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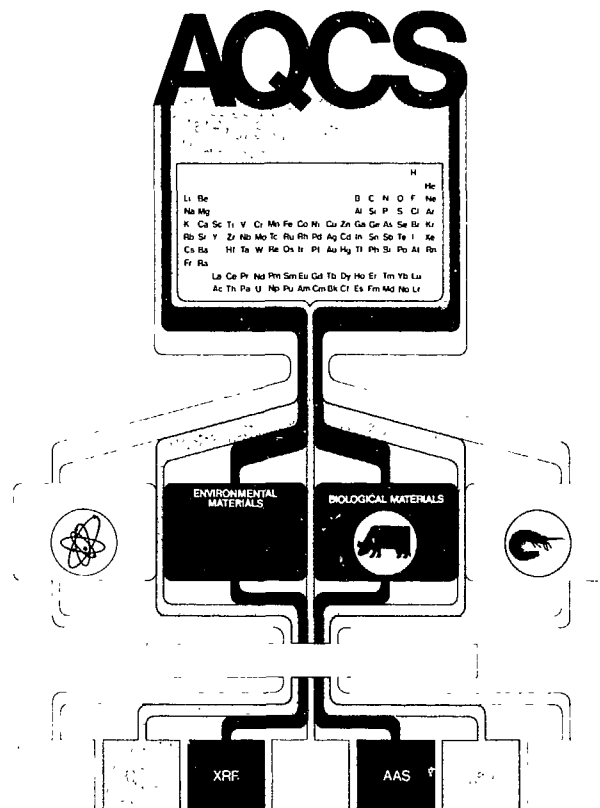
REPORT ON THE
INTERCOMPARISON RUN

IAEA-312

Ra-226, Th and U

IN

SOIL



ANALYTICAL QUALITY CONTROL SERVICES

INTERNATIONAL ATOMIC ENERGY AGENCY, P. O. BOX 100, A-1400 VIENNA, AUSTRIA



IAEA/AL/036

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**INTERCOMPARISON STUDY IAEA-312 ON THE DETERMINATION
OF U, Th and Ra-226 IN SOIL**

by

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**International Atomic Energy Agency
Agency's Laboratories
Analytical Quality Control Services
Vienna, January 1991**

WP1223k

Summary

This report contains the results of the intercomparison IAEA-312 on the determination of uranium, thorium and Ra-226 in soil. The participants included 39 laboratories located in 17 countries, and statistical evaluation of their data yield recommended values for these elements.

The elements, their recommended values and confidence intervals are listed below:

Ra-226	269	Bq/kg	(250-287)
Th	91.4	microg/g	(81.3-101.5)
U	16.5	microg/g	(15.7-17.4)

Reference date: 30 January 1988

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1. Introduction

Knowledge of the composition of soil, which is one of the main components of the environment and one of the most important elements in the production circle of human and animal nutrition, is of interest to the specialist in such different fields of research as geology, biology and environmental pollution. Its quality directly affects human health and, therefore, the level of its natural radioactivity and of its pollution by artificial radionuclides is of great interest.

2. Scope of study

Participating laboratories were requested to determine radium-226, uranium and thorium. The analysts were requested to make at least three, but preferably six, independent measurements for each element.

3. Description of the material

The bulk soil sample donated by the Indonesian Atomic Energy Commission (IAEC) was collected from the Sibolga area of north Sumatra.

The sun dried batch of the soil passing a 180 μ m sieve was further ground and homogenized.

Aliquots of 50 g were distributed in plastic bottles and all bottles were sealed and sterilized by gamma ray irradiation to a total dose of $2.5 \cdot 10^4$ Gy using a ^{60}Co source.

The homogeneity of the material (after bottling) was checked by determining the concentration of uranium by laser fluorimetry in two sub-samples taken from various bottles chosen at random.

By applying the F-test it was found that the results did not differ significantly for uranium and that this material could be considered homogeneous for a sample size greater or equal to 500 mg (significance level of 0.05).

4. Evaluation of results

The original data that were received from the participating laboratories were edited (converted to the same units and format) before being entered into a computer data file. This data file was processed by a computer program especially written for evaluating intercomparison results. Results which deviated significantly from the population were considered to be outliers and rejected if they failed either one of the following statistical tests at the significance level of $\alpha = 0.05$:

- 1) Dixon's
- 2) Grubb's
- 3) coefficient of skewness, and
- 4) coefficient of kurtosis.

Additional information on acceptance criteria can be found in reference [1].

[1] R. Dyczynski, A. Tugsavul, O. Suschny, *Analyst* 103 (1978) 733

4.1. Explanation of tables

4.1.1 Data tables

The laboratory mean values for a specific element for which at least two laboratory means were supplied are presented in Tables 1 to 3.

LAB. CODE NO.: Each laboratory was assigned a code number, which is the same throughout the report. To ensure anonymity these code numbers do not correspond to the sequence of the laboratories in the list of participants given at the end of the report.

METHOD CODE: The analytical techniques employed by the participating laboratories are represented in the form of codes (a letter and number). The key to the different analytical techniques is given in Table A.

NO. OF DETERMINATIONS: The number of individual results for a given element reported by the participating laboratory.

LAB. MEAN. The arithmetic mean computed from all the individual results reported by the participating laboratory. An asterisk (*) after the lab mean denotes that it was detected and rejected as an outlier. Outliers were not used to compute the overall mean for this element.

LAB. STANDARD DEVIATION: The absolute and relative standard deviations were calculated if at least three results were reported by the participating laboratory.

4.1.2. Summary of results tables

The summary of the results for IAEA-312 is given in Table B. Most of the terms used in the summary table have been already defined. The standard error (S.E.) is defined as the standard deviation of the mean values divided by the square root of the number of laboratory means.

4.2. Description of figures

A figure was plotted for an element when at least five or more laboratory means were reported. The laboratory means are plotted in ascending order (microg/g or Bq/kg) on the y-axis with their corresponding laboratory code noted along the x-axis.

The reported uncertainties or "error bars" (standard deviation of the laboratory mean) are also shown. The code above the error bar is the laboratory method code, while the value below the error bar is the number of individual determinations. If a "less than" value was reported, an arrow downwards was employed rather than the numerical value and these values were not used to compute the overall mean. The mean value and the 95% confidence interval for all the accepted laboratory means are listed in the figure caption

when appropriate. Finally, the solid points indicate those values that (filled in circles) were detected and rejected as outliers for the calculation of the overall laboratory mean.

4.3 Criteria for recommended values and confidence intervals

Please note that these criteria are especially designed for this report and do not apply for general consideration.

The following criteria have been used for data classification:

1. The relative uncertainty of the overall mean (\bar{x}) at the significance level of $\alpha = 0.05$ defined as $\frac{SE \cdot t_{0.05}}{\bar{x}}$ is lower than: a) 20%, b) 30%;
2. The overall mean was calculated on the basis of the results obtained from at least two different analytical methods;
3. The percentage of outliers was less than a) 20%, b) 30%.
4. At least 20 laboratory averages have been used for the calculation of the overall mean.

The overall mean for the particular element was classified as "reference value" (class A), when criteria 1a, 2, 3a and 4 were fulfilled. When criteria 1b, 2, 3b and 4 were fulfilled the overall mean of a given element was classified as "reference value" (class B).

5. Results and conclusion

The results obtained from this intercomparison are detailed in Tables 1-4.

Since a large number of laboratories provided their results using a different analytical methods, it was possible to establish "recommended values" for uranium, thorium and Ra-226. A survey of outlying results seems to indicate that a relatively small number of laboratories are mainly responsible for producing erroneous results, and not the analytical technique or the kind of element being determined. Certain differences between the methods, however, seem to exist in isolated cases and this problem deserves further investigation.

The recommended values for the activity concentration (Bq/kg) of Ra-226 and U, Th (microg/g) in IAEA-312 are summarized in Table C.

6. Acknowledgements

The authors of this report wish to thank Ms. Katalin Lewis-Goettler for processing the results and the Oesterreichisches Forschungszentrum for the ^{60}Co irradiation of these intercomparison samples. Last, we would also like to thank all the participating laboratories listed at the end of this report for their co-operation in providing the data for this intercomparison.

Table A

Laboratory method codes used in the IAEA-312 intercomparison

Method Code	Method
G2	Gamma ray spectrometry without sample pretreatment
G3	Gamma ray spectrometry with sample pretreatment
F1	Fluorimetry, without specification
F2	Fluorimetry, laser
K1	α -counting techniques
K2	α -spectrometry without specification
M1	Mass spectrometry without specification
N2	Neutron activation analysis, thermal, instrumental
N3	Neutron activation analysis, epithermal, instrumental
N7	Delayed neutron counting
R1	Radon emanation method
S2	Spectrophotometry without specification
T1	Fission track method
X1	X-ray fluorescence analysis

TABLE NO. 1 SIGNIFICANCE LEVEL 0.05

RESULTS OF INTERCOMPARISON FOR RA-226 IN SOIL-312, 1990

UNIT: BQ/KG

NO.	LAB. CODE NO.	METHOD CODE	NO.OF DETERM.	MEAN	STANDARD DEV.		ACCEPTANCE CODE **
					ABS	REL %	
1	3	G2	3	335.00	2.00	0.6	23.9
2	4	G2	5	270.40	4.73	1.7	OK
3	5	G2	6	229.10	10.36	4.5	-2.0
4	15	G2	6	228.63	4.74	2.1	-4.5
5	16A	R1	3	506.67*	15.01	3.0	14.6
6	16B	R1	3	516.67*	13.65	2.6	16.8
7	17	R1	4	204.67	4.03	2.0	-11.2
8	18	G2	2	483.50*	6.36	1.3	30.9
9	19	G2	6	185.27	1.90	1.0	-34.0
10	20	R1	6	206.67	27.33	13.2	-1.6
11	21	K1	6	292.83	46.35	15.8	0.1
12	22	G2	5	257.00	7.35	2.9	OK
13	23	R1	3	313.33	11.55	3.7	2.3
14	24	N2	6	227.50	9.33	4.1	-2.4
15	25	G2	6	314.50	15.93	5.1	1.7
16	26A	G2	6	231.17	11.44	5.0	-1.6
17	26B	K1	1	230.00			LO
18	27	R1	3	310.00	23.90	7.7	1.0
19	28	G2	6	280.83	11.63	4.1	OK
20	29	G2	6	282.50	14.82	5.2	OK
21	30	G2	6	240.55	7.09	2.9	-1.3
22	33	G2	3	312.30	1.30	0.4	19.4
23	35A	G2	5	322.94	4.54	1.4	7.9
24	35B	G2	4	318.70	3.63	1.1	8.7
25	36	G3	6	345.22	25.20	7.3	2.3
26	37	G2	2	269.00	0.00	0.0	OK
27	38	G2	6	261.50	2.07	0.8	OK
28	39	G2	5	243.60	2.22	0.9	-2.9

** FOR CONFIDENCE INTERVAL 249.95 TO 287.11

RA-226 IN SOIL 312, 1990 (BQ/KG)

MEAN VALUE: 268.53 BQ/KG

95% CONFIDENCE INTERVAL: 249.95 TO 287.11

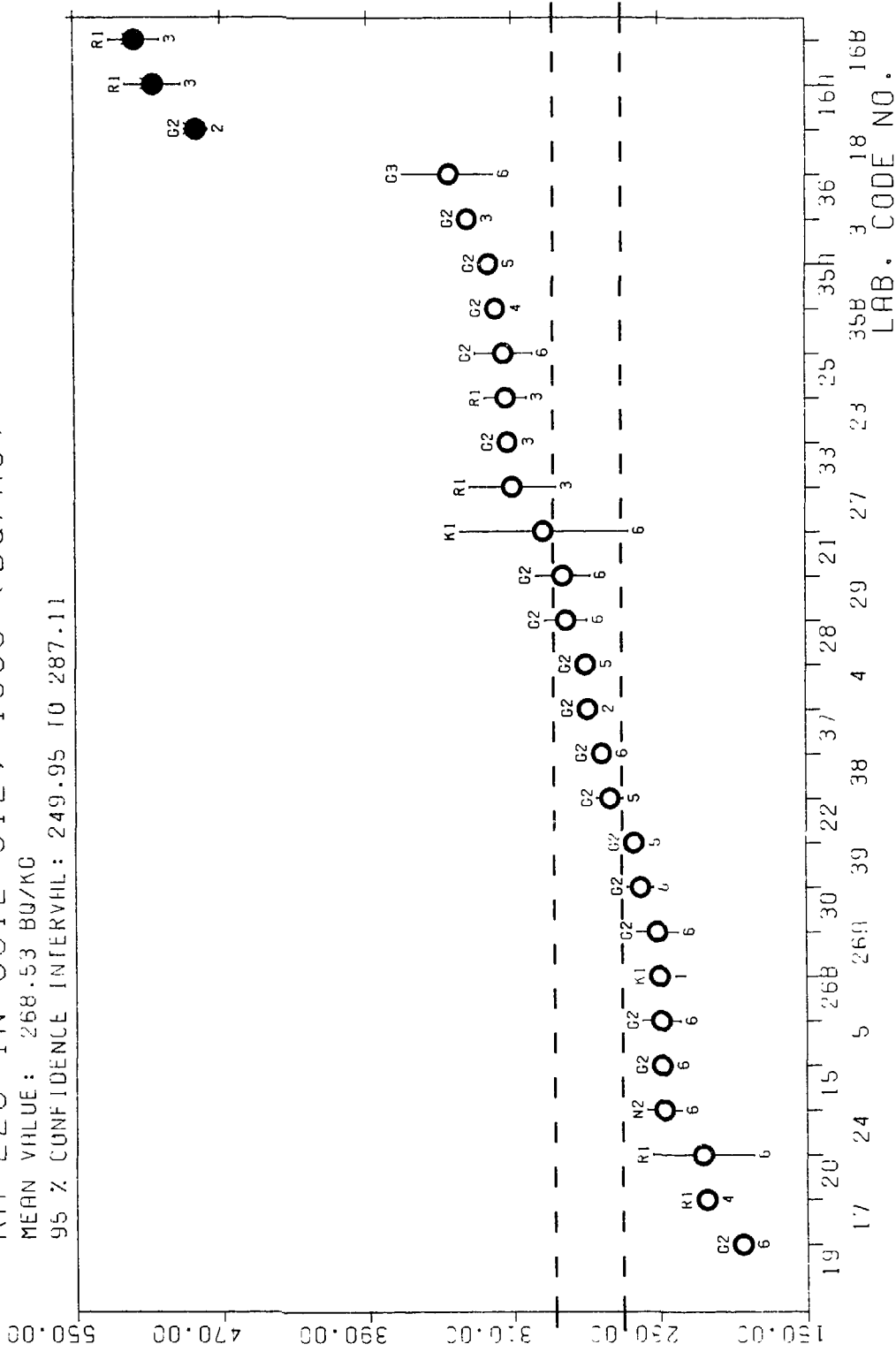


TABLE NO. 2 SIGNIFICANCE LEVEL 0.05

RESULTS OF INTERCOMPARISON FOR TH IN SOIL-312, 1990

UNIT: MICROG/G

NO.	LAB. CODE NO.	METHOD CODE	NO.OF DETERM.	MEAN	STANDARD DEV.		ACCEPTANCE CODE **
					ABS	REL %	
1	1	X1	6	103.17	0.98	1.0	1.7
2	2	G2	6	108.50	3.62	3.3	1.9
3	3	G2	3	122.77	1.40	1.1	15.2
4	4	G2	5	97.78	2.47	2.5	OK
5	5	G2	6	123.58	2.66	2.2	8.3
6	6	N2	6	151.30	5.81	3.8	8.6
7	8	X1	6	125.17	.98	0.8	24.1
8	9	X1	4	34.50	2.73	7.9	-17.1
9	10	N2	4	102.00	2.16	2.1	0.2
10	12	S2	3	52.57	3.27	6.2	-8.8
11	13	S2	4	85.65	2.16	2.5	OK
12	14	N2	6	93.89	2.87	3.1	OK
13	15	G2	6	93.52	7.04	7.5	OK
14	16A	N2	6	109.50	1.64	1.5	4.9
15	16B	N2	6	108.17	1.33	1.2	5.0
16	17	N2	5	94.40	2.30	2.4	OK
17	19	G2	6	764.55*	10.78	1.4	61.5
18	20	K1	6	88.83	5.95	6.7	OK
19	23	G2	3	31.00	4.00	12.9	-12.6
20	24	N2	6	68.08	2.20	3.2	-6.0
21	25	G2	6	103.42	6.19	6.0	0.3
22	26A	G2	6	95.13	4.59	4.8	OK
23	26B	K1	2	82.30	27.86	33.9	OK
24	28	G2	6	88.33	1.21	1.4	OK
25	29	N3	6	97.55	1.87	1.9	OK
26	30	N2	6	90.43	2.64	2.9	OK
27	31	T1	5	71.42	9.30	13.0	-1.1
28	32	T1	2	65.10	3.82	5.9	-4.2
29	33	G2	3	101.03	1.06	1.0	OK
30	34	N2	4	18.42	1.84	10.0	-34.1
31	35A	G2	5	106.78	2.70	2.5	2.0
32	35B	G2	4	105.75	2.42	2.3	1.8
33	39	G2	5	104.26	1.32	1.3	2.1

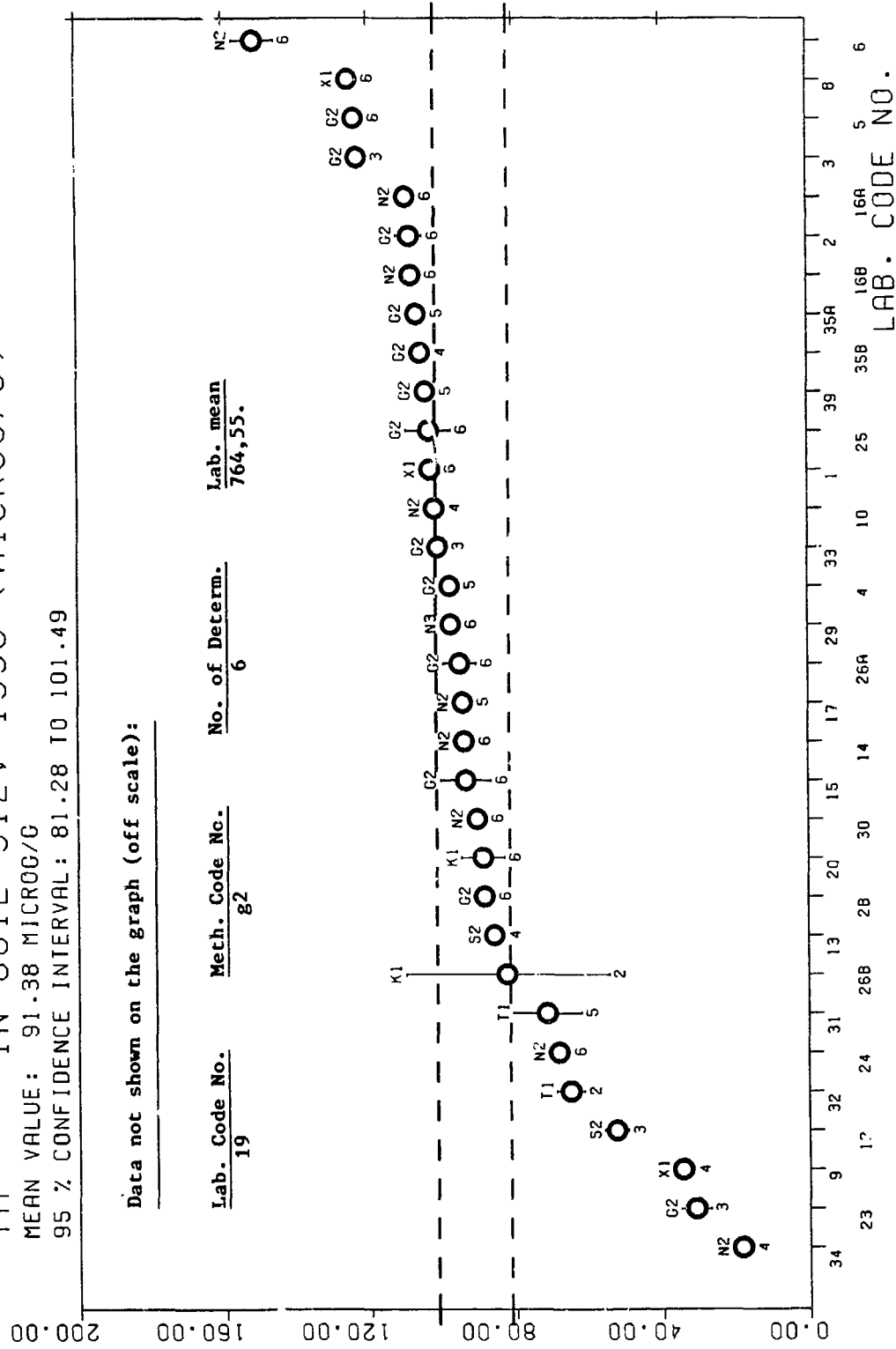
** FOR CONFIDENCE INTERVAL 81.28 TO 101.49

TH IN SOIL-312, 1990 (MICROG/G)

MEAN VALUE: 91.38 MICROG/G
 95 % CONFIDENCE INTERVAL: 81.28 TO 101.49

Data not shown on the graph (off scale):

Lab. Code No.	Meth. Code No.	No. of Determ.	Lab. mean
19	82	6	764,55.



LAB. CODE NO. 16A 16B 35B 35A 2 5 6 8

TABLE NO. 3 SIGNIFICANCE LEVEL 0.05

RESULTS OF INTERCOMPARISON FOR U IN SOIL-312, 1990

UNIT: MICROG/G

NO.	LAB. CODE NO.	METHOD CODE	NO.OF DETERM.	MEAN	STANDARD DEV.		ACCEPTANCE CODE **
					ABS	REL %	
1	1	X1	6	14.67	0.52	3.5	-1.9
2	2	G2	6	25.17*	1.17	4.6	6.7
3	3	K2	3	15.83	0.15	1.0	OK
4	4	G2	4	49.95*	3.88	7.8	8.4
5	5	G2	6	66.63*	4.62	6.9	10.7
6	6	N2	6	16.60	0.18	1.1	OK
7	7	F2	6	16.22	0.59	3.6	OK
8	10	M1	4	18.37	0.63	3.4	1.6
9	11	K2	3	43.40*	2.78	6.4	9.3
10	12	S2	4	13.47	2.59	19.2	-0.8
11	13	F1	4	13.72	0.35	2.6	-5.5
12	14	N2	6	13.60	0.40	2.9	-5.2
13	15	G2	6	15.08	4.24	28.1	-0.1
14	16A	N7	6	18.60	0.35	1.9	3.4
15	16B	N7	6	18.52	0.29	1.5	3.9
16	17	N2	5	16.48	0.62	3.8	OK
17	19	G2	6	30.32*	1.27	4.2	10.2
18	20	F1	6	123.33*	10.33	8.4	10.3
19	23	G2	3	105.67*	2.31	2.2	38.2
20	24A	N7	6	13.97	0.22	1.5	-7.8
21	24B	N2	6	15.63	2.26	14.5	-0.0
22	25	G2	6	18.73	1.47	7.9	0.9
23	26A	G2	5	36.02*	5.60	15.6	3.3
24	26B	K1	2	21.25	0.21	1.0	18.2
25	27	K2	3	18.00	1.06	5.9	0.6
26	28	G2	6	11.83	0.98	8.3	-3.9
27	29	N3	6	16.70	0.34	2.0	OK
28	30	N2	6	16.73	1.01	6.0	OK
29	31A	T1	6	17.53	1.16	6.6	0.1
30	31B	T1	6	16.78	1.56	9.3	OK
31	31C	T1	3	13.73	0.45	3.3	-4.3
32	32A	T1	6	18.97	0.39	2.0	4.1
33	32B	T1	6	17.85	0.64	3.6	0.7
34	32C	T1	3	13.73	0.25	1.8	-7.7
35	34	N2	4	43.37*	2.02	4.7	12.9
36	35A	G2	5	19.04	1.92	10.1	0.9
37	35B	G2	4	17.57	1.11	6.3	0.2
38	39	G2	5	19.94	0.35	1.8	7.3

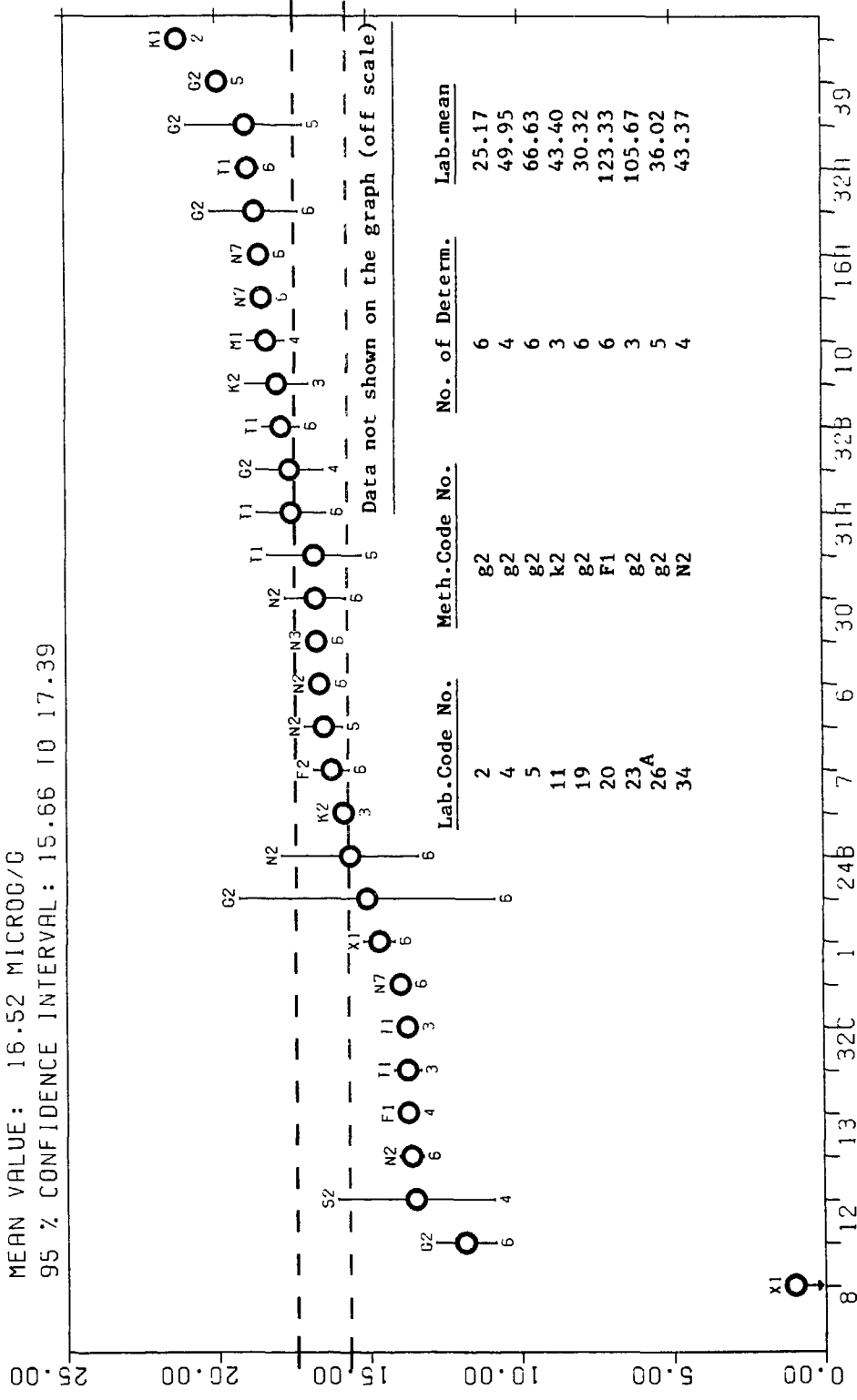
** FOR CONFIDENCE INTERVAL 15.66 TO 17.39

RESULTS BELOW LIMIT OF DETECTION REPORTED FOR U

NO.	LAB. CODE NO.	METHOD CODE	LAB. LOD
1	8	X1	1.00

U IN SOIL-312, 1990 (MICROG/G)

MEAN VALUE: 16.52 MICROG/G
 95 % CONFIDENCE INTERVAL: 15.66 10 17.39



28 8 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39

LAB. CODE NO.

TABLE NO. 4 SIGNIFICANCE LEVEL 0.05

RESULTS OF INTERCOMPARISON FOR U-238 IN SOIL-312, 1990

UNIT: MICROG/G

NO.	LAB. CODE NO.	METHOD CODE	NO.OF DETERM.	MEAN	STANDARD DEV.	
					ABS	REL %
1	33	G2	3	17.80	0.36	2.0

TABLE B

SUMMARY OF RESULTS OF THE INTERCOMPARISON SOIL-312, 1990

RADIONUCLIDE DETERMINED	RA-226	TH	U
UNIT	BQ/KG	MICROG/G	MICROG/G
NUMBER OF LABORATORY REPORTED RESULTS	28	33	38
INDIVIDUAL DETERMINATIONS	129	163	190
NUMBER OF LABORATORY ACCEPTED RESULTS	25	32	29
INDIVIDUAL DETERMINATIONS	121	157	147
TOTAL RANGE OF LABORATORY AVERAGES	185.27 - 516.67	18.42 - 764.55	11.83 - 123.33
RANGE OF ACCEPTED LABORATORY AVERAGES	185.27 - 345.22	18.42 - 151.30	11.83 - 21.25
PERCENTAGE OF OUTLYING LABORATORIES	11	3	24
OVERALL MEAN OF ACCEPTED LABORATORY AVERAGES	268.53	91.38	16.52
STANDARD DEVIATION (S.D.)	ABS 45.00 REL% 16.8	28.02 30.7	2.28 13.8
STANDARD ERROR (S.E.)	ABS 9.00 REL% 3.4	4.95 5.4	0.42 2.6
CONFIDENCE INTERVALS FOR THE MEAN OF POPULATION FOR SIGNIFICANCE LEVEL .05	249.95 - 287.11	81.28 - 101.49	15.66 - 17.39

Table C

Recommended values and confidence intervals for
Uranium, Thorium and Ra-226 in IAEA-312 soil

Element	Recommended value	Confidence Interval*
Ra-226	269 Bq/kg	250 -287 (Class A)
Th	91.4 microg/g	81.3-101.5 (Class A)
U	16.5 microg/g	15.7- 17.4 (Class B)

* Confidence intervals are for significance level 0.05.

Reference date: 30 January 1988

List of participating laboratories for the IAEA's intercomparison study
of the soil (IAEA-312) for Ra-226, uranium and thorium

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