Swedish interlaboratory trials on proximates and certain macro minerals

I. Torelm

National Food Administration, Box 622, S-751 26 Uppsala, Sweden

Summary. During the period 1980–1986 a number of samples representing different kinds of food items were distributed to about thirty laboratories for analysis. The objective was to test the laboratories with respect to their analytical skill in proximate analyses. Towards the end of the period the condition for analyses and the statistical technique had been developed in such a way that variations could be estimated within laboratories (repeatability) as well as between laboratories (reproducibility). An ellipse was constructed so that the probability for a randomly selected laboratory to fall within the ellipse would be 95%. This presentation also gives an example of wether mean values and standard deviations for a specific item change depending on the time between two courses of analysis.

Introduction

About thirty laboratories in Sweden and some other countries are participants in an intercalibration on proximates administered by the Swedish National Food Administration (NFA). When the period started in 1980 there were 24 laboratories, at the end 39. They represent authorized official food laboratories (about $^2/_3$) as well as approved private food laboratories. In many cases they have quite different specialities of routine samples. The authorized laboratories are supposed to handle all sorts of food samples, while the approved laboratories are connected to different food industries.

The intercalibrations run once every year and aim at enhancing the reliability of the results from the laboratories. The laboratories are allowed to use their own routine methods. Investigations have shown no statistical difference between the different methods used in analysing fat, calcium and iron [5].

Materials and methods

The kind of samples chosen and the conditions for analysing are shown in Table 1. The dry powders were bought in economy-size packets in ordinary food stores, were well mixed and packed in plastic bags or in small containers. The powder meant for nutrition was bought in a chemist's shop. In this case the individually packed batches on 77.5 g were used for distribution. The meat samples and the black puddings were specially produced for the purpose in meat product factories and canned or packed in vacuum plastic film. Samples were controlled with respect to homogeneity and sent by mail to the laboratories. All samples except the canned ones were kept frozen in airtight containers at the NFA until distributed.

The analyses asked for were dry weight, ashes, fat, nitrogen, phosphorous, calcium and iron. Not all laboratories use all these analyses in their routine work. They were told only to perform those analytical methods which were included in their routine program, in order to eliminate unskilled results.

Outlying results were eliminated using the normal probability test of the Minitab Statistical Program [3]. Repeatability standard deviation (SD) and reproducibility SD

Table 1. Samples and analysis plan

Sample No.	Type of sample	Value reported to the NFA
1.	Gruel powder	Mean of two determinations, analysed at two occasions within 7 months of each other
2.	Mashed potatoes powder	Mean of two determinations, analysed at three occasions, the second after 3 years, the third after 3 years plus 1 week
3.	Meat product I, canned	Open duplicates, analysed at two occasions within a week of each other
4.	Meat product II, canned	Open duplicates, analysed at two occasions within a week of each other
5.	Enteral nutrition product	Blind duplicates, analysed at the same occasion
6.	Pancake powder	
7.	Milk powder	Blind duplicates, analysed at the same occasion
8.	Milk powder	
9.	Gruel powder	Blind duplicates, analysed at the same occasion
10.	Gruel powder	
11.	Black pudding, frozen	Blind duplicates, analysed at the same occasion
12.	Black pudding, frozen	
13.	Meat product, frozen	Blind duplicates, analysed at the same occasion
14.	Meat product, frozen	

Fresenius Z Anal Chem (1987) 326:699–701

Table 2A. Results of analyses, one week between first and second determination. Values are mean and SD

	Dry weight (g/kg)	Ash (g/kg)	Fat (g/kg)	N (g/kg)	Ca (mg/kg)	P (mg/kg)	Fe (mg/kg)
Mashed potatoes powder							
n	31	31	31	30	23	20	22
1st det.	929 ± 4.0	57.2 ± 3.5	28.3 ± 10	13.4 ± 0.5	697 ± 53	2800 ± 190	26.0 ± 10
2nd det.	929 ± 4.0	57.5 ± 3.0	28.8 ± 10	13.3 ± 0.6	693 ± 43	2810 ± 170	25.0 ± 9
Meat product I, canned							
n	33	33	33	32	25	23	24
1st det.	461 ± 5.0	45.9 ± 0.9	303 ± 5.0	18.3 ± 0.5	486 ± 45	1850 ± 87	27.2 ± 1.9
2nd det.	464 ± 6.0	45.9 ± 1.0	304 ± 5.0	18.5 ± 0.4	481 ± 48	1860 ± 76	27.4 ± 2.1
Meat product II, canned							
n	31	31	31	30	23	20	
1st det.	327 ± 4.0	35.1 ± 0.8	120 ± 5.0	27.8 ± 0.9	891 ± 71	3630 ± 210	60 ± 5.0
2nd det.	327 ± 4.0	35.2 ± 0.8	122 ± 5.0	27.8 ± 0.8	882 ± 69	3590 ± 220	60 ± 6.0

Table 2B. Results of analyses, seven months (gruel powder) and three years (mashed potatoes powder) between first and second determination, respectively. Values are mean and SD

	Dry weight (g/kg)	Ash (g/kg)	Fat (g/kg)	N (g/kg)	Ca (mg/kg)	P (mg/kg)	Fe (mg/kg)
Gruel powder							
n	23	23	20	22	19	19	19
1st det.	970 ± 3.8	53.3 ± 1.9	159 ± 10	28.8 ± 1.4	7090 ± 363	5450 ± 348	102 ± 4.6
2nd det.	960 ± 7.0	53.6 ± 1.1	156 ± 10	28.4 ± 0.9	7000 ± 640	5370 ± 1450	103 ± 9.3
Mashed potatoes powder							
n	31	31	31	30	23	20	22
1st det.	928 ± 5.4	55.2 ± 5.0	26.3 ± 10	13.5 ± 0.5	690 ± 91	2900 ± 188	25.6 ± 7.3
2nd det.	929 ± 4.0	57.2 ± 3.5	28.3 ± 10	13.4 ± 0.5	697 ± 53	2800 ± 190	26.0 ± 10

Table 3
Reproducibility and repeatability obtained from five blind duplicates. Values are CV %. Figures in parentheses are numbers of eliminated results

Sample		Dry weight	Ash	Fat	N	Ca	P	Fe
5– 6	Number of labs	33	33	33	32 (2)	21 (1)	18 (2)	21
	CV between	0.318	5.25	14.6	1.82	[a]	4.78	9.43
	CV within	0.186	4.02	5.49	1.65	[a]	2.73	10.5
7– 8	*n*	32 (3)	35	29 (4)	32 (1)	17 (3)	19 13)	19 (4)
	CV between	0.30	1.08	3.39	1.26	5.13	5.55	41.0
	CV within	0.065	0.51	1.17	0.73	2.39	1.59	11.9
9–10	*n*	32 (3)	35	27 (7)	31 (2)	16 (3)	15 (5)	22 (1)
	CV between	0.31	0.97	3.59	1.22	3.14	5.67	4.13
	CV within	0.083	0.53	1.13	1.11	2.30	0.64	4.07
11–12	*n*	37	33 (2)	34	30 (3)	21 (1)	19 (1)	22 (1)
	CV between	0.70	1.70	2.41	1.21	14.3	4.00	9.73
	CV within	0.92	1.29	1.41	2.20	1.70	2.14	2.25
13–14	*n*	37	33 (2)	32 (2)	33	21 (1)	20	13 (10)
	CV between	0.64	2.07	1.82	2.62	19.5	4.74	8.47
	CV within	1.54	1.49	1.91	2.16	9.9	2.04	0.42

[a] Values are impossible to calculate because of too big differences in Ca levels in the two samples

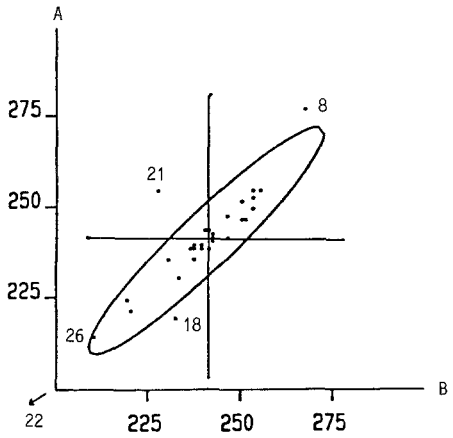

Fig. 1. Youden's two-sample diagram. Sample A and B. *Numbered points* are laboratories outside the 95% tolerance limit

were calculated using an analysis of variance technique as described by Youden [6].

Results and discussion

Results from analyses with an interval of only one week normally do not show any effect of storing, but only the lack of repeatability at the laboratory. The longer the time between two analysis occasions, the more the repeatability turns into reproducibility, and in addition greater differences occur in levels, depending on changes during storage. The standard deviations for the results in Table 2B include all possible variations like sample variation, possible methods difference, error of measurement, effects of storage.

As expected the total SD for the results in Table 2A were not large, nor were there any greater differences in the levels of the different nutrition values. The ability to reproduce the results within a week is evidently satisfying. Even in Table 2B when longer time has passed between the two analyses, there are no definite differences in levels, indicating that these sample materials tolerate storage. However, the total SD in the minerals was larger in the gruel powder after 7 months than at the first occasion. This might be a coincidence, coupled with the larger SD in the value for dry weight. After 3 years, in the mashed potatoes powder, the SD is again, if anything, lower.

Of course it is easy to believe that this depends on a more precise handling than 3 years earlier, and that the intercalibration has been worthwhile.

The variations in results when analysing the samples 5–14 distributed as blind duplicates from January 1984 to December 1985 are shown in Table 3. When the first of these samples were analysed, the trials had run for four years in one technique or another.

Eliminated outliers were rather few, with some exceptions. The determination of iron in samples 13–14 resulted in ten outliers. This error might be explained by the relatively low level of iron in this meat product combined with some difficulties in delivering the frozen samples still frozen.

Both the CV within and the CV between laboratories for ash and fat are remarkably high for samples 5–6 compared to the other samples. The analyses of dry weight and Ca for the frozen samples 11–14 are larger in variation than those for the dry products. The latter case might be explained by the greater difficulties in handling moist samples.

The results of the different intercalibrations were usually given to the laboratories as diagrams examplified in Fig. 1, [2] and [6]. The position of a point representing the results of a single laboratory has no general interpretation. The ellipse in the figure describes the 95% tolerance limit representing all participating laboratories. Frequent placing outside this limit gives a signal to a laboratory to check its routine.

Conclusions

As there are very few studies referred to in literature comparable to this one, it is difficult to comment on the results. The analyses of minerals of biological standard reference materials, certified by the National Bureau of Standards (NBS) [4], that are in common with this investigation, generally give lower variances. The conditions for nominating the laboratories working for the NBS are quite different from the present study, where any laboratory interested is included.

The results of the present investigation reflect the outcome of ordinary routine work at a number of laboratories, not always used to the type of samples, and with many different routine methods.

An investigation which is quite comparable in its design is the Eurofoods Interlaboratory Trial [1]. The CVs for the results here are as a rule larger. But this trial was only carried out once.

In order to reach the goal of enhancing the reliability in analysis work, it is necessary to run intercalibrations of this kind, and the calibrations must be carried through at intervals for longer periods.

References

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Received September 15, 1986