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Plant Reference Materials for Inorganic Chemical Analysis; are they Still Stable after 20 Years?

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Introduction

The "Comité inter-instituts d'étude des techniques analytiques (CII)" is a group composed of 32 European laboratories (table 1) which are principally involved in the fields of agronomy, forestry and environmental research. Some laboratories are governmental research centres or part of university departments, others were originally private laboratories. The group was founded in 1959 in Abidjan, following a colloquium on the control of plant nutrition.

The main goals of the CII are to prepare and make available agricultural or environmental reference materials to its members and the scientific community at large for use in inorganic chemical analysis, as well as the development of analytical methods.

From its origins until now, the CII has created 30 reference materials, 26 of which are still available. They can be classified in four main groups (table 2).

Table 1
CII Members: countries of origin

Countries	*Number of laboratories*
France	12
Belgium	6
Italy	2
Spain	2
Switzerland	2
Bulgaria	1
Denmark	1
Germany	1
Netherlands	1
Norway	1
Poland	1
Portugal	1
Russia	1

List of the CII-laboratories:
Centre de coopération internationale en recherche agronomique pour le développement, Montpellier (F), Centre d'études atomiques, Is/Tille (F), Centre national de la recherche scientifique, Strasbourg (F), Centre national de la recherche scientifique, Vernaison (F), Institut européen de l'environnement de Bordeaux (F), Institut national agronomique, Paris-Grignon (F), Institut national de la recherche agronomique, Centre de Bordeaux (F), Institut national de la recherche agronomique, Nancy (F), Institut Pasteur de Lille (F), Laboratoire SADEF, Aspach-Le-Bas (F), Office d'équipement hydraulique corse, Bastia (F), Université de Paris VI (F); Centre d'études et de recherches vétérinaires et agrochimiques, Tervuren (B), Hogeschool Gent (B), Station des plantes ornementales, Merlbeke (B), Université catholique de Louvain, Centre de Michamps (B), Université catholique de Louvain, Louvain-La-Neuve (B), Université libre de Bruxelles (B); Ente national energia atomica, Casaccia (I), Istituto Agrario di S. Michele a/A (I); Escuela tecnica superior de ing. agraria, Lleida (E), Estacion experimental del Zaidin, Granada (E); ConStat Consulting, Bern (CH), Eidg. Forschungsanstalt für Agrarökologie und Landbau, Reckenholz & Liebefeld (CH); Sofia University, (BU); Danish forest and landscape research institute, Hoersholm (DK); Bundesforschungsanstalt für Landwirtschaft, Braunschweig Volkenrode (D); Agricultural University, Wageningen (NL); Norvegian forest research institute, As (N); Institute for land reclamation and grassland farming, Falenty (PL); Laboratorio quimico agricola da Silva, Lisboa (P); St Petersburg State University, (RU).

For the whole of these materials, the contents are given for the following elements: $N_{Kjeldahl}$, P, K, Ca, Mg, Na, Cu, Fe, Mn, Zn. For some, the information is completed by the following indications: Al, B, Cl, S, $N\text{-}NO_3$, SiO_2, and the raw ash (useful for X-ray fluorescence analysis). The contents of Cd, Co, Mo and Pb are also occasionally included (table 3).

Methods of preparation and of analysis

The members decide during the regularly held CII meetings on the choice of reference materials to be prepared. The different steps of preparation and quality control are presented succinctly in table 4.

Soon after its founding, the CII defined a method of mineralization for plant material. It is based firstly on dry ashing at 450°C and solubilisation of the ashes in dilute hydrochloric acid. After filtration of this solution, a calcination of the filter and of the residue is followed by treatment with hydrofluoric acid and solubilisa-

Table 2
Reference materials available

Human nutrition	*Agricultural and animal nutrition*	*Plants substrats and soil improvers of organic nature*	*Environment and foresty*
Directly	Alfalfa	Barley straw	Carnation
	Hay	Blond peat	Pine needles
Apple-fruit	Rye-grass	Pine bark	
Cabbage			
Lettuce			
	Leaves of:		Leaves of:
Indirectly[a]	– Codia discolor*		– Eucalyptus*
	– Cotton*		– Hevea*
Rice straw	– Tobacco		– Oak
	– Sugarbeet		
Leaves of:			
– Golden apple*			
– Maize*			
– Olive*			
– Orange*			
– Peach*			
– Vine*			

[a] through the foliar diagnostic (initial trend of the CII)
* see text

Table 3
Content ranges (dry matter) of the reference materials

	g/kg		mg/kg
$N_{Kjeldahl}$	3.28– 44.9	Al	21.9 – 263.7
NO_3-N	0.09– 11.1	B	7.6 – 57.7
P	0.25– 7.20	Cd	0.19– 3.3
K	0.52– 70.8	Co	0.17– 25.8
Ca	2.15– 49.1	Cu	3.1 – 880
Mg	0.48– 7.0	Fe	55 –1814
Na	0.06– 11.6	Mn	11.1 –1684
Cl	0.22– 22.3	Mo	0.96– 1.2
S	1.7 – 3.48	Pb	2.6 – 6.4
SiO_2[a]	0.45–107	Zn	8.3 – 24.1
Ash	28.8 –222		

[a] total Si calculated as SiO_2
The individual values for the materials given in this table have been taken from the publications 2–7, 14–18

Table 4

Preparation and storage of the reference materials

- Selection of the material in accordance to the members' needs
- Growing/harvesting of the chosen material (between 20 and 40 kg of dry matter)
- Drying, grinding, homogenisation, 1st homogeneity control
- Packaging of 20 to 75 g of the material in PVC or polyethylene bottles or small plastic bags, 2nd homogeneity control
- Storage in a dark, dry room at 16 ± 4°C

tion in dilute hydrochloric acid. Finally, the two solutions are combined and adjusted to the desired end volume (1). The solution obtained is suitable for use in atomic absorption spectrometry (flame and electrothermal), inductively coupled plasma emission spectrometry (optical and mass spectrometry detection), polarography, titrimetry, photometry or ion chromatography. Nitrogen has always been determined by the method of Kjeldahl.

The CII has always given a lot of attention to the quality of its determinations. It has on numerous occasions used non-destructive neutron activation and X-ray fluorescence for the analysis of the dried plant material (2–4) to confirm the accuracy of its method of sample preparation using the treatment with hydrofluoric acid. A further example is the analysis of nitrogen by the method of Kjeldahl; various members have carried out the procedure using different catalysts to ensure the independence and accuracy of the determination.

Stability of the reference materials

A reference material is only of value, if it is homogeneous and its composition remains stable over time. The CII published the composition of the first reference materials around 1975 (5-7) and these are denoted with a (*) in table 2. Ten years later, a new round of analyses confirmed the stability of these materials (8).

So where are we now, twenty years later? A new round of analyses were carried out in 1992/93 to investigate the stability of the materials. The study involved only six of the original thirteen materials, because the amounts of material remaining were in some cases less than one hundred of the original sample-batch. They cover also the range of concentrations mentioned in table 3 as far as possible. For these reasons, the materials codia-, cotton-, eucalyptus-, olive-, orange-, vine-leaves and the elements $N_{Kjeldahl}$, P, K, Ca, Mg, Na, Cl, S, B, Cu, Fe, Mn, Zn were selected for investigation.

The analyses were carried out by half of the participants using the CII method of preparation with hydrofluoric acid, the others, for safety and technical reasons used classical wet digestions (sulfuric acid, nitric acid, perchloric acid, etc), microwaves or dry ashing with no hydrofluoric acid treatment.

A simple evaluation of the results was presented at the IXth International Colloquium for the Optimization of Plant Nutrition (9). It allows the conclusion, with some reservation, that the composition values published in 1975 and 1977 are still sound.

This article considers the same analytical results, but with a more critical approach in order to draw more reliable conclusions.

Results and Discussion

It would be very laborious to compare the results of 1993 for each element and each test material with the corresponding results of 1973 and also to test for any significant differences. If each of these tests were carried out at the level, $\alpha = 5\%$, significant differences would occur in certain cases, even if all the values were from the same normally distributed population. If the level of each comparison (of a total of 78) is reduced to $\alpha = 0.05/78 \approx 0.00064$ (in order to keep the global level within 5%) and considering that for some elements only five results were provided in 1993, it is obvious that no reliable conclusions would emerge from such a study.

A better approach than the mechanical and stereotypical strategy – one factor at a time – is the analysis of variance. The difficulties which result from too small sample sizes can be avoided by an appropriate pooling of the results of different analytes, provided that the variances are roughly homogenous. In this case however, the reproducibility standard deviations for the raw data tends to increase with increases in content. Figure 1 shows the logarithms of the mean content of each plant material for 1973 and 1993, plotted against the logarithms of the corresponding reproducibility standard deviations as well as the two regression lines. As the data are not exactly normally distributed robust techniques were used, for which algorithms and details are given in the Swiss Food Manual (10).

In both cases, a strong linear relationship is evident. Intercept *a* and slope *b* of the regression lines are respectively –0.74 and 0.885 for 1973, –0.73 and 0.875 for 1993 and –0.735 and 0.880 for the two years together. This functional relationship between contents and reproducibility standard deviations allows to stabilise the variances by a suitable transformation.

A Box-Cox-transformation (11) stabilises the variances and makes it possible to use analysis of variance methods:

$$y = \begin{cases} \dfrac{x^{\lambda}-1}{\lambda}, & \text{if } \lambda \neq 0 \\ \ln x, & \text{if } \lambda = 0 \end{cases} \qquad \text{where: } x = \text{raw data}, \quad y = \text{transformed data}$$

with parameter $\lambda = 1 - b = 0.12$.

For the years 1973 and 1993 taken separately, the residuals $r_{ijk} = y_{ijk} - \tilde{y}_{ij}$, for each test material *i*, for each analyte *j* and for each laboratory *k* are calculated, where $\tilde{y}_{ij}$ is the robust mean of the transformed results of test material *i* and analyte *j*.

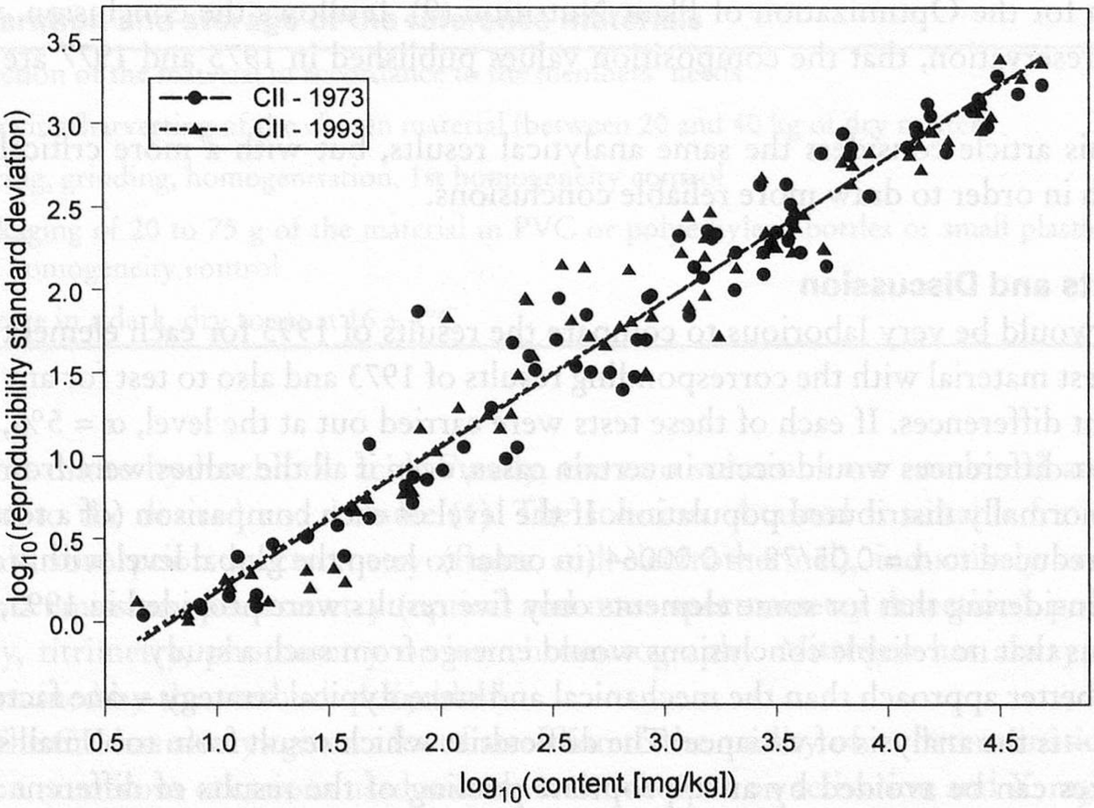

Figure 1 **Reproducibility standard deviation versus mean content of each plant material and regression lines**

As the transformed results y_{ijk} all have approximately the same variance, a pooling of residuals of the different test materials allows estimates with many more degrees of freedom and consequently more reliable estimates.

As an example figure 2 shows boxplots of the residuals of the transformed results of 1993. The standard deviations of the residuals (bottom line) of a particular element can be interpreted as coefficient of variation of the measurement results at content level c = 1 mg/kg.

The higher variability of the laboratory results for Na is obvious, slightly less for S and Fe. The spread of the sodium values is certainly influenced by the difficulties (usually contaminations) associated with the measurement of this element, especially at small contents as in olive-leaves (0.08 mg/kg) (7).

Table 5 lists the estimates of the standard deviations of the transformed residuals for the years 1973 and 1993.

The variance $\mathrm{Var}(\tilde{y}_{ij}^{(1993)} - \tilde{y}_{ij}^{(1973)})$ of the transformed paired differences can now be determined using the normal method for combining variances and taking into account the different number of laboratories which provided results.

An obvious method, to decide whether the 'true values' have significantly changed during the past 20 years, is to draw the uncertainty bars of these paired dif-

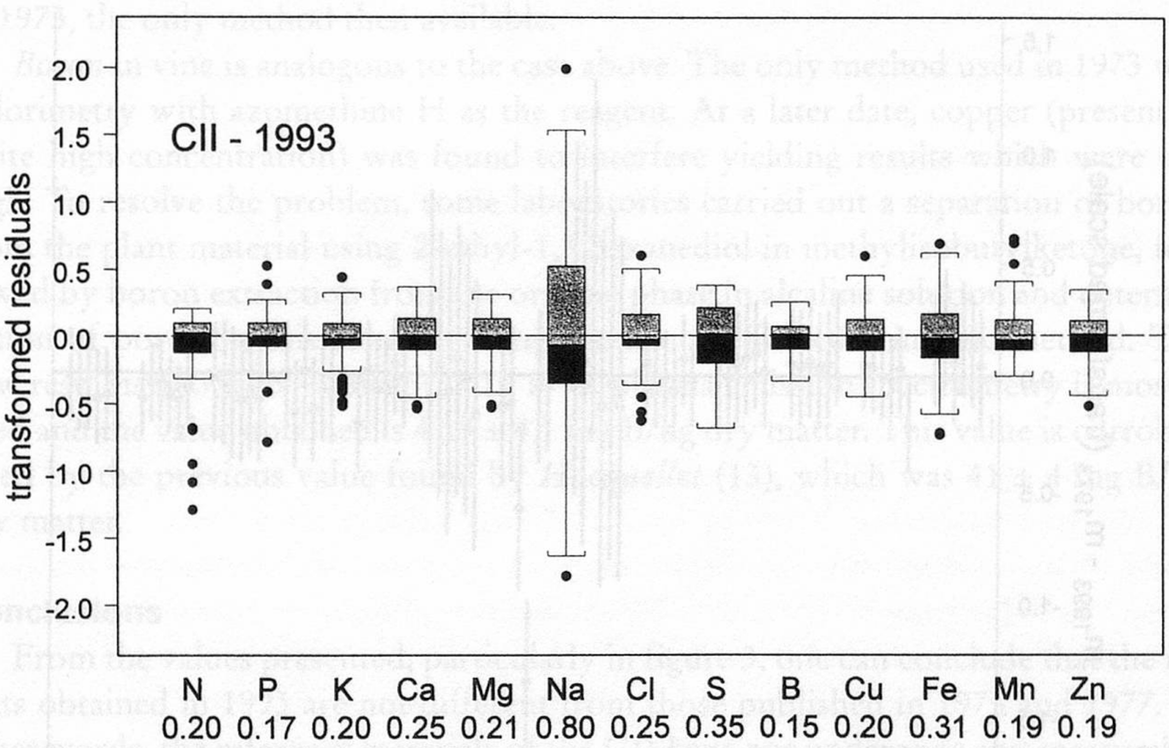

Figure 2 **Boxplots of the transformed residuals. The numbers at the bottom line indicate the standard deviations**

ferences and to check if the value zero is contained in it. The uncertainty of measurement is "the interval around the measurement that contains the true value with a high probability". The uncertainty bar is obtained by multiplying the standard deviation by a coverage factor *k*. In this case *k* = 3 was chosen (12). This coverage factor (*k* = 3) corresponds to a confidence-level of about 99%. The transformed paired differences for the 78 analytes and their uncertainty bars are shown in figure 3.

The difference of *chlorine* content in olive-leaves (0.33 g/kg in dry matter) is difficult to evaluate. One observes a decrease by a factor of about 1.5 during these 20 years, but more surprising is the increase in the coefficients of variation. For 1983 and 1993, they are 33.5% and 29.8% respectively (results not given in detail), both

Table 5
Estimates of the standard deviation of the transformed residuals

	N^a	P	K	Ca	Mg	Na	Cl	S	B	Cu	Fe	Mn	Zn
CII-73	0.177	0.177	0.265	0.185	0.147	0.320	0.138	0.369	0.202	0.167	0.166	0.105	0.153
CII-93	0.200	0.167	0.202	0.246	0.213	0.798	0.250	0.350	0.148	0.202	0.306	0.192	0.194

^{a}N$_{\text{Kjeldahl}}$

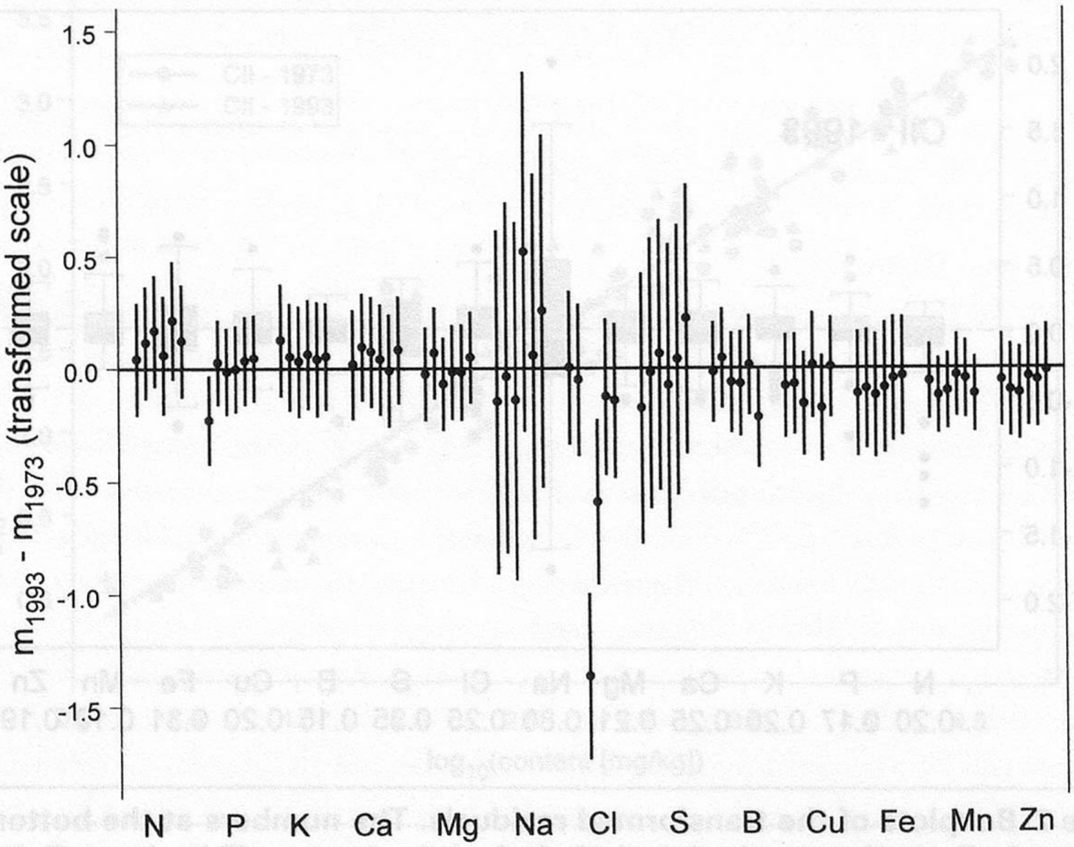

Figure 3 **Transformed paired differences with uncertainty bars for the six test materials: Leaves of Codia discolor(first bar), cotton (second bar), eucalyptus, olive, orange and vine (sixth bar). m: robust mean**

values being almost double that of the original one (15.8%), although the number of results is equivalent for the three studies (between 5 an 8). Whether new analytical problems, less rigorous quality control or an effective diminution of chlorine content in the material occurred, is difficult to assess. The content of chlorine in eucalyptus-leaves (3.02 g/kg dry matter) is a similar case, even if slightly easier. It was already known in 1983 that the decrease in chlorine content was statistically significant and it became even more evident in 1993. In this case, it is probably due to the loss of one or more volatile chlorinated compounds as the diminution is practically monotonous as a function of time. Between 1973 and 1983, the value decreased by 0.70 g/kg dry matter and between 1983 and 1993 by 0.56 g/kg dry matter; an almost linear decrease of about 0.06 g/kg dry matter per year.

Figure 3 shows also that there are differences between the 1973 and 1993 values for *phosphorus* in codia discolor-leaves and for boron in vine-leaves. Considering codia, this difference is probably due to the two following factors. The first one is the small concentration of phosphorus in the plant (0.25 g/kg dry matter) which makes measurement difficult. The second one is that in 1993 both colorimetry and plasma emission spectroscopy were used as methods in comparison to colorimetry in 1973, the only method then available.

Boron in vine is analogous to the case above. The only method used in 1973 was colorimetry with azomethine H as the reagent. At a later date, copper (present in quite high concentration) was found to interfere yielding results which were too high. To resolve the problem, some laboratories carried out a separation of boron from the plant material using 2-ethyl-1,3 hexanediol in methylisobutylketone, followed by boron extraction from the organic phase in alcaline solution and determination of boron in this solution using the azomethine colorimetric method. The new result is about 25% lower (8). In 1993, plasma emission spectrometry is mostly used and the value obtained is 41.9 ± 4.1 mg B/kg dry matter. This value is corroborated by the previous value found by *Hocquellet* (13), which was 41 ± 4 mg B/kg dry matter.

Conclusions

From the values presented, particularly in figure 3, one can conclude that the results obtained in 1993 are not different from those published in 1975 and 1977. In other words, the reference materials of the CII have not undergone any measurable changes, except for the reference values of chlorine in eucalyptus- and in olive-leaves which today cannot be considered as valid.

According to *Hocquellet* (13), the values obtained for phosphorus by plasma emission spectrometry are more accurate than those from colorimetry, considering the various mean values calculated in 1973, 1983 and 1993. It can therefore be deduced that the probable concentration of phosphorus in codia lies between 0.20 and 0.25 mg P/kg dry matter. It can further be stated that the analytical technical changes are in this case probably more important than an eventual alteration of the plant material in time.

Considering boron in vine-leaves, the CII adopts 42 ± 4 mg B/kg dry matter as the new reference value.

On the whole, the observed variations are mainly due to the evolution in the analytical methods rather than a change in the reference materials.

Summary

The "Comité inter-instituts d'étude des techniques analytiques (CII)", a group of 32 European laboratories, has as first objective to make available reference materials to its members and the scientific community for inorganic chemical analysis of plant materials.

Created in 1959, the CII published in 1975 the chemical composition of 13 reference materials. A first study, carried out in 1984, confirmed the stability of the reference plant materials. Twenty years after their preparation, the question was raised whether the initial characteristics have been preserved or changes have occurred. A new serie of analyses has confirmed that the original contents (78 values) are still valid, apart from three exceptions, two of which concern the chlorine contents. The influence of changes in analytical techniques are discussed briefly with reference to two real cases (boron and phosphorus).

Zusammenfassung

Das "Comité inter-instituts d'étude des techniques analytiques (CII)" besteht seit 1959 und ist eine Vereinigung von 32 europäischen Laboratorien. Seine Hauptaufgabe besteht darin, den Mitgliedern und einem weiteren Kreis von Interessierten, Referenzmaterialien pflanzlichen Ursprungs für chemisch analytische Bestimmungen zur Verfügung zu stellen.

Das CII publizierte 1975 die chemische Zusammensetzung von 13 pflanzlichen Referenzmaterialien. 1984 präsentierte es eine erste Studie, in der die Stabilität dieser Referenzmaterialien bestätigt wurde. Zwanzig Jahre nach deren Herstellung stellte sich die Frage der Stabilität erneut. In einer weiteren Serie von Analysen konnte nachgewiesen werden, dass die zu Beginn gefundenen chemischen Zusammensetzungen bis auf drei Ausnahmen (von insgesamt 78 Werten) ihre Gültigkeit behielten. Zwei dieser Ausnahmen betreffen das Element Chlor. An zwei konkreten Beispielen (Bor und Phosphor) werden die Konsequenzen des in den vergangenen Jahren erfolgten technischen Fortschritts in der Analytik kurz diskutiert.

Résumé

Le Comité inter-instituts d'étude des techniques analytiques (CII) est un groupement de 32 laboratoires européens dont le but principal est de mettre à la disposition de ses membres et de la communauté scientifique des matériaux de référence pour l'analyse chimique minérale de matériel végétal et environnemental.

Créé en 1959, il publiait en 1975 la composition chimique minérale de 13 matériaux de référence. En 1984 le CII présentait une première étude confirmant la stabilité de ses matériaux de référence végétaux. Vingt ans après leur création ceux-ci conservent-ils toutes leurs caractéristiques initiales ou des modifications sont-elles intervenues? Une nouvelle série d'analyses permet d'affirmer que les teneurs déterminées à l'origine (78 valeurs) gardent toute leur validité, à l'exception de trois d'entre elles, dont deux concernent des teneurs en chlore. Les influences provenant de l'évolution des techniques analytiques mises en jeu durant ces années sont brièvement discutées sur la base de deux cas concrets se rapportant au bore et au phosphore.

Key words

Plant chemical analysis, Macro elements, Micro elements, Reference materials, Stability

References

1 *Les Laboratoires membres du Comité inter-instituts d'étude des techniques analytiques du diagnostic foliaire:* Méthodes de référence pour la détermination des éléments minéraux dans les végétaux. Azote, phosphore, potassium, sodium, calcium, magnésium. Oléagineux **24**, 497–504 (1969).

2 *Daniel, R.Ch.* et *les membres du CII:* Les étalons végétaux du C.I.I. Résultats complémentaires. In: Martin-Prével, P. (ed), Proceedings 6th International Colloquium for the Optimization of Plant Nutrition, 1984 Montpellier (F). Vol. 3, 837–846 (1984). AIONP/CIRAD, Montpellier, 1986

3 *Daniel, R.Ch., Lischer, P., Ruf, D.* and *Theiller, G.:* Statistical approches to the determination of reference values for new CII standard substances: alfalfa, rye-grass, peat and pine bark. Recherche agronom. Suisse **31**, 117–126 (1991).

4 *Daniel, R.Ch., Lischer, P.* and *Theiller, G.:* Four new CII reference materials for the chemical analysis of plants: pine needles, oak leaves, barley-straw and apple-fruit. In: Fragoso, M.A.C., van Beusichem M.L. (ed), Optimization of Plant Nutrition: 31–35. Kulwer Academic Publishers 1993.

5 *Pinta, M.* et *le Comité inter-instituts d'étude des techniques analytiques de diagnostic foliaire:* Etalons végétaux pour l'analyse foliaire. Analusis **3**, 345–353 (1975).

6 *Pinta M.* et *le Comité inter-instituts d'étude des techniques analytiques de diagnostic foliaire:* Echantillons de référence pour l'analyse végétale. 1. Azote, phosphore, potassium, calcium, magnésium, manganèse, zinc. Geostandards Newsletter, **1**, 25–30 (1977).

7 *Pinta, M.* et *le Comité inter-instituts d'étude des techniques analytiques de diagnostic foliaire:* Echantillons de référence pour l'analyse végétale. 2. Sodium, chlore, soufre, bore, oligo-éléments. Geostandards Newsletter, **1**, 115–121 (1977).

8 *Daniel, R.Ch., Bonvalet, A.* et *les membres du CII:* Stabilité des étalons végétaux du C.I.I. Qu'en est-il après 10 ans? In: Martin-Prével, P. (ed), Proceedings 6th International Colloquium for the Optimization of Plant Nutrition, 1984 Montpellier (F). Vol **3**, 831–835 (1984). AIONP/CIRAD, Montpellier, 1986.

9 *Theiller, G., Daniel, R.Ch., Paul, J.L., Clément, A., Lischer, P.* and *Gabriels, R.:* The stability of reference materials as guaranteeing the quality of plant analysis. In: Martin-Prével, P., Baier, J. (ed), Optimization of Plant Nutrition: Presented papers from the IXth International Colloquium for the Optimization of Plant Nutrition 8th–15th September 1996 Prague (CZ). 21–25 Czech University of Agriculture, Prague 1998.

10 Schweizerisches Lebensmittelbuch, Kapitel 60. Statistik und Ringversuche. Eidg. Drucksachen- und Materialzentrale, Bern 1989.

11 *Box, G.E.P.* and *Cox, D.R.:* An analysis of transformations (with discussion). J. Roy. Stat. Soc. B 26, 211–252 (1964).

12 *Analytical Methods Committee:* Uncertainty of measurement: implication of its use in analytical science. Analyst **120**, 2303–2308 (1995).

13 *Hocquellet, P., Theiller, G.* et *les membres du CII:* Comité inter-instituts: évaluation de la spectrométrie d'émission atomique par plasma à couplage inductif (ICP) pour l'analyse foliaire. Analusis **19**, M45–M47 (1991).

14 *Daniel, R.Ch.:* Etalons pour l'analyse chimique des végétaux. Trav. chim. aliment. hyg. **71**, 242–247 (1980).

15 *Pinta, M., Daniel, R.Ch.* et *les membres du CII:* Nouveaux étalons CII pour l'analyse foliaire. In: Fregoni, M. (ed), Proceedings 5th International Colloquium on the Control of Plant Nutrition. Castelfranco Veneto (I) 1980. Edizioni Comunita Nuova-IPSA 1982. Vol **1**, 112–117 (1982).

16 *Daniel, R.Ch., Theiller, G.* et *les membres du CII:* Betterave, foin, laitue, 3 étalons du CII pour l'analyse chimique des végétaux. Résultats complémentaires. Trav. chim. aliment. hyg. **81**, 219–227 (1990).

17 *Daniel, R.Ch., Lischer, P., Bermond, A.* et *Ducauze, C.J.:* Laquelle est la «Vraie Valeur»? Une approche statistique pour déterminer la teneur en nitrates des étalons végétaux du C.I.I. Recherche agronom. Suisse 30, 11–21 (1991).

18 *Novozamsky, I., Houba, V.J.G., Daniel, R.Ch.* and *the members of CII:* Certification of cabbage and carnation sample and their use in an international proficiency study. Fresenius J. Anal. Chem. **345**, 198–201 (1993).

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