NAHRES-60
Vienna, 2001

Report on the

NAT-9 quality control exercise on uranium isotopes in two soil samples

A report prepared by

Andreas Bleise

Vienna, Austria, April 2001

INTERNATIONAL ATOMIC ENERGY AGENCY

EDITORIAL NOTE

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SUMMARY

The International Atomic Energy Agency (IAEA) section of Nutritional and Health related Environmental Studies (NAHRES) organized a quality control study for laboratories analysing samples form the UNEP field mission to Kosovo. Quality control was the major responsibility of the IAEA in the UN field assessment team.

The NAT-9 quality control study consists of two soil materials from the IAEA laboratories in Seibersdorf. The scope of this exercise was to determine the content of the uranium isotopes U-234, U-235 and U-238. The IAEA did not provide specific instructions, the participants were encouraged to apply their established analytical procedures to the samples. Five laboratories were invited to participate, four laboratories submitted results. For each soil sample 10 laboratory mean values were reported, using ICP-MS (3 laboratories) and α-spectrometry (1 laboratory).

The participating laboratories were capable to distinguish the different uranium isotopes. All laboratories obtained the natural uranium ratio between U-235 and U-238. However, the results highlight a particular analytical weak spot. Although the methods of measuring the analytical signals are highly dependable, the sample preparation steps, in particular the sample dissolution procedure appears to be lacking total quality control and has contributed to the deviations from the reported target values. One laboratory has documented evidence that extensive and well-controlled digestion methods can yield measurement results close to the target values.

INTRODUCTION

During the fact finding mission to Kosovo in November 2000 it was agreed that it was necessary to organize a quality control exercise for the laboratories analysing the samples from the mission [1]. Since most samples consist of soils, it was decided to take two soil materials for this exercise. The study (NAT-9) was organized by the section of Nutritional and Health Related Environmental Studies (NAHRES) of the International Atomic Energy Agency (IAEA).

This report is an evaluation of the results obtained for the NAT-9 quality control exercise on two soil samples. The purpose of this report is to display and discuss the results, to provide individual participants with feedback focusing mainly on the results and to show the performance of different analytical techniques. Participants were not instructed to use a specific leaching or digestion method; on the contrary they were encouraged to use their established analytical method. It is not intended to judge the performance of the laboratories, but to find out whether the applied analytical methods and the sample preparation is suitable for analyzing uranium isotopes.

The NAT-9 quality control exercise comprises two soil materials. Soil-1 was a podsolic soil, originating from the surface layer having a depth of twenty centimetre [2]. Soil-2 was a marine sediment collected in the vicinity of a nuclear power plant [3]. Five laboratories from five countries were invited, four laboratories participated in this exercise and reported four sets of results for both materials. Analytical methods used were: inductively coupled plasma mass spectrometry (ICP-MS), and alpha spectrometry.

CONTENT OF THE REPORT

This report contains mainly the results obtained in a tabular and in a graphical form (bar-plots). All results are expressed anonymously. The laboratories are only identified by a code number. The low number of participants did not allow a full statistical treatment of the results. In addition, the information sheet, which was sent out with the samples, is appended.

Tables and plots are arranged in order of increasing uranium isotope masses. The first two tables show the submitted mean values in ng/g and Bq/kg, the number of determinations, the analytical method applied and the way of dissolution of the samples. In addition, the U235/U238 ratio was calculated to demonstrate, that all laboratories revealed the natural uranium abundance in the samples (ratio ~ 0.0072) and no depleted uranium (DU) was present [4].

Tables 3-8 compare the results of the NAT-9 exercise with target values and includes the evaluation according the set accuracy and precision criteria (see paragraph data evaluation). The submitted mean values are compared with the target values and the differences are expressed in per cent and z-scores.

In the graphical presentation each point represents a mean value from one laboratory and the error bar shows the standard deviation if this information was provided by the laboratory. The values are compared with target values, and the standard deviation in the

reference sheet. The grey bands are two standard deviations away from the target value and have a width of one standard deviation. The laboratory codes are shown on the x-axis.

DATA EVALUATION

Results received from the laboratories were evaluated in relation to established target values. Deviation from the target value are expressed in per cent and z-scores. The z-scores are calculated using the following equation:

$$Z_{score} = \frac{Value_{lab.} - Value_{target.}}{\sigma}$$

σ: Standard deviation of the mean

In addition the results were evaluated against acceptance criteria for accuracy and precision. A result must pass both criteria to be assigned as passed. The following criteria was applied:

1. Accuracy:

The value is based on the u-test score [5], which is calculated according to the following equation:

$$u\_test = \frac{\left|Value_{target} - Value_{Lab.}\right|}{\sqrt{Unc._{target}^2 + Unc._{Lab.}^2}}$$

Unc.: Submitted uncertainty

The calculated u-test value is compared with the critical values listed in the t-statistic tables to determine if the reported value differs significantly from the target value at a given value of probability. For the evaluation the condition u > 3.29 was set, which means that the probability is less than 0.001 and the reported result differs significantly from the target value.

Result passes if

$$\left|Value_{target} - Value_{lab}\right| \le 3.29 \times \sqrt{Unc._{target}^2 + Unc_{lab.}^2}.$$

2. Precision:

For precision the limit was set to 30%. This limit is used in proficiency tests for medium activity samples. Results passes if :

$$\sqrt{\left(\frac{Unc._{target}}{Value_{target}}\right)^2 + \left(\frac{Unc._{lab.}}{Value_{lab.}}\right)^2} \times 100\% \le 30\%$$

RESULTS AND DISCUSSION

Sample S-1

For the soil sample S-1, 10 laboratory mean values for the three uranium isotopes (U-234, U-235 and U-238) were reported, using ICP-MS (3 laboratories) and α-spectrometry (1 laboratory).

U-234

The following methods were used to provide results: ICP-MS (3) and α-spectrometry (1). The results show some variation within the same analytical technique (0.0536ng/g to 0.14ng/g). All results are lower than the target value, which is 0.14ng/g. Three out of the four submitted results are inside the range of two standard deviations from the target value. One result was rejected due to the accuracy criteria.

U-235

Only ICP-MS (3) was used for establishing values for this measurand. The value of U-235 was too low for the laboratory using α-spectrometry. All submitted results are lower than the target value. The accuracy and the precision criteria were met by all results.

U-238

The following methods were used to provide results: ICP-MS (3), and α-spectrometry (1). The values cover a large range and are all lower than the target value. The result obtained with α-spectrometry (1) shows the highest value. One result does not fulfil the accuracy criteria and was rejected.

The sample Soil-1 consists of a podsolic soil and the natural uranium is not easily liberated. In this soil matrix the total uranium content can only be analysed by using total digestion methods or fusion. The uranium is strongly bonded to the mineral matrix. Most participating laboratories are using acid leaching (HNO_3+H_2O_2-leaching; HNO_3 / HF-leaching) and acid digestion, which is an established dissolution method according to international guidelines, but does not always lead to the total amount of uranium [6]. A similar result was discovered in the certification exercise of this material. Several results were refused, because they did not reveal the total amount of uranium. In the certification exercise all results obtained with alpha-spectrometry and acid leaching or total dissolution with HF were rejected.

The results show that not the analytical method is responsible for the discrepancies of the values, but the sample dissolution method. Laboratory 4 is using an extensive digestion method (melting with Na_2CO_3 + Na_2O_2, leaching with HCl, HNO_3 + HF and HNO_3 by heating) and obtained for all measurands results close to the target value.

Unfortunately no non-destructive technique was applied to the sample. Neutron activation analysis (NAA) would be suitable to establish the total U-238 value in the sample and as a non-destructive technique would lead to the total content of uranium. All results submitted using NAA were accepted in the certification exercise of this material. NAA is a capable method for analysing uranium at environmental levels. In the literature NAA was used for the determination of uranium in biological matrices [7].

Sample S-2

For the soil sample S-1, 10 laboratory mean values the three uranium isotopes (U-234, U-235 and U-238) were reported, using ICP-MS (3 laboratories) and α-spectrometry (1 laboratory).

U-234

The following methods were used to provide results: ICP-MS (3), and α-spectrometry (1). Three values are higher than the target value and are in good agreement. One value, determined with ICP-MS, is outside the range of three standard deviation from the target value. This result was rejected by the accuracy criteria.

U-235

Only ICP-MS (3) was used for establishing values for this measurand. The value of U-235 was too low for α-spectrometry. All submitted results are slightly lower than the target value, but are inside two standard deviation from the target value. The precision criteria had to be adjusted for this measurand because the target value is only an informational value with a high uncertainty, which reveals the low precision (see equation for precision).

U-238

The following methods were used to provide results: ICP-MS (3), and α-spectrometry (1). The values show a good agreement. Only the result obtained with α-spectrometry is higher than the target value. All results passed the criteria for accuracy and precision

The result of soil-2 prove that this sediment is an easier matrix than soil-1 with respect to determination of uranium isotopes. All but one submitted result are inside the interval of two standard deviations from the target value and for U-238 the results are evenly distributed around the target value.

CONCLUSION

This quality control exercise shows that the participating laboratories are capable to distinguish the different uranium isotopes. All laboratories obtained the natural uranium ratio between U-235 and U-238. However, the sample Soil-1, a complicated matrix, revealed some problems in determining the total uranium amount. For this sample, most results of the laboratories are lower than the target value. The applied digestion methods are not sufficient to leach all uranium. This shows that the problem is not the analytical method but the dissolution of the samples. For obtaining reliable results on the relative amount of depleted uranium in a real sample, it is essential to accurately determine the total content of uranium. Neutron activation analysis (NAA), a non destructive analytical technique, would be suitable and complementary to provide information about the total U-238 content avoiding any leaching problems.

Concerning precision and accuracy, all the laboratories met the criteria set for precision, but not for accuracy. One laboratory failed in meeting the accuracy criteria for 50% of the results. The results of this particular laboratory do significantly differ from the target value and would fail in a proficiency test.

ACKNOWLEDGEMENT

The author would like to thank the laboratories listed in Appendix IV for their contribution and their effort to meet the deadline for submitting results. Furthermore the assistance of Mr. Zbigniew Radecki (NAAL) in preparing the samples for shipment and the data evaluation is gratefully acknowledged.

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INFORMATION SHEET

NAT - 9

Quality Control Exercise

on

Uranium Isotopes

in

Soil

INTERNATIONAL ATOMIC ENERGY AGENCY

SECTION OF NUTRITIONAL AND HEALTH RELATED
ENVIRONMENTAL STUDIES

INTERNATIONAL ATOMIC ENERGY AGENCY

SECTION OF NUTRITIONAL AND HEALTH RELATED
ENVIRONMENTAL STUDIES

Quality control exercise on uranium isotopes in soil

Information Sheet

Description of the materials

The samples S-1 and S-2 have been selected as suitable materials for the determination of uranium isotopes in soil. Sample S-1 is a soil prepared and characterized by the Agency's laboratory in Seibersdorf. Sample S-2 was prepared by the Agency's laboratory in Monaco. The samples are provided in plastic containers, containing approximately 100g of material.

Scope of the study

Participants are requested to use their established and proven analytical techniques for the determination of uranium isotopes. The following measurands are to be reported:

U-234, U-235 and U-238

Reports on any other element that may be available in conjunction with the determination of the priority elements would be appreciated. Participants are requested to **perform 6 independent** determinations.

Preparation of samples for measurement

The materials are provided in white plastic containers. Segregation might have occurred during transportation and therefore the laboratories should carry out rehomogenization of the material according to their usual procedures.

Moisture determination

All results are to be reported on a dry weight basis. For this purpose, the volatile water content at the time of analysis should be determined in separate subsamples of at least 500 mg. The recommended procedure is oven drying at 105 °C for 4 hours or freeze drying for 48 hours.

Analytical quality control

Procedures of good laboratory practice (GLP) and laboratory quality assurance should be strictly applied to the performed analyses. Quality control (QC) with a certified reference material is obligatory, laboratories not providing information on the analysis of a suitable reference material will be rejected from the data evaluation. The analysis of a suitable QC material should be carried out together with the analysis of the intercomparison material, applying the same procedures and analysing the same elements. The number of QC determinations should be at least 3.

Reporting of results

The report should contain the following items:

A text file (Microsoft Word document, or printout):

- Short summary of the sample preparation procedure.
- Description of the analytical method, equipment and analytical parameters used.
- Limit of detection and linearity range for each element measured.
- The type and amount of QC material used.

A Microsoft EXCEL file:

- The results of each independent determination in mg/kg or Bq/kg of the material on a dry weight basis. Please avoid exponential numbers, %, or other units.
- The best estimate of the measurement uncertainty for each determination, in mg/kg or Bq/kg; the total uncertainty obtained by summing the individual standard uncertainties, using the law of propagation, is recommended.
- The results obtained for a suitable certified reference material (QC material).

The results should be reported to the address mentioned on the accompanying letter and the reporting forms as soon as possible but not later than the **15th December 2000.**

These data should be reported, both on the enclosed reporting forms and on the computer diskette provided with the material. If e-mail is available, reporting by appending the EXCEL file to an e-mail would be appreciated. The DOS formatted computer diskette contains two files having the extension .XLS (Microsoft EXCEL files).

TABLES OF SUBMITTED DATA

Lab. ID	Measurand	No. of Determinations	Mean Value [ng/g]	Mean Value [Bq/kg]	Total Uncertainty [ng/g]	Ratio U235/U238	Anal. Method	Dissolution
1	U-234	6	0.1007	23.3	0.00816		ICP-MS	HNO_3 / HF-Leaching
1	U-235	6	10.79	0.86	0.245	0.0072	ICP-MS	**EPA 3052**
1	U-238	6	1490	18.5	31		ICP-MS	
2	U-234	4	0.0536	12.4	0.00089		ICP-MS	HNO_3+H_2O_2-Leaching
2	U-235	4	5.75	0.46	0.062	0.0073	ICP-MS	**EPA 3050B**
2	U-238	4	785	9.8	8		ICP-MS	
3	U-234	3	0.14	32.3			ICP-MS	HNO_3+$HClO_4$+HF
3	U-235	3	15.71	1.25		0.0072	ICP-MS	microwave digestion
3	U-238	3	2190	27.2			ICP-MS	
4	U-234	6	0.138	31.9	0.0138		alpha-spec.	Melting with Na_2CO_3 + Na_2O_2
4	U-235							Leaching with HCl, HNO_3 + HF
4	U-238	6	2620	32.5	217		alpha-spec.	and HNO_3 by heating

Table 1 Submitted data for sample S-1

Lab. ID	Measurand	No. of Determinations	Mean Value [ng/g]	Mean Value [Bq/kg]	Total Uncertainty [ng/g]	Ratio U235/U238	Anal. Method	Dissolution
1	U-234	6	0.079	18.25	0.00648		ICP-MS	HNO_3 / HF-Leaching
1	U-235	6	8.81	0.71	0.174	0.0072	ICP-MS	**EPA 3052**
1	U-238	6	1220	15.2	23		ICP-MS	
2	U-234	4	0.0439	10.1	0.00082		ICP-MS	HNO_3+H_2O_2-Leaching
2	U-235	4	4.55	0.364	0.039	0.0072	ICP-MS	**EPA 3050B**
2	U-238	4	629	7.8	5.3		ICP-MS	
3	U-234	3	0.09	20.8			ICP-MS	HNO_3+$HClO_4$+HF
3	U-235	3	9.3	0.74		0.0072	ICP-MS	microwave digestion
3	U-238	3	1300	16.2			ICP-MS	
4	U-234	6	0.0857	19.8	0.00686		alpha-spec.	Melting with Na_2CO_3 + Na_2O_2
4	U-235							Leaching with HCl, HNO_3 + HF
4	U-238	6	1600	19.8	128		alpha-spec.	and HNO_3 by heating

Table 2 Submitted data for sample S-2

RESULTS FOR SAMPLE S-1

^{234}U

	Target Value		NAT-9							Acceptance criteria					
Lab. ID	Value	Unc.	Value	Unc.		Deviation	Z-score	u-statistic	Lab/Target Value	Accuracy			Precision		
	ng/g		ng/g		%										
1	0.141	0.025	0.1007	0.00816	8.10%	-28.6%	-1.43	1.53	0.71	0.040	0.087	passed	19.5%	passed	passed
2	0.141	0.025	0.0536	0.0089	16.60%	-62.0%	-3.10	3.29	0.38	0.0874	0.0873	failed	24.3%	passed	rejected
3	0.141	0.025	0.14	--	--	-0.71%	-0.04	0.04	0.99	0.001	0.082	passed	17.7%	passed	passed
4	0.141	0.025	0.138	0.0138	10.0%	-2.13%	-0.11	0.11	0.98	0.003	0.094	passed	20.4%	passed	passed

^{235}U

	Target Value		NAT-9							Acceptance criteria					
Lab. ID	Value	Unc.	Value	Unc.		Deviation	Z-score	u-statistic	Lab/Target Value	Accuracy			Precision		
	ng/g		ng/g		%										
1	17.87	4.10	10.79	0.245	2.27%	-39.6%	-1.98	1.72	0.60	7.080	13.513	passed	23.1%	passed	passed
2	17.87	4.10	5.75	0.062	1.08%	-67.8%	-3.39	2.96	0.32	12.120	13.491	passed	23.0%	passed	passed
3	17.87	4.10	15.71	--	--	-12.1%	-0.60	0.53	0.88	2.160	13.489	passed	22.9%	passed	passed
4	17.87	4.10	Not reported												

^{238}U

	Target Value		NAT-9							Acceptance criteria					
Lab. ID	Value	Unc.	Value	Unc.		Deviation	Z-score	u-statistic	Lab/Target Value	Accuracy			Precision		
	ng/g		ng/g		%										
1	2733.9	484.0	1490	31	2.08%	-45.5%	-2.27	2.56	0.55	1243.90	1595.62	passed	17.8%	passed	passed
2	2733.9	484.0	785	8	1.02%	-71.3%	-3.56	4.03	0.29	1948.90	1592.58	failed	17.7%	passed	rejected
3	2733.9	484.0	2190	--	--	-19.9%	-0.99	1.12	0.80	543.90	1592.36	passed	17.7%	passed	passed
4	2733.9	484.0	2620	217	8.28%	-4.17%	-0.21	0.21	0.96	113.90	1745.08	passed	19.5%	passed	passed

RESULTS FOR SAMPLE S-2

^{234}U

	Target Value		NAT-9							Acceptance criteria					
Lab. ID	Value	Unc.	Value	Unc.		Deviation	Z-score	u-statistic	Lab/Target Value	Accuracy			Precision		
	ng/g		ng/g		%										
1	0.0770	0.0080	0.079	0.00648	8.20%	2.6%	0.13	0.19	1.03	0.002	0.034	passed	13.2%	passed	passed
2	0.0770	0.0080	0.0439	0.0008	1.87%	-43.0%	-2.15	4.12	0.57	0.033	0.026	failed	10.6%	passed	rejected
3	0.0770	0.0080	0.09	--	--	16.9%	0.84	1.63	1.17	0.013	0.026	passed	10.4%	passed	passed
4	0.0770	0.0080	0.0857	0.0069	8.0%	11.3%	0.56	0.83	1.11	0.009	0.035	passed	13.1%	passed	passed

^{235}U

	Target Value		NAT-9							Acceptance criteria					
Lab. ID	Value	Unc.	Value	Unc.		Deviation	Z-score	u-statistic	Lab/Target Value	Accuracy			Precision		
	ng/g		ng/g		%										
1	10.50	6.00	8.81	0.71	8.06%	-16.1%	-0.80	0.28	0.84	1.69	19.88	passed	57.7%	passed	passed
2	10.50	6.00	4.55	0.039	0.86%	-56.7%	-2.83	0.99	0.43	5.95	19.74	passed	57.1%	passed	passed
3	10.50	6.00	9.3	--	--	-11.4%	-0.57	0.20	0.89	1.20	19.74	passed	57.1%	passed	passed
4	10.50	6.00	Not reported												

^{238}U

	Target Value		NAT-9							Acceptance criteria					
Lab. ID	Value	Unc.	Value	Unc.		Deviation	Z-score	u-statistic	Lab/Target Value	Accuracy			Precision		
	ng/g		ng/g		%										
1	1419.3	282.2	1220	15.2	1.25%	-14.0%	-0.70	0.71	0.86	199.30	929.8	passed	19.9%	passed	passed
2	1419.3	282.2	629	5.3	0.84%	-55.7%	-2.78	2.80	0.44	790.30	928.6	passed	19.9%	passed	passed
3	1419.3	282.2	1300	0	0.00%	-8.4%	-0.42	0.42	0.92	119.30	928.4	passed	19.9%	passed	passed
4	1419.3	282.2	1600	128	8.00%	12.7%	0.64	0.58	1.13	180.70	1019.5	passed	21.4%	passed	passed

GRAPHICAL PRESENTATION OF THE RESULTS

Sample S-1

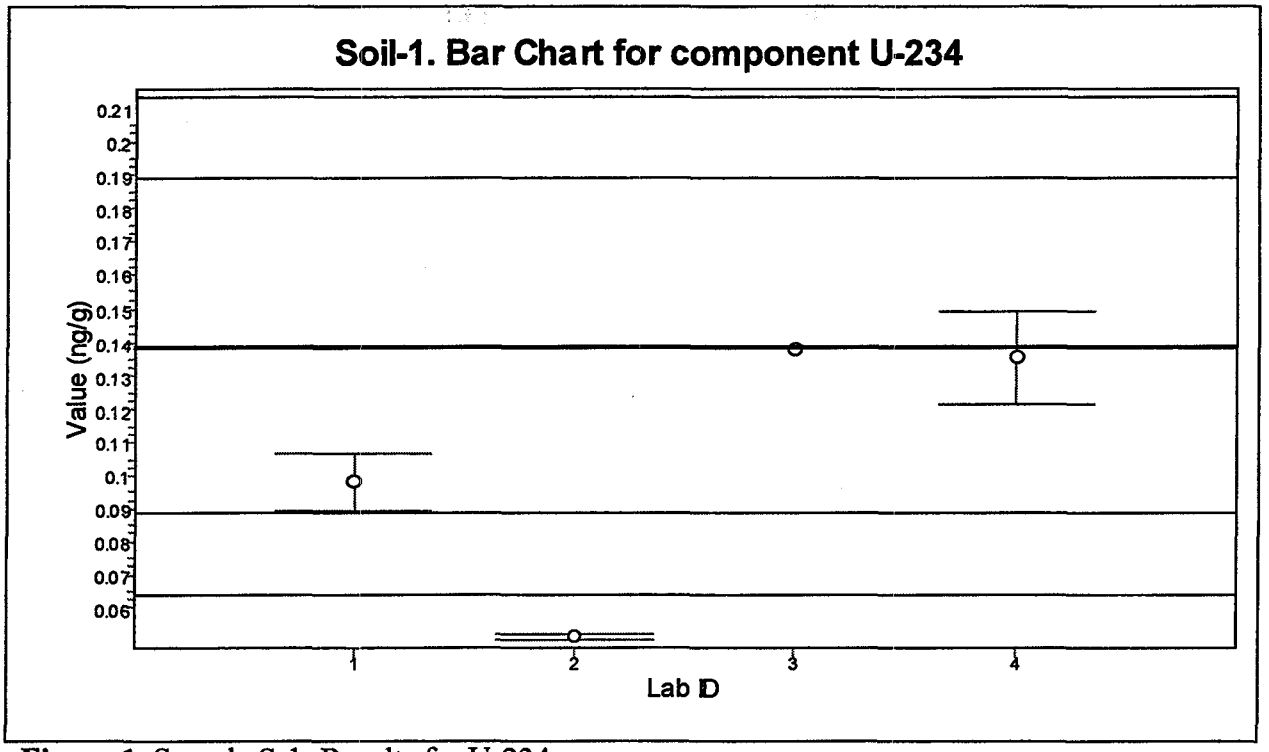

Figure 1 Sample S-1: Results for U-234

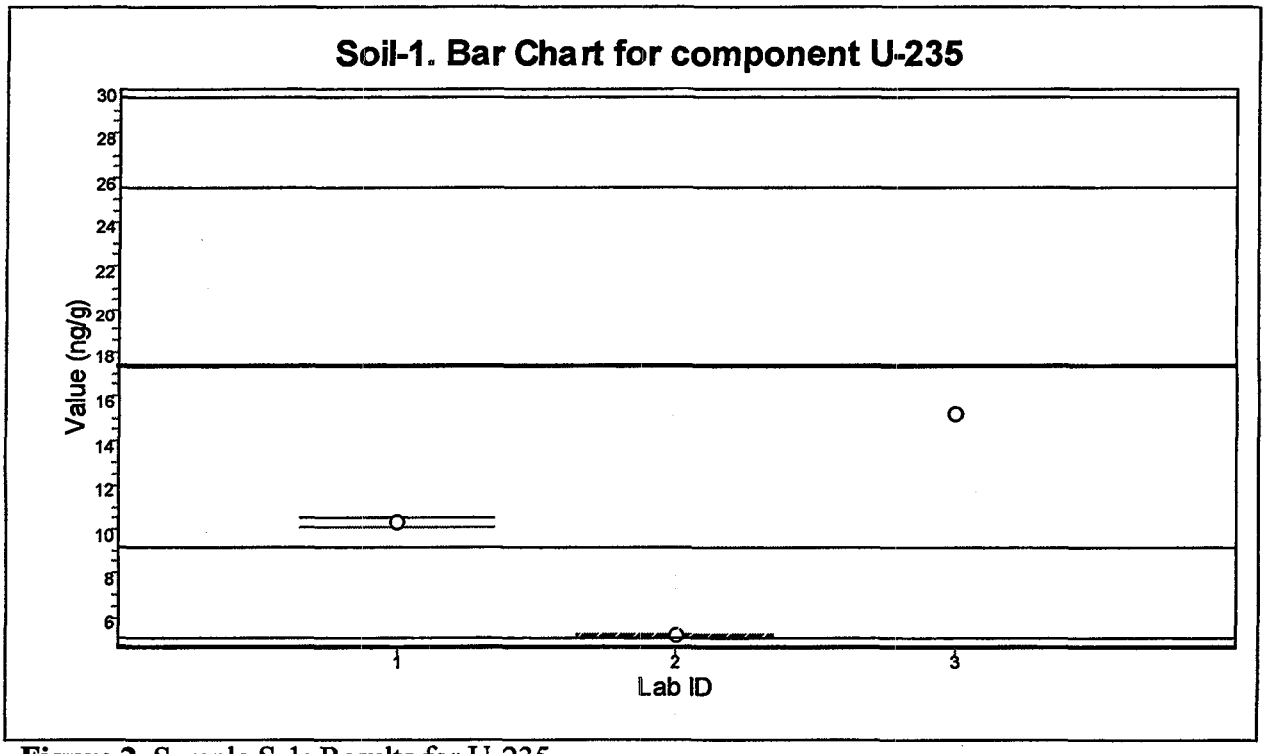

Figure 2 Sample S-1: Results for U-235

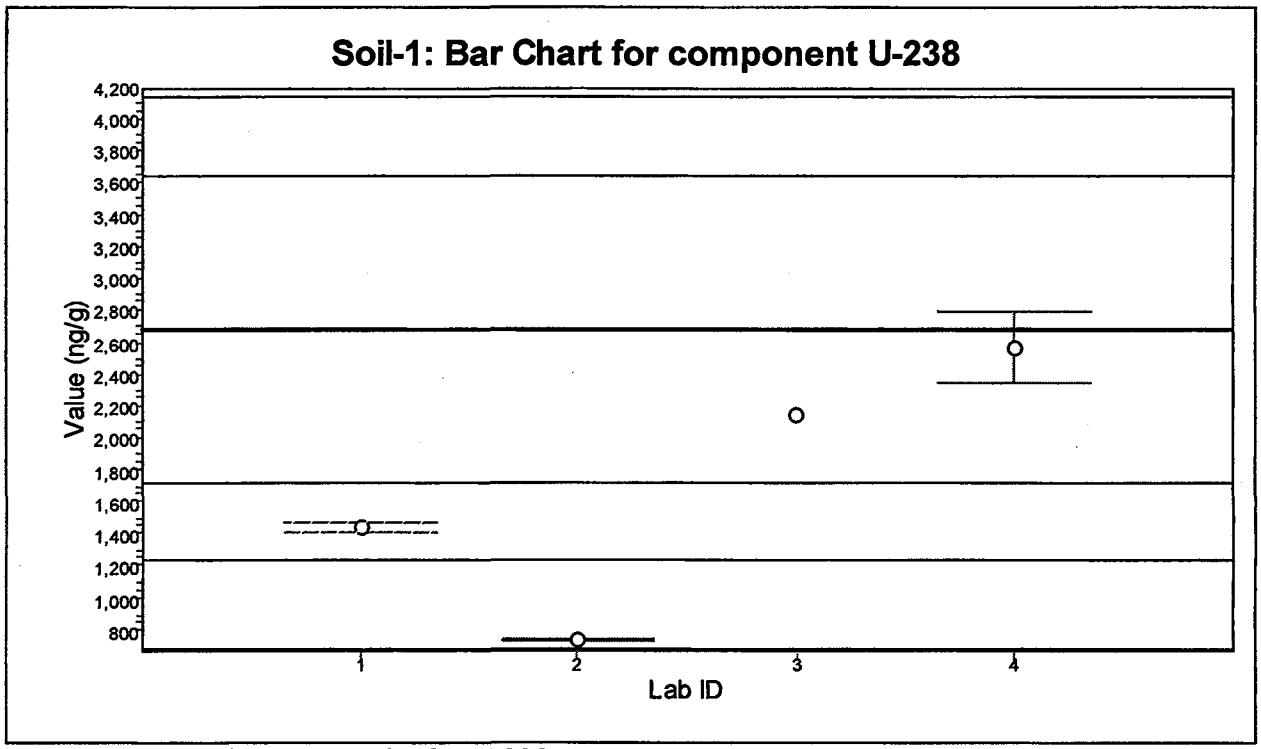

Figure 3 Sample S-1: Results for U-238

Sample S-2

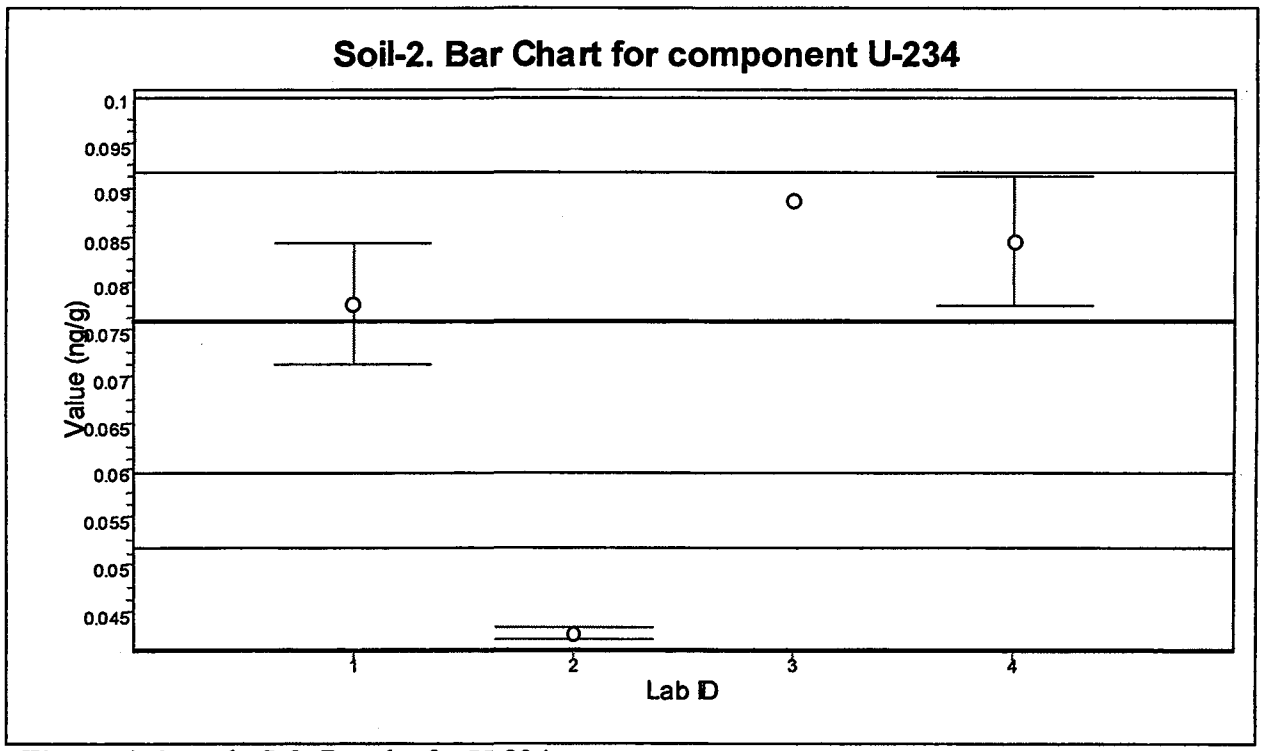

Figure 4 Sample S-2: Results for U-234

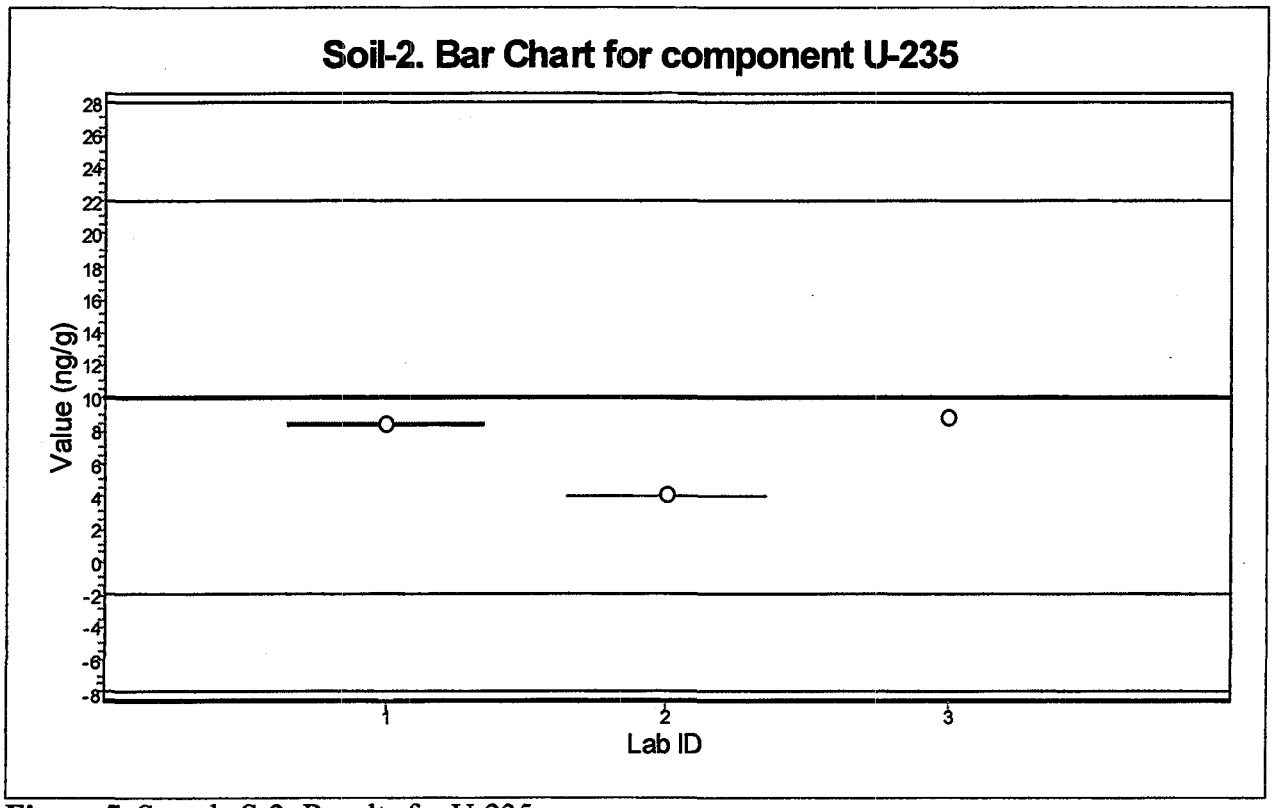

Figure 5 Sample S-2: Results for U-235

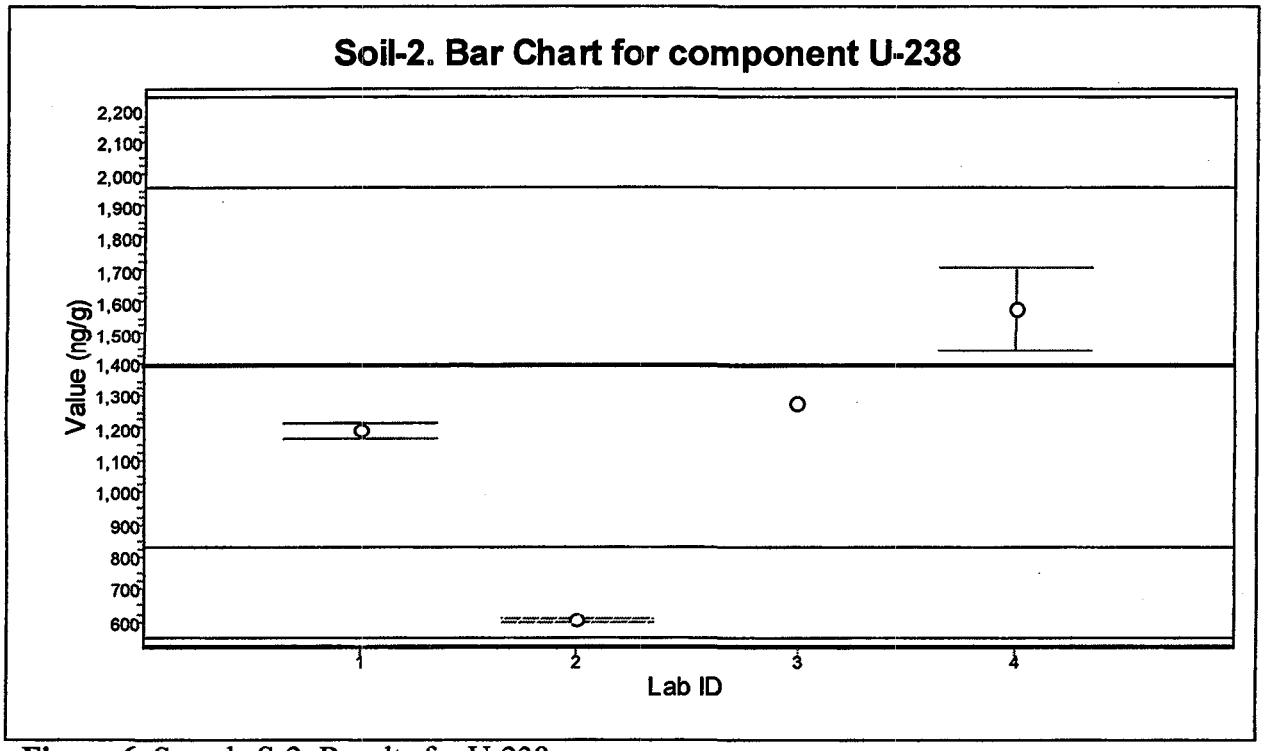

Figure 6 Sample S-2: Results for U-238

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