



Unified method for the determination of chemical composition in different types of materials using Wavelength Dispersive X-ray Fluorescence Spectrometry



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ABSTRACT

The aim of the article is to show that determination of the main chemical composition with Wavelength Dispersive X-ray Fluorescence Spectrometry method does not require the use of separate analytical applications and procedures for the tests of materials of different origin. This is however conditioned upon calcination of the tested initial sample at the temperature of 815 °C to remove organic matter and its preparation for X-ray measurements by fusing into a borate bead. Within the framework of the conducted research a special analytical application measuring 10 oxides: SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, Na₂O, K₂O, SO₃, TiO₂ and P₂O₅ was developed. Standards and certified reference materials (CRMs) were applied for calibration. Synthetic standards with the use of oxides and salts of purity of 99.99% were also prepared to complete the measuring points on the calibration curves. The curves determined based on the measuring points have high correlation coefficients and accuracy. The α empirical correction coefficients were applied to correct matrix effects. The range of the method was confirmed based on the measurements of 13 synthetic standards. The average values of the standard deviations in the lower range of the calibration curves were between 0.0008% for K₂O and 0.0056% for Na₂O and 0.0054% for MgO. The average values of the relative standard deviation were in the range between 1.81% for K₂O and 13.92% for MgO and 11.21% for Na₂O, respectively. In the upper range of the calibration curves, the average values of standard deviation were between 0.079% for TiO₂ and 0.962% for P₂O₅, and the relative standard deviation was between 0.05% for SiO₂ and 2.39% for P₂O₅. The accuracy of the developed WDXRF method was assessed based on the measurement of 10 certified reference materials representing all the tested materials (cement, coal ash, slag, fire clay, sediment and soil). Out of 98 conducted measurements (two CRMs did not contain the declared content of P₂O₅ and SO₃ respectively), in 68 measurements, relative errors were below 5%, and, in next 27 measurements, they were between 5% and 10%. The errors were comparable for all the tested materials which confirms that in WDXRF analyses of borax beads the type, kind and origin of a sample do not affect accuracy of the obtained measurements.

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1. Introduction

There are two main methods of preparing samples for Wavelength Dispersive X-ray Fluorescence Spectrometry (WDXRF) analyses. The first one is pressing a sample together with a binding material [1–4]. The most commonly applied binding materials are cellulose, boric acid and wax. In the other method a sample is fused into a borate bead with the use of lithium tetraborate or a mixture of boranes [5–7]. In the first method a sample to be

tested can be the initial sample. The pressing method is cheap and quick, it does not change the chemical composition of a sample, and the obtained results of the WDXRF analyses correspond to the real contents of particular components in a tested initial sample [7–11]. The main disadvantage of the X-ray measurements of pressed samples are high values of matrix errors which significantly influence accuracy of the obtained results. Matrix errors are associated with the differences in the mineralogical form of given elements in the tested samples [4,12]. As the dilution of a sample with the binding material is usually small, the matrix errors resulting from absorption or enhancement of the radiation emitted from a sample by the measured element by other elements

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occurring in the sample may reach high values. Due to the differences in the mineralogical composition of the tested samples, it is difficult to obtain homogenous grain size (preferably below 10 μm) through grinding which is both a prerequisite and necessary to minimize the errors associated with the effects in the WDXRF technique [7,13,14]. The WDXRF technique, like all other instrumental techniques of chemical analysis, compares the results with standards, hence it is based on calibration [2,14].

In the light of the potential errors mentioned above, which may occur when pressed samples are tested, it is obvious that accurate results can be obtained only if the standards used for calibration of the method and measured samples are similar. It is recommended to use the same objects or samples of the same origin. It complies with the guidelines, which recommend applying separate analytical procedures for specific objects [15,16]. For most industrial laboratories maintaining a quality system it is not a significant problem as they usually analyze one or at most a few objects. These are laboratories working for cement industry, metallurgical industry, glass industry and many others, where the tested object is usually a raw material or a product, and the aim of the analysis is not to determine accurately the full chemical composition of the tested sample. The analyses seek to confirm if the content of the parameter, strategic for realization of a process or significant for the quality of a product, meets the requirements of a relevant standard and falls within the required range [17–19]. In such cases, preparing samples for the X-ray measurements by pressing them with a binding material is an ideal solution as it is quick and cheap, and with good quality standards it enables to obtain accurate results.

The aim of the research presented in this article is to show that for samples prepared for WDXRF technique measurements by the fusion method their origin, kind and type does not matter, because differences in their structure and mineralogy as well as the variability of their chemical composition do not have any significant influence on the obtained results. In other words, as far as the accuracy of an analysis is concerned, it is not necessary to develop separate analytical applications for given materials tested with the Wavelength Dispersive X-ray Fluorescence Spectrometry if the samples are prepared by fusing into a borate bead. It is so as the borate beads form a homogeneous solid solution, in which the intensities of the analytical lines of the measured elements, which are emitted from a sample during the X-ray measurement, depend only on the content of the element in a given sample. Hence the causes of biggest errors in the WDXRF technique [11], which are associated with mineralogical and grain-size differences, disappear. It is also no longer important in what form or chemical compound the measured element occurs in a sample. In fused samples matrix effects associated with absorption or enhancement of the X-radiation emitted by the measured element as a result of the presence of other elements which form the matrix also exist. Yet, they are much smaller than in pressed samples and in many cases so insignificant that it is even not necessary to correct them mathematically applying matrix α correction coefficients empirical or theoretical. Nevertheless, in cases when analytical application comprises determination of several elements or more and obtained calibration curves are applicable in a wide range of content [7,11], it is recommended to apply matrix effects correction with the use of α coefficients even if the sample is highly diluted with a flux, at the ratio of e.g. 1:9. Large dilution with a flux facilitates fusing, minimizes losses of volatile components during the fusion process, yet it increases the determination limits in comparison with the pressed samples. It is insignificant for measuring the main components, but it is a problem when trace elements are measured [11]. They can also be determined, but with higher detection limits.

As it was shown in the paper, there is no need to create separate analytical applications for particular tested objects while perform-

ing analysis by means of X-ray fluorescence spectrometry with wavelength dispersion provided that samples are prepared for X-ray measurements by fusing into a borate bead.

2. Materials and methods

In the study presented in the paper the content of: SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , Na_2O , K_2O , SO_3 , TiO_2 and P_2O_5 in samples of building materials, soils, recovered secondary fuels, solid fuels and wastes of specified codes was determined. The procedure of sample preparation for X-ray measurements was identical for all the tested objects. All the measurements were carried out with the use of Rigaku Primus II X-ray Fluorescence Spectrometer (Japan) with wavelength dispersion in vacuum. The spectrometer is equipped with 4 kW X-ray Rh tube and two detectors: gas-filled and scintillation. The set of 6 diffraction crystals (RX25, RX35, RX60, PET, Ge and LiF2000) and 4 collimators (S1, S2, S3 and S4) cover the range of elements which can be analyzed from Boron to Uranium. $K\alpha$ analytical lines were used for all 10 elements. Crystal RX25 was used for Mg and Na, crystal Ge for P and S, crystal PET for Si and Al and crystal LiF200 for Fe, Ti, Ca and K. Both detectors were applied to measure the X-ray fluorescent radiation coming from Na, Mg, Al, Si, P, S, K and Ca. Two elements Fe and Ti were measured with the use of scintillation detector only. X-ray tube current parameters were the same: 50 kV and 60 mA.

A sample of $1.0000 \text{ g} \pm 0.0002 \text{ g}$ was fused with $9.0000 \text{ g} \pm 0.0005 \text{ g}$ of the flux into a borate bead in an electrical fusion machine at the temperature of 1050 $^\circ\text{C}$. The flux was a mixture of lithium borate with a small amount of lithium bromide as a non-wetting agent of the following composition: 66.67% $\text{Li}_2\text{B}_4\text{O}_7$, 32.83% LiBO_2 , 0.5% LiBr , respectively. The flux was of ultra-pure class in the anhydrous state. Experimentally optimized instrumental measurement conditions for the analytical lines of given elements were also identical for all the analyzed samples and all the tested materials and objects. All analyses were performed in the Laboratory of Solid Waste Analyses of the Department of Environmental Monitoring, Central Mining Institute accredited by Polish Centre for Accreditation.

Table 1 presents the determination ranges for all 10 oxides analyzed with the use of the WDXRF technique, which are the widest for wastes and for aggregates and soils. It is obvious that in different tested objects the measured elements may occur in various chemical compounds. Thus, these objects have different chemical composition and different mineralogical structure, but as written in the introduction, it ceases to have any significance after the sample has been fused into a borate bead. A homogeneous solid solution is obtained, in which the intensity of analytical lines of the determined elements emitted from the sample during X-ray measurement depends only on the content of this element in the tested sample.

The matrix effects associated with absorption and/or enhancement of emitted radiation by other elements present in the fused sample also exist, but they are much smaller and can be corrected mathematically at the stage of creating calibration curves by application of α empirical or theoretical correction coefficients. The matrix effects correction is not always necessary when flux to sample weight ratio is high, for example when a sample is diluted with the flux at the weight ratio of 1 : 9.

The software used for data treatment was the original Rigaku Corporation software provided with the spectrometer allowing for the creation of own analytical applications. Chemical elements to be analyzed may be selected and all measuring parameters for each element may be optimized experimentally. The software also allows selecting standards for calibration and a method of matrix effects correction. Each application is given a name and the appli-

Table 1

The determination ranges for 10 oxides analyzed with the use of the WDXRF technique.

Concentration [%]	Construction materials/binders	Construction materials/aggregates	Soils	Recovered fuels -alternative fuels	Solid fuel -Hard coal	Wastes of given codes	Solid fuels - biomass biofuel
SiO ₂	3.02–74.24	0.01–97.35	0.01–97.35	1.20–89.16	3.36–69.06	0.01–97.35	5.42–66.04
Al ₂ O ₃	1.01–39.92	0.01–95.50	0.01–95.50	0.12–43.72	2.18–43.23	0.01–95.50	0.36–7.90
Fe ₂ O ₃	1.06–19.79	0.01–95.75	0.01–95.75	0.29–70.72	1.15–50.20	0.01–95.75	0.48–23.00
CaO	9.96–70.72	0.01–99.24	0.01–99.24	0.18–70.81	0.40–34.58	0.01–99.24	2.91–41.94
MgO	0.11–3.95	0.01–82.25	0.01–82.25	0.15–23.51	0.80–17.84	0.01–82.25	0.80–8.91
Na ₂ O	0.21–5.22	0.01–39.28	0.01–39.28	0.01–10.52	0.07–5.75	0.01–39.28	0.16–3.89
K ₂ O	1.01–5.86	0.01–48.93	0.01–48.93	0.05–3.78	0.16–3.88	0.01–48.93	0.64–25.17
SO ₃	1.14–11.46	0.02–51.40	0.02–51.40	0.30–72.02	0.27–33.50	0.02–51.40	0.32–7.17
TiO ₂	0.16–2.55	0.01–39.79	0.01–39.79	0.01–3.25	0.10–3.25	0.01–39.79	0.02–0.90
P ₂ O ₅	0.03–0.48	0.01–44.84	0.01–44.84	0.04–14.66	0.02–8.84	0.01–44.84	0.75–27.96

cation created for the X-ray measurements performed within the study presented in the paper was called DEMO (short name for demonstration).

3. Results and discussion

Analytical application DEMO, including measurements of all 10 oxides, mentioned in Table 1, was developed to show that in Wavelength Dispersive X-ray Fluorescence Spectrometry it is not necessary to create separate analytical applications for particular materials and objects when the analyzed sample is a samples fused into a borate bead. High quality standards, certified reference materials, samples obtained from interlaboratory proficiency tests and synthetic standards prepared by mixing oxides and/or salts of purity over 99.99% in various proportions were used to prepare the calibration curves. The example of obtained calibration curves for SiO₂ and Al₂O₃ are presented in Fig. 1 (the remaining are presented in Supplement 1). The calibration curve for each element was determined based on 79 measuring points: wastes – 39 standards, building materials and binders – 16 standards, coal ashes – 14 standards, and 10 synthetic standards. The α empirical correction coefficients were applied to correct matrix effects. White circles in Fig. 1 show the position of a calibration standard without matrix effects correction. Blue squares show the position of this standard after matrix effects correction. One can easily observe that even in 10 times diluted samples by flux matrix effects still exist, but they are not as big as in pressed samples and can be significantly corrected by theoretical or empirical α correction factors. The measurements refer to the incinerated state and they should not be referred to the initial state, especially in a situation when a sample of a given object has high loss on ignition.

The calibration curves presented in Fig. 1 (in Supplement 1) confirm that when the oxide composition of any solid sample is measured with the use of a WDXRF method, after prior incineration at the temperature of 815 °C and preparation for X-ray measurements by fusing into a borate bead, neither origin of a sample nor its kind and type affect the obtained results. Additionally, the received calibration curves ensure high accuracy of results obtained for 10 oxides. One WDXRF method based on a big number of high quality standards representing all tested objects is considered to be giving better results than the use of several methods calibrated with a few standards only.

Proving the thesis that the origin and type of the sample does not affect the determination results obtained in the WDXRF technique when borate beads are analyzed significantly facilitates the performance of validation tests. It is enough to do it for the method with the widest content range. Confirmation of a laboratory's competence in obtaining accurate results in the lower and the upper content range of this method is equivalent to confirmation of its competence in obtaining accurate results in the lower and the

upper range of other accredited methods with a narrower content range of determined oxides. Another advantage of the proposed approach is the fact that any material can be a sample for the measurements. If there are no materials of extreme content of the measured oxides, then synthetic samples prepared from ultra-pure (over 99.99%) chemical reagents, can be used as samples. Preparing such synthetic standards is relatively easy and burdened only with the weighing error. To make this error even smaller it is recommended to prepare a bigger portion of each synthetic standard (several grams). The calculated contents of determined oxides in given synthetic standards can be compared with the determination results obtained by the WDXRF analysis and, based on it, the accuracy of the method in its upper and lower range can be assessed.

Thirteen synthetic standards which were mixtures of the following chemical compounds of purity over 99.99%: SiO₂, Al₂O₃, Fe₂O₃, CaO, CaSO₄, MgO, MgSO₄, Na₂SO₄, K₂SO₄, K₂HPO₄ and TiO₂ in various proportions were prepared to confirm the presented approach. The standards were marked from ZKS1 to ZKS13. The chemical composition of the series of ZKS standards was calculated from the weights of chemical reagents used for their preparation and it is presented in Table 2.

Three beads for each standard were prepared and next each bead was measured three times with the use of analytical application DEMO. The obtained measurement results were then subjected to the statistical analysis. Average values, the values of standard deviations and the relative standard deviation (RSD%) were calculated and they are presented in Table 3.

The lowest concentration of all 10 tested oxides in the standards used for calibration was 0.01%. The short distance between an X-ray tube window and a measured sample and a powerful 4 kW X-ray tube gave clear analytical signal for all 10 oxides (intensities of analytical lines were significantly higher than the intensities of the background measured in the neighborhood of the analytical lines), even when the content of an analyte in a sample was 0.01% or lower. In this case the lowest concentration on the calibration curve can be accepted as the limit of quantification (LOQ). Since this approach may be considered to be too simplistic, it was decided to use the series of synthetic standards marked from ZKS1 to ZKS13, which were prepared to confirm and verify the range of the developed WDXRF method. The average values of the standard deviation in the lower range of the calibration curves (Table 3) were the basis for calculating the real limits of quantification. The values of a standard deviation determining the LOQs for the developed method were: 0.017% for SiO₂, 0.020% for Al₂O₃, 0.023% for Fe₂O₃, 0.009% for CaO, 0.033% for MgO, 0.034% for Na₂O, 0.005% for K₂O, 0.023% for SO₃, 0.012% for TiO₂ and 0.008% for P₂O₅ respectively.

While creating the series of standards ZKS the amounts of introduced particular chemical reagents were selected in such a way that for each of the determined oxides at least three measuring points in the lower range of the calibration curve and one measur-

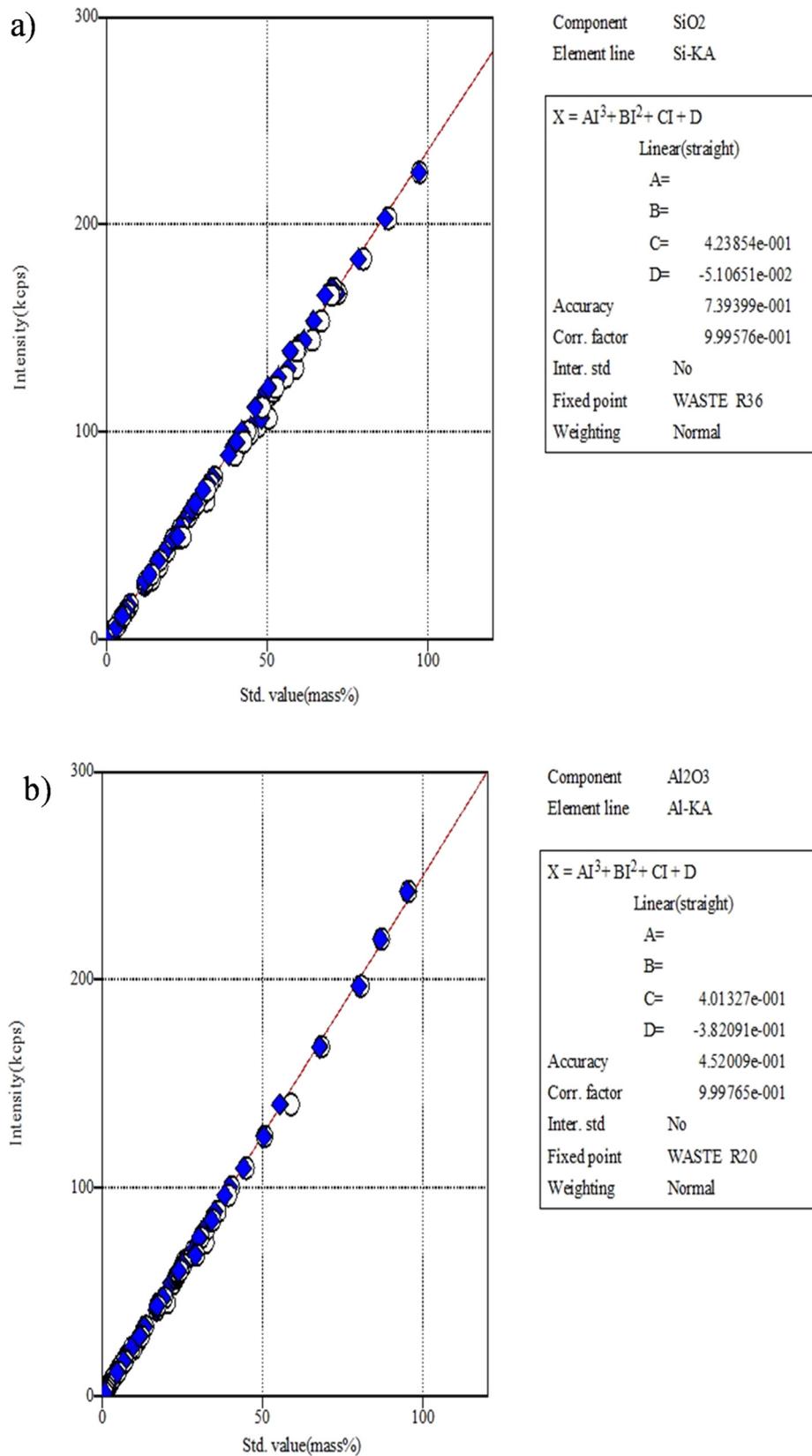


Fig. 1. Example of calibration curves for a) SiO₂, b) Al₂O₃.

ing point in the upper range were obtained. The selected measuring points, together with the relevant statistical calculations, are presented in Table 3.

The average values of standard deviation in the lower range of the calibration curves were between 0.0008% for K₂O and 0.0056% for Na₂O, and 0.0054% for MgO. The average values of

Table 2

The chemical composition of synthetic standards prepared to verify and confirm the range of the developed WDXRF method.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	TiO ₂	P ₂ O ₅
ZKS1	0.67	0.4	0.48	47.1	1.09	4.09	2.58	3.89	0.06	39.64
ZKS2	0.5	0.36	0.09	0.1	2.18	–	50.73	46.04	–	–
ZKS3	0.54	0.42	–	98.14	0.76	–	0.04	0.061	–	0.039
ZKS4	3.8	0.13	95.92	0.047	0.038	–	0.048	–	–	0.017
ZKS5	2.21	97.24	0.14	0.069	–	0.042	0.068	0.058	0.16	0.013
ZKS6	97.66	–	2.19	0.039	0.031	–	0.039	0.041	–	–
ZKS7	0.065	8.25	0.066	0.06	0.069	39.22	0.012	52.2	0.041	0.017
ZKS8	0.31	17.59	0.2	0.14	80.47	–	0.5	0.68	–	0.11
ZKS9	0.13	0.24	–	58.61	0.055	0.048	0.056	0.14	40.7	0.021
ZKS10	3.47	0.6	0.3	84.97	0.91	0.039	0.045	9.55	0.016	0.1
ZKS11	99.7	0.027	–	0.058	0.04	0.08	–	0.081	–	0.014
ZKS12	0.018	99.77	–	0.042	–	0.11	–	0.048	–	0.012
ZKS13	0.036	0.14	7.19	9.3	27.7	–	0.12	55.16	0.3	0.054

Table 3

Statistical data for the measuring points used for verification and confirmation of the range of the developed WDXRF method.

		Lower Range				Average value	Upper Range		Average value
		1	2	3	4		1	2	
SiO ₂	Standard	ZKS12	ZKS13	ZKS7	ZKS9		ZKS6	ZKS11	
	Standard deviation	0.0016	0.0029	0.0033	0.0029	0.0027	0.036	0.05	0.0043
	RSD (%)	11.49	6.74	6.07	2.66	6.74	0.04	0.05	0.05
Al ₂ O ₃	Standard	ZKS11	ZKS13	ZKS4			ZKS5	ZKS12	
	Standard deviation	0.0016	0.0028	0.0056		0.0033	0.15	0.127	0.138
	RSD (%)	7.44	2.23	3.77		4.48	0.15	0.13	0.14
Fe ₂ O ₃	Standard	ZKS7	ZKS2	ZKS5			ZKS4		
	Standard deviation	0.0039	0.0043	0.0031		0.0038	0.67		0.67
	RSD (%)	7.4	5.45	2.58		5.14	0.68		0.68
CaO	Standard	ZKS4	ZKS11	ZKS7	ZKS2		ZKS10	ZKS3	
	Standard deviation	0.0012	0.0017	0.0011	0.0019	0.0015	0.26	0.397	0.328
	RSD (%)	3.04	3.33	1.46	2.02	2.46	0.29	0.41	0.35
MgO	Standard	ZKS6	ZKS11	ZKS9	ZKS7		ZKS8		
	Standard deviation	0.0047	0.0026	0.0063	0.0081	0.0054	0.397		0.397
	RSD (%)	20.03	8.13	13.26	14.24	13.92	0.5		0.5
Na ₂ O	Standard	ZKS10	ZKS5	ZKS9	ZKS11		ZKS7		
	Standard deviation	0.0058	0.0075	0.0048	0.0041	0.0056	0.213		0.213
	RSD (%)	17.86	14.13	8.4	4.46	11.21	0.54		0.54
K ₂ O	Standard	ZKS6	ZKS9	ZKS3	ZKS5		ZKS2		
	Standard deviation	0.001	0.0005	0.0007	0.0009	0.0008	0.291		0.291
	RSD (%)	3.05	1.1	1.61	1.49	1.81	0.58		0.58
SO ₃	Standard	ZKS6	ZKS5	ZKS3	ZKS11		ZKS2	ZKS7	
	Standard deviation	0.0049	0.0031	0.0027	0.0047	0.0038	0.45	0.728	0.589
	RSD (%)	10.38	6.09	4.78	5.37	6.66	0.98	1.4	1.19
TiO ₂	Standard	ZKS10	ZKS7	ZKS1	ZKS5		ZKS9		
	Standard deviation	0.0014	0.0024	0.0012	0.0031	0.002	0.079		0.079
	RSD (%)	12.79	4.62	1.84	1.9	5.29	0.2		0.2
P ₂ O ₅	Standard	ZKS9	ZKS3	ZKS13	ZKS10		ZKS10		
	Standard deviation	0.0011	0.0004	0.0016	0.0015	0.0012	0.962		0.962
	RSD (%)	4.5	1.27	2.57	1.33	2.42	2.39		2.39

the relative standard deviation ranged from 1.81% for K₂O to 13.92% for MgO, and 11.21% for Na₂O. The highest values, obtained for Na₂O and MgO, result from the fact that sodium and magnesium are the lightest of the measured elements. The wavelength of their analytical lines is 11.91 Å for K α Na and 9.89 Å for K α Mg, respectively. The lines are in the range of so-called soft X-rays, hence lower accuracy of measurements of these elements with the WDXRF technique in comparison with heavier elements which analytical lines K α have shorter wavelength and higher energy. Considering the fact that the calculated values of standard deviation and relative standard deviation were obtained based on nine measurements (triple measurements of three borate beads prepared for every standard), and the fact that the range of content of the determined oxides was between 0.01% and 0.1%, the X-ray measurements performed with the use of WDXRF spectrometer are very precise, even at such a low range of concentrations, for all 10 analyzed oxides. Moreover, the differences between the results obtained from the single measurement of three borate

beads prepared for each of the standards used for the tests are not significantly bigger than the differences obtained from the triple measurement of the same bead.

In the upper measuring range, the average values of standard deviation are between 0.079% for titanium dioxide, at the content of 40.70% in the standard, and 0.962% for phosphorus pentoxide, at the content of 39.64% in the standard. The determined content of titanium dioxide in all three borate beads was almost identical. The average of the three measurements was respectively: 40.52% (bead 1), 40.35% (bead 2) and 40.38% (bead 3). Although these differences were small, they were much bigger than the differences between the results obtained for three measurements of the same borate bead, which were 0.061%, 0.020% and 0.008%, respectively for bead no. 1, 2 and 3. For phosphorus, the differences between the results for the same bead were also insignificantly small and were respectively 0.037%, 0.057% and 0.021% for bead no. 1, 2 and 3, comparable with the values obtained for titanium. Unfortunately, there were much bigger differences between the values of

average content of phosphorus pentoxide obtained during measurements of the three borate beads which were prepared at the same time. The values were respectively: 41.52% for bead 1, 39.63% for bead 2 and 39.58% for bead 3, which, as a result, gives 10 times higher value of the standard deviation.

In the X-ray analysis of the fused samples, the most important problem is the volatility of the measured components. The chemical agent – potassium phosphate dibasic used for the preparation of the standard for phosphorus, like all the oxides and salts used for preparing synthetic standards, was not calcined at the temperature of 815 °C but only dried at the temperature of 105 °C prior to preparing the test portions. Titanium dioxide, used for the preparation of the synthetic standards to confirm the measurement range of titanium, is not a volatile compound and that is why three repeatable beads were obtained. In the process of fusing of potassium phosphate dibasic K_2HPO_4 , despite significant surplus of the flux, small losses of phosphorus resulting from either its volatility or its decomposition at the fusion temperature of 1050 °C must have occurred. The problem of partial or complete volatilizing of components from tested environmental samples and wastes during fusion concerns not only phosphorus but also sodium, potassium, sulphur and a several volatile trace metals. Hence it is recommended that the initial sample for the WDXRF analyses prepared for X-ray measurements by borate fusion method ought to be first calcined or incinerated at the temperature of 815 °C or higher following the standards PN-EN 14775:2010 or PN-EN

18122:2016. All the volatile components are released from a sample at this temperature and there are no further significant losses in the temperature range between 815 °C and the fusion temperature 1050 °C.

The calculated average values of the relative standard deviation had values from 0.05% for silicon dioxide to 2.39% for phosphorus pentoxide, so they were much smaller than in the lower measuring range. It means that the determination of the main chemical composition with a sample preparation for the X-ray measurements by borate fusion method is also very accurate and repeatable in the upper measuring range of the elaborated method WDXRF. Next, in order to estimate the accuracy of the elaborated WDXRF method called DEMO application in its lower and upper range, calculated contents of all 10 determined oxides in these 13 synthetic standards were compared with the results of their X-ray measurements. The obtained values are presented in Table 4, along with the values of obtained absolute and relative errors taking as the reference values the calculated contents.

The calculated average values of absolute errors of determination of all 10 oxides in the lower range of the method did not differ much and ranged between 0.005% for titanium dioxide and 0.015% for aluminum oxide. The calculated relative errors of measurements were between 11.0% for sulfur trioxide (VI) and 19.5% for sodium oxide. Taking into consideration that the obtained errors concern the level of the oxide content in the tested standards between 0.02% and 0.1% for CaO, MgO, Na_2O , K_2O , SO_3 , TiO_2 and

Table 4
Estimation of accuracy of WDXRF method in its lower and upper range.

[%]		Lower range				Average value	Upper range		Average value
		1	2	3	4		1	2	
SiO ₂	Calculated content	0.018	0.036	0.065	0.13		97.66	99.7	
	Measured content	0.014	0.043	0.054	0.11		98.3	100.94	
	Absolute error	0.004	0.007	0.011	0.02	0.011	0.64	1.24	0.94
	Relative error	22.2	19.4	16.9	15.4	18.5	0.66	1.24	0.95
Al ₂ O ₂	Calculated content	0.027	0.14	0.13			97.24	99.77	
	Measured content	0.021	0.12	0.15			97.14	99.74	
	Absolute error	0.006	0.02	0.02		0.015	0.1	0.03	0.07
	Relative error	22.2	14.3	15.4		17.3	0.1	0.03	0.07
Fe ₂ O ₃	Calculated content	0.066	0.09	0.14			95.92		
	Measured content	0.053	0.08	0.12			98.57		
	Absolute error	0.013	0.01	0.02		0.014	2.65		2.65
	Relative error	19.7	11.1	14.3		15.00	2.76		2.76
CaO	Calculated content	0.047	0.058	0.06	0.1		84.97	98.14	
	Measured content	0.038	0.051	0.073	0.096		88.37	97.57	
	Absolute error	0.009	0.007	0.013	0.004	0.008	3.4	0.57	1.98
	Relative error	19.1	12.1	21.7	4.00	14.2	4.00	0.58	2.29
MgO	Calculated content	0.031	0.04	0.055	0.069	–	80.47		
	Measured content	0.024	0.032	0.047	0.057	–	79.99		
	Absolute error	0.007	0.008	0.008	0.012	0.009	0.48		0.49
	Relative error	22.6	20.00	14.5	17.4	18.8	0.6		0.6
Na ₂ O	Calculated content	0.039	0.042	0.048	0.08	–	39.22		
	Measured content	0.032	0.053	0.057	0.092	–	39.07		
	Absolute error	0.007	0.011	0.009	0.012	0.01	0.15		0.15
	Relative error	17.9	26.2	18.8	15.00	19.5	0.38		0.38
K ₂ O	Calculated content	0.039	0.056	0.04	0.068	–	50.73		
	Measured content	0.034	0.049	0.046	0.061	–	50.53		
	Absolute error	0.005	0.007	0.006	0.007	0.006	0.2		0.2
	Relative error	12.8	12.5	15.00	10.3	12.7	0.39		0.39
SO ₃	Calculated content	0.041	0.058	0.061	0.081	–	46.04	52.2	
	Measured content	0.047	0.05	0.056	0.087	–	45.8	52.06	
	Absolute error	0.006	0.008	0.005	0.006	0.006	0.24	0.14	0.19
	Relative error	14.6	13.8	8.2	7.4	11.00	0.52	0.27	0.4
TiO ₂	Calculated content	0.016	0.041	0.06	0.16	–	40.7		
	Measured content	0.011	0.052	0.064	0.16	–	40.42		
	Absolute error	0.005	0.011	0.004	0.00	0.005	0.28		0.28
	Relative error	31.2	26.8	6.7	0.00	16.2	0.69		0.69
P ₂ O ₅	Calculated content	0.021	0.039	0.054	0.1	–	39.64		
	Measured content	0.025	0.033	0.063	0.11	–	40.24		
	Absolute error	0.004	0.006	0.009	0.01	0.007	0.6		0.6
	Relative error	19.00	15.4	16.7	10.00	15.3	1.51		1.51

P₂O₅, and up to 0.13% for SiO₂, Al₂O₃ and 0.14% for Fe₂O₃, they are really small and difficult to reach with other instrumental or classical analytical techniques. In the upper range of the method the lowest value of relative error was obtained for aluminum oxide –

0.07% and the highest for iron(III) oxide– 2.65%, but at the Fe₂O₃ content in the sample of 95.92%.

In the validation process of any analytical method, including methods based on calibration curves, the most important is to

Table 5

Results of WDXRF analyses for two types of cement.

NIST SRM 1882a CEMENT	Declared value [%]	Measured value [%]			Relative error [%]
		Bead 1	Bead 2	Average	
SiO ₂	0.24	0.22	0.23	0.225	6.20
Al ₂ O ₂	39.14	38.81	39.10	38.96	0.46
Fe ₂ O ₃	14.67	14.45	14.51	14.48	1.30
CaO	39.29	39.60	39.32	39.46	0.43
MgO	0.51	0.53	0.53	0.53	3.90
Na ₂ O	0.021	0.034	0.03	0.032	52.4
K ₂ O	0.051	0.044	0.048	0.046	9.80
SO ₃	4.01	3.87	3.91	3.89	3.00
TiO ₂	1.786	1.74	1.76	1.75	2.00
P ₂ O ₅	0.07	0.074	0.072	0.073	4.30
NIST SRM 1885a CEMENT	Declared value [%]	Measured value [%]			Relative error [%]
		Bead 1	Bead 2	Average	
SiO ₂	20.91	20.74	20.80	20.77	0.67
Al ₂ O ₂	4.026	4.06	4.12	4.09	1.60
Fe ₂ O ₃	1.929	1.95	1.97	1.96	1.60
CaO	62.39	61.98	62.20	62.09	0.48
MgO	4.033	3.96	3.92	3.94	2.30
Na ₂ O	1.068	1.02	1.04	1.03	3.60
K ₂ O	0.206	0.20	0.19	0.195	5.30
SO ₃	2.83	2.74	2.78	2.76	2.50
TiO ₂	0.195	0.18	0.19	0.185	5.10
P ₂ O ₅	0.122	0.13	0.13	0.13	6.60

Table 6

Results of WDXRF analyses for three types of coal ash.

NCS FC 82,012 COAL ASH	Declared value [%]	Measured value [%]			Relative error [%]
		Bead 1	Bead 2	Average	
SiO ₂	46.77	47.16	47.02	47.09	0.68
Al ₂ O ₂	14.960	14.72	14.78	14.75	1.4
Fe ₂ O ₃	5.510	5.36	5.40	5.38	2.4
CaO	21.37	21.10	21.16	21.13	1.1
MgO	1.740	1.64	1.66	1.65	5.2
Na ₂ O	1.360	1.44	1.40	1.42	4.4
K ₂ O	1.410	1.36	1.38	1.37	2.8
SO ₃	3.94	3.82	3.84	3.83	2.8
TiO ₂	0.630	0.60	0.60	0.60	4.8
P ₂ O ₅	0.500	0.49	0.47	0.48	4.0
NCS FC 82,015 COAL ASH	Declared value [%]	Measured value [%]			Relative error [%]
		Bead 1	Bead 2	Average	
SiO ₂	62.88	62.32	62.46	62.39	0.78
Al ₂ O ₂	17.880	17.61	17.69	17.65	1.3
Fe ₂ O ₃	6.040	5.80	5.78	5.79	4.1
CaO	6.11	6.00	5.94	5.97	2.3
MgO	0.900	0.96	0.94	0.95	5.6
Na ₂ O	1.180	1.10	1.14	1.12	5.1
K ₂ O	0.870	0.84	0.82	0.83	4.6
SO ₃	1.20	1.26	1.28	1.27	5.8
TiO ₂	0.790	0.83	0.81	0.82	3.8
P ₂ O ₅	0.850	0.86	0.88	0.87	2.4
AS CRM 010–2 COAL ASH	Declared value [%]	Measured value [%]			Relative error [%]
		Bead 1	Bead 2	Average	
SiO ₂	52.20	53.02	52.86	52.94	1.4
Al ₂ O ₂	27.10	26.88	26.84	26.86	0.89
Fe ₂ O ₃	10.80	10.52	10.58	10.55	2.3
CaO	3.47	3.60	3.54	3.57	2.9
MgO	1.40	1.34	1.36	1.35	3.6
Na ₂ O	0.47	0.44	0.42	0.43	8.5
K ₂ O	0.92	0.94	0.96	0.95	3.3
SO ₃	0.21	0.18	0.18	0.18	14.3
TiO ₂	1.34	1.38	1.36	1.37	2.2
P ₂ O ₅	1.13	1.10	1.12	1.11	1.8

check and confirm its lower and upper range of applicability, which has already been achieved. However, it was not enough to prove the thesis that one calibration curve covering the full range of the variability of occurrence of a given measured element, may be applied for all the tested materials including natural environmental samples (e.g. soils, grounds, raw materials, ores, water sediments, rocks), as well as municipal and industrial waste and by-products (e.g. ashes, slugs). Further research was done with the use of selected for this purpose 10 commercially available certified reference materials (CRM), including 2 types of cement, 3 types of coal ash, 1 slag, 1 fire clay, 1 sediment and 2 types of soil. These standards represented different tested materials and were characterized by significant variability of the content of determined oxides. The selected CRMs were dried at 105 °C and prepared for X-ray measurements by fusing them into borate beads. Only soil CRMs, prior to preparing a bead, were calcined at the temperature of 815 °C to remove the organic substance. The determined losses on ignition of 4.4% and 14.3%, respectively were taken into consideration while recalculating the declared content into the calcined state. It was not necessary to calcine the other CRMs prior to preparing a borate bead. The values of losses on ignition declared for the certificates were 0%. The main chemical composition of CRM samples (10 main oxides) prepared for the tests by borate fusion method was determined according to DEMO application. The certified main chemical composition of the selected CRMs used for the final verification of the elaborated WDXRF method, given in the calcined state, is presented in Tables 5–8.

Two borate beads for each tested CRM sample were prepared and each bead was measured three times. The obtained results,

as the average of 3 measurements, were compared with the declared contents in the certificate and the absolute and relative errors of the determinations were calculated. The calculated values for all 10 determined oxides and for all 10 tested CRMs are presented in Table 5–8.

The determination results of the chemical composition of CRMs performed with the WDXRF method according to DEMO application (see Table 5–8), indicate that all 10 oxides were measured with comparable accuracy. They do not show tendency that any of the measured oxides was determined with a greater error in one CRM in comparison with the errors obtained for the same oxide for other objects. Out of 98 performed determinations (one CRM did not contain declared content of P₂O₅, and the other of SO₃) 68 ones had relative errors below 5%, and for the next 20 ones the values of the relative errors were between 5% and 10%. The highest values of the relative error were observed in the cases when the contents of the determined oxides in the measured CRMs were at a very low level. They were 52.4% for Na₂O with its content 0.021% and 41.9% and 29.7% for SO₃ with its content 0.031% and 0.037%, respectively.

In all techniques of instrumental chemical analyses based on calibration, including the WDXRF technique, the determination errors in the lower range of the calibration curve, are always very high [20–22]. Then, in the lowest range of applicability the accuracy of such a method should be characterized by the absolute error. The absolute errors in these three discussed cases had the values respectively: 0.011% for Na₂O and 0.013% and 0.011% for SO₃, which confirms the thesis that the WDXRF technique with borate fusion as a method of sample preparation for X-ray mea-

Table 7
Results of WDXRF analyses for one slag, fire clay and sediment, respectively.

FX RAW 03a SLAG	Declared value [%]	Measured value [%]			Relative error [%]
		Bead 1	Bead 2	Average	
SiO ₂	39.24	39.62	39.54	39.58	0.87
Al ₂ O ₃	6.24	6.50	6.44	6.47	3.69
Fe ₂ O ₃	0.79	0.82	0.84	0.83	5.1
CaO	31.39	30.92	31.06	30.99	1.3
MgO	19.01	18.78	18.72	18.75	1.4
Na ₂ O	0.24	0.22	0.20	0.21	12.5
K ₂ O	0.38	0.39	0.41	0.40	5.3
SO ₃	1.44	1.40	1.38	1.39	3.5
TiO ₂	0.392	0.38	0.36	0.37	5.6
P ₂ O ₅	–	–	–	–	–
JRRM 124 FIRE CLAY	Declared value [%]	Measured value [%]			Relative error [%]
		Bead 1	Bead 2	Average	
SiO ₂	73.90	72.64	72.86	72.75	1.6
Al ₂ O ₃	16.50	16.82	16.68	16.75	1.5
Fe ₂ O ₃	2.60	2.84	2.86	2.85	9.6
CaO	1.09	1.12	1.14	1.13	3.7
MgO	0.10	0.12	0.12	0.12	20.0
Na ₂ O	0.31	0.33	0.35	0.34	9.7
K ₂ O	1.79	1.86	1.84	1.85	3.4
SO ₃	–	–	–	–	–
TiO ₂	2.74	2.80	2.78	2.79	1.8
P ₂ O ₅	0.19	0.22	0.22	0.22	15.8
NIST SRM 1646a SEDIMENT	Declared value [%]	Measured value [%]			Relative error [%]
		Bead 1	Bead 2	Average	
SiO ₂	85.71	86.40	86.58	86.49	0.91
Al ₂ O ₃	4.339	4.12	4.18	4.15	4.4
Fe ₂ O ₃	2.87	2.78	2.74	2.76	3.8
CaO	0.727	0.76	0.78	0.77	5.9
MgO	0.647	0.60	0.62	0.61	5.7
Na ₂ O	0.999	0.94	0.96	0.95	4.9
K ₂ O	1.041	0.99	0.99	0.99	4.9
SO ₃	0.879	0.84	0.84	0.84	4.4
TiO ₂	0.773	0.74	0.76	0.75	3.0
P ₂ O ₅	0.063	0.082	0.078	0.080	27.0

Table 8
Results of WDXRF analyses for two types of soil.

NCS DC 73,320 SOIL	Declared value [%]	Measured value [%]			Relative error [%]
		Bead 1	Bead 2	Average	
SiO ₂	76.72	76.29	76.43	76.36	0.47
Al ₂ O ₃	10.78	10.98	11.08	11.03	2.3
Fe ₂ O ₃	3.68	3.90	3.84	3.87	5.2
CaO	2.47	2.38	2.34	2.36	4.5
MgO	1.09	1.13	1.11	1.12	2.8
Na ₂ O	1.69	1.62	1.64	1.63	3.6
K ₂ O	2.66	2.60	2.58	2.59	2.6
SO ₃	0.031	0.046	0.042	0.044	41.9
TiO ₂	0.47	0.49	0.47	0.48	2.1
P ₂ O ₅	0.107	0.099	0.097	0.098	8.4
NCS DC 73,325 SOIL	Declared value [%]	Measured value [%]			Relative error [%]
		Bead 1	Bead 2	Average	
SiO ₂	38.15	38.62	38.48	38.55	1.05
Al ₂ O ₃	34.14	33.96	33.84	33.90	0.70
Fe ₂ O ₃	20.72	20.56	20.64	20.60	0.58
CaO	0.19	0.19	0.18	0.185	2.6
MgO	0.30	0.31	0.33	0.32	6.7
Na ₂ O	0.093	0.079	0.081	0.080	14.0
K ₂ O	0.233	0.27	0.25	0.26	11.6
SO ₃	0.037	0.050	0.046	0.048	29.7
TiO ₂	3.93	3.88	3.84	3.86	1.8
P ₂ O ₅	0.31	0.32	0.32	0.32	3.2

measurements can be successfully applied to determine main oxides with the content below 0.1% in all kind of samples. Based on the results of the analyses presented in Tables 5-8, the conclusion may be drawn that the values of relative errors decreased when the content of the measured component in a given sample increased and they reached values below 2% for all 10 determined oxides in all analysed CRMs when their content was over 10%. In most cases in the upper ranges of the calibration curves the relative errors were below 1%. Thus, it has been presented that a type and origin of a tested sample does not have any effect on the obtained determination results under certain conditions. Firstly a tested sample has to be calcined in the temperature 815 °C or higher to remove all organic matter which presence could damage a crucible during fusion. Secondly a sample has to be prepared for X-ray measurements by borate fusion method and finally calibration should be based on a big number of high quality standards representing all tested materials.

4. Conclusions

- (1). It was proved that determination of the main chemical composition with the Wavelength Dispersive X-ray Fluorescence Spectrometry does not require the use of separate analytical applications to analyze materials of different type and origin provided that tested sample before analysis is calcined at the temperature 815 °C or higher and prepared for X-ray measurements by borate fusion method.
- (2). The calibration curves for all 10 determined oxides: SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, Na₂O, K₂O, SO₃, TiO₂ and P₂O₅ were based on 79 measuring points: wastes – 39 standards, building materials and binders – 16 standards, coal ashes – 14 standards, and 10 synthetic standards and had high correlation coefficient and accuracy when the α -empirical correction coefficients were applied to correct matrix effects.
- (3). The range of the method was confirmed based on the measurements of 13 synthetic standards. The average values of standard deviations in the lower range of the calibration curves were between 0.0008% for K₂O and 0.0056% for Na₂O and 0.0054% for MgO. The average values of the relative standard deviation were between 1.81% for K₂O and

13.92% for MgO and 11.21% for Na₂O. In the upper range of the calibration curves, the average values of standard deviations were between 0.079% for TiO₂ and 0.962% for P₂O₅. The relative standard deviation values were between 0.05% for SiO₂ and 2.39% for P₂O₅.

- (4). The accuracy of the developed WDXRF method was assessed based on the measurements of 10 certified reference materials (CRM) representing all the tested objects (2 types of cement, 3 types of coal ash, slag, fire clay, sediment and 2 types of soil).
- (5). The tests performed for the certified reference materials confirmed high accuracy of the WDXRF method in both the upper and the lower range of its applicability. They also proved that, in case of fused samples which were first calcined at the temperature of 815 °C or higher, one calibration curve based on measurements of a greater number of high quality standards and with matrix effects corrected with α empirical correction coefficients, may be applied to determine a given element in all types of tested materials and objects.

CRedit authorship contribution statement

Adam Smoliński: Methodology, Formal analysis, Investigation.
Marek Stempin: Conceptualization, Methodology, Formal analysis, Investigation.
Natalia Howaniec: Conceptualization, Formal analysis, Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.measurement.2020.108030>.

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