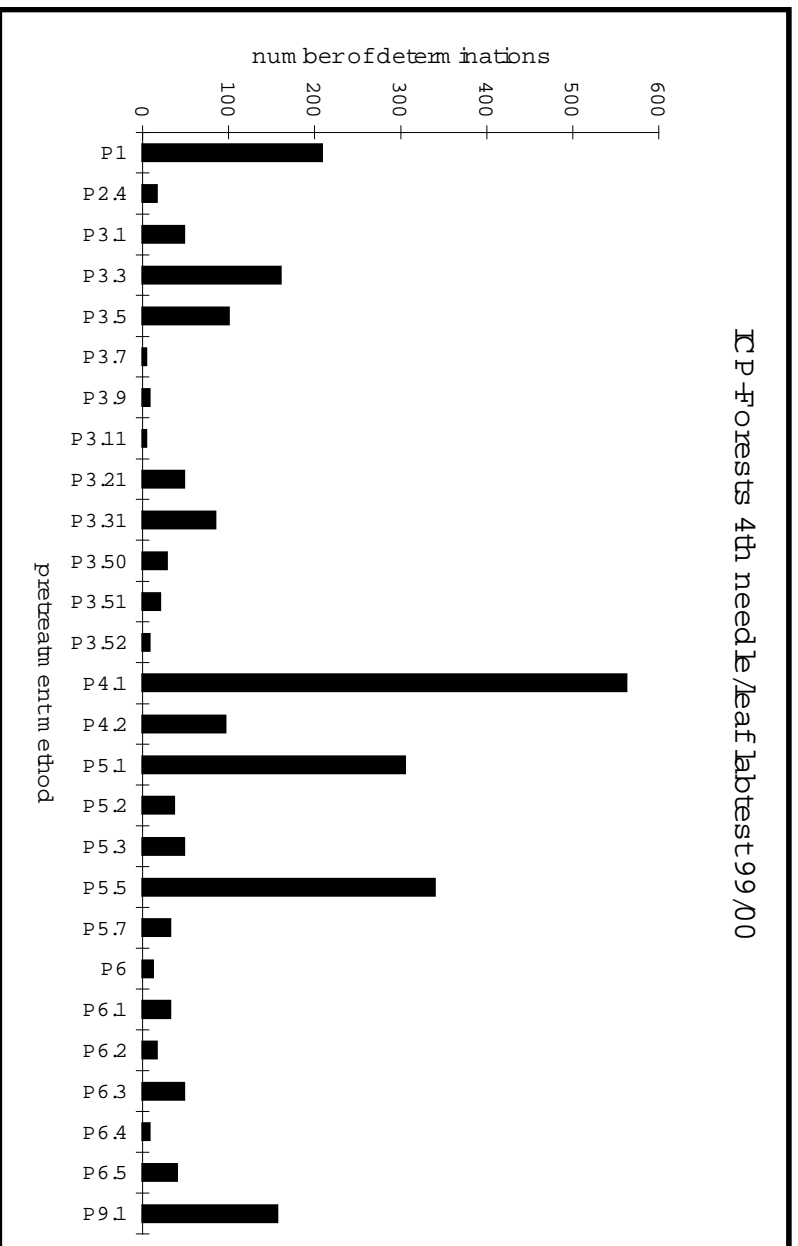
Only one results lies outside the recommended limits of  $\pm 5\%$ . Within these limits the analysis of carbon does not cause any problems and has not to be commented on further.

## **4. Conclusions**

The 4<sup>th</sup> ICP Forest Interlaboratory Test shows significant improvement in analytical quality despite a few unsatisfactory aspects. Nevertheless bigger efforts are necessary to improve especially the comparability of the analysis of trace elements. This can only be achieved by further periodical ringtests and by restricting the number of methods at the same time to as few as possible.

**Fig. 4** and **Table 6** show the frequency of methods applied. They show impressingly that the trend leads away from classic to more automatic methods (such as elemental analyzers, ICP, etc.) and to the restriction to simple HNO<sub>3</sub> digestions in closed systems.

Figure 4:



**Table 6:**

<b>Number of applied methods</b>				
<b>method</b>	<b>number</b>		<b>method</b>	<b>number</b>
P1-D10	12		P3.50-D11.2	8
P1-D11.1	4		P3.50-D11.3	4
P1-D11.2	12		P3.50-D51	4
P1-D12.2	12		P3.50-D51.2	4
P1-D12.3	12		P3.50-D82	8
P1-D13.1	4		P3.51-D11.1	4
P1-D14.1	12		P3.51-D11.2	8
P1-D15.1	4		P3.51-D82	8
P1-D15.2	7		P3.52-D11.2	4
P1-D15.3	8		P3.52-D82	4
P1-D15.4	16		P4.1-D21.1	40
P1-D16.1	4		P4.1-D22	37
P1-D17.1	84		P4.1-D31	413
P1-D18.1	12		P4.1-D32	68
P1-D18.2	4		P4.1-D53.1	4
P1-D71.1	1		P4.2-D31	80
P2.4-D21.1	4		P4.2-D32	16
P2.4-D28	8		P5.1-D21.1	64
P2.4-D53.2	4		P5.1-D22	20
P3.1-D21.1	4		P5.1-D28	8
P3.1-D28	4		P5.1-D31	209
P3.1-D31	12		P5.1-D53.1	4
P3.3-D21.1	48		P5.2-D31	36
P3.3-D22	4		P5.3-D31	48
P3.3-D28	13		P5.5-D21.1	11
P3.3-D31	83		P5.5-D31	263
P3.3-D52	4		P5.5-D32	13
P3.3-D53.2	4		P5.5-D35	52
P3.3-D82.3	4		P5.7-D31	28
P3.5-D21.1	28		P5.7-D53.1	4
P3.5-D22	8		P6.1-D21.1	20
P3.5-D31	44		P6.1-D28	8
P3.5-D35	12		P6.1-D53.2	4
P3.5-D52.1	8		P6.2-D52.1	8
P3.7-D53	4		P6.2-D53.1	4
P3.9-D52.1	4		P6.2-D54.2	4
P3.9-D53	4		P6.3-D31	44
P3.10-D31	28		P6.3-D32	4
P3.11-D51	4		P6.4-D53.2	4
P3.21-D21.1	44		P6.4-D54.1	4
P3.21-D53.1	4		P6.5-D21.1	35
P3.31-D11	4		P6.5-D53.2	1
P3.31-D11.1	4		P6.5-D54	4
P3.31-D21.1	12		P6-D31	8
P3.31-D22	16		P6-D60	4
P3.31-D31	32		P9.1-D41	42
P3.31-D51.3	8		P9.1-D42	114
P3.31-D53.3	8			

The variants that are described in detail in the method code are not needed any longer in such a comprehensive form. It is suggested to reduce the choice of proposed methods in favour of more automatic methods in the revised manual.

According to the author it would be reasonable to radically restrict methods to:

1. C-N-S elemental analyzers (for C, N, and S)
2. HNO<sub>3</sub> digestions in closed systems (pressure bomb or microwave) in combination with ICP-OES or ICP-MS (for S, P, Ca, etc.) or HGA-AAS (for Cu, Pb, Cd)
3. X-ray fluorescence analysis. This has not proved in each case to be as good as the before mentioned methods due to poorer sensitivity but should be kept and further developed as a quick automatic and non-destructive multi element analysis method (for S, P, Ca, Mg, K, (Na), Zn, Mn, (Fe, Cu, Pb, Cd) .

It is suggested to carry out a separate ringtest exclusively with these methods.

## 5. Literature

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## **7. ICP Forests Foliar Analysis Methods Code (1999/2000)**

### **7. 1 Code Numbers of Abbreviations of Pretreatments**

#### **P0 No information**

#### **P1 No pretreatment**

#### **P2 Extractions**

**P2.1** Extraction, H<sub>2</sub>O

**P2.2** Extraction, HNO<sub>3</sub>

**P2.2** Extracton, aqua regia

#### **P3 Wet ashings at room pressure (open system)**

**P3.1** Wet ashing, HNO<sub>3</sub>

**P3.2** Wet ashing, HNO<sub>3</sub>/HF

**P3.3** Wet ashing, HNO<sub>3</sub>/HClO<sub>4</sub>

**P3.4** Wet ashing, HNO<sub>3</sub>/HClO<sub>4</sub>/HF

**P3.5** Wet ashing HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>

**P3.6** Wet ashing HNO<sub>3</sub>/HClO<sub>4</sub> /H<sub>2</sub>SO<sub>4</sub>

**P3.7** Wet ashing, HNO<sub>3</sub>/HClO<sub>4</sub>/CaCl<sub>2</sub>

**P3.8** Wet ashing, HNO<sub>3</sub>/HClO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>

**P3.9** wet ashing, HNO<sub>3</sub>/HClO<sub>4</sub>/HCl

**P3.10** Wet ashing, HNO<sub>3</sub> /H<sub>2</sub>SO<sub>4</sub>

**P3.20** Wet ashing, HClO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>

**P3.21** Wet ashing, HClO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub>

**P3.31** Wet ashing, H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>

**P3.32** Wet ashing, H<sub>2</sub>SO<sub>4</sub>/K<sub>2</sub>CrO<sub>7</sub>

**P3.50** Kjeldahl, H<sub>2</sub>SO<sub>4</sub>/ Se-catalyst

**P3.51** Kjeldahl, H<sub>2</sub>SO<sub>4</sub>/Cu-catalyst

**P3.52** Kjeldahl, H<sub>2</sub>SO<sub>4</sub>/Ti-Cu-catalyst

**P3.53** Kjeldahl, H<sub>2</sub>SO<sub>4</sub>/Hg-catalyst

#### **P4 Pressure digestions (closed system)**

**P4.1** Pressure digestion, HNO<sub>3</sub>,

**P4.2** Pressure digestion, HNO<sub>3</sub>/HF

**P4.3** Pressure digestion, HNO<sub>3</sub>/HClO<sub>4</sub>,

**P4.4** Pressure digestion, HNO<sub>3</sub>/HClO<sub>4</sub>/HF,

**P4.5** Pressure digestion, HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>,

#### **P5 Microwave pressure digestions (closed system)**

**P5.1** Microwave digestion, HNO<sub>3</sub>,

**P5.2** Microwave digestion, HNO<sub>3</sub>/HF

**P5.3** Microwave digestion, HNO<sub>3</sub>/HClO<sub>4</sub>

**P5.4** Microwave digestion, HNO<sub>3</sub>/HClO<sub>4</sub>/HF

**P5.5** Microwave digestion, HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>,

**P5.6** Microwave digestion, HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/HF

**P5.7** Microwave digestion,  $\text{HNO}_3/\text{H}_2\text{O}_2/\text{HCl}$

**P6 Dry ashings**

**P6.1** Dry ashing, dissolution with  $\text{HNO}_3$

**P6.2** Dry ashing, dissolution with  $\text{HNO}_3/\text{MgNO}_3$

**P6.3** Dry ashing, dissolution with  $\text{HNO}_3/\text{HF}$

**P6.4** Dry ashing, dissolution with  $\text{HNO}_3/\text{HCl}$

**P6.5** Dry ashing, dissolution with  $\text{HCl}$

**P6.6** Dry ashing, dissolution with  $\text{HCl}/\text{HF}$

**P6.7** Dry ashing, dissolution with  $\text{H}_2\text{SO}_4$

**P7 Oxygen ashings**

**P7.1** Oxygen ashing, Schöniger

**P7.2** Oxygen ashing, Wickbold

**P7.3** Oxygen ashing, calorimetric bomb

**P9 X-ray-pretreatments and other pretreatments**

**P9.1** Material pressed (Pellet)

**P9.2** Material melted and formed (tablet)

**P9.5** Melting ( $\text{NaOH}$ )6. 2 Code Numbers of Abbreviations of Detections

## 7.2 Code Numbers of Abbreviations of Detectrions

**D0** No information

**D1** No detection

### **D10** Elemental-analyzers

**D11** Kjeldahl-apparatus

**D11.1** Kjeldahl-apparatus (Tecator)

**D11.2** Kjeldahl-apparatus (Gerhardt)

**D11.3** Kjeldahl-apparatus (Büchi)

**D12** N-Analyzer

**D12.1** N-Analyzer (Heraeus/Elementar )

**D12.2** N-Analyzer (Vario)

**D12.3** N-Analyzer(,Leco)

**D13** C-Analyzer

**D13.1** C-Analyzer (Leco)

**D14** S-Analyzer

**D14.1** S-Analyzer (Leco)

**D15** C/N-Analyzer

**D15.1** C/N-Analyzer (Carlo-Erba)

**D15.2** C/N-Analyzer (Leco)

**D15.3** C/N-Analyzer (Heraeus)

**D15.4** C/N-Analyzer (Vario)

**D16** C/S-Analyzer

**D16.1** C/S-Analyzer (Leco)

**D17** C/N/S-Analyzer

**D17.1** C/N/S-Analyzer (Leco)

**D17.2**

**D18** C/N/H-Analyzer

**D18.1** C/N/H-Analyzer (Leco)

**D18.2** C/H/N-Analyzer (Heraeus)

**D20 Mono-Atom-Spectrometry-Techniques**

**D21** AAS-flame technique

**D21.1** AAS-flame technique (C<sub>2</sub>H<sub>2</sub>/Air)

**D21.2** AAS-flame technique (C<sub>2</sub>H<sub>2</sub>/N<sub>2</sub>O)

**D22** AAS-flameless technique

**D24** AAS-hydride technique

**D25** AAS-cold vapor technique

**D26** AFS-hydride-technique

**D28** AES-Flame photometer

**D30 Multi-Atom-Spectrometry-techniques**

**D31** ICP-AES without Ultrasonic nebulisation

**D32** ICP-AES with Ultrasonic nebulisation

**D35** ICP-MS

**D40 Physical techniques**

**D41** X-ray-energy dispersive

**D42** X-ray-wavelength dispersive

**D45** Neutron activation analysis (NAA)

**D47**  $\gamma$ -spectroscopy

**D50 UV-VIS-spectrophotometric techniques**

**D51 Colorimetric N-Determination**

**D51.1** Indophenol-blue-method

**D51.2** Flow Injection (FIAS) - NH<sub>3</sub>-Membrane-diffusion, 566 nm

**D51.3** Continuous flow method, Indophenol blue

**D52 Colorimetric S-Determination**

**D52.1** BaCl<sub>2</sub>-methods (Nephelometry)

**D53 Colorimetric P-Determination**

**D53.1** Molybdene-blue-method

**D53.2** Vanadium-Mo-blue-method

**D53.3** Continuous flow method, Molybdene-blue

**D54 Colorimetric B-Determination**

**D54.1** Azomethin - H

**D54.2** Carmine

**D60 Ion-chromatographic techniques**

**D61.1** Anion-Chromatography w. chemical suppression

**D61.2** Anion-Chromatography w. electr. suppression

**D62.1** Kation-Chromatography w. chemical suppression

**D62.2** Kation-Chromatography w. electr. suppression

**D70 Electrochemical methods**

**D71** Conductimetry

**D71.1** Conductometric titration

**D72** Potentiometry

**D72.1** pH

**D72.2** other ion selective elektrodes

**D73** Potentiometric titrations

**D74** Stripping potentiometry

**D75** Voltammetry

**D76** Polarography

**D77** Amperometry

**D78** Electrophoresis

**D79** Redox potential

**D80 Classical analytical techniques**

**D81** Gravimetry

**D82** Titration

**D82.1** NH<sub>4</sub>-back titration

**D82.2** Thiocyanate-titration

**D82.3** FeNH<sub>4</sub>SO<sub>4</sub>-Titration

**D82.4** Barimetric titration

**D90 other detections**