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ELEMENTAL COMPOSITION OF SOLVOTHERMALLY SYNTHESIZED ZIF-8 STUDIED BY X-RAY FLUORESCENCE ANALYSIS

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Abstract: ZIF-8 prepared by a solvothermal route in methanol was studied by X-ray fluorescence (XRF) analysis using the fundamental parameters (FP) method in scatter mode. Zinc was the dominant element (8.62 wt%). Ten other elements (Cl, Si, S, K, Ca, Ti, Fe, Ni, Zr and Ag) were found only at trace levels, about 0.15 wt% in total. The measured zinc content is roughly 3.3 times lower than the value calculated for $Zn(C_4H_5N_2)_2$ (28.73 wt%). Because C, H and N are not determined by XRF, the reason for this difference cannot be established from the XRF data alone, and CHN analysis is needed to close the mass balance.

Keywords: *ZIF-8; X-ray fluorescence; elemental composition; fundamental parameters method; trace impurities; stoichiometry.*

Zeolitic imidazolate frameworks (ZIFs) are built from tetrahedrally coordinated

metal ions and imidazolate linkers. They form neutral frameworks whose topologies follow those of zeolites [1]. In ZIF-8 each Zn^{2+} ion is bound to four 2-methylimidazolate anions, so the ideal formula of the framework is $Zn(C_4H_5N_2)_2$, or $ZnC_8H_{10}N_4$ [1].

ZIF-8 is often prepared with a large excess of the ligand over the metal salt, and this excess is known to influence crystal size and growth [2, 3]. As a result, the composition of a real product can differ from the ideal formula, because unreacted ligand, residual solvent or inorganic impurities may stay in the pores or on the crystal surface. The characterization of MOFs therefore relies on several complementary methods [4], and elemental analysis is a simple first check of sample quality.

In this work the elemental composition of an activated ZIF-8 sample was measured by XRF analysis and compared with the composition calculated from the ideal formula. The sample was obtained by solvothermal synthesis from zinc nitrate hexahydrate and 2-methylimidazole in methanol, followed by thermal activation.

The composition was determined by XRF analysis with the fundamental parameters (FP) method in scatter mode. In the FP approach, concentrations are calculated from the measured line intensities with the help of physical constants such as absorption coefficients and fluorescence yields, so fewer reference standards are needed than in purely empirical calibration [5]. For every element the program gives the result in mass percent, the statistical error, the lower limit of detection (LLD) and the lower limit of quantification (LLQ). XRF is a non-destructive multi-element technique [6]. It is, however, poorly suited to the light elements that make up the organic part of ZIF-8: hydrogen gives no characteristic X-ray lines, and carbon and nitrogen are difficult to quantify with standard instrumentation.

The results are given in Table 1. Zinc is by far the main element, with a content of 8.62 wt% and a statistical error of 0.0284 wt% (0.33% of the measured value). Ten other elements were detected, all below 0.1 wt%, and together they add up to only

about 0.147 wt%. The zinc content is more than 100 times higher than that of any of them (the closest is Zr, 0.0729 wt%).

Table 1. Elemental composition of the ZIF-8 sample determined by XRF (FP method, scatter mode).

No.	Element	Result, wt%	Statistical error	LLD	LLQ
1	Cl	0.0348	0.0001	<0.0001	0.0003
2	Si	0.0179	0.0003	0.0003	0.0010
3	S	0.0103	0.0001	0.0002	0.0005
4	K	0.0027	0.0003	0.0006	0.0018
5	Ca	0.0026	0.0002	0.0003	0.0010
6	Ti	(0.0003)	<0.0001	0.0001	0.0004
7	Fe	0.0037	0.0002	0.0004	0.0011
8	Ni	0.0010	0.0001	0.0003	0.0009
9	Zn	8.62	0.0284	<0.0001	0.0002
10	Zr	0.0729	0.0012	0.0001	0.0003
11	Ag	0.0005	<0.0001	0.0001	0.0004

Note: the value in parentheses lies between LLD and LLQ. Results are in wt%.

Every value except titanium is above its LLQ. The titanium value (0.0003 wt%) is given in parentheses because it lies between LLD and LLQ, so titanium is detected but not reliably quantified. Nickel and silver are only slightly above their LLQ and should be regarded as approximate.

The origin of the trace elements cannot be proven from these data, but likely sources are easy to name. Chlorine and sulfur may come from the zinc salt or from laboratory ware. Silicon is a typical contaminant from glassware and glass-fiber filter

materials. Iron and nickel are the main components of stainless steel and may come from the autoclave body or the stirring equipment. Potassium and calcium are common impurities in reagents. Zirconium is the highest of the trace elements, and a contribution from the instrument or the sample holder is possible; a blank measurement of the empty holder would show whether this is the case.

The ideal formula $ZnC_8H_{10}N_4$ corresponds to a molar mass of 227.58 g/mol. The calculated mass fractions are compared with the XRF result in Table 2. The measured zinc content, 8.62 wt%, is only about 30% of the calculated value of 28.73 wt%. A difference of this size cannot be caused by the trace impurities, which add up to less than 0.15 wt%. Since C, H and N are not measured, a large part of the sample is invisible in the spectrum, and the software may treat it as an undetected part of the matrix. Residual methanol or water in the pores, and the way the powder was prepared for the measurement (for example, dilution with a binder), could also lower the apparent zinc fraction. XRF alone cannot decide between these explanations.

Table 2. Composition calculated for $ZnC_8H_{10}N_4$ and the XRF result.

Element	**Calculated for $ZnC_8H_{10}N_4$, wt%**	**XRF result, wt%**
Zn	28.73	8.62
C	42.22	not determined
H	4.43	not determined
N	24.62	not determined

For this reason the XRF result is used here only as evidence that zinc is the main metal component and that no other metal is present in a significant amount. It does not prove that the sample has the ideal composition. To check the Zn:ligand ratio and to complete the mass balance (Zn + C + H + N close to 100%), the XRF data should be combined with CHN analysis and thermogravimetry, and XRD would confirm the

phase purity.

XRF analysis showed that zinc is the main element of the synthesized ZIF-8 sample (8.62 wt%) and that other elements are present only at trace levels, about 0.15 wt% in total, probably coming from the reagents, glassware and equipment. The measured zinc fraction is about 3.3 times lower than the ideal value of 28.73 wt%, and the reason for this cannot be established from XRF data alone. CHN analysis is the next step needed to judge the purity and stoichiometry of the material.

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