Quantitative multi-element analysis of Argonne Premium Coal samples by ETV-ICP OES – A highly efficient direct analytical technique for inorganics in coal

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HIGHLIGHTS

- A novel direct solid sampling method for coal analysis was developed.
- Simultaneous quantitative multi-element analysis of major and trace elements.
- No need for any further sample pretreatment.
- Element release in dependence on temperature can be determined by ETV-ICP OES.
- The possibility of element speciation as result of release temperature is shown.

GRAPHICAL ABSTRACT
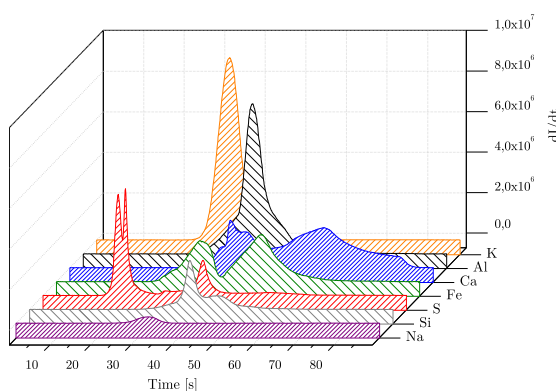
ARTICLE INFO

ABSTRACT

A new and highly efficient solid sampling method was developed for fast direct multi-element analysis in coals using electrothermal vaporization as sample introduction system for inductively coupled plasma optical emission spectrometry (ETV-ICP OES). With ETV coupled to ICP OES it is possible to analyze trace and major elements simultaneously in whole coal samples with a minimum effort of sample preparation and short analyzing times. The quantitative determination of Al, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Si, Ti, V and Zn by ETV-ICP OES in all eight Argonne Premium Coals, covering the rank range from lignite to semi-anthracite, is presented. The results are comparable with the reported element contents in literature. It is shown, that the fast direct solid sampling multi-element spectroscopic method, based on electrothermal vaporization of powdered samples, is proved to be a suitable alternative to labor intensive traditional methods.

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1. Introduction

The knowledge of inorganic constituents in coals is important for understanding the chemistry associated with coal formation and for evaluation of the coal quality. Especially for the processing industry, the prediction of the behavior of different coals in their

process is necessary, due to the possible negative impact of inorganics on system performance [1,2]. In addition to the problems during processing, like high temperature corrosion of material [3], catalyst poisoning [4], fouling and slagging [5], the total element contents and the knowledge of their species as well as their temperature dependent release behavior is required to determine the suitability of a specific coal treatment or cleaning strategy. Particularly the formation of deposits as a result of condensation on cool heat-transfer surfaces leads on the one hand to a sharp deterioration of efficiency, on the other to high-temperature corrosion of the installed materials [6]. Depending on the severity and the location of the deposits, they also lead to an increased need for cleaning systems. To prevent the formation of such deposits, to maximize the economics of coal processing and prevent downtime, empirical indices are needed to characterize the slagging, fouling and corrosion potentials of impurities in fuels. Bryers [5] and Hatt [7] provide a comprehensive study how the coal/ash chemistry correlate with furnace slagging, fouling and corrosion problems. According to this, the elements Al, Ca, Cl, Fe, K, Mg, Na, S, Si and Ti in coal, additionally Ni, Pb and V in other fuels (like coke, petroleum coke and refuse) occur in significant concentrations to contribute fireside problems [5,7]. In the case of biomass co-combustion attention should also be paid to the phosphorus content, caused by its normally high value in biomass in contrast to coal [8].

In literature a number of different techniques have been applied for characterizing the input materials used in processing. Vassilev et al. [9] and Huggins [10] provide a comprehensive review about the analytical methods for identification and quantification of major, minor and trace elements in coal. The manual "The Chemical Analysis of Argonne Premium Coal Samples", edited by Curtis A. Palmer [11], also presents analyzing methods for the chemical characterization of coal. Most of the described methods require time- and labor-consuming sample pretreatment, especially destroying the organic matrix or dissolve the samples for liquid sample introduction. Depending on the sample pretreatment it requires large amounts of high-purity or hazardous chemicals (like HF) and bears the risk of incomplete sample dissolution and contamination. Additionally certain elements are affiliated to organic phases (porphyrins, organometallics or acid salts) [12] and during ashing (preconcentration step for XRF – X-ray fluorescence spectroscopy), the losing of elements by volatilization is possible. Ideally the whole coal should be analyzed directly as solid sample to prevent chemical changes in the sample and consequently the possibility of element speciation is given.

As a result of the disadvantages of the traditional methods, there is a growing need for a rapid-process assisted analysis to assess the total content as well as the element distribution in energy resources and their combustion byproducts. The purpose of the present study was the development of a fast multi-element analytical method with simplified sample preparation, which is easy to calibrate, accurate and allows the simultaneous determination of all relevant elements in a high concentration range. The solid sampling technique electrothermal vaporization (ETV) in combination with the inductively coupled plasma (ICP) optical emission spectrometry (OES) combines these properties and overcomes the above described problems. Preliminary investigations on several samples of typical different quality sorts of rhenish lignite showed the potential of this fast direct analysis technique for simultaneously determination of major, minor as well as trace elements in whole coals.

For determination by ETV-ICP OES the sample, either liquid or solid, is placed in a graphite boat and is resistively heated up to a maximum temperature of 3000 °C in the ETV unit. During the heating process the analytes are vaporized with the assistance of a reaction gas and transported directly into the inductively coupled plasma of the emission spectrometer. Due to this working principle, different element species can be selectively and separated vaporized and so the possibility of element speciation is given. Thereby theoretically detection limits in the sub-ppm range are possible [13,14].

For validation of the developed multi-element method for quantitative analyses, the internationally recognized reference set of Argonne Premium Coals was analyzed by ETV-ICP OES. These coals, differing in rank, have been extensively characterized by a variety of other methods. The study "The Chemical Analysis of Argonne Premium Coal Samples", edited by Curtis A. Palmer, provided a good basis for comparison of obtained element concentrations by this study with published ones [11].

2. Experimental section

2.1. Reference materials and samples

(1) Reference materials (RM). Four multi element RM, two purchased from the National Institute of Standards and Technology (NIST) and two from the China National Analysis Centre for Iron and Steel (NCS) were used for calibration in this study. These coal standards were chosen, because they cover a wide rank range as well as a wide range of element contents.

(2) Argonne Premium Coals (APC). For identification and quantification of corresponding element contents by ETV-ICP OES, additionally to the reference materials the complete collection from the Argonne Premium Sample Coal Bank were measured (cf. Table 1). The set, a broad array of coals, collected, prepared and stored under controlled conditions, consists of a suite of eight samples of varying rank and have been used worldwide in numerous coal studies [15].

2.2. Instrumentation

2.2.1. ETV-ICP OES

The measurements were performed using two ICP OES spectrometers (ARCOS EOP and ARCOS SOP, SPECTRO Analytical Instruments, Kleve, Germany), differing in plasma view. In the case of axial viewing, the plasma torch operates in a horizontal orientation and the analytical zone is observed from the end of the plasma (end on plasma, EOP). In radial view mode, the plasma is observed from the side (side on plasma, SOP) in a vertical torch orientation. The analytical advantages and disadvantages of those kinds of spectrometer, using Rowland's circle for detection, are described in the article of Hou et al. in Encyclopedia of Analytical Chemistry [16].

For sample introduction both spectrometers were interfaced via PFA transport tubing to solid sampling ETV units (ETV 4000C, Spectral Systems, Fuerstenfeldbruck, Germany). For fully automatic sampling of the graphite sample boats, both ETV systems are

Table 1
Sample identification and rank of coal samples used in this work.

Sample ID	Seam	Rank
UF	Upper Freeport	Medium volatile bituminous
WY	Wyodak Anderson	Subbituminous
IL	Illinois	High volatile bituminous
PITT	Pittsburgh	High volatile bituminous
POC	Pocahontas	Low volatile bituminous
UT	Blind Canyon	High volatile bituminous
WV	Lewison Stockton	High volatile bituminous
ND	Beulap-Zap	Lignite
1632d	Pittsburgh	Bituminous
1635a	Wyodak Anderson	Subbituminous
FC28123	Not specified	Anthracite
FC28127	Not specified	Bituminous

equipped with an AD50 auto-sampler. The temperature of the ETV furnace can be regulated in the range from 20 to 3000 °C, but in the view of the durability of the graphite tubes a maximal temperature of 2600 °C should not be overrun. The temperature profile and heating time are free programmable. For the regulation of the furnace and exact temperatures, an internal pyrometer measures continuously the actual furnace temperature. The internal furnace pyrometer is calibrated with an external pyrometer (PL31 AF4, Keller MSR, Ibbenbueren-Laggenbeck, Germany) each measuring day, to ensure correct temperatures. During heating, the compounds of the sample are vaporized or transformed into volatile halogenated species. The usage of a halogenated reaction gas (here: CCl_2F_2), which is added to the inner gas phase of the oven (cf. Fig. 1), is necessary to ensure complete volatilization of carbide-forming and high-boiling elements and also to improve the transport efficiency of the dry aerosol to the plasma of the spectrometer [17].

The released elements are transported as hot vapor through the nozzle of the graphite tube. Immediately after the end of the nozzle cold bypass gas (Ar) flows around the hot vapor to form a transportable dry aerosol in the gas phase and prevent condensation on cold surfaces – this step is important for a high and stable transportation efficiency of more than 90% [13]. The dry aerosol is transported through a corundum aerosol-tube and a PFA transport-tube to the plasma of the spectrometer. In the plasma, after atomization respectively ionization and excitation, the atoms and ions emit electromagnetic radiation with specific wavelengths for each element. These emission lines were detected simultaneously in a Rowland-circle spectrometer in Paschen-Runge mount (130–770 nm).

For analyzing the total element contents of the samples, a heating program with a relatively slow heating rate was used to prevent a detector overflow due to a high release of analytes (cf. Table 2). For best results in respect of limit of detection (LOD), a fast heating rate would be advantageous but this is not necessary for coal samples due to the partly high element concentrations. The contents of elements in the investigated samples vary over a wide concentration range [11]. Due to the fact that LOD and working range are specific to the used spectral lines, the selection of appropriate wavelengths among the enormous variety of emission lines is very important. By the use of the solid sampling introduction system (ETV) the input of sample material to the plasma of the ICP is very high, therefore emission lines with low sensitivity and a wide linear calibration range had to be chosen. The selected

Table 2
ETV program.

Step	Ramp	
	t (s)	T (°C)
Preheating	5	50
Evaporation	55	2350
Cleaning	20	2350

emission lines and the other optimized instrumental operating conditions used for final analysis are summarized in Table S-1 in the Supporting Information.

2.3. Measurement procedure

The eight APC and the four RM were dried at 107 °C ± 2 °C in a drying cabinet without circulation. To ensure the use of clean graphite boats for measurement by ETV-ICP OES, the empty boats were purified by a thermal cleansing run up to a temperature of 2400 °C. In order to check the influence of rank of coal on the calibration, the element concentrations should be calibrated by using coal reference materials differing in rank. For subsequent quantification, ten samples of NIST SRM 1632d and five calibration samples of all other RM were weighed into the graphite boats in a range from 0.01 mg to 7 mg. As the concentrations of the elements are known from the certified values the absolute mass of the element content can be calculated from the respective sample weight. For the determination of the detection limits for the coal corresponding carbon matrix, twenty graphite boats, containing 3 mg high purity graphite powder, were measured as blanks.

For verification of accuracy of the developed method, two reference materials, NIST SRM 1632d and NIST SRM 1635a, were measured as control samples ten times. In addition to this, all APC were weighed in a known mass of about 3 mg into the graphite boats to validate the developed analysis method. Therefore, the APC were analyzed in triplicate.

3. Results and discussion

Additionally to the calibration functions and the detection limits, precision and trueness of the developed method was under study. For verification of the used solid sampling spectroscopic method the complete set of the Argonne Premium Coal sample
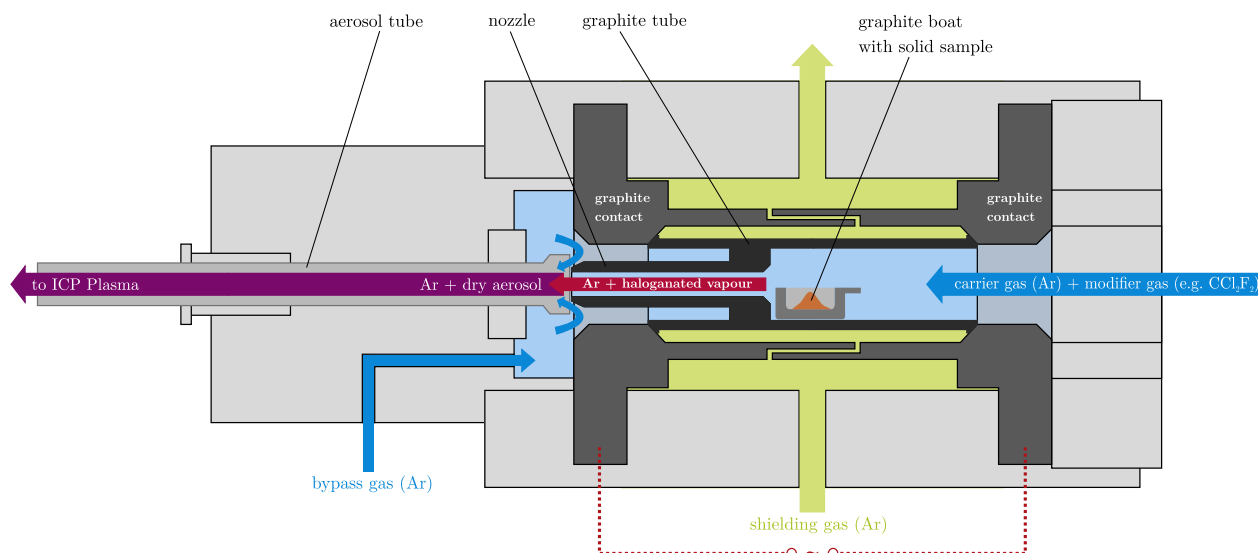

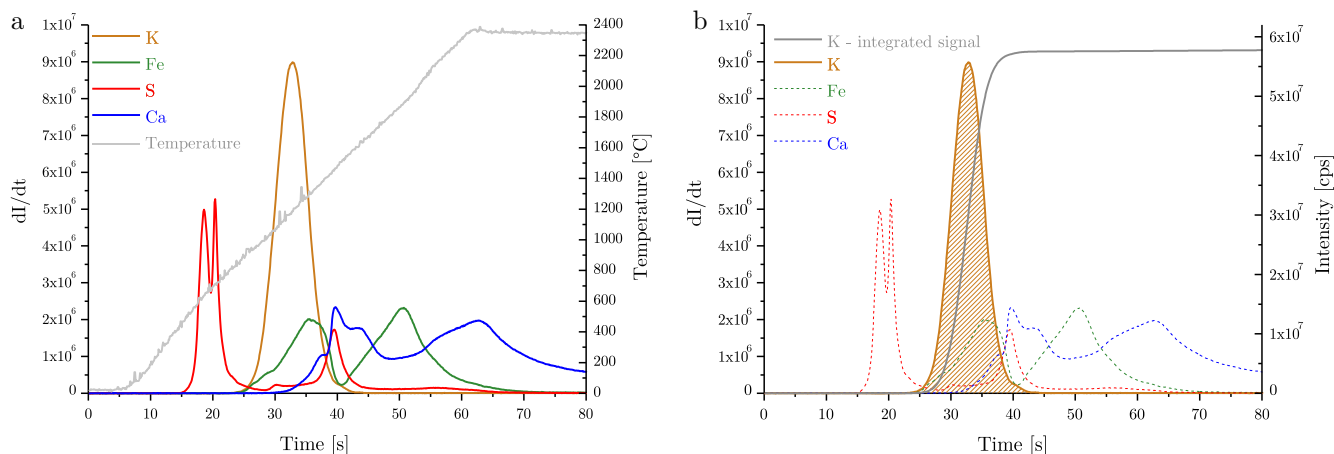**Fig. 1.** Basic construction of the ETV graphite furnace.

Fig. 2. a. Transient signals of selected elements for IL, measured by ETV-ICP OES (SOP). b. Integration of potassium signal.

program was analyzed. Detailed statistical data are given in the Supporting Information as box-and-whisker plots.

The quantitative multi-element analysis by ETV-ICP OES is based on the vaporization of elements depending on temperature. Exemplary the obtained transient emission signals of Ca, Fe, K and S of the APC from the seam in Illinois (IL) are shown in Fig. 2a. These signals alone can only be used for fast qualitative analysis. In order to offer a quantitative conclusion, the analysis must be based on a calibration for each element. Therefore the transient signals have to be integrated (10–80 s) and related to the respective sample masses (cf. integrated Signal of potassium in Fig. 2b) to get the peak area (cf. Fig. 2b).

3.1. Calibration

An external calibration with coal reference materials different in rank was developed. In addition to this, the stability of the system and the need for daily calibration was checked. The detected peak areas were plotted versus the calculated absolute element masses of the corresponding RM. As shown in Fig. 3, the obtained data are illustrated using the element potassium. The calibration-samples with the additional label "+7 days" were measured seven days later on equal conditions to check the stability of the system.

In accordance with IUPAC recommendations the relative standard deviation of the procedure (RSD_P) is an absolute measure of precision for the calibration. It was calculated from the standard error of the regression function divided by its slope, in relation to the mean value of all analyte masses used for the calibration

function (reference mass – m_{ref}), respectively. The detection limits (LOD) for the analytes were based on standard deviation of the blanks (3.3σ) divided by the slope of the calibration curve. The results, obtained by measuring with ETV-ICP OES in radial (SOP) and axial view (EOP), are summarized in Table 3. It was possible to calibrate with all four coal reference materials, different in rank. Linear calibration functions over three to four orders of magnitude were obtained and in compliance with the calibration functions received seven days later. This indicates on the one hand that there are no effects on calibration by the coal rank and on the other hand that daily calibration is not necessary. Upon closer observation of the statistical data, it is necessary to take into account that the obtained slopes and LODs based on low sensitive emission lines. Especially the high sensitive EOP requires lines with low emission, due to the partially very high analyte concentrations in the coal samples. With the chosen emission lines an average RSD_P of 11% (SOP) or 17% (EOP) was obtained (cf. box-and-whisker plot in Fig. S-1 in Supporting Information). Therefore the RSD_P are in the typical range of 20% for solid sampling spectrometry.

The higher RSD_P obtained by EOP are based on the higher effects on background and interferences caused by the very high concentrations of some elements in coal, especially of alkali metals. By measurements with radial view, it is possible to change the height of the plasma observation zone to avoid the emission in the hottest zones in the ICP-plasma. The high sensitivity of the solid sampling spectroscopy method could be demonstrated by the obtained LOD's in the difficult matrix coal, which are in the lower ppm range.
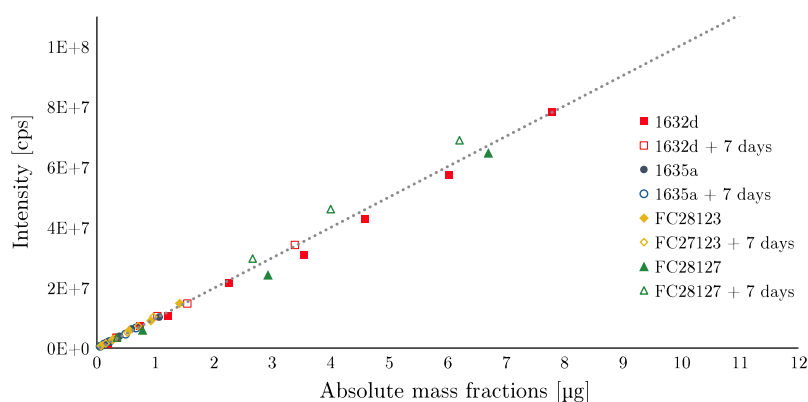

Fig. 3. ETV-ICP OES (SOP) calibration of the element potassium with different reference materials (cf. Table 1).

Table 3
Statistical data for the calibration functions, obtained by ETV-ICP OES.

	SOP					EOP				
	Slope (cts mg⁻¹)	RSD_P (%)	m_{ref} (µg)	LOD (ppm)	R^2	a [cts mg⁻¹]	RSD_P (%)	m_{ref} (µg)	LOD (ppm)	R^2
Al	1.437E+09	10.93	26.212	2.853	0.9865	6.259E+08	10.61	30.447	12.77	0.9891
Ba	6.540E+10	5.53	0.289	0.148	0.9982	n/s				
Ca	1.914E+09	12.34	19.081	2.755	0.9902	1.958E+09	24.07	15.840	1.880	0.9561
Cr	3.839E+10	14.50	0.021	0.076	0.9872	4.508E+11	22.60	0.032	0.010	0.9557
Cu	2.616E+11	5.84	0.035	0.050	0.9951	1.754E+12	14.76	0.027	0.450	0.9697
Fe	6.892E+08	12.27	10.305	4.350	0.9867	3.015E+11	18.79	16.210	3.179	0.9688
K	1.008E+10	11.11	1.854	0.567	0.9935	n/s				
Mg	9.687E+09	9.63	3.162	0.462	0.9926	4.295E+10	23.76	1.844	0.447	0.9410
Mn	1.403E+12	12.41	0.024	0.004	0.9893	8.949E+11	13.39	0.036	0.024	0.9828
Na	5.861E+08	7.19	1.497	6.451	0.9956	6.493E+09	15.64	1.914	1.262	0.9798
Ni	6.027E+10	11.06	0.015	0.053	0.9895	1.039E+12	19.02	0.021	0.326	0.9630
P	2.556E+10	11.16	0.439	0.118	0.9865	2.303E+11	13.21	0.329	0.685	0.9762
Pb	6.659E+10	11.28	0.008	0.032	0.9909	1.566E+11	24.17	0.013	0.693	0.9685
S	2.180E+08	3.79	25.291	32.630	0.9994	1.352E+09	14.45	2.905	59.79	0.9846
Si	1.679E+08	6.23	66.248	16.820	0.9950	1.152E+09	8.34	53.71	52.91	0.9912
Ti	9.685E+09	20.26	1.694	0.675	0.9760	4.104E+09	14.19	2.062	1.238	0.9798
V	n/s					1.034E+12	24.46	0.034	0.048	0.9262
Zn	1.437E+09	17.92	0.022	0.654	0.9861	2.771E+12	16.50	0.025	1.746	0.9682

Abbreviations: RSD_P – relative standard deviation of the procedure (%), m_{ref} – reference mass for the calculated RSD_P, LOD – limit of detection (sample mass 3 mg), R^2 – coefficient of determination for the calibration functions, n/s – not specified.

Table 4a
Comparison of concentrations for NIST SRM 1632d determined from this study with certified values and the resulting recovery.

	1632d – SOP		1632d – certificate	1632d – EOP	
	Mass fraction	R (%)	Mass fraction	Mass fraction	R (%)
Al	0.9526 ± 0.0394	104	0.912 ± 0.005	0.9441 ± 0.0192	104
Ca	0.1379 ± 0.0072	96	0.144 ± 0.003	0.1402 ± 0.0190	97
Fe	0.7459 ± 0.0445	100	0.749 ± 0.016	0.7450 ± 0.0367	99
K	0.1088 ± 0.0027	99	0.1094 ± 0.0026	n/s	
Mg	0.0377 ± 0.0012	97	0.0390 ± 0.0006	0.0150 ± 0.0022	38
Na	0.0309 ± 0.0010	104	0.0297 ± 0.0004	0.0316 ± 0.0011	106
S	1.3771 ± 0.0289	94	1.4620 ± 0.074	1.4560 ± 0.0273	100
Si	1.6224 ± 0.1046	98	1.65 ± 0.03	1.6487 ± 0.0536	100
Ti	0.0467 ± 0.0019	98	0.0477 ± 0.0010	0.0455 ± 0.0019	95
Ba	40.53 ± 1.90	100	40.42 ± 0.89	n/s	
Cr	15.66 ± 0.74	114	13.7 ± 0.1	15.64 ± 0.36	114
Cu	6.37 ± 0.41	109	5.83 ± 0.31	5.77 ± 0.23	99
Mn	12.99 ± 0.55	99	13.1 ± 0.4	13.87 ± 1.05	106
Ni	11.55 ± 0.47	116	10 ± n/s	11.36 ± 0.23	114
P	137.42 ± 9.02	n/s	n/s	130.10 ± 8.84	
Pb	3.93 ± 0.16	102	3.845 ± 0.042	3.95 ± 0.20	103
V	n/s	n/s	23.74 ± 0.01	19.04 ± 0.87	80
Zn	12.75 ± 1.09	99	12.9 ± 1.2	11.79 ± 1.18	91

The concentrations of the first nine elements (Al through Ti) are in % and for the remaining elements (Ba through Zn) they are in ppm, respectively. R – recovery, n/s – not specified.

Table 4b
Comparison of concentrations for SRM 1635a determined from this study with certified values and the resulting recovery.

	1635a – SOP		1635a – certificate	1635a – EOP	
	Mass fraction	R (%)	Mass fraction	Mass fraction	R (%)
Al	0.5430 ± 0.0079	100	0.5437 ± 0.0063	0.5507 ± 0.0074	101
Ca	1.1113 ± 0.0404	102	1.087 ± 0.014	1.4431 ± 0.0345	133
Fe	0.2769 ± 0.0041	112	0.2472 ± 0.0022	0.2737 ± 0.0059	111
K	0.0204 ± 0.0007	109	0.0187 ± 0.0008	n/s	n/s
Mg	0.2628 ± 0.0067	114	0.2303 ± 0.0031	0.2414 ± 0.0010	105
Na	0.1069 ± 0.0008	104	0.1031 ± 0.0078	0.1093 ± 0.0004	106
S	0.2965 ± 0.0021	101	0.294 ± 0.022	0.3156 ± 0.3389	107
Si	0.7965 ± 0.0105	n/s	n/s	0.9862 ± 0.0042	n/s
Ti	0.0601 ± 0.0008	115	0.0524 ± 0.0009	0.0594 ± 0.0003	113
Ba	378.52 ± 6.29	106	357.8 ± 9.1	n/s	n/s
Cr	3.58 ± 0.12	101	3.56 ± 0.18	3.40 ± 0.04	96
Cu	12.58 ± 0.68	110	11.42 ± 0.74	11.41 ± 0.21	100
Mn	6.59 ± 0.10	99	6.69 ± 0.14	6.77 ± 0.12	101
Ni	5.40 ± 0.08	101	5.37 ± 0.30	4.29 ± 0.08	80
P	219.06 ± 4.16	n/s	n/s	226.17 ± 3.00	n/s
Pb	2.78 ± 0.08	98	2.85 ± 0.51	3.99 ± 0.08	140
V	n/s	n/s	13.34 ± 0.59	16.00 ± 0.16	120
Zn	13.22 ± 1.46	181	7.3 ± 1.5	6.54 ± 0.26	90

3.2. Accuracy of the analytical method

To evaluate precision and trueness of the method, the reference materials NIST SRM 1632d and NIST SRM 1635a were included as control samples to each measuring run. Thereby the precision of the method was specified by replicate analyses and the trueness was calculated by the comparison of the analyte concentrations, determined by ETV-ICP OES and with those provided by the certificates. The results are summarized in Table 4, whereby the trueness is based on the percent recovery (R) and the precision is given as standard deviation (SD) for each element, respectively. Thereby the concentrations of major elements (Al through Ti) are reported in percent and them of trace elements (Ba through Zn) in ppm. Unfortunately, phosphorous has not been specified for the used NIST SRM 1632d and NIST SRM 1635a, so trueness and the resulting recovery cannot be determined. For the other elements, recoveries could be obtained in the range of 90–120% and precisions are clearly lower than 10% relative standard deviation (RSD). More detailed statistical information are shown in the box-and-whisker plots in Fig. S-2/3 in the Supporting Information. Therefore, the precision is higher than usually for ETV-ICP spectrometry, which have RSDs of about 10%, typically [18]. Additionally, the obtained RSDs in this study are lower than those given in the certificates. The results of measurements by ETV-ICP OES in radial view (SOP) are comparable to those determined in axial plasma view (EOP). In summary, adequate accuracy is achieved and the expectations of technologists who need fast analytical information is fulfilled with a measuring time of approximately two minutes per sample by the use of this direct sampling method.

3.3. Applicability of the analytical method

To validate the applicability of the developed method, the specific element contents in the APC were analyzed by ETV-ICP OES. To illustrate the comparison of the obtained values with the
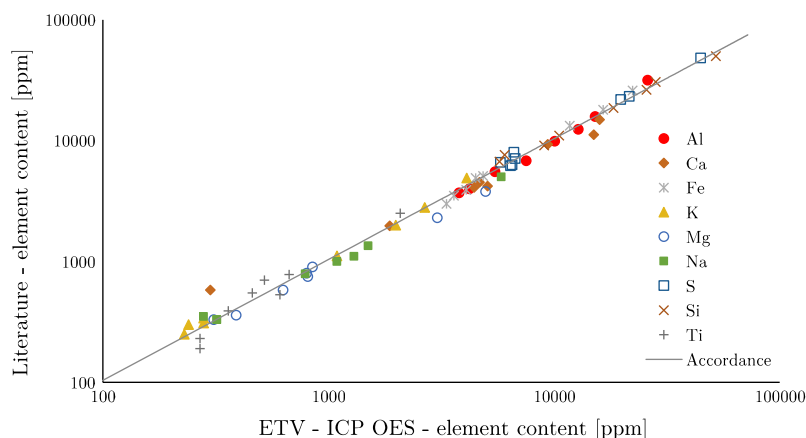
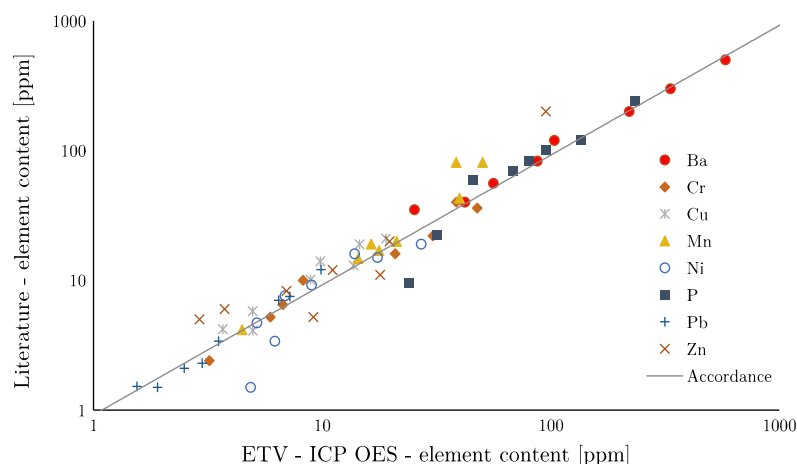**Fig. 4a.** Comparison of measured with literature values of all APC for major elements.

Fig. 4b. Comparison of measured with literature values of all APC for minor and trace elements.
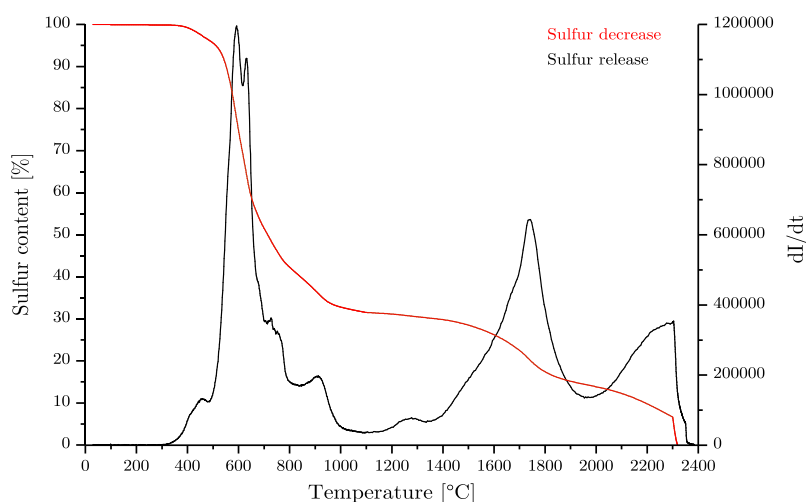

Fig. 5. Sulfur release or decrease depending on temperature for SRM 1632d, measured by ETV-ICP OES (EOP).

published ones, both sets of data were plotted against each other in Fig. 4a for major elements and in Fig. 4b for minor and trace elements. The lines in the figures represent the accordance between literature and measured values and it could be shown that the

obtained values and the published values are in sufficient agreement. The obtained recoveries were in the range of 80–140% (cf. Fig. S-4 in the Supporting Information). For all elements, the concentrations were well above detection limits by ETV-ICP OES. The

data of triplicate analyses of the eight coals, within their standard deviation, is given in comparison with APC reference values [11] in Table S-2 in the Supporting Information. The elements, which are out of the linear working range are underlined. By comparison the RSD's reported in the literature, the obtained standard deviations are thus in the area of the heterogeneity of the samples, due to considerably lower RSD's than 10 % (cf. Fig. S-5 in the Supporting Information). The obtained adequate accuracy is the proof that both applied methods offer a simple and rapid technique to determine elements with a wide concentration range in coals with different rank.

3.4. Analysis of element release–element speciation

In some cases the total element content will not provide sufficient information about the quality of coal for the processing industry, due to there is a strong influence of element species on their behavior during processing of energy resources. For example, the responsibility for formation of deposits during combustion is not based on the total sulfur content itself, but on the presence of minerals (e.g. pyrite) in a high-sulfur coal. Therefore additionally to the total element content the analysis of the different element species is reasonable. The direct determination of different sulfur forms additional to elemental sulfur in coals by ETV-ICP OES has been reported previously [19]. The method ETV-ICP OES, as solid sampling analysis technique for element speciation, is based upon the fact that different element compounds mostly are decomposed at specific different temperatures. Consequently, on controlled thermal decomposition of coal in argon atmosphere it is possible to determine the release of elements as a function of temperature and to draw conclusions about element species with qualitative and quantitative information. With the increase of temperature, various sulfur compounds of the sample are decomposed and the mass percentage of each resulting sulfur release can be measured. Results are plotted with temperature on the *X*-axis and mass loss on the *Y*-axis (cf. Fig. 5). For better illustration of the sulfur distribution the emission signal also can be plotted as the first derivative (2. *Y*-axis). In summary, additionally to the total element content, the possibility of element speciation and statements about element release as a function of temperature are given within the same short measurement-time.

4. Conclusions

The developed direct solid sampling ETV-ICP OES method enables simultaneous quantitative multi-element analysis of coals without need for any further sample pretreatment. The rapid method proved a high working range, a precision clearly lower than 10% RSD and low limits of detection in the sub ppm range. In addition to the determination of total element contents, states about the release temperature of an element and the possibility of element-speciation is given. This validated method can be automated to a large extent of samples and is applicable for processes accompanying analyses. Therefore it is time and cost effective and well suited for the fast characterization of elements and the possibility of speciation in coal is given. This demonstrates the high analytical capability and universal applicability of the direct solid sampling method ETV-ICP OES for the determination of elements in the matrix coal.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2014.12.057.

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