

Chemical analysis of solid residue from liquid and solid fuel combustion: Method development and validation

Chemische Analyse der Zusammensetzung von festen Rückständen nach Verbrennung von flüssigen und festen Treibstoffen: Methodenentwicklung und Validierung

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This paper deals with the development and validation of methods for identifying the composition of solid residue after liquid and solid fuel combustion in thermal power plant furnaces. The methods were developed for energy dispersive X-ray fluorescence (EDXRF) spectrometer analysis. Due to the fuels used, the different composition and the location of creation of solid residue, it was necessary to develop two methods. The first method is used for identifying solid residue composition after fuel oil combustion (*Method 1*), while the second method is used for identifying solid residue composition after the combustion of solid fuels, i.e. coal (*Method 2*). Method calibration was performed on sets of 12 (*Method 1*) and 6 (*Method 2*) certified reference materials (CRM). CRMs and analysis test samples were prepared in pellet form using hydraulic press. For the purpose of method validation the linearity, accuracy, precision and specificity were determined, and the measurement uncertainty of methods for each analyte separately was assessed. The methods were applied in the analysis of real furnace residue samples.

Keywords: ash / fuel oil / coal / EDXRF / validation

Diese Arbeit zeigt die Entwicklung und Validierung von Methoden für das Bestimmen der Zusammensetzung von festen Rückständen nach Verbrennung von flüssigen und festen Treibstoffen in den Verbrennungsöfen von Wärmekraftwerken. Die Methoden wurden für die Röntgenfluoreszenzanalyse entwickelt. Aufgrund der verwendeten Treibstoffe, der verschiedenen Zusammensetzungen und des Entstehungsortes der festen Rückstände war es notwendig, zwei Methoden zu entwickeln. Die erste Methode wird für die Bestimmung der Zusammensetzung von festen Rückständen nach der Verbrennung von Schweröl (*Methode 1*) benutzt, und die zweite Methode für das Bestimmen der Zusammensetzung von festen Rückständen nach der Verbrennung von festen Treibstoffen, d.h. Kohle (*Methode 2*). Die Kalibrierung der Methoden wurde in Sätzen von 12 (*Methode 1*) und 6 (*Methode 2*) zertifizierten Referenzmaterialien (CRM) durchgeführt. CRM und die Testproben für die Analyse wurden durch Pressen mit einer hydraulischen Presse in Pelletform vorbereitet. Zum Zwecke der Validierung der Methoden wurden die Linearität, Richtigkeit, Präzision und Selektivität bestimmt, wie auch die Messunsicherheit der Methoden gesondert für jeden Analyten. Die Methoden wurden für die Analyse von realen Rückständeproben aus Verbrennungsöfen benutzt.

Schlüsselwörter: Asche / Heizöl / Kohle / EDXRF / Validierung

1 Introduction

Combustion of liquid and solid fuels in thermal power plants results in creation of solid residue which differ in their composition and the place of creation, depending on the used fuel type and quality, furnace construction and other working parameters

during combustion. Due to the quantities created in thermal power plants throughout the world, solid residue after fuel combustion is becoming an increasingly grave problem. The importance of identifying the chemical composition of solid residue is crucial in predicting material properties for the purpose of its further use or disposal.

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Long-term practice of the use of heavy fuel oils in contemporary steam generators shows that in case exploitation problems occur in the zone with high temperatures of heating surface walls, the first cause to be mentioned is the occurrence of high temperature corrosion caused by liquid fuel ashes. Solid residue resulting from deposition to the furnace walls and pipe bundles are very dangerous for the proper functioning of the plant. For this reason the plant needs to be stopped more often and the created residue needs to be mechanically or chemically cleaned, which makes the plant operation more expensive. The problem of residue disposal occurs and additional engagement of the employed staff is required. The created residue has different melting temperatures depending on its composition, whose origin is mostly fuel. Vanadium, sodium and sulphur are very often mentioned as the most important elements in the deposition process as they can create new complex compounds, have different melting points and stick to the heating surfaces [1].

Creation of deposit in the furnace is not exclusively limited to thermal power plants using fuel oil. This problem also occurs in plants using coal as fuel [2], and even in those using biofuels [3, 4], and in incineration plants [5]. In spite of available technologies and ongoing research, only a small part of solid residue has commercial use, while the rest is disposed of at landfill sites.

Solid residue remaining after coal combustion are fly ash, bottom ash and flue gas desulphurization products. Their properties depend on the physical and chemical properties of coal, the size of the coal particles during combustion, the combustion process and the manner of gathering. The greatest part of solid products is fly ash, as much as 80%, of grey colour and of irregular form in appearance. Other ash type, bottom ash, consists of larger particles and melted material, is of coarser appearance and of a darker grey colour due to the presence of unburned carbon. It mostly remains in the furnace and is called slag [6–12].

Literature dealing with analyses of residue systems from different furnaces states energy dispersive X-ray fluorescence (EDXRF) as the most suitable technique for this kind of research due to its speed, economicality, and suitability for simultaneous quantitative identification of elements from many matrixes. For these reasons, this technique has several advantages over other spectrometric methods. The total time needed for EDXRF analysis is much shorter than for conventional chemical techniques, and the choice of analysis method always being a compromise of required accuracy and necessary analysis time [13–19].

The disadvantages of this technique are the influence of the sample matrix onto the analysis, problems of determining the content of sodium and other light elements and impossibility of identifying their low concentrations. For this kind of samples, inductively coupled plasma atomic emission spectrometry (ICP-AES) and neutron activation analysis (NAA) are often used as a supplement to the EDXRF technique in establishing the content composition with regard to trace elements [20–23].

The goal the research work described in this paper is to develop and validate two EDXRF methods for analysing solid residue after liquid and solid fuels combustion in thermal power plant furnaces. The first method is a method for establishing composition of residue resulting from fuel oil combustion in thermal power plant furnaces (Method 1), and the second

method is a method for establishing the composition of ash after solid fuel combustion in thermal power plant furnaces (Method 2). The methods were applied to real residue samples from thermal power plant using fuel oils and to ash samples resulting from coal and patent fuels combustion in experimental solid oil furnace.

2 Experiment

All determinations were performed using the energy dispersive X-ray fluorescence spectrometer EDXRF Oxford ED2000 (Great Britain). For method development Certified Reference Material (CRM), obtained via *MBH Analytical LTD* from Great Britain, was used. To obtain optimum instrument working conditions for each individual element in the tested sample, it is necessary to set a series of operating parameters: the voltage and current of the X-ray tube, primary beam (or tube) filter, spectrometer working atmosphere, detector pulse rate, energy range of the spectrum, measurement time, peak position check sample and reference element for fine calibration of the energy scale. The choice of working parameters is influenced by physical form, elemental composition, size and shape of the sample. The fix conditions contain a set of predetermined parameters, except for the current of the X-ray tube and the measurement time. It is only necessary to choose those conditions which are best suitable for the element to be determined. It provides same measurement quality which would be obtained by a complex optimisation of each parameter separately. There are a total of 21 fix conditions set by the instrument manufacturer. Each covers a specific area and measures mostly between 5 to 10 elements. In the quantitative analysis the working conditions are mostly sequentially combined in order to cover a large range of elements.

2.1 Methods

Method 1 was developed for determining the composition of furnace walls residue created by fuel oil combustion. This method enables to determine 14 different analytes simultaneously, but it is not standardized. Four different fix conditions have been used for measurement in vacuum medium, each lasting 100 s:

- **Light elements for:** sodium oxide, magnesium oxide, silicon dioxide, aluminium oxide, phosphorus pentoxide and sulphur,
- **Solids (S-V) for:** potassium oxide, calcium oxide, titanium dioxide and vanadium,
- **Steels for:** chromium, manganese oxide, iron oxide,
- **Medium elements for:** nickel.

Due to the specificity of those samples and the lack of information on their composition in literature, a standardless fundamental parameter analysis of actual residue samples was performed using the EDXRF spectrometer. The purpose of the analysis was to determine which analytes and in which concentrations are present in the samples, as well as to gain insight into the sample matrix. Based on this analysis the adequate CRMs were chosen, *Table 1*. Due to the wide scope of concentrations and the large number of analytes, 12 Certified Reference Materials were used for developing the test method.

Table 1. CRM chemical composition for developing *Method 1*.**Tabelle 1.** Chemische Zusammensetzung von CRM für die Entwicklung der *Methode 1*.

No. Code Type	1 COD 161b Pb-Zn Sulph	2 B 2780 Hard Rock	3 S JR-3 Rhyolite	4 S Jsy-1 Syenite	5 FER-1 Iron Formation	6 FER-2 Iron Formation	7 UM-2 Sulf- ultrama	8 UM-4 Sulf- ultrama	9 SA 1 Granite	10 SA 3 Lujavrite	11 SA 4 Novrite	12 SA 50 Dolerite
Na ₂ O (wt%)	1.00	0.30	4.69	10.74	0.02	0.5	0.32	0.45	3.36	8.37	2.46	2.3
MgO (wt%)	1.48	0.88	0.05	0.02	0.30	2.1	25.45	22.5	0.06	0.28	7.5	7.57
Al ₂ O ₃ (wt%)	13.23	16.76	11.9	23.17	0.50	5.17	7.23	8.98	12.08	13.64	16.5	15.28
SiO ₂ (wt%)	55.4	70.09	72.76	60.02	17.02	48.92	39.2	39.35	75.7	52.4	52.64	51.56
P ₂ O ₅ (wt%)	0.27	0.098	0.02	0.01	2.44	0.27	0.02	0.02	–	0.06	0.03	0.15
S (wt%)	2.29	1.26	0.01	0.001	0.25	0.17	0.94	0.44	–	0.07	–	0.03
P ₂ O ₅ (wt%)	4.1	4.07	4.29	4.82	0.02	1.3	0.11	0.18	4.99	5.51	0.25	0.61
CaO (wt%)	3.7	0.27	0.09	0.25	3.31	2.17	4.68	6.27	0.78	3.22	11.5	10.8
TiO ₂ (wt%)	0.42	1.17	0.21	0.002	0.03	0.19	0.24	0.35	0.09	0.48	0.2	0.86
V (mg/kg)	61	268	4.2	2.1	98	36.5	–	–	2	81	220	216
Cr (wt%, mg/kg)	0.06	44	3.5	2	7	46	1.03	1.77	12	10	30	357
MnO (wt%)	1.11	0.06	0.08	0.002	0.23	0.12	0.08	0.15	0.02	0.77	0.18	0.17
Fe ₂ O ₃ (wt%)	6.09	3.98	4.72	0.08	75.8	39.4	14.40	14.23	2	9.91	8.97	11
Ni (wt%, mg/kg)	13	12	1.6	1.1	12	25	0.39	0.25	8	–	120	85

Table 2. CRM chemical composition for developing *Method 2*.**Tabelle 2.** Chemische Zusammensetzung von CRM für die Entwicklung der *Methode 2*.

No. Code	1 SABS 106	2 SABS 108	3 NCS FC 82012	4 NCS FC 82014	5 NCS FC 82016	6 ASRM 010-2
SiO ₂ (wt%)	57.71	40.03	46.77	53.98	50.08	52.2
Al ₂ O ₃ (wt%)	24.5	34.36	14.96	31.7	33.78	27.1
Fe ₂ O ₃ (wt%)	3.87	2.42	5.51	7.8	4.36	10.8
CaO (wt%)	5.55	9.13	21.37	1.44	5.5	3.47
MgO (wt%)	1.46	1.98	1.73	1.08	0.76	1.4
TiO ₂ (wt%)	1.51	1.95	0.63	1.17	1.77	1.34
P ₂ O ₅ (wt%)	0.68	0.78	1.41	1.36	0.88	0.92
Na ₂ O (wt%)	0.19	0.2	1.36	0.22	0.41	0.47
P ₂ O ₅ (wt%)	0.67	2.69	0.5	0.28	0.18	1.13
S (wt%)	2.89	4.46	3.94	0.28	1.25	0.21

The test method was developed by creating calibration lines of the dependence of X-ray intensity (*counts per second, CPS*) of the analyte concentration (*wt%*).

Method 2 was developed for determining the composition of ash resulting from solid fuel combustion in a furnace. The method is standardised (ASTM D4326-04) [24] and enables to determine the ash composition by measuring the content of 13 different analytes. Due to the chemical composition of CRMs *Table 2*, the method could only be developed for 10 different analytes. The examination was conducted in helium, with two fix conditions, each lasting for 100 seconds:

- **Very light elements for:** sodium oxide, magnesium oxide, silicon dioxide, aluminium oxide, phosphorus pentoxide, potassium oxide, calcium oxide and sulphur,
- **Solids A for:** titanium dioxide, iron oxide.

Six certified reference materials (CRM) were used for calibration of *Method 2*.

2.2 CRM preparation for calibration of methods

All CRM were in powder form. Due to the laboratory equipment, the reference material for calibration of the methods was prepared in pellet form by pressing using a manual hydraulic press

(SPECAC, P/N 25011). The pressing power was 15 tons, pressing time 30 seconds.

CRMs for *Method 1* are of geological origin. In spite of the powder form, pellets of sufficient quality, appearance and compactness were obtained by pressing so it was not necessary to add any binder.

To develop *Method 2* CRMs with coal ash matrix were used. Before pressing, each CRM had to be returned in a furnace at 815 °C. For creation of compact pellets it was necessary to add binder, Hoechst wax C micropowder, *Merck*, in the ratio: CRM : Hoechst wax = 4:1.

2.3 Preparation of real samples for analysis

For determining the composition of residue resulting from fuel oil combustion (*Method 1*), residue samples from the steam generator furnace were taken, after the thermal power plant was put out of operation before cleaning the furnace. According to their appearance, the samples represent the products of combustion and deposition on the heating surface wall. In such samples where this was possible, the layers were separated, crushed and the resulting grains were separated according to the visual properties of the layers. The sampling locations in the steam genera-

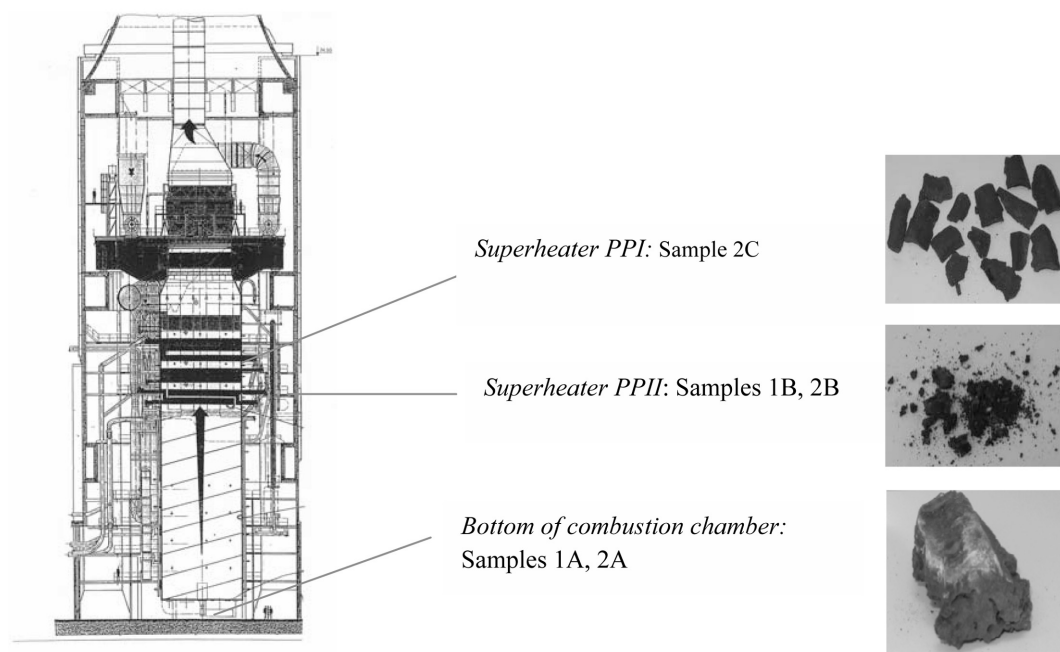


Figure 1. Sampling locations in combustion chamber.

Bild 1. Probeentnahmeorte im Verbrennungssofen.

tor furnace on liquid fuels, as well as pictures of the samples are depicted in *Figure 1*.

For determining the composition of ash after coal combustion (*Method 2*) residue samples resulting from combustion of steam coal ($w(\text{ash}) = 10.04 \text{ wt\%}$) and brown coal ($w(\text{ash}) = 17.93 \text{ wt\%}$) and a mixture of steam coal with patent fuel were used. According to its appearance, solid combustion residue, i. e. bottom ash taken from the furnace, represents inhomogeneous combustion products.

Preparation of samples for analysis has a great influence on the accuracy of the results. Since the combustion remains of both liquid and solid fuels are inhomogeneous samples, the process of preparation of a representative and homogeneous sample is very important and requires a series of steps. Additional effort was made to separate layers taken from the furnace bottom after fuel oil combustion. Those samples were usually larger pieces with visibly different layers. A layer created at the profile membrane could be distinguished, as well as other layers which mostly resulted from falling of higher parts of the furnace to this basis layer. In such samples where this was possible, the layers were separated, crushed and the resulting grains were separated according to the visual features of the layers. Samples taken from the steam superheater (PI and PII) were of smaller quantity, more homogeneous, without visible different layers. The sample preparation was carried out in the manner described in the diagram in *Figure 2*.

The residue samples after fuel oil combustion were analysed using *Method 1* (method for analysis of solid samples after liquid fuels combustion).

After the described preparation, bottom ash samples resulting from steam and brown coal combustion were analysed using *Method 2*. Sample pellets were prepared, in the same way as the

CRM were, with addition of Hoechst wax in 4:1 ratio. Besides steam and brown coal ashes, the method was also applied to ash resulting from combustion of coal with patent fuel addition.

3 Results and discussion

3.1 Method validation

Analytical method validation encompassed the review of parameters: linearity, accuracy, precision (reproducibility of measurement and reproducibility of sample preparation) and specificity. Since the methods were developed to determine main and secondary elements, the detection and quantification limits were not determined. Measurement uncertainty was assessed for all analytes of both methods.

Method linearity was checked for all points of the calibration lines of each of the analytes. The dependence of the X-ray intensity on the analyte concentration was expressed in the form of $y = ax + b$ (y being the X-ray intensity in counts per second, x being the known analyte concentration from the certificate of the reference material). Acceptability criterion is expressed via correlation coefficient R representing the measure of relation linearity of the two variables. For both methods the requirement that the correlation coefficient has to be higher or equal to 0.98 ($R = 0.98$) was fulfilled. Due to the number of analytes, the wide concentration range and the sample matrix it is to be expected that such correlation coefficient would occur especially with elements of wide concentration range (SiO_2). It was shown that the correlation coefficient in *Method 2*, in which case binder was used during pellet preparation, has worse values for all analytes as compared to those in *Method 1* in case which the pellets were prepared without binder.

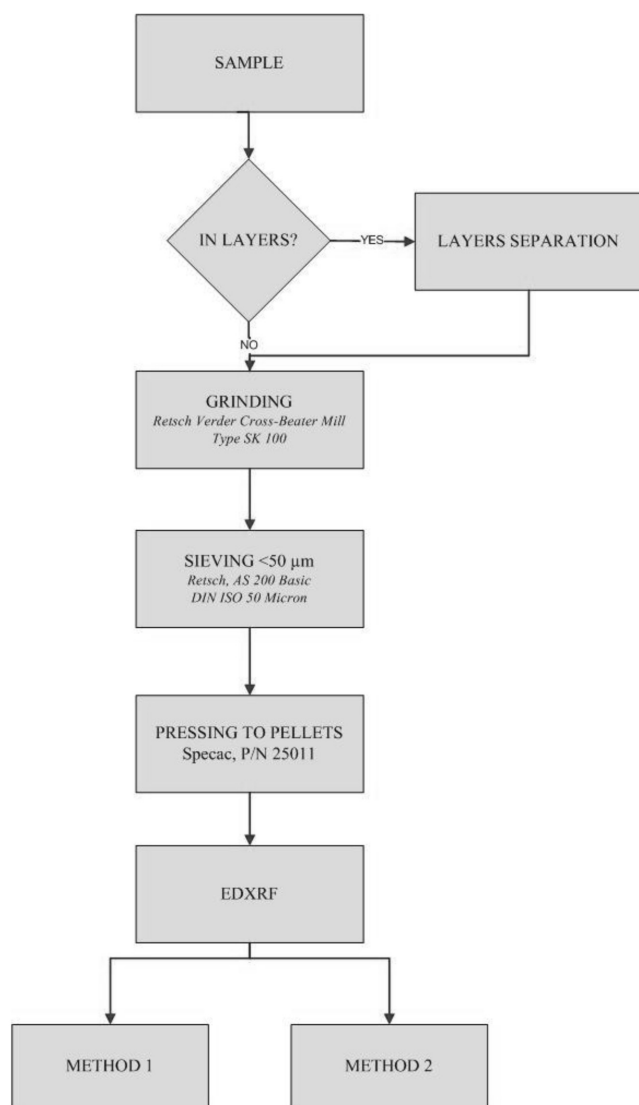


Figure 2. Depiction of solid samples preparation.

Bild 2. Darstellung der Vorbereitung von festen Rückständen.

Specificity of test methods was checked by comparative depiction of spectra of the sample and the reference material for each individual analyte, measured under same conditions.

The accuracy of the method represents the relation between the arithmetic mean of the analyte content measurement value and the certificate reference value. Accuracy was tested for 4 different concentration ranges and the values were compared to the known values of the Certified Reference Material. The acceptability criterion for accuracy is expressed by recovery factor:

$$R_f = \frac{\bar{x}}{x_{CRM}} \cdot 100\% \quad (1)$$

where \bar{x} is mean value from a series of analyte concentration measurements, x_{CRM} is the true (actual) analyte concentration value.

For *Method 1*, R_f of all analytes is within the interval: 98.15 to 102.58%. For *Method 2*, R_f of all analytes is within the interval: 94.03 to 103.50%. In spite of the wider factor interval used for

this method, the results of the accuracy check of all analytes from *Method 2* fulfil the set acceptability criteria from the ASTM D 4326:04 norm (data on method reproducibility were used).

Test method precision was checked by determining the reproducibility of measurement and reproducibility of sample preparation for analysis. Measurement reproducibility was checked for each analyte separately by subsequent measurement of one prepared sample tablet 9 times within the same day, by the same analyst. Relative standard deviation of measurement reproducibility for *Method 1* is within the interval 0.1–8.3%, and for *Method 2* within the interval 0.5–8.9%. Sodium has the highest relative standard deviation, which is a borderline element in determination using EDXRF technique, whose measurement is also problematic in other matrices. Since *Method 2* is standardized, the reproducibility results obtained were also checked using set reproducibility criteria of the standard. All deviation values are within the allowed limits.

Reproducibility of sample preparation was tested for each analyte separately by preparation of nine tablets of the same sample, and each was measured once within the same day. The tablet preparation and measurement was carried out by one and the same analyst. Relative standard deviation (RSD) of the measurement series for *Method 1* is within the interval 1.0–9.2%. For *Method 2*, RSD for preparation reproducibility is within the interval 0.5–13.3%. Sodium has the highest RSD again. Comparing the results gained, it is visible that RSD of each analyte is higher for preparation reproducibility than for measurement reproducibility, which indicates that the greater part of the total mistakes is introduced into the measurement system by preparation and handling of samples, rather than by the measurement itself.

Validation results for both methods are shown in *Tables 3 and 4*.

3.2 Measurement uncertainty

Assessment of the total measurement uncertainty encompassed the quantification of the uncertainty components of the calibration line for each analyte, and uncertainty due to reproducibility of sample preparation for analysis. Measurement uncertainty was calculated according to the Guide to the Expression of Uncertainty in Measurement – GUM [25].

The uncertainty of the calibration line was determined using the following expressions:

a) Concentration variance:

$$S_{xx} = \sum_{j=1}^n (c_j - \bar{c})^2 \quad (2)$$

b) Residual standard deviation

$$S = \sqrt{\frac{\sum_{j=1}^n (A_j - (ac_j + b))^2}{n - 2}} \quad (3)$$

c) Standard uncertainty of calibration line

$$u(c_0) = \frac{S}{a} \sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(c_0 - \bar{c})^2}{S_{xx}}} \quad (4)$$

where:

Table 3. Validation parameter results for *Method 1*.**Tabelle 3.** Resultate für Validierungsparameter für *Methode 1*.

Analyte	Unit	linearity		accuracy		reproducibility of measurement		reproducibility of sample preparation	
		$y=ax+b$	R	$R_f(\%)$		\bar{x}	RSD(%)	\bar{x}	RSD (%)
Na ₂ O	wt%	$y = 5.34x - 1.50$	1	98.42		2.29	4.3	2.17	5.5
MgO	wt%	$y = 41.59x - 23.56$	1	102.58		4.45	1.8	4.44	2.4
Al ₂ O ₃	wt%	$y = 133.63x + 46.49$	1	99.95		16.58	0.5	16.56	1.5
SiO ₂	wt%	$y = 300.28 - 2080.45$	0.98	101.23		53.82	0.1	53.79	1.1
P ₂ O ₅	wt%	$y = 961.37x - 41.47$	1	100.14		0.16	3.2	0.15	3.3
S	wt%	$y = 1313.24x - 26.28$	1	98.67		1.89	1.2	1.84	1.3
K ₂ O	wt%	$y = 112.88x + 4.04$	1	99.97		0.70	1.9	0.68	2.3
CaO	wt%	$y = 167.34x + 8.22$	1	100.22		11.08	0.3	11.06	1.0
TiO ₂	wt%	$y = 273.05x + 9.12$	1	98.15		0.79	2.0	0.80	2.3
V	mg/kg	$y = 0.05x + 0.07$	1	100.76		226.7	7.7	239.3	7.8
Cr	mg/kg	$y = 0.08x + 3.08$	1	99.69		365.1	2.2	370.5	2.3
MnO	wt%	$y = 840.47x + 11.94$	1	98.92		0.16	1.9	0.16	2.5
Fe ₂ O ₃	wt%	$y = 625.64x + 2939.13$	0.99	98.69		10.50	0.2	10.51	1.2
Ni	mg/kg	$y = 0.10x + 1.81$	1	101.45		84.7	8.3	74.7	9.2

Table 4. Validation parameter results for *Method 2*.**Tabelle 4.** Resultate für Validierungsparameter für *Methode 2*.

Analyte	Unit	linearity		accuracy		reproducibility of measurement		reproducibility of sample preparation	
		$y = ax + b$	R	$R_f(\%)$		\bar{x}	RSD(%)	\bar{x}	RSD (%)
Na ₂ O	wt%	$y = 8.69 - 1.57$	0.99	102.21		0.88	8.9	0.82	13.3
MgO	wt%	$y = 163.30x - 222.20$	0.98	99.08		1.69	3.6	1.69	3.6
Al ₂ O ₃	wt%	$y = 87.76x - 233.18$	0.99	98.94		15.22	1.7	15.22	1.7
SiO ₂	wt%	$y = 432.15x - 15594$	0.98	101.36		52.86	0.5	52.86	0.5
P ₂ O ₅	wt%	$y = 1939.50x - 2582.3$	0.98	94.03		1.39	6.4	1.39	6.4
SO ₃	wt%	$y = 995.46x - 1733.4$	0.99	103.50		9.52	3.0	10.02	3.2
K ₂ O	wt%	$y = 681.46x + 250.62$	0.98	97.31		1.30	5.7	1.3	5.7
CaO	wt%	$y = 690.5x - 997.56$	0.99	100.47		5.24	1.2	5.24	1.1
TiO ₂	wt%	$y = 951.82x - 233.69$	0.98	98.89		0.79	1.1	0.79	0.8
Fe ₂ O ₃	wt%	$y = 2015.1x - 1782.1$	0.99	101.84		10.87	0.6	10.74	0.9

c_j - is the concentration of the analytes covered by calibration,

A_j - X-ray intensity,

a - calibration line slope,

p - number of measurement in the test sample routine,

n - number of measurements in calibration line,

c_0 - analyte content in test sample,

\bar{c} - mean analyte concentration in calibration line.

Standard uncertainty of sample preparation reproducibility was calculated according to the expression:

$$u(x_{pon}) = s(x_{pon}) = \frac{SO(x_{pon})}{\sqrt{n}} \quad (5)$$

where:

SO - standard deviation of results when determining preparation reproducibility,

n - number of measurements in routine.

The uncertainty of the calibration line and the uncertainty of the sample preparation were calculated for each analyte in both

methods. In the comparative presentation of their relative standard uncertainties *Figure 3*, it is visible that the preparation of samples for analysis is accountable for the higher contribution to the total measurement uncertainty of the method. The total expanded measurement uncertainty of each analyte for both methods was calculated using a coverage factor $k = 2$.

The total expanded measurement uncertainties, along with the measurement results, are presented in *Table 5*.

3.3 Application of methods for analysis of real samples

Test method validation proved that both methods are suitable for the stated purpose and that they can be applied to actual samples of solid residue after liquid and solid fuel combustion in furnaces.

The described method validation showed that the sample preparation for analysis has a great influence on the result accuracy. The residue samples after fuel oil combustion were analysed using *Method 1*. The composition of these residues is to the greatest extent influenced by the content of vanadium (152 mg/kg),

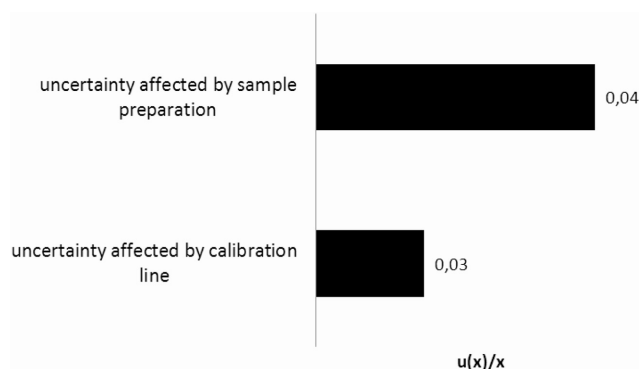


Figure 3. Comparison of relative measurement uncertainties. (Method 2)

Bild 3. Vergleich der relativen Messunsicherheiten. (Methode 2)

Table 5. Results of sample preparation reproducibility test presented with values of total measurement uncertainties of analytes for both methods.

Tabelle 5. Resultate der Prüfung der Wiederholbarkeit von Probevorbereitung mit Werten weiterer Messunsicherheiten für Analyten für beide Methoden

Total expanded measurement uncertainty		
Analyte	Method 1	Method 2
TiO ₂	U = 0.80 ± 0.03 wt%	U = 0.79 ± 0.04 wt%
Fe ₂ O ₃	U = 10.51 ± 0.73 wt%	U = 10.74 ± 0.28 wt%
Na ₂ O	U = 2.17 ± 0.29 wt%	U = 0.82 ± 0.11 wt%
MgO	U = 4.44 ± 0.27 wt%	U = 1.69 ± 0.11 wt%
Al ₂ O ₃	U = 16.56 ± 0.45 wt%	U = 15.22 ± 0.27 wt%
SiO ₂	U = 53.79 ± 3.50 wt%	U = 52.86 ± 3.83 wt%
P ₂ O ₅	U = 0.15 ± 0.03 wt%	U = 1.39 ± 0.15 wt%
S	U = 1.84 ± 0.16 wt%	U = 10.02 ± 0.80 wt%
K ₂ O	U = 0.68 ± 0.07 wt%	U = 1.30 ± 0.13 wt%
CaO	U = 11.06 ± 0.21 wt%	U = 5.24 ± 0.13 wt%
V	U = 239.3 ± 27.28 mg/kg	
Cr	U = 370.5 ± 16.73 mg/kg	
Ni	U = 74.7 ± 11.47 mg/kg	

sodium (6 mg/kg) and sulphur (2.28 wt%) in the fuel oil used for combustion. Table 6 shows the results of determination of the composition of residue samples after fuel oil combustion using Method 1.

Since the vanadium content is very important in residue from fuel oil combustion, its content was determined by separate

semiquantitative method on EDXRF spectrometer. The reason for determining it by another method is the high content of this element in the samples, which cannot be determined using Method 1, which limits the calibration line of vanadium to a range of less than 0.1 wt% of vanadium. The validity of the method for determining vanadium content was proved by one reference material with high vanadium content.

Table 6 shows that in the residue from the bottom of combustion chamber, the following analytes are the most represented ones: sodium oxide, potassium oxide, calcium oxide, vanadium and chromium, while on the steam superheater I and II the following are the most represented: magnesium oxide, aluminium oxide, silicon dioxide, phosphorus pentoxide, sulphur, iron oxide and nickel, which are also the most represented analytes determined in the second residue layer from bottom of combustion chamber, which proves the assumption that this second layer was created by falling from the higher furnace parts to the basic first residue layer from of combustion chamber bottom. TiO₂ and MnO are to be found in almost equal parts in the residue from bottom of combustion chamber and from superheater tubes.

Bottom ash samples gained from steam and brown coal combustion after the described preparation were analysed using Method 2. Besides steam and brown coal, the method was also applied to the ash resulting from combustion of coal with addition of patent fuel. The test results are shown in Table 7.

The test results of ash composition from Table 7 show that steam coal ash contains significantly more aluminium as compared to brown coal. The content of titan, silicon and calcium is somewhat higher in the steam coal ash than in brown coal ash. The content of magnesium, phosphorus, potassium and calcium is equal in both ashes.

A comparison of the steam coal ash and the ash from combustion of steam coal and patent fuel shows that the ash from the mixture has significantly lower silicon content, lower iron and aluminium content. In the combustion of the fuel mixture, the sodium and calcium content in the ash is significantly increased, and the titan and potassium content is increased. The magnesium and phosphorus content are equal in both samples.

4 Conclusions

This paper shows the development, validation and application of methods for determining the composition of solid residue after

Table 6. Results of chemical analysis of residue from fuel oil combustion gained using Method 1.

Tabelle 6. Resultate chemischer Analyse von Rückständen nach Schwerölverbrennung erhalten durch Anwendung der Methode 1.

Sample	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	S	K ₂ O	CaO	TiO ₂	V	Cr	MnO	Fe ₂ O ₃	Ni
1A-1. layer bottom of combustion chamber	5.75	3.81	3.16	5.79	0.80	3.60	1.15	3.85	0.37	58.58	4.36	0.034	5.20	4.83
1A-2. layer	3.03	5.59	5.70	12.94	1.01	1.47	0.51	2.76	0.41	32.89	2.92	0.026	11.27	10.49
1A	4.62	4.49	4.53	9.45	1.00	2.72	0.74	3.96	0.42	45.27	3.67	0.029	7.98	7.44
1B PPII	2.33	4.97	4.63	12.13	1.64	5.70	0.29	1.94	0.32	32.79	2.80	0.046	10.92	9.49
2A-1. layer bottom of combustion chamber	6.83	3.08	1.69	2.50	0.38	9.53	1.47	3.08	0.25	69.63	4.85	0.063	2.88	2.45
2A-2. layer	2.29	6.65	3.19	8.39	0.49	4.76	0.43	3.70	0.42	37.38	3.21	0.049	10.84	9.98
2A	3.27	5.62	2.68	6.57	0.47	6.33	0.67	3.77	0.39	44.42	3.62	0.049	8.69	8.44
2B PPII	1.35	7.48	4.43	9.79	0.79	4.43	0.21	2.14	0.40	34.21	3.20	0.034	11.12	10.50
2C PPI	2.36	5.99	3.88	6.11	0.65	4.05	0.49	2.76	0.39	54.15	4.53	0.05	5.74	5.80

Table 7. Results of chemical analysis of ash from steam and brown coal combustion and from combustion of coal with addition of patent fuel gained using *Method 2*.**Tabelle 7.** Resultate der chemischen Analyse von Asche von Stein- und Schwarzkohleverbrennung und von Verbrennung von Kohle unter Zusatz von Patenttreibstoff durch Anwendung der Methode 2.

Sample	Analyte Type	TiO ₂	Fe ₂ O ₃	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO
3.	Steam coal ash	1.39	6.95	0.47	1.67	21.03	54.89	1.14	0.22	1.50	6.91
4.	Brown coal ash	0.79	10.80	0.88	1.72	14.96	52.95	1.37	1.65	1.29	5.24
5.	Steam coal ash and patent fuel (combustion chamber)	1.97	4.06	0.99	1.65	19.53	45.88	1.11	0.74	2.06	18.64
6.	Steam coal ash and patent fuel (ash bin)	1.27	3.78	1.68	1.92	12.78	44.22	1.33	0.84	2.96	25.06

liquid and solid fuel combustion. Due to different composition of the initial fuels, the residue after their combustion could not be analysed by the same method. The method for determining the composition of residue created in steam generator furnaces in thermal power plants using fuel oil (*Method 1*) is not standardized, and encompasses simultaneous determination of 14 different analytes. The method for determining the ash composition after solid fuel combustion (*Method 2*) is standardized (ASTM D 4326-04) and comprehends determining 10 major and minor elements in ash. All measurements were conducted using an energy dispersive X-ray fluorescence (EDXRF) spectrometer: Oxford ED 2000. For the purpose of validation of *Method 1* and *2* the following validation parameters were determined: measurement reproducibility (*RSD* is from 0.1% to 8.9%), reproducibility of reference material preparation (*RSD* is from 0.5% to 13.3%), linearity ($r \geq 0.98$), accuracy (R_f is from 94.03% to 103.50%) and specificity.

The accuracy and reliability of the test depend mostly on the sample preparation, which is complex and must be carried out in several steps. The method linearity test showed greater deviations when the tablets were prepared with addition of binder.

The methods are suitable for the analysis of actual solid residue after fuel oil, coal and patent fuel combustion. The obtained results of the content of individual analytes in residue completely correspond to the data in literature, with a crucial significance of the initial fuel quality for their composition.

Energy dispersive X-ray fluorescence (EDXRF) proved to be an exceptionally good technique for determining the composition of solid residue after combustion. Its greatest advantages are speed, non-destructiveness and the possibility to simultaneously determine a large series of analytes in a wide concentration range.

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