

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

Objects of the experiment

- Recording the x-ray fluorescence spectrum of a brass sample.
- Determining the mass ratios of individual alloy components.

Principles

A sample irradiated with high-energy x-ray photons emits characteristic x-ray lines, whose energy depends on the atomic number of the element of the sample material. This dependence (Moseley's law) together with the x-ray fluorescence spectra of several elements was examined in the LD Physics Leaflets P6.3.5.4 and P6.3.5.5.

If the sample represents a chemical compound or mixture then its fluorescence spectrum is also of a complex nature. Since the inner electron shells (between which the x-ray transitions occur) are not incorporated in the chemical bond, the characteristic lines are also to a large degree *independent of the chemical bond of the element*. Hence the x-ray fluorescence spectra of a chemical compound are, as a first approximation, a superposition of spectra of its components.

To make a qualitative analysis of the chemical composition of a sample, all of the existing peaks in the fluorescence spectrum are firstly assigned to the elements. This is performed with the help of tabular values for the energies of the characteristic lines. In making the assignment the "pattern" of each spectral series is also considered: thus as well as the $K\alpha$ line, the $K\beta$ line with smaller (ca. 5 to 10 times) intensity must also be in the spectrum; the $L\alpha$ line appears together with the $L\beta$ line with similar intensity and the $L\gamma$ line with smaller intensity.

Conclusions can be made about the relative proportions of each element in the compound on the basis of the relative intensities of their fluorescent lines.

To make a quantitative analysis however, many other factors need to be taken into account, factors which influence the relationship of the line intensities of various elements. Matrix effects for example play a large role, whereby "matrix" here is understood to mean the physical and chemical neighbourhood of the element under scrutiny. Also the surface quality and the geometric properties of the sample need to be considered. Furthermore the influence of the measuring system

as well as the detector response probability and the dead time all need to be accounted for.

Since the intensity of the peaks depends not only on the concentration of the element but also on the position of its absorption discontinuities relative to the excitation spectrum, the matrix effects also occur via the absorption (especially the discontinuity absorption) of the primary radiation through the other elements of the compound. The fluorescence radiation of the element under scrutiny is also in part absorbed by the matrix to a considerable degree, before reaching the detector.

In this experiment, the quantitative analysis of the chemical composition of a brass sample containing lead is carried out. The components in this alloy were already identified in the LD Physics Leaflet P7.5.1.1. The matrix effects are not considered.

For calculating the mass ratios, the fact is made use of that the height of a peak is proportional to the number n of radiating atoms. In the reference spectrum this number n_0 is determined by the density of the substance ρ , its atomic weight A , the radiated area 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 type in the alloy, to first approximation the expression

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

can be used. In this H and H_0 are the peak heights in the spectrum to be analysed and in the reference spectrum is $V=S \cdot d$ the irradiated volume.

Apparatus

1 X-ray apparatus with X-ray tube Mo and goniometer or	554 811
1 X-ray apparatus with X-ray tube Cu and goniometer	
1 X-ray energy detector	559 938
1 Target set of alloys	554 848
1 Target set for K-lines fluorescence	554 844
1 Target set for L-lines fluorescence	554 846
1 Sensor-CASSY	524 010
1 MCA Box	524 058
1 CASSY Lab	524 200
1 BNC cable, 1 m	501 02
1 PC with Windows 98/2000 or higher version	

Using this information, the mass ratio C_i of the element number i in the alloy is

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

The X-ray apparatus fulfils all regulations on the design of an X-ray apparatus and fully protected device for instructional use and is type approved for school use in Germany (NW 807 / 97 Rö).

The built-in protective and shielding fixtures reduce the dose rate outside the X-ray apparatus to less than 1 $\mu\text{Sv/h}$, which is of the order of magnitude of the natural background radiation.

■ Before putting the X-ray apparatus into operation, inspect it for damage and check whether the high voltage is switched off when the sliding doors are opened (see instruction sheet of the X-ray apparatus).

■ Protect the X-ray apparatus against access by unauthorized persons.

Avoid overheating of the anode in the X-ray tube.

■ When switching the X-ray apparatus on, check whether the ventilator in the tube chamber starts rotating.

The goniometer is positioned solely by means of electric stepper motors.

■ Do not block the target arm and sensor arm and do not use force to move them.

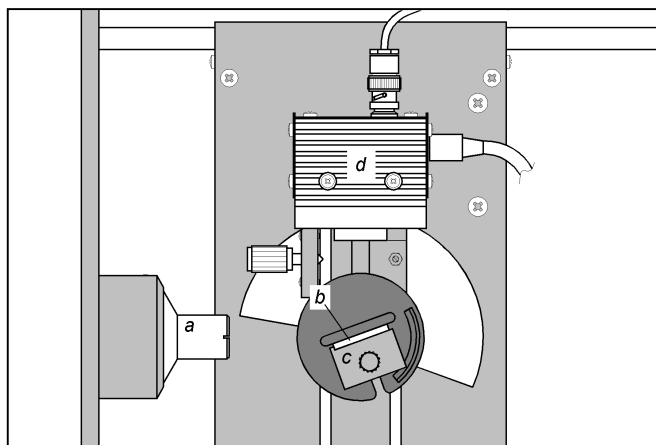



Fig. 1: Experiment setup: a – collimator, b – target, c – target stage, d – detector.

Setup

Fig. 1 shows the experiment setup.

- Guide the connection cable for the table-top power supply through the empty channel of the x-ray apparatus and connect it to the mini-DIN socket of the x-ray energy detector.
- Secure the sensor holder with the mounted x-ray energy detector in the goniometer sensor arm.
- Connect the signal output of the x-ray energy detector to the BNC socket SIGNAL IN of the x-ray apparatus by means of the BNC cable included.
- Feed enough connection cable through to make complete movement of the sensor arm possible.
- Press the SENSOR button and set the sensor angle with the rotary adjuster ADJUST manually to 90°.
- Connect Sensor-CASSY to the computer and connect the MCA box.
- Connect the SIGNAL OUT output in the connection panel of the x-ray apparatus to the MCA box by means of the BNC cable.
- Set the distances between the slit aperture of the collimator and the axis of rotation as well as between the axis of rotation and the window of the x-ray energy detector both to 5 to 6 cm.
- Place target 3 (brass containing lead) from the target set of alloys onto the target table.
- Press the TARGET button and adjust the target angle manually using the rotary button ADJUST to 45°.

Carrying out the experiment

- Connect the table-top power supply to the mains (after approx. 2 minutes the LED of the x-ray energy detector will glow "green" indicating that it is ready for use).
- Call CASSY Lab, and select the measuring parameters "Multichannel Measurement, 512 Channels, Negative Pulses, Gain 2.5, Measuring Time 180 s".
- Select the tube high voltage $U = 35 \text{ kV}$ and the emission current $I = 1 \text{ mA}$, and switch the high voltage on.
- Start recording the spectrum with  or with the F9 key.

- Finally, record the spectra for the targets Cu, Zn and Pb from the target sets for K lines and L lines fluorescence as reference spectra.
- Save the entire measurement using an appropriate name.

Measuring example

The recorded spectra are displayed in Fig. 2a-d.

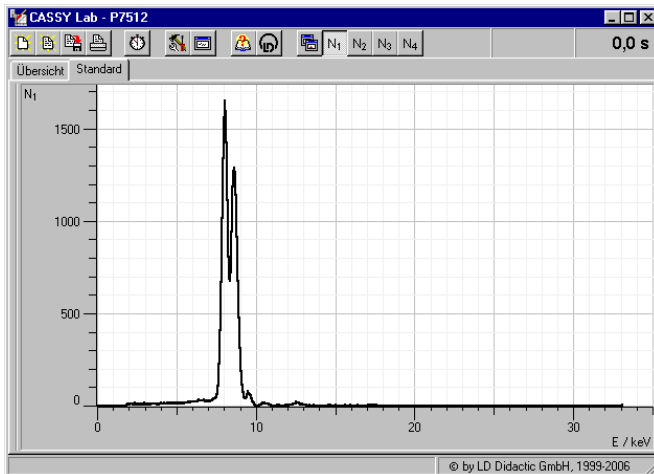


Fig. 2a Brass fluorescence spectrum.

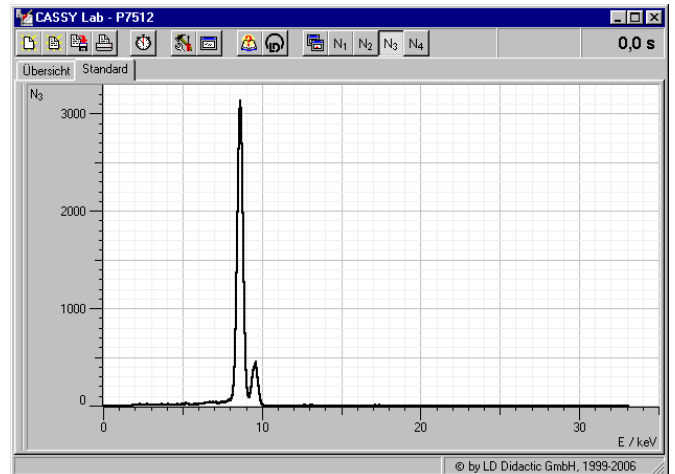


Fig. 2c Zinc fluorescence spectrum (reference spectrum).

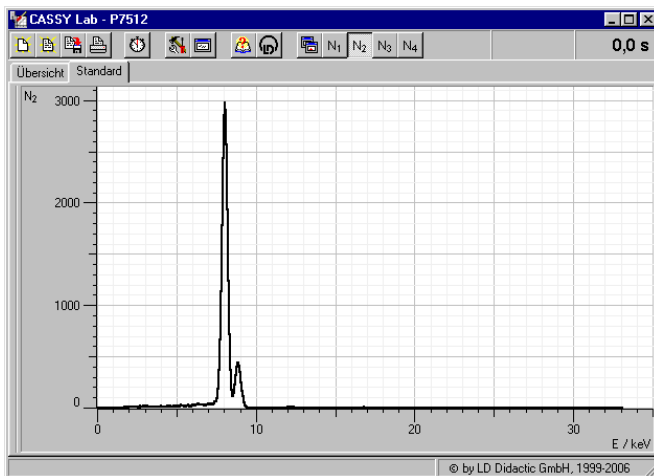


Fig. 2b Copper fluorescence spectrum (reference spectrum).

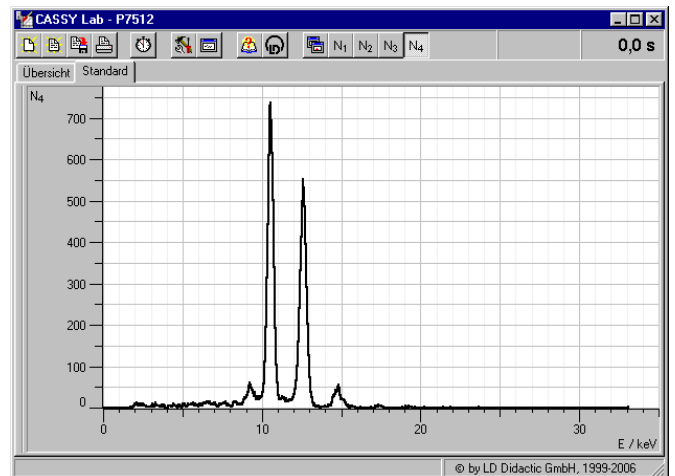


Fig. 2d Lead fluorescence spectrum (reference spectrum).

Evaluation

a) Energy calibration of the spectra

The energy calibration is carried out for the spectra of copper and lead from the reference spectra.

- Open the "Energy Calibration" dialog window with the shortcut Alt+E, select "Global Energy Calibration" and enter the energies of the Cu K α line (8.04 keV) and the Pb L α line (10.56 keV).
- Select the menu item "Other Evaluations" \rightarrow "Calculate Peak Center" in the pop-up menu of the diagram window, mark the Cu K α line, and enter the result in the "Energy Calibration" dialog window.
- Then determine and enter the centre for the Pb L α line.

b) Identifying the lines in the brass spectrum

For identifying and labelling the lines (see fig. 3a)

- In the pop-up menu of the diagram window select the item "X-ray Energies".
- Click on the element symbol Cu and select the button "Adopt".
- Finally plot the lines for zinc (Zn) and lead (Pb).

It is apparent that the second largest peak in the spectrum consists of two non-resolved lines: Zn K α and Cu K β . The Cu K α line is in part superimposed with the Zn K α line.

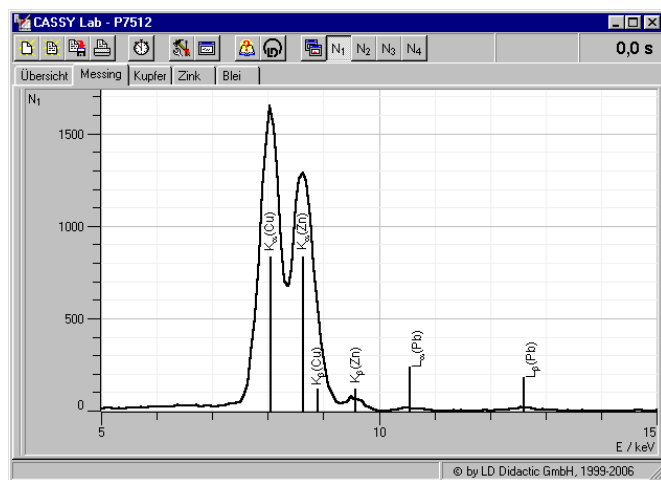


Fig. 3a Fluorescence spectrum of the brass sample with the identified lines of the alloy components.

c) Resolution of the superimposed lines in the fluorescence spectrum of the brass sample

The mass ratios of the alloy components are calculated by comparing the heights of the strongest lines in the brass fluorescence spectrum and the reference spectra. These lines are: the K α of copper, the K α of zinc and the L α of lead.

For the determination of the heights of the Cu K α and the Zn K α , the brass fluorescence spectrum must be resolved in the energy range from 7.5 keV to 9.1 keV. For this the spectrum in this range is fitted with three Gaussian curves of equal width at the known energies of the Cu K α line ($E = 8.04$ keV), the Cu K β line (8.91 keV) and the Zn K α line (8.64 keV).

- In the pop-up menu of the diagram window select the item "Other Evaluations" \rightarrow "Gaussians of specified energy".
- Mark measuring points in the energy range 7.5 keV to 9.1 keV (without the Pb L α line).

The result is a fitted contour of the fluorescence spectrum (see fig. 3b). The final values of the parameters should be taken from the status line and inserted in a table (H in Tab. 1).

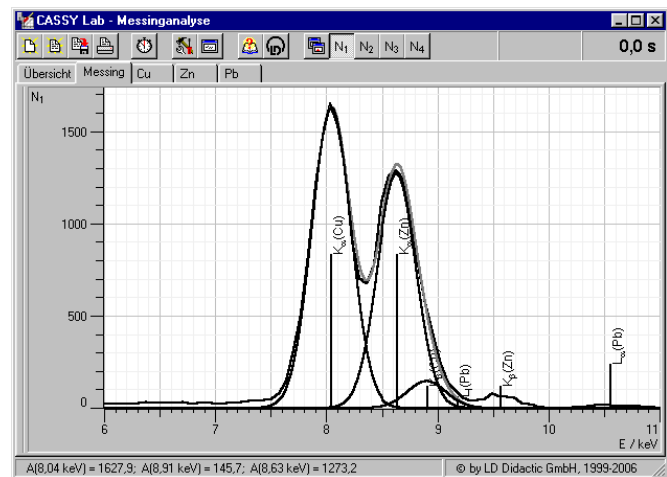


Fig. 3b Result of fitting the brass fluorescence spectrum with three Gaussian curves (lines) of given energies.

To determine the height of the L α line for lead in the fluorescence spectrum of the brass sample, a Gaussian curve is fitted to it:

- In the pop-up menu of the diagram window select the item "Other Evaluations" \rightarrow "Fit Gaussians" (Alt+G).
- Mark the Pb L α line (energy range from 10 keV to 11.5 keV).
- Insert the result (A_1) in Tab. 1 (H).

d) Determination of the line heights in the reference spectra

- In the pop-up menu of the diagram window select the item "Other Evaluations" \rightarrow "Fit Gaussians" (Alt+G).
- Mark the Cu K α line in the reference spectrum.
- Insert the result (A_1) in Tab. 1 (H_0).
- Finally determine the heights of the Zn K α line and the Pb L α line in their reference spectra and insert the values in Tab. 1.

e) Determination of the mass ratios

The mass ratios of the alloy components are determined according to Eq. (1). The values of the peak heights in the brass fluorescence spectrum (H) and in the reference spectra (H_0) are stated in Tab. 1.

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

Element	ρ , g/cm ³	Line	H	H_0	$\rho \cdot H/H_0$	C , %
Copper	8,96	K α	1628	2959	4,91	61,3
Zinc	7,10	K α	1273	3132	2,79	35,9
Lead	11,34	L α	14,6	711	0,23	2,9

Result

The determined mass ratios of the alloy components in the brass sample correspond well to the known chemical composition (CuZn39Pb3).

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

Element	Stated	Experimental
Copper	58%	61,3%
Zinc	39%	35,9%
Lead	3%	2,9%

Additional information

The example of the copper-zinc alloy (brass) shows how the *secondary fluorescence* modifies the spectrum shape. During the irradiation of such a sample with x-ray photons, the K lines of both copper and zinc are excited. But because the K β line of zinc ($E = 9.57$ keV) lies above the K edge of copper ($E = 8.99$ keV), it can also "secondarily" excite the copper K lines.

Therefore, in the fluorescence radiation emitted, the intensity of the copper lines is higher at the cost of the Zn K β line, and the ratio of the Zn K α and the K β lines does not correspond to the ratio found in pure zinc. For this reason, the mass ratio of the alloy components determined from the K α lines indicates a slightly too high proportion of copper.

