

Feasibility of employing permanent chemical modifiers for the determination of cadmium in coal using slurry sampling electrothermal atomic absorption spectrometry

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Abstract

Iridium and ruthenium, alone and in combination with tungsten, thermally deposited on the platform of a transversely heated graphite tube, were investigated for their suitability as permanent chemical modifiers for the determination of cadmium in coal slurries by electrothermal atomic absorption spectrometry (ET AAS). The conventional mixed palladium and magnesium nitrates (Pd–Mg) modifiers, added in solution, were also investigated for comparison. The latter one showed the best performance for aqueous solutions, and the mixed W–Ir and W–Ru permanent modifiers had the lowest stabilizing power. All of the investigated modifiers lost some of their stabilizing power when coal slurries were investigated. The Pd–Mg modifier, pure Ir and Ru, and a mixture of 300 µg W + 200 µg Ir could stabilize Cd at least to a pyrolysis temperature of 600 °C, whereas all the other combinations already failed at temperatures above 500–550 °C. Additional investigations of the supernatant liquid of the slurries supported the assumption that the high acid concentration of the slurries and/or a concomitant leaching out of the coal might be responsible for the reduced stabilizing power of the modifiers. The maximum applicable pyrolysis temperature of 600 °C was not sufficient to reduce the background absorption to a manageable level in the majority of the coal samples. High-resolution continuum source ET AAS revealed that the continuous background absorption was exceeding values of $A=2$, and was overlapping with the analyte signal. Although the latter technique could correct for this background absorption, some analyte was apparently lost with the rapidly vaporizing matrix so that the method could not be considered to be rugged. A characteristic mass of 1.0 pg and a detection limit of 0.6 ng g⁻¹ could be obtained under these conditions. © 2006 Elsevier B.V. All rights reserved.

Keywords: Electrothermal atomic absorption spectrometry; Slurry sampling; Cadmium determination; Coal analysis; Permanent chemical modifiers; Background correction; High-resolution continuum source AAS

1. Introduction

The interest in potentially hazardous metals in coal has increased significantly in recent years and many studies for their determination have been carried out [1]. The processes of mining, storage, beneficiation and combustion of coal release

these elements to the environment in gaseous form through stag gas, in solid form through atmospheric and waste deposition, and to surface and ground water through leaching processes [2,3]. The conventional way to analyze coal is after acid digestion, but to bring coal into solution is time consuming and includes the use of concentrated acids and high temperature ashing [4]. These procedures, however, include the risk of loss of volatile trace elements and contamination. Microwave-assisted acid digestion can be applied to speed up part of the

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process, but still requires prior ashing of coal [5], unless perchloric acid is added [6–8].

Due to these difficulties, several alternatives have been investigated to avoid coal digestion, such as direct solid sampling electrothermal atomic absorption spectrometry (ETAAS) [9–12] and sample introduction in the form of slurries. The latter technique was considered to have certain advantages over the former one, since it is possible to change the slurry concentration by simple dilution, hence combining the advantages of solid and liquid sampling [13]. Slurry sampling also allows the introduction of a small sample mass, using the same devices available for liquid sampling, such as autosamplers and pipettes [14]. The main advantages of slurry sampling and other important aspects that need to be considered are discussed recently by Cal Prieto et al. [15]. Slurry sampling has been successfully applied for coal analysis using electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) [16], Hydride-generation ET AAS [17], and particularly direct ET AAS [18–21].

The use of chemical modifiers has become an important part of the analytical procedure in ET AAS, mainly with the stabilized temperature platform furnace (STPF) concept, in order to obtain interference-free measurement conditions [22]. The most frequently used chemical modifier in ET AAS is a mixture of palladium nitrate and magnesium nitrate. This modifier can thermally stabilize at least 21 elements, allowing a high pyrolysis temperature without loss of the analyte [23,24]. More recently permanent chemical modifiers, applied as kind of a surface coating to graphite tubes or platforms, have been used increasingly [25] mainly in order to simplify the analytical procedure and to avoid contamination introduced by the modifier [26]. The platinum group metals (PGM), mostly Rh, Ru and Ir, have been used as modifiers either alone or mixed for the determination of a wide variety of volatile analytes [27–30]. da Silva et al. [26] used Ru as permanent modifier to analyze *aqua regia* extracts from sediments. Lima et al. [31,32] proposed various combinations of PGM with tungsten as permanent chemical modifiers for Cd and found better performance in the presence of tungsten than in its absence.

The aim of this work was to investigate the feasibility of the determination of cadmium in coal samples using slurry sampling and permanent modifiers, particularly as direct solid sampling requires special accessory for sample introduction that is not available for most commercial instruments, whereas slurries might be introduced using conventional equipment. High-resolution continuum source (HR-CS) ET AAS was used for method optimization in addition to conventional line-source (LS) ET AAS because of the significantly increased information available with the former one, and its improved background correction capability [33].

2. Experimental

2.1. Instrumentation

All measurements with conventional LS ET AAS were carried out using an AAS 5EA atomic absorption spectrometer (Analytik Jena AG, Jena, Germany) with deuterium background

correction, equipped with a transversely heated graphite tube atomizer. A NARVA cadmium hollow cathode lamp (GLE, Berlin, Germany) was used as the radiation source with a current of 4.0 mA. The main resonance line at 228.8 nm was used for all determinations with a spectral bandwidth of 0.8 nm. The spectrometer was interfaced to an IBM PC/AT-compatible computer. All experiments were carried out using pyrolytically coated graphite tubes with an integrated PIN platform (Analytik Jena Part No. 407-A81.025). An M2P micro-balance (Sartorius, Goettingen, Germany) was used for weighing the samples.

An MPE 5 furnace autosampler (Analytik Jena AG) was used for introduction of slurries and solutions. Argon with a purity of 99.996% (White Martins, São Paulo, Brazil) was the purge gas with a flow rate of 2.0 L min⁻¹ during all stages, except during atomization, where the flow was stopped. Integrated absorbance (peak area) was used exclusively for signal evaluation and quantification. The optimized graphite furnace temperature program used for all determinations with LS ET AAS is given in Table 1.

All measurements with HR-CS ET AAS were carried out using a prototype HR-CS atomic absorption spectrometer, built at ISAS, Department Berlin (Berlin, Germany). The prototype is based on a Model AAS 6 Vario (Analytik Jena AG, Jena, Germany), from which the entire optical compartment including detector and associated controls had been removed and replaced by a double monochromator (DEMON), similar to the system described by Heitmann et al. [34]. The DEMON consists of a prism pre-monochromator for order separation and an echelle monochromator for simultaneous recording of small sections of the high-resolved spectrum. Both units are in Littrow-mounting with focal lengths of 300 and 400 mm, respectively, resulting in a total spectral resolution per pixel of about 140,000. Variation of the width of the intermediate slit allows determining the recorded wavelength interval. A xenon short-arc lamp XBO 301 (GLE, Berlin, Germany) with a nominal power of 300 W, operating in a ‘hot-spot’ mode, and emitting intense radiation particularly in the UV region was used as the continuum radiation source. An S7031-0906 UV-sensitive, thinned back-illuminated CCD array detector (Hamamatsu Photonics, Herrsching, Germany) with 512 × 58 pixels, size 24 × 24 μm², operating in full vertical binning mode was used, providing an instrumental bandwidth of 1.9 pm per pixel at 228.802 nm, the main wavelength of Cd. An intermediate slit width of 428 μm was used, making possible the simultaneous evaluation of 200 pixels, corresponding to about ±0.2 nm around the

Table 1
Temperature program for the determination of cadmium in coal by slurry sampling ET AAS

Stage	Temperature (°C)	Ramp (°C s ⁻¹)	Hold time (s)	Ar flow rate (L min ⁻¹)
1 — Drying	100	100	5	2.0
2 — Drying	160	5	15	2.0
3 — Pyrolysis	Variable	40	20	2.0
4 — Auto zero	Same as 3	100	1	0.0
5 — Cool down	200	NP	2	2.0
6 — Atomization	1600	2000	6	0.0
7 — Cleaning	2100	1000	3	2.0

analytical wavelength at pixel No. 250. The cadmium absorption was measured using the central pixel (CP) and $CP \pm 1$, i.e. over a spectral interval of about 2 and 6 pm, respectively, but only results obtained at $CP \pm 1$ are reported in this work because of the better signal-to-noise (S/N) ratio obtained under these conditions. The DEMON also includes active wavelength stabilization via spectral lines from an internal Ne lamp. The system was controlled by a Pentium III, 1000 MHz personal computer, running a data acquisition program developed at ISAS, Department Berlin. An important feature of the software is that all data of a measurement can be stored in the computer, and parameters, such as the time interval for integration, and pixel(s) used for measurement and background correction can be optimized after the measurement. The system and its special features have been described in detail elsewhere [33]. The graphite tube atomizer, the graphite parts and the graphite furnace temperature program were identical to those used with the AAS 5 atomic absorption spectrometer.

2.2. Reagents and reference materials

Analytical grade reagents were used throughout. The nitric acid (Merck, Germany), used to prepare the slurries and aqueous calibration standards, was further purified by sub-boiling distillation in a quartz apparatus (Kürner Analysentechnik, Rosenheim, Germany). All containers and glassware were soaked in 3 mol L^{-1} nitric acid for at least 24 h and rinsed three times with deionized water before use. Distilled, deionized water with a resistivity of $18 \text{ M}\Omega \text{ cm}$ from a Millipore water purification system (Millipore, Bedford, MA, USA) was used for the preparation of the samples and standards. The water did not contain any detectable concentration of Cd. The Cadmium stock solution (1000 mg L^{-1} in 0.014 mol L^{-1} nitric acid) was prepared from cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$), Merck. The working standards were prepared by serial dilution of the stock solution using the autosampler device, programmed to aspirate sequentially different amounts of Cd standard and diluent solution.

The following reference materials were used in this work: BCR No. 180 Gas Coal (Community Bureau of Reference, Brussels, Belgium); SARM 20 Coal Sasolburg and SARM 19 Coal O.F.S (South Africa Bureau of Standards, Pretoria, South Africa); NIST SRM 1630a Trace Mercury in Coal, SRM 1632b Trace Elements Coal, and NIST SRM 1635 Trace Elements in Coal (National Institute for Standards and Technology, Gaithersburg, MD, USA). In addition, a coal sample from the Candiota mine in Rio Grande do Sul, Brazil, termed 'Candiota', was used as in-house standard

Table 2

Temperature program for treatment of the platform with permanent modifiers; for details see text

Stage	Temperature (°C)	Ramp (°C s ⁻¹)	Hold time (s)	Ar flow rate (L min ⁻¹)
1	130	20	40	2.0
2	160	20	50	2.0
3	1000	100	25	2.0
4	1400	200	5	2.0
5	2000	1000	5	2.0

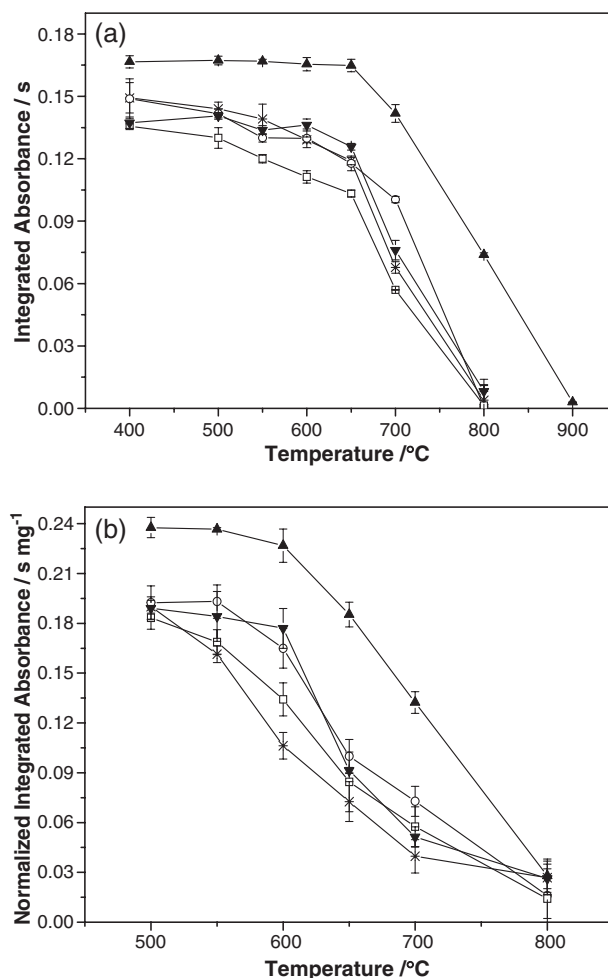


Fig. 1. Pyrolysis curves for Cd using different Ru-based permanent modifiers; atomization temperature: $1600 \text{ }^\circ\text{C}$; LS ET AAS; ($-\blacktriangledown-$) $400 \mu\text{g Ru}$; ($-*-$) $300 \mu\text{g W} + 200 \mu\text{g Ru}$; ($-O-$) $300 \mu\text{g W} + 300 \mu\text{g Ru}$; ($-□-$) $300 \mu\text{g W} + 400 \mu\text{g Ru}$; ($-\blacktriangle-$) Pd+Mg in solution; (a) 50 pg Cd in aqueous solution; (b) Cd in Candiota coal slurry; integrated absorbance normalized for a sample mass of 1 mg.

for method development. For all experiments the samples were ground manually in an agate mortar to a particle size $\leq 50 \mu\text{m}$.

2.3. Slurry preparation

For the slurry preparation we were following the procedure described by Silva et al. [20]; 10–60 mg of sample were weighed directly into the autosampler cups and a 1.5 mL aliquot of diluent consisting of 5% v/v HNO_3 , 0.05% v/v Triton X-100 and 10% v/v ethanol was added using a micropipette. The bigger particles of the slurry started to settle quickly, so that the homogeneity of the slurry had to be re-established by manual stirring before each sample injection, using the same micropipette. The slurry volume delivered into the atomizer was $20 \mu\text{L}$ in all cases. Aqueous standards were prepared with the same reagents as the slurries.

2.4. Permanent chemical modifiers

In order to apply the different permanent modifiers, the graphite platforms were treated as follow: for the mixed W+Ir

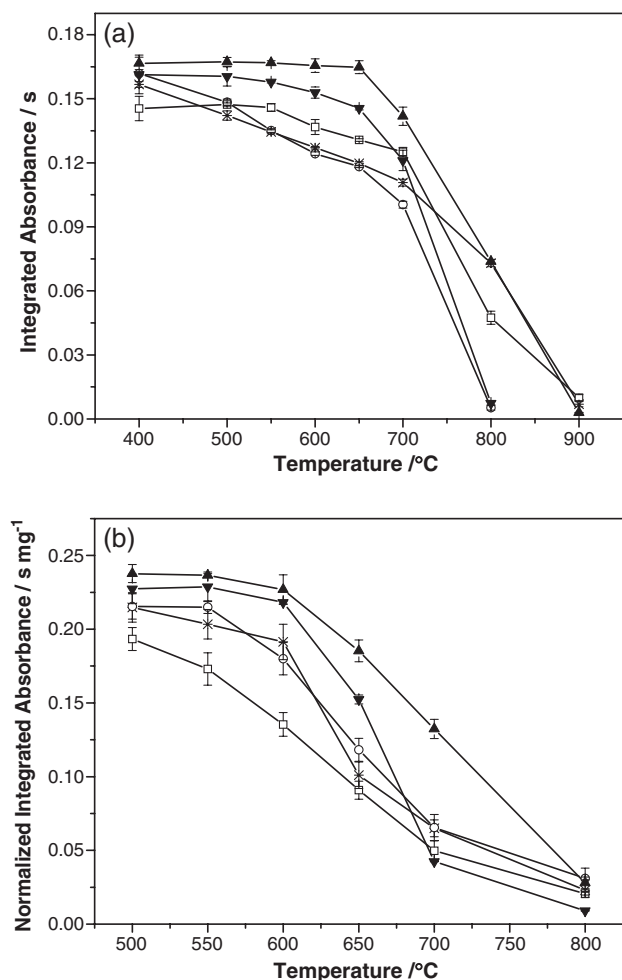


Fig. 2. Pyrolysis curves for Cd using different Ir-based permanent modifiers; atomization temperature: 1600 °C; LS ET AAS; (—▼—) 400 μg Ir; (—*—) 300 μg W+200 μg Ir; (—○—) 300 μg W+300 μg Ir; (—□—) 300 μg W+400 μg Ir; (—▲—) Pd+Mg in solution; (a) 50 pg Cd in aqueous solution; (b) Cd in Candiota coal slurry; integrated absorbance normalized for a sample mass of 1 mg.

and W+Ru modifiers by injecting 10 times 30 μL of 1000 mg L^{-1} of W standard solution onto the platform and submitting the graphite tube after each injection to the first four stages of the temperature program shown in Table 2. After the last treatment, when a total of 300 μg of W had been applied, the full program was executed. After this, Ir or Ru was deposited by injecting 10 times 20, 30 or 40 μL of 1000 mg L^{-1} Ir or Ru standard solution (as the chloride) and submitting the tube again after each injection to the first four stages of the temperature program shown in Table 2. After the last treatment, when a total of 200, 300 or 400 μg of Ir or Ru had been applied, the full program was executed. For the pure Ir or Ru treatment, 10 times 40 μL of 1000 mg L^{-1} Ir or Ru standard solution was injected onto the platform, and the tube submitted to the same heating program described above. The treatment with the permanent modifiers was repeated after 300 and 600 determinations, and a new tube was used after 900 determinations. For comparison, a conventional chemical modifier prepared from a mixture of 0.03% m/v Pd and 0.05% m/v Mg solutions, both as nitrates (Merck), was

investigated as well. This Pd–Mg modifier was added in solution to each coal slurry and calibration solution, using the autosampler.

3. Results and discussion

3.1. Furnace program and chemical modifiers

Two PGM, ruthenium and iridium, were chosen as potential permanent modifiers because of their high melting points, which make it unlikely that they are lost easily during the atomization and clean stages. Both modifiers were used alone and in combination with tungsten, which has been reported to result in longer tube lifetime and better sensitivity [31,32]. The performance of all modifiers and modifier combinations was investigated for the determination of cadmium in aqueous solution and in coal slurry using the in-house coal “Candiota”. The pyrolysis curves for the ruthenium-based modifier combinations are shown in Fig. 1a and b, and those for the iridium-based modifiers in Fig. 2a and b. For comparison the conventional palladium and magnesium nitrates (Pd–Mg) modifiers added in solution were investigated as well and included in all figures. It is quite obvious that the Pd–Mg modifier exhibited the best performance in all cases, both with respect to sensitivity and stabilizing power. In aqueous solution the Pd–Mg modifier could stabilize cadmium up to a pyrolysis temperature of 650 °C, which is in agreement with literature data [35]. The second best performance was found for the pure PGM without tungsten, which could stabilize Cd to a pyrolysis temperature of 550–600 °C, which is in agreement with the findings of Lima et al. [31,32], whereas most of the combinations with tungsten lost their stabilizing power already around 500 °C, which is in contrast to the results of the above authors, who reported a pyrolysis temperature of 650 °C for the W–Ir and W–Ru modifiers.

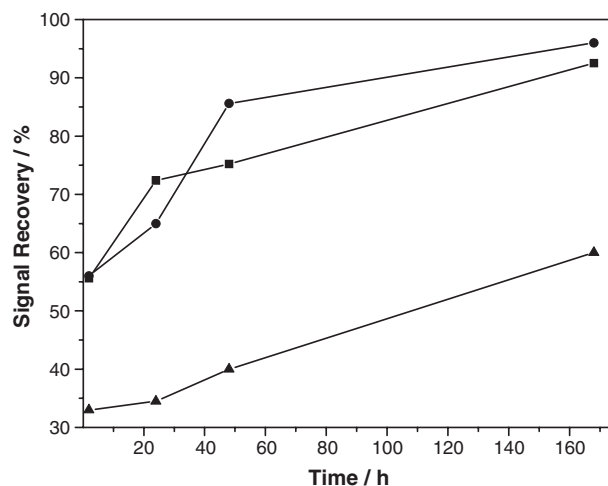


Fig. 3. Extraction of cadmium into the liquid phase relative to the total content found in the whole slurry in dependence of the extraction time, using 400 μg Ir as permanent modifier; pyrolysis temperature: 600 °C; atomization temperature: 1600 °C — LS ET AAS. (—●—) SARM 19; (—■—) Candiota; (—▲—) BCR No180 Gas Coal.

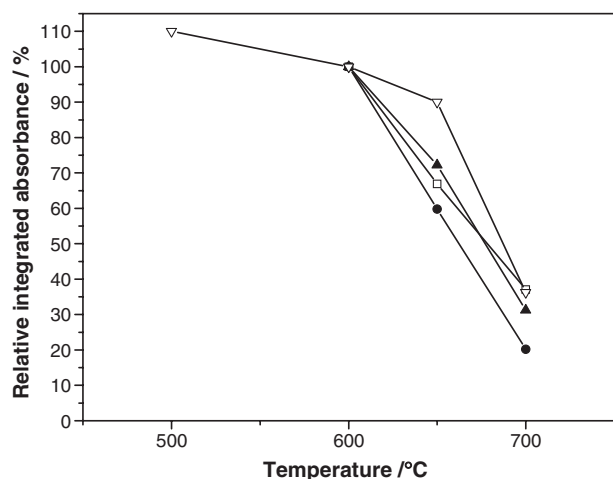


Fig. 4. Relative integrated absorbance obtained for Candiotia coal slurries using pyrolysis temperatures between 500 and 700 °C (A_{int} at 600 °C=100); (□) fresh slurry; (●) after 24 h; (▲) after 48 h; (▽) supernatant only.

The situation changed somewhat when coal slurries were investigated, as the Pd–Mg modifier lost some of its stabilizing power, and the maximum applicable pyrolysis temperature dropped to 600 °C. The same pyrolysis temperature could also be used with the pure PGM permanent modifiers Ru and Ir, whereas all the combinations of these modifiers with tungsten lost their stabilizing power already between 500 and 550 °C. These results were kind of surprising, as in recent investigations on cadmium determination in coal using direct solid sampling iridium, applied as permanent modifier, were found to allow pyrolysis temperatures of 700–800 °C without any analyte loss [11]. We were therefore suspecting that the high acid concentration used for slurry preparation and/or some compound that was leaching out of the coal during slurry preparation could impair the performance of the permanent modifiers. A number of leaching experiments were therefore carried out in order to get more insight into that process.

3.2. Leaching experiments

First the extraction of the analyte from the coal matrix to the liquid phase of the slurry was investigated, and three significantly different coal samples were chosen in order to get representative information. Slurries of BCR No180 Gas Coal,

SARM 19 and Candiotia were prepared as described in the Experimental part, but weighing the samples into 10 mL polyethylene closed vessels. After the addition of the diluent, the slurries were submitted to ultrasonic agitation for 5 min and left to stand for 24 h, 48 h and one week, respectively, of extraction at room temperature. Prior to transfer to the autosampler cup, the slurries were put one more time into the ultrasonic bath for 5 min.

The average integrated absorbance obtained for the slurry was adopted as 100%. Then the slurries were left in the autosampler cup for about one hour in order to allow sedimentation of the solid phase. The depth of the autosampler capillary was adjusted to aspirate 20 μL of the supernatant into the atomizer tube. Fig. 3 shows the fraction of analyte extracted into the supernatant in comparison to the values obtained for the bulk slurry ($n=10$). The measurements were performed using the tube treated with 400 μg of Ir, at pyrolysis and atomization temperatures of 600 and 1600 °C, respectively. It is obvious that the extraction of cadmium to the liquid phase is not complete, not even after one week. However, different coal samples might show significantly different leaching behavior, as more than 50% of the analyte was leaching out of SARM 19 and Candiotia already during slurry preparation, and about 90% were in the aqueous phase after one week, whereas the extraction from the gas coal reached only about 50% after this period of time.

In another set of experiments pyrolysis curves were established for fresh slurries, after one and after two days of standing, and for the supernatant liquid. A typical example is shown in Fig. 4. The curves were normalized to 100% for the integrated absorbance obtained with 600 °C pyrolysis for better comparison, firstly because the supernatant always had a lower analyte content, and secondly to eliminate differences in sensitivity, because the measurements obviously had to be made at different days. There was no significant difference in the drop of sensitivity between 600 and 700 °C between fresh slurries and those that have been standing for 1–2 days. The supernatant usually exhibited a less pronounced drop in sensitivity between 600 and 650 °C, compared to the slurries, but this difference disappeared for a pyrolysis temperature of 700 °C, where the signal had dropped to about 30–40% of its original value for all slurries and the supernatant. This means that the solid phase of the slurries had no detectable contribution to the loss in sensitivity (and analyte) between 600 and 700 °C. This is also in

Table 3
Determination of cadmium in coal using slurry sampling LS ET AAS

Sample or CRM	Certified or reference value ($\mu\text{g g}^{-1}$)	Found/ $\mu\text{g g}^{-1}$			
		400 μg Ru	300 μg W + 400 μg Ru	400 μg Ir	300 μg W + 300 μg Ir
Candiotia	0.081 \pm 0.009 ^a	0.074 \pm 0.009	0.078 \pm 0.002	0.082 \pm 0.005	0.086 \pm 0.004
BCR 180	0.212 \pm 0.011	n.d.	n.d.	n.d.	0.129 \pm 0.010
SARM 19	0.13 \pm 0.016 ^b	0.099 \pm 0.01	0.093 \pm 0.002	0.089 \pm 0.004	0.099 \pm 0.001
NIST 1635	0.03 \pm 0.01	n.d.	n.d.	n.d.	0.006 \pm 0.001

n.d. = not determined.

^a From Ref. [20].

^b From Ref. [11].

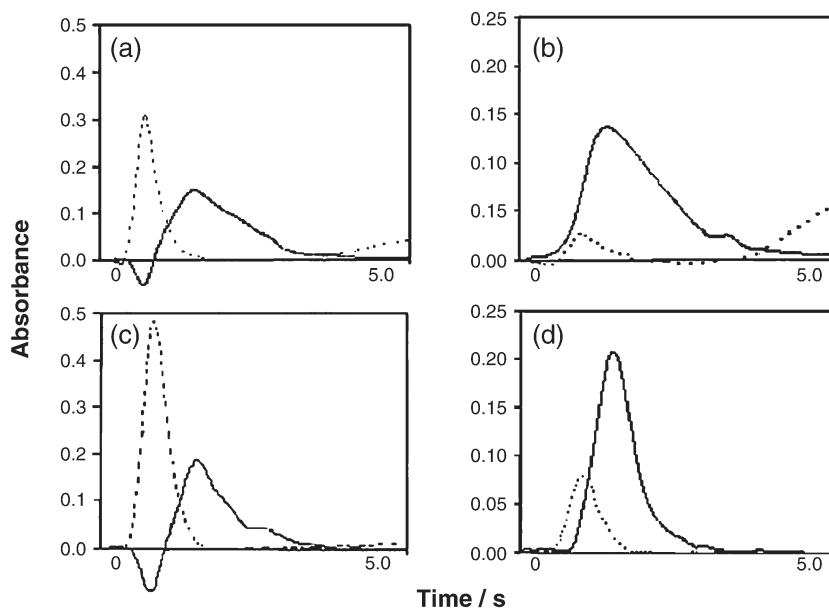


Fig. 5. Absorption signals for cadmium (solid line) and background (dotted line) in coal slurries using LS ET AAS with an atomization temperature of 1600 °C and W–Ir permanent modifier; (a) Candiota, $T_{\text{pyr}}=500$ °C; (b) Candiota, $T_{\text{pyr}}=600$ °C; (c) BCR 180 Gas Coal, $T_{\text{pyr}}=600$ °C; (d) BCR 180 Gas Coal, $T_{\text{pyr}}=650$ °C.

agreement with results obtained with direct solid sampling, using the same samples and the same permanent modifier, where no loss in sensitivity has been observed for cadmium at least up to 700 °C [11]. The results therefore support the assumption that the high acid concentration and/or some matrix component that is leaching easily to the aqueous phase is deactivating the permanent modifier in part, resulting in the observed losses above 600 °C.

3.3. Analytical results using LS AAS

Independent of the apparent losses at pyrolysis temperatures above 600 °C, an attempt was made to determine cadmium in coal slurries using this pyrolysis temperature and calibration against aqueous standards. The results are shown in Table 3 using the two PGM permanent modifiers and two combinations with tungsten. The results for the Candiota coal were in

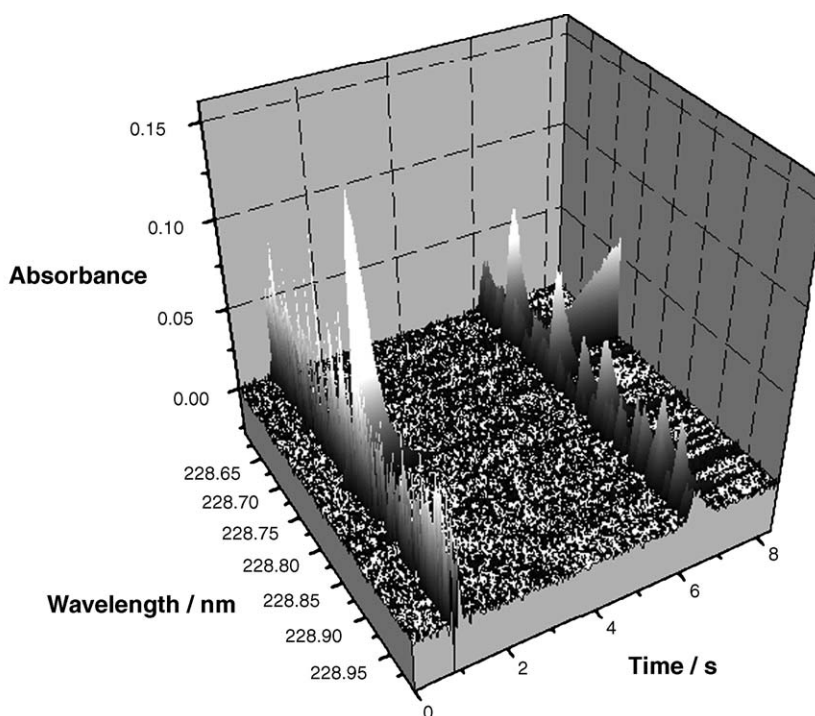


Fig. 6. Time-resolved absorbance spectrum for BCR 180 Gas Coal in the vicinity of the Cd line at 228.802 nm line, using HR-CS ET AAS; $T_{\text{pyr}}=600$ °C; $T_{\text{at}}=1600$ °C. Registration starts with the atomization stage and continues through the clean stage.

agreement with the value established previously using independent techniques [20], and the results for SARM 19 were reasonably close to the values obtained by solid sampling ET

AAS and ETV-ICP-MS [11]. However, the results for BCR 180 Gas Coal and NIST 1635 coal were far too low.

The explanation for this poor performance could be found by investigating the peak profiles, which are shown in Fig. 5. In the case of the Candiota coal an overcorrection was observed only for pyrolysis temperatures $<600\text{ }^{\circ}\text{C}$ (Fig. 5a), which, however, completely disappeared at a pyrolysis temperature of $600\text{ }^{\circ}\text{C}$ (Fig. 5b), explaining the accurate results for this sample. In the case of the BCR 180 Gas Coal, however, there was a very pronounced overcorrection due to a spectral interference under the analytical conditions used for cadmium determination, i.e. a pyrolysis temperature of $600\text{ }^{\circ}\text{C}$ (Fig. 5c), which could only be overcome using a pyrolysis temperature of at least $650\text{ }^{\circ}\text{C}$ (Fig. 5d). At this temperature, however, a significant part of the analyte is already lost in the pyrolysis stage, so that only a slight improvement in the recovery could be obtained. This means that the slurry sampling technique did not show the ruggedness required for a routine method with any of the investigated permanent modifiers.

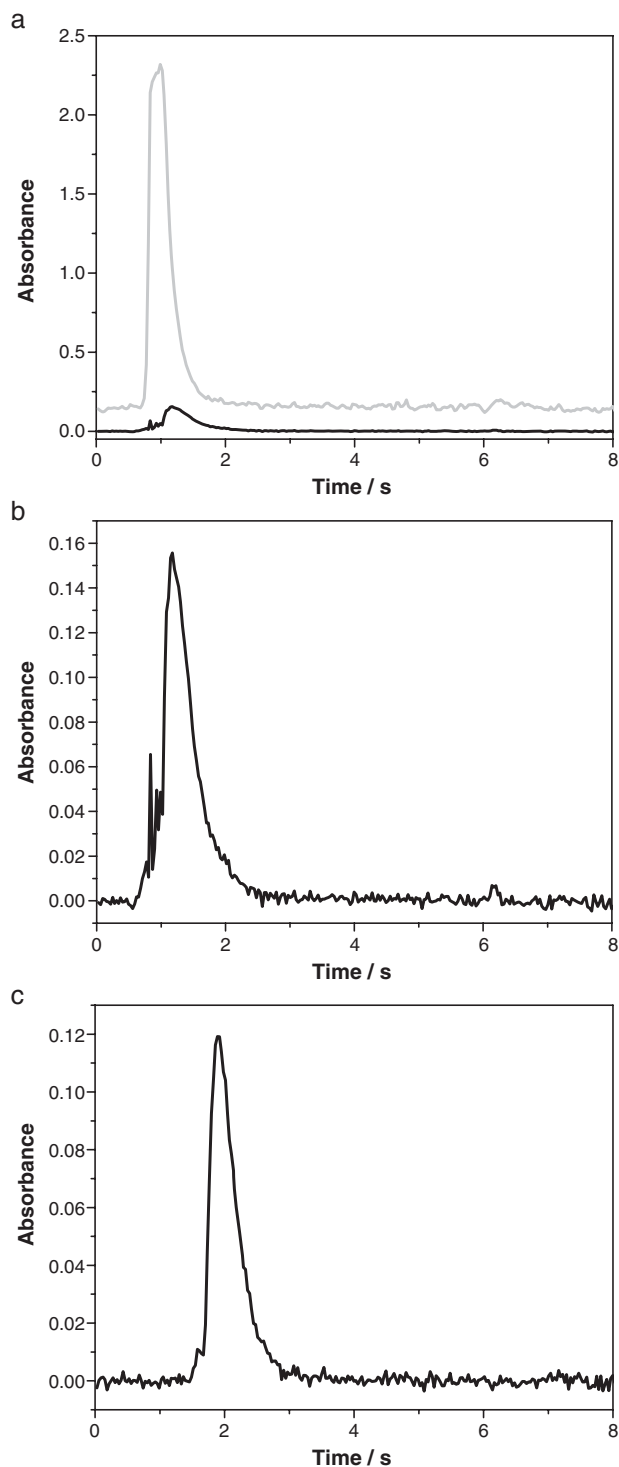


Fig. 7. Absorbance over time for BCR 180 Gas Coal measured at the center pixel at 228.802 nm only, using HR-CS ET AAS; registration starts with the atomization stage and continues through the clean stage; (a) absorbance signals without (gray) and with (black) automatic background correction $T_{\text{pyr}}=600\text{ }^{\circ}\text{C}$; (b) background-corrected absorbance for Cd, $T_{\text{pyr}}=600\text{ }^{\circ}\text{C}$; (c) background-corrected absorbance for Cd, $T_{\text{pyr}}=700\text{ }^{\circ}\text{C}$.

3.4. Measurements using HR-CS ET AAS

In order to further investigate the spectral interference that had caused the overcorrection shown in Fig. 5c, additional investigations were carried out using HR-CS ET AAS. As exactly the same graphite furnace design and the same tubes were used in both instruments, the results would be directly comparable. The design of the two spectrometers, however, was completely different, as the latter one, among many other things, makes it possible to visualize the entire spectral environment of the analytical line at high resolution, which makes the detection and the avoidance of spectral interferences relatively easy [33]. Fig. 6 shows the time-resolved absorbance spectrum of BCR 180 Gas Coal under exactly the same conditions that have been used in Fig. 5c. Obviously the information contained in Fig. 6 is orders of magnitude greater. The registration starts at the beginning of the atomization stage and the cleaning stage begins at 6 s, and it was in this stage that fine-structured background absorption appeared. However, neither this molecular absorption, nor the secondary iron line at 228.725 nm [33], which appeared even later, could have caused any problem in LS ET AAS using deuterium background correction, but only the noisy signal preceding the cadmium absorption pulse.

This phenomenon is illustrated in more detail in Fig. 7a, where only the absorbance over time, recorded at the center pixel at 228.802 nm , is shown without and with automatic background correction. The rapidly appearing background absorption signal, which is due to radiation scattering at volatilized matrix particles, reaches values of $A\sim 2.5$, which is beyond the capabilities of any background correction system, particularly of deuterium background correction. The background absorption is directly overlapping with the analyte atomization signal, and the very rapid increase of the background peak would cause additional problems for any sequential correction system, as are all systems used in LS AAS.

In HR-CS AAS, however, background measurement and correction are strictly simultaneous, resulting in much more

Table 4
Determination of cadmium in coal with slurry sampling HR-CS ET AAS using different modifiers and pyrolysis temperatures

Sample or CRM	Certified or reference value ($\mu\text{g g}^{-1}$)	Found/ $\mu\text{g g}^{-1}$				
		400 $\mu\text{g Ir}$		400 $\mu\text{g Ru}$		Pd–Mg
		$T_{\text{pyr.}} 600\text{ }^{\circ}\text{C}$	$T_{\text{pyr.}} 700\text{ }^{\circ}\text{C}$	$T_{\text{pyr.}} 600\text{ }^{\circ}\text{C}$	$T_{\text{pyr.}} 700\text{ }^{\circ}\text{C}$	$T_{\text{pyr.}} 700\text{ }^{\circ}\text{C}$
Candiota	$0.081 \pm 0.009^{\text{a}}$	0.073 ± 0.006	0.083 ± 0.008	0.092 ± 0.003	0.093 ± 0.01	0.079 ± 0.01
BCR 180	0.212 ± 0.011	0.163 ± 0.01	0.201 ± 0.021	n.d.	0.124 ± 0.012	0.210 ± 0.04
SARM 19	$0.073 \pm 0.016^{\text{b}}$	0.093 ± 0.009	0.120 ± 0.012	0.089 ± 0.006	0.079 ± 0.01	0.090 ± 0.01
SARM 20	$0.05 \pm 0.01^{\text{b}}$	0.068 ± 0.006	0.082 ± 0.004	0.066 ± 0.009	0.054 ± 0.002	0.066 ± 0.001
NIST 1630 a	$0.13 \pm 0.003^{\text{b}}$	0.046 ± 0.01	0.050 ± 0.007	n.d.	0.041 ± 0.009	0.042 ± 0.004
NIST 1632 b	0.0573 ± 0.0027	n.d.	0.057 ± 0.005	0.045 ± 0.008	0.036 ± 0.02	0.053 ± 0.01
NIST 1635	0.03 ± 0.01	n.d.	0.018 ± 0.003	0.018 ± 0.004	0.01 ± 0.002	0.016 ± 0.005

n.d. = not determined.

^a From Ref. [20].

^b From Ref. [11].

efficient correction, as can be seen in Fig. 7b. The background absorption is perfectly corrected without leaving any artifact except for an increased noise level at the beginning of the atomization stage due to the extreme attenuation of the radiant flux reaching the detector under these conditions. It is also worth mentioning that no molecular absorption appeared 6 s after the onset of the atomization stage, i.e. during the cleaning stage. This means that this fine structured absorption, which clearly appeared in Fig. 6, was not only resolved from the analyte absorption in time, but also in wavelength from the analytical line.

Only minor background absorption was observed, and a perfectly shaped absorption pulse for Cd was obtained when a pyrolysis temperature of 700 °C was used, as shown in Fig. 7c. This was in agreement with results obtained using direct solid sampling [11], however, the absorbance was clearly lower than that for a pyrolysis temperature of 600 °C (Fig. 7b), indicating analyte losses, as expected from the pyrolysis curves established earlier.

3.5. Analytical results obtained with HR-CS ET AAS

Based on the above investigations, a number of coal reference materials were analyzed with the HR-CS ET AAS equipment using Ir and Ru permanent modifiers and pyrolysis temperatures of 600 and 700 °C, as well as the conventional

Pd–Mg modifier added in solution, using a pyrolysis temperature of 700 °C. The results are reported in Table 4 except for a few situations, where no reproducible values could be obtained. Unfortunately the results were not very consistent, and there was not a single modifier–pyrolysis temperature combination that gave satisfactory results for all coal samples investigated. The quality of the result obviously depended on the individual coal and its matrix composition. There was only one coal, Candiota, for which the results were not significantly different from the reference value under all the various conditions. In contrast, for NIST SRM 1630a and 1635, all the results were lower than the certified or reference values. For the other coals investigated, the most consistent results were obtained with the conventional Pd–Mg modifier. Low results obtained with a pyrolysis temperature of 600 °C in spite of a successful background correction, as shown for BCR 180 in Fig. 7b, could only be explained by a reduced residence time of the analyte atoms in the absorption volume. As the background signal, which is caused by the rapidly volatilized matrix, is directly overlapping with the analyte signal, it is quite likely that some analyte atoms are carried out of the tube with the matrix. The fact that both high and low values were obtained for pyrolysis temperatures of 700 °C indicates that analyte losses from the coal slurries might be higher or lower than for aqueous standards, depending on the individual coal and the modifier.

3.6. Figures of merit

In spite of the not really satisfactory analytical results, some figures of merit were established in order to characterize the method for comparison with other approaches. Only the values for HR-CS ET AAS are shown in Table 5; the sensitivity obtained with LS AAS was lower, but the overall trend was similar. The characteristic mass of 1.0 pg and the slope of the calibration curve were similar for the Ir permanent modifier and a pyrolysis temperature of 600 °C and the Pd–Mg modifier and a pyrolysis temperature of 700 °C. For the Ru permanent modifier the characteristic mass was higher and the slope of the calibration curve lower than for the Ir permanent modifier for a pyrolysis temperature of 600 °C. The sensitivity deteriorated

Table 5
Figures of merit for the determination of cadmium in coal by slurry sampling HR-CS ET AAS

Modifier	Pyrolysis temp./°C	Detection limit (ng g^{-1})	Characteristic mass (pg)	Linear regression	r
400 $\mu\text{g Ir}$	600	0.6	1.0	$A=0.00582+$ 0.0041 m	0.9989
	700	1.5	1.5	$A=0.000142+$ 0.0029 m	0.9998
400 $\mu\text{g Ru}$	600	3.0	1.3	$A=0.000857+$ 0.0034 m	0.9999
	700	2.6	1.4	$A=0.00366+$ 0.0031 m	0.9990
Pd–Mg	700	3.0	1.0	$A=-0.00114+$ 0.0047 m	0.9998

for both permanent modifiers when a pyrolysis temperature of 700 °C was used, but less for Ru than for Ir. The best detection limit of 0.6 ng g⁻¹, defined as three times the standard deviation of ten measurements of the blank divided by the slope of the calibration curve, calculated for an average mass of 40 mg of coal in 1.5 mL of slurry, was obtained for the Ir permanent modifier and a pyrolysis temperature of 600 °C.

4. Conclusion

The current investigations have brought about a number of interesting results and findings. Firstly, it has been shown clearly that slurry sampling need not be the better way of analyzing solid samples, as the easier handling of samples is certainly less important than the accuracy of the results and the robustness of the method. The reason for this was the inferior stabilizing power of the permanent modifiers investigated for cadmium in the form of slurries, compared to direct solid sampling. This is the second interesting finding that permanent chemical modifiers, although for sure not in intimate contact with the sample, exhibit higher stabilizing power in direct solid sample analysis compared to slurry sampling. Thirdly, in contrast to some published results, the mixed W–PGM permanent modifiers exhibited inferior stabilizing power compared to the pure PGM modifiers. Fourthly, HR-CS ET AAS could reveal the nature of the interference observed in this work; although even rapidly changing background absorption up to $A \sim 2.5$ could be corrected without problems, low recoveries were obtained for some coals, proposing that the analyte was lost in part with the rapidly volatilizing matrix.

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References

- [1] A. Ohki, T. Nakajima, H. Yamashita, A. Iwashita, H. Takanashi, *Fuel Process. Technol.* 85 (2004) 1089–1102.
- [2] D.J. Swaine, *Fuel Process. Technol.* 65–66 (2000) 21–33.

- [3] E. Zjusz-Zubek, J. Konieczynski, *Fuel* 82 (2003) 1281–1290.
- [4] E.N. Pollock, Trace impurities in coal by wet chemical methods, in: S.P. Babu (Ed.), *Trace Elements in Fuel*, ACS, Washington, DC, 1975, pp. 23–34.
- [5] H.M. Kingston, S. Haswell, *Microwave enhanced chemistry*, American Chemical Society Professional Book Series, ACS, Washington, DC, 1997.
- [6] S. Fadda, A. Rivoldini, I. Cau, *Geostand. Newsl.* 19 (1995) 41–54.
- [7] H. Lachas, R. Richaud, K.E. Jarvis, A.A. Herod, D.R. Dugwell, R. Kandiyoti, *Analyst* 124 (1999) 177–184.
- [8] J. Liu, R.E. Sturgeon, *Ciencia* 3 (1995) 127–138.
- [9] M.G.R. Vale, M.M. Silva, B. Welz, E.C. Lima, *Spectrochim. Acta, Part B: Atom. Spectrosc.* 56 (2001) 1859–1873.
- [10] A.F. Silva, D.L.G. Borges, B. Welz, M.G.R. Vale, M.M. Silva, A. Klassen, U. Heitmann, *Spectrochim. Acta, Part B: Atom. Spectrosc.* 59 (2004) 841–850.
- [11] A.F. Silva, D.L.G. Borges, F.G. Lepri, B. Welz, A.J. Curtius, U. Heitmann, *Anal. Bioanal. Chem.* 382 (2005) 1835–1841.
- [12] D.L.G. Borges, A.F. Silva, A.J. Curtius, B. Welz, U. Heitmann, *Microchim. Acta* (in press).
- [13] C. Bendicho, M.T.C. de Loos-Vollebregt, *J. Anal. At. Spectrom.* 6 (1991) 353–374.
- [14] N.J. Miller-Ihli, *J. Anal. At. Spectrom.* 9 (1994) 1129–1134.
- [15] M.J. Cal Prieto, M. Felipe-Sotelo, A. Carlosena, J.M. Andrade, P. López-Mahia, S. Muniategui, D. Prada, *Talanta* 56 (2001) 1–51.
- [16] S.M. Maia, J.B.B. da Silva, A.J. Curtius, B. Welz, *J. Anal. At. Spectrom.* 15 (2000) 1081–1086.
- [17] M.A. Vieira, B. Welz, A.J. Curtius, *Spectrochim. Acta, Part B: Atom. Spectrosc.* 57 (2002) 2057–2067.
- [18] L. Ebdon, H.G.M. Parry, *J. Anal. At. Spectrom.* 2 (1987) 131–134.
- [19] L. Ebdon, H.G.M. Parry, *J. Anal. At. Spectrom.* 3 (1988) 131–134.
- [20] M.M. Silva, M.G.R. Vale, E.B. Caramão, *Talanta* 50 (1999) 1035–1043.
- [21] U. Schäffer, V. Krivan, *Spectrochim. Acta, Part B: Atom. Spectrosc.* 51 (1996) 1211–1222.
- [22] W. Slavin, D.C. Manning, G.R. Carnrick, *At. Spectr.* 2 (1981) 137–145.
- [23] G. Schlemmer, B. Welz, *Spectrochim. Acta, Part B: Atom. Spectrosc.* 41 (1986) 1157–1271.
- [24] B. Welz, G. Schlemmer, J.R. Mudakavi, *J. Anal. At. Spectrom.* 7 (1992) 1257–1271.
- [25] D.L. Tsalev, V.I. Slaveykova, L. Lampugnani, A. D’Ulivo, R. Georgieva, *Spectrochim. Acta, Part B: Atom. Spectrosc.* 55 (2000) 473–490.
- [26] J.B.B. da Silva, M.A.M. da Silva, A.J. Curtius, B. Welz, *J. Anal. At. Spectrom.* 14 (1999) 1737–1742.
- [27] D.L. Tsalev, V.I. Slaveykova, *Spectrosc. Lett.* 25 (1992) 221–238.
- [28] D.L. Tsalev, A. D’Ulivo, A. Lampugnani, M. di Marco, R.J. Zamboni, *J. Anal. At. Spectrom.* 10 (1995) 1003–1009.
- [29] A.B. Volynski, V. Krivan, *J. Anal. At. Spectrom.* 12 (1997) 333–340.
- [30] A.B. Volynski, S.V. Tikhomirov, *J. Anal. Chem.* 53 (1998) 718–721.
- [31] E.C. Lima, R.V. Barbosa, J.L. Brasil, A.H.P. Santos, *J. Anal. At. Spectrom.* 17 (2002) 1523–1529.
- [32] E.C. Lima, R.V. Barbosa, C.P. Vaghetti, L.S. Ferreira, *At. Spectr.* 23 (2002) 135–142.
- [33] B. Welz, H. Becker-Ross, S. Florek, U. Heitmann, *High-Resolution Continuum Source AAS*, Wiley-VCH, Weinheim, New York, 2005.
- [34] U. Heitmann, M. Schütz, H. Becker-Ross, S. Florek, *Spectrochim. Acta, Part B: Atom. Spectrosc.* 51 (1996) 1095–1105.
- [35] B. Welz, M. Sperling, *Atomic Absorption Spectrometry*, Wiley-VCH, Weinheim, New York, 1999, pp. 492–493.