DETERMINATION OF THE LEAD OXIDE CONTENT OF LEAD CONTAINING GLASSES ON THE BASIS OF THE ATTENUATION OF GAMMA RADIATION

By

D. Bódizs and G. Keömley

Nuclear Training Reactor of the Technical University Budapest

Introduction

In the production of lead-containing glasses, the concentrations of lead oxide are different in the raw mixture, the melt and the final product. Consequently, the PbO concentration, which determines the quality of the product, can be adjusted only approximately to the desired value. The critical value for the quality of the glass is about 24% PbO content.

This requires a fast, reliable and relatively simple measurement method for the determination of PbO during manufacturing.

Methods for the determination of lead oxide concentration

There are relatively few examples for industrially applicable methods of lead analysis. Some authors reported activation methods [1, 2, 3, 4, 5], but they are hard to use in industrial environment, requiring expensive and complex instrumentation (e.g. neutron generator or other neutron sources of high intensity, multichannel analyser, etc.). It is a further problem that lead has unfavourable properties in activation analysis.

For the determination of PbO other analytical methods can also be applied, such as complexometric method [6], atomic absorption method [7], gravimetric method.

These methods, however, due to their time consuming nature, cannot be applied in intermediate product control.

Theory of the method applied

Three basic interactions take place between gamma radiation and matter: photo-effect, Compton scattering and pair production. Owing to the interactions, a gamma beam of intensity I_0, after passing a homogeneous layer of thickness x, is attenuated in intensity to

$$I = I_0 \exp\left(-\mu' x\right) \tag{1}$$

where μ' is the linear absorption coefficient. The probability of interactions depends on the energy of the gamma radiation and on the atomic number of the absorbent.

Equation (1) can be transformed into the following form [8]:

$$I = I_0 \exp\left(\frac{-\mu'}{\rho}\rho x\right) = I_0 \exp(-\mu d) \tag{2}$$

where μ is the mass absorption coefficient ($cm^2\ g^{-1}$),

　　d is surface density (gcm^{-2}), and

　　ρ is the density of absorbent (gcm^{-3}).

When the absorbent is a mixture of different substances, the mass absorption coefficient can be given by the relationship

$$\mu = \sum_{i=1}^{n} w_i \mu_i \tag{3}$$

where

　　i runs from 1 to n (the number of components),

　　μ_i is the mass absorption coefficient of component i, and

　　w_i is the mole fraction of component i, which can be determined from the atomic and molecular weights [9].

The above considerations hold for parallel, monoenergetic beams. If these conditions are not fulfilled, multiple scattering of gamma photons in the absorbent should also be taken into account.

The mass absorption coefficient strongly varies with the atomic number of the absorbent. Accordingly, lead — owing to its high atomic number — is known to particularly well absorb gamma radiation. The measurement is based on this behaviour.

In the given case relatively high (20–30%) lead concentrations are to be determined. The other constituents of glass (SiO_2, Al_2O_3, CaO, MgO, K_2O, Na_2O, Fe_2O_3, TiO_3) have either low atomic numbers (hence low μ_i'), or appear in low concentrations, thus their share in the attenuation process is negligible with respect to that of lead.

The actual measurement is a relative method. Using a series of standard glass specimens with known lead oxide concentrations an attenuation vs. lead oxide concentration curve is constructed, and by means of this calibration curve the lead oxide content of an unknown sample can easily be determined, provided that the conditions of measurements are the same.

Factors affecting the accuracy of measurement

Preparation of specimen and standard

There were examined two methods for preparation of the sample (and standard):

The sample taken from the *glass melt* to be analysed is pulverized after solidification, and pressed into form with the addition of some binding material, and then the solvent of the binding agent is evaporated. This process has the following disadvantages: according to Equation (2) the attenuation due to the absorbent also depends on the density and thickness of the sample in addition to the composition. These parameters (grain size, density, sufficiently accurate geometry) are difficult to reproduce with the thus prepared samples, and as a relative method is used, reproducibility in preparing the samples is a particularly important requirement.

Most of the above difficulties can be overcome with the application of *glass sheet* specimens. The identical thickness can be ensured by grinding the sheets. Problems arising from inhomogeneous density are also eliminated, care should be, however, excercised that inclusions of air bubbles do not occur in the glass.

Considering the above factors, we decided in favour of glass sheet specimens.

Radiation source

In this respect the required activity and the optimum gamma energy with respect to sensitivity were investigated.

1. Calculation of activity

Let us take a sample of 24% lead oxide concentration with a density of 2.9 gcm^{-3}.

To estimate the necessary minimum activity of radiation source, three specimens 4 cm in diameter and different in thickness were taken. From the volume and density data an "effective lead thickness" was determined; this is the thickness of a lead sheet that can be substituted for the specimen if the absorption effect of the other components of the sample is neglected.

Under these assumptions the activity of the radiation source can be estimated by the relationship

$$A_0 = \frac{I}{f \cdot \varepsilon \cdot \Omega \exp\left(-\mu\rho x_i\right)} \tag{4}$$

where I is the count rate expected after the absorbent (cps);

   f is the number of gamma quanta produced in one decay (taken as 1 until the radiation source is not selected);

   ε is the total efficiency. Its values can be found e.g. in Ref. 10 as a function of gamma energy, detector size and radiation source — detector distance;

   Ω is a solid angle factor which takes into account the decrease in efficiency due to the collimators, its value can be determined from the source — detector distance and the bore length and diameter of the collimator [10];

   x_i is the effective lead thickness.

The calculations were performed for three specimens differing in thickness (0.5, 1.0 and 1.5 cm), and for three gamma energies (60, 300 and 600 keV), assuming a count rate of 100 cps after the specimen. In the calculations a radiation source — detector distance of 10 cm, a scintillation detector of 1 1/4″ × 1″ size, and a collimator of 1 cm thickness and 0.2 cm bore diameter, placed 2 cm before the detector, were assumed. The calculated results are given in Table 1.

Table 1

Specimen thickness (cm)	Gamma energy (keV)		
	60	300	600
	Activity (MBq) A_0		
0.5	46.3	20.1	21.3
1.0	242	22.8	22.2
1.5	1267	25.9	23.1

$\varrho_{Pb} = 11.34 \ \text{gcm}^{-3}$
$\Omega = 1.88 \times 10^{-3}$
$I = 100 \ \text{cps}$
Pb O concentration: 24%

The activity of the radiation source to be used for the measurements should presumably be higher than the A_0 values shown in Table 1, since generally $f < 1$, and with the differential discriminator counting method preferably applied the count rate further decreases. This fact was disregarded in the theoretical considerations.

2. Gamma energy

It can be seen from Equation (2) that the intensity attenuation of the specimen depends, in addition to the effective lead thickness, x, exponentially on the mass absorption coefficient. Regarding the relationship between absorption coefficient and gamma energy for lead, the strongest attenuation can be expected for gamma photons of about 20 keV. The absorption coefficient has an extremum at 88.01 keV (K-edge). Accordingly, the highest sensitivity can be expected to occur in the gamma energy regions of 20–70 keV and 90–150 keV. Of course, in selecting the radiation source, certain practical aspects (half-life, availability, price, etc.) should also be observed.

The concentration scale of the standard

The analytical curve is constructed from the measured attenuations of standards. It is plausible that with only a few measuring points the accuracy of determination will be poor. On the other hand, the points of the analytical curve are subject to statistical errors. On this basis, an upper limit may be estabilshed for the density of points of the curve.

Assuming standards 1 cm in thickness, and a gamma energy of about 60 keV, it can be calculated that the lead-oxide content of the standards for taking the calibration curve should differ in steps about 0.1–0.2%.

On the basis of the theoretical considerations ^{241}Am was applied as radiation source (half-life 458 y, gamma energy 59.64 keV, gamma abundance 0.353 [11]). The activity of the source was 3780 MBq.

Experimental

Preparation and measurement of standards

Standard glass specimens were lead-glass discs 4 cm in diameter and 1 cm in thickness. The amount of PbO varied in steps of 1% in the 20–30% concentration range, and in steps of 0.1% between 23.5 and 24.5%. Several (4 to 5) specimens were prepared for each concentration. The PbO concentration was measured by gravimetric method with an accuracy of ±0.2%.

Measuring apparatus

The measuring apparatus consisted of the following parts:

Detector: Product of Gamma Works. Measuring head ND 131/F, containing an S 1144 type scintillation crystal with a good effeciency for low-

energy gamma radiation. Due to the small volume of the crystal the
background also decreased.

Measuring instrument: Product of Gamma Works. NK-350 type single-
channel, energy selective scaler with IC, operated in differential mode.

Data output: GNP-516 type numeric printer of Gamma Works. The
scintillation head, the sample, the radiation source and the lead collimators
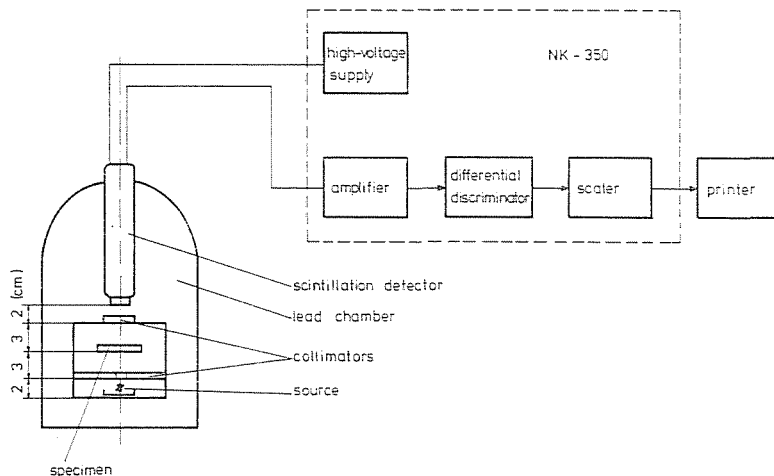ensuring "good-geometry" were placed in a lead chamber.

Fig. 1. Block diagram of the measuring apparatus

The source — detector distance was 10 cm. Above the source and before
the detector lead collimators, 10 mm in thickness and with a bore of 2 mm in
diameter, were installed. The glass samples to be measured were placed
between the two collimators (Fig. 1).

The relatively high activity of the source permitted the application of thin
beam and differential counting (with narrow energy window). Thus the number
of scattered photons and the intensity of background could be reduced
substantially.

Experimental results

The first purpose of the measurements was to determine the intensity
attenuation of gamma radiation by the standards as a function of the lead oxide
content (calibration curve).

Geometry and measuring parameters should be selected in a way that the
value of I_0 does not cause appreciable dead time loss, and I_x should not be too
low. Some typical count rates were as follows:

background: 50 counts/100s
I_0 370 000 counts/100 s
I_x 10 000 counts/100 s   (cca. 20% PbO)
                          5 500 counts/100 s   (cca. 24% PbO)
                          2 000 counts/100 s   (cca. 30% PbO)

    Figure 2 shows the calibration curve, the measured values of the intensity attenuation as a function of lead oxide concentration, their statistical errors, and the calculated points of the fitted exponential curve. ($y = ae^{bx}$). The agreement, with the exception of one concentration (26.28%), is good. This exception can be attributed to the inhomogeneity of the samples. Figure 3 illustrates the concentration dependence of the logarithm of intensity attenuation.
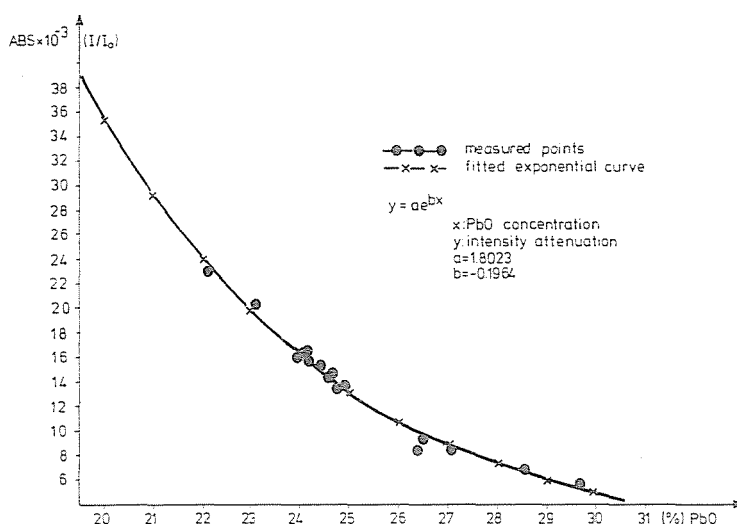

Fig. 2. Intensity attenuation of lead glass as a function of PbO concentration

    Concerning the error of the final results, the following estimation can be given. The statistical error in the measurement of I_x/I_0 is cca. 1% in the neighbourhood of 24% PbO. In the preparation of standard glass specimens two sources of error may occur. On the one hand, the concentrations can be determined with a relative error of cca 1% by means of the traditional method, and on the other hand a relative error of cca. 0.1% may be introduced at the measurement of thickness. Due to the independence of these errors, the laws of error propagation lead to cca. 1.4% as the relative error of concentration. This means that a lead oxide concentration of e.g. 24% can be given as (24 ± 0.34) %.
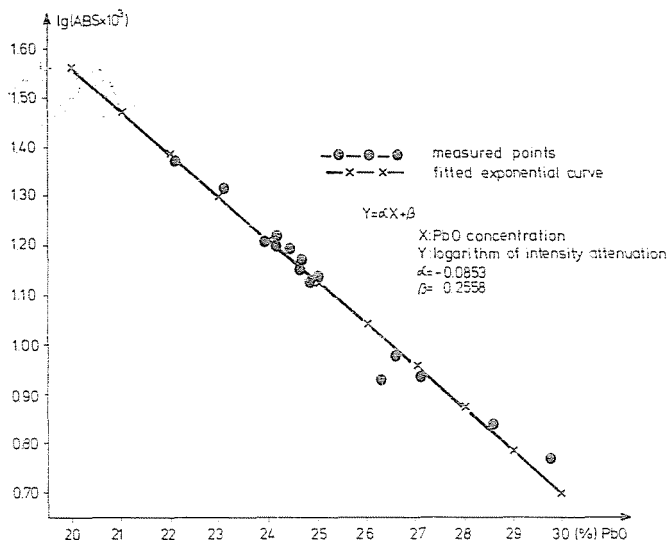
Fig. 3. The logarithm of intensity attenuation of lead glass as a function of PbO concentration

Summary

In the possession of theoretical considerations and experimental results it can be stated that the above method for the determination of lead is simple, and can therefore be easily introduced in industry, is fast, thus it enables to perform intermediata product quality control and, if necessary, intervention into the technological process. The measurement requires a series of standard glass specimens in which the lead concentration is known with the demanded accuracy. The standards and the test specimens should be homogeneous, and may not contain bubbles or inclusions. The duration of measurement is cca. 60 min, accuracy is $\pm 0.4\%$ in the PbO concentration range of 20–30%.

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Dr. Dénes BÓDIZS
Dr. Gábor KEÖMLEY $\Big\}$ H-1521 Budapest