

X-ray fluorescence analysis of the chemical composition of various alloys

Aims of the experiment

- To learn how to use an x-ray apparatus.
- To understand x-ray fluorescence analysis.
- To calibrate an x-ray apparatus for x-ray fluorescence analysis.
- To apply x-ray fluorescence analysis to various samples (alloys).
- To analyse the composition of alloys.

Principles

When atoms are irradiated with high-energy x-rays, the energy supplied can cause electrons to be ejected from the inner electron 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. This phenomenon is called x-ray fluorescence.

If electrons are ejected from the innermost electron shell, also referred to as the K shell, this results in the so-called K spectrum (the K spectral series). This is caused by electron jumps out of the second ($K\alpha$) or the third ($K\beta$) electron shell. The L spectrum originates analogously when electrons fall back into the second electron shell (L shell).

The energy of the radiation emitted from an electron shell depends on the nuclear charge (Moseley's Law). This makes it possible to determine precisely the nuclear charge of an element and made an historically important contribution to completing the periodic table system.

Every element (each with a different nuclear charge) emits x-rays with a characteristic energy. This energy is practically

independent of the bonding form of the element, as the inner electrons have practically no involvement in chemical binding. The composition of materials can therefore be determined using x-ray fluorescence analysis, even if the elements are present in chemically different forms.

The x-ray fluorescence spectrum of a homogenous sample having several components is, as a first approach, the addition of the individual spectra. It is therefore possible using this method to determine qualitatively the composition of any sample. To do this, it is first necessary to assign all of the signals present in the fluorescence spectrum to an element. This is achieved with the help of table values for the energy of the characteristic lines. The pattern of each spectral series is also taken into account for the assignment. Every $K\alpha$ line has an associated $K\beta$ line with about 5 - 10 times lower intensity.

In this experiment, an energy calibration of the spectrum will first be carried out. For this, an alloy with a known composition is measured and the lines in the spectrum are assigned to energy values from the literature. Thereafter, other substances of any kind, e.g. alloys, can be measured and their composition determined.



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 R0) 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 $1 \mu\text{Sv/h}$, 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 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 set-up of the experiment 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 the calibration target supplied with the x-ray energy detector onto the target table. Press the TARGET pushbutton and adjust the target angle to 45° using the ADJUST rotation adjuster.

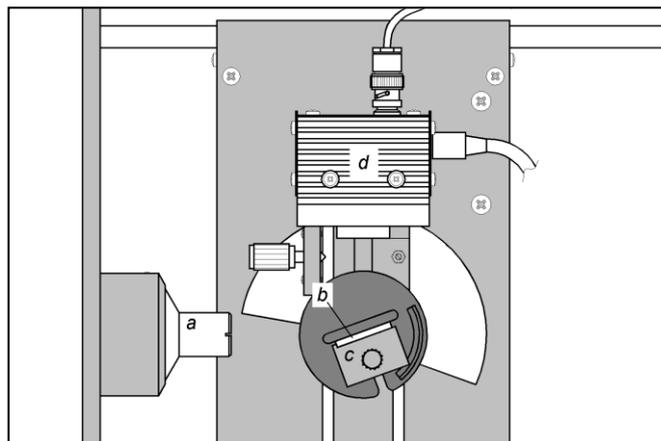


Fig. 1: Experimental set-up: a – Collimator, b – Target, c – Target table, d – Detector.

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 $U = 35 \text{ kV}$ and the emission current to $I = 1 \text{ mA}$ and switch on the high voltage supply.
4. Start recording the spectrum by pressing  or the button on the Pocket-CASSY.
5. Following this, record spectra for all targets from the alloys target set.

Results

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

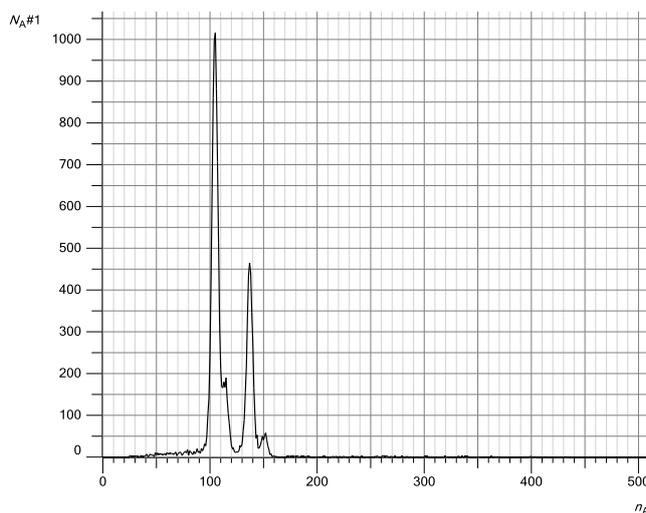


Fig. 2a: Fluorescence spectrum of the calibration target.

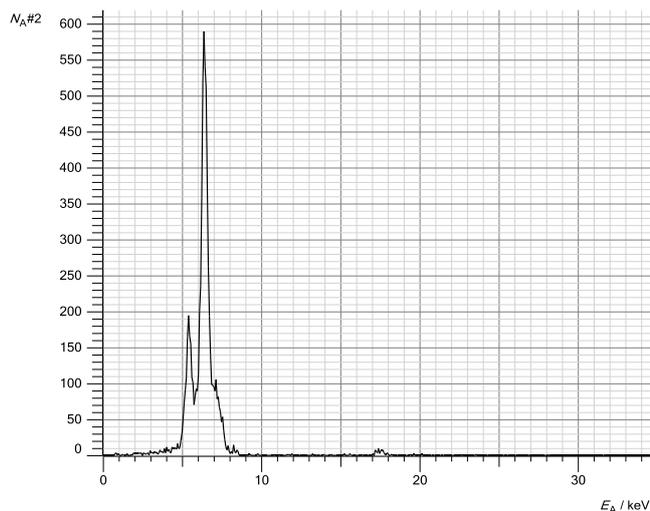


Fig. 2b: Fluorescence spectrum of target 1.

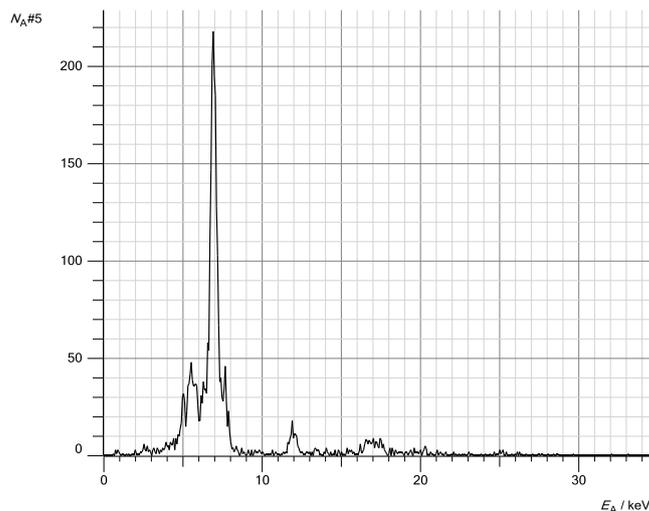


Fig. 2e: Fluorescence spectrum of target 4.

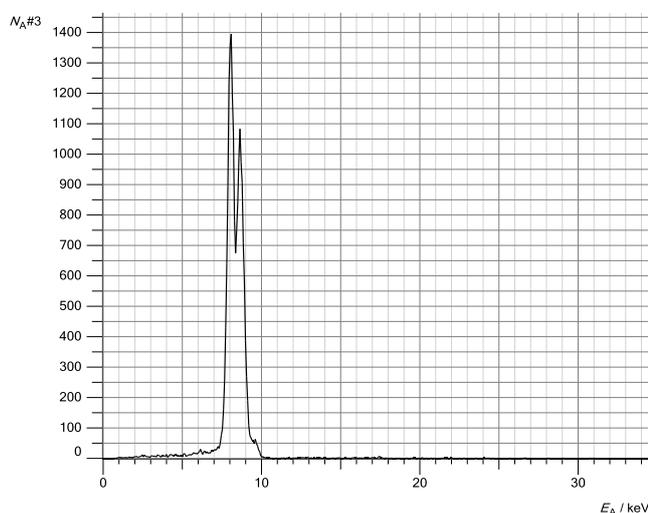


Fig. 2c: Fluorescence spectrum of target 2.

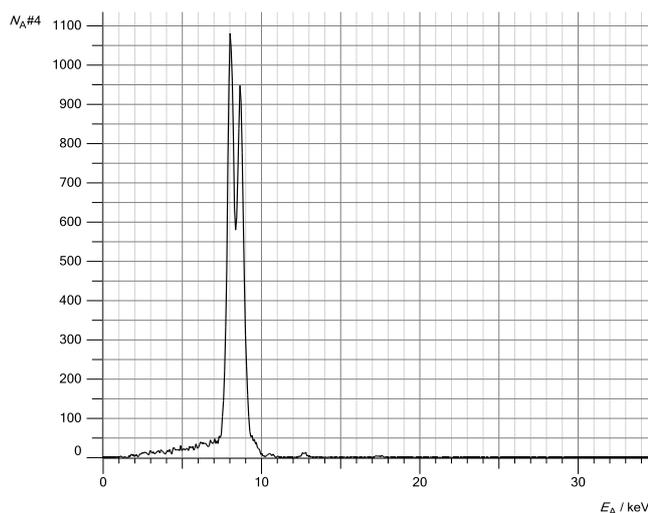


Fig. 2d: Fluorescence spectrum of target 3.

Evaluation

Energy calibration of the spectra

The energy calibration of the spectra is carried out using the calibration target (Fe + Zn) (see Fig. 3a).

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 Fe-K α line (6.40 keV) and the Zn-K α line (8.64 keV) (preset values).

2. Mark the median point of the peak of the iron-zinc signals. To do this, select "Calculate peak median point" in the context menu of the diagram  and mark the Fe-K α 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 line).

3. Determine the median point of the Zn-K α 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 "Display 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 \rightarrow keV X-ray energy values \rightarrow Fe and + place mark \rightarrow keV X-ray energy values \rightarrow Zn).

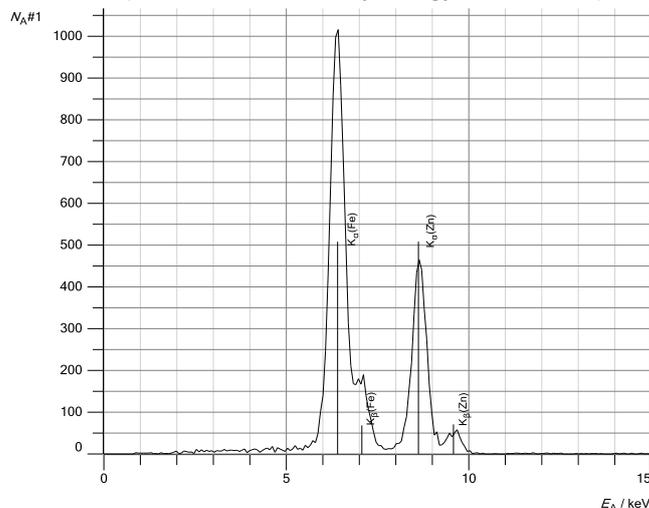


Fig. 3a: Lines identified in the fluorescence spectrum of the calibration target. It contains iron and zinc.

The four visible peaks can be attributed to the fluorescence of the main constituents iron (Fe) and zinc (Zn) of the zinc-plated sheet steel. Both the $K\alpha$ and the $K\beta$ lines are visible.

Identification of lines in the spectra of the targets

The constituents of the various targets can now be identified.

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. Alternatively one can zoom in.
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.

Results

The spectra of the targets are shown in Figures 3b to 3e. The results of the qualitative investigation of the alloys based on the x-ray fluorescence spectra agree with the known chemical compositions:

Target 1 (Fig. 3b): Stainless steel X5CrNi18-10, contains 72 % iron (Fe), 18 % chromium (Cr) and 10 % nickel (Ni).

Target 2 (Fig. 3c): Brass CuZn36, contains 64 % copper (Cu) and 36 % zinc (Zn).

Target 3 (Fig. 3d): Brass CuZn39Pb3, contains 58 % copper (Cu), 39 % zinc (Zn) and 3 % lead (Pb).

Target 4 (Fig. 3e): Praseodymium-samarium-cobalt magnet. Apart from cobalt (Co), samarium (Sm) and praseodymium (Pr), these magnets can also contain iron (Fe), copper (Cu) and zirconium (Zr).

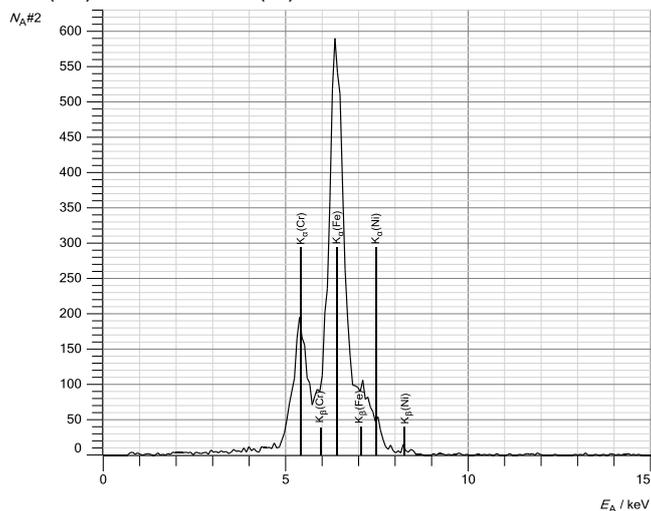


Fig. 3b: Determination of the components of target 1: Chromium, iron and nickel (stainless steel).

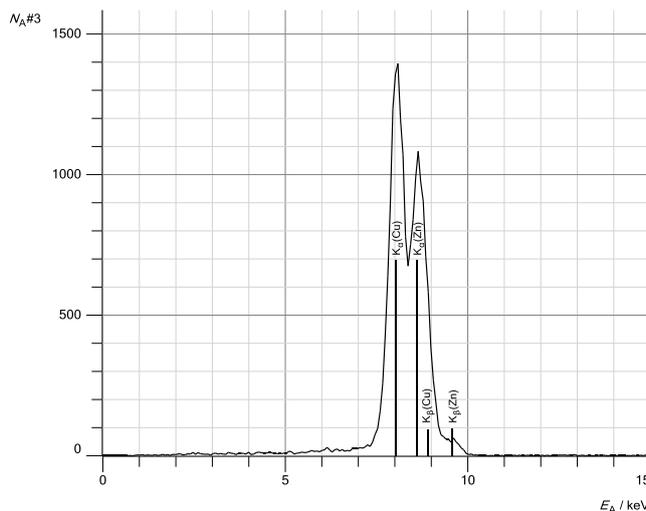


Fig. 3c: Determination of the components of target 2: Copper and zinc (brass).

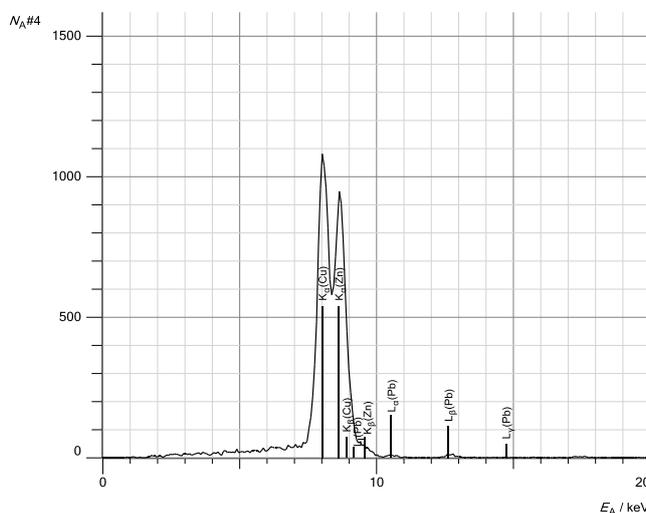


Fig. 3d: Determination of the components of target 3: Copper, zinc and lead (lead brass).

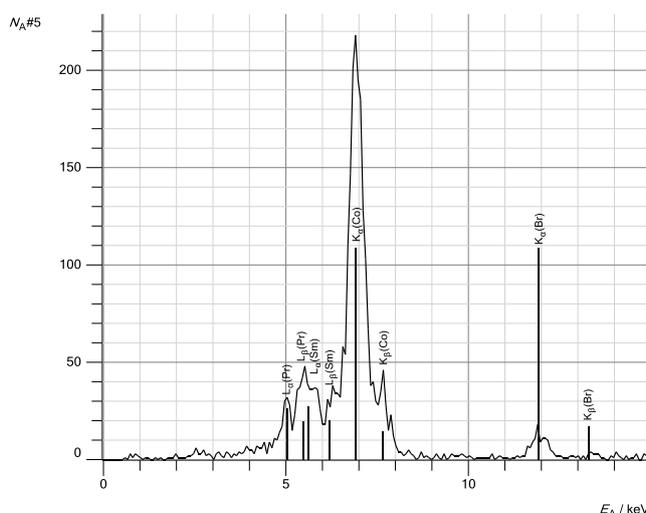


Fig. 3e: Determination of the components of target 4: Praseodymium, samarium and cobalt (rare-earth magnet). The fluorescence lines of bromine come from the plastic underlay (flame retardant).