

Article

Application and Validation of Analytical Software (SQX) for Semi-Quantitative Determination of the Main Chemical Composition of Solid, Bulk and Powder Fuel Samples by Wavelength Dispersive X-ray Fluorescence Technique

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Abstract: Determination of the content of chemical elements occurring in waste in large, small and trace amounts was performed using two instrumental analysis techniques: ICP-OES—Inductively Coupled Plasma Optical Emission Spectrometry and WDXRF—Wavelength Dispersive X-ray Fluorescence Spectrometry. Since such analyses are expensive and time-consuming, the objective of the work presented in this paper was the development of a quick and inexpensive method for preliminary, scanning-based identification of the chemical composition of tested samples (solid, bulk or powder) using standardless, semi-quantitative analysis. An optimized method of preparing samples for X-ray measurements by pressing into a durable tablet, universal for all materials tested, was developed. Moreover, limits of quantification were determined, and the uncertainty of the results obtained was estimated by comparing them with the results acquired with the use of the accredited calibration method, employing standards and certified reference materials.

Keywords: XRF; WDXRF; ICP-OES; X-ray fluorescence spectrometry



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1. Introduction

While performing monitoring of solid waste and other environmental samples [1–3], one often encounters the problem of quick, approximate information about the chemical composition of an analysed sample. In many cases, such knowledge is sufficient to make conclusive decisions regarding the further fate of the tested material, regardless of its type, covering among others the industrial or municipal waste, coal-derived fly ash from energy systems, and soil or ground samples analysed [4,5] for the purposes of environmental monitoring and protection [6–8]. It is often required to determine only the selected chemical elements in a sample and not the full chemical composition with high accuracy [9,10]. Furthermore, performing the full analytical process according to an accredited method is expensive, and it also happens that the object of analysis may be a chemical element rarely found in waste and therefore not covered by the scope of accreditation [11,12]. Determination of uncommon elements in untypical solid samples is always a difficult analytical challenge reluctantly undertaken by most chemical laboratories, including the accredited ones.

Practically all accredited determinations of basic chemical composition performed with the use of the WDXRF technique concern samples initially burnt in a muffle furnace at the temperature of 815 °C and then prepared for X-ray measurements by fusing them into borate beads [13]. Sample fusing has many advantages as well as some disadvantages. Fusing is necessary for samples containing organic matter. Removal of the organic matter

prevents destruction of the platinum crucible during the fusion process. The undoubted advantage of the analysis of fused samples is that in a bead, which is a homogeneous solid solution, the matrix effects associated with the variation in mineralogical forms in which an element may occur in the samples disappear. Diluting the sample with flux at a weight ratio of 1:9 ensures that the sample is completely dissolved and minimizes the matrix effects of enhancing or weakening the intensity of the X-ray fluorescent radiation emitted from the sample by a given element by other elements present in the measured sample. As a result, the accuracy of the results obtained in the WDXRF technique with sample preparation for X-ray measurements by a fusion method is much higher than those in the analysis of pressed samples [14,15]. Another advantage is the ease of calibration, for which one may use any standards and certified reference materials (CRM) as well as make one's own standards by mixing in appropriate proportions and then fusing various high-purity chemical reagents [16]. The preparation and analysis of fused samples involves many problems. Firstly, the fusion method is expensive because it requires a fusing machine and a set of platinum crucibles and casting dishes, and it is time-consuming because of the need to incinerate the sample before making the bead. Secondly, the incineration process does not provide a 100% safety guarantee for the platinum crucible, and it changes the chemical composition of the sample analysed, which is no longer the initial sample. At a loss on ignition of 20% or more, the results obtained from the analysis of the initial sample submitted for testing and those obtained from the analysis of the incinerated and then fused sample after, recalculated to the initial state, taking into account the simultaneously determined value of loss on ignition, may differ significantly. Obviously, the magnitude of these differences depends primarily on the chemical composition of the sample. If the loss on ignition includes chemically bound water, carbonates or even organic carbon released during the incineration process, the problem is negligible. If, on the other hand, partial or total emissions of volatile compounds occur in the combustion process when some components are oxidized and transformed into other chemical compounds, the problem becomes much more significant [17,18]. Thus, based on the results reported for the incinerated state, incorrect information on the chemical composition of the sample in the state as provided for testing may be obtained. The general principle is that if the sample submitted for testing is not a sample obtained in a high-temperature industrial process (e.g., binder, cement, refractory material, slag, coal/biomass/alternative fuel fly ash) and there is a risk that it may contain organic matter before preparing the borate bead, it needs to be incinerated with a simultaneous determination of the loss on ignition [19–22]. Another inconvenience arising from the analysis of fused samples is that, due to the high dilution with flux, many heavy metals occurring in the tested sample at trace levels (from a few to several ppm) cannot be determined or are determined with low accuracy due to the low intensities of the analytical lines, which may be considered as a serious drawback in environmental protection applications.

In this paper, the new, quick and inexpensive method for preliminary, scanning-based identification of the chemical composition of tested samples (solid, bulk or powder) using standardless, semi-quantitative analysis was developed. The sample for X-ray measurements has to be prepared by pressing it into a durable tablet with the use of a binding agent. The grinding and pressing method therefore also has to be fast, cheap and, most importantly, effective and applicable to any sample. The pressing efficiency depends on the sample grain size. The smaller the grain size, the more durable the received tablet is. It was therefore crucial to obtain the smallest possible grain size in the developed method, especially since the biggest source of errors in the WDXRF pressed methods are the matrix effects related to the grain size distribution and mineralogical composition of the sample [23,24]. The necessary condition, the fulfilment of which allows for minimizing such errors, is that the standards used for calibration of the WDXRF method and the samples tested with the use of this method are identical objects, since only this ensures consistency of mineralogical composition and grain size and enables the obtaining of comparable fineness of the sample after grinding. Meeting the above requirements, ensuring accurate

results in the WDXRF technique, with the preparation of samples for X-ray measurements using the method of pressing with a binding agent, is possible in industrial laboratories dealing with the analysis of chemical composition of only one or several objects (e.g., in cement plants, glass and ironworks, factories of building and refractory materials) [25]. In this case, all that is needed is to have several standards or certified reference materials (CRMs), develop a grinding and pressing method and perform calibration measurements of the prepared standard tablets on the X-ray fluorescence spectrometer.

2. Materials and Methods

The Rigaku analytical software (SQX) for semi-quantitative standardless analysis was applied to determine the chemical composition of various solid samples, representing different objects, both covered and not covered by the present laboratory accreditation range. Twenty-four certified reference materials (CRMs) representing various test objects, such as waste, coal ash, soil, rock, construction materials including aggregates and binders and biomass, were selected for the study. The results obtained with the use of the software were compared with both the results acquired with the use of the WDXRF-accredited method and the certified contents of the determined oxides stated in the certificates related to the selected CRMs, which were used as reference values.

The key issue in the study presented was to develop an adequate method of samples preparation for X-ray measurements, being a compromise between the simplicity of the procedure and the effectiveness of grinding, ensuring pressing of a sample into a tablet durable enough for multiple X-ray measurements on one hand and obtaining correct results by mitigation of matrix errors with increasing sample fineness on the other hand.

A sample in an analytical state with a fineness below 212 μm prepared for testing according to ISO 13909-4 [26] and dried to constant weight at 105 $^{\circ}\text{C}$ is not suitable for testing with the use of the WDXRF technique, and it needs to be ground to a smaller grain size. The HSM 100A pulverizing mill (HERZOG, Munich, Germany) was used for the final grinding of samples before making tablets for X-ray measurements [27]. Grinding the sample represents several challenges itself. When it is performed on a few gram quantities needed to make a tablet, a part of the ground material sticks to the walls of the mill, and therefore the sample cannot be quantitatively transferred from the mill to the press. Grinding the sample in larger amounts, on the other hand, provides no guarantee that the portion of the sample that has been successfully swept out from the mill represents the same chemical composition as the initial sample, before grinding. Furthermore, since the waste materials are mixtures of different chemical compounds, varying in hardness and viscosity, mainly soft and viscous components will settle on the walls of the mill.

3. Results and Discussions

3.1. Optimization of Sample Preparation for X-ray Measurements

In the search for the optimum tablet preparation method, it was assumed that the sample would be ground together with the binding agent. The usefulness of four commonly applied binding agents, i.e., boric acid, cellulose, wax and starch, was tested. Two specially prepared samples, differing significantly in chemical and mineralogical compositions (coal ash and soli), were selected, homogenized, dried to room temperature, ground to an analytical state and burnt to a constant weight in a muffle furnace at 815 $^{\circ}\text{C}$. The samples were prepared in larger quantities, sufficient to perform all the intended tests, and stored in hermetic plastic containers in a desiccator. It is generally accepted that matrix errors associated with differences in grain size and mineralogical composition become negligibly small for WDXRF measurement when a sample is ground to a particle size below 10 μm . This is technically unfeasible with the use of conventional grinding methods, even for a single material, let alone a sample that is a mixture of several components of varying hardness. A sample suitable for X-ray measurements should have a minimum grain size between 30 μm and 63 μm or smaller, if possible.

Grinding of the selected samples with boric acid, cellulose and starch at different sample-to-binder weight ratios (4:1, 3:2 and 3:3) did not improve the grinding efficiency. Since wax deposited on the walls of the mill, it was not ground with the sample, but instead it was added during the pressing stage. Even then, it was not possible to obtain a homogeneous distribution of wax throughout the sample volume, which resulted in production of a non-durable tablet, crumbling at the edges. As a consequence, wax was rejected as an unsuitable binding agent. The addition of graphite enabled the ability to obtain the intended grain size and improved the grinding efficiency for all binders tested, with the definitely best results observed for cellulose as a binding agent. The mixture of the sample, cellulose and graphite did not stick to the walls of the mill, and the quantitative transferring of the ground mixture to the press was possible. Thus, cellulose was finally chosen as the universal binding agent. Once dried at 105 °C, cellulose and graphite stored in hermetic plastic containers are suitable for a long-term use. After implementing the developed grinding method into a laboratory practice, the vast majority of solid samples pressed and analysed with the use of the WDXRF technique is removed from the mill after grinding without any residue, which also significantly reduces the time required to prepare the sample for X-ray measurements.

3.1.1. Optimization of the Grinding Procedure

The experimentally determined optimum composition of the sample and binder mixture subjected to grinding and subsequent pressing into a tablet durable enough for multiple X-ray measurements is as follows: 4.0 g of sample, 2.0 g of cellulose and 0.6 g of graphite.

At the stage of optimization of the grinding procedure, different rotational speeds of the mill and different grinding times were tested. It was found that the best grinding effects are obtained at a maximum speed of 1400 rpm with a grinding time of 3 min. Longer grinding time did not result in a further reduction of a grain size.

The selected samples of coal ash and soil were mixed with cellulose and graphite in the ratio given above. For each sample, five such mixtures were prepared and then ground in a mill using different grinding times of: 30, 60, 120, 180 and 240 s, respectively. The ground mixtures were next transferred to a hydraulic press (HTP 40, HERZOG) and pressed under 300 kN pressure. The obtained tablets were then subjected to X-ray analysis in accordance with the test procedure accredited according to the standard PN EN 15309 [28] for the determination of the main chemical composition of solid waste using the WDXRF technique. The obtained results of the analysis of all 10 analysed oxides at different milling times are presented in Table 1.

Table 1. Effect of grinding time on X-ray fluorescence analysis results.

Component	Grinding Time, s									
	30	60	120	180	240	30	60	120	180	240
	Concentration in the Coal Ash Sample, wt%					Concentration in the Soil Sample, wt%				
SiO ₂	42.69	45.52	47.99	48.1	47.92	81.17	88.51	91.97	91.82	92.03
Al ₂ O ₃	26.93	24.81	23.93	23.86	24.00	8.98	5.16	3.83	3.90	3.85
Fe ₂ O ₃	6.28	6.93	7.51	7.49	7.54	2.71	1.43	1.01	0.992	1.00
CaO	7.31	6.95	6.74	6.71	6.72	0.569	0.332	0.263	0.261	0.257
MgO	2.49	2.81	3.02	3.04	3.02	0.626	0.365	0.239	0.24	0.242
Na ₂ O	0.913	0.862	0.835	0.834	0.837	0.429	0.287	0.233	0.227	0.228
K ₂ O	6.53	5.4	5.10	5.12	5.07	3.28	1.54	1.28	1.28	1.30
SO ₃	3.02	2.61	2.38	2.35	2.42	0.164	0.101	0.074	0.074	0.072
TiO ₂	1.53	1.36	1.21	1.19	1.20	0.58	0.306	0.214	0.21	0.211
P ₂ O ₅	1.36	1.19	1.02	1.03	1.04	0.198	0.099	0.056	0.058	0.055

The data in Table 1 are an excellent illustration of the influence of a grain size on the X-ray measurement results. As it can be seen from Table 1, the errors of determination in the

WDXRF technique resulting from this alone are significant and affect all components present in the analysed sample. It is worth noting that in the case of the coal ash sample, with increasing grinding time and thus decreasing grain size, the determined oxide contents for SiO_2 , Fe_2O_3 and MgO increased, while the remaining ones, i.e., for Al_2O_3 , CaO , Na_2O , K_2O , SO_3 , TiO_2 and P_2O_5 , decreased. For the soil sample, a respective increase in content was observed only for SiO_2 . Keeping in mind that X-ray analysis is a surface analysis, it can be concluded that after pressing an insufficiently ground sample, the chemical composition of the analysed surface is not the same as inside the obtained tablet. In the process of pressing, the components of lower hardness (grinding faster and therefore present in the smaller grain size) are densely packed on the measured surface of the tablet and give a greater intensity of secondary X-ray fluorescent radiation emitted from the tablet, which has a direct effect on higher values of the results. For hard components, such as silica, the opposite effect is observed: the distribution of larger grains on the measured surface is looser, and therefore the results obtained for hard components, when the sample is insufficiently ground prior to tablet preparation, are always lower than expected. An interesting and important observation arising from the analysis of the data contained in Table 1 is also that for a given mill, at a given composition of the ground material (sample + binding agent), the optimum grinding effects achievable under the given conditions are obtained after some particular period of time, the extension beyond which does not result in further decreasing the sample grain size. In a HERZOG impact mill model HSM 100A at a high speed of 1400 rpm and for the optimized sample composition (4.0 g of the test sample, 2.0 g of cellulose and 0.6 g of graphite), the maximum possible grinding effects are achieved after 2 min. Bearing in mind that the waste materials analysed in the laboratory are of very diversified chemical and mineralogical compositions, in order to maintain a safety margin, the grinding time accepted as the final for use in preparing samples for X-ray measurements both in the semi-quantitative and the calibration-based methods was extended to 3 min.

3.2. Development of a Method for Determining the Main Chemical Composition of Solid Waste with the Use of the WDXRF Technique with Sample Preparation for X-ray Measurements by Pressing with a Binding Agent—Calibration-Based Method

3.2.1. The Problem of Obtaining a Durable Tablet for Multiple X-ray Measurements with the Use of Rigaku ZSX Primus II Spectrometer

After the implementation of the newly purchased sequential wavelength dispersive X-ray fluorescence spectrometer type Primus II (Rigaku, Japan) into laboratory practice, it seemed that the development of a method for determining the main chemical composition of solid waste with the use of the WDXRF technique with the preparation of samples for X-ray measurements by pressing with a binding agent using the new spectrometer would not be problematic, as it would not be a development of a new method but rather an adaptation, with some minor modifications and improvements, of the proven method successfully applied for several dozen years for Philips PW 1404 X-ray fluorescence spectrometer with wavelength dispersion and accredited by the Polish Centre for Accreditation. It turned out, however, that the Rigaku ZSX Primus II spectrometer, apart from many undoubted advantages, seems to have one disadvantage: the pressed sample can be measured practically only once, because every subsequent measurement gives higher results. This phenomenon is particularly pronounced for samples pressed with a binding agent. Following the suggestion of the manufacturer, that cellulose as a binding agent might not be the best choice, although it is the most versatile and best of all binding agents currently used in the WDXRF technique, especially in the analysis of solid wastes due to their great diversity in terms of chemical and mineralogical composition, other binding agents were also tested, including boric acid, starch and wax mixed with different tested wastes in different proportions with and without the addition of graphite, as were different pressing forces: 200 kN, 300 kN and even 400 kN, which also resulted in obtaining the same effect each time, i.e., a systematic increase in the intensity of the analytical lines. The results of these tests are not presented here in detail, as they are not the main subject of this paper, but to illustrate the scale of the problem, the results of the seven-fold measurement of one

tablet of coal ash prepared for X-ray measurement according to the developed procedure used for both the quantitative calibration-based method and the semi-quantitative method, using the SQX analytical software supplied with the software controlling the operation of the spectrometer by the manufacturer (Rigaku), are presented in Table 2. These results were compared with those obtained from a single measurement of seven tablets made from the same coal ash tested and prepared for X-ray measurements in an identical way (Table 3). The results in Table 3 show that both the tablet preparation method and the X-ray measurement itself are very precise, as evidenced by the small values of standard deviations ranging from 0.005% for TiO₂ and 0.006% for Na₂O at content levels of 1.10% and 0.84%, respectively, to 0.06% for Al₂O₃ and 0.13% for SiO₂ at content levels of 23.92% and 50.00%, respectively, and the low coefficient of variation values ranging from 0.24% for MgO (3.02% content) to 0.74% for CaO (5.24% content).

Table 2. Results of 7-fold X-ray measurement of 1 tablet prepared from a test coal ash sample.

Measurement No./Parameter	Component Concentration, wt%									
	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
1	50.244	24.035	7.489	5.222	3.014	0.835	4.306	2.072	1.106	0.922
2	53.743	25.654	7.460	5.309	3.115	0.937	4.437	2.152	1.092	1.001
3	54.727	26.099	7.465	5.372	3.128	0.964	4.482	2.166	1.087	1.017
4	55.437	26.408	7.474	5.396	3.136	0.976	4.512	2.183	1.087	1.027
5	55.920	26.612	7.470	5.428	3.157	0.999	4.534	2.191	1.089	1.040
6	56.342	26.865	7.456	5.423	3.171	1.011	4.555	2.202	1.082	1.050
7	56.696	26.986	7.466	5.443	3.164	1.009	4.575	2.207	1.087	1.058
Average	54.730	26.094	7.469	5.370	3.126	0.962	4.486	2.168	1.090	1.016
Maximum	56.696	26.986	7.489	5.443	3.171	1.011	4.575	2.207	1.106	1.058
Minimum	50.244	24.035	7.456	5.222	3.014	0.835	4.306	2.072	1.082	0.922
Range	6.452	2.951	0.033	0.221	0.157	0.176	0.269	0.135	0.024	0.136
Standard deviation	2.0521	0.9404	0.0100	0.0735	0.0496	0.0572	0.0849	0.0429	0.0071	0.0426
Coefficient of variation (RSD), %	3.75	3.60	0.13	1.37	1.59	5.95	1.89	1.98	0.65	4.19

Table 3. X-ray measurement results of 7 tablets prepared from a test coal ash sample.

Tablet No./Parameter	Component Concentration, wt%									
	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
Tablet 1	49.859	23.858	7.474	5.324	3.025	0.846	4.270	2.140	1.096	0.924
Tablet 2	49.929	23.876	7.539	5.236	3.032	0.833	4.300	2.121	1.107	0.923
Tablet 3	50.201	23.995	7.464	5.229	3.013	0.834	4.298	2.076	1.102	0.929
Tablet 4	49.917	23.902	7.491	5.224	3.012	0.834	4.295	2.054	1.111	0.909
Tablet 5	50.100	23.964	7.443	5.207	3.016	0.837	4.306	2.076	1.103	0.920
Tablet 6	50.110	24.002	7.474	5.247	3.023	0.835	4.313	2.084	1.110	0.926
Tablet 7	49.900	23.879	7.511	5.220	3.016	0.827	4.290	2.085	1.106	0.921
Average	50.002	23.925	7.485	5.241	3.020	0.835	4.296	2.091	1.105	0.922
Maximum	50.201	24.002	7.539	5.324	3.032	0.846	4.313	2.140	1.111	0.929
Minimum	49.859	23.858	7.443	5.207	3.012	0.827	4.270	2.054	1.096	0.909
Range	0.342	0.144	0.096	0.117	0.020	0.019	0.043	0.086	0.015	0.020
Standard deviation	0.1319	0.0603	0.0317	0.0387	0.0074	0.0059	0.0135	0.0296	0.0051	0.0063
Coefficient of variation (RSD), %	0.26	0.25	0.42	0.74	0.24	0.71	0.31	1.42	0.46	0.69

From the analysis of the results contained in Table 2 it can be seen that the highest absolute increase in the content concerns the components which occur in the examined coal ash in the highest concentrations, i.e., for SiO₂, for which the content between the first and the seventh measurement increased from 50.24% to 56.70%, i.e., by 12.6% in relation to the result obtained in the first measurement, and for Al₂O₃, for which an increase was observed from 24.04% to 26.99%, i.e., by 12.3% of the first result. For the other determined oxides, the relative increases in content expressed as a percentage relative to the result of the first measurement are: 4.2% for CaO, 5.0% for MgO, 21.0% for Na₂O, 6.3% for K₂O, 6.8%

for SO_3 and 15.2% for P_2O_5 , respectively. Only in the case of two oxides, Fe_2O_3 and TiO_2 , was there no increase in the content; on the contrary, the result of the first measurement was the highest.

An interesting observation is also that the highest increase in content always occurs between the first and second measurement, while after the fourth or fifth measurement the result stabilizes. It was also observed that when the previously tested (even several times) tablet is ground again in the mill and pressed, the results obtained in the first measurement on the spectrometer of this re-prepared tablet return to the initial state, i.e., are identical to those obtained at the beginning, and then in each subsequent measurement the determined content systematically increases. It has to be clearly stated, however, that in case of routine analysis of pressed samples this problem is not an issue, since the prepared tablet is used for the measurement only once, and even if it had to be used again it is not very time-consuming to crush the pellet and press it for the second time. Nevertheless, the prepared pressed standards can only be used once for calibration and are not applicable for re-calibration. Higher intensities of the analytical lines of the elements determined in the method, obtained in subsequent X-ray measurements made for the standard tablets, would result in lower determination results. In the laboratory practice this meant that the standard tablets carefully stored in a desiccator and used for years in case of the Philips spectrometer became useless, and it was necessary to develop the entire analytical method for the wavelength dispersive X-ray fluorescence spectrometer Rigaku ZSX Primus II from scratch with the use of newly purchased certified reference materials (CRMs) and standards (STDs).

3.2.2. Method of Preparing Calibration Standards and Test Samples for X-ray Measurement by Pressing with Binding Material

The method of preparing the tablet for X-ray analysis experimentally established, proven in many years of laboratory practice and universal for all types and kinds of solid, bulk and powder materials was as follows: The starting sample was a standard or CRM previously dried in a laboratory dryer at $105\text{ }^\circ\text{C}$ for 2 h. An amount of 4.0000 g of standard sample, 2.0000 g of cellulose and 0.6000 g of graphite were weighed successively with accuracy of 0.0002 g using the analytical balance type CP224S-OCE (Sartorius, Goettingen, Germany). Both cellulose and graphite were also previously dried under the same conditions and stored in sealed plastic containers in a desiccator. Both reagents were pure for analysis (p.a.). The weights were quantitatively transferred into a 45×45 mm weighing vessel and thoroughly stirred for 5 min to obtain a homogeneous mixture, after which they were ground for 3 min at 1400 rpm in an impact mill HSM 100A (HERZOG, Munich, Germany) and pressed in a hydraulic press model HTP 40 (HERZOG, Munich, Germany) with a pressing force of 300 kN. The final result was a durable tablet ready for X-ray measurements with the use of the spectrometer.

3.2.3. Selection and Measurement of Standards to Obtain Calibration Curves

The assumption was to use for calibration all high-quality standards and CRMs at the laboratory disposal. In total, 22 such standards and 2 blends of two standards mixed in a weight ratio of 1:1 were selected. The standards represented all the objects tested in the laboratory: bottom coal ashes, fly coal ashes, soils, rocks, cements, sediments and ores. In spite of diversified chemical compositions of these standards, it was not possible to obtain for all determined oxides a wide range of calibration curve fully covering the range of variability of occurrence of these oxides in solid samples provided to the laboratory for testing, in particular for wastes. Such standards are also not available on the market, and therefore, it was decided to create such standards using natural waste samples provided to the laboratory for testing. Twenty-two such samples were selected, and their main chemical compositions (oxide contents) were determined using the accredited WDXRF method with sample preparation for X-ray measurements by fusion into a borate bead [13] and the ICP-AES method. In total, the calibration curves for all 10 oxides determined in

the research study presented in this paper were based on 42 standards. These selected standards were prepared for X-ray measurements as presented in Section 3.2.2, and the resulting standard tablets were then measured with the use of the spectrometer to obtain intensities for the calibration curves. Experimentally determined optimum instrumental measurement conditions for all 10 oxides are given in Table 4.

Table 4. Measurement conditions.

Chemical Element	Analytical Line	Background One	2 θ Degree		Measurement Time, s		Current Parameters of the Tube		Analysing Crystal	Collimator	Detector
			Peak	Background Two	Peak	Background	Voltage, kV	Current, mA			
Si	K α	106.15	109.05	111.90	20	10	50	60	PET	Course	PC
Al	K α	143.35	144.61	147.85	20	10	50	60	PET	Course	PC
Fe	K α	56.00	57.50	58.90	20	10	50	60	LiF200	Fine	SC
Ca	K α	110.30	113.12	115.85	20	10	50	60	LiF200	Course	PC
Mg	K α	37.05	40.07	42.40	30	14	50	60	Rx25	Course	PC
Na	K α	45.70	48.70	51.15	30	14	50	60	Rx25	Course	PC
K	K α	133.20	136.68	139.70	20	10	50	60	LiF200	Course	PC
S	K α	107.35	110.82	113.85	20	10	50	60	Ge	Course	PC
Ti	K α	84.80	86.11	87.90	20	10	50	60	LiF200	Fine	SC
P	K α	139.50	141.19	143.85	20	10	50	60	Ge	Course	PC

The α -empirical correction coefficients were applied to correct matrix effects at the stage of creating the final calibration curves. All calibration curves, shown in Figure 1, are linear despite the wide content range and have high correlation coefficients from 0.9995 for SiO₂ and TiO₂ to 0.9999 for SO₃ and P₂O₅.

The blue colour represents the position of the measurement points relative to the statistically determined curve after correction of matrix effects, and the white colour represents those before correction. The interval between these colours for each measurement point can be taken as a measure of the matrix effect. Observation of the attached calibration curves shows that the matrix effects are largest for the lightest of the oxides determined, that is, Na₂O, and for the heaviest, TiO₂ and Fe₂O₃. It is also an interesting observation that the standards prepared in the laboratory do not differ in quality from the purchased international standards and certified reference materials. On the basis of the deviation of the measuring points from the determined calibration curve it cannot be stated whether a point represents the laboratory-made or an international standard, since the observed deviations are comparable for both types of standards and are generally small for all 10 tested oxides considering that the method is based on very different standards with sample preparation for X-ray measurements by pressing with a binding agent. Assuming that the declared contents of all oxides in the certificate and determined in the laboratory are close to the actual contents and that the tablet preparation error is small, as will be shown later in this paper, the deviations obtained are a measure of matrix effects. Based on previous experience, it may be stated that the matrix effects associated with the absorption and enhancement of the X-ray fluorescence emitted from the sample by a given element by the other matrix-forming elements present in the sample have only a small effect on the value of this deviation, since they are effectively minimized by α -empirical or theoretical matrix effects correction factors. In this study, α -empirical coefficients were applied because α -theoretical coefficients could not be used, taking into account their one major limitation, consisting of the fact that they can only be used if the sum of all the components determined in a given analytical application is above 99%. Not all standards applied in calibration met the above criterion. A much larger share of the observed deviations of standard points from the calibration curve constitute matrix errors associated with differences in the mineralogical composition of the standards applied in calibration, and unfortunately mineralogical effects, as mentioned in Section 2, cannot be corrected by means of correction factors α . As a result, in the WDXRF technique, the determination accuracy of the main components in methods with sample preparation for measurement by pressing with a binding agent is always worse than for samples fused into a borate bead. In light of the above statement, an attempt to investigate the applicability of the SQX software for semi-quantitative analysis

by comparing the results received from this software with those obtained in the calibration method and in the reference to certified values becomes even more justified.

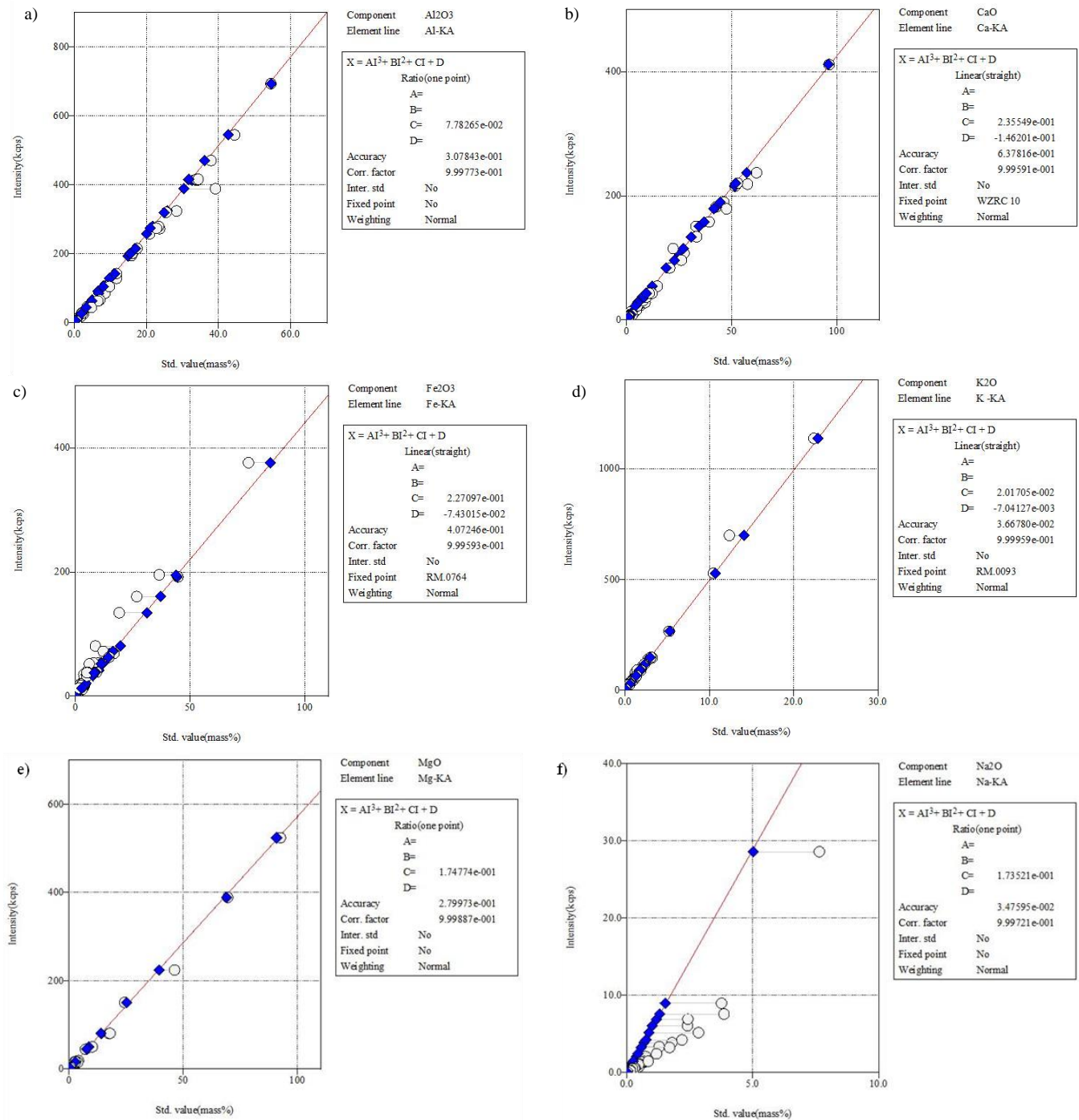


Figure 1. Cont.

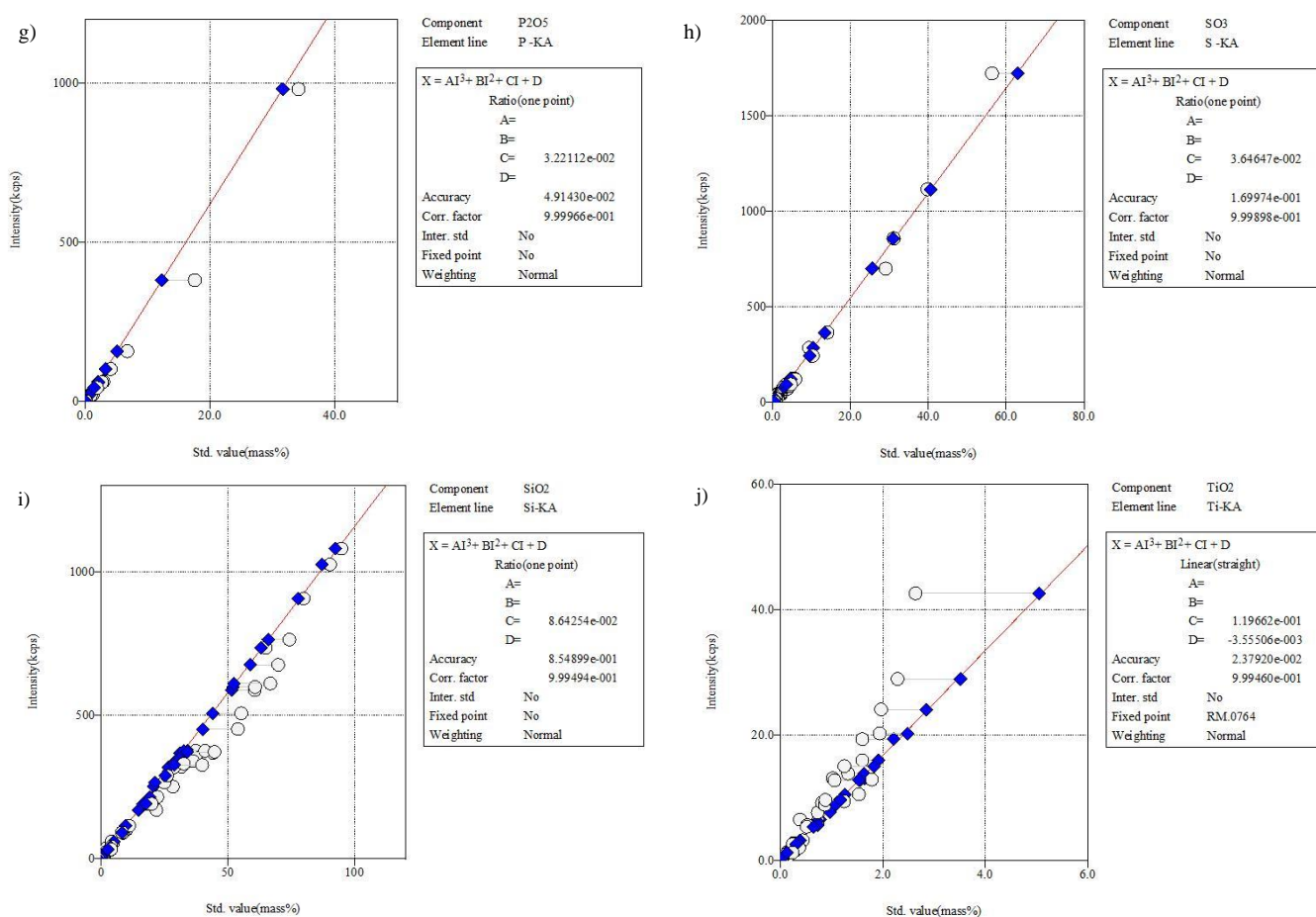


Figure 1. Calibration curves for (a) Al₂O₃, (b) CaO, (c) Fe₂O₃, (d) K₂O, (e) MgO, (f) Na₂O, (g) P₂O₅, (h) SO₃, (i) SiO₂ and (j) TiO₂.

3.2.4. The Principle of Semi-Quantitative Analysis and Optimization of the Method of Performing the Determination in Terms of the Correctness of the Obtained Results

Any determination of elemental composition with the use of the WDXRF technique is based on calibration. In standard calibration methods, the user prepares standards for X-ray measurements, develops an analytical application, optimizes instrumental measurement conditions, makes calibration measurements and finally develops calibration curves without or with correction of matrix effects. WDXRF spectrometry ensures high accuracy of the results provided that the standards applied to calibrate the method and the unknown samples determined in this method represent the same object (and thus differ only slightly in mineralogical and chemical compositions) and are prepared for X-ray measurements in an identical way. It is a valuable and useful research tool because of the ease of sample preparation and short analysis time. However, X-ray analysis applied to a sample that differs significantly from the standards employed in calibration may lead to unsatisfactory results even after applying a correction for matrix effects. Therefore, every leading manufacturer of X-ray fluorescence spectrometers also provides analytical software for semi-quantitative determination of the content of elements in any unknown sample as a part of the computer operational software accompanying the spectrometer. This software is also based on calibration, but the difference is that it is prepared by the manufacturer. In this case, calibration is based on a series of synthetic standards covering a wide range of elemental content over a large range of matrix variation; hence, this method is commonly referred to as a standardless analysis. This analytical software takes into account various factors at the stage of calculating the elemental content of the sample, such as coincidence of spectral lines, matrix effects, geometry of the optical system of the spectrometer, char-

acteristics of the detectors and how the sample was prepared for X-ray measurement. It enables the determination of elements ranging from sodium to uranium and in the content range from 0.01% to 100%. Rigaku bases the calibration of the standardless software on six standards designated DSC 1–DSC 6. The most important advantage of this software seems to be that the sample does not have to be analysed itself, but it can be mixed and pressed with a binding agent before X-ray measurement. After the analysis, at the stage of calculating the results, the type of a binding material, its chemical formula and the weight ratio in which the binding agent was mixed with the tested sample are specified, and the software recounts the obtained results into percentages of the initial sample. The analysis of a completely unknown sample by means of the SQX program is possible because the spectrometer is equipped with a set of analysing crystals allowing the determination of elements ranging from boron to uranium, and thus also oxygen and carbon, as important elements in waste analysis. This is especially important since the software summarises the contents of all detected elements to 100% with the possibility of converting them to oxides. In this situation, the only potential source of additional error is the inability to determine the hydrogen content, which may be, however, overcome in two ways. The first is to analyse dry samples to eliminate hydrogen present in the water. The second is to determine the hydrogen content by elemental analysis, if the laboratory is equipped with a suitable analyser, and enter the determined hydrogen into the program as a fixed value during the calculation of final results. The same can be done with carbon and nitrogen because, as very light elements, they will always be determined in WDXRF with high error. No corrections were applied in testing the SQX software, and the samples analysed were dried at 105 °C. The analysis of the chemical composition of the tested sample using the SQX software may be performed optionally in three time variants: short, standard and long. In all analyses performed for the purpose of this study, the “long” option was used. The time of full analysis is only a few minutes longer, but due to the use of a larger number of measuring points at the stage of scanning the spectral range, the spectrometer is able to detect elements that, due to their low content, are not detectable in the standard option. Depending on the chemical composition of the analysed sample, the software itself automatically selects the optimum measuring conditions for each of the determined elements by choosing the appropriate analysing crystal and changing the current parameters of the X-ray tube. In order to obtain the lowest possible limits of detection in our tests, the measured surface was always the maximum surface, a circle of 35 mm diameter.

3.2.5. The Effect of the Type and Amount of Binding Agent on the Result of the SQX Software Analysis

The first test was to verify how the SQX software handles the conversion of the results obtained from the measurement of the tablet, which is a mixture of the test sample and the binding agent, to the content of determined elements in the initial sample. In order to carry out the test, the test samples previously mentioned in Section 3.1.1 were used, i.e., a soil sample and a coal ash sample. For both test samples, seven tablets were prepared according to the adopted procedure presented in Section 3.2.2, by mixing the samples with different binding agents and in different weight ratios (Table 5).

Table 5. Compositions of tablets tested.

Tablet Name	Mass of the Sample	Mass of the Binding Agent and the Kind of Binding Agent Used
A	4.0000 g	2.0000 g of cellulose
B	3.0000 g	3.0000 g of cellulose
C	4.0000 g	2.0000 g of boric acid
D	3.0000 g	3.0000 g of boric acid
E	5.0000 g	1.0000 g of wax
F	4.0000 g	2.0000 g of cellulose + 0.6000 g of graphite
G	4.0000 g	2.0000 g of boric acid + 0.6000 g of graphite

The tablets were then analysed using the SQX software. The results obtained after conversion by the software into the contents of 10 main oxides in the initial soil and coal ash samples along with statistical calculations are presented in Table 6.

Table 6. The effect of the binding agent on the results of the analysis performed with the use of the SQX semi-quantitative software.

Tablet/Parameter	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
Coal sample										
Tablet A	47.22	23.97	7.41	6.77	3.10	0.831	5.16	2.47	1.21	1.03
Tablet B	46.29	24.18	7.63	6.98	3.05	0.801	5.35	2.64	1.29	1.06
Tablet C	46.61	24.24	7.26	6.88	3.26	0.856	5.16	2.43	1.46	1.05
Tablet D	47.19	25.24	6.74	6.41	3.40	0.907	4.89	2.32	1.22	0.99
Tablet E	45.35	24.91	7.84	7.21	2.85	0.810	5.37	2.48	1.39	1.07
Tablet F	46.74	24.35	7.62	6.98	2.98	0.822	5.37	2.66	1.27	1.08
Tablet G	46.73	24.72	7.25	6.74	3.23	0.831	5.11	2.46	1.27	1.06
Total number of tablets	7	7	7	7	7	7	7	7	7	7
Average	46.59	24.52	7.39	6.85	3.12	0.84	5.20	2.49	1.30	1.05
Maximum	47.22	25.24	7.84	7.21	3.40	0.91	5.37	2.66	1.46	1.08
Minimum	45.35	23.97	6.74	6.41	2.85	0.80	4.89	2.32	1.21	0.99
Range	1.87	1.27	1.10	0.80	0.55	0.11	0.48	0.34	0.25	0.09
Standard deviation	0.5888	0.4202	0.3322	0.2319	0.1723	0.0329	0.1637	0.1103	0.0846	0.0280
Coefficient of variation (RSD), %	1.26	1.71	4.49	3.38	5.51	3.93	3.15	4.42	6.50	2.67
Relative error, %	4.01	5.18	14.88	11.67	17.60	12.67	9.23	13.63	19.21	8.58
Soil sample										
Tablet A	92.19	3.78	1.13	0.326	0.208	0.239	1.30	0.109	0.209	0.0582
Tablet B	92.04	3.96	1.10	0.293	0.217	0.256	1.33	0.105	0.217	0.0660
Tablet C	91.74	4.02	1.07	0.304	0.223	0.227	1.35	0.097	0.230	0.0613
Tablet D	91.53	4.25	1.08	0.286	0.231	0.264	1.37	0.098	0.225	0.0642
Tablet E	91.76	4.27	1.15	0.322	0.229	0.243	1.38	0.102	0.241	0.0629
Tablet F	92.30	3.82	1.11	0.285	0.204	0.252	1.29	0.081	0.212	0.0554
Tablet G	92.19	3.91	1.13	0.307	0.215	0.249	1.32	0.094	0.220	0.0578
Total number of tablets	7	7	7	7	7	7	7	7	7	7
Average	91.96	4.00	1.11	0.30	0.22	0.25	1.33	0.10	0.22	0.06
Maximum	92.30	4.27	1.15	0.33	0.23	0.26	1.38	0.11	0.24	0.07
Minimum	91.53	3.78	1.07	0.29	0.20	0.23	1.29	0.08	0.21	0.06
Range	0.77	0.49	0.08	0.04	0.03	0.04	0.09	0.03	0.03	0.01
Standard deviation	0.2675	0.1798	0.0267	0.0152	0.0094	0.0112	0.0316	0.0084	0.0102	0.0035
Coefficient of variation (RSD), %	0.29	4.49	2.41	5.02	4.32	4.53	2.37	8.55	4.61	5.83
Relative error, %	0.84	12.25	7.21	13.52	12.38	14.97	6.75	28.57	14.41	17.43

On the basis of the analysis of the results given in Table 6, it may be concluded that the effect of the type of a binding agent applied on the results of the determination of the main chemical composition using the Rigaku SQX software for semi-quantitative analysis is not significant. As previously mentioned, all that is needed is to define the binding agent applied in the preparation of a tablet after the X-ray measurement, and the mathematical algorithm included in the software effectively converts the results obtained into the content of oxides in the initial sample. The effectiveness of the conversion algorithm is evidenced by the small differences between the results obtained for all the tested binding agents mixed with tested samples of coal ash and soil at different weight ratios, which is directly reflected in the low values of standard deviations and coefficients of variation. In case of the coal ash sample, the standard deviation values are the highest for SiO₂ (0.5888%) at its average determined content in ash of 46.59% and for Al₂O₃ (0.4202%) at its content of 24.52%, and the lowest is for Na₂O (0.0329%) at its average determined content of 0.84% and for P₂O₅ (0.0280%) at its average determined content of 1.05%. The coefficients of variation are also

low and range from 1.26% for SiO₂ and 1.71% for Al₂O₃ to 5.51% for MgO and 6.50% for TiO₂. These trends are similar for the tested soil sample: the highest values of standard deviation were reported for SiO₂ (0.2675%) at its average determined content in soil equal to 91.96% and for Al₂O₃ (0.1798%), at 4.00%; the lowest were reported for SO₃ (0.0084%) at its average determined content of 0.10% and for P₂O₅ (0.0035%) at its average determined content of 0.06%. The coefficients of variation are also at similar levels to those of coal ash and range from 0.29% for SiO₂ and 2.37% for K₂O to 5.83% for P₂O₅ and 8.55% for SO₃.

3.2.6. Estimation of the Reproducibility of the Tablet Preparation Procedure for the Standardless Analysis and the Repeatability of the Results Obtained Using the SQX Software

These tests were performed on the test sample of coal ash. Seven tablets were prepared according to the adopted procedure, and each of them was subjected to X-ray analysis with the use of the SQX software. The results obtained after conversion into the contents of the 10 determined oxides in the initial coal ash sample along with statistical data are included in Table 7.

Table 7. The reproducibility of the results obtained with the SQX software for coal ash sample.

Measurement No./Parameter	Component Concentration, wt%									
	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
1	46.00	24.40	7.64	7.07	3.04	0.838	5.31	2.71	1.27	1.07
2	46.10	24.40	7.46	7.03	3.03	0.799	5.36	2.71	1.25	1.07
3	46.20	24.50	7.62	6.90	3.02	0.806	5.33	2.63	1.24	1.07
4	46.10	24.50	7.66	6.91	3.02	0.812	5.33	2.61	1.27	1.05
5	46.10	24.50	7.61	6.93	3.00	0.815	5.32	2.65	1.26	1.07
6	46.10	24.40	7.63	6.96	3.03	0.819	5.32	2.66	1.26	1.06
7	46.10	24.50	7.67	6.99	3.01	0.802	5.32	2.65	1.25	1.08
Average	46.10	24.46	7.61	6.97	3.02	0.813	5.33	2.66	1.26	1.07
Maximum	46.20	24.50	7.67	7.07	3.04	0.838	5.36	2.71	1.27	1.08
Minimum	46.00	24.40	7.46	6.90	3.00	0.799	5.31	2.61	1.24	1.05
Range	0.20	0.10	0.21	0.17	0.04	0.04	0.05	0.10	0.03	0.03
Standard deviation	0.0535	0.0495	0.0654	0.0588	0.0125	0.0121	0.0148	0.0351	0.0103	0.0088
Coefficient of variation (RSD), %	0.12	0.20	0.86	0.84	0.41	1.49	0.28	1.32	0.82	0.83

The results show that the preparation of the sample for X-ray measurements by pressing with a binding agent and the measurement of the obtained tablet using the SQX program are not a serious source of error. Very small differences between the maximum and minimum results obtained from measurements of 7 tablets and for all 10 determined oxides prove that the procedure of tablet preparation and the analysis itself using the SQX program are very reproducible and repeatable. The calculated values of standard deviations range from 0.0088% for P₂O₅ and 0.0103% for TiO₂ to 0.0588% for CaO and 0.0654% for Fe₂O₃. The values of coefficients of variation (RSD) do not exceed even 1.5% and are the lowest for SiO₂ (0.12%) and Al₂O₃ (0.20%). The highest values have been found for SO₃ (1.32%) and Na₂O (1.49%).

3.2.7. Results Accuracy Estimation of the Determination of the Main Chemical Composition of Solid Samples with the Use of the SQX Software for Semi-Quantitative Analysis of the Rigaku ZSX Primus II Wavelength Dispersive X-ray Fluorescence Spectrometer

In order to estimate the accuracy of the results of determining the main composition of solid samples by means of the SQX software, 22 certified reference materials (CRMs) representing various objects under the study were used. These included waste, coal ash, construction materials (binders and aggregates), soils, rocks and biomass. In addition, two more samples were prepared, which were blends of two different CRMs mixed in a weight ratio of 1:1. Thus, the total number of samples for the study was 24, and these samples differed among themselves in mineralogical composition and were also characterized by a wide range of variation in the content of all 10 oxides determined (Table 8).

Table 8. Content range of the determined oxides in the standards (CRMs) applied in estimation of the accuracy of the SQX semi-quantitative analysis—content range of the method.

Oxide	Content Range in the Standards (CRMs), et%
SiO ₂	0.505–90.36
Al ₂ O ₃	0.0419–54.50
Fe ₂ O ₃	0.0154–14.67
CaO	0.0180–61.87
MgO	0.0120–18.00
Na ₂ O	0.0070–3.86
K ₂ O	0.0100–5.80
SO ₃	0.0022–2.64
TiO ₂	0.0080–2.69
P ₂ O ₅	0.0090–3.07

Selected CRMs were then prepared for X-ray measurements according to the procedure adopted and presented in Section 3.2.2., and the tablets were subjected to chemical analysis on a spectrometer, first by the method based on calibration and then using the SQX software. The results obtained by both methods for all 24 CRM samples tested were compared with the certified values, and relative errors of determinations were calculated (Table 9).

Table 9. Results accuracy estimation for the semi-quantitative analysis of the Rigaku ZSX Primus II wavelength dispersive X-ray fluorescence spectrometer.

Oxide	Content Certified, wt. %	Content Determined with the Use of the Semi-Quantitative Method, wt. %	Relative Error of the Semi-Quantitative Method, %	Content Determined with the Use of the Calibration Method, wt. %	Relative Error of the Calibration Method, %	Content Certified, wt. %	Content Determined with the Use of the Semi-Quantitative Method, wt. %	Relative Error of the Semi-Quantitative Method, %	Content Determined with the Use of the Calibration Method, wt. %	Relative Error of the Calibration Method, %	
Mixed standards: RM.0764–RM.0054 (ratio 1:1)						Mixed standards: RM.0093–RM.0061 (ratio 1:1)					
SiO ₂	31.775	27.528	13.37	31.34	1.37	31.775	27.528	13.37	31.34	1.37	
Al ₂ O ₃	11.715	10.381	11.39	11.96	2.09	11.715	10.381	11.39	11.96	2.09	
Fe ₂ O ₃	2.578	2.644	2.56	3.29	27.62	2.578	2.644	2.56	3.29	27.62	
CaO	20.53	25.815	25.74	21.26	3.56	20.53	25.815	25.74	21.26	3.56	
MgO	10.268	10.584	3.08	10.33	0.60	10.268	10.584	3.08	10.33	0.60	
Na ₂ O	0.175	0.1323	24.40	0.166	5.14	0.175	0.1323	24.40	0.166	5.14	
K ₂ O	0.632	0.733	15.98	0.654	3.48	0.632	0.733	15.98	0.654	3.48	
SO ₃	0.192	0.294	53.13	0.165	14.06	0.192	0.294	53.13	0.165	14.06	
TiO ₂	0.435	0.485	11.49	0.436	0.23	0.435	0.485	11.49	0.436	0.23	
P ₂ O ₅	0.658	0.58	11.85	0.548	16.72	0.658	0.58	11.85	0.548	16.72	
RM.0126: NIST 1881a—Portland Cement						RM.0764: NCS DC 70310—Carbonate Rock					
SiO ₂	22.26	18.935	14.94	21.55	3.19	8.25	7.488	9.24	7.96	3.52	
Al ₂ O ₃	7.06	5.872	16.83	7.39	4.67	0.10	0.141	41.00	0.168	68.00	
Fe ₂ O ₃	3.09	3.036	1.75	3.66	18.45	0.057	0.0831	45.79	0.057	0.00	
CaO	57.58	62.01	7.69	56.27	2.28	33.07	36.024	8.93	34.01	2.84	
MgO	2.981	2.136	28.35	2.82	5.40	18.00	16.135	10.36	18.01	0.06	
Na ₂ O	0.199	0.165	17.09	0.185	7.04	0.026	0.0156	40.00	0.02	23.08	
K ₂ O	1.228	1.454	18.40	1.27	3.42	0.01	0.0227	127.00	0.015	50.00	
SO ₃	3.366	3.823	13.58	3.31	1.66	0.01	0.081	710.00	0.018	80.00	
TiO ₂	0.3663	0.367	0.19	0.412	12.48	0.003	0.00	100.00	0.003	0.00	
P ₂ O ₅	0.1459	0.131	10.21	0.142	2.67	0.124	0.114	8.06	0.128	3.23	

Based on the data presented in Table 9, one major conclusion may be drawn that the calibration method is more accurate than the semi-quantitative analysis using the SQX software because the results obtained by the calibration method are closer to the certified contents as evidenced by the lower values of relative determination errors compared to the corresponding errors calculated for the SQX method. The Fe₂O₃, and for some CRMs the relative error of determination in the method based on calibration, is larger than that with the use of the SQX software. It should be noted that the range of content of a few oxides in the 24 tested CRMs samples comprises even three orders of magnitude. For example,

the SiO₂ content is in the range of 0.505% to 90.36%, while the Al₂O₃ content is in the range of 0.0419% to 54.50% (Table 9), and the minimum and maximum CaO contents in the tested certified reference materials are 0.0180% and 61.87% (Table 8), respectively. For the remaining seven oxides these ranges are narrower but also include two or even three orders of magnitude as, for example, SO₃, whose minimum content in the selected CRMs is 0.0022% and maximum is 2.64% (Table 8). Thus, the calculation and adoption of a single mean determination error for the entire range would not be substantively justified and would contradict commonly applied statistical principles. Therefore, in the work presented in this paper the principle of dividing the full range of applicability of the semi-quantitative analysis, i.e., the range from 0.01% to 100%, into four sub-ranges and calculating the mean relative error of determination of a given oxide in a given sub-range was adopted. These four subranges hereinafter referred to as “Ranges” are:

- Range 1: below < 0.1%;
- Range 2: between 0.1% and 1.0%;
- Range 3: between 1% and 10%;
- Range 4: above 10%.

The calculated mean values of relative errors in relation to certified content obtained for the semi-quantitative method with the use of the SQX software and for comparison for the method based on calibration are presented in Table 10.

As it can be seen, for various oxides, the ranges are represented by a different number of measurement points. This is mainly due to the range of variation in the occurrence of a given oxide in the selected objects. For example, in 24 tested standards, in none of them is the content of SiO₂ below 0.1%, and in the case of Al₂O₃ and CaO there is only one such standard. In contrast, Range 4 (content above 10%) is represented by as many as 15 standards for SiO₂ and 13 standards for Al₂O₃, but Na₂O, K₂O, SO₃, TiO₂ and P₂O₅ are not represented in this range at all. Thus, the largest number of standards is located in the middle ranges (Ranges 2 and 3), and therefore, the calculated mean error of determination of a given oxide in these two ranges reflects the real state best and can actually be accepted as uncertainty of determination of this oxide in a given content range. This is also true for Range 4 but only for the oxides SiO₂, Al₂O₃ and CaO, which are represented in this range by a larger number of standards: 15, 13 and 9, respectively. In general, the data included in Table 10 only confirm the conclusion already quoted, that for all the determined oxides, except for Fe₂O₃, the calibration method is more accurate than the semi-quantitative SQX method, but even for the SQX method, the mean relative errors of determination do not have very high values and decrease with increasing content of the given oxide in the standard. The highest error value was reported for Al₂O₃ in Range 2, equal to 63.08%, but for the same oxide in Range 3 the mean error is only 15.51%. As for Range 2, the second highest mean error is 28.75% for SO₃, and the lowest is 10.10% for SiO₂. For Range 3, the mean error values are between 5.12% for Fe₂O₃ and 33.83% for CaO. The mean relative errors of determination in Range 1 are from 298.5% for SO₃ (the second highest is 84.14% for K₂O) to 16.61% for P₂O₅, and taking into consideration the fact that the contents of the determined oxides in this range are below 0.1%, these errors are also acceptable. Further analysis of the data presented in Table 10 allows us to conclude that all 10 oxides are determined with comparable accuracy, which proves that the SQX software at the stage of calculating the content of individual oxides in the tested sample deals with matrix effects very well and is therefore universal and can be successfully applied in semi-quantitative determination of the main chemical composition of any unknown solid, bulk or powder sample with satisfactory accuracy. This last statement leads to another and better way of estimating the accuracy of this standardless semi-quantitative method.

Table 10. The mean values of the relative errors (MRE) obtained for the semi-quantitative method and for the method based on calibration in the reference to the certified contents.

Oxide	Parameter	Range 1	Range 2	Range 3	Range 4
SiO ₂	No. of standards in the range	0	1	8	15
	MRE for the semi-quantitative method	—	10.10	7.66	7.74
	MRE for the method based on calibration	—	15.64	6.13	1.68
Al ₂ O ₃	No. of standards in the range	1	6	4	13
	MRE for the semi-quantitative method	70.41	63.08	15.51	5.17
	MRE for the method based on calibration	15.57	29.25	4.60	1.12
Fe ₂ O ₃	No. of standards in the range	4	3	15	2
	MRE for the semi-quantitative method	23.48	19.64	5.12	2.25
	MRE for the method based on calibration	16.06	23.66	10.67	1.17
CaO	No. of standards in the range	1	5	9	9
	MRE for the semi-quantitative method	51.17	23.96	33.83	8.69
	MRE for the method based on calibration	25.00	10.95	13.48	2.13
MgO	No. of standards in the range	3	9	10	2
	MRE for the semi-quantitative method	29.68	17.34	15.81	13.07
	MRE for the method based on calibration	22.12	10.19	4.05	6.13
Na ₂ O	No. of standards in the range	8	11	4	0
	MRE for the semi-quantitative method	26.05	15.69	9.06	—
	MRE for the method based on calibration	31.79	3.21	2.86	—
K ₂ O	No. of standards in the range	4	9	11	0
	MRE for the semi-quantitative method	86.14	18.86	21.48	—
	MRE for the method based on calibration	20.48	10.43	2.84	—
SO ₃	No. of standards in the range	4	12	7	0
	MRE for the semi-quantitative method	298.50	28.75	16.50	—
	MRE for the method based on calibration	67.05	9.98	2.54	—
TiO ₂	No. of standards in the range	7	9	8	0
	MRE for the semi-quantitative method	69.78	10.13	8.01	—
	MRE for the method based on calibration	16.61	5.53	1.67	—
P ₂ O ₅	No. of standards in the range	7	12	4	0
	MRE for the semi-quantitative method	16.61	19.43	9.21	—
	MRE for the method based on calibration	19.86	9.75	7.00	—

Before starting the work we had at our disposal only 22 certified reference materials plus 2 extra samples prepared by us by mixing 2 different CRMs in a weight ratio of 1:1. Thus, the estimation of the accuracy of the determination of each oxide in the wide range of variation of its occurrence in the analysed CRMs (see Table 9) by four ranges was based on 24 measurement points, and in the case of Na₂O, SO₃ and P₂O₅, on 23, because there was no certified content of these oxides in one of the standards. If the determination errors are on the same level for all 10 determined oxides and depend mostly on the content of the oxide in the standard, the accuracy of the method can be expressed as the mean determination error in each of four selected content ranges. The accuracy estimated in this way better characterises the validated method since it is calculated based on a much larger number of measurement points more evenly distributed over all four content ranges. In this case,

since the method concerns the determination of 10 oxides, and 24 standard samples were at disposal, its accuracy was estimated on the basis of 237 measurement points (one certified content was missing for Na₂O, SO₃ and P₂O₅), which were distributed among the selected content ranges as follows: 39 results below 0.1% (Range 1), 77 results between 0.1% and 1% (Range 2), 80 results between 1% and 10% (Range 3) and 41 results above 10% (Range 4). Thus, the calculated average determination errors for all 10 determined oxides present in the selected CRMs in a given content range, which can be equated with measurement uncertainty, are presented in Table 11. For a more complete illustration, they are compared with the average determination errors calculated in the same way in the calibration method.

Table 11. Mean values of the relative errors for 4 content ranges in the SQX semi-quantitative method and the method based on calibration.

Content Range, wt%	Number of Results in the Range	Mean Relative Error of Determination, %	
		SQX Semi-Quantitative Method	Calibration Method
<0.1	39	68.11	26.43
0.1–1	77	22.53	10.71
1–10	80	14.40	6.14
>10	41	7.13	1.79

The analysis of the data in Table 11 shows that in both the semi-quantitative SQX method and the calibration method the accuracy of the determination increases with increasing oxide content in the sample as evidenced by the decreasing values of relative errors. The accuracy of the SQX method compared to the calibration-based method is more than two times lower for an oxide content of up to 10% and even three times lower for oxide contents above 10%. However, keeping in mind that it is, by design, a semi-quantitative method, the estimated accuracy is surprisingly high when one realises how diverse certified reference materials were applied to validate the method. Only in the lowest range (below 0.1%) is the estimated uncertainty 68.11%, but it increases significantly with increasing oxide content, reaching only 7.13% for contents above 10%.

In summary, the Rigaku software for semi-quantitative analysis supplied by the manufacturer with the wavelength dispersive X-ray fluorescence ZSX Primus II spectrometer is an ideal analytical tool for determining the chemical composition of unknown solid, bulk and powder samples with very satisfactory accuracy. The ease of sample preparation for X-ray measurements, the low cost of analysis and the short time leading to a result make the SQX program a valuable and necessary tool for any chemical laboratory equipped with a WDXRF spectrometer.

4. Conclusions

1. Rigaku software for semi-quantitative analysis provided by the manufacturer with its wavelength dispersive X-ray fluorescence ZSX Primus II spectrometer is an ideal analytical tool for determining the chemical composition, including 10 main oxides: SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, Na₂O, K₂O, SO₃, TiO₂ and P₂O₅ of any unknown solid, bulk and powder samples.
2. The uncertainty of determination of the above-mentioned oxides based on measurements of 24 certified reference materials estimated at the validation stage of the method after dividing the entire range of its applicability into four content sub-ranges is: 68.11% for contents below 0.1%; 22.53% in the content range 0.1–1%; 14.40% for the results between 1–10%; and 7.13% for the results above 10%.
3. Rigaku SQX software enables direct analysis of the initial samples as well as samples mixed and then pressed with the binding agent since, at the stage of calculating the determined contents, the software deals with the correction of matrix effects very well and efficiently. The effectiveness of the mathematical conversion algorithm is demonstrated by the small differences between the results obtained for the different

- binding agents tested and mixed at different weight ratios with coal ash and soil samples selected for this purpose.
4. The preparation of the sample for X-ray measurements by pressing with a binding agent and then the measurement of the obtained tablet itself using the SQX software are not significant sources of determination error. This is evidenced by the small differences between the maximum and minimum results obtained from the measurement of 7 tablets and for all 10 determined oxides. The calculated values of standard deviations range from 0.0088% for P_2O_5 and 0.0103% for TiO_2 to 0.0588% for CaO and 0.0654% for Fe_2O_3 . The values of coefficients of variation (RSD) do not exceed even 1.5% and are the lowest for SiO_2 and Al_2O_3 (0.12% and 0.20%, respectively) and the largest for SO_3 (1.32%) and for Na_2O (1.49%).
 5. The ease of sample preparation for X-ray measurement, the low cost of analysis and the short time leading to correct results make the SQX software a valuable, useful and even necessary analytical tool for any chemical laboratory equipped with a WDXRF spectrometer.

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