IAEA/AQ/17

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Reference Material IAEA 434: Naturally Occurring Radionuclides in Phosphogypsum

IAEA
International Atomic Energy Agency

REFERENCE MATERIAL IAEA 434: NATURALLY OCCURRING RADIONUCLIDES IN PHOSPHOGYPSUM

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INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 2010

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FOREWORD

The IAEA helps its Member State laboratories to maintain their readiness and improve the quality of their analytical results by producing and distributing reference materials, through the development of standardized methods for sample collection and analysis, and by conducting interlaboratory comparisons and proficiency tests as tools for quality control of analytical results.

The IAEA started to produce reference materials in the early 1960s to meet the needs of the analytical laboratories in its Member States that required reference materials for the quality control of their measurements. Reference materials are a basic requirement for any sort of quantitative chemical and radiochemical analysis. Laboratories need them for calibration and quality control throughout their analytical work. Today, the IAEA has more than 90 reference materials and maintains a customer base of about 5000 members from more than 85 Member States.

To fulfil this obligation and ensure reliable, accurate and consistent analytical results, the IAEA Terrestrial Environment Laboratory in Seibersdorf, Austria produces reference materials and organises interlaboratory studies and proficiency tests.

As part of the continuous renewal and production efforts, the Reference Materials Group of the IAEA Terrestrial Environment Laboratory has prepared and certified a new phosphogypsum reference material the IAEA-434 characterized for Pb-210, Ra-226, Th-230, U-234 and U-238 by a group of National Metrology Institutes and expert laboratories, in cooperation with the Committee Consultative on Ionization Radiation (CCRI) of the Bureau International des Poids et Mesures (BIPM).

In this publication, details are given on the production and certification of the reference material IAEA-434 and data evaluation.

The IAEA officer responsible for this publication is A. Shakhashiro of the IAEA Environment Laboratories.

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CONTENTS

1. INTRODUCTION

Phosphogypsum is generated as a by-product of the phosphoric acid based fertilizer industry. The discharge of phosphogypsum on earth surface deposits is a potential source of enhanced natural radiation and heavy metals, and the resulting environmental impact should be considered carefully to ensure safety and compliance with environmental regulations. In addition, phosphogypsum can be used to make several building materials and it is used in agriculture as a conditioner to maintain soil productivity in areas where soils are poor and erode easily.

A reliable determination of naturally occurring radionuclides in phosphogypsum is necessary to comply with the radiation protection and environmental regulations. The IAEA-434 will assist laboratories in the IAEA Member States in validating their analytical methods for the determination of naturally occurring radionuclides in phosphogypsum and to control the quality of the produced analytical results.

Reference values for the massic activities and associated standard uncertainties were established for: Pb-210, Ra-226, Th-230, U-234 and U-238.

During sample production and certification, the requirements for reference material production and certification as stated in ISO guides 34 and 35 [1, 2] were taken into account. This report summarizes the preparation and certification process.

2. DESCRIPTION OF THE PHOSPHOGYPSUM REFERENCE MATERIAL

The IAEA-434 reference material (RM) was collected from a processing plant located in Gdansk (Poland) in 2003. The matrix composition is: $CaSO_4*2H_2O$ (96%), P_2O_5 (1-2%), F Total (1.2%), SiO_2 (1%), Al_2O_3 (0.2%).

The bulk material of phosphogypsum was received in 60 litre drums at a very high level of moisture. Then it was initially dried at 80 ºC for 36 hours. Three hundred kilograms of bulk material were processed with a grinder to a mesh size below 250 µm. Then the bulk material was dried again for 12 hours at 80 ºC down to approx 8% of moisture content.

The dried phosphogypsum was processed with an air jet-mill. The particle size distribution of the milled material was determined using Mastersizer X, Malvern Instruments. Figure 1 shows the particle distribution of the IAEA-434. It can be seen from Figure 1 that the maximum of the particle size is located around 10 µm which indicates high level of homogeneity of the material.

The milled material was homogenised in one lot in a clean atmosphere at a temperature of 20±2 °C and a relative humidity of 55%. The used homogeniser was a mixer of a 1000 litre capacity.

Bottling of IAEA-434 was done under normal laboratory conditions; 1000 bottles were filled in one day taking all precautions to avoid segregation. The bottles were labeled arranged into plastic boxes and sterilized using gamma ray irradiation with a total dose of 25 kGy using a Co-60 source.

The bottle size was 900 ml with wide secure-sealed cover to preserve the integrity of the reference material in the bottle. The amount of the material in each bottle was 250 g.

2.1. Homogeneity study

For the homogeneity study 10 bottles covering the whole bottling range were randomly selected, three independent sample portions at 12.5 g from each bottle were analyzed using gamma spectrometry for Pb-210, Ra-226, Th-230, U-234 and U-238. The homogeneity of Ra-226 was also tested by analysing three test portions of one gram from five bottles using alpha spectrometry technique. The analysis of homogeneity study was performed under repeatability conditions to minimise variations.

The standard uncertainty associated with the material heterogeneity was calculated using the formulas stated in ISO Guide 35 [2]. Single way ANOVA results were used to apply formulas 1 to 5. The slope and its uncertainty of the analytical results of 10 bottles were calculated for each measurand. The calculated statistical values were compared to the t-student critical value for a degree of freedom of 9 and probability level of 95%. From the statistical calculations there was not any significant trend observed due to the bottling process. Table 1 shows the results of the homogeneity study and trend analysis results. The outcome of the homogeneity study demonstrated that the uncertainties due to between-bottles heterogeneity u_{bb} were generally very small and the material could be considered sufficiently homogeneous for the tested radionuclides at the range of mass used.

TABLE 1: HOMOGENEITY STUDY AND TREND ANALYSIS RESULTS

Element	Pb-210	Ra-226	Th-230	U-234	U-238
u_{bb} [Bq.kg^{-1}]	5.0	3.4	0.79	0.52	0.40
u_{bb} [%]	0.76	0.45	0.36	0.41	0.33
b_1	-0.044	0.091	-0.122	-0.002	-0.001
$u(b_1)$	0.013	0.061	39.785	0.0020	0.002
$b_1 / u(b_{1)}$	-3.41	1.49	-0.003	-0.916	-0.74
Critical value: $t_{0.95,n-2}$	2.262	2.262	2.262	2.262	2.262

$$s_{wb}^2 = MS_{within} \quad (1)$$

$$s_{bb}^2 = \frac{MS_{amon\,g} - MS_{within}}{n_0} \quad (2)$$

$$s_{within}^2 = M_{within} \quad (3)$$

$$s_{between\_bottles}^2 = \frac{M_{between} - M_{within}}{n_0} \quad (4)$$

$$u_{bb} = \sqrt{\frac{s_{within}^2}{n_{bot} \cdot n} + \frac{s_{bb}^2}{n_{bot}}} \quad (5)$$

The abbreviations in Table 1 and formulae are explained in the list of abbreviations.

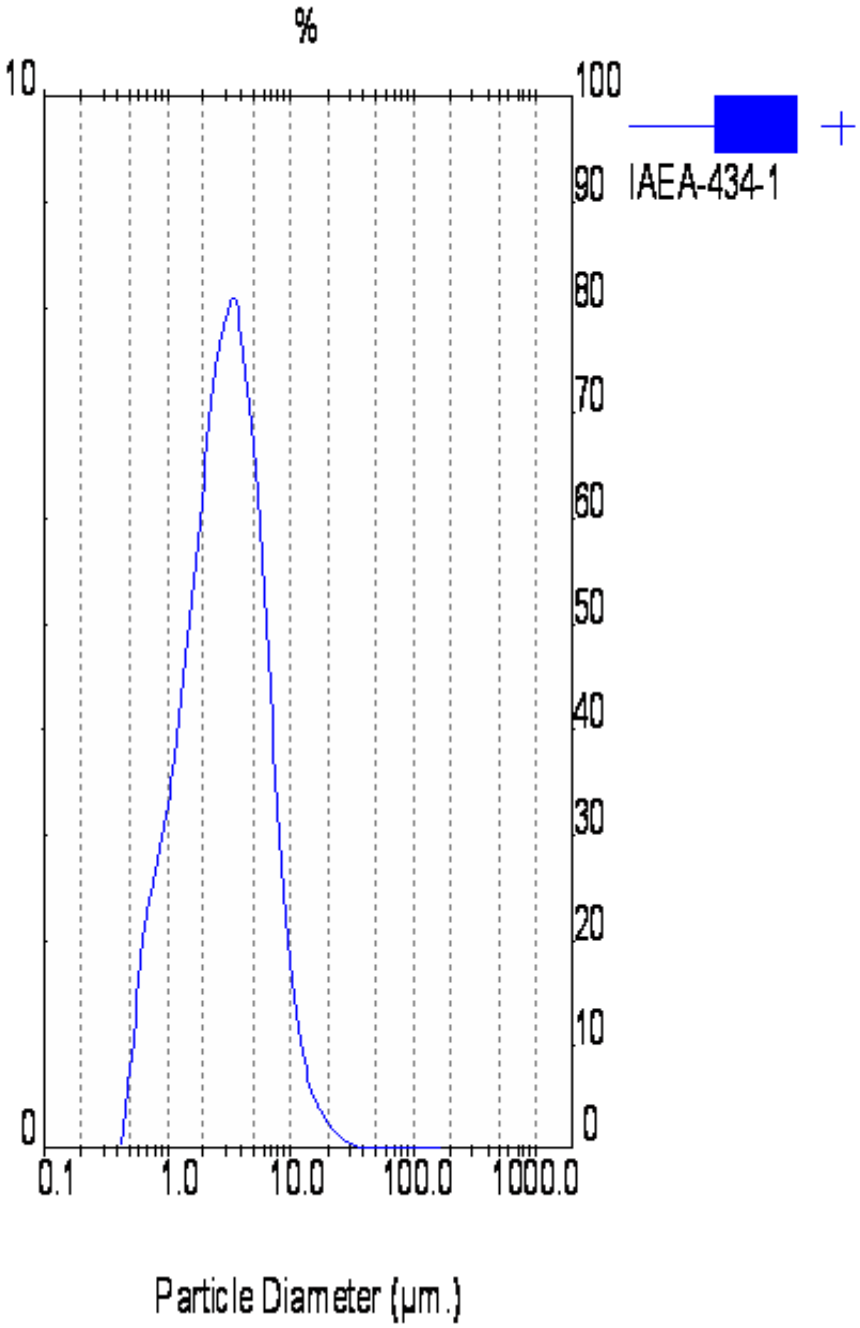

Figure 1. Particle size distribution of the IAEA-434 reference material.

Although there are indications that due to the small particle size of this material the homogeneity of the material is generally suitable even for smaller test portions, it is recommended that the minimum test portion used for analysis should be 1g. If a smaller test portion is taken the uncertainty of the property value should be expanded taking into account the relationship of mass and heterogeneity explained in the concept of Ingamels sampling constant or other related concepts [3,4,5].

3. CHARACTERIZATION

The material was initially characterized at the Terrestrial Environment Laboratory in Seibersdorf during the feasibility study phase. Then the characterization of the material took place within the interlaboratory comparison piloted by the Terrestrial Environment Laboratory in cooperation with the Consultative Committee on Ionization Radiation (CCRI) of the International Bureau des Poids et Mesure (PIBM). The results reported in this comparison were used to derive the property values of the measurands of interest.

Four National Metrology Institutes (NMI) and seven expert laboratories nominated by their respective NMI took part in the IAEA-434 interlaboratory comparison; namely: ERISS (Australia), PTB (Germany), HAA (Hungary), ARPA (Italy), KINS (Korea), KRISS (Korea), LNHB (France), MNA (Malaysia), IJS (Slovenia), AECS (Syria), and the Terrestrial Environment Laboratory (Austria). A complete list and information on the participating laboratories is given in section 7.

The interlaboratory comparison was aimed at:

- supporting calibration and measurement capability claims of National Metrology Institutes for naturally occurring radionuclides and,
- assigning the property values and associated uncertainties of the IAEA-434 phophogypsum reference material.

During the planning phase, a short analytical protocol in addition to reporting forms were prepared. The participants were asked to report the details of their analytical procedure, metrological traceability of standards and calibration, quality control procedure, uncertainty budget details, test portion mass and dissolution techniques.

Each analyst received one bottle of the phophogypsum material (randomly selected covering the whole bottling sequence) and was requested to analyze from each bottle at least 3 sub-samples following the established protocol.

Test portion mass for the analysis was proposed to be at least 1 gram for radiochemical analysis and 50 grams for gamma spectroscopy analysis. To assess the digestion difficulty of the phosphogypsum, and to assist users of the IAEA-434 in selecting the dissolution technique, the Terrestrial Environment Laboratory performed several dissolution experiments, the most effective one was based on using of HNO_3 and HF acids. The details of this dissolution procedure are reported in Appendix II.

The results of laboratories with codes 5 and 7 plotted on the charts in Appendix I were obtained using radio-chemical procedures, it can be seen that a good agreement was observed between the results obtained using gamma spectrometry and radiochemical procedures.

4. EVALUATION OF RESULTS

4.1. General

All results were collected and used as a basis for evaluation. The participating laboratories were asked to report the standard uncertainty associated with the measurement result and to report details of the uncertainty budget estimation in addition to the details of the applied quality control procedure.

4.2. Statistical screening of the combined data sets

Since the number of data sets was relatively small for many radionuclides, their statistical evaluation was expanded to cover all individual results of all methods and analysts and not only the laboratory mean values. An in-house software package developed by the Terrestrial Environment Laboratory for statistical evaluation of data was used for data screening and evaluation. Beside general descriptive statistics, the following tests are included in the program:

- Outlier tests (Dixon, Grubbs, Skewness, Kurtosis)
- Directional tests (Skewness, Kurtosis)
- Normality tests (Kolmogorov-Smirnov, Kolmogorov-Smirnov-Lilliefors)

The relative standard deviation of all measurements was below 10% for all measurands. No outlying data were observed. The directional tests did not always pass the acceptance criteria but still the Kolmogorov-Smirnov and Kolmogorov-Smirnov-Lilliefors normality tests showed normal distributions of the data sets.

4.3. Calculation of property values and associated uncertainties

The property values of all radionuclides were established on the basis of a robust approach proposed by David L. Duewer [6] and the Mixture Model Median (MM-median) of the analytical results reported by the expert laboratories was calculated. The MM-median is a direct analogue of the median. It is the location which divides the Mixture Model Probability Density Function (MM-PDF) into two sections of equal area. The MM-median is closely related to the median. It is robust to outliers and also accounts for the reported uncertainty of each measurement result.

To estimate the standard uncertainty associated with the property value the MM-median based Standard Deviation S(MM-median) was calculated from the span of the central 50% of the MM-PDF density function [6].

The calculated parameters of the homogeneity study are listed in Table 2. It can be noticed that the uncertainty associated with the between-bottles heterogeneity is reasonably small.

The variances in Table 2 (within-bottle (S^2_{wb}), between-bottle (S^2_{bb}) were obtained from single way ANOVA calculations.

TABLE 2: VARIANCES AND BETWEEN-BOTTLES UNCERTAINTIES ASSOCIATED WITH THE HETEROGENEITY OF IAEA-434

Nuclide	S^2_{wb}	S^2_{bb}	s_{bb} [%]	u_{bb} [%)]
Pb-210	210	211	2.2	0.76
Ra-226	108	35	0.8	0.45
Th-230	33	0.008	0.04	0.36
U-234	10.6	0.56	0.59	0.41
U-238	7.8	0.06	0.2	0.33

The calculations of S^2_{wb}, S^2_{bb}, s_{bb} and u_{bb} are according to formulas 1-5 which can be also found in ANNEX A of the ISO Guide [2]. The abbreviations in Table 2 are explained in the list of abbreviations.

Table 3 shows the assigned recommended values of the massic activities and associated standard uncertainties of the measurands of interest.

TABLE 3: RECOMMENDED MASSIC ACTIVITIES AND STANDARD UNCERTAINTIES OF IAEA-434

Nuclide	Reference values of the massic activities [Bq/kg dry mass]	Standard combined uncertainty* [Bq/kg dry mass]
**Pb-210	680	58
Ra-226	780	62
Th-230	211	9
U-234	120	9
U-238	120	11

**Uncertainty is expressed as a Mixture model median based standard deviation S(MM-median) at 95 % confidence level [6].*
***Reference date: 2008-January-01*

4.4. Traceability of results

The quantity values assigned to the IAEA-434 reference material are massic activities of Pb-210, Ra-226, Th-230, U-234 and U-238 expressed in the derived SI unit Bq/kg. Consensus values were derived from individual results reported by National Metrology Institutes and expert laboratories using the Mixture Model Median [6]. For all results used in the calculation of the consensus values, the utmost care was taken regarding the metrological traceability of the property values assigned to this reference material already at the planning phase and during the entire characterization process. Laboratories participating in the characterization campaign have been requested to carefully choose the calibrants and to provide the IAEA with all related information. However, the selection of measurement methods and measurement procedures, as well as respective calibrants, was based on the decision of the participating laboratory. A consequence of the use of different calibrants is the fact that the metrological chain(s) for each of the assigned quantity values respectively (combined from number of results), cannot easily be described. Therefore, the assigned property values, the massic activities, although expressed in the derived SI unit, are not intended for calibration purposes, and the reference material as such is not to be used as a calibrant.

4.5. Intended Use

This reference material is intended to be used for quality assurance purposes, basically as a quality control material for the measurement of the radiological composition of materials similar in composition to phosphogypsum, especially construction materials, for the assessment of a laboratory's analytical work and for the validation of analytical methods.

The estimated standard uncertainty is relatively large due to the consideration of the between laboratories dispersion in the calculation of the S(MM-median). It is expected that individual laboratories applying a single analytical procedure will produce results with smaller dispersion. Therefore it is recommended that the users establish their own reproducibility standard deviations to be used as a control limits for precision.

4.6. Instructions for use

Before each sub-sampling, the bottle should be shaken thoroughly to re-homogenize the powder. The recommended minimum test portion is 1 gram.

Analysts are reminded to take appropriate precautions to avoid contamination of the sample and the remaining material in the bottle.

It is recommended to store the material after the opening of the bottle in a room temperature (at 20-25 °C) or dessicator. Exposure to sunlight should be avoided.

Storage at room temperature and even temperatures up to 40 °C did not show degradation of the originally sealed phosphogypsum material.

4.7. Dry mass determination

Reference values are expressed on a dry mass basis. Therefore the analytical results need to be corrected for the moisture content of the sample at the time of analysis.

It is recommended to dry a separate sample portion of at least 1 gram for 12 hours at 80 °C. If smaller sample test portions are taken, the uncertainty on the dry mass correction factor is increased and should be taken into account for the total uncertainty calculation.

4.8. Expiry date

Based on the experience with similar materials the expiry date of the reference sheet is set to December 2020. The certificate is valid as long as the material is handled and stored in accordance with the instructions given above and the plastic container is not damaged. The IAEA is monitoring the long term stability of the material and customers will be informed in case of extension of the reference sheet beyond the expiry date and if any observed changes.

4.9. Compliance with ISO Guide 31:2000

The content of this report and associated IAEA Reference Sheet of the IAEA-434 reference material is in compliance with the ISO Guide 31:2000: Reference materials: Content of certificates and labels.

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ABBREVIATIONS

List of abbreviations in the equations and tables (number of equation and table in brackets) if not explained in the text

b_1	Slop (Table 1)
$u(b_1)$	Uncertainty of the slope (Table 1)
MS_{among}	Mean square (ANOVA) between bottles (2)
MS_{within}	Mean square (ANOVA) within bottles (1, 2, 3)
n	Number of observations (5)
n_{bot}	Number of bottles (5)
n_0	(Effective) number of (sub) group members (for complete data sets $n=n_0$) (2, 3)
s_{bb}^2	Variance between bottles (Table 2)
$S(MM\text{-}median)$	Standard deviation of Mixture Model Median
s_{wb}^2	Variance within bottles (Table 2)
u_{bb}	Uncertainty related to between bottle variations (Table 2)
U	Expanded uncertainty (coverage factor 2 for 95% probability) (Appendix I)

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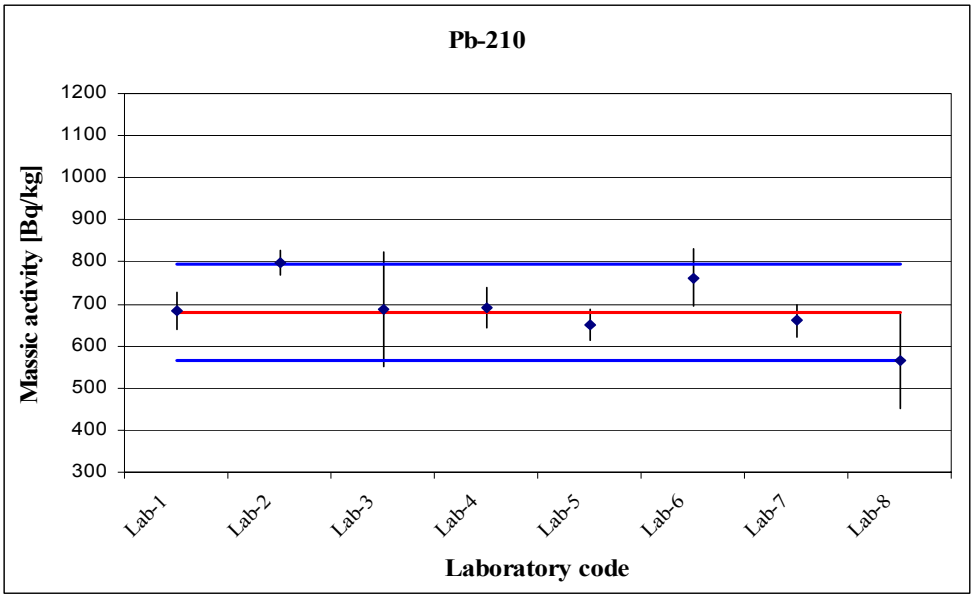
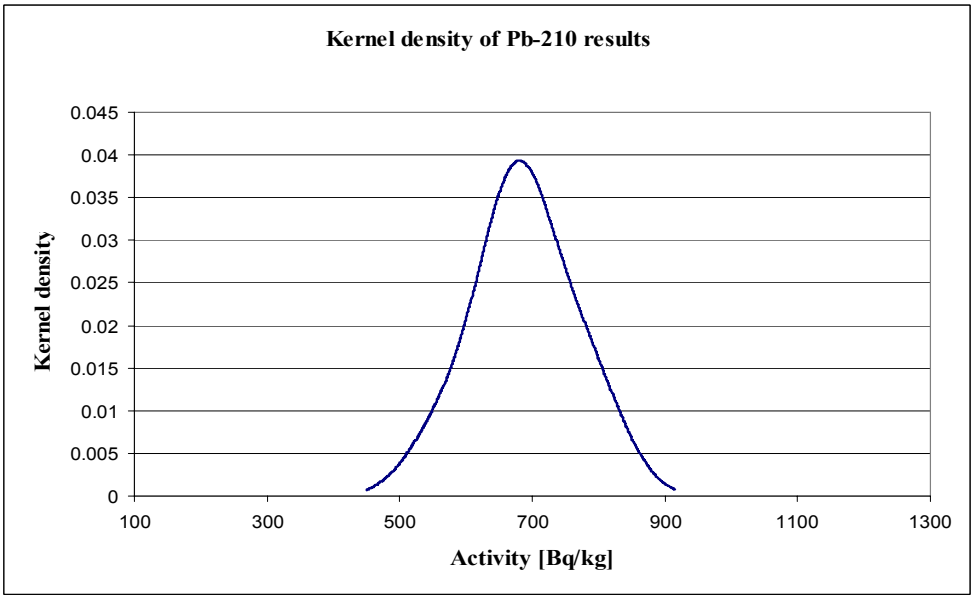
APPENDIX I
GRAPHICAL PRESENTATION OF THE RECOMMENDED VALUES AND ASSOCIATED UNCERTAINTIES

The recommended values are reported as Mixture model median of the analytical results for all techniques and laboratories used for the certification. Recommended values are reported with expanded uncertainty U (k = 2) which was derived from the standard deviation of the Mixture model median.

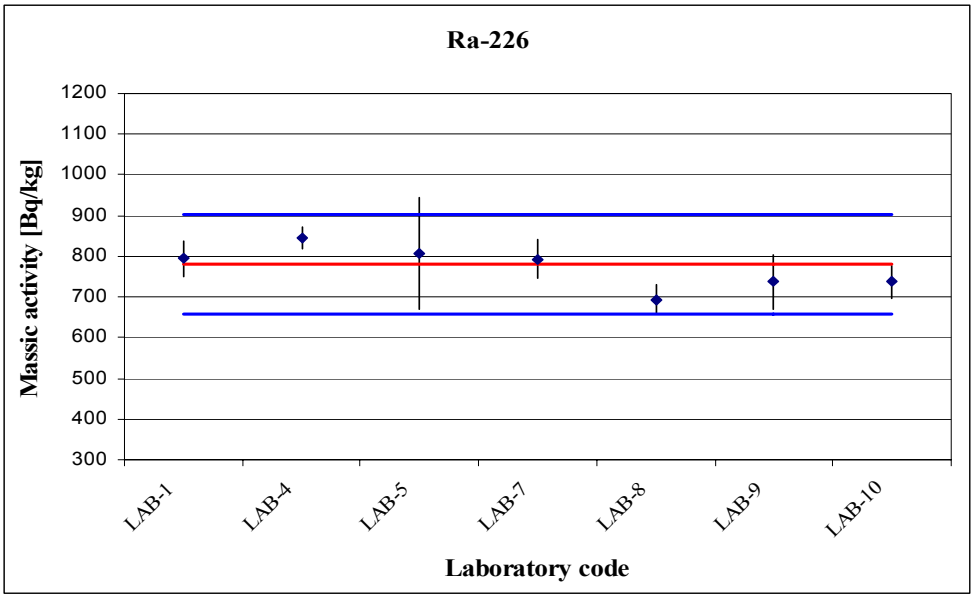
The red line represents the derived recommended value, the blue line represents the property value ± U (k = 2).

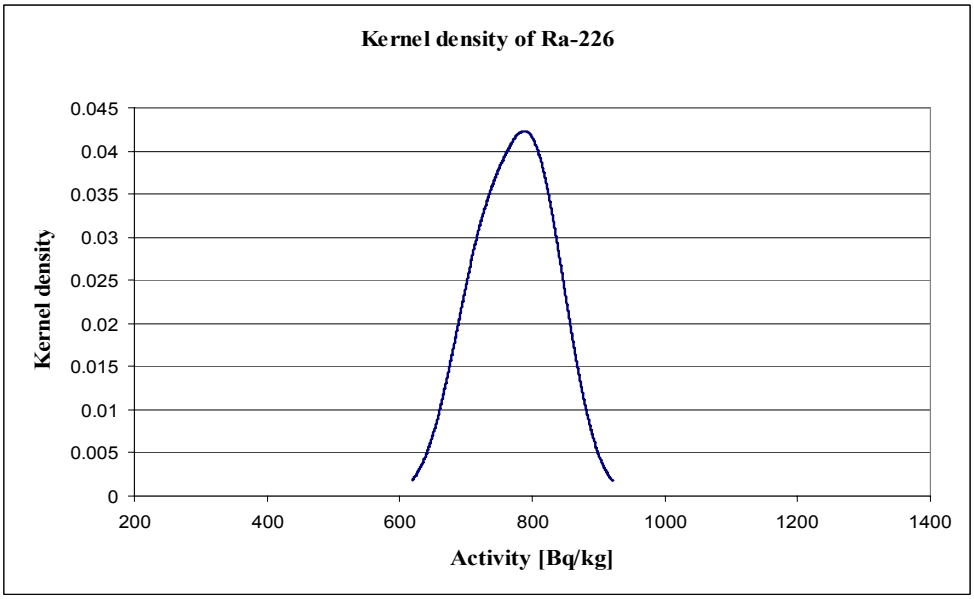
IAEA 434: Naturally occurring radionuclides in phosphogypsum
Laboratory means and recommended value ± U for Pb-210



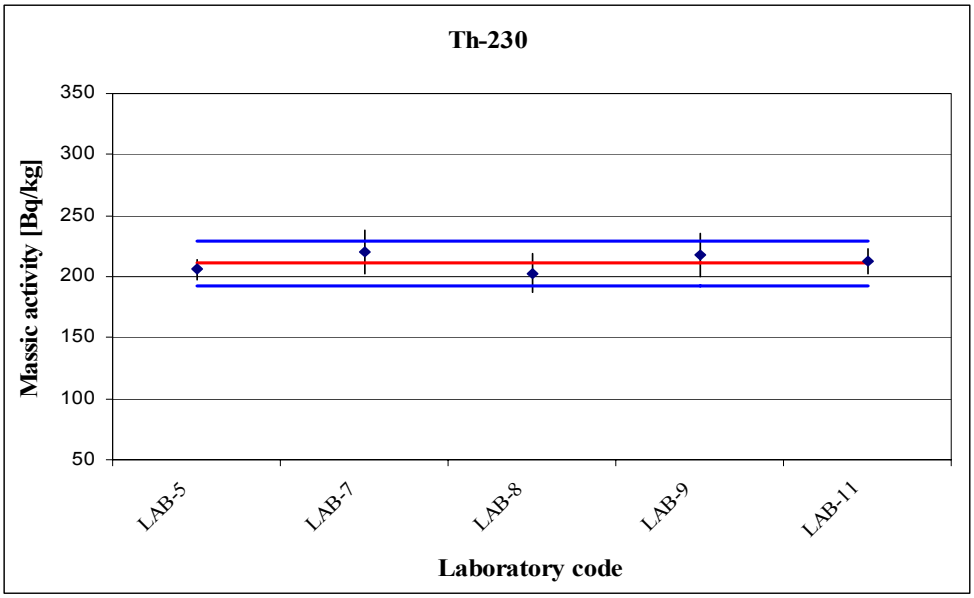


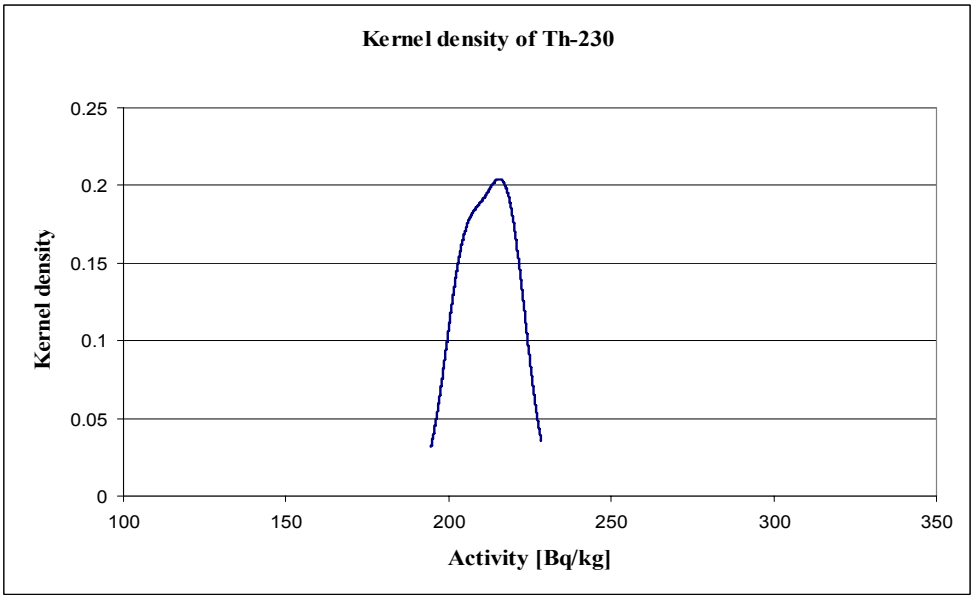
IAEA 434: Naturally occurring radionuclides in phosphogypsum
Laboratory means and recommended value ± U for Ra-226





IAEA 434: Naturally occurring radionuclides in phosphogypsum
Laboratory means and recommended value ± U for Th-230





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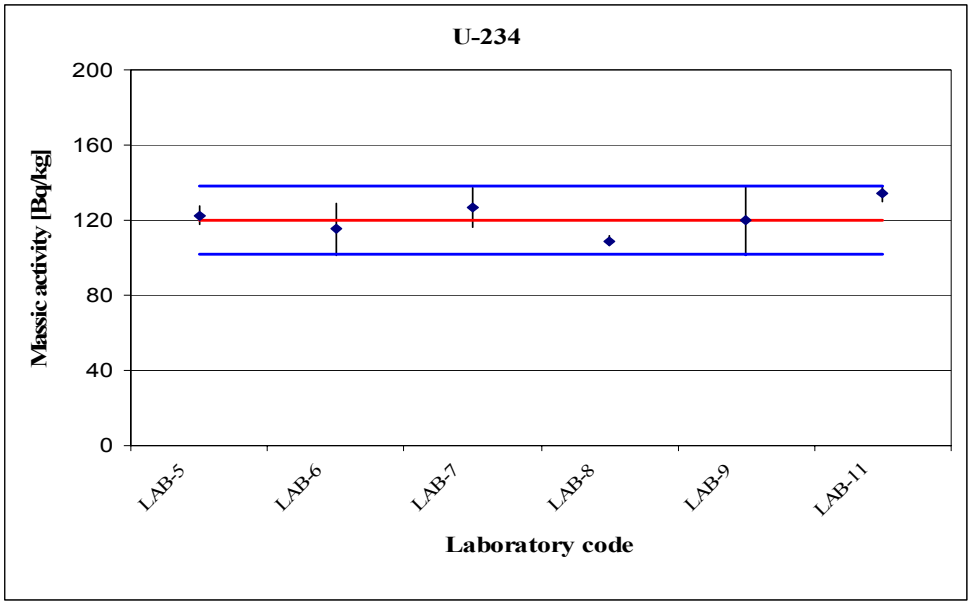
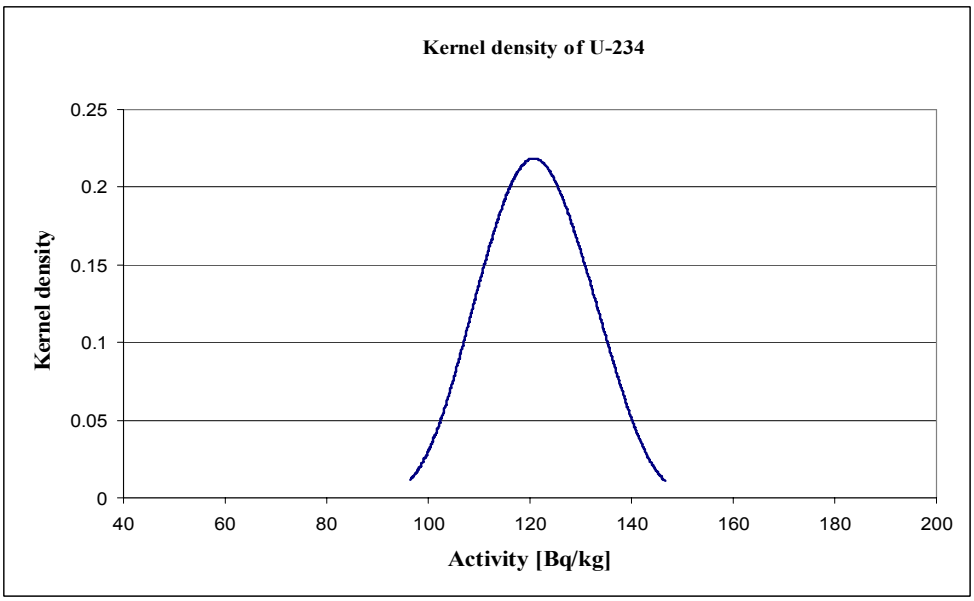
Laboratory means and recommended value ± U for U-234





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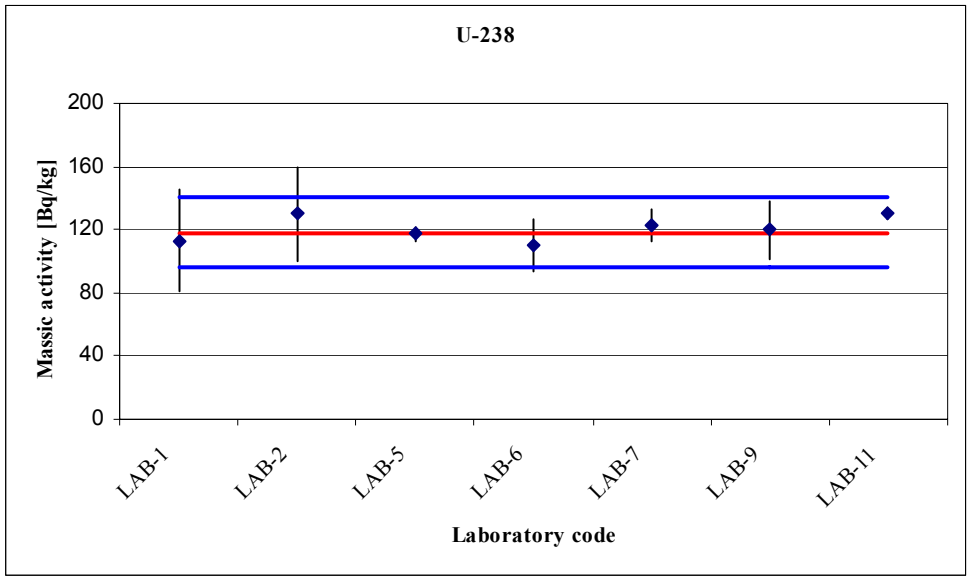
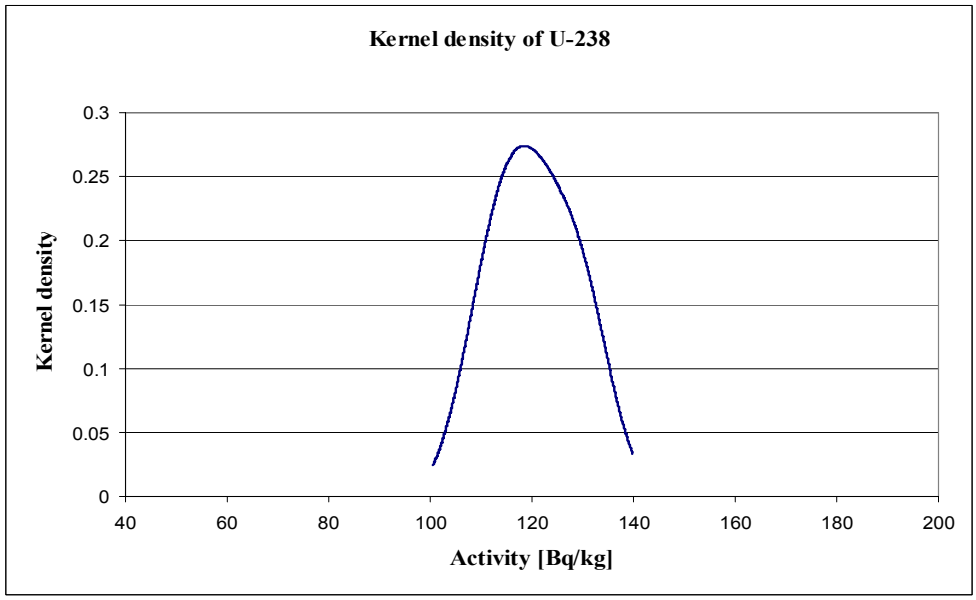
Laboratory means and recommended value ± U for U-238





APPENDIX II
TECHNICAL INFORMATION ON THE DISSOLUTION PROCEDURES USED IN THE IAEA LABORATORIES

Technique and method used

The Po-210, Pb-210 and the U and Th isotopes were separated applying a sequential radiochemical procedure, using extraction chromatography. Than U, Th isotopes and Po-210 were determined by isotope dilution alpha-spectrometry and Pb-210 by Liquid Scintillation Spectrometry.

Description of analytical method

(1) Dissolution of phosphogypsum

0.5 g aliquots of the phosphogypsum were transferred into microwave containers, about 30 mg of Pb^{2+} carrier, about 0.4 Bq of Po-209 and 0.04 Bq of U-232 (containing Th-228 daughter in known ratio close to 1) tracers and 15ml 65% HNO_3 were added, and the microwave digestion shown in Figure 1 was applied. After digestion the sample solutions were then transferred to plastic centrifuge tubes and centrifuged for 10 minutes at 3000 rpm. The supernatants were transferred to Teflon beakers and the residues were transferred back into the microwave containers with 3 ml HNO_3 and 2 ml of 40% HF. The residues were digested again using the same microwave program achieving complete sample dissolution. The solutions of the residues were combined with their supernatants, and then evaporated with three portions of 5 ml of 65% HNO_3 to remove HF and than dissolved in 30 ml of 2M HCl and 0.1 g H_3BO_3.

(2) Separation of Pb-210, U and Th radioisotopes using SrResin, TEVA and UTEVA

After sample digestion, polonium and lead were separated using the method proposed by Vajda et. al [7]. The solution was loaded on SrResin column preconditioned in advance with 100 ml 2 M HCl. The column was rinsed with 100 ml of 2 M HCl and 25 ml 6 M HNO_3 to remove the non-retained ions. The effluent and washing solutions were combined and used for analysis of uranium and thorium. Polonium was stripped with 60ml 6 M HNO_3, and then lead was eluted with 60 ml 6 M HCl.

The effluent and the washing solution from SrResin column were combined and then evaporated to dryness. The residue was dissolved in 20 ml 3 M HNO_3 and then loaded onto TEVA column which was in advance preconditioned with 20 ml of 3 M HNO_3. The columns were washed with 10 ml of 3 M HNO_3. The washing solution was combined with the effluent from the TEVA column for analysis of uranium. After additional washing with 20 ml of 3 M HNO_3, 20 ml 8 M HCl was used to elute Th.

The combined effluent and washing solution from the TEVA column was directly loaded onto UTEVA column which was in advance preconditioned with 20 ml of 3 M HNO_3. The column was washed with 30 ml of 3 M HNO_3, 5 ml 9 M HCl and followed by 15 ml 6 M HCl to remove any Po and Th remaining on the column. Finally, the uranium on the UTEVA column was eluted with 6 ml H_2O.

(3) Source preparation

Polonium solution was carefully evaporated to dryness. The residue was taken with 10 ml 0.5 M HCl transferred into a Teflon deposition cell, the pH of the solution was adjusted to 1 using 6 M NaOH. Polonium was auto-deposited onto silver disc at 90°C for 90 min with stirring the solution, and then measured by alpha-spectrometry.

The Pb fraction was evaporated 3 times with 2 mL of 65% HNO_3. The residue was dissolved in 20 ml 1 M HNO_3, add 0.400 g oxalic acid to warm solution and adjust the pH to 3-5 with $NH_{3(aq)}$ to precipitate Pb-oxalate. The Pb-oxalate precipitate was filtered through a pre-weighed filter paper (∅ 24 mm). The filter was washed with 3*1 mL water and 2 mL of ethanol, dried in oven at 40-50 ^{o}C, cooled in a desiccator and weighted to determine the mass of lead-oxalate and the chemical recovery gravimetrically. The lead-oxalate precipitate was transferred together with the filter into liquid scintillation vial, dissolved in 1 mL 6 M HNO_3 and mixed it with 14 mL 'INSTA-GEL PLUS' liquid scintillation cocktail. $^{Pb-210}$ was determined by liquid scintillation spectrometry.

U and Th fractions were three times evaporated with few ml of 65% HNO_3, respectively. The residues were dissolved in 10 ml of 10% $(NH_4)_2SO_4$ plating solution with pH 2 and transferred into electro-deposition cell. U and Th were electrodeposited onto stainless steel discs at 0.97A for 90 min, respectively and then measured by alpha-spectrometry.

The activities of U, Th and Po-210 were determined by isotope dilution alpha-spectrometry.

The Th-228 daughter of U-232 was used as a tracer for the determination of Th-230 and Th-232.

The natural Th-228 content of the samples was low, and it was taken into correction by analysing the Th isotopic ratios of sample blanks (samples analysed without addition of tracers and carrier).

(4) Instrumentation

Alpha-spectrometer system: EG & G ORTEC OCTETE, with EG & G Ultra BU-020-450-AS PIPS detectors, Canberra AMX 884 multiplexer, RPI 554, ADC 8701 and AIM556 modules.

The alpha spectra were collected and evaluated using Canberra Genie 2000 software.

WALLAC QUANTULUS 1220 Liquid Scintillation Spectrometer: Liquid Scintillation Spectra were collected and evaluated using Wallac WINQ v. 1.1 and EASY view v.1.0.3.4.

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