

Nondestructive analysis of potassium in ancient glass on the base of its natural gamma activity

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The concentration of K_2O in historical glass objects was measured by gamma ray spectrometry. The method involved using moulds of the objects filled with material of known K_2O content. The results obtained were found to be close to results previously obtained by traditional methods and well within accepted tolerances in such cases. Gamma ray spectrometry produces results based on the whole object, not just on a sample of it which in the case of historical glass may not be representative. The method is completely nondestructive as no sample is taken, which allows it to be used for museum glass when destruction may not be permitted.

Zerstörungsfreie Kaliumbestimmung in historischen Gläsern auf der Basis ihrer natürlichen Gammastrahlung

Die K_2O -Konzentration in historischen Gläsern wurde mit der Gamma-Spektrometrie gemessen. Dieses Verfahren beinhaltet, daß von den Objekten Formenimitationen hergestellt werden, die für Vergleichsmessungen Füllmaterial mit bekanntem K_2O -Gehalt enthalten. Die ermittelten Ergebnisse stimmen gut mit denen früherer, auf traditionellen Methoden basierender Untersuchungen überein. Die Gamma-Spektrometrie erfaßt das ganze Objekt und nicht nur einen Teilbereich, der bei historischem Glas keineswegs repräsentativ sein muß. Das Verfahren ist völlig zerstörungsfrei und kann deshalb für Museumsgläser, von denen in der Regel keine Teilproben zur Verfügung stehen, angewendet werden.

1. Introduction

The determination of the concentration of a particular element can be crucial in the classification of historical glass objects. This is the case in the discrimination between potassium and sodium in medieval glass and many younger objects. Most historical glasses produced up to the end of the 18th century contain only the radioactive nuclide ^{40}K in more than trace concentrations. Higher concentrations of uranium may be found in glass made in the 19th century. Other radioactive elements, for example rubidium, can be ignored because of their trace abundances.

The use of the natural radioactivity of historical glass in order to classify them has received little attention as yet. Only a few examples are reported in the literature. Murray and Haggith [1], and later Festag, Gentner and Müller [2] measured the uranium content. Hudson and Newton [3 to 5] used radiation-monitoring films to determine the amounts of potassium in medieval glass by measuring beta activity. Their results have been used by Cox and Gillies [6].

Measuring the concentration of potassium by the natural radioactivity is carried out on various objects, including glass. In the case of gamma spectrometry, it

is usually a destructive method, because the sample is powdered. The purpose of this research was to explore the possibility of measuring the potassium content of historical glass objects by gamma ray spectrometry in a nondestructive manner. The fundamental problem of adopting gamma spectrometry to historical glass is to achieve stable and comparable parameters in the measurements of both the historical objects and the calibration materials.

Natural potassium contains 0.0119% of isotope ^{40}K . ^{40}K decays with a half-life of $1.28 \cdot 10^9$ years in accordance with the branching of electron capture and beta activity. The radiation emitted consists of beta particles with 1314 keV endpoint energy (89.3% yield) and gamma rays of 1460.8 keV energy (10.5%). The latter is important for this investigation.

2. Analytical procedure and equipment

The measurement of the 1460.8 keV radiation of ^{40}K was performed by 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 natural background spectrum contains a 1460.8 keV peak. Therefore, natural background radiation was reduced by a 10 cm passive lead shield

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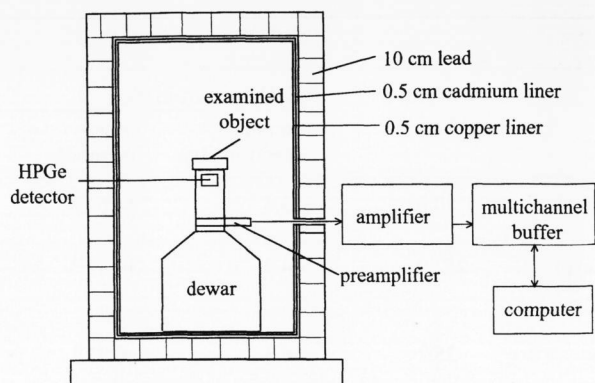


Figure 1. Standard gamma ray spectrometry system with a passive shield.

Table 1. Comparison of gamma spectrometry and AAS results of glass plates.

no.	weight in g	K ₂ O content in %	
		AAS ¹⁾	gamma spectrometry
1	13.751	19.7	20.0
2	14.666	15.7	16.1
3	14.317	11.5	11.6
4	14.292	9.57	9.21
5	14.385	5.15	5.04
6	14.672	1.09	1.04
Standard for calibration	K ₂ SO ₄ 9.475		54.1

¹⁾ AAS analysis of samples conducted by the Polish Geological Institute, Warsaw.

lined with 0.5 cm cadmium and 0.5 cm copper. The block diagram of the gamma spectrometry system is shown in figure 1.

For objects of irregular geometry it was necessary to make moulds of the specimens to be analysed. Initial experiments included measurements of: a) the empty mould (the background), b) the mould with the glass object inside, c) the mould filled with potassium sulphate powder which was used for calibration. As the natural background radiation did not vary during the course of analysis, subsequent tests were exclusively carried out on b) and c). Silicon rubber (room temperature vulcanization) was found to be the best material for the moulds. However, aluminium foil and dental wax is also suitable. The type of material for the mould is not significant. But it should not contain any potassium. To ensure satisfactory precision a counting time in the range of 10000 to 120000 s was selected. For this counting time the statistical error was less than 6%. The following calculation for the intensity of gamma rays was used:

$$n = (I - I_B)/m \quad (1)$$

where n = net counts per 80000 s for 1460.8 keV peak per unit mass; I = counts per 80000 s for 1460.8 keV peak; I_B = the number of counts in the 1460.8 keV peak of natural background per 80000 s; and m = weight of glass object in g.

The K₂O content in the glass objects was calculated by comparing their gamma ray intensity to that of the potassium sulphate filled moulds used for calibration. For this method, where the sample under study and a reference sample were measured under the same geometrical conditions, the concentration of potassium in the examined glass was calculated as follows:

$$c_x = c_r(n_x/n_r) \quad (2)$$

where c_x, c_r = concentrations of potassium in the unknown and the reference samples, respectively; and n_x, n_r = 1460.8 keV net peak count rate per unit mass of the unknown and the reference samples, respectively.

3. Preliminary experiment

During the preliminary stage of the experiment the authors used ordinary glass plates (about $(35 \times 35 \times 5)$ mm³) with different K₂O contents. Their K₂O concentrations were obtained by atomic absorption spectrometry (AAS). The results including that on the standard K₂SO₄ are shown in table 1. The agreement of the results was acceptable.

4. Measurements of museum objects

The preliminary experiments were restricted to one single mould with the shape of the glass plates. In the case of museum objects, each specimen was of different shape for which special moulds were made. These were filled with potassium sulphate powder, so that there would be an independent calibration source. It should be stressed that no calibration curve was needed. In table 2, the results by gamma spectrometry on eleven historical objects are presented. All these artefacts had been analysed earlier by various laboratories and analytical methods, often by an unspecified procedure, but an analytical sample was always used. The original results are also listed in table 2.

5. Comments

The procedures used permitted the authors to ignore the self-absorption effect of gamma radiation of ⁴⁰K, as the measured objects were small. The first results have proved encouraging, although the number of glass objects investigated was limited. The differences between the results obtained by gamma ray spectrometry and the other methods (final two columns of table 2) are not large and compare favourably with normal discrepancies between different samples examined in different labora-

Table 2. Data on K₂O concentrations in historical glass objects.

no.	glass object	weight in g	K ₂ O content in %	
			gamma spectrometry	other methods
1	body and neck of bottle; greenish; weathered; 1st half 18th c. (Royal Castle, Warsaw [ZK/95/6/98])	80.8	13.4	14.69 ²⁾
2	stem of goblet; colourless; unweathered (with the naked eye); around 1730; Lubaczów (?); (National Museum, Warsaw [SZS mag. 486])	252.0	14.9	14.82 ²⁾
3	foot of glass; green glass; weathered; 18th c. (Royal Castle, Warsaw [ZK/95/23/0])	25.7	6.3	6.33 ³⁾
4	fragment of bracelet; dark brown, weathered; K ₂ O–PbO–SiO ₂ type; 12/13th c. (?); (PMA, Warsaw [V/VI/1235, no. 4])	3.3	18.6	15.8 ⁴⁾ see [7]
5	fragment of bracelet; dark brown, weathered; K ₂ O–PbO–SiO ₂ type; 12/13th c. (?); (PMA, Warsaw [V/VI/1235, no. 2])	2.562	16.5	17.0 ⁴⁾ see [7]
6	fragment of glass; weathered; (Józwiów, district Radoszyce, voivodeship Kielce [inv. no. 56/94/17])	8.98	9.0	8.0 ⁴⁾
7	fragment of greenish glass; weathered; (Biała Głina, district Mniów, voivodeship Kielce [inv. no. 2c/94/7])	21.06	7.1	6.2 ⁴⁾
8	fragment of colourless glass; weathered; (Nowa Wieś, district Strawczyn, voivodeship Kielce [inv. no. 1c/94/3])	14.59	11.4	11.4 ⁴⁾
9	fragment of greenish glass; weathered; (Wieleńki, district Daleszyce, voivodeship Kielce [inv. no. 13/94/6])	15.72	15.7	14.4 ⁴⁾
10	fragment of green glass; weathered; (Cisów, district Daleszyce, voivodeship Kielce [place 1, inv. no. 7/94/8])	11.742	6.01	6.0 ⁴⁾
11	goblet; colourless; unweathered (with the naked eye); Naliboki; 18th c. (National Museum, Warsaw [SZS mag. 446])	73.440	20.0	18.6 ⁴⁾

²⁾ Atomic absorption spectrometry, conducted by Polish Geological Institute, Warsaw.

³⁾ Electron microprobe analysis, conducted by Central Laboratory of the Institute of Archaeology and Ethnology, Polish Academy of Sciences, Warsaw.

⁴⁾ Flame photometry, conducted for glass objects nos. 4 and 5 by A. Girdwoyń and H. Pawłowska and for glass objects nos. 6 to 11 only by A. Girdwoyń at the Central Laboratory of Institute of Archaeology and Ethnology, Polish Academy of Sciences, Warsaw.

Note:

Objects nos. 6 to 10 were made available by Prof. Dr. J. Olczak of the Institute of Archaeology and Ethnology, Copernicus University, Toruń. The museums which made available the remaining objects have been indicated with objects nos. 1 to 5 and 11 where PMA stands for State Archaeological Museum.

tories. The difference between the results of object no. 4 stands out. It requires further examination. It is well known that historical glass is not always homogeneous, so the sample in this case may not have been representative, but on the other hand, a gamma spectrometry result of a badly weathered glass object of a very small mass may not be representative of the original glass. It should be mentioned again that the gamma spectrometry, as used here, is a nondestructive method of analysis (as no sample is required), and that the results faithfully represent the average amount of K₂O within a glass object. No result obtained by the analysis of a single sample of historical glass can be treated as an average

concentration of the element throughout the whole object. In many cases, however, where it is not possible to destroy an object or its surface in any way (as is very frequently the case with objects from museum collections), XRF, EMPA or other related methods are not allowed to be used. Gamma spectrometry appears to be a valuable tool in these cases.

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