

ACCURACY CONTROL IN LOW-LEVEL MEASUREMENTS

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Abstract—One practical way to determine the accuracy of low-level measurements consists in organizing series of inter-comparison measurements amongst the largest possible number of qualified laboratories. These measurements should be executed on samples possessing the same characteristics as those which are routinely employed, and following the same measurement techniques. The IAEA has been organizing inter-comparison measurements since 1964 and the results of these two years confirm the necessity of this inter-comparison.

The following samples have been analyzed: milk, soil, rice, meat, bone, different kinds of vegetables and a mixture of dried food.

The following radionuclides have been determined: ^{90}Sr , ^{137}Cs , ^{226}Ra , ^{210}Po , and the stable elements calcium, strontium and potassium.

The results obtained cover a wide range. Statistical analysis proves the existence of systematic and accidental errors, the first being easier to identify than the second.

It has been observed that some laboratories which at the beginning of the measurement series gave results which were far from the average, have little by little improved their findings after the results of other laboratories were made known to them.

The participation, except for some items and some radionuclides, has been quite remarkable, about 80 laboratories in 27 countries. It is hoped that the number of laboratories participating in this inter-comparison will still increase, so that all data in relation to the environmental radioactivity may be comparable.

INTRODUCTION

It is well known that laboratories may at times experience difficulties in the determination of the accuracy of their low activity measurements. The use of suitable standards provides means for reducing these difficulties, but the most practical way consists probably in organizing a series of inter-comparison measurements amongst the largest possible number of qualified laboratories, with samples of the same matrix as those which are employed routinely. This method has also the advantage of giving a general picture of the accuracy of such types of measurements, accuracy which is quiet often overestimated.

The IAEA carried out a first small-scale inter-comparison run in 1962/3.^(1, 2) The results were so discouraging that it became necessary to carry out the project on a larger scale. Table 1 summarizes the results of inter-comparison runs in 1964/5.^(2, 3) It will be seen that a wide range of results was obtained. Unfortunately

no questionnaires on the analytical methods and the standards adopted were used for this first inter-comparison run. The reason for possible errors is therefore unknown. The data obtained from this first run indicated that of 70 laboratories which submitted results of analyses of ^{90}Sr , 26 were always correct, 8 gave results containing systematic errors, and 36 with accidental errors. Of 51 laboratories which submitted results of analyses of ^{137}Cs , 24 were always correct, 3 gave results containing systematic errors, and 36 results with accidental errors. Of 51 laboratories which submitted results of analyses of ^{137}Cs , 24 were always correct, 3 gave results containing systematic errors, and 24 results with accidental errors. We come therefore to the conclusion that less than 50% of low-activity measurements are correct within $\pm 15\%$ error, and the remaining are doubtful.

On looking at these results it could be argued that the samples submitted for analysis could not

Table 1. Value in $\mu\text{Ci/kg}$

Nuclide	Matrix	No. of results	No. of laboratories	General mean (95% C.L.)	Best verified values (95% C.L.)	No. of laboratories giving the best verified value
^{90}Sr	Bone ash	181	31	6450 ± 1600	6560 ± 930	25
	Bone ash	125	26	$185,000 \pm 66,000$	$181,000 \pm 28,000$	18
	Meat dry	159	32	18.9 ± 40	7.6 ± 2.8	17
	Meat ash	177	27	$4470 \pm 30,000$	1620 ± 300	20
	Milk powder	342	56	57 ± 28	53 ± 8	34
	Vegetation	167	34	804 ± 680	837 ± 152	18
	Vegetation	117	23	2333 ± 1700	2522 ± 327	15
	Soil	90	19	254 ± 600	193 ± 41	14
	Rice	98	15	64 ± 17	62 ± 8	10
	Meat dry	138	30	86 ± 128	51 ± 13	16
^{137}Cs	Meat ash	174	28	$57,000 \pm 19,000$	$57,000 \pm 8000$	22
	Milk powder	194	37	2220 ± 1170	2400 ± 400	29
	Vegetation	146	33	800 ± 745	674 ± 145	21
	Vegetation	117	23	2333 ± 1700	2522 ± 327	15
^{226}Ra	Bone ash	40	8	290 ± 1200	114 ± 45	6
	Milk	33	8	193 ± 1000	1.33 ± 45	5
	Vegetation	23	5	140 ± 630	9.7 ± 2.7	3

Table 2. Value in $\mu\text{Ci/kg}$ or g/kg

Nuclide	Matrix	No. of results	No. of laboratories	General mean (95% C.L.)	Best verified values (95% C.L.)	No. of laboratories giving the best verified value
^{137}Cs	Mixed diet	177	35	355 ± 170	350 ± 36	18
^{90}Sr	Mixed diet	172	31	139 ± 34	136 ± 15	23
^{226}Ra	Mixed diet	37	7	5.16 ± 7.90	2.93 ± 1.06	4
K	Mixed diet	179	34	7.06 ± 2.48	7.26 ± 0.44	21
Ca	Mixed diet	150	31	3.48 ± 1.36	3.58 ± 0.34	18
Sr	Mixed diet	49	12	$(7.7 \pm 15.6) \times 10^{-3}$	$(5.6 \pm 4.8) \times 10^{-3}$	10
^{210}Po	Tobacco	27	5	1257 ± 2100	775 ± 435	3
^{210}Po	Meat	18	4	31 ± 24	—	—
^{210}Po	Bone	19	5	169 ± 285	242 ± 58	4

have been well homogenized. This, however, can reasonably be excluded since of 100 samples submitted 10 were completely analyzed and 30 were controlled by gamma spectrometry in the IAEA laboratory to ensure that the measurements were within $\pm 5\%$. It could also be argued that because the precise weights of the samples distributed were not reported, and the results were required in pCi/kg of original matter, it is possible that differences in the humidity content could have affected the results to a small extent. From now on all samples contain the indication of the original weight. To eliminate this possible source of error, in

measurements of ^{226}Ra and ^{210}Po . Unfortunately the percentage of laboratories which submitted the results of their analyses is very low: less than 20% for nuclides such as ^{226}Ra and ^{210}Po , and about 40% for the others.

Figure 1 relates to ^{137}Cs in mixed diet. In this figure, as in all others, the y -axis indicates the number of laboratories and the x -axis the reported specific activities. The plotted step-curve indicates the number of those laboratories which accept as a result, within the standard error limit (95% C.L.), the corresponding specific activity values. This way of presenting data is made so as to give an idea of the

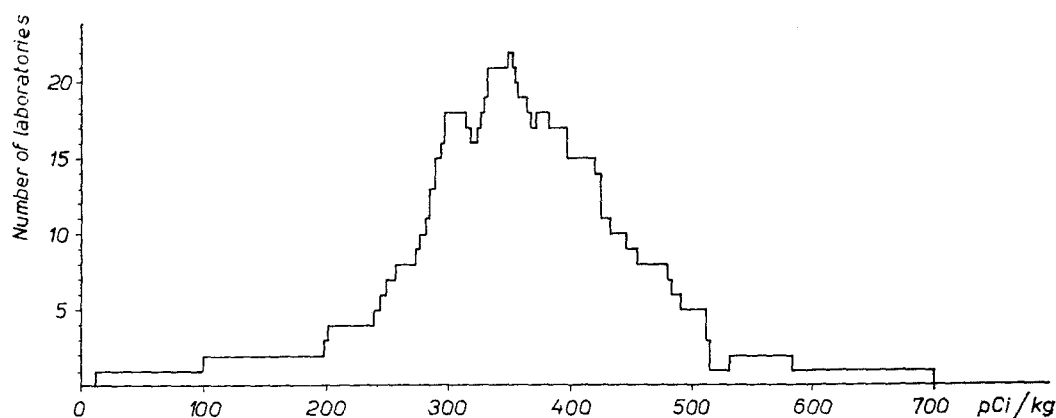


FIG. 1. Distributions of results of the analysis of ^{137}Cs in mixed diet.

some cases we also request data concerning other nuclides in the same sample.

Data are elaborated by means of analysis of variances with several criteria of sorting ^(4,5) nuclide, matrix, methods, etc. In this way data are classified in consistent groups which may be observed in the tables.

RECENT RESULTS

Table 2 contains data obtained after the 1965/6 run (until 5 August 1966). It will be observed that these results are more homogeneous than those of the former run. It must be noted, however, that most of these results come from laboratories which gave already the more homogeneous results in the former run. Only very few results have been received for

frequency of the different values, independent as much as possible of the number of results submitted by each laboratory. Table 3 shows the results after a statistical analysis. As may be observed, apart from two laboratories which have submitted "extreme" results, the others are sufficiently in agreement, even if they could be divided into four distinct groups. Nine analytical methods are adopted by the laboratories, the most common of which are:

- (a) ashing of the sample followed by a gamma spectrometry of the ashes, this method is adopted by 11 laboratories, 8 of which are in the range 350 ± 36 ;
- (b) gamma spectrometry of the original sample, adopted by 8 laboratories, 3 of

Table 3. ^{137}Cs in Mixed Diet, $\mu\text{Ci/kg}$

No. of laboratories	No. of countries	No. of results	Mean (95% C.L.)
1	1	5	120 ± 107
4	4	23	270 ± 52
5	4	26	298 ± 35
18	8	97	350 ± 36
8	4	31	414 ± 52
1	1	5	689 ± 157
35	12	177	355 ± 170

which are in the range 350 ± 36 and 4 in the range 414 ± 52 ;

- (c) Cs separation by means of AMP followed by gamma spectrometry adopted by 4 laboratories, 1 of which is in the range 350 ± 36 , 2 in the range 414 ± 52 , and 1 in the range 298 ± 35 ;
- (d) Cs separation by means of AMP followed by beta counting adopted by 4 laboratories, 3 of which are in the range 350 ± 36 and 1 in the range 689 ± 157 (most probably this last one was still contaminated by K).

The other methods are adopted by one or two laboratories.

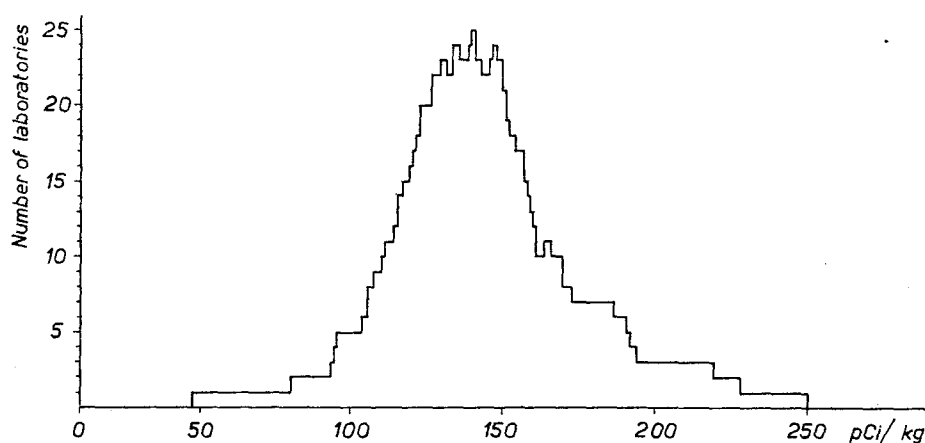
As can be seen, no method may be rejected *a priori*. The comparatively high number of

laboratories adopting the gamma spectrometry of the original sample giving results slightly over the probable true value is surprising. It could be argued that the other laboratories may have lost some Cs during the ashing, but this is hardly credible. It is more probable that some errors may come from background subtraction or from the geometry of the sample.

Figure 2 relates to ^{90}Sr in mixed diet. The relevant data (after statistical analysis) are summarized in Table 4. It will be observed that the homogeneity of the results is better than for ^{137}Cs . This happened also in the previous inter-comparison run. It is surprising if one thinks that the ^{90}Sr analysis involves generally a higher number of chemical manipulations than ^{137}Cs . Nineteen laboratories

Table 4. ^{90}Sr in Mixed Diet, $\mu\text{Ci/kg}$

No. of laboratories	No. of countries	No. of results	Mean (95% C.L.)
1	1	5	93 ± 13
2	2	12	121 ± 13
23	11	125	136 ± 15
5	4	27	158 ± 16
2	2	12	175 ± 55
31	12	172	139 ± 34

FIG. 2. Distributions of results of the analysis of ^{90}Sr in mixed diet.

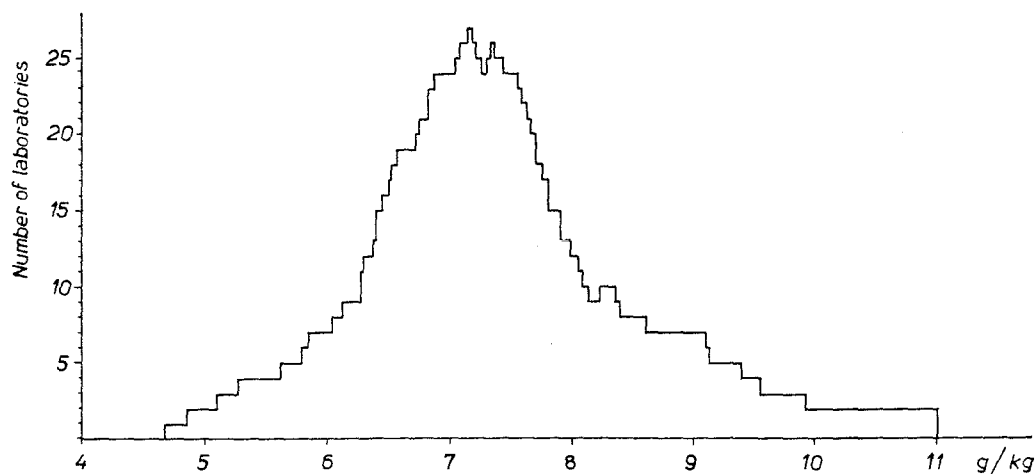


FIG. 3. Distributions of results of the analysis of K in mixed diet.

have adopted the fuming nitric acid separation of Sr followed by Y separation and ^{90}Y beta counting (there are, however, some differences in the determination of chemical yield of Sr separation). Fifteen of these laboratories are in the 136 ± 15 range. Two laboratories have adopted the nitric separation for Sr but do not separate Y and count $^{90}\text{Sr} + ^{90}\text{Y}$. Both are in the 136 ± 15 range. Two other laboratories used the Sr separation by means of ion exchange, Y separation and beta counting of ^{90}Y . One of these two laboratories is in the range of 136 ± 15 whereas the other is in the 121 ± 13 range. Four laboratories used other methods for Sr separation, three of which are in the 136 ± 15 range. Only two laboratories do not use anticoincidence counting, and both have the results in the 136 ± 15 range. From the foregoing it can be stated that all methods are good.

As regards the measurements of ^{226}Ra in mixed diet (Table 2) it is interesting to compare the results with those shown in Table 1. The range of measurements is reduced and there are no more differences of order of magnitude.

Figure 3 relates to normal potassium in mixed diet. One laboratory gave results in the range of 0.81 ± 0.30 , which are not included in the figure. Data (after statistical analysis) are shown in Table 5. As regards the analytical methods used, 18 laboratories employed gamma

spectrometry, 15 flame photometry and one used tetraphenylborate. All methods gave equivalent results. Figure 4 concerns normal calcium in mixed diet. One laboratory's results, in the 0.09 ± 0.08 range, are not included in the figure. Table 6 shows the relevant data

Table 5. K in Mixed Diet, g/kg

No. of laboratories	No. of countries	No. of results	Mean (95% C.L.)
1	1	6	0.81 ± 0.30
2	2	10	6.30 ± 0.20
6	4	36	6.65 ± 0.36
21	10	93	7.26 ± 0.44
5	4	27	7.85 ± 0.39
3	3	14	8.38 ± 3.54
34	11	179	7.06 ± 2.48

(after statistical analysis). Also in this case all methods used gave equivalent results. For the measurements of Sr it can be seen from Table 2 that with concentrations in the order of 100 mg/kg the accuracy of the measurements is not better than $\pm 100\%$. Only two laboratories gave results out of this range. It is possible to justify this poor result because in all likelihood, the analysis was carried out with small quantities

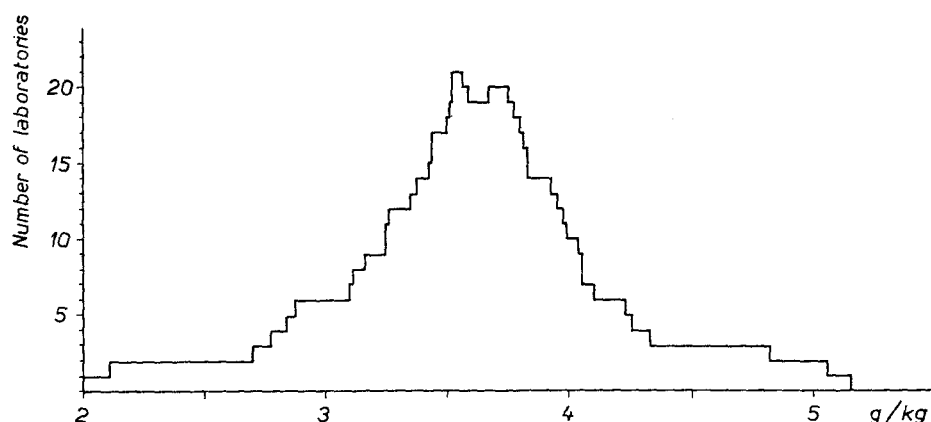


FIG. 4. Distributions of results of the analysis of Ca in mixed diet.

of original matter. It is very surprising that classical analysis like those for potassium and calcium should give results covering so wide a range.

Figures 5 and 6 concern the ratios $pCi^{137}Cs/gK$ and $pCi^{90}Sr/gCa$ in mixed diet. Tables 7 and

Table 6. *Ca in Mixed Diet, g/kg*

No. of laboratories	No. of countries	No. of results	Mean (95% C.L.)
1	1	6	0.09 ± 0.08
2	1	7	2.97 ± 0.83
5	5	28	3.32 ± 0.23
18	7	85	3.58 ± 0.34
6	4	38	3.88 ± 0.18
2	1	6	4.37 ± 0.95
31	11	150	3.48 ± 1.36

8 contain the relevant data (after statistical analysis). From these ratios it can be seen that only three laboratories gave results which were affected by errors in the same direction; this is a confirmation of the homogeneity of the samples sent by IAEA.

Unfortunately no conclusion may be drawn from the measurements of ^{210}Po in tobacco, meat and bones. As may be seen from Table 2 the range of measurements is of the order of

Table 7. *$pCi^{137}Cs/gK$ in Mixed Diet*

No. of laboratories	No. of countries	Mean (95% C.L.)
1	1	14.3 ± 32.6
4	4	36.3 ± 6.7
4	4	39.4 ± 6.4
18	7	48.6 ± 5.8
10	5	54.4 ± 4.4
1	1	64.1 ± 9.3
1	1	93.5 ± 34.5
1	1	470 ± 540
34	11	61.4 ± 146

Table 8. *$pCi^{90}Sr/gCa$ in Mixed Diet*

No. of laboratories	No. of countries	Mean (95% C.L.)
1	1	20.4 ± 4.3
9	6	33.5 ± 3.7
17	7	39.8 ± 5.0
5	3	46.1 ± 3.1
1	1	50.3 ± 135
1	1	1922 ± 358
30	11	101.2 ± 690

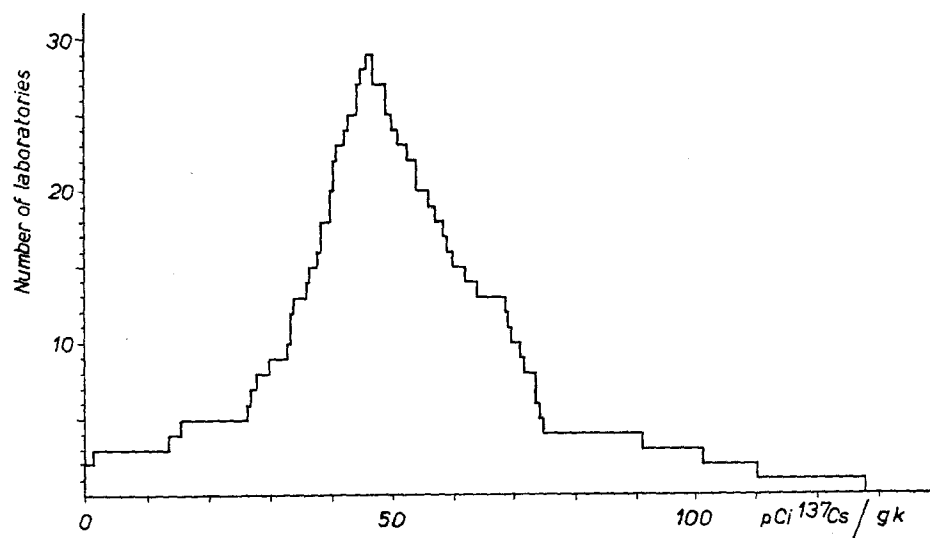


FIG. 5. Distribution of ratio $\text{pCi } ^{137}\text{Cs/g K}$ in mixed diet.

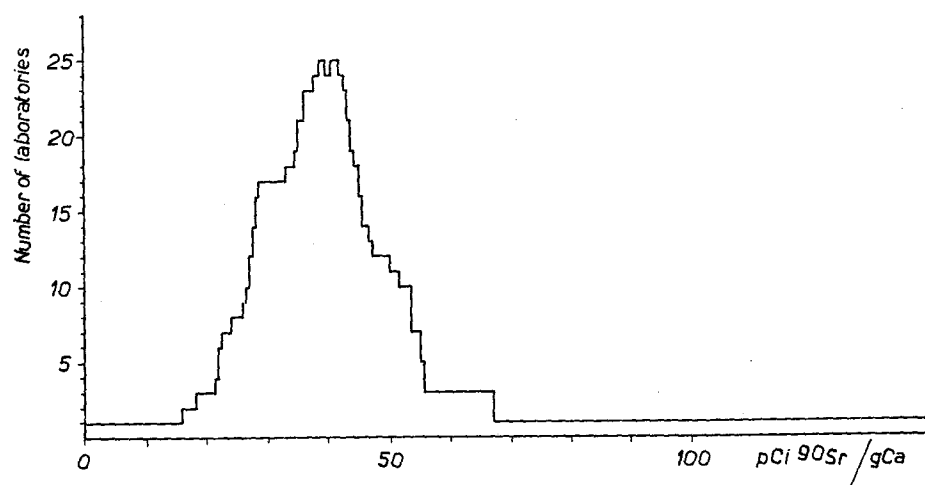


FIG. 6. Distribution of ratio $\text{pCi } ^{90}\text{Sr/g Ca}$ in mixed diet.

$\pm 100\%$. It cannot be admitted that these differences are due to a different grown-in of ^{210}Po since all samples are older than one year, and the equilibrium between ^{210}Pb and ^{210}Po is attained.

THE PRECISION OF MEASUREMENTS IN VARIOUS LABORATORIES

For ^{137}Cs and ^{90}Sr the average standard deviation is about 4% and 5% respectively. There are two laboratories giving results for ^{137}Cs and one for ^{90}Sr which give a standard deviation of less than 1%. On the other hand there are three laboratories giving results for ^{137}Cs and one for ^{90}Sr which give a standard deviation higher than 15%, and in one case even 33%. The average standard deviation for the analyses of potassium and calcium is about 1.5%. That is a little too optimistic after this intercomparison. There is one laboratory which gives a standard deviation for both elements higher than 15%.

Over 10% of all laboratories made errors in calculation. When we received results far from the normal range of measurements we requested that they check their calculations and often detected errors.

A comparison of the results of the laboratories participating in the inter-comparison run 1964/5 and 1965/6 has shown that seven laboratories are improving the measurements of ^{90}Sr , and

two the measurements of ^{137}Cs . The total number of laboratories participating in this inter-comparison is about 80 in 27 countries. ⁽⁶⁾

ACKNOWLEDGEMENTS

We wish to thank all the laboratories which have sent to us the results of their analyses. Without their valued co-operation this work would not have been possible. It is hoped that the number of laboratories participating in such inter-comparisons will increase in the future in order to improve the accuracy not only of the low-level measurements, but also of those more classic.

REFERENCES

1. D. MERTEN. Panel on the Standardisation of Low-Level Activity Measurements, Vienna, 28-31 October, 1963.
2. G. BERGERHOFF, M. M. FERRARIS and D. MERTEN. Some critical remarks on environmental radio-activity measurements, *Minerva Fisiconuclear*, in press.
3. G. BERGERHOFF, M. M. FERRARIS and D. MERTEN. Qualitätskontrolle analytischer Methoden in Internationalen Rahmen, *Zeit. Anal. Chem.*, in press.
4. R. E. SCOSSIROLI. *Manuale di Statistica per Ricercatori*, Olivetti, 1962.
5. G. W. SNEDECOR. *Statistical Methods*. The Iowa University Press, Ames, Iowa, 1956.
6. IAEA Laboratory Activities, Third Report, Technical Report Series No. 55, 1966.