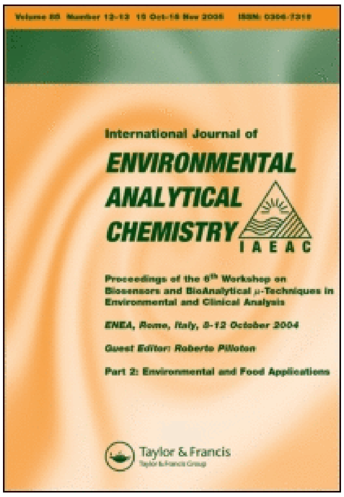

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Influence of Milling or Cutting Procedures on Trace Element Contents of Plant Samples

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INFLUENCE OF MILLING OR CUTTING PROCEDURES ON TRACE ELEMENT CONTENTS OF PLANT SAMPLES

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Several milling and cutting procedures have been tested for their suitability in trace element analysis of non - contaminated plant samples. Barley and wheat were selected because of their low trace element contents, and lucerne in order to test cutting with rotating steel knives. Grains and lucerne plants were distributed as a ring test, in order to yield processed and homogenized samples ready for decomposition and determination. The samples were collected and analyzed for their trace element contents in one lab, in order to avoid differences due to systematic errors of analysis. The trace elements of interest were chosen to detect abrasion of the mills (Fe, Cr, Ni, Mo, Co), contamination from dust (Pb, Cd), and cross contamination from animal feed premixes (Cu, Mn, Zn), which are often processed in the same labs as well. Whereas the results for Mn, Mo, and Cd approached Gaussian frequency distribution, the results for Cr, Ni, and Fe were clearly asymmetrically distributed, presumably due to many contaminated samples. In order to recognize outliers for asymmetric frequency distributions, construction of a symmetrical frequency distribution around the median is proposed, to which Gaussian statistics was applicable. The precision of the subsequent analytical procedure was evaluated with the same barley sample and among the same labs in a ring test one year afterwards. As a result, the precision of the median- corrected frequency distribution of milling/cutting and of the analysis were within then same range, whereas the scatter of data from elements prone to abrasion like Fe, Cr, Ni, was much larger from the original data set. As sources for contamination, bad maintainance of the milling room, as well as abrasion of rotor and sieve from continuously operating mills (stainless steel - titanium) could be recognized. There was no significant difference between continously and discontinously operating devices, nor between different modes of cleaning, like washing, discarding the first portion, or just blowing and brushing.

Keywords: Milling; trace elements; contamination; cereals; lucerne; asymmetrical frequency distribution

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INTRODUCTION

In more specialized laboratories, analysis of total contents of common trace element contents in agricultural and environmental matrices is frequently routinely done. To ensure reliability and compatibility of analytical procedures and issued data, homogenized samples of the matrices of interest are regularly distributed among participating laboratories by various organisations. After some time, the individual results are collected, statistically evaluated, and issued as round robins. This kind of quality control covers digestion, separation and determination methods.

Before the start of the analytical procedure, however, the delivered samples have to be pretreated to yield homogenous subsamples to be weighed for decomposition. Agricultural and environmental samples, like green plants, composts, processed food, or soils, which are routinely analyzed in our laboratories, are usually inhomogenous mixtures of various kinds of solids, which require to be characterized for their analytical contents, representative for the entire mixture. The preparation of these samples prior to the proper analysis may include drying, crushing, sieving, dividing, and milling procedures. However, the quality of all kinds of manipulations with solid samples, starting from the originally supplied material, till a representative subsample is achieved for the decomposition step, cannot be checked by the analysis of dried and finely ground certified reference materials.

In routine labs, these procedures (e.g. for whole plants, cereals etc.) are usually done with the total sample. Thus, these steps are hardly repeatable, and changes of the sample composition cannot be checked further. Afterwards, the homogenized fine- ground sample can be submitted to various analytical procedures many times, till the results are satisfactory.

Until now, only few authors have investigated the influence of sample preparation procedures on trace element contents of non- contaminated samples. For treatment of geological materials, the abrasion of various grinding devices was investigated by grinding of 50 g of pure quartz sand down to < 200 mesh, and subsequent trace element determination by X-ray-fluorescence. A high-carbon-steel disk grinder released appreciable amounts of Cr, Cu and Mn, and also some Zn and Ni. As might be expected, treatment in a shatterbox/ring grinder made of chrome steel, led to severe contamination of the sample with Cr. A tungsten carbide shatterbox/ ring grinder enhanced the Co-contents found in the samples, because the tungsten carbide contained 6% Co. On the other hand, corundum ceramics containing a lot of trace elements, did not contaminate the sample except with Ba. An agate mortar was the only device which did not introduce any measurable contamination of the 31 elements studied[1]. As agricultural and environmental solid samples hardly approach the hardness of quartz, these results can be regarded as upper limits of contamination by abrasion. Similarly, pure cellulose filter flocks (Macherey& Nagel) were milled like common samples in continuously operating mills, and analyzed before and after the treatment. As the contact time of filter flocks is much shorter than for a real sample of cereals, the result would rather give the lowest expectable level for abrasion and carry- over. For the investigated elements Cr/Cu/Fe/Mn/Ni/Zn, results could be explained by carry-over from higher levels in the feedstuffs treated before, rather than by abrasion, because contamination with Cr and Ni, which are at trace levels in feedstuffs, but alloyed in the tools, was negligible[2].

Houba et al.[3] give an example of the influence of grinding on the trace element contents of barley. Treatment in a mill with an Al- casing rose the mean Al-contents from 16 to 106 mg/kg, and vice-versa, parts of cast iron in another mill enhanced the mean Fe contents from 86 to 454 mg/kg.

The primary goal of the preparation of a certified reference material is to obtain a homogenous sample. Contamination and changes of speciation during the entire preparation procedure do not harm their ability to ensure comparable results. Therefore, certified reference materials do not necessarily represent the composition and speciation of constituents with respect to their original matrix.

Possible Changes of Sample Composition

During sample preparation, the composition of a proper sample can be influenced by abrasion from the milling and cutting tools, contamination from dust, carry - over from preceding samples, and locally high temperatures which lead to volatilization, oxidation and decomposition of reactive components (e.g. vitamins). Whereas for the analysis of vitamins and other degradable products, main alterations may be due to locally high temperatures, trace element analysis rather suffers from abrasion, dust and carry-over. Abrasion depends on the material of the tool, and the hardness of the samples. The carry- over can be largely influenced by cleaning procedures for the tools, and contamination from dust is due to the level of dirt in the milling room as well as its environment (rural or urban, floor number).

Combustion processes, metal corrosion, erosion from soils, rocks and various buildings may act as sources for the emission of dust. On mass basis, trace element contents in dust can be expected to be much higher than the average crustal abundance, with a tendency of enrichment towards the fine fraction. Air condition systems redistribute those fine fractions, which pass the filters (< 2 μm), and usually enhance dust contamination. In dust from private homes in Vienna 0.9-90 mg/kg As, 2.5- 46 mg/kg Cd, 144-381 mg/kg Cu, 1.2-5.5 mg/kg Hg, 90 -3340 mg/kg Pb, and 330 - 1700 mg/kg Zn were found[2], depending on the site and the floor number, but Cr and Ni remained at mean crust levels. A compilation of trace element levels of in-house dusts and street dusts on a mass basis shows[4] that sources contributing to street dust will also contribute to house dust. Except for As, Cd, and Zn, trace element contents in house dusts are likely to be lower than in street dusts. Paints, coatings, rubber, and metal corrosion may contribute to dust production in households.

With respect to the normal level encountered in plant samples, Pb, Zn and Cd may occur in urban dust enriched more than 1000 fold, whereas they are presumably hardly alloyed within the tools.

Animal food and its premixes, which are quite often analyzed in our laboratory, may sometimes contain Fe, Zn, Cu and Mn at a higher level, and may cause a carry-over into subsequently treated low-level samples.

Stainless steel knives, blades and castings may contain (in alphabetical order) Co, Cr, Mn, Mo, Ni , Si, V, and W alloyed to Fe, at the percent level, but they are usually low in Mn. The scope of this study is to ensure the validity of our sample preparation techniques used in our routine labs, as well as to detect and to avoid systematic errors for further improvements.

EXPERIMENTAL

In order to validate the entire procedure in the routine lab, proper round robins were designed. Samples of barley grains, lucerne plants and wheat grains were mixed in batch, bottled to samples of about 1 kg, and sent to various Austrian and foreign institutes, which were interested to participate. The barley sample was distributed in October 1993, the lucerne in October 1994, and the wheat sample in November 1995.

From each device, a proper sample was collected and returned to the author for the determination of trace elements. A form was designed to obtain more information about the entire procedure.

The determination of trace elements was carried out by standardized ALVA - methods (ALVA= Arbeitsgemeinschaft Landwirtschaftlicher Versuchsanstalten Österreichs). To ensure representative sample weights, at least 2 times 4 grams of each sample were dry -ashed at 550°C, dissolved in 1+3 HCl, and submitted to graphite furnace and flame-AAS techniques. The validity of the procedure was checked by decomposition of a series of samples by the standard dissolution procedure with nitric/perchloric acid in parallel. For each batch, blanks were made and substracted from the results; fortunately they were much lower than the results. No detectable blanks in any case were observed for Co and Mo (graphite furnace), as well as for Mn (flame AAS). The accuracy of the overall decomposition and determination procedures was tested by regular participation in the

International Plant Exchange programme of Wageningen Agricultural University (The Netherlands). The barley sample was taken as a sample for a round robin among Austrian agricultural laboratories (see below). Some wheat samples were analyzed in parallel in Vienna and Linz.

Dry ashing restricts the elements to be determined to non- volatiles, but it ensures a much higher sample mass to be treatable. This largely avoids the problem to determine the minimum sample mass which has to be regarded as representative.

For analysis of the processed samples, Fe, Cr, Ni, Co, Mo were chosen as indicative for abrasion, Pb and Cd as indicative for contamination from dust, as well as Cu and Mn as indicative for contamination from carry- over from preceding samples.

The sample matrices for testing the entire sample preparation procedure were selected due to their low trace element contents, our capabilities of pre- homogenization (splitting from 50 kg down to 1 kg), and similarity to our routine samples. In the first run, seed- barley harvested from one field (at St. Florian / Upper Austria) was chosen, purified by washing with distilled water and dried at 80°. It was grown without additional supply of trace elements. Barley tends to be the cereal lowest in trace element contents, and it has hard grains. Within a second run, lucerne (all parts growing above the ground) was investigated, to utilize devices different to the treatment of the barley sample one year before; mainly mills with rotating knives were used. In the third run, a sample of winter wheat, proved to be of one single genetic sort ("Capo"), was taken from an experimental field at Fuchsenbigl / Lower Austria, grown without additional supply of fertilizers and trace elements. This should above all test repeatability and improvements with regard to the first run with barley. To get a sample of obviously zero - contamination level, about 50 kg of the winter wheat were treated in a corundum mill under definitely clean room conditions.

Each sample was decomposed 2-6 times, and each solution was measured 2-3 times to yield a mean value as a result for each parameter in each sample within an acceptable precision.

Statistical evaluation of results was done by means of SPSS - software programme. The individual participants and their respective results are kept confidentially by issuing hidden numbers.

RESULTS AND DISCUSSION

Descriptive Statistics of the Data Sets

If there are no systematic errors during the sample preparation, the resulting data set should be Gaussian. This reflects both the uncertainty of the initial and final homogenization, milling and/or cutting, sample decomposition and final measurement.

Contamination leads to higher trace element concentrations found in the sample. As only non-volatiles are analyzed, volatilization losses need not be considered. If contamination is restricted to single cases, values significantly too high appear as outliers, and can be recognized as such. They can be discarded prior to the calculation of the „true" value. If contamination is approximately equal for any of the samples submitted, Gaussian distribution remains.

In Table I, descriptive statistics of the results for wheat are given as an example, together with the results of transformation to log - statistics. The data for barley and lucerne are included in Tables II and III.

TABLE I Descriptive statistics and log statistics for the wheat sample (mg/kg)

Element	$\mu \pm \sigma$ *(corrected for outliers)*	*Median*	*Range (entire data set)*	*Outliers found from original data*	*Mean corrected by log statistics*	*Median corrected by log statistics*
Cd	0.0153 ± 0.0032	0.0149	0.011 - 0.108	1	0.0149	0.0145
Co	0.015 ± 0.007	0.015	0.005 - 0.095	2	0.013	0.014
Cr	0.24 ± 0.14	0.19	0.08 - 3.20	3	0.24	0.23
Cu	3.54 ± 0.46	3.46	2.35 - 4.20	2	3.51	3.45
Fe	30.6 ± 3.2	30.1	24.1 - 93.0	3	30.9	30.1
Mn	32.2 ± 1.4	32.5	17.9 - 34.3	1	32.1	32.5
Mo	0.25 ± 0.05	0.25	0.11 - 0.36	0	0.26	0.25
Ni	0.26 ± 0.10	0.24	0.11 - 1.26	3	0.25	0.20
Pb	0.28 ± 0.07	0.27	0.13 - 0.43	0	0.28	0.27
Zn	22.4 ± 2.3	22.7	16.1 - 26.4	0	22.5	22.7

TABLE II

BARLEY	*Precision of milling*			*Precision of analysis*	
mg/kg	*Median*	*Mean ± Std. dev.*	*Corrected*	*Median*	*Mean ± Std. dev.*
Cu	4.05	4.10 ± 0.35	--------	4.6	4.6 ± 0.3
Mn	16.9	17.0 ± 0.8	--------	18.1	18.2 ± 1.7
Fe	42.1	43.4 ± 10.6	39.5 ± 6.5	37.6	38.3 ± 6.6
Zn	23.2	23.2 ± 0.8	--------	26.3	27.2 ± 2.0
Cr	0.23	0.49 ± 0.52	0.23 ± 0.19	0.11	0.18 ± 0.16
Ni	0.34	0.55 ± 0.44	0.34 ± 0.17	0.36	0.39 ± 0.22
Pb	0.135	0.155 ± 0.069	0.135 ± 0.046	0.09	0.09 ± 0.03
Co	0.02	------	--------	0.08	0.06 ± 0.03

TABLE III

LUCERNE	*Precision of milling*			*Precision of lucerne IPE 93.6*	
mg/kg	*Median*	*Mean ± Std. dev.*	*Corrected*	*Median*	*± Std. dev.*
Cu	7.0	7.0 ± 0.35	--------	5.1	± 0.50
Mn	30.3	30.9 ± 7.4	--------	42.9	± 1.9
Fe	192	242 ± 136	181 ± 49	204	± 16
Zn	17.0	17.5 ± 2.1	--------	18.0	± 1.3
Cr	0.75	1.11 ± 0.77	0.62 ± 0.29	0.86	± 0.16
Ni	1.09	1.56 ± 0.96	0.96 ± 0.20	1.15	± 0.27
Pb	0.34	0.41 ± 0.255	0.30 ± 0.11	1.54	± 0.23
Cd	0.023	0.024 ± 0.008	--------	0.063	± 0.006
Mo	0.70	0.74 ± 0.20	--------	0.29	± 0.024
Co	0.13	0.135 ± 0.065	--------	0.244	± 0.024

For so-called log- statistics, the data set for the wheat sample was transferred to logarithms, and subsequently submitted to descriptive statistics. This might be a reasonable approach for data sets, which both cannot be negative, and which have tailings towards high values. The skewness of the original log- data set approaches the ideal Gaussian value of 1 only for Co, Cr, and Cr. After rejection of the 2σ - outliers, the skewness of the resultant data set shows less Gaussian behaviour than before. The mean and the median of the resultant frequency distribution, after rejection of outliers, is given in Table IV. They coincide fairly well with the data from the Gaussian distribution around the median, whereas the ruggedness towards outliers is much larger.

Statistical Treatment of Data

From the overall data sets, three groups of parameters can be distinguished:

a. The data set is symmetric and about Gaussian. No outliers are detected by the t-test. As examples for symmetric and about Gaussian distribution, Mn, Pb in barley, Cu in lucerne, and Cu/Mn/ Mo/Pb/ Zn in wheat were found. Whereas the standard deviation for Cu, Mn and Zn was only about 10% of the mean, the scatter for e.g. Mo and Pb was much larger, due to sample homogeneity and/or precision of analysis.

b. The data set is approximately Gaussian, if 1-3 obviously contaminated samples are excluded from statistics, which are recognized by the t-test. Exam-

TABLE IV Effect of proposed correction on descriptive statistics

	Element	$\mu \pm \sigma$	*Range corrected*	*Outliers corrected*	*Outliers range corrected*	*Outliers Gaussian*	*Outliers Gaussian*
Barley	Cr	0.175 ± 0.07	0.09 - 0.31	10	0.48 - 4.30	1	4.30
	Co	---	<0.01 - 0.03	7	0.03 - 2.16	X	2.16
	Ni	0.26 ± 0.08	0.18 - 0.43	10	0.62 - 4.60	1	4.60
Lucerne	Cr	0.62 ± 0.29	0.20 - 0.84	8	1.10 - 2.70	1	2.70
	Fe	181 ± 49	95 - 280	6	313 - 663	2	573/663
	Mo	0.67 ± 0.10	0.47 - 0.89	4	0.97 - 1.20	2	1.17/1.20
	Ni	0.96 ± 0.20	0.68 - 1.47	9	1.69 - 4.27	2	3.51/4.27
	Pb	0.30 ± 0.11	<0.05 - 0.53	4	0.78 - 0.97	2	0.96/0.97
	Zn	16.8 ± 1.0	15.0 - 18.5	3	20.8 - 24.4	1	24.4
Wheat	Cd	0.0145 ± 0.0024	0.011 - 0.019	4	0.020 - 0.108	1	0.108
	Co	0.014 ± 0.005	0.005 - 0.022	4	0.031 - 0.095	2	0.079/0.095
	Cr	0.21 ± 0.09	0.09 - 0.43	6	0.43 - 3.20	3	0.82/0.89/3.2
	Fe	30.3 ± 3.0	24.1 - 37.5	4	37.5 - 93	3	46.3/74.6/93
	Ni	0.24 ± 0.08	0.11 - 0.42	5	0.46 - 1.26	2	1.23/1.26
	Pb	0.27 ± 0.06	0.13 - 0.40	2	0.41 - 0.43	2	0.42/0.43

ples for this type of data were Cu/ Fe/ Zn in barley, Cd/ Co/ Mn/ Mo/ Pb/ Zn in lucerne, and Cd/ Co/ Fe in wheat.

c. The data set is clearly asymmetric, and thus non- Gaussian. It is assumed that the data set is composed of a Gaussian distribution around a presumably true value, and deviations to the larger side only. To approach the presumably true value, construction of a symmetrical frequency distribution within the double distance between minimum and median is thus proposed. This leads to a classification of much more samples to be contaminated, than the t-test would reveal.

In Table IV, the effect of the proposed correction of data sets from the most asymmetric frequency distributions are shown. If a Gaussian distribution around the median of the all-over data set is constructed, the median of this corrected data set does not change much, but the mean and the standard deviation get much smaller. Kurtosis and skewness indicate a closer approach of the corrected data set towards Gaussian conditions.

Influence of the Operating Mode of the Mill

The data set for those elements, which have turned out to be most critical, was split up, to reveal possible differences between continuously and discontinuously operating devices. After rejection of all outliers recognized by the t-test, mean and standard deviation had to be calculated under the assumption of normal distribution, which is, however, not quite realistic (see above).

The results for continuously and discontinuously operating mills were not significantly different for any of the parameters investigated, if the criterium of ± 2 σ is used. This was contrary to expectations, because mortar mills are made of materials much more suitable for trace element analysis (e.g. agate, corundum), whereas the continuously operating mills are usually made of stainless steel. Whereas for continuously operating tools the contact time is only some seconds with a minimum of handling, mortar mills require about 10 min., and some handling for input and output, for less sample mass.

Influence of the Type of Mill

Tools made by various manufacturers, were utilized. Fortunately, in the barley run, one type of mill appeared 5 times; the results yielded the same scatter than the overall data set. Two years afterwards, with the wheat sample, the same type was used 10 times, and produced severe contamination with Cr and Ni in 4 cases, but did not obviously influence sample trace element composition in 6 further cases.

The name of the mill, given by the manufacturer, stands for a certain style of construction. The most frequently mills utilized for grains have a rotor rotating inside a sieve (Table V). The sample is ground by impact rather than by cutting, and exits the sieve into a proper vessel by centrifugal force. Rotor and sieve can be made of stainless steel, or e.g. of titanium. Surface corrosion of the grinding tools leads to enhanced abrasion of metals. This explains the differences observed, obtained with the same type of mill. The wheat samples A38, A40, A51, A63, A82, A83 were ground with rotor and sieve made of titanium, whereas the samples A45, A49, A65, A84 were ground with rotor and sieve of stainless steel.

TABLE V Differences due to material of the device (wheat sample)

	Fe	*Cr*	*Ni*
Ti - tools	30,3 ± 0,6	0,16 ± 0,05	0,21 ± 0,04
stainless steel tools	33,3 ± 2,5	0,63 ± 0,27	0,63 ± 0,43

Another type of mill, which was 2 times used in the barley run, produced too high values for Cu and Co both times, but was very low for Cr and Ni.. The same type of mill, but in another institute, yielded a severe Co and Cd- contamination with the wheat sample, but was again very clean for Cr and Ni, which were the most critical trace elements. This tool is made of tungsten carbide, which contains about 5% Co and also some Cu, but there are no stainless stell parts within this system.

The mill used for the wheat sample A33 is usually used for soils, and not for plant material, which explains the observed contamination with Fe, Cr and Ni.

In the series with the wheat, and the barley, Cr and Ni contamination were clearly correlated, but only weakly with Fe contamination. All the other trace element contents found were rather independent from one another, like Pb/Cd, or Co/Ni. For the wheat sample, no outliers were detectable for Zn and Mo, and only 2 were slightly "suspicious" for Pb.

Influence of the Cleaning Procedure

After rejection of the outliers recognized by the t- test, the data were grouped according to different cleaning procedures, according to the informations given on the form accompanying the samples. Some participants performed blowing/brushing and wiping only. Others additionally cleaned their devices with the sample itself, discarding the first fraction. A third group even washed and dried their mills after every sample (Table VI). The "human factor", like cleaning procedures, additional devices and the maintenance of the room, seems to exert more influence on the result, than the type of the mill, however.

TABLE VI Split according to cleaning procedure

		samples	*Fe*	*Pb*	*Cr*	*Ni*
barley	washing	4	45.2 ± 4.9	0.13 ± 0.08	0.72 ± 0.92*	0.67 ± 0.73*
	discarding 1st	13	43.7 ± 10.2*	0.17 ± 0.08	0.57 ± 0.53	0.63 ± 0.42
	blowing/brushing	4	36.9 ± 20.9	0.14 ± 0.07	0.24 ± 0.08	0.24 ± 0.17
lucerne/washing		5	141 ± 51*	0.18 ± 0.15*	1.68 ± 0.61*	1.81 ± 0.83*
	blowing/brushing	16	223 ± 71	0.39 ± 0.20	1.01 ± 0.67	1.31 ± 0.65
wheat	washing	8	30.1 ± 3.2	0.29 ± 0.06	0.16 ± 0.05	0.25 ± 0.12
	discarding 1st	10	31.1 ± 4.0*	0.29 ± 0.07	0.31 ± 0.17*	0.29 ± 0.09
	blowing/brushing	7	30.5 ± 1.1	0.26 ± 0.09	0.21 ± 0.10	0.20 ± 0.11

For treatment of the lucerne stalks, discarding of the first fraction in order to clean the mill with the sample, was done in only 2 cases, and is therefore not included in Table VII .

TABLE VII Effect of the environment on lucerne cutting

ug/g:	*Mn*	*Fe*	*Zn*	*Co*	*Mo*	*Pb*	*Cr*	*Ni*
Usual procedure	47.0*	663*	24.4	0.312*	1.20	0.97*	2.70*	4.27*
	50.0*	573*	21.5	0.335*	0.97	0.96*	1.61	3.51
Washing the room	22.3	132	17.8	0.099	0.48	0.08	0.84	0.87
gloves + plastic scissors	23.0	116	20.8	0.067	0.47	<0.05	0.20	0.88

* ... outliers, recognized by the t-test.

The surprisingly better performance of cleaning with respect to Cr and Ni by just blowing/brushing has not been ascertained, and seems to have occurred accidentally. In a brief discussion about the results of the barley test, some participants already knew about the bad performance of their devices,and wanted to test, if this kind of investigation would prove their experience. Others were surprised about their results.

In spite of the same procedures, operators and apparatus utilized for analysis in all three runs, the scatter of results for Fe/Cr/Ni was less for the wheat sample, than for the barley sample issued two years before. This may indicate further improvement in sample preparation techniques.

In case of lucerne, whole plants like harvested on the field, were distributed. Homogenization was thus more difficult to ensure. The levels of trace elements in lucerne are higher than for the cereals, but precleaning of the various cutters with the sample itself was less effective or impossible at all.

The Question, How to Approach the True Value

None of the cleaning and operational procedures had been proven to cause systematic errors, in comparison with the others. Contamination might be rather due to the operator, the maintenance of the devices, and the dirt in the milling room.

An example is given for the lucerne in Table 7. The first two samples were cut in the milling room as usual, after blowing/brushing the mill. Prior to the treatment of the third sample, another cutting mill was demonted, washed completely, and dried with pure cellulose. Additionally, all tables and the floor in the milling room were washed. The fourth sample was cut with a pair of scissors made of plastics (children's toy) and wearing medical gloves, on clean cellulose in the office. As a result, most trace element contents found, drop dramatically (Table VII). The values achieved after cutting with gloves and plastic scissors, were the minimum levels of the respective investigation for Cr, Co, Mo, and Pb.

These effects cannot be read, however, from a form, and they are valid for all types of devices used.

Similarly, the wheat sample was processed under definitely clean conditions with a corundum mill at the laboratory of the German specimen bank at Jülich, to obtain a sample of "zero-contamination" for comparison. The values for Cu, Mn, Fe, Zn, Cd and Mo closely approached the means of our milling test, but the values for Pb, Cr and Ni were lower. The wheat sample processed under definitely clean conditions had only 127 ug/g Pb and 75 ug/g Cr, whereas the other results were 280 ± 70 ug/g Pb and 240 ± 140 ug/g Cr. This may indicate a kind of overall contamination, which had occurred more or less in all other participating laboratories.

Precision of Milling/Cutting Versus Analytical Precision

Discussion of the precision of the sample preparation procedure is only valid, if data about the precision achieved in the analytical procedure, are given. For some elements, low contents to be determined by graphite furnace AAS, as well as subtraction of blanks, worsens the analytical precision, with respect to the level usually achieved.

The barley sample was milled under proved clean conditions in the Bundesanstalt für Agrarbiologie in Linz, and distributed as a round robin of an unknown sample, a year afterwards. The interlaboratory precisions achieved in milling/cutting are shown together with similar results of interlaboratory analyses of processed samples of the same matrix in Table II, Milling and proper analytical procedure yield approximately the same precision, if the proposed correction of the data set is made.

For the lucerne sample, the precision of the milling/cutting series presented in this work, is compared with the results of interlaboratory analyses from the International Plant Exchange programme (Wageningen Agricultural University, lucerne sample IPE 93.6) in Table III, in which many of the test laboratories also take part. Differences in the median values of Pb/Cd/Co/Mo may be due to different soils, on which the two test plant samples were grown. Again, the milling/cutting and proper analytical procedure yield approximately the same precision, if the proposed correction of the data set is made. For Fe, Cr and Mo, precision of analysis was better than cutting, for Pb, precision of analysis was worse.

In Table VIII, the variation coefficient of the analytical procedure are shown, which have been achieved within the analyzing laboratory, and calculated with the primary data from the wheat sample. Cases of poorer precision than usual are certainly due to the small amounts to be determined (the contents is clearly below the optimum range), and the blanks which had to be substracted (except for Mn, Mo and Co).

TABLE VIII Variation coefficients (%) for the analytical procedure (wheat sample)

Cu	flame AAS	± 13.1 %
Mn	flame AAS	± 6. 1 %
Fe	flame AAS	± 7.0%
Zn	flame AAS	± 6.8%
Pb	graphite furnace AAS	± 18.0 %
Cd	graphite furnace AAS	± 10.5 %
Cr	graphite furnace AAS	± 12.3%
Ni	graphite furnace AAS	± 12.1 %
Co	graphite furnace AAS	± 18.3 %
Mo	graphite furnace AAS	± 15.9 %

Remark: the coefficient of variation covers the entire procedure - decomposition + measurement + subtraction of individual blanks.

CONCLUSIONS

In order to check the validity of sample preparation techniques for trace element analyses in cereals and green plants at non contaminated levels, samples of barley, lucerne and wheat were sent to various routine labs in Austria, just for milling and cutting. The processed samples were analyzed in one laboratory for their Cd/ Co/ Cr/ Cu/ Fe/ Mn/ Mo/ Ni/ Pb/ Zn contents. For Cu/Fe/Mn/Zn, the scatter of data was small, and some contaminated samples were recognized easily by a t-test. For Cd/Mo/Pb, the data set was Gaussian as well, but scattered more, due to the lower contents, possible inhomogeneity and lower analytical precision. The data sets for Cr and Ni were asymmetric in all cases. A correction procedure implying construction of a Gaussian distribution around the median, is proposed. In order to compare the inter- laboratory precision of milling and analysis, the barley sample was milled under proved clean conditions, and distributed as a round robin for trace element analysis as well. Checking the approach towards the true value, the lucerne was cut with gloves and plastics scissors, and the wheat was ground under liquid nitrogen in a clean room. Cr and Ni turned out to be the most crucial for contamination. For the same type of construction, the influence of the material of the milling tools could be demonstrated.

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