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Determination of heavy metals in activated charcoals and carbon black for Lyocell fiber production using direct solid sampling high-resolution continuum source graphite furnace atomic absorption and inductively coupled plasma optical emission spectrometry

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ABSTRACT

Reactivity and concentration of additives, especially activated charcoal, employed for the Lyocell process, enhance the complexity of reactions in cellulose/*N*-methylmorpholine-*N*-oxide monohydrate solutions. Analytical control of the starting materials is a basic requirement to know the concentration of heavy metals, which are potential initiators of autocatalytic reactions. Seven activated charcoal and two carbon black samples have been analyzed regarding their content of seven elements, Cr, Cu, Fe, Mn, Mo, Ni and V using direct solid sampling high-resolution continuum source graphite furnace AAS (SS-HR-CS GF AAS) and inductively coupled plasma optical emission spectrometry (ICP OES) after microwave-assisted acidic digestion as a reference method. The limits of detection of the former technique are 1–2 orders of magnitude lower than those of ICP OES and comparable to those of more sophisticated techniques. For iron the working range of HR-CS GF AAS has been expanded by simultaneous measurement at two secondary absorption lines (344,099 nm and 344,399 nm). Partial least-squares regression between measured and calculated temperatures for beginning exothermicity (T_{on}) has been used to investigate the prediction capability of the investigated techniques. Whereas the ICP OES measurements for seven elements resulted in an error of prediction of 3.67%, the results obtained by SS-HR-CS GF AAS exhibited a correlation coefficient of 0.99 and an error of prediction of only 0.68%. Acceptable correlation has been obtained with the latter technique measuring only three to four elements.

1. Introduction

Direct dissolution of cellulose in *N*-methylmorpholine-*N*-oxide monohydrate (NMMO) was established as the well-known Lyocell process in the last decade [1–3]. Compared to conventional fiber-making processes, cellulose is dissolved without chemical derivatization, and the solvent can be recovered almost completely. Using the Lyocell technology beyond the textile sector, new fields are opened up for generating innovative materials. The physical dissolving process of cellulose and the high loading capacity of the solution enable novel opportunities for incorporating soluble blend components or even insoluble substances with particle sizes in the micrometer and nanometer ranges [4]. Accompanied by an only moderate deterioration of the textile-physical properties, the incorporation of ion exchange resins, super absorbing polymers, charcoal, carbon black, ceramics, etc. results in functional products such as filters for heavy metals, water absorption articles, adsorbers for organic compounds or conductive materials [5,6]. Neutral adsorbers, especially activated charcoal, are used to remove contaminations from liquids and gases. Technological applications of adsorbers are often limited by their granular shape that makes immobilization in cartridges or embedding methods necessary. Based on a cellulose matrix, a new class of materials with tailored adsorption characteristics is produced; additionally, fleeces can be manufactured from such adsorbing fibers. Preliminary

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studies show that Lyocell fibers, modified e.g. with activated charcoal, possess a rough and irregular exterior. Owing to the enlarged surface, extraction of organic compounds from vapor might be easier compared to a pure Lyocell fiber. Moreover, the addition of conductive carbon black produces fibers with a conductivity behavior across a wide electrical resistance range by keeping satisfactory textile-physical properties. Interesting applications in the form of electrical shielding materials for use in sensitive production areas and as heatable textiles are opened.

Although the dissolution of cellulose in NMMO and the fiber spinning are entirely physical processes, chemical alterations may appear under industrial conditions, and so-called thermal runaway reactions might occur, which could end up in deflagrations. The solvent NMMO is thermally instable and reactive, particularly in the presence of heavy metals [7–9]. Furthermore, higher amounts of additives have to be incorporated to reach an efficient effect. Thus, reactivity and concentration of the additives enhance the complexity of reactions in cellulose/NMMO solutions [10,11]. Most additives decrease the onset temperature (T_{on}), which is defined as the beginning of exothermicities and has to serve as a reference for the evaluation. In general, T_{on} is measured precisely by means of reaction calorimetry, but this is very time-consuming and only possible after having prepared the solution [10]. Nevertheless the thermal stability has to be characterized by other variables, apart from T_{on}. Impurities in additives can severely attract reactions in the cellulose/NMMO system resulting in a lower thermostability; namely metals and halogens are embedded in meso- and micropores of activated charcoals and carbon black. Depending on their valence state heavy metals might interfere with the hydrogen bond system of cellulose and NMMO, initiating redox or radical reactions. Precise evaluation of additive properties such as surface topology and metal content is therefore a must for the choice of the proper materials.

Usually the determination of metallic elements in additives is carried out after acid digestion or extraction using atomic absorption spectrometry (AAS) or inductively coupled plasma optical emission spectrometry (ICP OES). However, activated charcoal and carbon black samples are particularly difficult to bring into solution, requiring long and complex procedures. Digestion methods including ash fusion [12] or wet digestion using a mixture of concentrated hydrofluoric, nitric and sulfuric acids [13] have been proposed for that purpose. Microwave-assisted digestion can speed up dissolution and diminish losses of volatile trace elements and contamination from reagents and sample handling [14,15]. However, most digestion mixtures contain explosive $HClO_4$ and/or toxic HF. Efforts have therefore been undertaken to replace these acids by using only HNO_3 and H_2O_2 [16,17].

The direct analysis of solid samples has a number of advantages over solution analysis, particularly in cases where the samples are difficult to digest, such as: (i) a significantly reduced risk of contamination and loss of analytes; (ii) an increased sensitivity, as samples are not diluted; (iii) the use of expensive and/or hazardous reagents is not required, resulting in both economic and environmental benefits; (iv) results are obtained more rapidly [18,19]. However, only a few reports were published about direct solid sampling (SS) for coal analysis. Apart from the determination of Cd and Pb by graphite furnace AAS (GF AAS) using Ru as a permanent modifier and calibration against a solid certified reference material (CRM) [20] and the determination of As [21] using the same technique, most of the non-digestion procedures use slurry sampling and the application of electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) [22] or GF AAS [23].

Meanwhile, initial limitations of direct SS-GF AAS have been overcome; firstly, introduction of solid samples is nowadays supported by state-of-the-art equipment [19]; secondly, aqueous standards can often be used in solid sample analysis, particularly when high-resolution continuum source AAS (HR-CS AAS) [24] is used for the analysis [19]; thirdly, relative standard deviations (RSD) $\leq$10% can often be accomplished. Schaeffer and Krivan [25] determined 14 elements in high-purity graphite using SS-GF AAS and aqueous standards for calibration; the authors found that the limits of detection (LOD) of this technique were better than those obtained by ETV-ICP OES and instrumental neutron activation analysis. Direct SS analysis using HR-CS GF AAS has been applied for the determination of Cd in coal with Ir as the permanent modifier [26] and of Tl [27] and Pb [28] without a modifier, using calibration against aqueous standards in all cases.

The aim of this work has been to investigate the heavy metal content of activated charcoals and carbon black (soot) of different reactivity employed for the Lyocell process. The feasibility of direct determination of Cr, Cu, Fe, Mn, Mo, Ni and V in solid coal samples using SS-HR-CS GF AAS and the possibility of calibration against aqueous standards has been investigated, and the results have been compared with those obtained by ICP OES after microwave-assisted digestion. Furthermore, the results obtained with both techniques have been compared for their ability to predict the onset temperatures (T_{on}) of modified cellulose/NMMO solutions.

2. Experimental

2.1. Instrumentation

A prototype high-resolution continuum source atomic absorption spectrometer, built at ISAS, Berlin, has been used for all AAS measurements in this work. The equipment is based on a Model AAS 6 Vario (Analytik Jena AG, Jena, Germany) from which all optical components, including the detector and associated controls have been removed and replaced by a HR-CS spectrometer similar to that described by Becker-Ross et al. [29]. This spectrometer consists of a high-intensity xenon short-arc lamp operating in a hot-spot mode, a high-resolution double monochromator and a charge coupled device (CCD) array detector. The double monochromator consists of a pre-dispersing prism monochromator and a high-resolution echelle grating monochromator, both in Littrow mounting, resulting in a resolution of $\lambda/\Delta\lambda \approx 140{,}000$, corresponding to a resolution per pixel of ~2–3 pm within the spectral range used in this work. The system is controlled by a Pentium III personal computer (1000 MHz), running a data acquisition program developed at ISAS Berlin. Details of this equipment have been described previously [24,27]. The peak volume selected absorbance (PVSA) [30], i.e., the integrated absorbance summated over three pixels around the line core ($A_{\Sigma 3,\mathrm{int}}$) has been used for signal evaluation, unless stated differently, as the best signal-to-noise (S/N) ratio has been obtained under these conditions.

The conventional transversely heated graphite tube atomizer system supplied by Analytik Jena together with the Model AAS 6 Vario has been used throughout. All experiments were carried out using pyrolytically coated SS graphite tubes without dosing hole (Analytik Jena Part No. 407-A81.303) and SS platforms (Analytik Jena Part No. 407-152.023). Solid samples were weighed directly onto the SS platforms using an M2P microbalance (Sartorius, Göttingen, Germany, accuracy 0.001 mg) and inserted into the graphite tube using a pre-adjusted pair of tweezers, which is part of the SSA 5 manual solid sampling accessory (Analytik Jena). Aqueous standards were injected manually onto the SS platform using micropipettes with disposable tips. Argon (99.996%, White Martins, São Paulo, Brazil) was used as purge and protective gas. The general graphite furnace temperature program is shown in Table 1, and the operating parameters for the determination of seven elements in activated charcoal and carbon black samples are shown in Table 2.

Table 1
Graphite furnace temperature program for the determination of Cr, Cu, Fe, Mn, Mo, Ni and V using SS-HR-CS GF AAS.

Program stage	Temperature (°C)	Ramp (°C s^{-1})	Hold time (s)
Drying 1	90	15	10
Drying 2	130	10	15
Pyrolysis	Table 2	100	15
Atomization[a]	Table 2	3000	10
Cleaning	2650	1000	5

[a] Purge gas (argon) flow rate 2 L min^{-1} in all stages except during atomization where the gas flow was interrupted; reading in this stage.

The ICP OES analyses have been carried out using an OPTIMA 2000 DV ICP optical emission spectrometer (PerkinElmer, Shelton, CT, USA). Table 3 shows the instrumental parameters used for ICP OES analysis. Argon with a purity of 99.996% (Air Liquide, Saalfeld, Germany) has been used as plasma gas. A laboratory microwave oven (MIKROWAVE, PerkinElmer, Shelton, CT, USA) has been used for sample digestion.

2.2. Reagents, samples and standards

All reagents were at least of analytical grade (p.a.). Hydrogen peroxide, 30% (v/v) and nitric acid, 65% (v/v) were purchased from Merck (Darmstadt, Germany). De-ionized water from a Milli-Q system (Millipore, Bedford, MA, USA) with a resistivity of 18 MΩ cm has been used throughout. Stock standard solutions containing 1000 mg L^{-1} each of Cu, Mn, Mo, Ni and V have been prepared by dissolution of high-purity Cu, $Mn(C_2H_3O_2)_2 \cdot 4H_2O$, $(NH_4)_2MoO_4$, Ni and NH_4VO_3, respectively (SPEX, Edison, NJ, USA). For Fe and Cr stock standard solutions (1000 mg L^{-1}) from Merck have been used. Calibration solutions have been prepared by appropriate dilution of the stock standard solutions with 0.5% (v/v) HNO_3. For ICP OES analysis the ICP multi-element standard IV and a Mo ICP standard (both from Merck, Darmstadt, Germany) have been used.

The following samples have been used in the present investigations: two samples of carbon black (CB) from Degussa (Frankfurt/Main, Germany), and seven activated charcoals (A1–A7) from A.U.G. (Döberitz, Germany), Blücher GmbH (Erkrath, Germany), Kureha GmbH (Düsseldorf, Germany), Pica (Levallois, France) and three laboratory samples. All samples were ground to a particle size of ≤77 μm. The following coal CRM have been used for method validation: SARM 18 Coal Witbank and SARM 19 Coal OFS (South African Bureau of Standards, Pretoria, South Africa); NIST 1632a Bituminous Coal and NIST 1635 Sub-bituminous Coal (National Institute for Standards and Technology, Gaithersburg, MD, USA); BCR 180 Gas coal and BCR 181 Coking coal (Community Bureau of Reference, Brussels, Belgium).

2.3. Microwave-assisted acid digestion

Sample solutions for ICP OES analysis have been prepared using microwave-assisted acid digestion. A 0.1-g sample mass was weighed into a quartz vessel, 2.5 mL of hydrogen peroxide was added and the mixture was allowed to stand for 24 h. Afterwards 2.5 mL of concentrated nitric acid was added, the vessel sealed and placed into the rotor of the microwave oven. Six vessels were used in each run using the temperature program shown in Table 4. After treatment, the clear solutions were diluted to 25 mL with distilled, de-ionized water and used directly for measurement. In the case of incomplete digestion the solution has been filtered before measurement. Each sample has been digested at least three times.

Table 3
Instrumental parameters used for the analysis of activated charcoal and carbon black samples after microwave-assisted acid digestion.

RF generator frequency (MHz)	40
RF generator power (W)	1300
Type of RF generator	Solid state
Plasma gas flow rate (L min^{-1})	15
Auxilliary gas flow rate (L min^{-1})	0.5
Nebulizer flow rate (L min^{-1})	0.7
Sample pump rate (mL min^{-1})	1
Type of nebulizer	Crossflow
Type of spray chamber	Scott
Shear gas	Air
Purging gas	Argon
Read delay (s)	50
Read time (s)	2–5
Repetitions	3
Plasma observation	Axial
Background correction	Double
Wavelengths (nm)	Cr: 267.716; Cu: 327.393; Fe: 238.204; Mn: 257.610; Mo: 202.030; Ni: 231.604; V: 292.464

Table 4
Temperature program for the digestion of activated charcoal and carbon black.

Step	Power (W)	Time (min:s)	Power (W)	Cooling
1	300	04:00	300	1
2	400	08:00	600	1
3	600	08:00	800	1
4	800	15:00	800	1
5	0	15:00	0	3

3. Results and discussion

3.1. Determination using SS-HR-CS GF AAS

Chromium, Cu, Fe, Mn, Mo, Ni and V have been determined using SS-HR-CS GF AAS using the temperature program given in Table 1. Pyrolysis and atomization curves have been established for each element using a solid charcoal or carbon black sample, a coal reference material and an aqueous standard solution; the optimized pyrolysis and atomization temperatures are shown in Table 2. The addition of a chemical modifier has been found unnecessary for all of the analytes due to their inherent thermal stability, particularly in the carbon matrix. Significantly higher pyrolysis temperatures than those shown in Table 2 could actually have been used for most analytes; however, these higher temperatures did not bring any advantage, and would only have reduced tube lifetime.

The GF AAS technique is well suited for trace and ultra trace analysis, particularly when direct SS is used, as no dilution is involved. Hence, the determination of iron has been a challenge, firstly because of its ubiquitous character in the environment (blank values), and secondly, as it is often present not as a trace element, but at relatively high concentration, especially in coals. For this reason suitable iron lines had to be searched for, the sensitivities of

Table 2
Operating parameters for the analysis of activated charcoal and carbon black samples using SS-HR-CS GF AAS.

Parameter	Cr	Cu	Fe	Mn	Mo	Ni	V
Wavelength (nm)	357.869	324.754	344.099/344.388	403.076	313.259	232.003/232.138	318.540
Calibration	NIST 1635	Aqueous Standards	Aqueous Standards	NIST 1635	Aqueous Standards	Aqueous Standards	NIST 1635
Pyrolysis temperature (°C)	1000	1000	1000	700	1000	1000	1000
Atomization temperature (°C)	2500	2400	2400	2400	2650	2500	2650

Table 5

Figures of merit obtained for the analysis of activated charcoal and carbon black samples using SS-HR-CS GF AAS based on the introduction of 0.2 mg of sample into the graphite tube; all values are based on the PVSA of three pixels ($A_{\Sigma 3,\mathrm{int}}$), except for the determination of Ni at 232.003 nm, which is based on the integrated absorbance (A_{int}) measured at the center pixel only.

	Cr	Cu	Fe		Mn	Mo	Ni		V
Wavelength (nm)	357.869	324.754	344.099	344.388	403.076	313.259	232.003	232.138	318.540
Calibration range (ng)	0.1–0.5	0.05–0.5	2–16	8–50	1–5	0.1–0.4	0.1–1.0	1.0–10	0.5–5.0
Slope (s ng^{-1})	0.913	1.370	0.019	0.005	0.332	0.637	0.156	0.027	0.172
R	0.9927	0.9992	0.9995	0.9992	0.9900	0.9992	0.9995	0.9979	0.9982
m_0 (pg)	4.8	3.2	240	890	5.5	7.0	25	162	26
LOD (mg kg^{-1})	0.05	0.03	0.9	n.d.[a]	0.03	0.04	0.006	n.d.[a]	0.01
LOQ (mg kg^{-1})	0.15	0.09	3.2	n.d.[a]	0.09	0.1	0.02	n.d.[a]	0.03

[a] n.d., not determined; used for the determination of high concentrations only.

which were appropriate for the iron concentration. Fortunately iron has more than 600 absorption lines that are all available for analytical purposes in HR-CS AAS due to the use of a high-intensity continuum radiation source [24]. Measurements have been carried out simultaneously at two secondary lines at 344.099 nm and 344.388 nm, which are both within the spectral range covered by the array detector, resulting in an increase of the linear dynamic range available for iron determination. Nickel, which also occurs occasionally in high concentration in coals, has also been determined simultaneously at the primary resonance line at 232.003 nm and a secondary line at 232.138 nm, which appears within the same spectral range.

The figures of merit for the determination of the seven elements and all the analytical lines using HR-CS GF AAS are summarized in Table 5. The characteristic mass (m_0) is defined as the mass of analyte corresponding to a PVSA of 0.0044s. The limit of detection has been calculated as three times the standard deviation of 10 measurements of the blank divided by the slope of the calibration curve. Blank measurements have been carried out according to the “zero mass response”, introducing repeatedly an SS platform and running a full atomization cycle [31]. The limit of quantification (LOQ) is based on the same measurements, using 10 times the standard deviation of the blank readings divided by the slope of the calibration curve. No LOD or LOQ values have been calculated for the less sensitive lines of Fe and Ni, as these lines have only been used for the determination of high concentrations of these analytes.

The accuracy of the method has been evaluated by analyzing a number of coal CRM. The determination of Cu, Fe and Mo could be carried out using aqueous standards for calibration, indicating the absence of any interference. In the case of Ni there has been some overlap of structured molecular background absorption with the wing of the resonance line at 232.003 nm as can be seen in Fig. 1(a). Nevertheless, the determination could be carried out with calibration against aqueous standards when only the center pixel was used to evaluate the analytical signal. To investigate the origin of the interfering molecular spectrum, 20 μL of an aqueous solution containing 1000 mg L^{-1} Si has been vaporized using the same temperature program as for sample analysis, resulting in the time-integrated spectrum shown in Fig. 1(b). This spectrum has been identified as part of the $\Delta\nu = +1$ sequence of the SiO band system of the $X\ ^1\Sigma^+ \rightarrow A\ ^1\Pi$ electronic transition [24]. To correct for the structured background absorption and also to confirm the identity of the interfering molecule, the spectrum shown in Fig. 1(b) was subtracted from the sample spectrum in Fig. 1(a) using a least-squares algorithm for background correction (LSBC), and the result is shown in Fig. 1(c). It is obvious that only three absorption lines remain after LSBC, two of which are due to Ni at 232.003 nm and 232.138 nm, and the third one is due to a secondary Fe absorption line at 232.036 nm. The molecular absorption has been corrected to the baseline, showing the efficiency of this background correction procedure and also confirming the identity of the interfering diatomic molecule as SiO.

There has also been significant structured molecular background absorption in the vicinity of the vanadium triplet at 318.341/318.397/318.538 nm, as shown in Fig. 2(a), and all three vanadium lines were affected by this spectral interference. The origin of this molecular spectrum is still unknown; however, the spectrum generated by the volatilization of 20 μL of an aqueous solution containing 1000 mg L^{-1} S, as $(NH_4)_2SO_4$, which is shown in Fig. 2(b), exhibited sufficient similarity. After this spectrum has been subtracted from that in Fig. 2(a) using LSBC, the spectrum shown in Fig. 2(c) was obtained. There is still some remaining structured background absorption that might be due to a second molecule; however, at least at the V line at 318.538 nm the molecular absorption has been corrected to the baseline, so that this wavelength could be used for analytical purposes.

Nevertheless, some additional non-spectral interference has been encountered in the determination of V, as well as for Cr and Mn, so that a solid coal CRM (NIST 1635) had to be used for calibration. This can be easily explained, at least in the case of Cr and V, by the tendency of these analytes to form strong carbides that might impede their complete release from the high-carbon matrix. The time-resolved absorbance signals for 1.2 ng V in aqueous solution and 4.0 ng V in a coal CRM shown in Fig. 3 reveal at least part of the problem. The descending part of the two peaks is essentially coinciding, demonstrating that there is no excessive tailing due to a slow release from the coal matrix. The major difference in the two signals is clearly in the early part of the atomization stage and in the much smaller total area of the atomization signal found in the presence of the coal matrix; a similar behavior has been found for Cr and Mn. This might well be explained by the atomization mechanism for V, proposed by Wendl and Müller-Vogt [32,33] via the thermal decomposition of the carbide $VC_{(s)}$ at temperatures above 2000 K; the same authors proposed a similar atomization mechanism for Cr via the thermal decomposition of the carbide $Cr_3C_{2(s)}$ [32,33]. Veillon et al. [34] reported that a substantial portion of Cr is retained irreversibly in the graphite tube, an effect that was explained by Castillo et al. [35,36] as being due to the formation of higher carbides that decompose only very slowly. Considering these mechanisms it appears quite logic that the thermal decomposition of these carbides is much less efficient in the presence of the coal matrix, compared to pure aqueous solutions, resulting in a lower atomization signal for these analytes.

The results for all elements in the coal CRM are summarized in Table 6. All values are the average of $n = 5$ measurements. The standard deviation represents the repeatability of the direct SS method. All results are in agreement with certified or informed values according to a Student *t*-test at a 95% confidence level indicating that the method is suitable for the purpose.

3.2. Determination using ICP OES

The ICP OES analysis of the coal and carbon black samples has been carried out for comparison after a microwave-assisted diges-

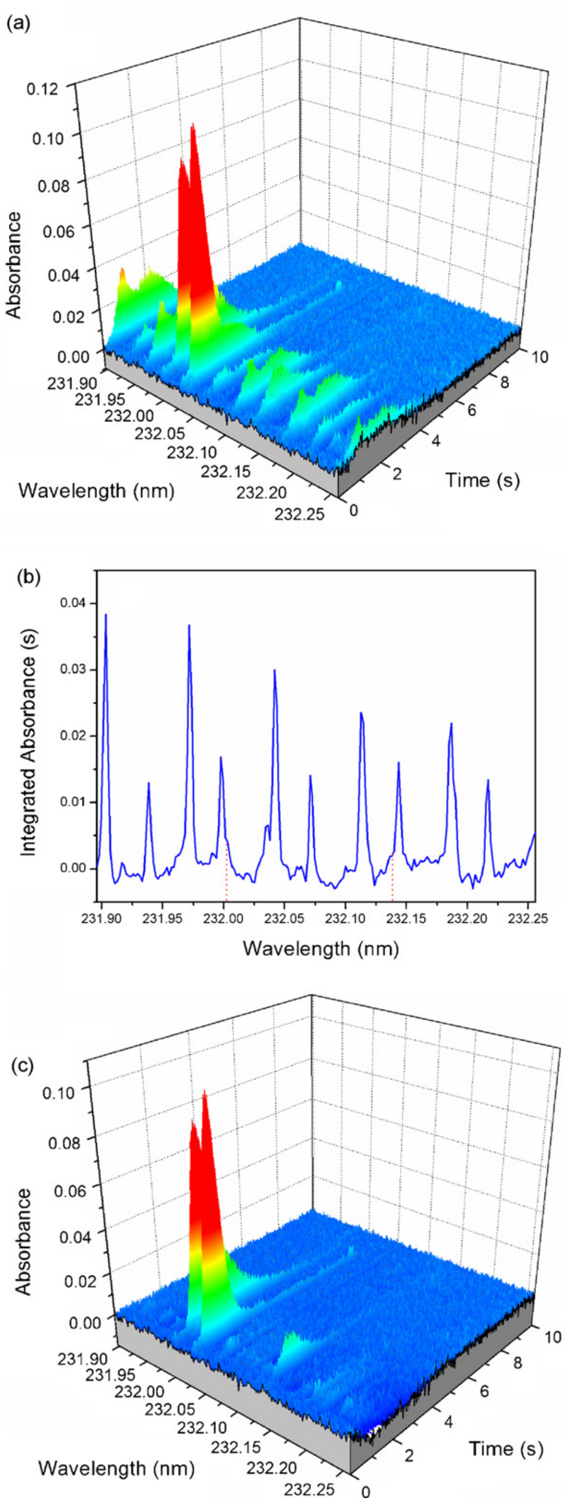

Fig. 1. Least-squares background correction for the determination of Ni in NIST SRM 1635; (a) time- and wavelength-resolved absorbance spectrum for NIST 1635 in the vicinity of the two nickel lines at 232.003 nm and 232.138 nm after automatic correction for continuous events; (b) time integrated absorbance spectrum for 20 μg Si in aqueous solution and (c) time- and wavelength-resolved absorbance spectrum for NIST 1635 after LSBC using (b) as the reference spectrum.

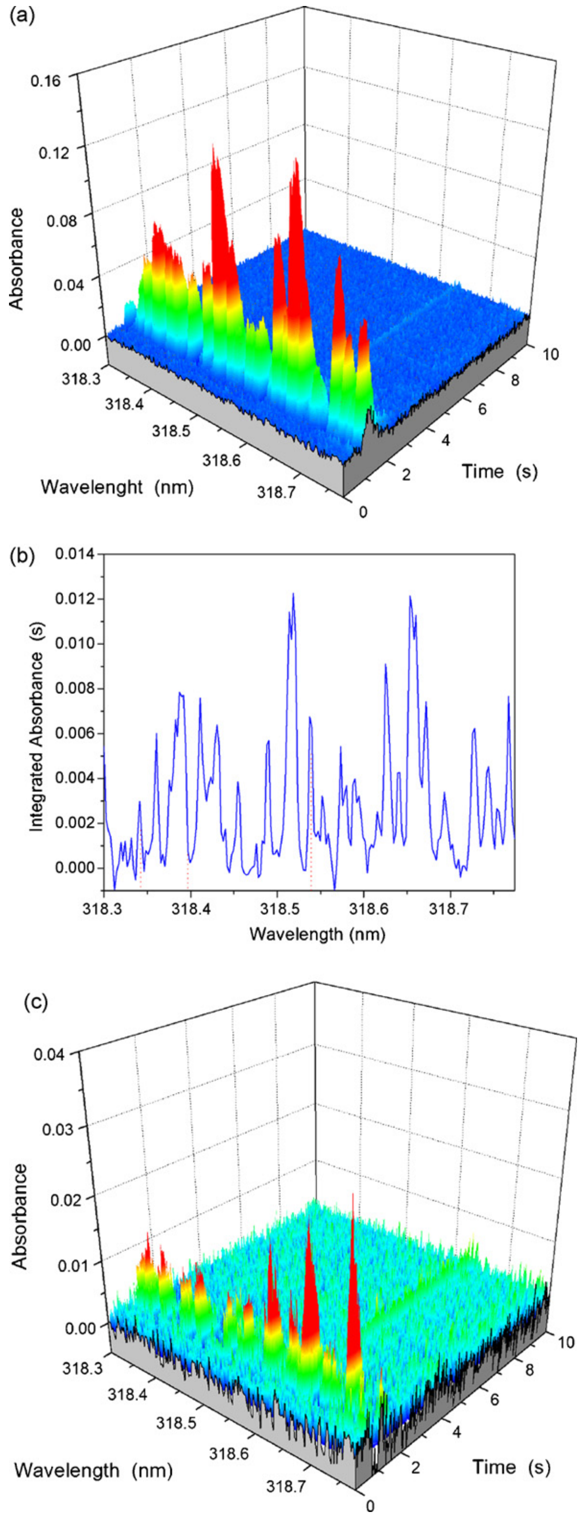

Fig. 2. Least-squares background correction for the determination of V in sample A6 (a) time- and wavelength-resolved absorbance spectrum for sample A6 in the vicinity of the vanadium triplet at 318.341/318.397/318.538 nm after automatic correction for continuous events; (b) time integrated absorbance spectrum for 20 μg S as $(NH_4)_2SO_4$ in aqueous solution and (c) time- and wavelength-resolved absorbance spectrum for sample A6 after LSBC using (b) as a reference spectrum.

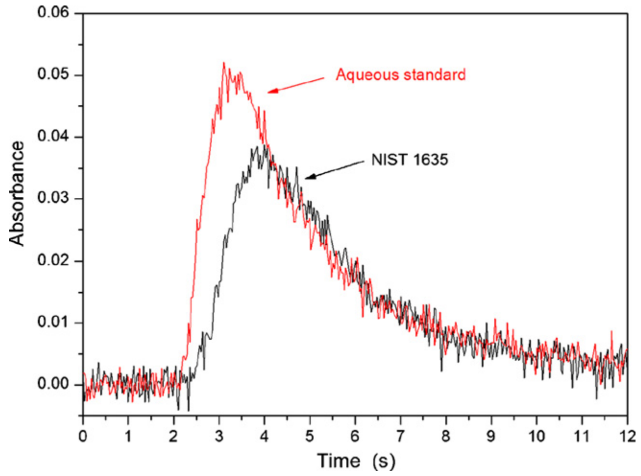

Fig. 3. Time-resolved absorbance signals for vanadium recorded at 318.540 nm for an aqueous standard (1.2 ng V) and the solid coal NIST SRM 1635 (corresponding to 4.0 ng V); pyrolysis temperature 1000 °C, atomization temperature 2650 °C.

tion using HNO_3 and H_2O_2, which could be considered the method of choice [17]. In this work the proposed method has been modified, expanding the standing time of the coals with H_2O_2 to 24 h. Addition of HNO_3 after that long period of time simplifies the access to the reaction sites, resulting in complete digestion for most samples. Microwave-assisted digestion of the investigated coals has been successful without using HF mainly because they were originating of plant materials; lower alumina and silica contents promote complete or almost complete digestion. The concentrations of the various elements are significantly different, with higher amounts of Fe and traces of the other elements. Ni and V could be determined in one carbon sample only with a concentration of 307 mg kg^{-1} and 653 mg kg^{-1}, respectively. Except for non-specific interferences there have been only slight spectral coincidences with the analytical lines. As an example, the copper line at 327.393 nm is affected by sodium (327.422 nm); however, the resolution of the spectrometer and the reading of only two or three pixels in the middle of the analyte line guarantee an accurate measurement.

3.3. *Comparison of the results*

The proposed methods have been applied for the determination of Cr, Cu, Fe, Mn, Mo, Ni and V in activated charcoal and carbon black samples; in Table 7 the results of HR-CS GF AAS are compared with those obtained by ICP OES after microwave-assisted acid digestion. The AAS values are the average of five weighings and measure-

Table 6
Results obtained in the analysis of coal certified reference materials (CRM) using SS-HR-CS GF AAS; mean value ± standard deviation.

Element	CRM	Certified (mg kg^{-1})	Found (mg kg^{-1})
Cr	SARM 18	16 (14–18)	16.6 ± 2.6
	BCR 180	12–15.7	14.7 ± 1.9
Cu	NIST 1635	3.6 ± 0.3	3.4 ± 0.5
	SARM 18	5.9 (5.2–6.4)	5.7 ± 0.4
Mn	NIST 1632a	28 ± 2	27.1 ± 1.2
	SARM 18	22 (21–23)	21.2 ± 3.4
Ni	NIST 1635	1.70 ± 0.10	1.69 ± 0.11
Mo	SARM 18	1	± 0.2
	SARM 19	2	1.6 ± 0.2
Fe[a]	NIST 1635	239 ± 5	268 ± 21
V	BCR 181	12.0 ± 0.4	14.1 ± 1.5

[a] Determined at 344.388 nm.

Table 7
Comparison of the results (mg kg^{-1}) obtained for the analysis of activated charcoal and carbon black samples using ICP OES and SS-HR-CS GF AAS (n.d., not determined).

Sample	Cr		Cu		Fe		Mn		Mo		*Ni*		V	
	ICP OES	SS-HR-CS GF AAS	ICP OES	SS-HR-CS GF AAS	ICP OES	SS-HR-CS GF AAS	ICP OES	SS-HR-CS GF AAS	ICP OES	SS-HR-CS GF AAS	ICP OES	SS-HR-CS GF AAS	ICP OES	SS-HR-CS GF AAS
A1	<1	n.d.	2.4 ± 0.2	1.4 ± 0.1	14.2 ± 1.0	n.d.	<1	18.9 ± 0.9	<2	<0.12	10.2 ± 0.6	6.57 ± 0.37	<1	<0.03
A2	106 ± 3.5	n.d.	8.5 ± 0.6	7.3 ± 0.2	684 ± 7.5	n.d.	4.9 ± 0.3	7.5 ± 0.5	<2	2.90 ± 0.23	18 ± 2.7	9.35 ± 0.09	<1	0.22 ± 0.02
A3	<1	0.86 ± 0.3	<1	2.5 ± 0.1	78 ± 3.9	75.2 ± 8.7	<1	1.5 ± 0.3	<2	<0.12	5.0 ± 0.6	0.78 ± 0.04	<1	0.09 ± 0.01
A4	4.1 ± 0.8	5.3 ± 0.5	18 ± 1.8	n.d.	307 ± 29	n.d.	9.6 ± 0.5	13.7 ± 0.1	<2	0.16 ± 0.03	7.3 ± 0.6	2.56 ± 0.12	<1	1.88 ± 0.02
A5	<1	n.d.	10 ± 1.0	n.d.	174 ± 17	n.d.	8.1 ± 0.7	13.9 ± 0.7	12 ± 2.3	<0.12	7.9 ± 0.7	1.07 ± 0.05	<1	1.90 ± 0.06
A6	<1	1.5 ± 0.2	10 ± 0.9	7.8 ± 0.3	61 ± 6.0	44.4 ± 5.7	5.0 ± 0.4	4.2 ± 0.1	<2	<0.12	6.5 ± 1.1	1.43 ± 0.12	<1	0.11 ± 0.01
A7	<1	2.6 ± 0.4	12.7 ± 0.8	11.4 ± 0.3	62 ± 2.2	77.8 ± 6.4	4.3 ± 0.1	7.5 ± 1.1	<2	<0.12	7.4 ± 1.3	2.01 ± 0.14	<1	0.15 ± 0.01
R1	<1	1.3 ± 0.1	<1	0.2 ± 0.03	28 ± 2.5	12.7 ± 0.7	<1	0.8 ± 0.2	<2	<0.12	5.0 ± 0.8	0.44 ± 0.04	<1	<0.03
R2	<1	8.4 ± 0.3	<1	1.2 ± 0.2	204 ± 19	n.d.	<1	2.9 ± 0.2	<2	<0.12	307 ± 15	n.d.	653 ± 62	n.d.

Table 8
Results of PLS regression for the prediction of T_{on} with different groups of variables measured by ICP OES after acid digestion and SS-HR-CS GF AAS.

Variable group	Significant variables (loadings)	Correlation coefficient of validation	Error of prediction (RMSEP) (%)
Microwave digestion/ICP OES (Cr, Cu, Fe, Mn, Mo, Ni, V and Fe^{2+})	Fe, Ni, V	0.416	3.67
Microwave digestion/ICP OES (16 elements and Fe^{2+}) [41]	Fe, Fe^{2+}, K, V	0.77	2.66
SS-HR-CS GF AAS (Fe)	Fe	0.92	0.99
SS-HR-CS GF AAS (Fe, Mn)	Fe, Mn	0.15	4.02
SS-HR-CS GF AAS (Cr, Fe, Mn)	Fe, Mn	0.016	4.06
SS-HR-CS GF AAS (Fe, Mn, Ni)	Fe, Mn	0.66	3.10
SS-HR-CS GF AAS (Cr, Fe, Mn, Ni)	Fe, Mn, Cr	0.69	2.98
SS-HR-CS GF AAS (Cr, Cu, Fe, Mn, Mo, Ni, V)	Fe, Mn	0.99	0.68

ments (confidence interval at the 95% level); the data of the ICP OES analysis are the average of three digestions. As mentioned before SS-HR-CS GF AAS is a technique primarily for determinations at trace and ultra trace level; consequently, not all samples could be analyzed with this technique due to excessively high analyte concentration. On the other hand, quite a number of samples could not be measured with ICP OES as the concentrations were below the LOQ of this technique. Nevertheless, there have been a sufficiently large number of samples that could be analyzed with both techniques, particularly in cases where less sensitive lines have been used for HR-CS GF AAS, making possible a comparison of the results.

Considering the data in detail, most of the values showed an acceptable conformity, such as in the case of Cu and Fe. However, there are also significant differences; the AAS values for Ni are throughout lower than those obtained by ICP OES, which might indicate a contamination with Ni in the acids used for digestion. In contrast, Cr and in part also Mn and V values are higher than those obtained by ICP OES. Here, it can be supposed that microwave-assisted acid digestion did not result in all cases in complete dissolution/extraction; it is well known for example that chromite [(Fe, Mg)Cr_2O_4] is practically insoluble in acids. In such cases, analysis using SS-ET AAS is of obvious advantage, as the successful determination depends mostly on the similar behavior of the analyte in samples and in the reference (calibration) matrix. It is worth mentioning in this context that non-spectral interferences have been encountered for the same analytes, Cr, Mn and V also with direct SS-GF AAS, which, however, could be controlled using calibration against solid CRM.

The RSD values for both methods are between 1 and 25%, depending on the concentration level, and with typically higher values for ICP OES measurements, except for high analyte concentrations. As expected the LOD values obtained with SS-HR-CS GF AAS are far lower than those of ICP OES. Even Mo and V can be determined much more accurately and with higher sensitivity. Moreover, in comparison to other methods described in the literature, including ICP-MS, the LOD values of SS-HR-CS GF AAS are quite comparable and, in the case of Cr and Ni, even significantly lower values could be reached [17,37]. Obviously, comparison of LOD is not straight-forward, as they depend on the type of device used and the sampling method. Resano et al. for example obtained much better LOD for Cr using sector field ICP-MS [38] compared to quadrupole ICP-MS [39] due to the removal of carbon-based polyatomic interference.

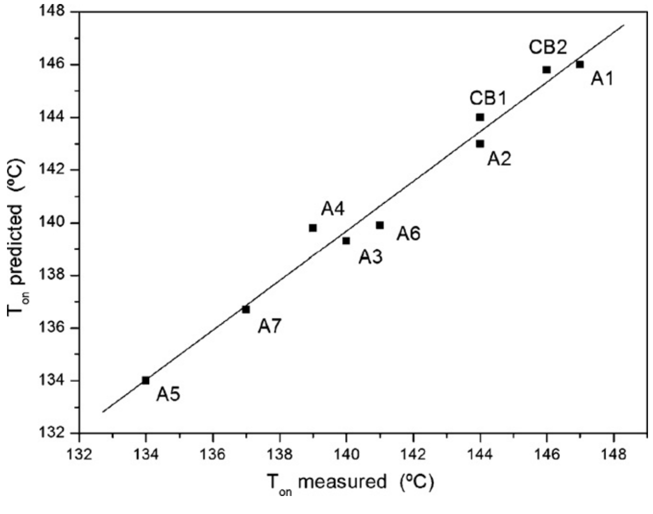

Fig. 4. Recovery function of the prediction for the onset temperature (T_{on}) from heavy metal measurements by direct SS-HR-CS GF AAS (9 samples, 7 variables).

3.4. Prediction capability of T_{on}

For further comparison of both methods the correlation between the concentration of heavy metals and the onset temperatures (T_{on}) of cellulose/NMMO solutions modified with the activated charcoals and carbon black ought to be considered. Regarding a statistical interpretation partial least-squares regression (PLS) between measured values for T_{on} and those calculated from metal concentrations has been found to be a useful tool [40]. T_{on} is a very convincing variable to investigate the beginning of exothermicities and has to be served as a reference for the evaluation. Hierarchical agglomeratic cluster analysis (CA) and principal component analysis (PCA) have been applied before the data were treated with PLS to evaluate the data structure and to discover classes among the samples. Table 8 summarizes the results of PLS regression for the calculation of T_{on} using 7 and 17 variables for ICP OES [41] and between 1 and 7 variables for SS-HR-CS GF AAS. Whereas the ICP OES measurement gives a satisfactory correlation only when 17 variables are used, results obtained by SS-HR-CS GF AAS exhibit a much better correlation coefficient of 0.99 when only 7 variables are considered, as is also shown in Fig. 4 for all the investigated samples. It is evident that Fe belongs to the significant variables with the highest variance and, consequently, the most information concerning the thermostability. Including only Fe into the PLS statistics, correlation of onset temperatures of the solutions and Fe content of the coals measured by SS HR-CS ETAAS provides a quite good correlation coefficient (0.92), however, only four samples are considered because SS-HR-CS GF AAS is a technique primarily for determinations at trace and ultra trace level; consequently, not all samples could be analyzed with this technique due to excessively high analyte concentration. Therefore, concise evaluation of thermostability necessitates measurement of at least three, better four elements. In this case Fe, Mn and Ni have to be measured to receive an acceptable correlation coefficient of 0.66; with Cr, Fe, Mn and Ni 0.69 has been obtained. It has to be mentioned that the aim of the study among others was the application of statistics on heavy metal analysis and, consequently, to find out the efficiency of SS-HR-CS ETAAS compared to conventional methods, especially multi-element ones, and the advantages of this technique have been clearly demonstrated.

4. Conclusion

Precise evaluation of properties such as metal content is a must for the choice of additives for the Lyocell process, particularly activated charcoals, as such impurities can severely attract reactions in the cellulose/NMMO system leading to lower thermostability. SS-HR-CS GF AAS has been shown to be a versatile technique for samples that are difficult to be brought into solution. All in all, due to its better accuracy and its much higher detection power, SS-HR-CS GF AAS has been found to be an extremely useful tool for the prediction of T_{on} of cellulose/NMMO solutions. The prediction capability of this technique is much higher and requires a smaller number of input data to arrive at an accurate forecast. This is in accordance with the results obtained by Krivan and co-workers [19,25] for the determination of a large number of trace metals in a wide variety of refractory materials, where SS-GF AAS always provided the lowest LOD and the most reliable results. The determination of six of the seven elements, Cr, Fe, Mn, Mo, Ni and V in coal using SS-GF AAS has been reported for the first time in this work. The fact that three of them, Cr, Mn and V required a solid CRM for calibration might require further investigation in order to get the residual non-spectral interference under control. Nevertheless, even these analytes could be determined with good accuracy, demonstrating the robustness of the technique.

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