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# RADIOCHEMICAL PROCEDURES FOR DETERMINATION OF NATURALLY OCCURRED URANIUM ISOTOPES IN ENVIRONMENTAL SAMPLES

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ABSTRACT

In the present paper different methods for uranium determination in the environmental samples are discussed. The developed procedure in the framework of IAEA Contract No 11298 for more precise determination of the uranium isotopes concentration in the soil and rock materials is presented. This methodology is very suitable for the regions where geo-ecology of uranium is disturbed. The main steps in the procedure described and discussed in this study are: 1) isotopic delution by use of the tracer $^{232}$U for chemical yield estimation; 2) full acid digestion of the sample in several consecutive steps with HF, $HNO_3$, HCl; 3) radiochemical separation of uranium from other matrix elements by ion exchange resin (BIO-Rad AG1-X8) and further purification by recently developed chromatographic material UTEVA.Spec of Eichrom Ind. (USA); 4) source preparation for alpha spectrometry by a) microprecipitation as fluorides whit c $NdF_3$ и b) electrodeposition. After extensive investigation of the specific parameters for every step the developed procedure was tested successfully on soil reference materials. Large number of analyses of uranium isotopes content in samples of the new developed reference material from the region of the village of Eleshniza were performed. The results proved the homogenity of the material and its applicability for use as reference material for naturally occurring uranium series.

## INTRODUCTION

Uranium industry has been developed during the second half of the XX century mainly in connection with nuclear energy generation chain. Mining, enrichment, nuclear fuel preparation and waste management require a number of chemical methods for extraction, purification and enrichment. The industry leads to the environmental impact with remarkable spread pollution in some regions of the uranium mining and milling.

Uranium, which is metal has the highest atomic weight of the naturally occurring elements. The primary isotopes of natural uranium are $^{238}$U (99.28 wt%), $^{234}$U(0.71 wt%), and $^{235}$U(0.0054 wt%), Merck Ind. 1989. Average concentration of Uranium in soil is 2 mg/kg (about 25 Bq/kg of $^{238}$U) ranging from <1mg/kg for basalt rocks to >8 mg/kg for granites, Canadian SQG for Uranium (2002).

Widely used methods for measuring uranium in environmental samples are fluorimetry, gamma-spectrometry and alpha spectrometry. Although high concentrations of uranium can be measured successfully without destruction of the sample (instrumental analysis) by gamma spectrometry it is not appropriate when determination of isotopic composition of Uranium in the material is sought. The method estimates the $^{238}$U through its daughter $^{234}$Th (requiring long period for equilibrium –approx. 1 year) can measure accurately $^{235}$U if the $^{226}$Ra (daughter до $^{238}$U) does not exceed significantly $^{235}$U activity, and $^{234}$U can not be measured directly in soil and rock samples.

Fluorimetry is historically first developed method and widely used for elemental determination of the uranium. The method is significantly improved by use of laser fluorimetry. For low level concentrations of uranium in food and other biological materials after pre-concentration and purification neutron activation analyses NAA is used, Dang and Chatt (1986) for example. The use of ICP MS and AMS (accelerated mass spectrometry) is the other method with extending use during the last decade for actinides including uranium. For chemical separation adsorption and ion exchange are common processes for soluble substances among others such solvent extraction and precipitation. It is hard to present in limited space a review of references of the analytical methods for determination of uranium but it is worth to mention that more than 14 analytical methods are standardized in ISO-95 (10): ASTM-95 (4), and in Bulgaria - BDS 12578-75 about uranium in drinking waters.

## EXPERIMENTAL SECTION

One of the approaches for evaluation of the isotopic ratio necessitates an application of a radiochemical procedure for extraction of uranium and measurement of uranium isotopes by its alpha energies on alpha spectrometer.

Therefore in the frame of the IAEA Research contract No 11298 "Development and characterization of a reference material for naturally occurring uranium series" a radiochemical procedure for isotopic analysis of Uranium in samples from the area of former uranium mines in the village of Eleshniza was developed. The main steps of the developed procedure: total acid digestion, anion exchange separation of the uranium from the basic matrix, further separation and purification by employing recent solvent extraction resin UTEVA-Spec, and thin alpha source preparation of alpha source is summarized in Fig.1.

Alpha spectrometry was performed by ORTEC Octete Alpha Spectrometric system equipped with 8 Ortec ULTRA-SA™ low background ion implanted detectors with 300mm$^2$ active area. The alpha spectrometric system was obtained under IAEA TCP RER 2/003. More information about the features of the spectrometric system are given in Veleva (1998).

The measured total system resolution FWHM for $^{241}$Am 5.486 MeV alphas is close (or even lower) to 19keV for 4cm source to detector distance for all detectors. Energy calibration as well as efficiency calibration for one of source geometry (co-ppt. Source) is done by mixed radionuclides standard containing $^{238}$U, $^{234}$U, $^{239}$Pu and $^{241}$Am with known activity, and for geometry of electroplated sources the efficiency calibration is estimated by Amersham $^{241}$Am standard.

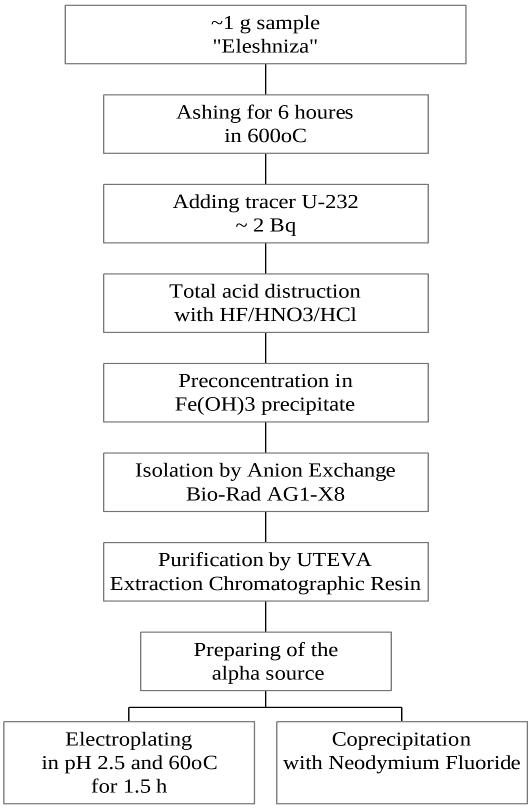

*Figure 1. Main steps of radiochemical procedure for extraction of uranium*

For correct determination of the uranium isotopes by alpha spectrometry the source preparation is essential. A number of experiments were carried out on two techniques with purpose to achieve higher yields and finer alpha spectra.

### Experiments on optimization of co-precipitation with $NdF_3$ for alpha source preparation:

The technique of co-precipitation of three and four valent actinides with lantanides (or micro-precipitation) for preparation of source for alpha spectrometry is developed by C. Sill (1987) and was successfully used by Taskaev et al. (1996) for determination of Plutonium in soils, following La Rosa (1990).

Because first results on analyzing of this material were with stable but low yields (around 20%), the behavior of the solution with known U concentration on different steps of the procedure was tested extensively. We analyze the condition of micro co-precipitation according to the quantity HF needed for forming the fine $NdF_3/UF_4$ precipitation, Table 1.

Table 1. The Results of samples with different quantity of HF and their recoveries:

| Sample | HF (ml) | Recovery % |
|---|---|---|
| U+5HF | 5 | 19.1 |
| U+7HF | 7 | 18.1 |
| U+10HF | 10 | 18.4 |

The conclusion that could be drawn from this data is that the quantity of added HF does not influence on the low recovery results, it remains unchanged.

The second test was connected with finding the optimum quantity of 15% $TiCl_3$ used for reduction of U (VI) to U (IV) for precipitation of $NF_3/UF_4$, Table 2.

The need of reduction of the Uranium high valency states with strong reduction agent was demonstrated by experiments where no Ti $^{(3+)}$ was added and there was no uranium in precipitation.

Table 2. The results of samples with different quantity of $TiCl_3$:

| Sample | Weigh (g) | Ti$^{(3+)}$ (μl) | Recovery % |
|---|---|---|---|
| 10A1 | 0.1899 | 200 | 55 |
| 10A2 | 0.1930 | 400 | 55 |
| 10A3 | 0.1973 | 600 | 52 |
| 10A4 | 0.1748 | 800 | 50 |
| 10A5 | 0.2472 | 1000 | 41 |

As we can see, the quantity of Ti $^{(3+)}$ also doesn't influence on the recovery. The fact that the recoveries reach about 50% is because of the smaller samples taken for this experiment (note that it is five times smaller than previous experiment).

Finally a doubled amount of the $Nd^{3+}$ increased the recovery almost twice. Further increase of $Nd^{3+}$ could lead to thickner source and degradation of alpha spectrum and was not tested.

The conclusion is that not the quantities of HF and $TiCl_3$, but the deficiency of co-precipitated $NdF_3$ micro-precipitation in high concentration uranium samples is the reason for low recoveries. It is questionable whether so called matrix effect - smaller samples have low level of salinity plays some role to obtain the higher recovery than it in the larger samples. The dependence of the observed recovery from the sample mass, respectively U concentration is shown on Fig.2.

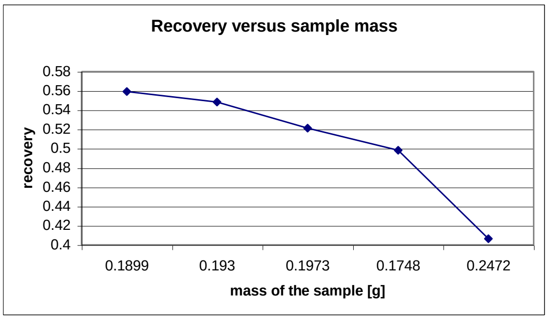

*Figure 2. Initial dependence of recovery from the sample mass*

Alpha spectrometry of the samples was performed at distance of ~ 1cm to the detector and at the typical range of 15-35 mbar pressure in the vacuum chambers, thus preventing detector contamination with recoil atoms. Every sample was measured at least twice. The recovery is estimated with some uncertainty, because it is not possible to reproduce exactly the geometry of the uniform standard. This uncertainty is different from the statistical one, depending on the number of counts in the peak of certain isotope.

**Experiments on optimization of electrodeposition for the preparing of alpha source**

We decided to implement electroplating as an optional technique for preparation of alpha sources with the purpose to achieve thinner source and respectively finer alpha spectrum. Some tests for spontaneous deposition of uranium on aluminum disks were done but the received recovery does not exceed 10%. In the literature there are described different conditions of electroplating of Uranium. One of the important points for successful electroplating is the electrolyte. In classic Talvitie (1972) method $(NH_4)_2SO_4$ is used, in DIN 38404-20 and ASTM C1000-90 it is $NaHSO_4$ + $6MH_2SO_4$ and $NaHSO_4$ + $1NH_2SO_4$ respectively, B. Burnett (2002) applyed $H_2SO_4$. In this study $(NH_4)_2SO_4$ was chosen and proved. Other characteristics of the listed methods are summarized in Table 3. The optimal distance of 10mm between cathode and anode was held. Several experiments were carried out on electroplating conditions, mainly changing pH and temperature. The tests for electrodeposition of uranil nitrate show an average 72% recovery ranging from 25 to near 100%. The best results with the highest yields were achieved at pH 2.5 and without cooling the solution (it reaches around 50-60°C during the process of electrodeposition)

The main advantage of the electrodeposition compare to micro-precipitation is the source thickness, estimated by energy resolution FWHM (Full Weight at Half of Maximum) of the alpha peak. This spectrometric characteristic is widely used in alpha spectrometry both for spectrometer and for source features and depends on the source to detector distance. The average FWHM in case of co-precipitation with 50 $\mu$g of Nd is about 80 KeV, for 100$\mu$g increases to 90KeV, but for electroplating sources is as better as 35-45 KeV.

Table 3. Specific characteristics of the electrodeposition methods

| **Ref.** | **DIN 38404-20** | **ASTM C1000-90** | **Talvitie (1972)** | **Burnett (2002)** | **This study** |
|---|---|---|---|---|---|
| Sample type | Water | Soil | Envir. Objects | Envir. objects | Soil |
| *Ph* | 2.4-2.5 | 2-2.3 | 1.2-2.8 | 3.2 | 2.5 |
| *Depos. Time, (min)* | 60 | 60 | 120 | - | 90 |
| *Volume (ml)* | 11 | 15 | 10 | 50 | 8 –11 |
| *Anode-Source d, (mm)* | - | 10 | 13 | 10 | 10 |
| *Current (A)* | 1.2-2 | 1.2 | 1.2 | 1.2 | 5min-0.5<br>90min-0.75 |

**Radiochemical separation**

During the process of development of the procedure three types of materials were used: depleted uranil nitrate solution; IAEA reference materials; and samples from new prepared and evaluated for possible reference material Eleshniza uranium ore. The initial tests for radiochemical separation were done with uranil nitrate solution spiking the tests solution with known amount of uranium mass Richter et al. (1999).

The main part of the analyzed samples of developed new reference material consists of a fine fraction of the raw grounded material (passed through the sieve with pore size of 0.074-mm). The non- homogeneity of the material in relation to particle size was established to be less than 1.5 %. The material was sampled and prepared according to BSS 8.892 (1996) and Claude&David (1995). The initial gamma measurements showed about 2 Bq/g of $^{238}$U therefore about 1 g of this fine powder was weighted to have enough material for alpha measuring.

Prior acid digestion, the sample to be analyzed is ignited in a porcelain crucible in an electric muffle furnace up to 600°C and held at that temperature for 6 hours to burn off all carbonaceous material. The final ash should be homogeneous like a fine powder.

The applied technique of total acid digestion of soil samples is close to J. La Rosa (1990) and has been used many times by the authors for analysis of radionuclides in environmental samples. The main advantages are: a) all quantity of radionuclides is transferred to the sample solution, and b) the conditions ensure full isotope exchange between radioactive tracer $^{232}$U and the natural isotopes of uranium - $^{234,\ 235,\ 238}$U. Use of a tracer provides the most accurate estimation of the chemical yield for every sample.

Discarding the main matrix of the rock sample was the next step in procedure. To achieve this purpose, we used co-precipitation of Uranium with $Fe(OH)_3$ in pH 9-10 and removed all soluble hydroxides in this conditions – mainly alkali and alkaline-earth metals. The precipitate was dissolved in 9M HCl and anion exchange chromatographic column of Bio - Rad AG 1-X8, 100-200 mesh was prepared for radiochemical separation of Uranium.

There are many procedures for extraction of uranium, all dealing with water, soil and rock samples with low content of uranium. The classic ion exchange resins (organic and inorganic) are recently replaced or supported by UTEVA.Spec chromatographic material (Renpo Wu et all., 1998, B. Burnet, 2002, Ann.Rep.of Helsinki University, 2001). Chemical separation of the spiked with uranil nitrate 9M HCl solution started with extraction by ion exchange resin only. Uranil nitrate spike vary from 0.0003 to 0.2019 mg uranium, the last value, equivalent to 2.49Bq $^{238}$U is closed to the activity in typical 1g sample from the Eleshniza material. The test showed that some Thorium impurities ($^{228, 230}$ Th ) presents in the alpha spectra, thus interfering determination of $^{234}$U and $^{235}$U. Therefore the second UTEVA.Spec column was introduced for purposes of further purification of the Uranium fraction from some actinides and Iron employing a recent chromatographic resin, commercially available product of Eichrom Ind. (USA).

The uranium eluat from BIO-Rad AG1-X8 column is coverted in nitrate form and loaded in 3M $HNO_3$+1.0M $Al(NO_3)_3$ solution. Prior the Uranium other elements and radionuclides (Th, Am, Al, Pa, Pu) are removed. The final uranium strip of 0.01M HCl is ready for source preparation.

Finally alpha sources were prepared by using two techniques: (1) co-precipitation as fluorides with Neodymium Fluoride and (2) electroplating.

## RESULTS AND DISCUSSION

Every set of samples was accompanied by spiked with $^{232}$U blank. The concentration of U isotopes in blank was very low and it was considered only in 2 sets. Typical alpha spectra of electroplated sample source is shown on Fig.3

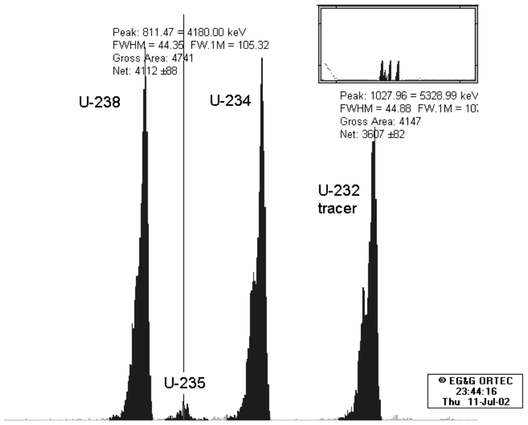

*Figure 3. Alpha spectra obtained by elctroplating. One of the Eleshniza sample from the final test serie.*

The activity of every uranium isotope is calculated according to the Equation 1.

$$A= (N_a.A_{tr}) / (N_{tr}.w) \qquad (1)$$

where, A is activity of the analyzed isotope in Bq/kg, $N_a$ is the number of counts in the peak of the analyzed isotop, $N_{tr}$.is the number of counts in the tracer peak, $A_{tr}$ is the activity of the added tracer ($^{232}$U), w is the weight of the sample. When some of detectors has background counts in the peak energy regions they are subtracted.

The first tests of the procedure on real samples were done by IAEA reference materials, Table 4. The $^{235}$ U concentrations are not listed, but are taken into account. Soil-5 is certified for U content (3.15 +/- 0.45 µg/g ), so the value ( Bq/kg) for uranium isotopes in Soil-5 was calculated using data for uranium isotopes content in natural uranium.

Table 4. Results of analysis of two types of reference materials.

| **Sample** | **$^{238}$ U Bq/kg** | **$^{234}$ U Bq/kg** | **Total U ±2 σ Bq/kg** *Recovery (%)* | **Cert. Value Bq/kg** |
|---|---|---|---|---|
| Soil-5 | 35.7 | 37.1 | 75.4±5.2<br>*(93)* | 79.6+/11.4 |
| Soil-5 | 35.2 | 36.3 | 71.5±5.8<br>*(91)* | 79.6+/11.4 |
| IAEA 135 | 27 | 26.5 | 54.9±2.3<br>*(93)* | 58.3 |
| IAEA 135 | 23.2 | 23.8 | 48±2.8<br>*(79)* | 58.3 |

The value for uranium in IAEA 135 reference material is not certified but is information value only. Nevertheless the results are very close and accepted as satisfying.

The samples from new reference material from Eleshniza were analyzed after the material was homogenized, sieved and packed in 0.5-kg vials. From each two samples of approximately 1g of the material were taken for radiochemical separation of uranium. Both samples passed through the same radiochemical procedure of uranium separation and purification. At the final step from one alpha-source was prepared by microprecipitation and from the other by electroplating. The summarized results are presented in Table 5 and Table 6.

Table 5. Results of determination of uranium isotopes by micro co-precipitation

| **Micro co-precipitation** | **U-238 Bq/kg** | **U-235 Bq/kg** | **U-234 Bq/kg** | **Recovery %** |
|---|---|---|---|---|
| **Average** | **2.260** | **0.113** | **2.232** | **35.3** |
| sd 95% | 0.135 | 0.010 | 0.117 | |
| Rsd | 6.0 | 8.8 | 5.2 | |
| sd av | 0.043 | 0.003 | 0.037 | |
| rsd av | 1.9 | 2.8 | 1.7 | |
| | | | | |
| **Min** | **1.95** | **0.09** | **1.97** | **14** |
| **Max** | **2.41** | **0.126** | **2.35** | **58** |
| **Confidence** | **0.084** | **0.006** | **0.072** | |

Where

Sd 95% = $\sqrt{\sum (\mathrm{Xi} - \mathrm{Xav})^2 / (\mathrm{n} - 1)}$ (2)

Rsd s = 100*Sd s/Xav

Sd av = Sd s/ $\sqrt{n}$

Rsd av = 100*Sd av/Xav

Table 6. Results of determination of uranium isotopes by electroplating

| **Electro-plating** | **$^{238}$U Bq/kg** | **$^{235}$U Bq/kg** | **$^{234}$U Bq/kg** | **Recovery %** |
|---|---|---|---|---|
| **average** | **2.284** | **0.114** | **2.247** | **24.5** |
| sd 95% | 0.078 | 0.009 | 0.071 | |
| rsd | 3.4 | 8.0 | 3.2 | |
| sd av | 0.026 | 0.003 | 0.024 | |
| rsd av | 1.1 | 2.7 | 1.1 | |
| | | | | |
| **min** | **2.18** | **0.103** | **2.15** | **13.3** |
| **max** | **2.43** | **0.126** | **2.36** | **38.4** |
| | | | | |
| **Confidence** | **0.041** | **0.006** | **0.047** | |

The results in the tables above are based on 10 samples proceeded by microprecipitation and 9 by electroplating. Other five electroplated samples were taken out because were apparently spoiled during the procedure (recovery below 10%).

It was mentioned that the occurrence of natural uranium in the environment consists of the three isotopes, $^{238}$U, $^{235}$U and $^{234}$U. $^{234}$U is a decay product of the $^{238}$U series and given sufficient time it approaches secular equilibrium with its parent activity. However under some circumstances secular equilibrium may not always be reached. On the other hand, $^{235}$U isotope is associated with a separate decay chain (the actinium series) and it is anticipated that $^{235}$U/$^{238}$U ratio in geological materials should provide a consistent activity ratio. It can be seen from the tables that isotopic ratios in the analyzed material corresponds within the standard deviation to the ratios of naturally occurring uranium series – 0.0466 for $^{235}$U/$^{238}$U and about 1 for $^{234}$U/$^{238}$U. The last ratio in our case is slightly lower than 1 that according to Larsen (2000) is observed in rocks, soils and sediments where some depletion in the ratio can occur under certain environmental conditions.

## CONCLUSIONS

The developed procedure for uranium naturally occurring isotopes determination in environmental samples is producing reliable and reproducible results. The procedure gives the possibility to determine $^{238}$U, $^{235}$U and $^{234}$U concentrations and their isotopic ratio. The procedure could be used for low activity samples with high chemical yield and in environmental samples with approximately high uranium content, where the lower yield does not affect the accuracy of uranium isotopes determination.

The new method for alpha source preparation by electrodeposition is worked up and is considered a task for further improvement.

The results obtained contributed in the process of certification of the new reference material from the region of the village of Eleshniza.

## REFERENCES

Annual Report, 2001. University of Helsinki. Department of Chemistry,*www.chemistry.helsinki.fi/radlab/ xtrafiles/rap2001.doc*

ASTM D 3972-90, 1990. Radiochemical Standard Test Method for Determination of Uranium Isotopes in Water.

Bulgarian State Standard 8.892, 1996. Standard Material: Determination of the Uniformity of a Disperse Material for Standard Material for Composition.

Burnett Bill, 2002. *Personal communication.*

Canadian Soil Quality Guidelines for Uranium: Environmental and human Health, 2002. Draft Scientific Supported Document.

Claude, Still, David, 1995. “Solid Standards for Quality Control in Radiochemical Analysis*”. - Radioactivity& Radiochemistry, v.6, No 2,* 28-39.

Dang H.S. and A.Chatt, 1986. Preconcentration Neutron Activation Analyses of Uranium and Thorium in Standard Reference Materials and Food. - *In: American Nuclear Society (ANS). Trace Elements in Nutritional Materials. Transactions. November 16-20. 1986, Winter meeting, Vol. 53,* Washington, DC. 169-170.

La Rosa J., 1990. Plutonium Radiochemical Procedure for Soil”, IAEA Manual - Seibersdorf Laboratories, Chemistry Unit.

Larsen, Ingvar, 2000. Some Notes and Comments Regarding Natural and Processed Uranium Isotopes. - *Radioactivity&Radiochemistry, v.11, No 2,* 6-10.

Merck Index. 1989. The Merck Index. *An encyclopedia of Chemicals, Drugs and Biologicals. Budavary, S. (ed) Eleventh Edition. Merck and Co., Inc.,* Rahway, NJ.

Microprecipitation source preparation for alpha spectrometry, 1997. *G-03,Vol.I Rev.0,HASL-300,28th Edition February, Environmental Measurments Laboratory,* U.S. Department of Energy

Renpo Wu, Noyce J. R., Lih-Ching Chu. 1998. Developing an efficient method for the measurements of isotopic uranium and thorium in small samples of soils and environmental waters. - *44th Annual Conference on Bioassay, Analytical, Environmental and Radiochemistry, November 19,* Albuquerque, New Mexico. *www.state.il.us/idns/pdfs/projectsPDF/rapiduth.pdf*Still,

Richter S., A.Alonso, R.Wellum and P.D.P.Taylor, 1999. The isotopic composition of commercially available uranium chemical reagent. - *Journal of Analytical Atomic Spectrometry, 14,* 889-891.

Sill, C. W., 1987. Precipitation of actinides as fluorides or hydroxides for high resolution alpha-spectrometry. - *Nuclear Chemical Waste Management, 7,* 201-215.

Talvitie, N.A, 1972, Electrodeposition of Actinides for Alpha Spectrometric Determination - *Analitical. Chemistry, vol.44, No2,* 280.

Taskaev E., Taskaeva M., Veleva B., Penev I., Grigorov T., Genchev T., 1994. E. Fast analyses of the samples from the region of national center of radiobiology and radiation protection. – *In Proc.: III Scientific-practical conference on* *population protection in case of disasters and accidents, Sofia 8-9 December, Vol.2,* 131-135.

Uranium in Water", June 1999. Eichrom Industries, Inc.Analytical Procedures,

Veleva B. 1998. Low level alpha spectrometry. Application in radioecology. - *Proc. Of XX Colloquium "Physics in human and environmental protection, 26-28 June 1998,* Gjuletchiza, 40-47.

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