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**DETERMINATION OF EXTRAFRAMEWORK
METAL CONTENT IN ZEOLITIC CATALYSTS
BY MEANS OF WD XRF SPECTROMETRY**

Petr KNOTEK^a, Miloslav POUZAR^b, Roman BULÁNEK^{a1}
and Kateřina NOVOVESKÁ^a

^aDepartment of Physical Chemistry, ^bInstitute of Environment Protection,
The University of Pardubice, CZ-532 10 Pardubice

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XRF spectroscopy is not widely used for zeolites analysis, but its known advantages are indispensable, i.e. small consumption of the sample (5 mg), analysis of the sample without dissolution, quickly and easy pre-treatment and low-cost analysis. Therefore, development of methodology for determination of metal (Cu, Co, Ga, V) content in zeolites using wavelength dispersive X-ray fluorescence analysis is described in this paper. XRF spectrometer was calibrated for each metal using model pellets containing oxide and boric acid. Response of detector on the amount of metal can be reliably fitted by a linear model. Copper (resp. cobalt) zeolites showed good agreement in metal content determination by XRF and standard validated analysis (AAS and ICP-OES after zeolite dissolution).

¹ To whom correspondence should be addressed.

Introduction

In the last decades, zeolites exchanged with transition metal ions due to their bifunctional behaviour (acid and redox centers) have received increasing interest as promising catalysts for a variety of important reactions [1]. Zeolites can serve as hosts for activation of transition metal ions, offering a unique ligand system with multiple types of coordination for cations.

Copper, cobalt, gallium and vanadium are most often used metals incorporated into zeolite. Cu-zeolites have unique activity for decomposition of NO_x into elements [2,3]. Cobalt zeolites are used for their high potential to remove NO_x with CH_4/O_2 even in the presence of water [4] or production of acetonitrile by ammoxidation of ethane [5,6]. Zeolites with gallium or zinc or nickel are well known catalysts for aromatization or dehydrogenation of alkanes [7] and vanadium doped zeolites are used for oxidative dehydrogenation or partial oxidation of alkanes [8]. Many other potential applications of metal exchanged zeolites are being researched.

Zeolite topology, type and exchange level of cations belong among the factors controlling catalytic activity of catalysts. Therefore composition of catalyst is one of the most important basic information. There is currently a wide range of analytical methods, which could be applied to deal with this particular problem. The most frequently applied methods for elemental analysis of these materials involve AAS (atomic absorption spectrometry) and ICP-OES (inductively coupled plasma optical emission spectrometry) [9]. Besides these ones there are many other methods for determination of the composition (e.g. NMR [10], PIXE [11], LIBS [12], IR after adsorption of the probe molecules [13], temperature programmed techniques [14] and many other techniques based on physical-chemical processes) but each of them has some disadvantages: very complicated calibration or applicability only to some types of catalysts. A disadvantage of the most often used methods (AAS, ICP-OES, titration) is the necessity of dissolution of analyzed material, e.g. consumption of ca. 0.25 – 1 g catalyst and working with dangerous acid (e.g. HF) using high temperature and pressure.

Some other problems (for example sample contamination and its losses) may occur during any of the mentioned procedures. And, therefore, these standard methods do not satisfy basic analytical requirements (minimum sample pre-treatment, quick analysis, small consumption of sample). That is why there are attempts to create new, quick and reliable analytical methodology.

Among the potential instrumental techniques, wavelength dispersive X-ray fluorescence spectrometry is highly attractive, allowing the quantification of exchanged elements in different matrixes. The main problem of analysis of materials such as zeolites by XRF is the signal influence by matrix effects [11,16]. Preparation of samples like pellets from a mixture of small amount of zeolite with plenty of X-ray inert material is the easiest way how to avoid problems caused by

matrix of the samples, and another, no less important, advantage of this method is the really small consumption of sample for analysis. Preparing of glass bead from analyzed material with lithium tetraborate is another pre-treatment possibility of zeolite [9,15].

Although this techniques gained major significance as a routine means of elemental analysis more than 25 years ago [16], either XRF techniques are not a widely used method, or the methodology for analysis of zeolite by means of XRF was not published. And that is why preparation of methodology for determination of metal (Cu, Co, V and Ga) content in various zeolite matrices was the aim of this work.

Experimental

Instrumentation

Samples and standards were analyzed as pellets using a bench-top vacuum wavelength dispersive X-ray spectrometer Spectroscan V (Spectron, Russia). X-ray tube with Pd anode with maximum output 200 W was used for excitation of characteristic radiation of the elements determined (used voltage 40 kV, optimized excitation current $i = 1$). The characteristic X-rays were detected with the aid of dispersive part created from curved crystals in Johanson's arrangement and a sealed gas proportional detector filled with Xe. All pellets were continuously rotated during analysis for removing potential heterogeneity of the pellet. The XRF parameters are summarized in Table I.

Background correction was based on two-points linear interpolation (see below). Software Spectroscan V 717 ver. 2 was used for controlling spectrometer and for optimization of integration time. The data were statistically processed by OPGM software [17].

Standard and Sample Preparation

Samples of metal doped zeolite catalysts were prepared by standard ion exchange at the Department of Physical Chemistry (University of Pardubice) or Heyrovsky Institute of Physical Chemistry (for the detailed description of zeolite preparation see Refs [6,18]).

For pellets preparation 5 mg zeolite was homogenized with 350 mg boric acid (Lachema Brno, p.a.) in a ball mill model 3110-3A (Crescent Dental Mfg. Co., USA). This mixture was transported onto the press adapter (Elmet, CZ) and compressed (3 min. by pressure 10 kN m^{-2} followed 7 min. by pressure 50

Table I Condition of measurement of WD XRF Spectroscan V for each of analyzed metals (X-ray tube with Pd target, voltage 40 kV, excitation current 1mA)

Metal	Cu	Cu	Co	Ga	V
Metal source	CuO	Cu(NO ₃) ₂ ·3H ₂ O	Co ₃ O ₄	Ga ₂ O ₃	V ₂ O ₅
Analytical line, mÅ	Kα 1541.9	Kα 1541.9	Kα 1790.4	Kα 1341.5	Kα 2504.9
Crystal	LiF 200	LiF 200	LiF 200	LiF 200	LiF 200
Integration time, s	30	30	30	30	60
Background ^a , mÅ	1500; 1630	1500; 1630	1720; 1840	1300; 1370	2460; 2540
Integration time, s	30	30	10	10	30

^a position of points for determination of background intensity

kN m⁻²) into pellets of 12 mm diameter and average thickness 2 mm.

The maximum metal content in zeolite materials modified by metal ions depends on the ion exchanged capacity of matrix, i.e. on the aluminium content in the zeolitic framework. Therefore, 5 – 7 wt. % of considered metal can be maximally dispersed into any analyzed zeolite. Real concentration of metal in the pellets of zeolite and boric acid is in the range from 0 to 1000 ppm.

The respective metal oxides were used as a source of metal atoms for preparation of the WD XRF calibration standards. CuO (p.a.) was purchased from Riedel-de Haën and Ga₂O₃ (purity 99.99 %) was purchased from Fluka. Co₃O₄ and V₂O₅ were prepared by thermal decomposition of cobalt (II) nitrate and ammonium metavanadate, respectively, according to Ref. [19]. Cu(NO₃)₂·3H₂O (Poliskie odczynniki chemiczne, Glivice, p.a.) was used as copper source.

Because the metal content in pellet is relatively small, five supply mixtures of metal source with 0.1 wt. % of metal in boric acid were prepared. Twelve standard pellets for each calibration were prepared in the same way as the pellets with zeolites; instead of 5 mg of zeolite known quantity of supply mixture was homogenized with boric acid.

WD XRF Method Validation

In order to validate the determination of copper and cobalt content by means of XRF spectrometry, the concentrations of mentioned metals in zeolites were determined by standard analytical methods AAS and ICP-OES after microwave sample decomposition. Zeolites were decomposed by means of two step process in microwave apparatus BM 1S/II (Plazmatronika, Poland). 150 mg zeolite was suspended in 2 ml hydrofluoric acid in a PTFE vessel and decomposed in

microwave apparatus for 20 min. Saturated solution of boric acid (8 ml) was added into the PTFE vessel after the first step of decomposition to remove the rest of hydrofluoric acid. The resulting solution was diluted by double distilled water to 50 ml.

The concentration of copper or cobalt in the solution achieved after digestion of zeolite was determined by flame atomic absorption spectroscopy by means of a GBC 906 AA spectrometer (GBC, Australia) and by ICP-OES measurement on a GBC Integra XL spectrometer (GBC, Australia).

Results and Discussion

Optimization of WD XRF method parameters

Determination of suitable analytical line together with background correction technique is an important part of each WD XRF method. The most intensive line ($K\alpha$) was chosen for all the metals investigated. The measured intensity of $K\alpha$ line is a sum of net line intensity (I) of metal and intensity of background (I_B). The net line intensity was calculated as total intensity minus background intensity, which was determined using "two points background correction" [16]. This method is based on linear interpolation of intensity of two points to the position of $K\alpha$ line. The position of points used for correction of background (Table I) was determined on the basis of the spectra measured with the highest-concentrated calibration standard to avoid interference of metal to background.

There are many other parameters which are worth optimizing. Signal integration time and X-ray tube current are the most important of them affecting accuracy as well as the spectrometer wear. For the optimization of these ones we prepared a homogenous mixture of CuO in H_3BO_3 with Cu content in the middle of the range of copper calibration standard (295 ppm of Cu). Three pellets of different weight (225, 300 and 368 mg) were prepared from this mixture. The thin layer sample was prepared by deposition of this powder onto adhesive side of insulating foil, too.

These samples were measured by XRF with changing excitation current of X-ray tube (i) in the range from 0.05 mA to 5 mA (Fig. 1). Cu $K\alpha$ net line intensity increases linearly below the excitation current of 3 mA. Above this value, the detector lost sensitivity to incident fluorescence X-ray photons due to the enormous number of them (detector began to be filled up [16]). The deviation from linear dependence due this problem occurred only for the copper net line intensity, because this signal is enlarged by that of coherent radiation of used Cu-shell of X-ray tube (see below).

Increasing the depth of penetration [16] and the number of radiating transitions participate in the net line intensity increasing. The second effect

mentioned (the number of radiation transitions) is important below the current of 1 mA, and above this value it is not changed and, therefore, does not influence the shape of the dependence intensity I vs. current i (see Fig. 1). Increasing of penetration depth is the most important, generally occurring, effect. The penetration depth (1 – 100 μm [16]), i.e. the number of irradiated ions, increases with the intensity of X-ray photons, and/or excitation current until they reach thickness of pellets and/or the maximum of output of X-ray tube, respectively. Because the net line intensity for each excitation current is independent of the weight of pellets, it has been proved that the penetration depth is more narrow than the thickness of all pellets. In the opposite case, the response of detector would exhibit different values for pellets of different weight.

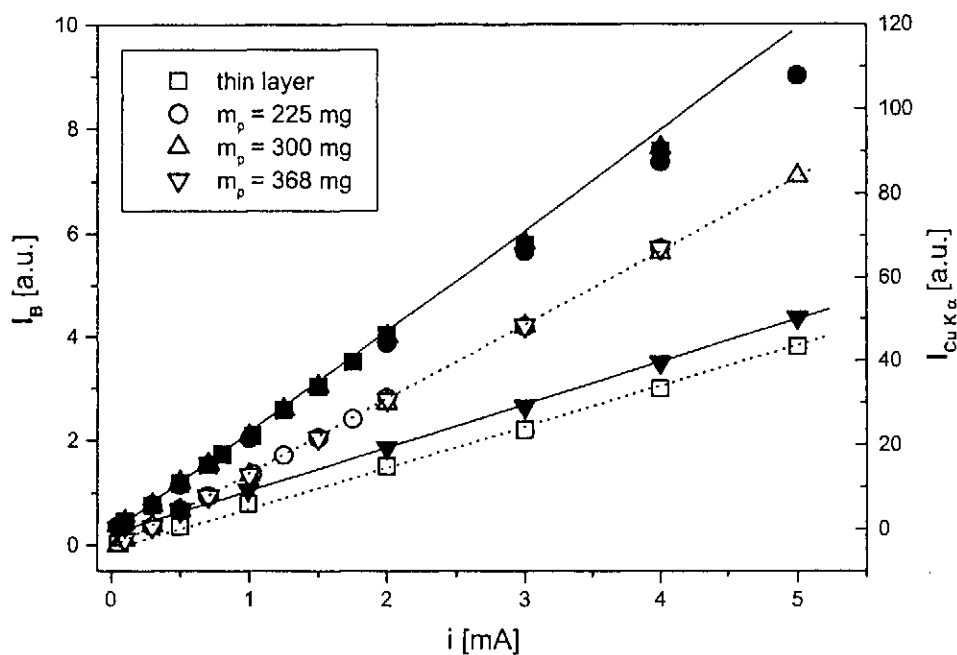


Fig. 1 Dependence of net line intensity I (full points) and intensity of background I_B (open points) on excitation current of X-ray tube i for pellets with different weights and the same copper concentration (295 ppm Cu)

Differences between pellets and thin layer are caused by different basic principle of these samples. The net line intensity measured from pellets depends on the concentration of analyzed metal in pellets (in the case that penetration depth is narrower than the thickness of pellets). If a beam of X-ray photons passes through the sample in the case of thin layer, all atoms of sample are irradiated and, therefore, the calibration is done on the absolute amount of metal in sample not on

its concentration [20]. Accurate measurement of weight of sample is a problem disproving the advantage of absence of problematic matrix effect and lost linearity of detector. Due to the half absolutely measured total intensity of compared to pellets, deviation of detector response from linearity is not important for high values of excitation current.

All three effects mentioned (increasing of penetration depth, changing number of radiation transitions and the problem with detector) influence the shape of signal-to-background ratio (SBR, Fig. 2). The dependence of SBR on excitation current exhibits a maximum in the range from 0.5 to 2 mA for pellets and a sigmoid curve for thin layer. Increasing of SBR value for low current is caused by increasing of number of radiation transitions of copper (for pellets and thin layer) and the decrease in SBR value for high current can be explained by depression of detector sensitivity induced by filling up of detector. The higher signal-to-background ratio makes the better determination of net line intensity I possible [9,16,20] and, therefore, the excitation current in the range from 0.5 to 2 mA seems to be optimal.

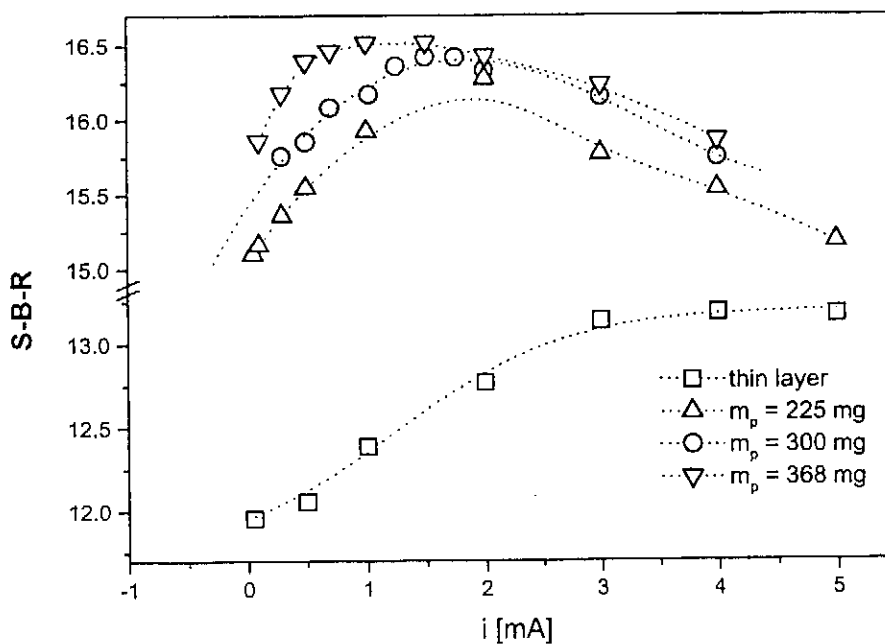


Fig. 2 Dependence of Signal-to-Background Ratio (SBR) on excitation current (i) and different weights of pellets (and thin layer) prepared from homogenous mixture of H_3BO_3 and CuO (295 ppm of copper)

The time of integration is another parameter worth optimising. The time of integration of analytical line as well as two points creating points for correction of background were determined by the software tools based on the calculation of instrument error from measured spectra of analytical line surroundings. The optimized time was determined as 30 seconds signal integration (Table I).

Calibration Model of the XRF Spectrometer for Analysis of Copper in Zeolites

The calibration was carried out using twelve pellets of known copper content in the range corresponding to the maximal copper content in zeolite. The copper concentration in each pellet was calculated from the amount of supply mixture brought into the grinding ampoule with inert material (H_3BO_3). This mixture was measured like pellets, which were formed by pressing of these mixtures. The intensity of Cu $K\alpha$ line in pellets was measured by means of X-ray fluorescence spectrometer with three different excitation current values of X-ray tube (0.5; 1 and 2 mA). The net intensity values I (total intensity corrected for background) were plotted against the calculated copper content in pellets (see Fig. 3).

The following calibration model was suggested for all three sets of measured data

$$c = \beta_0 + \beta_1 I + \beta_2 I^2$$

where c is concentration of Cu in pellets (ppm); I – net line intensity of corrected $K\alpha$ line in impulses per seconds (s^{-1}).

The statistical significance of parameters β_i was tested with the use of the Student test [17]. The absolute magnitude of tested criterion $abs(t)$ was in all cases for β_2 below the critical value $t_{1-0.05/2}(12-2) = 2.28$ and, therefore, it is possible to assume that term I^2 is statistically insignificant for all models tested and for all excitation currents tested.

The significance of parameters β_0 and β_1 was tested after leaving out the insignificant term β_2 . Both of them are statistically significant and new calibration model is

$$c = \beta_0 + \beta_1 I$$

The calibration parameters for three different excitation currents are summarized in Table II, and the calibration curve for excitation current 1 mA is shown in Fig. 3. There are numbers of global regression characteristics for comparison of different calibration curves and models. The correlation coefficient R [17]

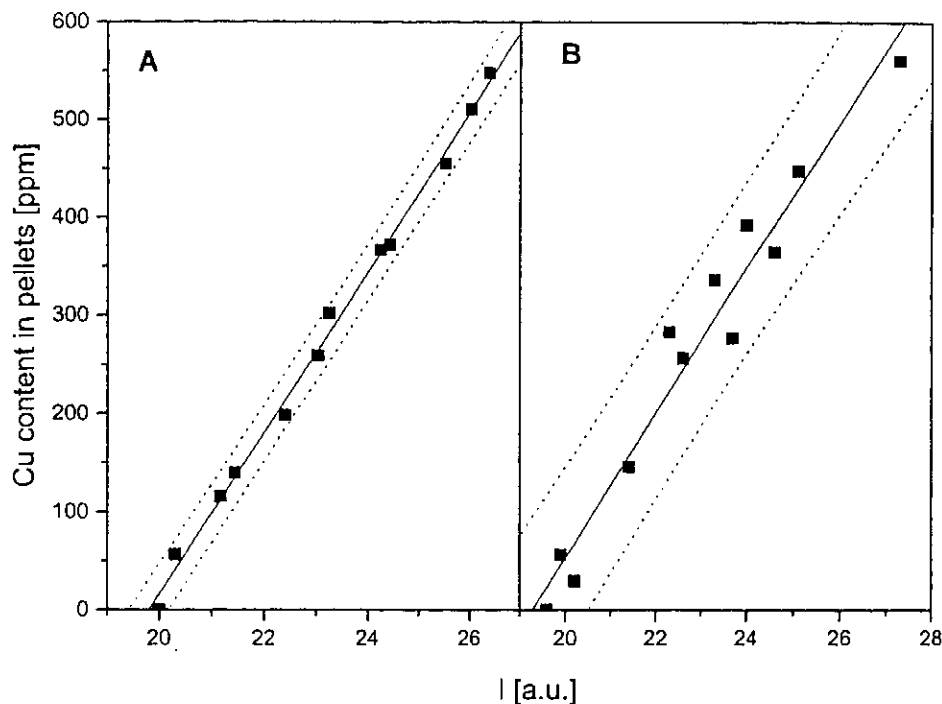


Fig. 3 Calibration curves for determination of copper prepared from CuO (A) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (B). Conditions of measurement: 12 pellets; excitation current $i = 1$ mA; voltage 40 kV; time of integration 30 s. solid line – calibration curve, dashed line – predicted values (probability of 95 %), squares – experimental points

Table II Parameters of calibration model $c = \beta_0 + \beta_1 I$ for copper analysis prepared from CuO for different excitation currents i . Comparison with the calibration curve prepared from sample from $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. Experimental condition: $t = 30$ s; i varies from 0.5 to 2 mA

i , mA	0.5	1	2	$\text{Cu}(\text{NO}_3)_2^a$
β_0	-1720 ± 40	-1660 ± 40	-1800 ± 40	-1400 ± 100
β_1	0.169 ± 0.004	0.0838 ± 0.001	0.0433 ± 0.0009	0.074 ± 0.005
R	0.9975	0.9979	0.9978	0.9794
Acaic	64.76	62.99	64.2	88.48

^a parameters of nitrate calibration curve for optimal current $i = 1$ mA

($R_{\text{linear calibration}} = 1$) and Acaic criterion [17] (a better calibration exhibits a lower value of the criterion) are the well-known. The comparison of three calibrations based on Acaic criterion and also the correlation coefficient indicate that the excitation current of X-ray tube adjusted on value 1 mA is optimal (see Table II).

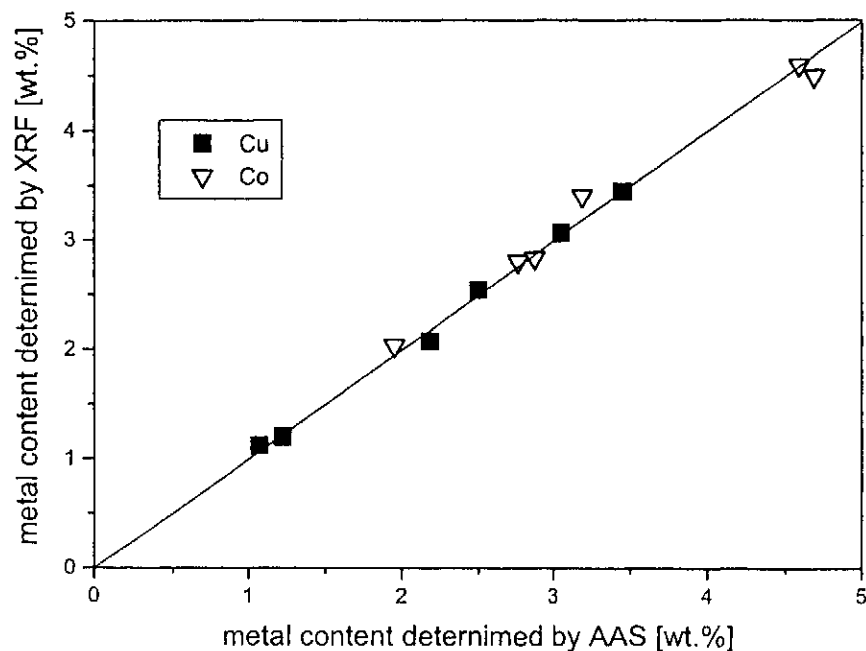


Fig. 4 Correlation between copper (full squares) (or cobalt (open triangles)) content determined in the zeolites investigated by means of AAS and XRF. The line represents theoretical values of total agreement between these methods

The signal of X-ray spectrometry should be relatively insensitive to chemical nature of metal source used for preparation of pellets [16,20]. Therefore, we tried to prepare other calibration standards from copper(II) nitrate, because nitrates are more commonly used for standards preparation in laboratory. The calibration curve was constructed in the same way as the oxide calibration curve, i.e. twelve pellets were prepared from a mixture of copper(II) nitrate and boric acid. The intensities of Cu K α line were measured at the excitation current adjusted at 1 mA and the signal was collected for 30 s. The data measured were fitted by the same calibration models as in the case of oxide. The parameters β_0 and β_1 for nitrate calibration are given in Table II. Another tested hypothesis was the equality of parameters β_0 and β_1 for both calibrations (alternative hypothesis (at least one parameter is different) was disproved by Chow's F-test [21] based on the change of sums of squares, $F_{crit}(3.49) > F(2.23)$) and the result confirmed the theory that the signal is not affected by chemical compound used in pellets. Based on comparison of global regression characteristic, the oxide calibration seems to be better. This may be caused by potential inaccuracy of standards resulting from hygroscopic behaviour of nitrates.

The detection limits as well as validity of the calibration models were

confirmed too. The detection limit defined as threefold standard deviation of the background [20] was 40 ppm in pellets (and after multiplication by diluting factor (inert/sample) was 0.3 wt. % of copper in zeolite).

The validation of method was based on analysis of zeolites with known copper concentration measured by means of standard analytical method (AAS after microwave zeolite decomposition). The same procedure, as the one used for the pellets of the standard, was also used for the pellets of six zeolites. The concentration of copper in these samples was determined by the suggested XRF spectrometry method. The results of the analyses of these samples by XRF on the basis of calibration were compared with the concentration of copper determined by AAS (Fig. 4). A linear dependence between the measured and calculated copper concentrations was found ($c_{\text{Cu}}^{\text{XRF}} = 0.005 + 0.99c_{\text{Cu}}^{\text{AAS}}$), and therefore, the hypothesis that the slope of this correlation is 1 and intercept is 0, was tested. This hypothesis is confirmed by means of *t*-test on the significance level 0.05 [17] ($t_{\text{int}} = 0.0695$; $t_{\text{slope}} = 0.0181$; $t_{\text{crit}} = 2.13$). The results of AAS and XRF are accordingly concurrent.

The reproducibility of determination of copper content was tested by preparing two sets of five pellets of zeolites with copper content 1.22 and 3.05 wt. %. These pellets were measured and the results of metal content are 1.21 ± 0.06 and 3.06 ± 0.08 wt. %. The error of copper content determination is in the range of 5 rel. %. Errors of Cu K α net line intensity measurement and errors connected with weigh of zeolite and boric acid participate in the overall error mentioned above.

Calibration Model of the XRF Spectrometer for Analysis of Cobalt, Vanadium and Gallium in Zeolites

The other metals introduced into zeolites and screened by XRF spectrometry were cobalt, vanadium and gallium. Parameters were accepted from their optimizing for copper analysis, it means excitation current was 1 mA, time of integration adjusted on 30 s for each from twelve standards prepared from oxides. The results are summarized in Table III.

Small differences were observed in comparison of copper calibration with these metals' calibrations. The intercept was practically zero (statistically insignificant). Copper calibration intercept is higher in connection with coherent scattering of copper shell of X-ray tube. The fact that the net line intensity of other metals was not affected by short term instability of Cu-shell explains the order decrease in detection limits for Co, Ga and V as compared with Cu detection limit. The sequential increase of slopes of calibration curves with increasing atomic number is caused by increase of fluorescence yield of analyzed metal [16,22,23].

This methodology of determination of metals content in zeolites by XRF

spectrometry was also validated for cobalt ions using zeolites with known Co content (measured by means of ICP OES). The regression curve (Fig. 4) was evaluated in a similar way as copper regression, and the resulting curve is $c_{Co}^{XRF} = 0.25 + 0.93 c_{Co}^{AAS}$. The hypothesis about zero intercept and slope equal to one was verified on the statistical significance $\alpha = 0.05$ [17] ($t_{int.} = 1.14$; $t_{slope} = 1.37$; $t_{crit} = 2.13$). Since the optimization of measurement parameters for copper can be used for cobalt analysis, it is possible to assume that these parameters are applicable to gallium and vanadium too. The reproducibility of measurement was studied in the same way as with copper content. Two sets, five pellets each, were prepared from zeolites of known Co content determined by means of ICP OES: 4.59 and 2.76 wt %. The results from XRF are 2.7 ± 0.1 wt. and 4.6 ± 0.1 wt. %. Relative errors of determination of cobalt content are lower than 5 % and are caused by the same reasons as in the case of copper determination.

Table III Parameters of calibration model $c = \beta_0 + \beta_1 I$ for analysis of cobalt, vanadium and gallium (in comparison with copper). R – correlation coefficient; Acaic – Acaic criterion; DL – detection limit in wt. % of determined metal in zeolites; $t_{int.}$ – testing criterion for hypothesis of intercept significance. Experimental conditions: 12 pellet standards prepared from oxides, $t = 30$ s; $i = 1$ mA

Metal	Co	Ga	V	Cu
β_0	-40 ± 10	-4 ± 10	0.3 ± 3	-1660 ± 40
β_1	0.066 ± 0.001	0.0565 ± 0.0008	0.311 ± 0.004	0.0838 ± 0.001
R	0.9987	0.9989	0.9991	0.9979
Acaic	71.97	80.6	44.42	62.99
DL	0.01	0.04	0.05	0.3
$t_{int.}$	-4.45	-0.349	0.0922	41.5

Conclusion

The determination of metal concentrations in the zeolitic materials modified by copper, cobalt, gallium or vanadium was carried out by means of XRF spectrometry. It was proved that the detector response of XRF spectrometer is able to be calibrated by the help of appropriate oxides. The response of detector to the amount of metal can be reliably fitted by a linear model. The calibration standards used in our laboratory were satisfactory. The obtained calibrations were tested on the real catalysts and validated by means of standard analytical methodology for these materials (e.g. AAS after dissolution).

The presented WD XRF method is fast, cheap, simple and the sample preparation requires only very small amount of sample (ca. 5 mg) in contrast to other analytical methods used for this kind of materials (ca. 300 mg). The detection limits, precision and accuracy were acceptable for standard laboratory purposes.

Acknowledgements

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Symbols

AAS	atomic absorption spectrometry
Acaic	Acaic criterion for global regression characterization
$c_{\text{Cu(Co)}}^{\text{AAS(XRF)}}$	concentration of Cu (or Co) measured by means of AAS (or XRF)
F	value of Fisher–Snedecor’s F -test
i	excitation current, mA
I	net line intensity, s^{-1}
I_B	background intensity, s^{-1}
ICP–OES	inductively coupled plasma optical emission spectrometry
IR	infra red spectroscopy
LIBS	Laser-induced breakdown spectroscopy
NMR	nuclear magnetic resonance
NO_x	nitric oxides
PIXE	particle induced X-ray excitation
ppm	part per million ($1 \text{ ppm} = 10^{-6}$)
SBR	signal-to-background ratio
$t_{\text{crit.}}$	critical value of Student t -test
$t_{\text{int.}}$	value of t criterion for intercept
t_{slope}	value of t criterion for slope
WD XRF	wavelength dispersive X-ray spectroscopy
wt.	weight

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