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Validation of Cadmium Determination in Polyethylene Reference Materials by Means of Solid Sampling Zeeman Atomic Absorption Spectrometry

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Abstract

Direct solid sampling Zeeman atomic absorption spectrometric (SS-ZAAS) method was developed for validation of cadmium determination in polyethylene. Measurements were performed by a third generation Zeeman atomic absorption spectrometer combined with an automatic solid sampler. Applied on alternative wavelength (326.1 nm) the magnetic-3-field-measurement mode extended the linear range of the calibration up to 2500 ng cadmium. High analyte contents (up to 3500 ng Cd) were detectable without laborious dilution of solid samples. Limit of detection was calculated to be 12 ng cadmium according to the 3σ-criterion, the maximum sample weight was about 10 mg. The use of matrix-matched solid certified reference materials (CRMs) allowed simple calibration and modifier-free determination of cadmium in polyethylene resulting in high accuracy of the method.

Keywords: Cadmium; Polyethylene; Solid Sampling Zeeman Atomic Absorption Spectrometry; Method Validation; Certified Reference Materials

1. Introduction

Cadmium is widely used in the industry as additive in paint, stabilizer for plastic materials against ageing and heat effect or for plating metal surfaces thus preventing corrosion [1]. On the other hand, it is a pollutant of high toxicity for the environment, and in 1991 the European Council issued a Directive on Cadmium [2], which prohibited the use of cadmium and its compounds in three areas: pigments, stabilisers and surface treatment. Furthermore, it provided for a general exemption clause where justification exists on the grounds of safety and reliability in case the use of cadmium is unavoidable. However, legal limits or threshold values must be based on strict analytical control, and quality assurance of analytical results requires certified reference materials (CRMs).

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Analytical methods associated with European directives include atomic spectrometry and are usually restricted to analysis of solutions. Dissolution of plastic materials as polyethylene requires complex and time consuming procedure involving concentrated acids and heating [3-6] or toxic organic solvents [7]. Because of the high volatility of cadmium there is a risk of analyte losses by methods using wet digestion in sample preparation.

Solid sampling Zeeman atomic absorption spectrometry (SS-ZAAS) with no chemical sample pretreatment reduces to minimum the risk of contamination and analyte loss. The short analysis cycle after calibration delivers one result every 3 minutes and avoiding any dilution step the method achieves lower detection limits, than conventional wet-digestion AAS-techniques [8,9].

Four polyethylene reference materials with cadmium concentrations in the range of 40 to 400 μg g^{-1} Cd have been certified for cadmium by the Institute for Reference Materials and Measurements (IRMM) on behalf of Verband der Automobilindustrie e.V. (VDA), Frankfurt, Germany. The material was used within the scope of IRMM's International Measurement Evaluation Programme (IMEP) [10]. The cadmium content was determined by Isotope Dilution Mass Spectrometry (IDMS) using quadrupole thermal ionization mass spectrometer [11]. The homogeneity of the materials was verified using Grün SM30 solid sampling ZAAS instrumentation (Grün Analytische Meß-Systeme GmbH, Germany) [1, 12].

In the present work a direct solid sampling ZAAS-method was validated for cadmium determination in polyethylene samples.

2. Experimental

2.1. Apparatus

For the determination of cadmium in polyethylene a third generation solid sampling Zeeman atomic absorption spectrometer ZEEnit 60 (Analytik Jena AG, Germany) supplied with an automatic solid sampler model SSA 61Z was used. The solid sampling system SSA 61Z automates the sample handling for the spectrometer. It consists of a modified microbalance (M2P Sartorius), a sample boat transfer with handling system and a microprocessor control unit with display and key panel. The transfer system picks the boat up at start position, transports it twice to the balance, first for tare and then for weighing the sample. Consecutively the sample boat is transferred to the furnace and after the measurement procedure brought back to the start.

The spectrometer features a transverse-heated graphite furnace atomiser and inverse Zeeman-effect background correction (variable magnetic field with two different correction modes). The magnetic field orientation is horizontal relatively to the furnace axes and transverse relatively to the optical radiation beam. The magnet field strength can be adjusted between 0.0 and 1.0 T with increments of 0.05 T.

Three measurements modes are available: the most sensitive 2-field [13], the less sensitive 3-field [14] and a combination of both, the dynamic mode [15]. In the 2-field mode single values of the integrated intensity levels are obtained at a frequency of 200 Hz. In the 3-field mode the measurement data are formed from the signals obtained at maximum and medium magnetic field strengths. In the dynamic mode the magnetic field is switched in the same way as in the 3-field mode. However, the measurement data are handled sequentially by the 2-field and 3-field modes. In this case two simultaneously valid analytical curves are obtained [15,16]. In 3-field and dynamic mode the concentration working range can be substantially extended depending on the element [17,18].

The experimental conditions for the SS-ZAAS determination of cadmium in polyethylene samples are listed in Table 1.

Table 1. Experimental conditions for the SS-ZAAS determination of cadmium in polyethylene

Experimental parameters	**ZEEnit 60**
Wavelength	326.1 nm
Bandpass	0.8 nm
Lamp type	HCL
Lamp current	3.5 mA
Measurement mode	Peak area
Integration time	4 s
Magnet field mode	3-field mode
Magnet field strength H_{med}/H_{max}	0.5 T / 0.8 T

The optimized time/temperature program is presented in Table 2.

Table 2. Time/temperature program for SS-ZAAS determination of cadmium in polyethylene

Step	**Temp [°C]**	**Ramp [°C s^{-1}]**	**Hold [s]**	**Ar flow**
1. Drying	100	50	10	Middle
2. Drying	200	50	20	Middle
3. Pyrolysis	550	200	50	Middle
4. Auto zero	550	0	5	Stop
5. Atomization	2000	1500	4	Stop
6. Cleanout	2400	1000	4	Max

2.2. Reference Materials and Samples

Six high-density polyethylene certified reference materials (CRMs) were used for method validation – four of them (sicolen yellow, sicolen orange, sicolen red and sicolen Bordeaux), certified by IRMM on behalf of VDA and two polyethylene European Reference Materials (ERM) CRMs [19].

The certified Cd concentrations in the CRMs are as follows:

1. Sicolen yellow - **VDA-001: 40.9±1.2 μg g^{-1} Cd**

2. Sicolen orange - **VDA-002: 75.9±2.1 μg g^{-1} Cd**

3. Sicolen red - **VDA-003: 197.9±4.8 μg g^{-1} Cd**

4. Sicolen Bordeaux - **VDA-004: 407±12 μg g^{-1} Cd**

5. Polyethylene (high level) **ERM–EC-680: 140.8±2.5 μg g^{-1} Cd**

6. Polyethylene (low level) **ERM–EC-681: 21.7±0.7 μg g^{-1} Cd**

Calibration was performed with different solid certified reference materials and variation of their sample weight. By ZEEnit 60 AA-spectrometer maximum four calibration standards could be used for one calibration curve.

The sample pieces were cut to the desired size with ceramic knife on a PTFE-plate and then taken with titanium tweezers to avoid sample contamination. They were weighed on a small boat platform which was brought then into the graphite tube. The weighed sample amounts were usually less than 1 mg, but in some cases their weight was several milligrams or more. Pyrolytically coated graphite platforms were used for all determinations and the integrated absorbance was measured.

3. Results and Discussion

3.1. Linearity and Working Range

The cadmium content in the polyethylene CRMs was relatively high (from 21.7 μg g^{-1} Cd for ERM–EC-681 to 407 μg g^{-1} Cd for VDA-004) and measurements were performed at the wavelength of 326.1 nm (500x less sensitive than the most sensitive resonance line).

For the determination of cadmium in polyethylene with the ZEEnit 60 spectrometer the 3-field measurement mode was applied. Using the 3-field mode the sensitivity could be optimized by varying the magnetic field strength ratio, i.e. the ratio between medium (H_{med}) and maximum (H_{max}) magnetic field strength - H_{med}/H_{max} (Table 1). With increasing this ratio, the absorption signals for Cd diminish, and system sensitivity gradually decreases. In this way a substantial reduction of sensitivity could be obtained [14].

Calibration curve made by using four polyethylene certified reference materials (ERM-EC-681, CRM-VDA-002, CRM-VDA-003 and CRM-VDA-004) is presented on Fig. 1.

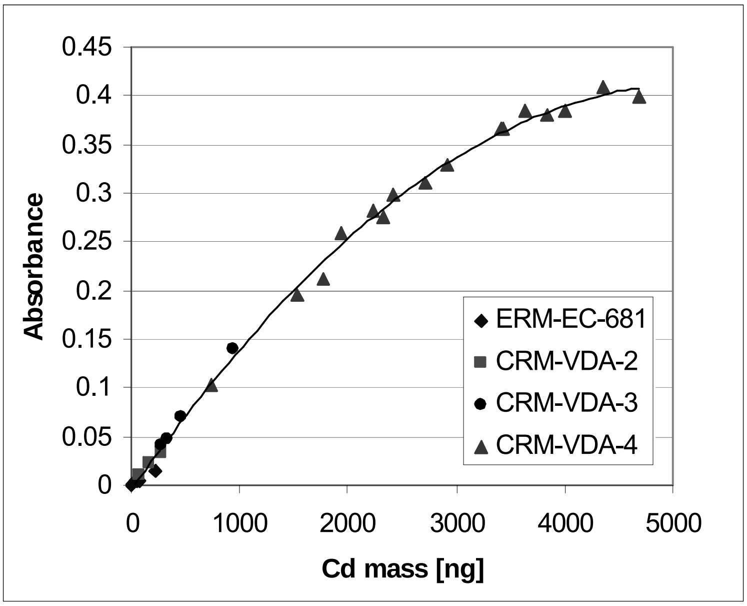


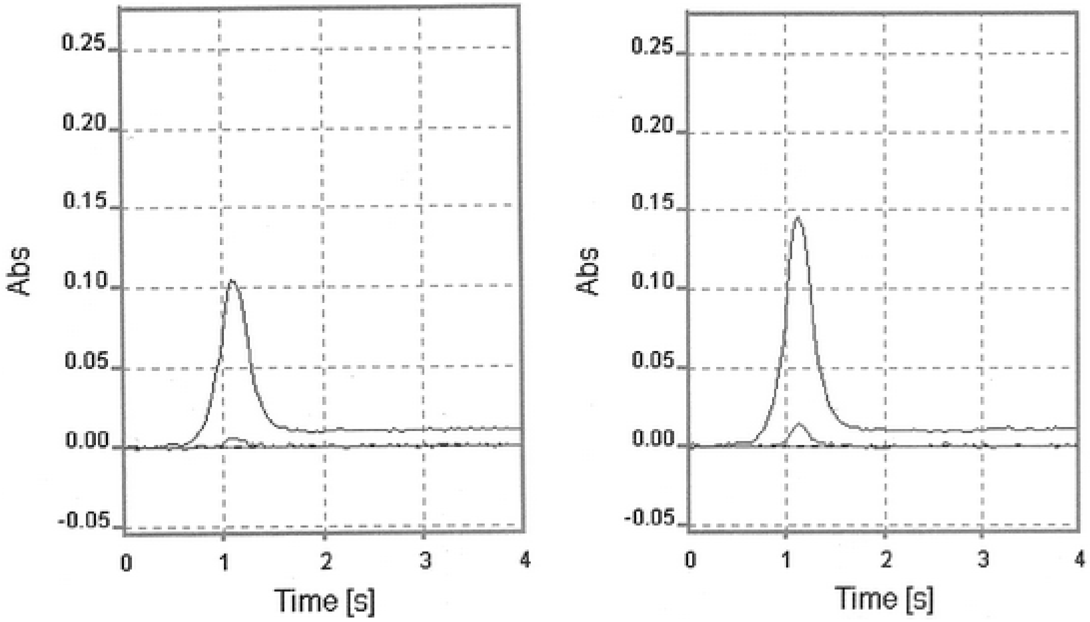
Fig. 1. Calibration curve for cadmium determination in polyethylene. Calibration standards used: Polyethylene (low level) ERM-EC-681 (21.7±0.7 μg g^{-1} Cd); CRM-VDA-002 (75.9±2.1 μg g^{-1} Cd); CRM-VDA-003 (197.9±4.8 μg g^{-1} Cd) and CRM-VDA-004 (407±12 μg g^{-1} Cd).

Linear and working ranges of the method were established from the calibration curve. Linear range is up to 2500 ng Cd and working range is up to 3500 ng Cd (non-linear calibration). For higher analyte content self-absorption is observed. Using the 3-field measurement mode by the optimized experimental conditions, the linear and working ranges were extended up to three orders of magnitude. This allows polyethylene samples with up to 10 mg of weight to be analysed.

3.2. Limit of Detection

The limit of detection was estimated according to the 3σ-criterion and was calculated to be 12 ng Cd.

Looking at the absorbance peaks for 9 ng Cd and 19 ng Cd (Fig. 2, a and b respectively), it may be concluded that even an absorbance signal of 9 ng Cd can be distinguished from the baseline (Fig. 2, a). The absorbance signal which corresponds to Cd content of 19 ng is already a well-pronounced peak (Fig. 2, b).



(a) (b)

Fig. 2. Absorbance peak for **(a)** 9 ng and **(b)** 19 ng cadmium (on both pictures the higher peak is background signal).

3.3. Precision and Accuracy

Determination of precision is hampered by the intrinsic heterogeneity of the materials. For small sample intakes, variation is heavily influenced by the micro heterogeneity. This effect cannot be eliminated by using more material of a lower concentration; as such materials are expected to be more heterogeneous.

Therefore solid samples inclusive reference materials are not suitable for precision determination. Especially for micro-analytical methods as SS-ZAAS the heterogeneity of solid samples substantially contributes to standard deviation of replicate measurements and makes them useless for precision calculations [9].

Comparison of the measured value with the certified value allows an assessment of accuracy.

Cadmium content was determined in two polyethylene CRMs, namely ERM-EC-680 and CRM-VDA-001. The cadmium concentrations in both CRMs were calculated using the calibration curve based on the other four polyethylene CRMs available - ERM-EC-681, CRM-VDA-002, CRM-VDA-003 and CRM-VDA-004 (Fig. 1). The experimental results are compared with the certified values in Table 3. There is an excellent agreement between experimental and certified values which is a proof for the good accuracy of the method. The relative standard deviation does not exceed 5.4 % RSD.

Table 3. Measurement results from the SS-ZAAS determination of cadmium in two polyethylene CRMs: VDA-001 and ERM-EC-680

	Cadmium concentration [μg g^{-1}]	
Reference material	**CRM-VDA-001**	**ERM-EC-680**
Single values	40.5	140.8
	40.2	148.7
	43.6	145.7
	39.9	139.0
	44.8	136.4
Mean value	**41.8**	**142.1**
SD	2.2	5.0
RSD%	5.4	3.5
Certified value	**40.9±1.2**	**140.8±2.5**

4. Conclusions

The validation of cadmium determination in polyethylene by means of SS-ZAAS without any sample pretreatment was successfully performed by analysing polyethylene CRMs. With the ZEEnit 60 combined with an automatic solid sampler it was possible to perform the measurements in routine. Using the less sensitive wavelength (326.1 nm) and the 3-field measurement mode the following figures of merit were obtained: linear range up to 2500 ng Cd; working range up to 3500 ng Cd; limit of detection (3σ-criterion) – 12 ng Cd; maximum sample weight – 10 mg. Results obtained are in excellent agreement with the certified values. Precision and accuracy are comparable to conventional analytical methods after sample decomposition.

The short analysis cycle after calibration delivers one result every three minutes. SS-ZAAS proved to be a rapid and accurate method for the determination of cadmium in polyethylene.

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