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Portable X-ray fluorescence system to measure Th and U concentrations

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ABSTRACT

This study reports the results obtained in the analysis of waste material samples generated by the industries of phosphate fertilizers, in particular, the use of specific filters in a portable X-ray fluorescence system, a simple equipment allowing the characterization, identification and quantification of low concentrations of Th and U (ppm). The industrial byproduct is classified as a Technologically-Enhanced, Naturally-Occurring Radioactive Material - TENORM, and therefore requires monitoring for its radio-toxic activity due to the presence of radioactive thorium and uranium families. From the results obtained, it is concluded that this technique is able to determine the contents of these elements to concentrations of tens of ppm in measurements of about 300 s, and a small sample amount (~0.1 g).

1. Introduction

The identification and detection of naturally occurring radioactive elements with low concentrations, such as Th and U are important in earth sciences, e.g., chronology, paleoclimatology (Broecker and Thurber, 1965), archeology (Holen et al., 2017), hydrology, geochemistry and oceanography due to their application as a chronometer and tracers in these areas (Schumann et al., 2017). In nuclear research, specifically in dosimetry, the radionuclides in the uranium and thorium decay chains are major contributors to gamma-emitting natural radiation from primordial radionuclides (UNSCEAR, 2002; UNSCEAR, 2008). Therefore, the development of analytical techniques to be used in the identification and the determination of their concentration play a major role in this research area (Nielson et al., 1977; Docenko et al., 2009). To determine thorium and uranium concentrations standard techniques are used (Tuovinen et al., 2015; Bártová et al., 2017; Chuan-Chou et al., 2002). In the ICPMS technique (Inductively Coupled Plasma Mass Spectrometry) (Chuan-Chou et al., 2002; Gennari et al., 2013), several steps in the sample preparation are required. This is an accurate technique, but the results may be strongly dependent on the sample solubilization process (Gennari et al., 2013).

For NAA (Neutron Activation Analysis) (Landsberger et al., 2015; Zamboni et al., 2007), another technique widely used, access to a Nuclear Reactor Facility is necessary. In this methodology, the gamma-ray activities induced by thermal and epithermal neutrons are measured. This technique requires an acquisition system and analysis of specified data for gamma-ray spectrometry (Pereira et al., 2013; Medina et al., 2013; Gamma Spectrometry and Last, 2017; Silveira et al, 2010, 2015). It is noted that the aforementioned techniques require sophisticated equipment, properly prepared samples and sometimes, in the case of NAA, difficult accessibility. A simpler and widely used method to quantify thorium and uranium concentration is Gamma-ray Spectrometry (Medina et al., 2013; Gamma Spectrometry and Last, 2017; Silveira et al, 2010, 2015), which requires large quantity of samples, compared to the other two techniques. In this case, the detection is performed with a scintillator detector such as NaI(Tl) or a semiconductor HPGe detector, which requires low temperature. Given the above, it is necessary to develop an alternative analytical methodology to measure low concentrations of these radioactive elements in small amounts of material. The main goal of this work is the development of a methodology of identification and quantification of Th and U in naturally radioactive materials through rapid analysis (seconds), sensitive (ppm) and non-destructive, since it can be used for the analysis of small amount of materials (~mg), and with a simple preparation.

1.1. TENORM materials

Naturally occurring radionuclides of terrestrial origin, also called primordial radionuclides, are present in various degrees in the environment, however, only those radionuclides with half-lives comparable to the age of the earth, and their decay products, exist in significant quantities in these materials. Therefore, since these radionuclides are

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present at trace levels in all soils, which are related to the types of rock from which the soils and rock originate, the exposures to natural radiation sources can be modified by human practices.

Industries use many different raw materials containing naturally occurring radioactive materials (NORM) which are mined, transported, and processed for further use (UNSCEAR, 2002; UNSCEAR, 2008; Pereira et al., 2013; Aguiar et al., 2010). Among the main industries that produce materials leading to naturally radioactive waste is the industry of phosphate processing to fertilizer production. During all physical and chemical processing steps used in the extraction of rock phosphate to produce the primary product, phosphoric acid, several by-products can be generated, known to contain naturally-occurring radioactive material (TENORM) (Pereira et al., 2013; Silveira et al, 2010, 2015; Aguiar et al., 2010).

Due to the large production of phosphoric acid and waste, it is very important to reduce the waste production or to reuse the wastes generated during the production processes (Silveira et al., 2010; Aguiar et al., 2010). This research was developed with samples, provided by Vale Fertilizantes S.A., a Brazilian industry, of waste from a magnetic separation step of the phosphate rock physical treatment process during phosphoric acid production (Pereira et al., 2013; Silveira et al., 2015). This waste is naturally radioactive and presents a large content of titanium, which has great commercial interest (Pereira et al., 2013). In order to reuse this waste through the extraction of titanium oxide, which is in the solid form, it was submitted to a series of solubility tests using sulfuric, hydrochloric and nitric acids and sodium hydroxide in order to concentrate the titanium dioxide present in the sample (Pereira et al., 2013; Li et al., 2006).

The resulting solid material from this extraction was properly identified and quantified by Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF). Specifically, the traces of the elements U and Th were also identified. This methodology to determine Th and U concentration in low mass samples is very important to better understand the extraction process that creates the waste considered TENORM (Nielson et al., 1977; Docenko et al., 2009; Pereira et al., 2013; Mazumder and Mishra, 2010).

2. Methodology and experimental procedure

It is important to investigate and quantify natural radiation present in TENORM materials, since these materials are generated in large quantities (UNSCEAR, 2002; UNSCEAR, 2008; Pereira et al., 2013; Silveira et al., 2015). This justifies the need for efficient analytical techniques, rapid and capable of analyzing samples in small quantities. A method using Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF) may be a viable alternative to be implemented as an analytical technique for determining the presence of Th and U in these samples (Pereira et al., 2013; Mazumder and Mishra, 2010; Vogel, 2002; Natarajan et al., 2012; Trojek and echák, 2015; Bleicher and Sasaki, 2000; Central Analítica, 2012). The X ray fluorescence methods have high practicality and ability to resolve the characteristic peaks of energy, showing a high efficiency for heavier elements. The data acquisition system is simple and portable, using an X-ray source to excite the chemical elements and a silicon detector for the emitted radiation (Potts and West, 2008). It is noteworthy that the EDXRF presents high potentiality to identify and quantify the chemical element constituents of the samples with atomic number greater than that of Al.

The waste material samples generated by the industries of phosphate fertilizers were subjected to a series of solubilization procedures using sulfuric acid, hydrochloric acid, nitric acid and sodium hydroxide in order to concentrate the titanium dioxide (Trojek and echák, 2015; Bleicher and Sasaki, 2000; Central Analítica, 2012). After solubilization, a solid phase was obtained. This small sample was analyzed using a portable EDXRF (Potts and West, 2008) in order to identify and quantify the uranium and thorium among the elements that were concentrated.

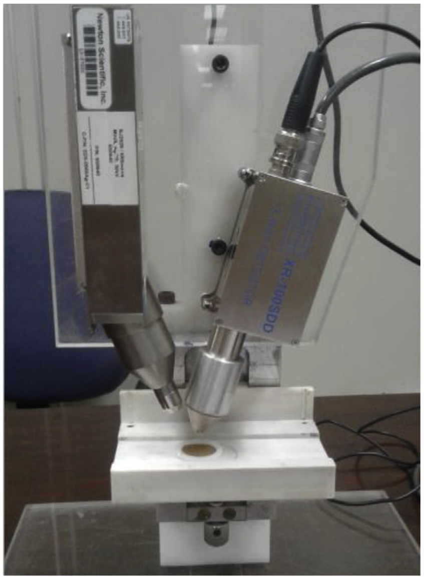

Fig. 1. Portable XRF System with a mini X-ray tube and a Si-Drift X-ray semiconductor detector. The W and Al foil filters were placed in front of the X-ray emission tube.

Due to the low concentration of U and Th in the material and the small amounts of sample obtained after the chemical process (0.07(1) g), the EDXRF technique was applied for thorium and uranium investigation, allowing determination of the radionuclide contribution to the natural radioactivity in several different regions of the thin powder sample.

The portable X-ray fluorescence (pXRF) Amptek® setup, a commercial system, uses a mini X-ray tube which operates with voltages ranging from 10 to 50 kV and currents of 5–200 μA with a silver (Ag) transmission target. The detector used is a Si Drift X-ray semiconductor (25 mm^2 × 500 μm/0.5 mil) with a thin beryllium end window of 3.8 cm, which is a new high-performance X-ray detector, with an energy resolution of 125 eV FWHM at @ 5.9 keV (^{55}Fe). The pXRF system used in this work is shown in Fig. 1. This whole system is very light (~0.5 kg) and can be mounted in other geometries depending on the sample size, being much more versatile than other X-ray bench systems. The measurements were carried out with 30 kV voltage applied on the tube, 5 μA of tube current and an excitation/detection time of 300 s (live time) with a fixed distance of13(1) mm.

The characteristic X-ray emitted by the Ag source is predominantly $E_{K\alpha}$ = 22.16 keV and $E_{K\beta}$ = 24.94 keV. However, the voltage applied to the X-ray tube was 30 kV, allowing the production of X-rays with energy up to 30 keV.

In the U and Th measurements, a filter of W and Al foil in the exit of the X-ray tube was also used. The spectra were analyzed with QXAS-AXIL software from the International Atomic Energy Agency (IAEA) (QXAS, 2007).

In Fig. 2, the best filter sequence found to reveal the X-ray energy

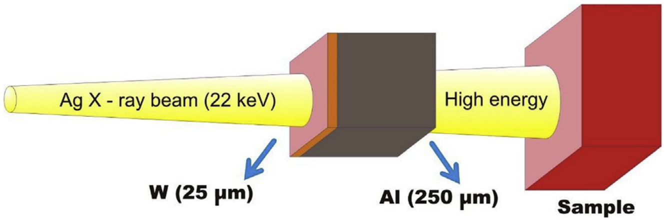

Fig. 2. Schematic view of the filter sequence used to absorb the low-energy emissions and reduce the background with the advantage of an improved discrimination.

peaks emitted by Th and U elements is shown. In this case, the filters absorb the low-energy emissions of the X-ray tube and reduce the background with the advantage of an improved X-ray peak discrimination. Without the filters, low energy X-rays emitted by the silver source excite low atomic number elements without exciting the heavy element atoms such as Th and U. With the filters, the excitation probability of Th and U atoms will be the same, but now without the background contribution due to low-energy excitation. The apparatus used permitted easy placement of filters in any desired order, making it possible to detect high-Z atoms easily.

In this study, the samples were analyzed in powder form with granulometric homogeneity. Measurements were made in various regions of each sample analyzed in order to verify the reproducibility of the results. In this analysis, the sample concentration values were obtained by using the IAEA quality assurance reference materials: RGU-238 and RGTh-232, prepared in the same geometry of the sample (IAEA). The standard concentration values for ^{238}U and ^{232}Th are (400 ± 2) μgU/g and (800 ± 16) μg Th/g.

3. Results and discussion

In Figs. 3 and 4, the filter effect in the EDXRF spectra obtained for thorium and uranium standard samples can be clearly observed. It can be noted that the use of filters decreases the count in the acquisition of data, reducing drastically low-energy emission signals of the sample below 10 keV and the Compton scattering. By means of the X-ray spectra presented in these figures, the main lines for Uranium ($L_\alpha = 13.61$ keV, $L_\beta = 17.22$ keV) and Thorium ($L_\alpha = 12.97$ keV, $L_\beta = 16.20$ keV) are very clear.

Due to the easier detection of Th and U X-ray peaks with the filter system discussed above, this technique was used to analyze a residue derived from one of the steps of physical handling of the phosphate rock. In Fig. 5, the X-ray fluorescence spectrum of a solid sample obtained after HCL treatment is shown. This X-ray spectrum shows evidence of the Th and U characteristic peaks using the filters. It is worth emphasizing that the sample analyzed was a small quantity, about 10 mg, containing thorium and uranium as trace elements, this being a reason to invest in X-ray fluorescence for analysis. This technique requires simple data analysis, is a non-destructive technique and requires no prior preparation. Since it is a non-destructive technique, the sample can be further analyzed by other techniques. The acquisition time used to obtain this X-ray spectrum was about 300 s.

In Fig. 5, the X-ray fluorescence spectrum allows us to obtain also information on the presence of Ti, Fe, Sr and Ni elements, with high precision, for elements with atomic number equal to or greater than Z = 14. Through the analysis of this spectrum, it is possible to quantify the concentrations of elements Th and U as 50 (5) ppm and 200 (20) ppm, respectively. In this analysis the X-ray peak areas of this spectrum were normalized with the standard peak areas. The results show that this technique can be used to extract, with the proper use of X-ray filters, information on the heavy elements, due to the ionization of the L layer (Nielson et al., 1977). In Figs. 6 and 7, X-ray fluorescence spectra obtained with different acquisition times are displayed. These spectra indicate that it is possible to detect traces of thorium and uranium with low acquisition times (tens of seconds) with a small amount of mass (only few milligrams) without complex sample preparation. With this methodology, even with a low acquisition time of about 50 s, it is possible to obtain the suggestion of a measurable peak in the Lα energy region of Th and U.

The time detection limits for the standard samples were estimates using the integrated area of each spectrum as a function of a different acquisition times. In Fig. 8, the X-ray peak area for Th and U as a function of the acquisition time are presented, indicating that less than one minute is enough to have about 10% error in the Th and U sample concentration.

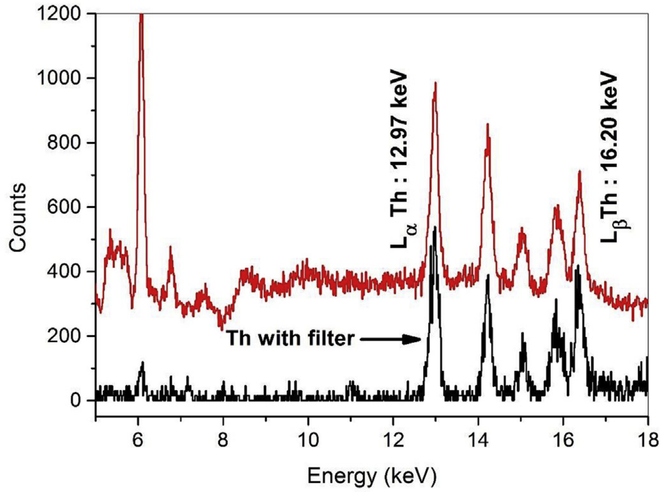

Fig. 3. X-ray spectra obtained for a thorium standard sample (IAEA-RGTh-232) with and without filter. The X-ray peaks with energies lower than 10 keV practically disappear when the filters are used.

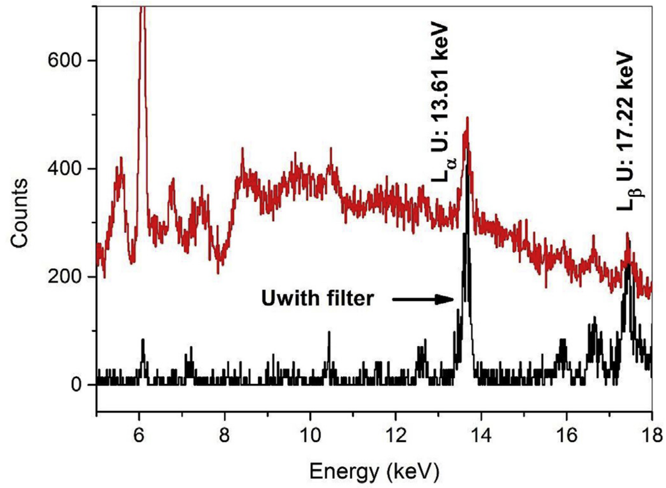

Fig. 4. X-ray spectra obtained for a uranium standard sample (IAEA – RGU-238) with and without filter. The X-ray peaks with energies lower than 10 keV practically disappear when the filters are used.

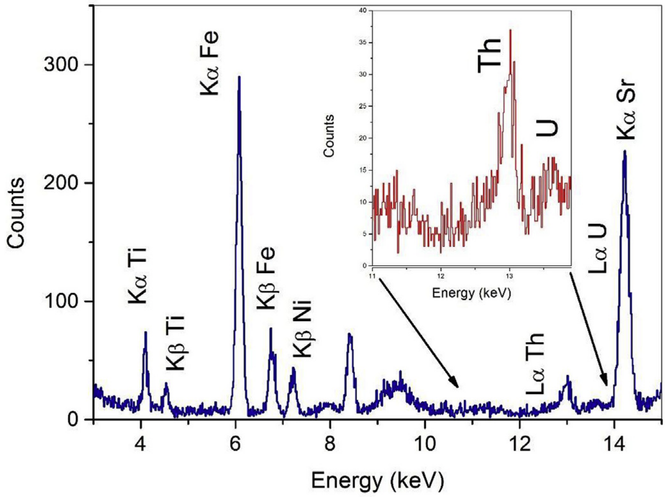

Fig. 5. Typical X -ray fluorescence spectrum of solid sample obtained after HCl treatment. It is possible to identify the presence of Th and U X-ray peaks.

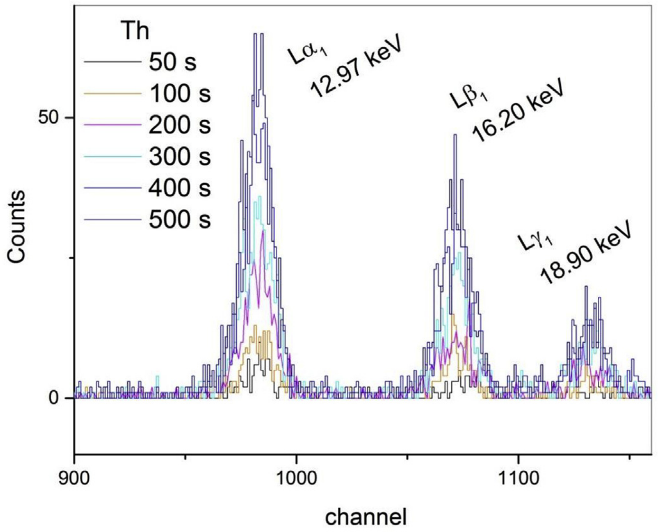

Fig. 6. X -ray fluorescence spectra obtained with different acquisition times. The X-lines for the solid sample, obtained after HCl treatment, are shown.

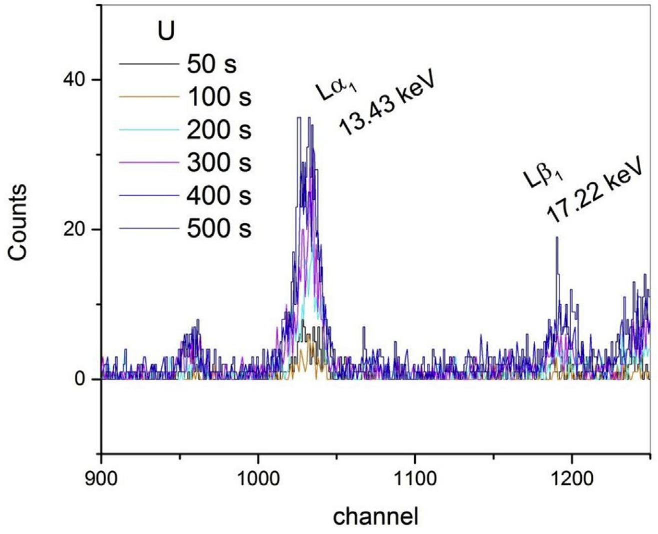

Fig. 7. X -ray fluorescence spectra obtained with different acquisition times. U X-lines for the solid sample, obtained after HCl treatment, are shown.

4. Conclusions

In this work, the concentrations of Th and U in a sample of about 100 mg, obtained after the chemical processing of an industrial waste considered TENORM, were determined through the Energy Dispersive X-ray Fluorescence (ED-XRF) technique. Using a filter system, with an acquisition time of hundreds of seconds, it is possible to identify and quantify Th and U elemental traces with concentrations of the order of tens of ppm. These results indicate that the ED-XRF, using appropriate filters, is fast, inexpensive and an efficient technique to analyze Th and U even with small concentrations. This non-destructive technique is able to determine the contents of elements with concentrations of the order of tens of ppm, with a short measurement time using a portable ED-XRF spectrometry.

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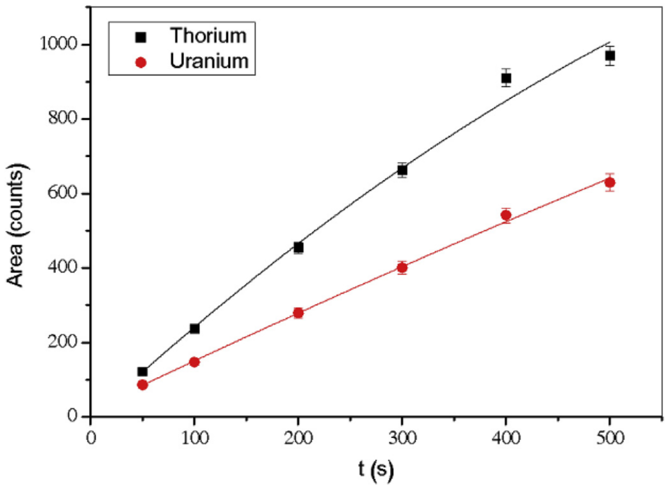

Fig. 8. X-ray peak area for Th and U as a function of the acquisition time. This plot indicates the time detection limit for Th and U using W and Al sandwich filters.

References

Aguiar, V.A.P., Medina, N.H., Moreira, R.H., Silveira, M.A.G., 2010. Absorbed gamma-ray doses due to natural radionuclides in building materials. In: AIP Conference Proceedings, vol. 1245. pp. 98.

Bártová, H., Kučera, J., Musílek, L., Trojek, T., Gregorová, E., 2017. Determination of U, Th and K in bricks by gamma-ray spectrometry, X-ray fluorescence analysis and neutron activation analysis. Radiat. Phys. Chem. 140, 161–166.

Bleicher, L., Sasaki, J.M., 2000. Introdução à difração de raio X em cristais. Universidade Federal do Ceará, Fortaleza Last accessed July 2017. http://www.agracadaquimica.com.br/quimica/arealegal/outros/173.pdf.

Broecker, W.S., Thurber, D.L., 1965. Uranium-series dating of corals and oolites from Bahaman and Florida key limestones. Science. 149, 58–60.

Central Analítica, 2012. Espectrometria de emissão atômica. Instituto de Química-USP, São Paulo Last accessed July 2017. http://ca.iq.usp.br/conteudo2.php?itemid=31&alt=ICP-AES&c=&paiid=16.

Chuan-Chou, Shen, Lawrence Edward, R., et al., 2002. Uranium and thorium isotopic and concentration measurements by magnetic sector inductively coupled plasma mass spectrometry. Chem. Geol. 185, 165–178.

Docenko, D., Gostilo, V., Sokolov, A., Rozite, A., 2009. On-line measurement of uranium in ores using XRF analyzer P2 Con-X. Available in IAEA-TECDOC-CD—1739. In: Proceedings of an International Symposium Organized by the International Atomic Energy Agency in Cooperation with the OECD Nuclear Energy Agency, the Nuclear Energy Institute and the World Nuclear Association Held in Vienna, Austria, pp. 22–26.

Gamma Spectrometry, Last accessed July 2017 http://www.gammaspectrometry.co.uk/examples.

Gennari, R.F., Garcia, I., Medina, N.H., Silveira, M.A.G., 2013. Sequential chemical extraction for a phosphogypsum environmental impact evaluation. In: Aip Conf. Proc., XXXV Brazilian Workshop on Nuclear Physics, vol. 1529. pp. 52–55.

Holen, R., Deméré, T.A., et al., 2017. A 130,000-year-old archaeological site in southern California, USA. Nature 544, 479–483.

Landsberger, S., Lara, R., Landsberger, S.G., 2015. Non-destructive determination of uranium, thorium and 40K in tobacco and their implication on radiation dose levels to the human body. Radiat. Protect. Dosim. 167 (1–3), 243–246.

Li, C., Liang, B., Chen, S., Jul. 2006. Combined milling dissolution of Panzhihua ilmenite in sulfuric acid. Hydrometallurgy 82, 93–99. http://www.sciencedirect.com/science/article/pii/S0304386X06001010.

Mazumder, B., Mishra, B.K., 2010. Managing Wastes from Aluminum Smelter Plants. Woodhead Publishing.

Medina, N.H., Silveira, M.A.G., Santos, R.B.B., 2013. Dynamic distribution of potassium in sugarcane. Journal of Environmental Radioactivity. 126, 172–175.

Natarajan, V., Porwal, N.K., Godbole, S.V., 2012. Indian J. Chem. Technol. 19, 399–402.

Nielson, K.K., Wogman, N.A., Brodzinski, R.L., 1977. X-ray fluorescence capabilities for uranium ore analysis. K. K., BNWL-SA-6223 available. 26. In: Annual Conference on Applications of X-ray Analysis, Denver, CO, USA.

Pereira, B.R., Silveira, M.A.G., et al., 2013. Titanium extraction from waste NORM. In: X Latin American Symposium on nuclear Physics and Applications (X LASNPA), PoS.

Potts, P.J., West, M., 2008. Portable X-Ray Fluorescence Spectrometry: Capabilities for in Situ Analysis. RSC Publishing, Cambridge England and references therein.

IAEA Referential Materials, Last accessed July 2017. http://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials/Radionuclides/index.htm.

Schumann, R.R., Zielinski, R.A., Otton, J.K., Pantea, M.P., Orem, W.H., 2017. Stratigraphic, Geochemical, and Hydrologic Data for the Boston Peak Wetland, Larimer County, CO, USA. U.S. Geological Survey data release. .

Silveira, M.A.G., et al., 2010. VIII Latin American symposium on nuclear physics and applications. In: American Institute of Physics Conference Proceedings, vol. 1265. pp. 465–466.

Silveira, M.A.G., Cardoso, L.L., Medina, N.H., 2015. Natural radiation in byproducts of the production of phosphoric acid. Brazilian Journal of radiation Science 3 (No 1A).

Trojek, T., echák, T.C., 2015. Detection of terrestrial radionuclides with x-ray fluorescence analysis. Radiat. Protect. Dosim. 164 (No. 4), 529–532.

Tuovinen, H., Vesterbacka, D., Pohjolainen, E., Read, D., Solatie, D., Lehto, J., 2015. A comparison of analytical methods for determining uranium and thorium in ores and mill tailings. Journal of Geochemical Exploration Volume 148, 174–180.

UNSCEAR, 2002. Annex B. New York. United Nations Scientific Committee on the Effects of Atomic Radiation, New York.

UNSCEAR, 2008. Annex B. New York. United Nations Scientific Committee on the Effects of Atomic Radiation, New York.

Vogel, A.L., 2002. Análise Química Quantitativa. 6°. LTC, Rio de Janeiro, pp. 347–350.

Zamboni, C., Silveira, M.A.G., Medina, N.H., 2007. In: AIP Conf. Proc, VII Latin American Symposium on Nuclear Physics and Application, Cuzco.

QXAS – Quantitative X-ray Analisis System. Last accessed July 2017, http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/41/115/41115593.pdf.