Quantitative X-ray fluorescence analysis of solutions

Physics > Modern Physics > Production & use of X-rays

Difficulty level	Group size	Preparation time	Execution time
hard	2	45+ minutes	45+ minutes

This content can also be found online at:

http://localhost:1337/c/5f8051117fb8b40003cb5b07

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General information

Application

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Setup

Most applications of X rays are based on their ability to pass through matter. Since this ability is dependent on the density of the matter, imaging of the interior of objects and even peaple becomes possible. This has wide usage in fields such as medicine or security.

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Other information (1/2)

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Prior knowledge

The prior knowledge for this experiment is found in the Theory section.

Main principle

Various solutions, with known element concentrations, are subjected to polychromatic X-rays. The energy and intensity of the resulting fluorescence radiation of the dissolved elements are analysed with the aid of a semiconductor detector and a multichannel analyser. In order to determine the unknown element concentrations in the solutions, calibration is performed. For this purpose, the known element concentrations of the calibration solution are plotted against the corresponding fluorescence intensities of the dissolved elements.

Other information (2/2)

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Learning objective

The goal of this experiment is to get to investigate the spectra of fluorescence radiation.

Tasks

1. Calibrate the semiconductor energy detector with the aid of the characteristic radiation of the tungsten X-ray tube.
2. Record the fluorescence spectra of potassium bromide solutions with various concentration levels.
3. Determine the intensity of the characteristic bromine radiation, based on the spectra.
4. Create a calibration function that is based on the concentration values as well as the intensity of the associated fluorescence radiation.

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Safety Instructions

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When handling chemicals, you should wear suitable protective gloves, safety goggles, and suitable clothing. Please refer to the appendix for detailed safety instructions.

Theory

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The X-ray fluorescence analysis is particularly suitable for determining the elements and their concentration levels in liquids. The method can be applied, for example, in order to determine the concentration levels of heavy metals in sewage water. In order to determine the concentration of the elements in a sample with the aid of X-ray fluorescence analysis, a qualitative analysis must first be performed. During the assignment of the fluorescence lines, it must be taken into consideration that the relaxations that follow the primary ionisation process can only take place if they fulfil the quantum-mechanical selection rules $\Delta \mathrm{j} = 0, \pm 1$ and $\Delta \mathrm{l} = \pm 1$ (j = total angular momentum, l = orbital angular momentum). In addition, it should be noted that every element has groups of X-ray lines that have a certain intensity relation. If, for example, one considers a specific line as the K_α-line of an element, it should be possible to detect the correspondingK_β-line in the correct intensity relation, provided that it is not overlaid by a line of another element. When the lines have been assigned to the elements, the line intensity allows for conclusions to be drawn about the concentration of the elements. In general, matrix effects make it difficult to determine the concentration directly, since the fluorescence radiation that is stimulated by the primary radiation is not only a function of the element concentration but also of the element combination. If one changes, for example, the solvent, then the fluorescence intensity of the element that is analysed may differ even though the concentration is the same.

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Equipment

Position	Material	Item No.	Quantity
1	XR 4.0 expert unit, 35 kV	09057-99	1
2	XR 4.0 X-ray goniometer	09057-10	1
3	XR4 X-ray Plug-in Cu tube	09057-51	1
4	XR 4.0 X-ray material upgrade set	09165-88	1
5	Potassium bromide, 100 g	30258-10	1

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Setup and Procedure

Setup (1/2)

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- Screw the adapter ring onto the inlet tube of the energy detector and connect the signal and supply cables to the corresponding ports of the detector with the aid of the right-angle plugs.
- Connect the signal and supply cables to the corresponding ports in the experiment chamber of the X-ray unit. In Figure 1, the port for the signal cable is marked in red and the port for the supply cable is marked in green. Connect the external X RED ports of the x-ray unit (see Fig. 2) to the multi-channel analyser (MCA). Connect the signal cable to the “Input” port and the supply cable to the “X-Ray Energy Det.” port of the MCA.

Fig. 1: Connectors in the experiment chamber

Fig. 2: Connection of the multi-channel analyser

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Setup (2/2)

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- Secure the energy detector in the holder of the swivel arm of the goniometer. Lay the two cables with sufficient length so that the goniometer can be swivelled freely over the entire range.
- Connect the multi-channel analyser and computer with the aid of the USB cable.
- Insert the tube with the 2-mm-aperture.
- Bring the goniometer block and the detector to their respective end positions on the left. Bring the detector to the 90° position in the 1:2 coupling mode (Fig. 3).

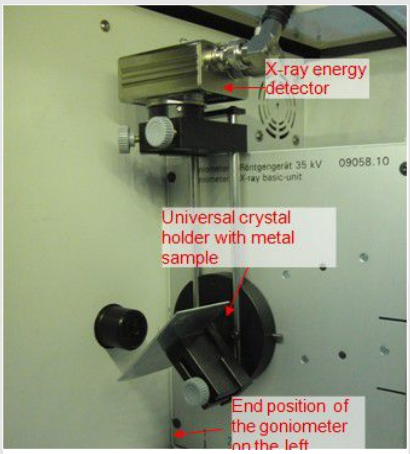

Fig. 3: Goniometer set-up

Procedure (1/5)

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- Bring the goniometer block and the detector to their respective end positions on the right.
- Insert the tube with the 1mm-aperture into the exit tube of the X-ray tube.
- With the X-ray unit switched on and the door locked, bring the detector to the 0° position. Then, shift the detector by some tenths degree out of the zero position in order to reduce the total rate.
- Operating data of the tungsten X-ray tube: Select an anode voltage U_A = 25 kV and an anode current I_A = 0.02 mA and confirm these values by pressing the “Enter” button.
- Switch on the X-radiation

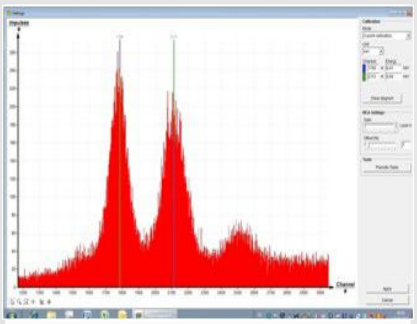

Fig. 4: calibration of the multi-channel analyser

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Procedure (2/5)

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- In the MEASURE program, select “Multi channel analyser” under “Gauge”. Then, select “Settings and calibration”. After the “Calibrate” button has been clicked, a spectrum can be measured. The counting rate should be < 300 c/s. Energy calibration settings: - 2-point calibration, - Unit = keV, Gain = 2 – Set the offset so that low-energy noise signals will be suppressed (usually a few per cent are sufficient), See Fig 4.
- Measuring time: 5 minutes. Use the timer of the X-ray unit.
- Make the two coloured calibration lines congruent with the line centres of the two characteristic X-ray lines. The corresponding energy values (see e.g. P2544705) $\mathrm{E}(\mathrm{L_3M_5}/\mathrm{L_3M_4})$ = 8,41keV and $\mathrm{E}(\mathrm{L_2N_4})$ = 9,69 keV are entered into the corresponding fields, depending on the colour. (Note: Since a separation of the lines $\mathrm{L_3M_4}$ and $\mathrm{L_3M_5}$ Lines is not possible, the mean value of both lines is entered as the energy of the line).
- Name and save the calibration.

Procedure (3/5)

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Sample preparation

In order to perform two series of measurements, two parent solutions with different starting concentrations must be prepared. To do so, add approx. 10 g of KBr into 100 ml of water, and approx. 65 g of KBr into another 100 ml of water. Fill the weighed potassium bromide portions separately into beakers that have been filled with 100 ml of water beforehand. Stir with the glass rod in order to completely dissolve the potassium bromide.
Now, prepare the diluted solutions based on parent solution 1. In order to prepare 10 ml in a defined way, use one pipette for the water and one for the solution (attach the pipette ball alternately). The pipettes are calibrated for delivery. Fill the two liquids into a snap-cap vial. It is important to thoroughly mix the new solution. Then, fill the plastic cuvettes to 3/4 with the mixed solutions.For a second series of measurements, those solutions with lower concentration levels must be prepared in the same way, only this time based on parent solution 2.

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Procedure (4/5)

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Spectrum recording

- Insert the tube with the 2-mm-aperture.
- Bring the goniometer block and the detector to their respective end positions on the left. Bring the detector to the 90° position in the 1:2 coupling mode.
- Insert the metal sample with the universal crystal holder (sample at 45°).
- Operating data of the molybdenum X-ray tube: Adjust an anode voltage U_A = 35 kV and an anode current so that the counting rate is $\leq$ 200 c/s.
- Measuring time: 10 minutes (use the timer of the X-ray unit).

Procedure (5/5)

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Evaluation of the measurement curves

- In order to determine the line energy, switch from the bar display to the curve display. To do so, click “Display options” and then “Interpolation and straight lines”.
- Extend the relevant line section with the aid of the zoom function
- Then, select the curve section with Open the window “Function fitting Then, select “Scaled normal distribution” and confirm.
- Find the line centroid of the normal distribution with “Peak analysis” or determine it with the function “Survey”

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Evaluation

Task 2

Figure 5 shows the fluorescence spectrum of an aqueous potassium bromide solution. Based on the characteristic fluorescence lines of potassium bromide, Figure 6 shows the method for evaluating these curves.

Table 1 shows a comparison of the experimental energy values of the lines and the corresponding table values.
The lines 1 (E = 7.5 keV) and 2 /E = 8.1 keV) are caused by nickel and copper. The scattered primary radiation generates fluorescence radiation on the material components of the detector housing. This fluorescence radiation is also detected by the detector. Line 5 (E = 16.7 keV) can be assigned to the Compton-scattered primary Mo-K_α-radiation. The energy of the characteristic fluorescence radiation of potassium is close to the sensitivity limit of the energy detectors, which is why it cannot be identified in this experiment due to the low concentration level.

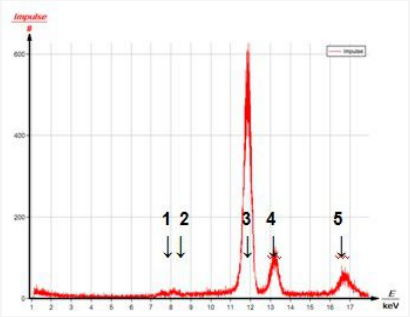

Fig. 5: Fluorescence spectrum of a potassium bromide solution

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Task 2 (part 2)

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Line	E_{exp} [keV]	E_{lit} [keV]
3-K_α	11.90	11.92
4-K_β	13.26	13.29

Table 1: Energy of the fluorescence lines of bromine

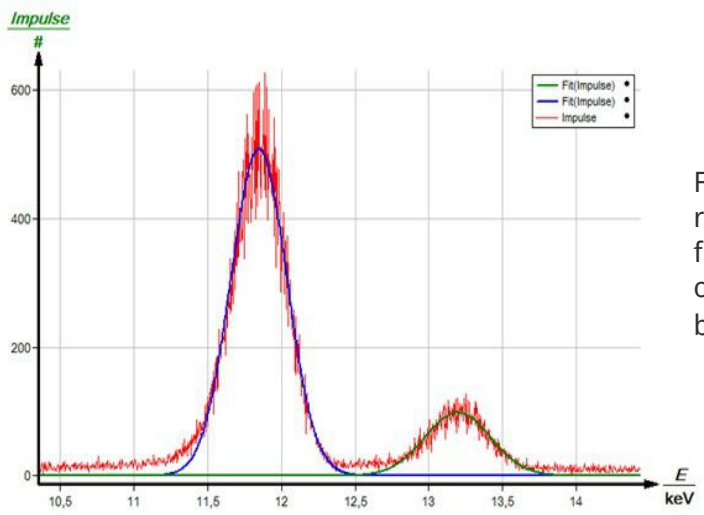

Fig. 6: Zoomed representation with a fitted normal distribution of the K_α- and K_β-line of bromine.

Task 3

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Figure 7 shows the linear course of the intensity of the K_α-line of bromine as a function of the bromine concentration (with the background taken into consideration) for a solution that is not too strongly concentrated (measurement with parent solution 1). This calibration can now be used for determining the bromine concentration of other bromine solutions. One cannot assume, that this calibration function can be used for all concentration levels. As the evaluation of the corresponding measurement with the saturated parent solution 2 shows (Fig. 8), the calibration functions only apply to a limited extent to liquids. In the case of strongly saturated solutions, the linear relation between the intensity and concentration is disturbed by matrix effects.

Fig. 7: Calibration function of a KBr solution of a low concentration

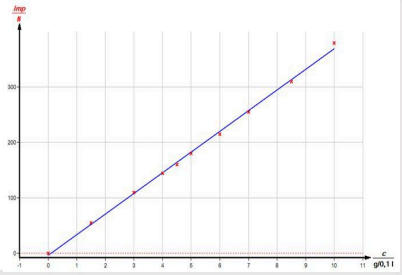
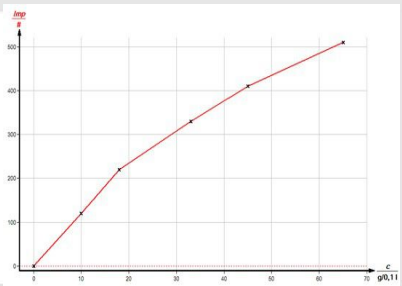


Fig. 8: Calibration function of a KBr solution of a high concentration



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Appendix

Security Information

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Hazard symbol, signal word	Hazard statements	Precautionary statements
Potassium bromide (KBr)		
	H315: Causes skin irritation H319: Causes serious eye irritation H335: May cause respiratory irritation	P261: Avoid breathing dust/fume/gas/mist/vapours/spray. P305 + P351 + P338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. .

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