Original Paper

Measurements of natural radioactivity in historical glasses

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Natural radioactive components of historical glasses and two methods of the respective measurement of the radioactivity are discussed. The evaluation of radioactivity of glass objects using a Geiger-Müller counter and high-resolution gamma ray spectrometry is presented. A survey of the Warsaw National Museum glass collection with a Geiger-Müller counter allowed distinguishing the vessels made of potassium and sodium glass by their level of natural radioactivity. Gamma spectrometry, on the other hand, enables estimating a specific radionuclide content. Special attention is given to uranium glasses. One 19th century Bohemian vessel, coloured with a uranium compound, was carefully examined using gamma spectrometry. K_2O and U content were estimated to be 16.2 and 0.33 %, respectively.

Messung von natürlicher Radioaktivität bei historischen Gläsern

Es werden natürliche radioaktive Komponenten historischer Gläser sowie zwei Methoden zur Messung der Radioaktivität vorgestellt. Die Bestimmung der Radioaktivität erfolgt mit einem Geiger-Müller-Zähler zusammen mit einem hochauflösenden Gammastrahlspektrometer. Eine Untersuchung der Glassammlung des Warschauer Nationalmuseums mit Hilfe des Geiger-Müller-Zählers ermöglichte es, an Hand der natürlichen Radioaktivität, zu unterscheiden, ob die Objekte aus einem Kalium- oder Natriumglas hergestellt wurden. Die Gamma-Spektrometrie erlaubt ferner die Bestimmung des spezifischen Gehalts an Radionukliden. Besonderes Gewicht wird auf die Untersuchung von Uran-Gläsern gelegt. Ein mit einer Uranverbindung gefärbtes böhmisches Glasgefäß aus dem 19. Jahrhundert wurde mit der Gamma-Spektrometrie eingehend untersucht und Gehalte von 16,2 % K_2O bzw. 0,33 % Uran festgestellt.

1. Introduction

Historical glasses contain natural radioactivity. Such a nuclide could be introduced with the raw materials as their major or minor component. The natural radioactive elements, regardless of their radioactivity, are used as constituents of glass and ceramics at present, too [1]. Most of the papers on radioactivity of historical glasses appeared in the sixties and seventies [2 to 6]. They were mainly concerned with dating of uranium glasses [3], qualitative and quantitative determination of uranium in glass [4 and 5], identification of high-potassium glass items and quantitative analyses of potassium [6 and 7], and with the study of chemical homogeneity of glass objects [8]. Some radioactive surveys of glass collections in several museums have also been performed using simple Geiger-Müller counters. Brill et al. [3] stated that by the use of such a counter, the detectable level of radioactivity corresponds to at least 0.2 wt% of uranium. Therefore, for a lower activity, other types of detectors are required, e.g. an alpha-particle counter, high-resolution gamma spectrometry system or track detector.

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2. Natural radioactive elements in historical glasses

In historical glass objects the potassium and uranium radioisotopes may be identified in some circumstances. Radiorubidium may occur in these objects only in trace concentrations.

2.1 Potassium

Potassium was a main chemical constituent of one of the principal glass raw materials, i.e. a woodash, as well

as a potash being a purified product of the woodash. At the beginning of glassmaking, sodium and potassium were indistinguishable by the producers. Potassium was discovered in 1807. It may be then assumed that potassium, as an element in our contemporary meaning, was introduced to a glass batch rather by chance. Simply, a certain alkali source, of a known technological flux property, was added to the batch. In some geographical regions or historical periods, the land-plant ash was used in the natural or, later, in the refined state, and in much more recent time, as e.g. saltpetre. In other regions or periods, e.g. the desert, marine or shore-plants' ashes, mineral natron or synthetic sulphate (the latter was introduced to glass fabrication in the 19th century) were used. In many cases, however, a definite flux that was used contained both sodium and potassium. The published results of chemical analyses of the so-called mixed alkali glasses have confirmed such an opinion. This is also connected with the forest glasses that, until quite recently, were considered to be typical high potassium glasses [9]. In many papers [10 to 15] the potassium content in historical glasses is discussed in terms of a variety of the alkali sources. The utilization of glass cullet should also be considered [16]. The potassium content in historical glass may be even higher than 20 wt% K_2O.

Potassium contains 0.0119 % ^{40}K, which is the only radioactive isotope of the element. The ^{40}K decays with a half-life of $1.28 \cdot 10^9$ years by an electron capture (10.5 % yield) and a beta particle emission (89.3 % yield). The maximum energy of beta particles is 1314 keV. The gamma-ray energy of 1460.8 keV has a branching ratio of 10.5 %.

2.2 Uranium

The German chemist M. H. Klaproth discovered uranium in 1789. Uranium is responsible for a characteristic yellow-green colour of glass. Most of such glasses are easily identified by a characteristic fluorescence under the ultraviolet radiation [17]. Supposedly, M. H. Klaproth was the first one to add intentionally an uranium compound as colourant to glass. In Bohemia Josef Riedel introduced glass coloured with the uranium compounds on an industrial scale in the early thirties of the 19th century. The transparent Annagrün and Annagelb glasses as well as an opaque glass called Chrysoprase belong to the well-known examples [18]. Some years later, uranium glass was melted also in some other countries. It came into vogue at the turn of the 19th century. The most common uranium raw material was pitchblende. The uranium content in historical glasses often exceeds one per cent.

Mention of a measurable uranium content has only once been made in an ancient Roman glass by J. J. Manley and E. G. Laws in 1912 [19]. They analysed green tesserrae of glass mosaics from an imperial Roman villa on Cape Posilipo on the shore of the Naples Bay. However, the results of these analyses are questionable [2, 4 and 20]. The mosaics disappeared during World War II and no re-examination is possible. Other analyses of Roman mosaics, including samples of the above mentioned green tesserrae, have not led to identification of any new examples of Roman uranium glass [4].

Natural uranium consists of three isotopes: ^{234}U (0.0058 %), U^{235} (0.714 %) and ^{238}U (99.28 %). They decay with a half-life of $2.46 \cdot 10^5$, $7.04 \cdot 10^8$ and $4.47 \cdot 10^9$ years, respectively. All these isotopes decay by the emission of alpha particles. Some of their daughters also emit beta and gamma radiation. Only ^{235}U is also a gamma ray emitter. The initial part of the ^{238}U and the ^{235}U decay series with the energies and intensities of the main gamma lines are reported in table 1. Only these members of the decay chains are shown which can be useful in measuring the uranium content in historical glass objects. The strong 63.29 and 92.6 keV gamma lines of ^{234}Th appear to be suitable for uranium determination in the little objects. In the case of larger ones, a significant error can arise as a result of the self-absorption effect. For the objects of irregular shapes, the determination is rather difficult to accomplish. The 143.76, 163.36, 185.71 and 205.31 keV gamma lines that are accompanying the ^{235}U decay, as well as the 766.38 and 1001.03 keV gamma lines that are accompanying the ^{234m}Pa decay via beta-particle emission (99.87 %) could be used to determine the uranium content. The ^{238}U decays through an alpha-particle emission to its daughter product, ^{234}Th, which, with a half-life of 24.1 d, decays to ^{234m}Pa. A secular equilibrium for this chain is reached within less than one year (about 250 d).

3. Experimental

3.1 Measurements of natural radioactivity of historical glass vessels with a Geiger-Müller counter

A conventional radiometer with a Geiger-Müller counter (SBT 10A type, manufactured by POLON-EKO-LAB, Bydgoszcz (Poland)) was used. An active window area was about 50 cm^2 and a window thickness was about 2 to 3 mg/cm^2.

The radiometer enabled the measurement of the sum of beta, gamma and X-ray intensities. The intensities are recorded in counts per second. All measurements were performed in the storage rooms of the Warsaw National Museum. The natural radioactive background was equal to about 2 counts/s.

3.1.1 Uranium glass

The results of uranium glass measurements are given in table 2. In many cases, the count rates for an object varied

Table 1. Schematic diagram of the ^{238}U and ^{235}U decay series down to ^{230}Th and ^{231}Th, respectively, energies and intensities of the main gamma lines

radionuclide	half-life	main gamma ray lines in keV	intensity in %
^{238}U	$4.47 \cdot 10^9$ a		
↓ α			
^{234}Th	24.1 d	63.29	4.8
		92.60	5.58
↓ β^-			
IT (0.13 %) ^{234m}Pa 99.87 %	1.17 m	766.38	0.318
		1001.03	0.845
^{234}Pa β^-	6.75 h		
β^-			
^{234}U	$2.46 \cdot 10^5$ a		
↓ α			
^{230}Th	$7.54 \cdot 10^4$ a	67.67	0.38
		143.87	0.049
↓ α			
^{235}U	$7.04 \cdot 10^8$ a	143.76	10.97
		163.36	5.08
↓ α		185.71	57.25
		205.31	5.02
^{231}Th	25.52 h		
↓ β^-			

Table 2. Measurements of natural radioactivity of historical objects of the uranium glass using a Geiger-Müller counter (all the objects belong to the Warsaw National Museum collection)

no.	glass object	inventory no.	measurements conducted from the following directions in counts/s			
			from above	from below	side view	side view
			close-contact distance			25 cm distance
1	footed beaker; green cut-glass; gilded; Bohemian, 1840s	158619	55	40	45	4
2	footed beaker; green cut-glass; gilded; Bohemian, 1840s	188645	75	55	50	5
3	lamp; opaline, green glass covered with blue glass; Silesian?, 2nd half (3rd quarter?) of 19th c.	SZSmag129	x	40	25	2
4	jug; opaline, blue cut-glass; Bohemian, c1850	SZSmag485	6	4	x	x
5	cameo-glass vase; acid-etching; French, E. Gallé, after 1904	SZS106	60	70	35	4
6	jug; opaline, cut-glass; gilded; Bohemian or French, before 1855	34069	110	115	105	15
7a	goblet; opaline, cut-glass; gilded and white enameled; Bohemian, c1850	32328/a	120	120	60	8
7b	cover for goblet above mentioned	32328/b	x	115	x	x
8	carbide lamp; opaline, green glass; gilded and enameled; Bohemian, c1850	30092	130	120	90	10
9	beaker; opaline, flashed cut-glass (green and colourless layers); Bohemian, 1840s	188648	115	5	5	2.5

Note: x = lack of measurement.

even by more than one order of magnitude. These discrepancies occurred when measurements were carried out from the different directions or at the different distances. The intensity of the radioactivity measured depended on the size and the shape of the examined surface. The exposed glass surface played an important role during the

experiments. This resulted from the self-absorption effect, which is particularly significant for the low energies.

3.1.2 Glasses without uranium

For measurements of the glass objects that contain uranium below detection limit, and were melted according to the sodium recipe, the detected level of their radioactivity did not exceed the background.

On the other hand, glass objects that contain uranium below detection limit, and were melted according to the potassium recipe gave two or three times greater count rates than the background did. The counts registered from a very close distance and from a 25 cm distance did not vary essentially for the potassium glass vessels. Hence, for measurements from a larger distance, in many cases it was impossible to distinguish between the potassium glass with and without uranium, exclusively on the basis of their radioactivity level. The count rates were almost the same (see: 1 to 3, 5, and 9 in table 2). For the potassium glass without uranium, and in contrast to the uranium glass, the count rates depended to a higher degree on mass, than on measurement direction and surface of the object examined. This originates in higher radiation energy emitted by potassium as compared to radiation that comes from the uranium isotopes and their daughters. The detected part of the gamma radiation from uranium chains comes to a larger extent from the surface layers of the objects studied.

Having in mind that most of the uranium glass objects were manufactured using the potassium flux, it should be stressed once again that the radioactivity of historical glass pieces detected with a Geiger-Müller counter refers to the overall radioactivity.

The radiometric measurements of the museum glass objects, performed through the showcase walls made of 0.5 cm thick ordinary sodium glass, showed only the background radioactivity. This depended neither on the distance of an object and a detector from the glass walls nor on the formulae of the examined glass object (i.e. with or without uranium). So, no doubt common glass walls in museum showcases constitute a sufficient shield for radioactivity emitted by historical glass items.

3.2 Measurement of the natural radioactivity of glass vessels using gamma spectrometry

A Bohemian footed green glass beaker made in 1840s was examined. The vessel has been made available for examination by the Warsaw National Museum (object inventory no. 188645, compare sample 2 in table 2). The weight of the object is 448.8 g. The measurements were carried out nondestructively at the Institute of Nuclear Chemistry and Technology in Warsaw.

Table 3. Gamma spectrometry of glass vessel (National Museum, Warsaw, inventory no. 188645)

isotope	gamma line in keV	net peak intensity[1)] in counts/(d · g)	U content in %	K_2O content in %
^{235}U	143.76	418	0.36	
	163.36	190	0.33	
	185.71	2114	0.33	
	205.31	189	0.32	
^{234m}Pa	766.38	143	0.30	
	1001.03	338	0.31	
^{40}K	1460.75	367		16.2

[1)] Background corrected.

The radiometric measurements were performed with the use of a gamma ray spectrometer, containing an HPGe detector with the resolution of 1.9 keV, and a relative detection efficiency of 92.4 % for a 1.33 MeV gamma line. The 10 cm passive lead shield lined with 0.5 cm cadmium and 0.5 cm copper was applied for reducing the natural background radiation. The full block diagram of the gamma spectrometry system and more detailed experimental information were given in an earlier paper [7].

The full examination consisted of two measurements. The counting time of each measurement was one day. The first step included measurement of a silicon mould with the glass vessel inside. For the second measurement, the same mould was filled with the powdered material that was used for calibration. A mixture of 22.5 g U_3O_8 and 385.4 g K_2SO_4 was used for this purpose. The mixture was homogenized in a ball mill and it contained 4.68 wt% U. The weight of the standard for calibration, which filled the silicon mould, was 274.7 g.

The results obtained are listed in table 3. The uranium content that was computed on the basis of intensity of the individual gamma lines showed a good agreement. Only one value computed on the basis of the 143.76 keV gamma line was higher. It was due to the impossibility of separating the 143.76 keV gamma line from the 143.87 keV one accompanying the decay of ^{230}Th ($t_{1/2} = 8.0 \cdot 10^4$ a). The ^{230}Th nuclide is a part of the ^{238}U decay chain (see table 1). If we reject this last extreme result (0.36 wt%) as the outlier, the mean uranium content in the examined glass, computed on the basis of intensities of the five remaining lines, amounts to 0.32 wt%. K_2O content is equal to 16.2 wt%.

On the basis of this historical glass object, the limits of detection of uranium and potassium were estimated for the gamma ray energies used in the measurements. For the objects in the mass range of 200 to 500 g and a time of measurement of 1 d, the uranium and potassium limits of detection are about 0.0002 and about 0.025 %, respec-

tively. For the same mass of the objects, and for the time of measurement of 1 h, a limit of uranium detection is 0.0010 %, and that of potassium it is about 0.1 %.

4. Discussion

The measurements of natural radioactivity of historical glass are useful as an alternative analytical procedure to determine the potassium and uranium contents. It should be remembered that most of the historical uranium glass pieces contain also potassium. The potassium content influences the overall level of natural radioactivity of the uranium glass. It is especially important, when one carries out radioactivity measurements using a Geiger-Müller counter. In such radiometric measurements, many parameters may disturb the obtained results, especially for comparison studies. These parameters are mainly connected with geometry of measurement. The measurements should be done from a close and constant distance for all the objects studied. In the case of uranium glass, the area of the exposed glass surface plays a very important role.

The showcase glass walls, commonly used in museums, reduce the radioactivity level measured with a Geiger-Müller counter to the background level. Therefore, the radioactivity of historical glass objects cannot be measured through them.

The high-resolution gamma spectrometry enables simultaneous determination of the uranium and potassium content nondestructively. Due to the low uranium detection limit, this method can be used for determining even the trace amounts of the element. The reliable knowledge of the uranium as well as of the potassium contents may be useful for further studies on dating the artefacts and in some other technological comparisons.

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