Analytical Chemistry

Applied analysis
Material analysis

Determination of the chemical composition of a brass sample using x-ray fluorescence

Aims of the experiment

■ To learn how to use an x-ray apparatus.

■ To perform an x-ray fluorescence analysis.

■ To analyse the composition of an alloy.

■ To determine the quantitative content of the constituents of an alloy.

Principles

When atoms are irradiated with high-energy x-rays, x-rays with a characteristic energy are emitted. This phenomenon is described as x-ray fluorescence. The emitted energy depends on the atomic number of the sample material (Moseley's Law).

The energy supplied causes electrons to be shot out of the inner shells. The gaps in the inner electron shells are then filled by electrons from the outer electron shells. These electrons lose energy in the process, which is then emitted in the form of x-rays (x-ray fluorescence).

The K spectrum (the K spectral series) is caused by electron jumps out of the second (Kα) or the third (Kβ) electron shell to the K shell. The L spectrum originates analogously when electrons fall back into the second electron shell (L shell).

Every element, each with a different atomic number, emits x-rays with different energy levels. This energy is practically independent of the bonding form of the element, as the inner electrons have practically no involvement in chemical binding.

The x-ray fluorescence spectrum of a sample containing several components is, as a first approach, the addition of the individual spectra. The relative proportions of the individual elements in a sample can be stated based on the relative intensities of their fluorescence lines. Unfortunately, the physical and chemical environment of the elements investigated can have an influence on this, referred to as the matrix effect. The surface quality and the geometrical properties of the sample must also be considered. And finally the measuring system also has an influence on the measurement. In order to obtain a reliable quantitative measurement in spite of this, calibrations must be carried out in the same instrument using materials of a similar matrix and surface consistency.

In this experiment, the quantitative analysis of the chemical composition of a leaded brass sample will be carried out. The components of this alloy were identified in the LD Chemistry Leaflet C3.6.1.1. By comparison of the peak heights of the sample with those of the pure elements, the composition is determined quantitatively.

Risk assessment

The x-ray apparatus complies with the regulations regarding the design of a school x-ray apparatus and fully protected device and is type approved in Germany (NW 8907/97 Rö) as a school x-ray apparatus and a fully protected device.

Owing to the built-in protection and screening measures, the dose rate outside of the x-ray apparatus is reduced to less than 1 μSv/h, a value which is in the order of magnitude of natural background radiation.

Before putting the x-ray apparatus into operation, inspect it for damage.

Protect the x-ray apparatus against access by unauthorised persons.

When switching on the x-ray apparatus, check to make sure that the ventilator in the tube chamber is turning.

The goniometer is moved exclusively by electric stepper motors. Do not block the target arm and sensor arm of the goniometer and do not use force to move them.

Equipment and chemicals

1 X-ray apparatus	554 800
1 X-ray tube, Mo	554 861
1 Goniometer	554 831
1 X-ray energy detector	559 938
1 Set of target alloys	554 848
1 K-line fluorescence target set	554 844
1 L-line fluorescence target set	554 846
1 Pocket-CASSY 2 Bluetooth	524 018
1 CASSY Lab 2	524 220
1 MCA box	524 058
1 BNC cable, 1 m	501 02

also required:
PC with Windows XP/7/8

Set-up and preparation of the experiment

The experimental set-up is illustrated in Figure 1.

1. Feed the connection cable of the power supply through the empty channel of the x-ray apparatus and connect it to the mini DIN socket on the x-ray energy detector.

2. Attach the sensor holder assembled with the x-ray energy detector to the sensor arm of the goniometer.

3. Connect the signal output of the x-ray energy detector to the BNC socket SIGNAL IN of the x-ray apparatus using the supplied thin BNC cable.

4. Continue to feed the cable in so that it is sufficient to allow the sensor arm to rotate fully.

5. Press the SENSOR pushbutton and adjust the sensor angle to 90° using the ADJUST rotation adjuster.

6. Mount the MCA box onto the Pocket-CASSY and connect it to the computer using a USB cable.

7. Connect the output SIGNAL OUT in the connections field of the x-ray apparatus to the MCA box using a BNC cable.

8. Set the separation between the slit diaphragm of the collimator and the rotational axis and between the rotational axis and the entrance to the x-ray energy detector to 5 - 6 cm in each case.

9. Lay target 3 (leaded brass) onto the target table. Press the TARGET pushbutton and adjust the target angle to 45° using the ADJUST rotation adjuster.
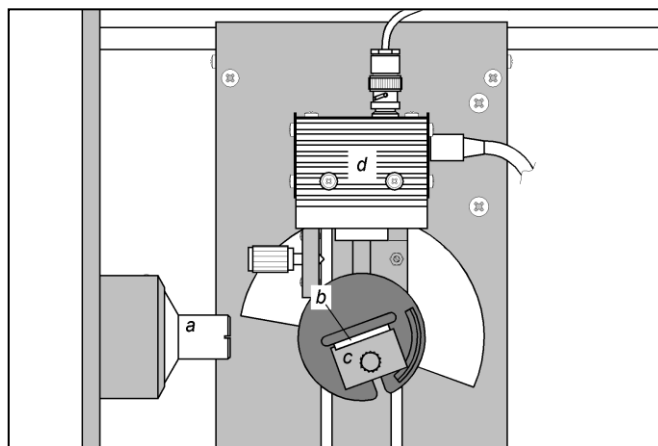

Fig. 1: Experimental set-up: a – Collimator, b – Target, c – Target table, d – Detector.

Performing the experiment

1. Connect the power supply to the mains socket. The "green" LED on the x-ray energy detector will light up after about 2 minutes and it is then ready for operation.

2. Load CASSY Lab settings.

3. Set the tube high voltage to U = 35 kV and the emission current to I = 1 mA and switch on the high voltage supply.

4. Start recording the spectrum by pressing 🕓 or the button on the Pocket-CASSY.

5. Then record the spectra for the targets copper (Cu), zinc (Zn) and lead (Pb) from the K-Line and L-line fluorescence target sets.

Results

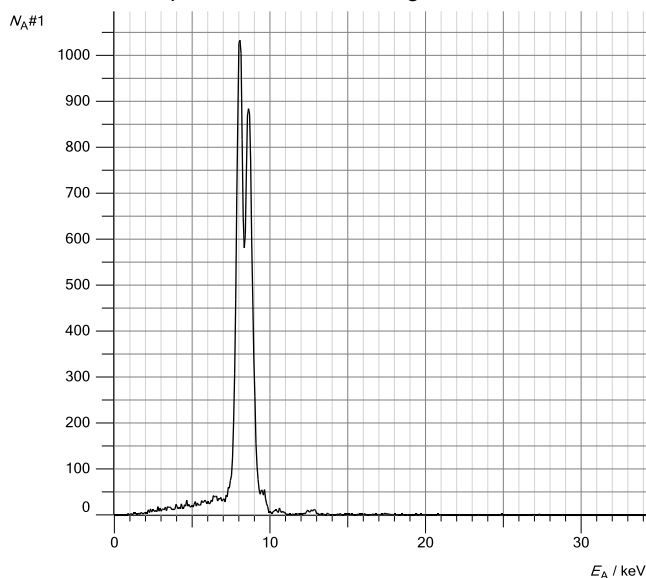The recorded spectra are shown in Figures 2a to 2d.
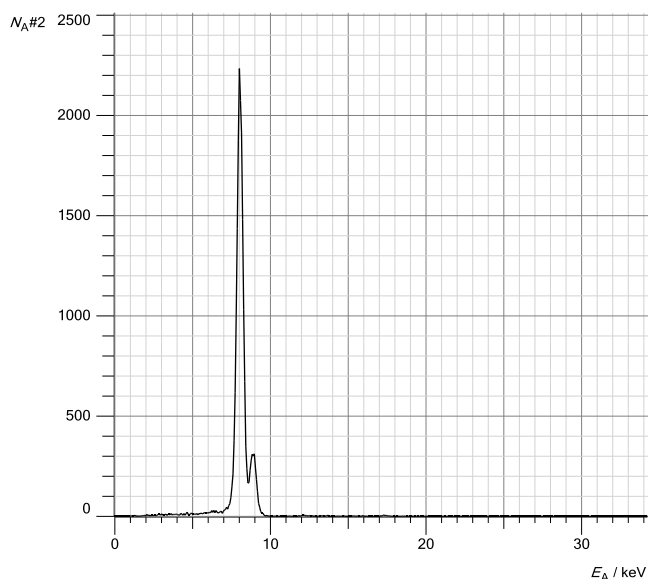

Fig. 2a: Fluorescence spectrum of brass (target 3).

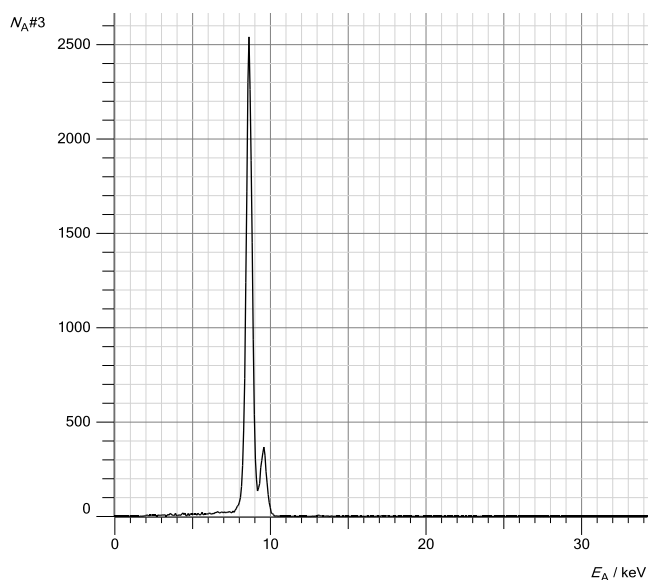**Fig. 2b:** Fluorescence spectrum of copper (reference spectrum).

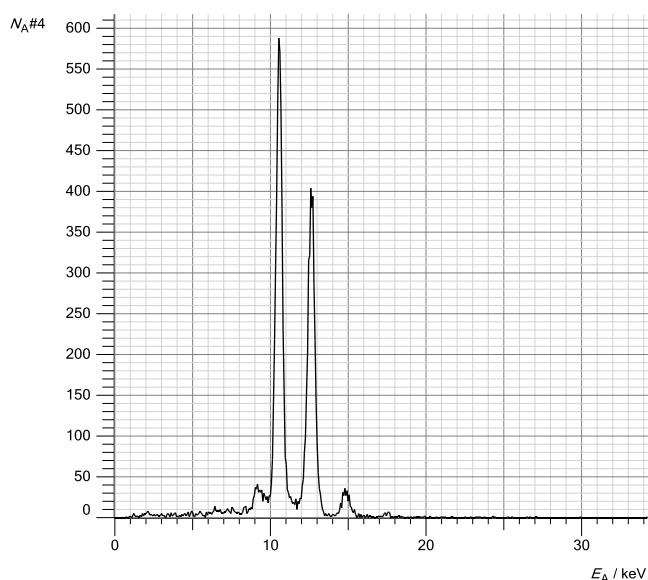**Fig. 2c:** Fluorescence spectrum of zinc (reference spectrum).

Fig. 2d: Fluorescence spectrum of lead (reference spectrum).

Evaluation

Energy calibration of the spectra

The energy calibration will be carried out based on the reference spectra of copper and lead.

1. Open "Energy calibration" in the Energy E_A settings. Select "Global for all spectra on this input" and on the right select the energy values for the Cu-Kα line (8.04 keV) and the Pb-Lα line (10.56 keV).

2. Mark the median point of the peak of the copper and lead signals. To do this, select "Calculate peak median point" in the context menu of the diagram ⋀ and mark the Cu-Kα line. The value is entered automatically into the first row. If this does not happen, enter the result manually into the energy calibration (e.g. by drag-and-drop from the status bar).

3. Determine the median point of the Pb-Lα line in an analogous way and also enter it on the left.

4. Display the energy on the x-axis. For this, drag the button E_A into the diagram using drag-and-drop.

5. Identify the lines through the context menu of the diagram and label them (✛ place mark → keV X-ray energy values → Cu and ✛ place mark → keV X-ray energy values → Pb).
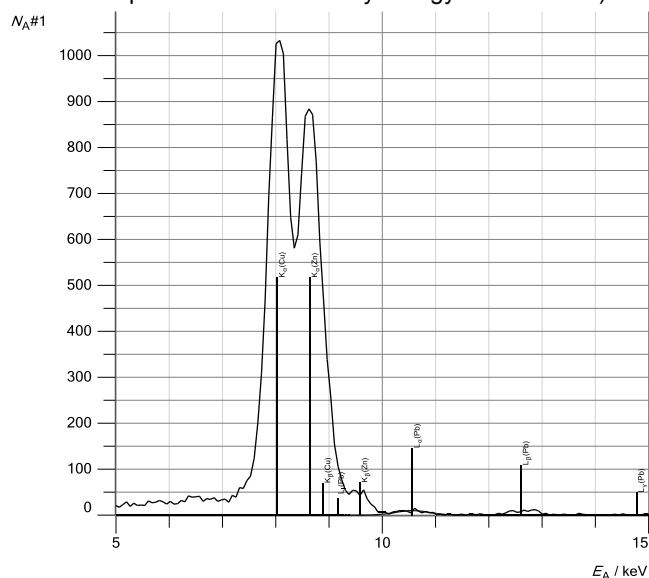

Fig. 3a: Fluorescence spectrum of the brass sample with the lines identified of the alloy components.

Identification of lines in the spectra of brass

The components of the brass sample can now be identified (see Fig. 3a).

1. Select the spectrum and establish a suitable section of the spectrum. To do this, right click on the x-axis (Energy E_A) and select a suitable section.

2. In the context menu, load the periodic table to identify the components of the alloy (✛ place mark → keV x-ray energy values).

3. Hover with the mouse over the element symbols. When an element has been "selected" in this way, its relevant lines appear in the spectrum. Determine the appropriate element by visual comparison and place the mark in the diagram by clicking on this element symbol. Determine the other components of the alloy in the same way.

4. Close the periodic table window.

It can be seen that the second-highest peak in the spectrum consists of two unresolved lines. Zn-Kα and Cu-Kβ. The Cu-Kβ line partially overlaps the Zn-Kα line.

Determination of the mass proportions

The number of irradiated atoms n is proportional to the area of a peak. As the peaks here are symmetrical, the number of irradiated atoms n is also proportional to the height H of a peak. In the reference spectrum, this number n_0 is determined by the density of the material ρ, its atomic weight A, the area irradiated S and the effective thickness d of the irradiated layer:

$$n_0 = S \cdot d \cdot \frac{\rho}{A} \ .$$

For the number of atoms of each kind in the alloy, the expression

$$n = n_0 \cdot \frac{H}{H_0} = V \cdot \frac{\rho}{A} \cdot \frac{H}{H_0}$$

can be used as a first approach. Where H and H_0 are the heights of the relevant peaks in the spectrum to be analysed or in the reference spectrum, $V = S \cdot d$ is the irradiated volume. Thus the mass proportion C_i of element number i in the alloy becomes

$$C_i = \frac{n_i \cdot A_i}{\sum_i n_i \cdot A_i} = \frac{\rho_i \cdot \dfrac{H_i}{H_{0i}}}{\sum_i \rho_i \cdot \dfrac{H_i}{H_{0i}}} \ . \qquad (I)$$

In order to calculate the mass proportion in accordance with equation I, the heights of the strongest lines in the fluorescence spectrum of brass (H) and the reference spectrum (H_0) are compared with one another. These lines are: Kα of copper, Kα of zinc and Lα of lead.

Determination of the peak heights in the fluorescence spectrum of the brass sample and deconvolution of the overlapping lines.

To determine the heights of the Cu-Kα and the Zn-Kα line, the fluorescence spectrum of brass is deconvoluted in the energy range 6 keV to 11 keV (see Fig. 3b). The spectrum is adjusted in this range using three Gauss curves of the same width at the known energy values of the Cu-Kα line ($E = 8.04$ keV), the Cu-Kβ line (8.91 keV) and the Zn-Kα line (8.64 keV).

1. Delete the Pb Ll line. This causes only a small error, but allows a clearer evaluation. To do this, double-click on the line to take hold of it and pull it out of the diagram.

2. In the context menu of the diagram, select the menu item **f(x)** "Further evaluations" → 🔲 "Gauss curves with predefined energy".

3. Mark measurement points in the energy range of about 7.5 keV to 9.1 keV.

The result is three Gauss curves (red) and an adjusted contour of the fluorescence spectrum (see Fig. 3b).

4. The peak heights (H) of the three peaks are now in the status bar. Using drag-and-drop, drag the Kα peak heights of copper and zinc from the status bar into the prepared table (on tab "Mass proportion") (see also column H in Table 1). The Cu-Kβ peak is automatically subtracted from the Zn-Kα peak in this evaluation.

To determine the height of the Lα line of lead in the fluorescence spectrum of the brass sample, it is adjusted using a Gauss curve:
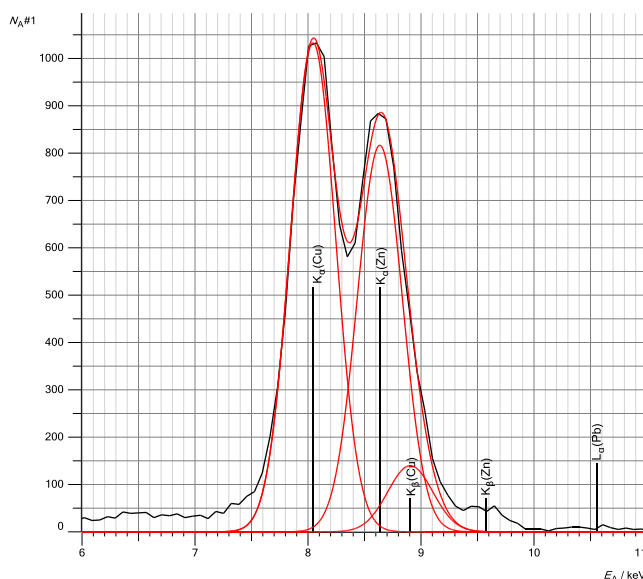

Fig. 3b: Result of the adjustment of the fluorescence spectrum of brass using three Gauss curves with predefined energy (red lines). The adjusted contour is also shown in red.

5. In the context menu of the diagram, select the menu item **f(x)** "Further evaluations" → 🔲 "Gauss curves with predefined energy".

6. Mark the Pb-Lα line (energy range of about 10 keV to 11,5 keV).

7. Using drag-and-drop, drag the Lα peak height of lead from the status bar into the prepared table (on tab "Mass proportion") (see also column H in Table 1).

Tab. 1: Determination of the mass proportion C of the alloy components of the brass sample.

	ρ g/cm^3	Line	H	H_0	ρ H/H_0	C %
Copper	8.96	Kα	1035	2153	4.30	62.4
Zinc	7.10	Kα	823.6	2427	2.40	34.9
Lead	11.34	Lα	9.3	574.7	0.18	2.7

Determination of the heights of the lines in the reference spectra

1. Select the reference spectra.

2. In the context menu of the diagram, select the menu item **f(x)** "Further evaluations" → 🔲 "Adjust Gauss curves (Alt + G)".

3. Mark the Cu-Kα line in the reference spectrum.

4. Using drag-and-drop, drag the Kα peak height of copper from the status bar into the prepared table (on tab "Mass proportion") (see also column H_0 in Table 1).

5. Then determine the heights of the Zn-Kα line and the Pb-Lα line in their reference spectra and drag the values into the prepared table (on tab "Mass proportion") (see also column H_0 in Table 1).

Determination of the mass proportions

The mass proportions of the alloy components are determined in accordance with equation (I) and automatically calculated in CASSY Lab in the prepared table (on tab "Mass proportion"). The values for the peak heights in the fluores-

cence spectrum of brass (*H*) and in the reference spectra (*H₀*) are entered into Table 1.

Results

The mass proportions of the alloy components of the brass sample as determined agree well with the known chemical composition ($CuZn_{39}Pb_3$).

Tab. 2: Comparison of the experimental values with the stated values for the mass proportions of the alloy components.

Element	stated	experimental
Copper	58%	62.4%
Zinc	39%	34.9%
Lead	3%	2.7%

Additional information

The example of the copper-zinc alloys (brass) demonstrates how *secondary fluorescence* can alter the shape of the spectrum. When such a sample is irradiated with x-ray photons, excitation of the K lines of both copper and zinc occurs. However, as the Kβ line of zinc lies over the edge of the K line of copper (E = 9.57 keV and 8.99 keV, respectively), it can also cause excitation "secondarily" of the K lines of copper.

For this reason, the intensity of the copper lines in the fluorescence emission from the sample is higher, at the expense of the Zn-Kβ line, and the ratio of the intensities of the Zn-Kα and Zn-Kβ lines is not the same as the ratio in the sample made of pure zinc. This is why the mass proportion determined from the Kα lines of the alloy components shows a somewhat higher proportion of copper.