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Uranium Glass in Museum Collections

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Vidro de Urânio em Colecções Museológicas

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Sumário

A presença de vidros de urânio em colecções museológicas e privadas tem vindo a suscitar preocupações na área da protecção radiológica relativamente à possibilidade de exposição à radiação ionizante emitida por este tipo de objectos. Foram estudados catorze objectos de vidro com diferentes concentrações de óxido de urânio.

A determinação da dose de radiação β/γ foi efectuada com um detector β/γ colocado a diferentes distâncias dos objectos de vidro. Na maioria dos objectos, a dose de radiação não é preocupante, se algumas precauções forem tidas em conta.

O radão 226 (^{226}Rn), usualmente o radionuclido que mais contribui para a totalidade da dose de exposição natural, e que resulta do decaimento do rádio 226 (^{226}Ra) nas séries do urânio natural, foi também determinado e os valores obtidos encontram-se próximos dos valores do fundo.

Com o objectivo de determinar a concentração de urânio foram testados dois métodos analíticos não-invasivos; num mediu-se a radiação α/β emitida por cada objecto e no outro utilizou-se a fluorimetria. Os resultados obtidos foram comparados com as concentrações determinadas por espectrometria de micro-fluorescência de raios X.

Recolheram-se amostras de quatro objectos para determinar a composição isotópica do urânio por espectrometria alfa, com o objectivo de distinguir os vidros produzidos com urânio natural e urânio empobrecido. Os resultados obtidos poderão contribuir para a atribuição da data de produção dos objectos de vidro de urânio.

Uranium Glass in Museum Collections

Filipa Lopes

Abstract

The presence of uranium glass objects in museum and private collections has raised radiation protection concerns resulting from possible exposure to ionizing radiation emitted by this type of object. Fourteen glass objects with different uranium contents were studied. Dose rates (β + γ radiation) were measured with a beta/gamma probe at several distances from the glass objects. In general the determined dose rates did not raise any concern as long as some precautions were taken. Radon (^{222}Rn), usually the most important contributor for the overall natural dose exposure resulting from radium (^{226}Ra) decay in the uranium natural series, was also evaluated and it was found to be within the background values.

Non-invasive analyses of the uranium content in fourteen glass objects were made using micro energy dispersive X-ray fluorescence spectrometry, measuring the radiation emitted by the objects and using fluorescence spectroscopy.

Alpha spectrometry was tested in four glasses to determine the uranium isotope composition in order to distinguish which objects used depleted and non-depleted uranium. This information is useful to dating the objects.

Part of this work was presented in a poster[1] with the title "Uranium glass in museum collections", in the II International Conference: Glass Science in Art and Conservation, Valencia, March 2008.

The same conference originated a special volume of the Journal of Cultural Heritage, where an article with the same title was submitted and accepted.

[1] Filipa Lopes, Andreia Ruivo, Vânia Muralha, Pedro Duarte, Isabel Paiva, Romão Trindade, Augusta Lima and António Pires de Matos, "Uranium glass in museum collections", Glass Science in Art and Conservation – II International Conference, Valencia, Spain, 5-7 March 2008 (Appendix I).

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1. Introduction

Uranates such as $Na_2U_2O_7$, $K_2U_2O_7$ and $(NH_4)_2U_2O_7$ (sodium, potassium and ammonium uranate, respectively), and uranium oxides have been used for colouring glass and as colouring agents in ceramic glazes since the 19th century [1]. In spite of Klaproth, who became the first to recognize uranium as a chemical element in 1789 [2], and other authors that mentioned its role as a colouring agent for glass objects, the history of uranium in glass is not very clear. As reported by F. Lole, the earliest reference appears to date from 1817 in the book of C. S. Gilbert "An Historical Survey of The Country of Cornwall" where it is written that uranium oxides impart bright colour to glass [3]. Paolo Brenni states that due to secrecy maintained by the glass manufacturers there is no reliable literature that can be referred to [4]. Franz Anton Riedel (1786-1844) began the production of uranium glass in the 1830s and Josef Riedel (1816-1894) developed two types of uranium coloured glass named by him as *Annagelb* (yellow) and *Annagrün* (green), in honour of his wife Anna. About the same time similar uranium glasses were produced in England and in France under the name *canary glass* and *verre canari* [5-9]. Due to its translucent yellow-greenish appearance uranium glass was named *vaseline glass* [10]. Uranium glass continued to be used in a great variety of objects, such as lamps, jewels, beads, necklaces, plates, bottles, jars and buttons [4]. It is found today displayed in antique shops and museums and enjoys increasing popularity as a collector's item.

The U^{6+} ions in the uranyl form $(UO_2)^{2+}$ show luminescent emission of very high efficiency and are responsible for the distinct green fluorescence of uranium glasses [11] (Figure 1.1). Soda-lime-silicate glasses are characterized by a luminescence spectra starting around 490 nm and extending above 600 nm with two main emission bands at 530 and 565 nm [11].

Figure 1.1. Uranium glasses from a private collection under UV light (stemmed plate, toothpick holder and oil cruet).

Natural uranium has three isotopes, all of them radioactive [^{238}U (99.27%), ^{235}U (0.72%) and ^{234}U (0.0055%)] [12,13]. The radioactivity emitted by uranium glass objects arises mainly from ^{238}U and its daughter products ^{234}Th and ^{234}Pa [14]. In 1943, in the United States and the United Kingdom, new legislation introduced safeguards and controls for radioactive substances [15]. Between 1943 and 1958 the American government banned uranium salts from any commercial use due to their strategic importance during the Second World War [5]. Since then, the use of natural uranium for glazes, enamels and glasses has been discontinued throughout the world and depleted uranium started to be used.

In order to produce fuel for certain types of nuclear reactors, uranium has to be 'enriched' in the ^{235}U isotope, which is responsible for nuclear fission [16]. During the enrichment process

the fraction of ^{235}U is increased from its natural level (0.72%) to about 3% [17]. The remaining uranium after removal of the enriched fraction is referred to as depleted uranium (Table 1.1). Another less common source of depleted uranium is reprocessed spent nuclear reactor fuel, which can be identified by the presence of ^{236}U.

As natural uranium was used as a coulorant in the production of glass between 1830s and 1940s, its isotopic composition can be useful in authenticity studies.

Table 1.1. Relative mass abundances of uranium isotopes (by weight % and by activity %) in natural and an example of depleted uranium [12,13,16,17].

Isotope	Natural uranium		Depleted uranium	
	by weight	by activity	by weight	by activity
^{238}U	99.27%	48.8%	99.8%	83.7%
^{235}U	0.72%	2.4%	0.2%	1.1%
^{234}U	0.0055%	48.8%	0.0006%	15.2%

The decay of uranium gives rise to other radioactive daughter products which include radon gas. Uranium emits α particles and its fission products produce β particles and γ radiation, so that appropriate safety measures are very important when working with uranium compounds [1,18].

As far as is known, even at low doses, radiation may act as a mutational initiator of tumorigenesis [19]. This is the reason why in this work dose rates were measured on uranium glasses.

Radioactivity measurements on uranium glass objects have also been made by Donna Strahan from the Asian Art Museum, San Francisco [5] and Kierzek et al. [20], yet no radon exhalation measurements were made. Kierzek et al. used gamma radiation spectrometry to evaluate the uranium concentration in one object.

The objective of this work was to assess the contribution of uranium glass objects radiation dose for the total dose received by museum workers and general public in order to verify compliance with dose limits. Three non-invasive analytical methods were used for the determination of the uranium content in fourteen uranium glass objects from a private collection (Figure 1.1 and 1.2).

Figure 1.2. Uranium glasses from a private collection (1 - squared bottle; 2 – footed beaker; 3 - Czech jug; 4 - beaker; 5 - stemmed plate; 6 - oil cruet; 7 - salt-cellar; 8 - candlestick; 9 - toothpick holder; 10 - children's plate; 11 - paperweight; 12 - ballot; 13 - box; 14 - ashtray).

Description of uranium glasses from a private collection [10]:

1. Squared bottle, mould-pressed, green glass showing brilliant green fluorescence under ultraviolet light.

2. Footed beaker, pressed in a four-section mould; bright greenish-yellow glass showing brilliant green fluorescence under ultraviolet light [2].

3. Czech jug, mould-blown, light-green glass showing brilliant green fluorescence under ultraviolet light.

4. Beaker, mould-pressed, eight-petalled base, greenish-yellow glass showing brilliant green fluorescence under ultraviolet light.

5. Stemmed plate, mould-pressed, diamond cut decoration, greenish-yellow glass showing brilliant greenish-yellow fluorescence under ultraviolet light.

6. Oil cruet, hobnail pattern mould-blown, light yellow glass showing brilliant green fluorescence under ultraviolet light.

7. Salt-cellar, American, made at the Mosser Glass (established in 1971). Mould-pressed glass (Mosser Glass catalog ref. no. 115V) [21]. Light yellow glass showing brilliant green fluorescence under ultraviolet light.

8. Candlestick, mould-pressed in a four section mould and squared base; bright yellow glass showing brilliant green fluorescence under ultraviolet light [2].

9. Toothpick holder, mould-pressed, bright greenish-yellow glass showing brilliant green fluorescence under ultraviolet light.

10. Children's plate, American, made at the Mosser Glass (established in 1971) Children’s tableware: ABC plate (Mosser Glass catalog ref. no. 304V) [21]. Mould-pressed light yellow glass showing brilliant green fluorescence under ultraviolet light.

11. Paperweight, Czech Republic, made at Jizerské Sklo Co., ‘INIS’ engraved (International Nuclear Information System); bright yellow glass showing brilliant green fluorescence under ultraviolet light.

12. Ballot, bright yellow glass showing brilliant green fluorescence under ultraviolet light.

13. Box with lid, mould-pressed, bright yellow glass showing brilliant green fluorescence under ultraviolet light.

14. Ashtray, mould-pressed, bright yellow glass showing brilliant green fluorescence under ultraviolet light.

2. Experimental

2.1. Chemical composition using Micro-EDXRF

Preliminary chemical characterisation of the glass objects was made using non-destructive analysis by micro energy dispersive X-ray fluorescence spectrometry (μ-EDXRF). This analysis was carried out at the Departamento de Conservação e Restauro of the Faculdade de Ciências e Tecnologia of the Universidade Nova de Lisboa using a portable spectrometer ArtTAX, which consists of an air-cooled low-power X-ray tube with a molybdenum target, a silicon drift detector electro-thermally cooled and a measurement head fixed on a tripod with a motor-driven XYZ stage for sample positioning. This system is combined with a colour CCD camera that provides a magnified digital image of the area under investigation. The primary X-ray beam is focused by means of polycapillary X-ray minilens and the excitation and detection paths can be purged with helium to allow the detection of low-Z elements.

Measurements were carried out directly on the surface of the objects without any previous preparation. Each object was measured in three different points of the surface, and in each point just a single measurement was made. The measuring conditions were the following: voltage 40 kV, intensity 0.6 mA and live time 300 s.

Helium purging was used to allow the determination of elements down to aluminium. Sodium oxide was determined by difference after analysing all the other oxides.

WinAxil analytical software was used for quantification of major and minor element oxides. Calibration was made using two reference glasses prepared by adding 1 and 1.2 wt% of uranium oxide to a soda-lime silicate glass standard from the Society of Glass Technology (SGT 7) which was further heated in a crucible at 1500ºC for about 24 hours (Appendix III).The accuracy of the method, determined by the quantification of the reference glasses, was found to be less than 10% for the major elements oxides (≥ 1%) and 15% for the minor elements oxides (< 1%). The detection limit for uranium was 50 ppm [22].

2.2. Dose rate

The dose rate was measured using a beta/gamma probe in contact with the objects and at two different distances, 20 and 50 cm. Beta/gamma probe contains two G-M tubes with a minimum detectable level of 0.1 μGy/h and was coupled to a RadiacSet AN/VDR-2 unit. This probe detects beta radiation from background (0.001 μGy/h) to 50 mGy/h and gamma radiation from background to 9990 mGy/h. The measurements were made with the end window opened. The accuracy was about 20% at 5 μGy/h.

2.3. Radon exhalation assessment

For the radon exhalation measurements, objects were inserted in closed cylindrical containers, used as accumulation chambers. After an accumulation period of about 30 days, an air sample was taken from each container, filtered through a Millipore type AA 0.8 µm filter and collected into a 125 cm^3 scintillation cell (Lucas cell). Radon (^{222}Rn) concentration was measured in equilibrium (after three hours) using a photomultiplier counter (NOVELEC®).

2.4. Uranium content estimation measuring the emission of radiation

In order to estimate the uranium concentration in the glass objects, their radiation was measured with a Ratemeter type RM2/1 with a dual phosphor probe (sensible to alpha and beta radiation) and a scintillation counter using plastic phosphor, coated on one face with zinc sulphide with a thickness of 12 m/cm^2. The radiation was measured through a window with 2x2 cm made of lead sheet, in order to measure the same area for both the small and large objects.

2.5. Luminescence intensity

The luminescence intensity of the objects was measured under UV light of 380 nm wavelength in order to evaluate if luminescence intensity is proportional to the uranium concentration in the glass objects. The emission spectra were measured with an Avantes AvaSpec-2048 fibre optic spectrometer. It is a fibre optic spectrometer with a 300 lines/mm grating. The operational range is 200-1100 nm and the instrument has a FWHM resolution of 2.4 nm. The light emitted was measured using a 200 µm reflection probe (Avantes FCR 7-UV-200). It consists of six illuminating fibres surrounding one central reading fibre; the diameter of each of these fibres is 200 microns.

2.6. Uranium isotopic composition

Alpha spectrometry was tested on four glass objects to determine the content of uranium isotopes. The objective was to distinguish depleted and non-depleted uranium for dating purposes.

The samples needed for this analysis were removed using a new method developed for neutron activation analysis of glass objects [23]. It consisted in placing a small strip of plastic adhesive tape with a hole of ca. 2 mm^2 over the glass surface. A drop of 40 % hydrofluoric acid (v/v) was placed in the hole and after a short period (up to 1 minute) was transferred to an ultra pure polyethylene container and heated to dryness [23].

Measurement of radionuclides was performed with surface barrier silicium detectors 450 mm^2, 100 µm depletion depth, and with 450 mm^2 UltraAs ion implanted detectors. Detectors were used in the assemblage OCTETE Plus from Ortec EG&G and in dual chambers.

Vacuum in detector chambers, performed with pumps (Edwards RV8), was set at 10-20 mTorr. Counting time for measurement of radiation emitted by the source discs was performed for 12 to 240 hours, as needed to obtain relative uncertainties around 5% or lower. Analysis of spectra was performed with Maestro 5.0 software package [24].

3. Results and discussion

3.1. Chemical composition using Micro-EDXRF

Uranium coloured glasses may contain 0.5 - 4 wt% uranium oxide in their composition. However, the colour intensity does not increase significantly with increasing uranium oxide content, reason why commercial glasses usually contain ca. 0.5 wt% of U_3O_8 [1]. The results obtained by µ-EDXRF show that uranium oxide content in the objects varies between 0.14 - 1.40 wt% being in agreement with the values reported in the literature (Table 3.1.1). The analysis also shown that the fourteen objects are made of soda-lime-silicate glasses (Appendix II).

Due to the geometry of the µ-EDXRF probe and the irregular surface of the toothpick holder, the measurement conditions for this object were not ideal, and so the standard deviation was very high.

Table 3.1.1. Silicon, calcium, aluminium and uranium oxides content and standard deviation (wt %), of the glass objects analysed by µ-EDXRF.

N.	Description	SiO_2	CaO	Al_2O_3	U_3O_8
1	Squared bottle	80.0 ± 0.00	5.3 ± 0.17	1.53 ± 0.06	0.14 ± 0.01
2	Footed beaker	74.0 ± 0.00	10.0 ± 0.00	0.80 ± 0.00	0.46 ± 0.00
3	Czech jug	78.0 ± 3.46	5.3 ± 0.31	1.03 ± 0.23	0.36 ± 0.03
4	Beaker	75.5 ± 0.71	5.2 ± 0.14	0.79 ± 0.01	1.25 ± 0.07
5	Stemmed plate	73.0 ± 0.00	6.0 ± 0.06	0.92 ± 0.17	1.40 ± 0.00
6	Oil cruet	78.3 ± 2.89	4.9 ± 0.06	1.47 ± 0.06	0.49 ± 0.00
7	Salt-cellar	77.7 ± 2.08	3.3 ± 0.1	2.47 ± 0.25	0.43 ± 0.01
8	Candlestick	79.0 ± 1.73	5.6 ± 0.15	0.97 ± 0.12	0.56 ± 0.04
9	Toothpick holder	65.3 ± 8.08	7.4 ± 1.40	0.79 ± 0.11	0.42 ± 0.10
10	Children's plate	80.0 ± 0.00	3.6 ± 0.35	1.57 ± 0.42	0.44 ± 0.02
11	Paperweight	73.0 ± 0.00	5.5 ± 0.10	0.81 ± 0.16	0.91 ± 0.01
12	Ballot	63.0 ± 1.00	2.8 ± 0.06	2.10 ± 0.44	0.80 ± 0.05
13	Box	74.0 ± 0.00	5.3 ± 0.06	0.82 ± 0.07	1.40 ± 0.00
14	Ashtray	80.0 ± 0.00	4.7 ± 0.00	1.15 ± 0.35	1.08 ± 0.00

3.2. Dose rate

The results obtained for dose rate measurements are reported in Table 3.2.1. The values for 20 and 50 cm distances decrease significantly when compared to the contact measurements, which is in agreement with the fact that the radiation involved is basically provided by beta emitters such as ^{234m}Pa (^{238}U daughter). Stemmed plate corresponds to the

object that emits more radiation in contact. In terms of radiological protection, the worst case scenario would be the public exposed at a dose rate of 0.28 (µGy/h, therefore an annual dose of 0.56 mSv, which is well below the dose limit for the public, 1 mSv (Council Directive 96/29 /EURATOM). This value 0.28 µGy/h is the highest dose rate obtained for 50 cm measurements. This is the distance at which usually objects are displayed in museums. It was also measured the dose rate placing a soda-lime-silicate glass in front of the object to simulate a showcase glass wall, which reduced radioactivity to the background level.

Table 3.2.1. Dose rate at three different distances, in contact with the object and at 20 and 50 cm.

N.	Description	**Dose rate** (µGy/h)		
		contact	**20 cm**	**50 cm**
1	Squared bottle	0.62	0.22	*
2	Footed beaker	1.78	0.24	*
3	Czech jug	1.45	0.35	*
4	Beaker	4.06	0.5	0.28
5	Stemmed plate	5.07	0.47	0.26
6	Oil cruet	1.66	0.2	*
7	Salt-cellar	2.60	*	*
8	Candlestick	1.38	0.32	0.23
9	Toothpick holder	1.75	0.19	*
10	Children's plate	2.34	0.33	0.25
11	Paperweight	2.26	0.31	*
12	Ballot	2.27	*	*
13	Box	4.25	1.04	0.26
14	Ashtray	3.64	0.34	0.2

* identical to background (0.15 µGy/h)

3.3. Radon exhalation

Using the accumulation chamber method and Lucas cells to sample air, radon exhalation results were found to be within the background values. This result would be expected if all natural isotopes present in raw uranium ore ^{238}U, ^{235}U and ^{234}U had been chemically removed from the decay chain of the daughter products.

However if ^{226}Ra had been removed from the uranium breaking decay chain of the daughter products, and ^{230}Th was left, the quantity of radium in a glass with 150 years would be appreciable. Probably radon is not detected due to the low diffusion through the uranium glass matrix. Nevertheless, due to the large glass surface of the objects it could be possible to detect some radon emanation. That was the reason why the radon emanation was tested.

3.4. Uranium content estimation measuring the emission of radiation

The alpha and beta radiation of the objects was measured with a Ratemeter type RM2/1 in counts per second (cps). The values measured ranged between 2.5 and 25 cps showing a very good correlation (r = 0.97) between this technique and the μ-EDXRF results (Figure 3.4.1).

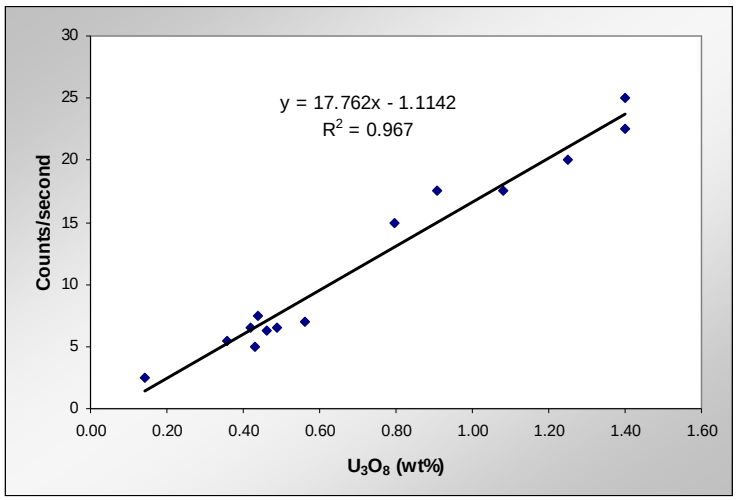

Figure 3.4.1. Plot of α and β radiation (cps) vs U_3O_8 concentration (wt%) of the fourteen objects.

3.5. Luminescence intensity

Accordingly with W. A. Weyl [25], not only the shape of the spectrum and distribution of intensities of uranium glass change considerably when base glasses of different composition are compared. As expected, in the studied objects no significant shape differences were observed in the spectra as all glasses are soda-lime-silicate. The emission spectra obtained showed the characteristic bands of U^{6+} at 530 and 565 nm [11] (Figure 3.5.1). It was possible to observe that the luminescence intensity increases with the concentration of uranium in the glass. There are some exceptions, namely stemmed plate, children's plate and paperweight, probably because of the geometry of the objects and different glass thicknesses. Accordingly with J. Navarro [11], the luminescence intensity decreases with increasing calcium oxide content.

The fluorescence of uranium glasses is promoted by the presence of excess of oxygen, which leads to the formation of uranyl group $(UO_2)^{2+}$. All the conditions that suppress the formation of the uranyl group also suppress fluorescence [1]. This is just clearly observed in the emission spectrum obtained for sample number 2 (footed beaker) with 10% of calcium oxide content and near the lower value of luminescent intensities (Table 3.5.1).

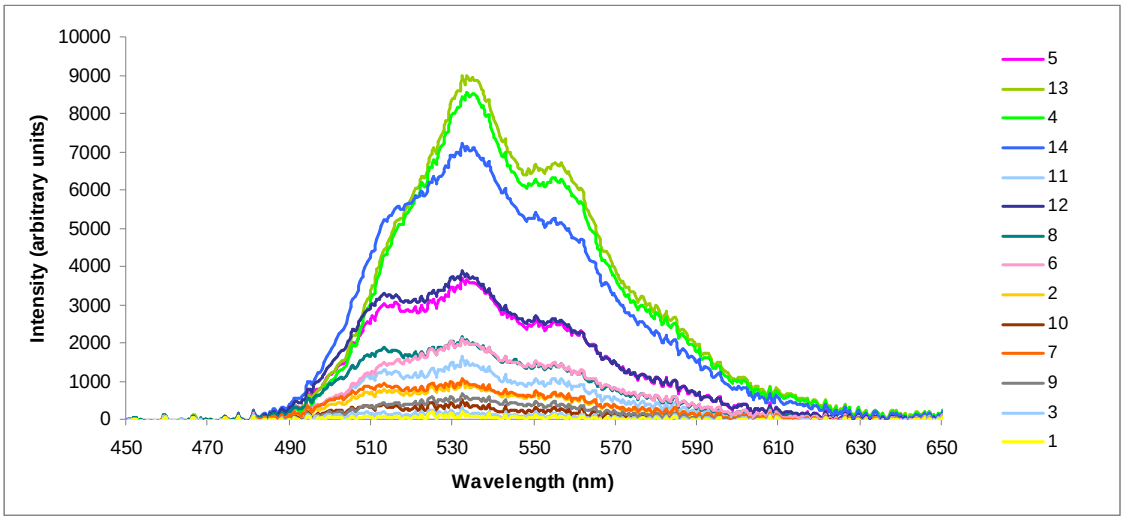

Figure 3.5. 1. Luminescence spectra of the uranium glass objects.

Table 3.5.1. Maximum values of luminescence spectra at ca. 530 nm of the uranium glass objects.

N.	**Description**	**Intensity** (ca. 530 nm)
1	Squared bottle	120.47
2	Footed beaker	966.53
3	Czech jug	301.95
4	Beaker	8449.2
5	Stemmed plate	3569.1
6	Oil cruet	2023.6
7	Salt-cellar	966.53
8	Candlestick	2023.6
9	Toothpick holder	606.17
10	Children's plate	531.42
11	Paperweight	1637.1
12	Ballot	3882.8
13	Box	8975.2
14	Ashtray	7200.3

3.6. Uranium isotopic composition

Results of the analysis of alpha-emitters in the samples collected from the four uranium glass objects are reported in Table 3.6.1. Accordingly with Table 1.1, all analysed objects are made of natural uranium with the exception of the children's plate which results are in agreement with depleted uranium content. Children's plate has ^{238}U (99.78%), ^{235}U (0.21%) and ^{234}U (0.00069%) and also ^{236}U (0.0034%).

Accordingly with the obtained results, we can state that the children's plate was made after 1958. The other analysed objects could have been produced before or after this date as it is possible that natural uranium continued to be used for glassmaking after the prohibition date.

Table 3.6. 1. Relative mass abundances of radionuclides (wt %) analysed by alpha-spectrometry in four uranium glass objects.

N.	Description	^{238}U	^{235}U	^{236}U	^{234}U
1	Squared bottle	99.265 ± 1.799	0.729 ± 0.046	n.d.	0.0060 ± 0.0001
10	Children's plate	99.78 ± 1.68	0.21± 0.02	0.0034 ± 0.0006	0.00069 ± 0.00003
12	Ballot	99.33 ± 2.73	0.66 ± 0.07	n.d.	0.0042 ± 0.0001
13	Box	99.34 ± 1.83	0.65 ± 0.04	n.d.	0.0053 ± 0.0001

n.d. – not detected

4. Conclusions

The objective of this work was to assess the contribution of uranium glass objects radiation dose for the total dose received by museum workers and general public in order to verify compliance with dose limits. Three non-invasive analytical methods were used for the determination of the uranium content in fourteen uranium glass objects from a private collection.

Concerning the dose rates, it was shown there is no danger for the public or for conservators. The uranium glasses should be placed safely with at least 50 cm distance from people. The showcase glass walls, soda-lime-silicate glasses commonly used in museums, reduce the radioactivity to the background level. For the conservators it is recommended that each object should be handled separately (with gloves) to maintain the radiation exposure as low as possible.

The measurement of the emitted radiation and luminescence intensities used for the determination of uranium content were evaluated in comparison with X-ray fluorescence analysis.

The measurement of the emitted radiation through the window gave only the relative uranium concentration, which showed a good relation to the uranium concentration determined by X-ray fluorescence. The thickness variation of the glass objects does not influence significantly the results obtained. If uranium glass standards were used, it would be a simple method to determine the concentration of uranium in an object.

Concerning the luminescence measurements under UV light, the results obtained indicate that for the majority of the objects the luminescence intensity is proportional to the uranium concentration. The surface morphology of some of the objects which were measured revealed to be quite critical.

Further studies are in progress to use a fluorimeter where UV light and light emission can be conducted within the probe. This process could probably eliminate the errors due to geometry effects and only the thickness of the glass walls of the uranium objects could slightly affect the results. Standards with several thicknesses have to be prepared for comparison.

Uranium isotope abundances determined by alpha spectrometry analysis in uranium glass objects gave the possibility to distinguish natural uranium from depleted uranium.

If alpha spectrometry analysis shows that a uranium glass object was made with depleted uranium, we can now conclude that the glass was made after 1958.

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Appendix I – GLASSAC Conference Poster

FACULDADE DE CIÊNCIAS E TECNOLOGIA UNIVERSIDADE NOVA DE LISBOA

VICARTE - VIDRO E CERÂMICA PARA AS ARTES

Uranium glass in museum collections

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Introduction

The presence of uranium glass objects in museum and private collections has recently raised concerns about exposure to ionizing radiation possibly emitted by this type of objects.

Fig. 1. Oil cruet in uranium glass.

Non-destructive analyses of the uranium content were made to fourteen glass objects from a private collection (Fig.1) using three methods: micro-EDXRF analysis, measuring the radiation emitted by the objects and measuring the intensity of their luminescence under UV light (Fig.2).

Fig. 2. Uranium glasses from a private collection under UV light (stemmed plate, toothpick holder and oil cruet).

Experimental

Table1 shows that for 20 and 50 cm distance, dose rate values show a significantly decrease when compared to the contact measures which is in agreement with the fact that the radiation involved is basically provided by beta emitters such as ^{234m}Pa (^{238}U daughter).

Table 1. Uranium dose rate was measured with RadiacSet AN/VDR-2 probe in contact with the objects and at two different distances, 20 and 50 cm.

Object	Dose rate (μGy/h)		
	contact	20 cm	50 cm
Squared bottle	0,62	0,22	*
Beaker 1	1,78	0,24	*
Czech jug	1,45	0,35	*
Beaker 2	4,06	0,5	0,28
Stemmed plate	5,07	0,47	0,26
Oil cruet	1,66	0,2	*
Salt-cellar	2,6	*	*
Candlestick	1,38	0,32	0,23
Toothpick holder	1,75	0,19	*
Children's plate	2,34	0,33	0,25
Paper weight	2,26	0,31	*
Ballot	2,27	*	*
Box	4,25	1,04	0,26
Ashtray	3,64	0,34	0,2

* identical to background (0,15 μGy/h)

In terms of radiological protection, the worst scenario considering a worker exposed at a dose rate of 0,28 μGy/h will give an annual dose of 0,56 mSv which is well below the dose limit for the public,1 mSv, (Council Directive 96/29 /EURATOM).

To determine the uranium content micro Energy-Dispersive X-Ray Fluorescence (μ-EDXRF) with a portable spectrometer ArtTAX was used. Results are shown in Table 2.

Table 2. Uranium oxide (wt %) content in each object analysed by μ-EDXRF.

Object	U_3O_8
Squared bottle	0,14
Beaker 1	0,46
Czech jug	0,36
Beaker 2	1,25
Stemmed plate	1,4
Oil cruet	0,49
Salt-cellar	0,43
Candlestick	0,56
Toothpick holder	0,42
Children's plate	0,44
Paper weight	0,91
Ballot	0,8
Box	1,4
Ashtray	1,08

Using the accumulation chamber method and Lucas cells to sampling air, radon exhalation results, as expected, were found to be within the background values.

With a Ratemeter type RM2/1 with a dual phosphor probe (alpha and beta radiation) the radiation of objects was measured in counts per second (cps). Figure 2 shows that there is a good correlation between these two measuring techniques.

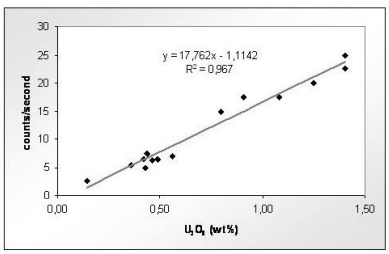

Fig. 3. Alpha and beta radiation in counts per second (cps) of the objects for different concentrations of U_3O_8.

Uranium has twenty two isotopes, all of which are radioactive. In 1943, in United States and United Kingdom legislation was implemented introducing safeguards and radioactive substances control [2]. Only afterwards, the use of uranium for glazes, enamels and glasses has been discontinued throughout the world.

Final remark

The first results were encouraging and the optimization of experimental conditions is still under study.

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Appendix II - Chemical compositions obtained by Micro-EDXRF

Table 1. Chemical composition of the glass objects analysed by µ-EDXRF, oxides content and standard deviation (wt %).

N.	Description	SiO_2	CaO	K_2O	PbO	TiO_2	Al_2O_3	U_3O_8	As_2O_5	SO_3	Fe_2O_3
1	Squared bottle	80.0 ± 0.00	5.3 ± 0.17	0.33 ± 0.02	0.14 ± 0.02	0.04 ± 0.01	1.53 ± 0.06	0.14 ± 0.01	0.09 ± 0.01	0.14 ± 0.01	0.05 ± 0.00
2	Footed beaker	74.0 ± 0.00	10.0 ± 0.00	3.00 ± 0.00	0.20 ± 0.03	n. d.	0.80 ± 0.00	0.46 ± 0.00	0.31 ± 0.01	0.15 ± 0.00	0.02 ± 0.00
3	Czech jug	78.0 ± 3.46	5.3 ± 0.31	4.27 ± 0.35	0.20 ± 0.03	0.01 ± 0.00	1.03 ± 0.23	0.36 ± 0.03	0.10 ± 0.01	0.17 ± 0.04	0.03 ± 0.00
4	Beaker	75.5 ± 0.71	5.2 ± 0.14	5.60 ± 0.00	7.40 ± 0.14	2.10 ± 0.00	0.79 ± 0.01	1.25 ± 0.07	0.19 ± 0.01	1.70 ± 0.00	0.02 ± 0.00
5	Stemmed plate	73.0 ± 0.00	6.0 ± 0.06	5.17 ± 0.06	n. d.	0.05 ± 0.00	0.92 ± 0.17	1.40 ± 0.00	0.59 ± 0.01	0.15 ± 0.00	0.02 ± 0.00
6	Oil cruet	78.3 ± 2.89	4.9 ± 0.06	0.61 ± 0.02	0.58 ± 0.03	0.02 ± 0.00	1.47 ± 0.06	0.49 ± 0.00	0.28 ± 0.01	0.15 ± 0.01	0.04 ± 0.00
7	Salt-cellar	77.7 ± 2.08	3.3 ± 0.1	1.27 ± 0.06	n. d.	0.03 ± 0.00	2.47 ± 0.25	0.43 ± 0.01	n. d.	0.08 ± 0.00	0.02 ± 0.00
8	Candlestick	79.0 ± 1.73	5.6 ± 0.15	3.17 ± 0.15	9.53 ± 0.47	n. d.	0.97 ± 0.12	0.56 ± 0.04	n. d.	1.93 ± 0.06	0.05 ± 0.00
9	Toothpick holder	65.3 ± 8.08	7.4 ± 1.40	0.97 ± 0.20	0.16 ± 0.05	n. d.	0.79 ± 0.11	0.42 ± 0.10	0.32 ± 0.08	0.17 ± 0.01	0.02 ± 0.00
10	Children's plate	80.0 ± 0.00	3.6 ± 0.35	0.50 ± 0.06	n. d.	0.03 ± 0.01	1.57 ± 0.42	0.44 ± 0.02	n. d.	0.14 ± 0.00	0.03 ± 0.00
11	Paperweight	73.0 ± 0.00	5.5 ± 0.10	4.73 ± 0.06	0.20 ± 0.02	0.03 ± 0.00	0.81 ± 0.16	0.91 ± 0.01	0.37 ± 0.01	0.14 ± 0.00	0.02 ± 0.00
12	Ballot	63.0 ± 1.00	2.8 ± 0.06	2.53 ± 0.06	0.81 ± 0.05	n. d.	2.10 ± 0.44	0.80 ± 0.05	n. d.	0.21 ± 0.00	0.02 ± 0.00
13	Box	74.0 ± 0.00	5.3 ± 0.06	5.63 ± 0.06	8.90 ± 0.17	2.23 ± 0.06	0.82 ± 0.07	1.40 ± 0.00	n. d.	1.80 ± 0.00	0.02 ± 0.00
14	Ashtray	80.0 ± 0.00	4.7 ± 0.00	0.24 ± 0.01	n. d.	0.02 ± 0.00	1.15 ± 0.35	1.08 ± 0.00	0.29 ± 0.00	0.14 ± 0.00	0.06 ± 0.00

n.d. – not detected

Appendix III - Reference glasses composition

Table 1. Theoretical composition of two reference glasses prepared by adding 1 and 1.2 wt% of uranium oxide to a soda-lime silicate glass standards from the Society of Glass Technology (SGT 7). Natural uranium was from Instituto Tecnológico e Nuclear.

Oxides	Reference glasses (wt %)	
	SGT7.U-A	**SGT7.U-B**
SiO_2	71.86	72
Na_2O	13.74	13.76
CaO	10.9	10.92
Al_2O_3	1.48	1.48
K_2O	0.73	0.43
SO_3	0.19	0.19
MgO	0.14	0.14
TiO_2	0.04	0.04
Fe_2O_3	0.04	0.04
U_3O_8	1.19	1