

DETERMINATION OF ALPHA EMITTERS IN ENVIRONMENTAL SAMPLES OF SOME EGYPTIAN INDUSTRIAL CITIES.

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Abstract

The activity concentration of uranium isotopes, thorium isotopes, and the radioelement Polonium-210 has been measured in some soil samples collected from two industrial cities in Egypt. The analytical method is based on isotopes selective separation by Anion exchange method after digestion and extraction with Dowex ion - exchange resin. Tracers (^{232}U , ^{229}Th , and ^{209}Po) are added into the samples as chemical yield monitors. The uranium and thorium sources are prepared by electrodeposited onto a stainless steel disk. The polonium source is prepared by spontaneous deposition onto a silver disk. The measurement were carried out using alpha-particle spectrometry. The QC were achieved by using IAEA reference materials. The analytical results of the total uranium was found to be in the range from 16.71 to 34.17 Bq/kg with an average value of 26.21 Bq/kg, the results of the total thorium was found to be in the range from 16.23 to 62.62 Bq/kg with an average value of 44.32 Bq/kg, and ^{210}Po contents vary between 4.0 to 19.3 Bq/kg with an average value of 11.73 Bq/kg.

1.Introduction

^{235}U , ^{230}Th , and ^{210}Po in the environmental samples, such as soil, are frequently analyzed for both emergency and routine radiation monitoring. Health physicists use the analytical results of environmental samples to estimate the amount of radioactive material present in the environment, calculating its burden for the radiological workers and general public [1]

Many methods for the determination and separation of actinides from environmental samples have been developed during the last decades. Most of them are highly strong acid wastes. New, highly specific resins have added interest in extraction chromatography as a separation method for actinides in environmental samples [2]

The determination of actinide concentrations in low activity samples can be performed by alpha spectrometry, whereby a chemical separation is needed. Any possible losses of the analyte during the analysis can be determined by use of a tracer. It is assumed that the chemical behavior of the tracer is identical to the analyte [3]

Polonium-210 ($t_{1/2}=138.38$ d) occurs naturally via ^{210}Pb ($t_{1/2}=22.3$ y) and ^{210}Bi ($t_{1/2}=5.15$ d) in the ^{238}U decay chain. The contribution of ^{210}Pb , ^{210}Bi , and ^{210}Po to the internal radiation dose to human has been estimated to be around 8%.

Polonium occurs widely in nature and is considered as an important component of man's radiation background. Its presence in soil may be traced to the decay of radionuclides of the ^{238}U chain in the soil. This decay leads to the formation of ^{222}Rn (half-life of 3.82 days), so there is enough time for its diffusion from soil to atmosphere. The fraction of ^{222}Rn escaping into the air can vary in the range of 18-87% depending upon soil type [4]

2. Methodology

2.1 Sample preparation

Nine soil samples were collected from the two industrial cities (Sadat and 6th of October), in addition to one sample as a reference IAEA-300 and one sample as a blank. The samples were dry ashed with the blank in a porcelain crucible in an electric muffle furnace up to 600 °C for 24 hours. The ashing program is given in Table 1

Table (1): Ashing program carried out in this work.

Steps	T ₁	T ₂	T ₃
Temp. (°C)	200	350	550
Time (hours)	2h	4h	24h

Four g of the sample and one g from the reference material were used in addition one sample as a blank were treated for uranium and thorium isotopes. Samples were placed into porcelain beakers for digestion process. To each beaker (including the reagent blank), 50µl ^{229}Th (21.64 dpm/ml) and 200 µl ^{232}U (5.465 ± 0.164 dpm/ml) were added. The dry to ash weight ratio averaged 1.03 for all soil samples.

2.2 Sample digestion

For digestion of the soil samples, the blank and the reference material were digested in Teflon beaker with a mixture of mineral acids (HNO_3 , 40% HF, ml 32% HCL, and Boric acid).

The chromatography column is prepared and conditioned before introduction of the sample solution using (distilled water, AG1-X8, 100-200 mesh, and 9M HCL). Load the sample solution on the conditioned anion exchange column with the adjustment of the flow rate (1drop/6 seconds) under gravity flow.

Finally, strip thorium fraction from the column by passing 50 ml 9 M HCL solution through the column. In the mean time strip uranium fraction from the same column by passing 100 ml 0.01 M HCL (warm) solution through the same column. Then further purification for both thorium and uranium fractions were done.

2.3 Thorium elution method

After purification, finally, thorium from the column by passing 100 ml 0.01 M HCL solution through the column is stripped. Then it is evaporated to near dryness. After dryness, 20 ml 65% HNO₃ is added, then evaporated to dryness. After dryness, 10 ml 65% HNO₃ + 1 ml 0.3 M Na₂SO₄ is added and evaporated to dryness. After dryness, the source of thorium is prepared by electro-deposition method. And finally, it has to be counted by alpha spectrometry.

2.4 Uranium elution method

The eluted uranium fraction solution from the first anion exchange column were evaporated on the hot plate to near dryness. Then after dryness 30 ml 65% HNO₃ is added and evaporated to near dryness. After dryness, 20 ml 2.5 M HNO₃ is added with 4 ml 0.6 M ferrous sulfomate.

The UTEVA column (Eichrom) is prepared and conditioned before introduction of the sample solution (2.5M HNO₃ for conditioning). The sample solution (20 ml 2.5 M HNO₃ +4 ml 0.6 M ferrous sulfomate) is loaded on to the conditioned UTEVA column. Then 2.5 ml 9 M HCL is added to the column and discarded. Then 20 ml 5 M HCL-0.05 M H₂C₂O₄ is passed to strip any Th, Pu, Np, etc.

While leaving U on the column. finally, uranium is stripped from the column by passing 30 ml 0.01 M HCL solution through the column. Then it is evaporated to near dryness. After dryness, 30 ml 65% HNO₃ is added and the solution is evaporated to near dryness. Then electro-deposition is carried out.

2.5 Electro-deposition method

Electro-deposition method was chosen for U and Th isotopes in this work because of higher recoveries. The anode (platinum wire of horizontal helix shape) has to be adjusted to make the distance to the disc about 3mm. Electroplating is carried out at 1.2 A for one hour. Occasional adjustment may be necessary to maintain the current at 1.2 A during the plating period [5]. Before discarding the plating solution and washing from columns, the sample has to be counted by alpha spectrometry for recovery [6].

2.6 Radiochemical procedure for Po-210

0.1g of dry soil sample and two IAEA reference material samples (0.1 gm from IAEA-375 and 3 gm from IAEA-327) in addition to one sample as a blank were placed in a Teflon Bomb. (approximately 1 dpm per sample from the tracer ²⁰⁹Po (4979.2 keV and 102 years). Sample was digested with a mixture of mineral acids (HF 40%, HCL 32%, HNO₃ 65%, ascorbic acid, and Boric acid) in a digestion microwave oven. After digestion, silver disks and plate are washed with alcohol. The silver disks are placed inside the solution, and the solution is placed on a hot plate with magnetic stirring system. The plating temperature should be between 60–85 °C. Plating time is about 3-6 h. After plating, the disk is dried and kept inside a plastic dishes.

2.7 Apparatus

The alpha spectrometry system equipped with 72 planar ion-implanted silicon semiconductor detectors was used for determining alpha emitters radionuclides. The detectors were divided among twenty-four EG&G Ortec model 576 dual alpha spectrometers and three EG&G Ortec 8-unit Octete model alpha spectrometer systems. All the units were connected by means of mixer/routers and multi-channel buffers to a computer-based operating system using the EG&G Ortec Alpha Vision software system for acquisition, analysis and storage of alpha spectra. The chemical procedures used for separation of alpha emitters and the measurements were carried out at IAEA-MEL-Monaco.

3. Results and discussion

3.1. Alpha Spectrometric Analyses of Uranium Isotopes.

The specific activities in nine soil samples in Bq/kg dry weight together with one sample as a reference IAEA-300 and one sample as a blank is shown in Table 2. It is necessary to determine not only the concentration of the total uranium but also the ratio of different uranium isotopes to detect any man-made radioactivity. The concentration of ²³⁴U, ²³⁵U, and ²³⁸U in addition to ²³⁴U/²³⁸U, and ²³⁵U/²³⁸U ratios were determined. The specific activities of ²³⁸U ranged from 8.05 to 16.52 Bq/kg with an average of 12.75 Bq/kg. The ratios ²³⁴U/²³⁸U ranged from 0.76 to 1.09 Bq/kg with an average of 1.01 Bq/kg with correlation coefficient of 0.969 as shown in Figure 1. The specific activities of ²³⁵U ranged from 0.341 to 0.652 Bq/kg with an average of 0.47 Bq/kg. The ²³⁵U/²³⁸U ratios ranged from 0.03 to 0.04 Bq/kg with an average of 0.038 Bq/kg with correlation coefficient of 0.906 as shown in Figure 2. The specific activities of ²³⁴U ranged from 7.41 to 16.12 Bq/kg with an average of 12.98 Bq/kg. From the above mentioned results, good agreement for the results of the IAEA reference materials indicates the reliability of the analysis methods.

Table (2) Activity concentrations (Bq kg⁻¹ dry weight) measured by α -spectrometry in soil sample.

Sample	²³⁵ U	²³⁸ U	²³⁴ U	Total Uranium	²³⁴ U/ ²³⁸ U ratio	²³⁵ U/ ²³⁸ U ratio
S.Oc 1	0.341±0.03	8.05±0.24	8.32±0.23	16.71	1.03	0.04
S.Oc 2	0.513±0.04	14.90±0.41	15.31±0.41	30.72	1.03	0.03
S.Oc 3	0.362±0.03	9.77±0.29	7.41±0.21	17.54	0.76	0.04
S.Oc 4	0.415±0.06	13.98±0.72	14.49±0.73	28.89	1.04	0.03
S.Oc 5	0.56±0.04	14.48±0.37	15.02±0.37	30.06	1.04	0.04
S.Sa 1	0.375±0.04	9.29±0.31	9.30±0.29	18.97	1.00	0.04
S.Sa 2	0.652±0.03	16.52±0.03	17.00±0.46	34.17	1.03	0.04
S.Sa 3	0.510±0.04	13.12±0.35	13.89±0.36	27.52	1.06	0.04
S.Sa 4	0.540±0.04	14.66±0.42	16.12±0.44	31.32	1.09	0.04
IAEA-300	2.71±0.08	67.13±2.60	71.54±2.71	141.38	1.07	0.04

3.2 Alpha Spectrometric Analyses of Thorium Isotopes

Table 3 shows the specific activities in the same soil samples with one sample as a reference IAEA-300 and one sample as a blank. The concentration of ^{232}Th , ^{230}Th , ^{228}Th , and $^{232}\text{Th}/^{228}\text{Th}$ ratios (Bq/kg dry weight), were determined in the same above mentioned samples. The specific activities of ^{232}Th ranged from 5.00 to 24.53 Bq/kg with an average of 11.85 Bq/kg. The specific activities of ^{230}Th ranged from 6.42 to 14.46 Bq/kg with an average of 11.37 Bq/kg. The specific activities of ^{228}Th ranged from 4.81 to 27.15 Bq/kg with an average of 16.75 Bq/kg. The $^{232}\text{Th}/^{228}\text{Th}$ ratios ranged from 0.86 to 1.04 with an average of 0.97 and correlation coefficient of 0.986 as shown in Figure 3 .

It was found that, good correlation between the activity concentration of thorium isotopes measured by alpha spectrometry. The existence of secular equilibrium between the ^{232}Th and the other members of its series in the studied soil samples was found.

Table (3): Activity concentrations (Bq kg⁻¹ dry weight) measured by α spectrometry in soil.

Site No.	^{232}Th	^{230}Th	^{228}Th	Total Thorium	$^{232}\text{Th}/^{228}\text{Th}$ ratio	$^{238}\text{U}/^{230}\text{Th}$ ratio
S.Oc 1	5.00±0.27	6.42±0.34	4.81±0.49	16.23	1.04	1.25
S.Oc 2	24.53±1.49	13.42±0.78	24.67±1.75	62.62	0.99	1.11
S.Oc 3	10.61±0.63	9.36±0.57	11.41±0.91	31.38	0.93	1.04
S.Oc 4	24.25±1.36	13.85±0.83	23.95±1.58	62.05	1.01	1.01
S.Oc 5	15.54±0.79	13.57±0.71	15.57±1.02	44.68	0.99	1.07
S.Sa 1	9.09±0.39	6.68±0.19	8.78±0.58	24.55	1.04	1.39
S.Sa 2	23.31±1.2	14.46±0.79	27.15±1.39	64.92	0.86	1.14
S.Sa 3	23.83±1.11	13.24±0.66	23.45±1.29	60.52	1.02	0.99
S.Sa 4	9.59±0.62	11.34±0.32	10.98±0.95	31.90	0.87	1.29
IAEA-300	62.72±2.40	81.22±3.05	56.21±2.89	200.15	1.12	0.83

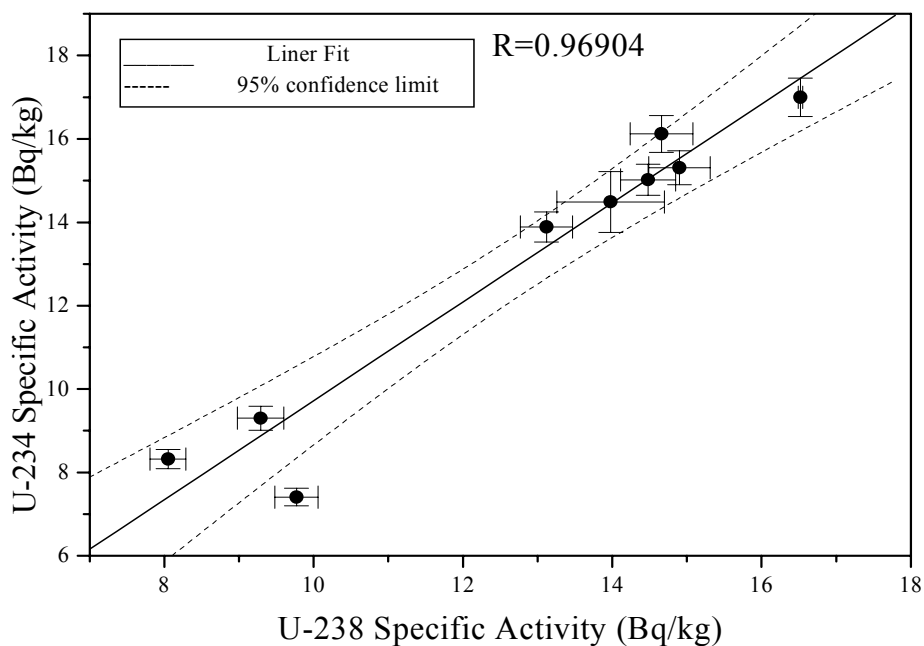


Fig. (1): Correlation between U-238 and U-234 measured by Alpha analyses

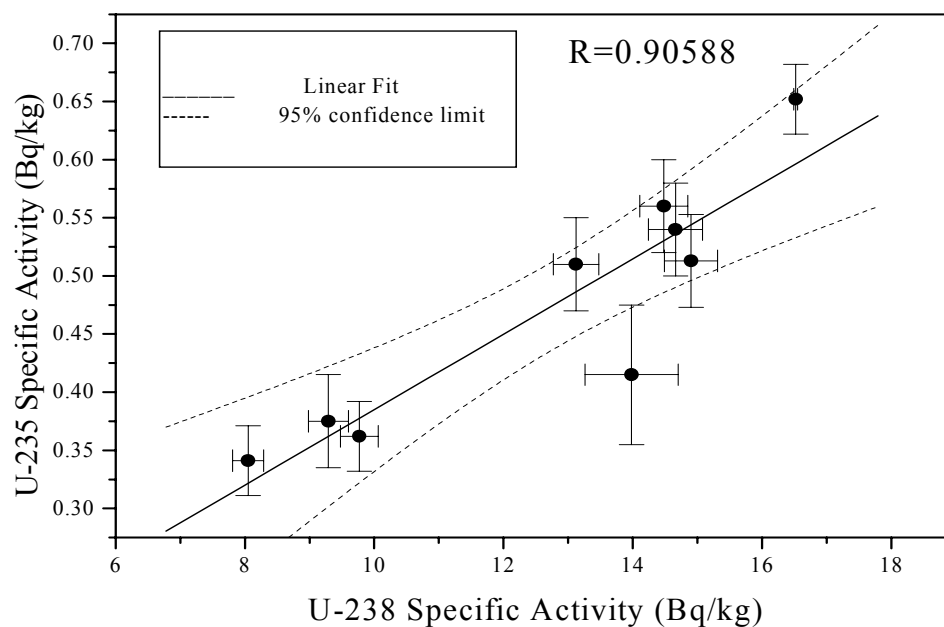


Fig. (2): Correlations between U-238 and U-235 measured by Alpha analyses

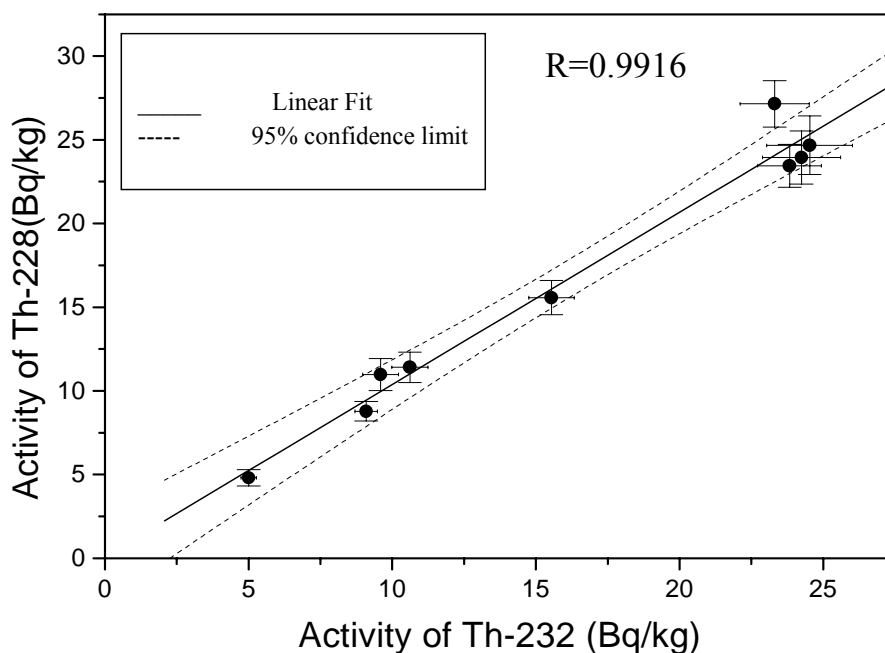


Fig. (3): Correlation between Th-228 and Th-232 measured by Alpha analyses

3.3 Alpha spectrometric analyses of polonium-210 in soil samples.

Polonium-210 ($t_{1/2}=138.38$ d) occurs naturally via ^{210}Pb ($t_{1/2}=22.3$ y) and ^{210}Bi ($t_{1/2}=5.15$ d) in the ^{238}U decay chain. The contribution of ^{210}Pb , ^{210}Bi , and ^{210}Po to the internal radiation dose to human has been estimated to be around 8%.

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Twelve soil samples were measured to determine ^{210}Po after radiochemical separation using alpha spectrometry. Table 4 shows that, the activity concentrations of polonium-210 ranged from 4.0 to 19.3 Bq/kg with an average value of 11.7 Bq/kg. For comparison, the average value of the activity concentration of ^{210}Po in soil samples for the two cities with the literature values reported for north Sinai in Egypt and other environments are given in Table 5.

Table (4): Activity concentration of Po-210 measured by Alpha analysis in soil samples.

Sample Code	²¹⁰ Po Bq/kg by Alpha analysis
S.Sa 4	6.9±1.9
S.Sa 5	4.7±2.4
S.Sa 6	17.0±3.2
S.Sa 7	10.1±1.8
S.Sa 8	18.8±4.4
S.Sa 9	10.5±2.2
S.Oc 1	17.0±3.2
S.Oc 2	-
S.Oc 3	4.0±1.6
S.Oc 4	9.0±1.1
S.Oc 5	-
S.Oc 6	19.3±3.4
IAEA-375	14.8±3.2
IAEA-327	8.2±2.3

Table (5): Comparison of ²¹⁰Po activity in the surface soils

Region	Activity Concentration of Po-210 (Bq/kg)
Present work	11.7
North Sinai, Egypt	16.2-133.7
Colorado, USA	28.86-58.83
USA (country wide)	8.1-128
Blackforest, Germany	33.3-207.2
CIPC, Brazil	32.07-70
Mysore, India	7.6-37.3
Kiaga, India	17.1-228.2
World range	8.14-219

3.4 Quality Control and Acceptance criteria

Blank samples were introduced at the beginning of the analysis at the time of allocation to trace any cross contamination which might occur during any of the analysis steps. The data obtained shows good accuracy without any cross contamination during all the steps of the analyses.

Another test for QC for the analyzing samples is the u-test. The criteria was to get a value of $u \leq 3.29$ to pass the accuracy test [8] and given in equation 1.

$$U_{test} = \frac{|Value_{Certified} - Value_{Analyzed}|}{\sqrt{Unc_{Certified}^2 + Unc_{Analyzed}^2}} \quad (1)$$

The quality control results were evaluated to be assigned the status of passed. Tables 6 and 7 presents the data obtained for both the quality control (reference and blank samples). It was found that all the QC samples analyzed passed this test. This indicates that the analyses performed in this study showed a good accuracy and precession.

Conclusions

The results indicate that these radioactivity concentrations are of natural origin. This confirms that the resulting public average radiation exposure is within the international acceptable limits (UNSCEAR, 2000). The $^{238}\text{U}/^{232}\text{Th}$ ratios were found to be normal, suggesting no detectable impact from the industrial activities on the environment of the two cities.

The measured average isotopic values of $^{234}\text{U}/^{238}\text{U}$ indicate the presence of secular equilibrium between the uranium isotope with its daughters in the studied soil samples in the two cities.

Good correlations were found between the activity concentration values of uranium and thorium measured using alpha spectrometry.

The activity concentrations of polonium-210 in the studied soil samples were found to be within the international level.

-In summary the results obtained in this study are considered as part of the data base established by the Central Laboratory for Environmental Radioactivity Measurements Intercomparison and Training (CLERMIT) in the frame of radiation protection objects of the National Center for Nuclear Safety and Radiation Control (NCNSRC).

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