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Properties and characterization of materials (mod.2)

Qualitative and quantitative phase analysis of a mixture of inorganic compounds by XRD and ICP-OES

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1. Introduction

The aim of this laboratory experience was to perform an elemental analysis of a mixture of inorganic compounds through ICP-OES, a qualitative and semi-quantitative analysis of the same system by XRD. Combining the results of the two techniques it was possible to carry out the identification of the components of the sample and the estimation of the amount of the different phases.

2.Materials and Methods

The sample studied, called sample black, was an unknown crystalline mixture of different components with an initial mass of 121.8 g.

To perform the ICP-OES analysis a Spectro Ciros Vision CCD machine was used on a solution containing distilled water and the sample that was previously dissolved in 5mL of concentrated hydrochloric acid.

For the XRD the instrument utilised was a Italstructures IPD3000/CPS120 with a 1200W Cobalt source multilayer monochromator on incident beam. The detector of this apparatus is an Inel CPS 120, that has a detection interval from 5° to 125°. To perform the qualitative analysis the software QualX was used, whereas for the semi-quantitative analysis the software Maud [1] was employed.

3.Experimental Results

Through the ICP-OES analysis the mean concentration of Ca, Fe and Zn calculated on three specimens of 50mL of solution were provided by the instrument and are reported in table 1.

	Ca	**Fe**	**Zn**
Mean Concentration (mg/L)	10.173 ± 0.089	4.090 ± 0.012	1.937 ± 0.001

Table. 1. – Concentration of elements collected thorough ICP-OES.

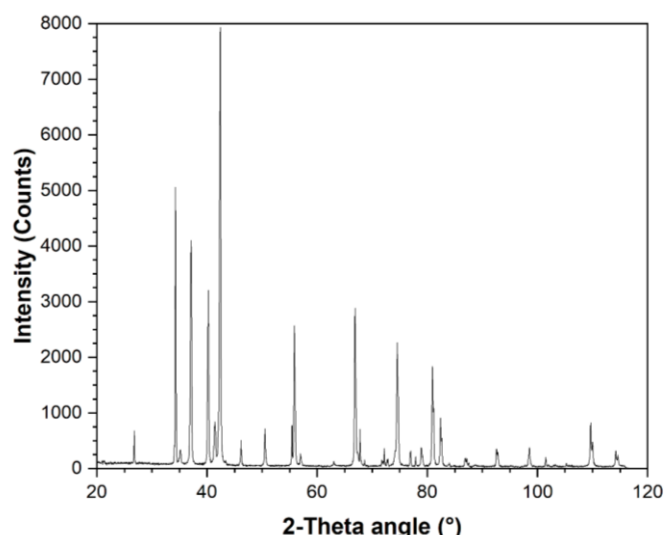In Fig.1 the spectrum collected by the XRD instrument is reported.

Fig. 1 – XRD spectrum of the unknown sample.

4. Data Analysis

From the data collected in ICP-OES experiment it was possible to evaluate the relative percentage of Ca, Fe and Zn and the percentage of these elements considering whole mass of the sample. Both values calculated and their related error are presented in Table 2.

	Ca	**Fe**	**Zn**
Relative Percentage (%)	62.769 ± 0.676	25.279 ± 0.175	11.952 ± 0.075
Percentage in the sample (%)	41.761 ± 0.521	16.819 ± 0.158	7.952 ± 0.071

Table 2 – Percentage of the elements in the sample calculated thorough ICP-OES data

From this first data is possible to observe how these elements are present in great measure but, to further understand the composition of the unknown compound, a qualitative analysis of the XRD spectrum was done using the program QualX.

Starting from the results of the ICP-OES analysis, the search was refined excluding some elements like Mn, Co, Mg, and looking for phases containing Fe, Ca and Zn. Zincite (ZnO) and calcium carbonate ($CaCO_3$) were chosen, since they showed a very good fitting. Furthermore, the main matches founded for these phases presented the same crystal structure hexagonal and trigonal for zincite and calcium carbonate respectively.

Concerning the iron-containing phase magnetite (Fe_3O_4) was selected but, in this case, different crystal structures fitted the data. Monoclinic and trigonal showed a good fitting for the peaks, but their spectra contained many other different peaks and therefore, since the experimental spectrum presented sharp peaks, they were excluded. Cubic crystalline structure, instead, showed the same good fitting mainly exclusively in correspondence of the peaks of the experimental spectrum and therefore this final structure was picked. Presented in Fig.2 (a) is the XRD spectrum containing also the peaks representing the selected phases.

	Pdf Number	**Space group**	**Crystal system**	**Cell Parameters**
ZnO	00-230-0450	P 63 m c	Hexagonal	a = 3.2493 Å c = 5.2057 Å
CaCO₃	0-900-0095	R -3 c :H	Trigonal	a = 4.9900 Å c = 17.0615 Å
Fe₃O₄	00-210-1926	F d -3 m :2	Cubic	a = 8.3750 Å

Table 3-Parameter for each chosen phase after qualitative analysis

In Table 3 are reported the number of the power diffraction file (pdf), the space group, the crystal system and the cell parameters for each chosen phase.
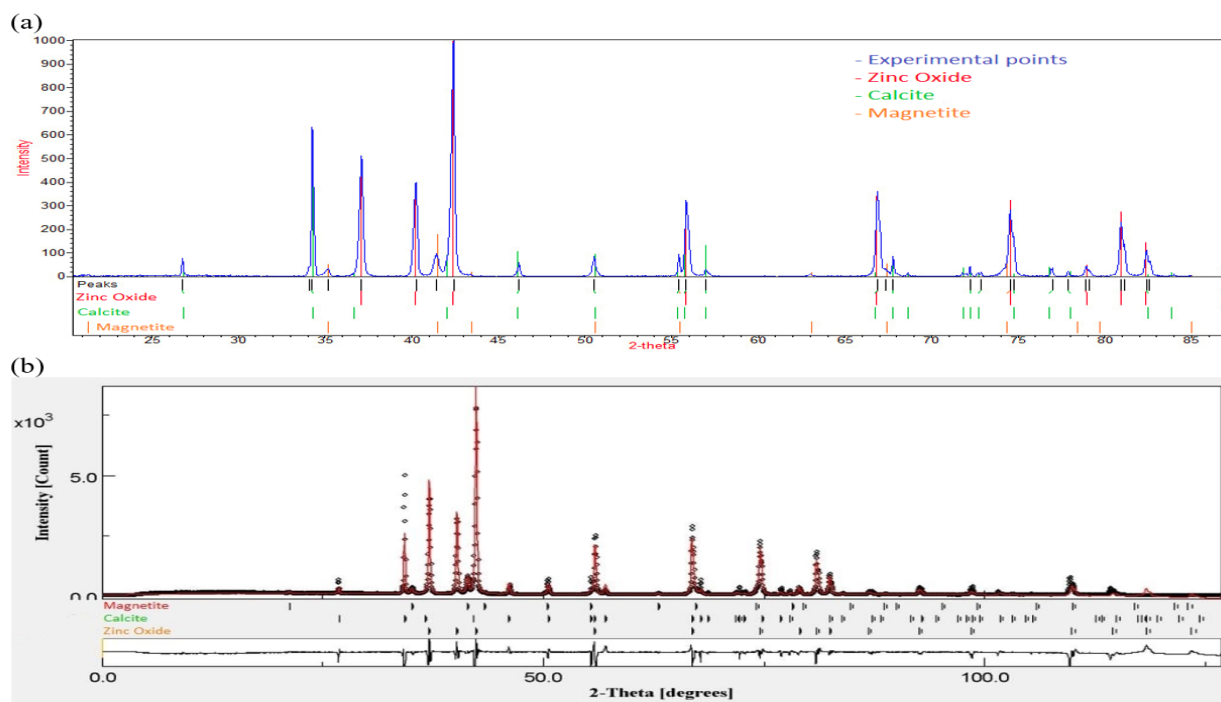

Fig.2 –(a) QualX analysis of the peaks with the relative phases. (b) Maud simulation of the XRD spectrum of the sample.

Afterwards, using Maud to do a quantitative analysis, the percentages of the crystalline phases in the compound were calculated. In Fig. 2(b) the spectra with the fitting of the phases obtained using CIF files corresponding to the pdf of the phases selected [2] [3] [4] is presented whereas, in Table 4, the numerical results are reported. In order to obtain the quantitative analysis results 21 iterations were done and it was obtained an error of sig of 2.58 and %Rwp of 23.85. Due to the software it was not possible to obtain an error to the value of the percentage of ZnO, that is therefore reported as 0.0.

	ZnO	CaCO₃	Fe₃O₄
Percentage in the sample (%)	62.920 ± 0.0	25.696 ± 0.477	11.384 ± 0.308

Table 4-Quantitative results XRD analysis.

Once the crystalline phases of the unknown sample were identified in order to corroborate the results of the XRD quantitative analysis the percentage of the phases in the sample calculated through the ICP-OES analysis were evaluated. The estimated values are reported in Table 5.

	CaCO₃	Fe₃O₄	ZnO
Percentage in the sample (%)	49.519 ± 0.516	40.012 ± 0.255	10.469 ± 0.061

Table 5 – Quantitative results of ICP-OES analysis

It's possible to observe how there's no correspondence between the phase percentages calculated from the XRD and the ICP-OES analysis and this may be due to many factors.

Using the Maud software, a XRD semi-quantitative analysis was carried out, and no calibration process was done. On the other hand, when an ICP-OES analysis is carried out the calibration is performed, so the results can be considered more reliable. Moreover, from picture 3 is clear how not all the peaks are so well fitted, especially the ones corresponding to the CaCO₃ and this also can explain the discrepancies in the calculated percentages.

To further explain the divergence between the percentages calculated also the sample preparation must be taken into account. For the XRD, due to the fact that a narrow laser beam was used, a really good homogenization of the powders composing the sample must be obtained and, when this result is not achieved, the XRD analysis can result in misleading percentages of phases of the sample that differ from the true ones as this seems to be the case.

5. Conclusions

The unknown powder was identified through the XRD qualitative analysis as a material containing three main phases: zinc oxide (ZnO), Magnetite (Fe_3O_4) and Calcite ($CaCO_3$). In addition, performing an elemental and then quantitative ICP-OES analysis, it was calculated that the sample contained $49.519 \pm 0.516\%$ of ZnO, $10.469 \pm 0.061\%$ of Fe_3O_4 and $40.012 \pm 0.255\%$ of $CaCO_3$. These values differ from the ones obtained through the XRD semi-quantitative analysis that resulted to be $62.920 \pm 0.0\%$ for ZnO, $11.384 \pm 0.308\%$ for Fe_3O_4 and $25.696 \pm 0.477\%$ for $CaCO_3$.

To perform a ICP-OES elemental analysis a calibration process is needed, whereas in the XRD is not necessary and, for this last technique, also a good carried out sample preparation, especially the homogenization process, is required to avoid incorrect results. For these reasons the results of the ICP-OES were considered more reliable.

References

[1] Lutterotti L., 2006, MAUD tutorial-Instrumental Broadening Determination.

[2] Bragg W., 1915, The Structure of Magnetite and the Spinels, *Nature* **95,** https://doi.org/10.1038/095561a0

[3] Tyutyunnik A., Slobodin B., Samigullina R., Verberc k B., Tarakina N., 2012 , K2CaV2O7: A pyrovanadate with a new layered type of structure in the A2BV2O7 family. Dalton transactions (Cambridge, England : 2003). 42. 10.1039/c2dt31246h.

[4] Sowa H., Ahsbahs H., 2006, High-pressure X-ray investigation of zincite ZnO single crystals using diamond anvils with an improved shape. Journal of Applied Crystallography - J APPL CRYST. 39. 169-175. 10.1107/S0021889805042457/ko5022zno87sup6.hkl.