Determination of Trace Cadmium in 24-h Diets by Graphite Furnace Atomic Absorption Spectrometry

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An analytical procedure for the determination of trace Cd in 24-h diets with graphite furnace atomic absorption spectrometry is developed and validated. Closed-vessel microwave acid digestion was used for the sample dissolution. To evaluate the bias of the method, reference materials were analyzed, and the results are in good agreement with the certified values. The precision of the method was evaluated by the analysis of a total diet sample and the repeatability and reproducibility (RSD) are 1.4% and 7.3%, respectively. The limit of detection and the limit of quantification in the dry product are 0.004 and 0.012 μg/g, respectively. Cd is determined in 28 total diet samples collected during 7 days at four locations in Belgium. The estimated daily Cd dietary intake in Belgium is 18.4 ± 6.0 μg, which is acceptable compared with the ADI (60 μg/day) established by the FAO/WHO.

Keywords: *Trace cadmium; graphite furnace atomic absorption spectrometry; closed vessel microwave acid digestion; food analysis; total diets*

INTRODUCTION

Cadmium (Cd), together with lead and mercury, is of major concern as an environmental contaminant. Cd has a tendency to accumulate in human organs (a half-life of 30 years). Long-term chronic exposure to Cd has been implicated in kidney lesion, osteomalacia, cardiovascular diseases, and hypertension (Bernard and Lauwerys, 1984; Lu, 1991; Robards and Worsfold, 1991). In 1976, the International Agency for Research on Cancer (IARC) classified Cd with those chemicals that are probably carcinogenic to man (IARC, 1976). The acceptable daily intake (ADI) established by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) is 60 μg/60 kg of body weight (WHO, 1972).

In the general population, Cd exposure occurs via food, air, and water. It has been shown that food is a major source of Cd intake (Robards and Worsfold, 1991). JECFA observed that the Cd dietary intake in 21 countries over the period 1980–1988 is below the ADI and is usually between 8.6 and 34.3 μg/day (WHO, 1989; Galal-Gorchev, 1993). JECFA concluded that there is only a relatively small safety margin between exposure and the ADI. It is therefore recommended that levels of Cd in foods and total diet should continue to be monitored and should not increase further.

Surveys on Cd dietary intake conducted in Belgium were reported in 1980 (Noirfalise and Fouassin, 1980; Fouassin and Fondu, 1980) and 1983 (Buchet et al., 1983). The estimated Cd intake reported in 1980 (Fouassin and Fondu, 1980) was between 45 and 50 μg/day. The intake decreased to 18 μg/day in the report of 1983 (Buchet et al., 1983). The latter survey employed duplicated portion studies (DPS), which is one of the study types in total diet studies (TDS) (Ockhuizen et al., 1991).

TDS are specifically designed to establish by chemical analysis the dietary intake of food constituents by a person consuming a typical diet. WHO has recommended TDS for the assessment of the potential risk of food contaminants (WHO, 1985; Kumpulainen, 1991). The outcome of TDS is compared with available standards such as ADI to evaluate potential risks of exposure.

Besides DPS mentioned earlier, the other two types of TDS are market basket studies (MBS) and individual food items (IFI) (Ockhuizen et al., 1991). For DPS, a selected group of individuals is invited to duplicate their daily meals, drinks, and snacks. The portions are aggregated and chemically analyzed. The advantages of DPS are the accurate duplication of all processes that are applied to the food before consumption and the provision of direct information on the actual intake by the individuals involved. The major drawbacks are the limited time period of the study and the possibility of altered food patterns during participation in the study. In MBS, according to the known average dietary intake of the population at large, all food items that are part of the diet are purchased. These food items are prepared following standard household procedures and combined into food groups, which are subsequently analyzed. IFI studies are based on data available from national food consumption surveys. The most commonly consumed food items are analyzed.

Our laboratory has been involved in a joint project for the assessment of daily intakes of food constituents by the Belgian population. Different approaches are considered, such as the analysis of individual foodstuffs in combination with data concerning food consumption and the analysis of total diets. For the former approach, an analytical method for the determination of trace Al in fish and bread with graphite furnace atomic absorption spectrometry (GFAAS) was developed (Yang et al., 1994). The sample preparation employed a closed-vessel acid microwave digestion, which assures an effective, fast, and contamination-free sample dissolution. The procedure was also found to be useful for the determination of K, Na, Ca, Mg, and Mn in some natural products by means of capillary electrophoresis (Yang et al., 1995). In this work the same digestion procedure was applied to decompose total diets, and an analytical method for the determination of trace Cd with GFAAS

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0021-8561/95/1443-2652$09.00/0

Table 1. Instrumental Conditions and Temperature Program

light source	EDL
power (W)	5
wavelength (nm)	228.8
spectral bandwidth (nm)	0.7
injection volume (μL)	10 of sample + 15 of matrix modifier

step	furnace temp (°C)	ramp time (s)	hold time (s)	Ar flow rate (mL/min)
1	90	1	10	300
2	160	60	20	300
3	750	30	15	300
4	1700	0	6	0
5	2650	1	5	300
6	20	1	5	300

Table 2. Microwave Heating Program

	step							
	1	2	3	4	5	6	7	8
power (W)	180	360	600	0	600	360	180	0
time (min)	3	3	3	3	3	3	3	2

was established. Eventually, 28 total diets, which were collected at four locations in Belgium, were analyzed to estimate the daily dietary intake of Cd in Belgium.

EXPERIMENTAL PROCEDURES

1. Apparatus. All measurements were performed with a Perkin-Elmer Zeeman 3030 atomic absorption spectrometer equipped with an HGA-600 graphite furnace, an AS-60 autosampler, and a PR-100 printer. Pyrolytic graphite coated tubes with a pyrolytic graphite platform were used. The instrumental conditions and the furnace program are given in Table 1. Signal evaluation was by means of the integrated absorbance values (A) computed by the instrument.

The digestions were performed with a programmable Milestone 1200 microwave digestion system with a maximum power supply of 1200 W and equipped with the ACM-100 automatic capping module (Milestone, Germany). Teflon HPV 80 high-pressure vessels (80 mL) with safety shields which can withstand up to 120 bar of pressure and a temperature of 300 °C were used. The microwave heating program is given in Table 2.

2. Reagents. A Titrisol concentrate containing 1000 mg/L Cd (Merck, Darmstadt, Germany) was used for preparing standard solutions (add 0.2 mL of nitric acid per 100 mL). Nitric acid (65% w/w) of the highest purity (Suprapur; Merck) was used for the preparation of the standards and for the digestion. Hydrogen peroxide (30% w/w) was of analytical reagent grade (pro analysi; Merck). For labware cleaning, analytical reagent nitric acid of 65% (w/w) was used (pro analysi; Merck). The water used for the preparation of all solutions was obtained from a Milli-Q water purification system (Millipore, Milford, MA) and contained no detectable Cd.

3. Samples and Their Decomposition. The 24-h diets were collected during 7 consecutive days at four locations in Belgium: the University Hospital in Liège, the Royal Military School in Brussels, the University Hospital in Antwerp, and the Barrack Major Houssiau in Peutie. The composition of the diets and their weights were noted. Per day, the meals consumed by one person were collected in a container and stored at −20 °C. In the laboratory, the samples were thawed and thoroughly homogenized with a mixer. From each diet, two subsamples (indicated further as a and b) were weighed in acid-rinsed plastic recipients (200 mL). These subsamples were freeze-dried and subsequently thoroughly homogenized in a mortar. The water contents of the subsamples were noted.

For digestion, two portions of ±0.4 g were taken from each subsample, and 2 mL of nitric acid, 0.5 mL of hydrogen peroxide, and 1 mL of Milli-Q water were added to each portion. They were digested in a microwave digestor using the heating program given in Table 2. The resulting digests were diluted to 10 mL in quartz volumetric flasks. The solutions were directly used for the determination with GFAAS. More details about the digestion procedure and the contamination control can be found in a previous publication (Yang et al., 1994).

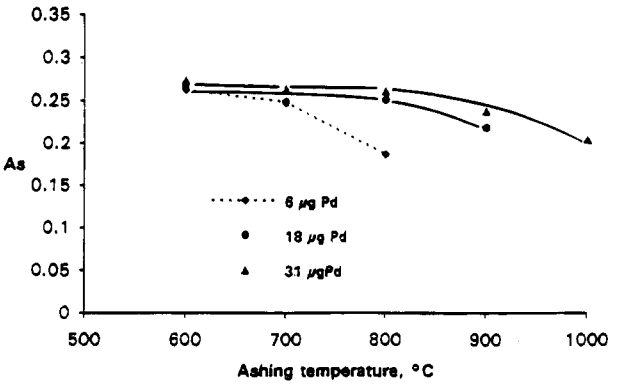

Figure 1. Thermal pretreatment curves for a total diet reference material digest spiked with 40 pg of Cd in the presence of different modifiers. Other experimental conditions are as given in Table 1.

Corresponding digestion blank solutions were prepared according to the above procedure.

4. Standard Reference Materials. Total diet with a certified Cd value of 0.028 ± 0.004 μg/g (NIST 1548) (National Institute of Standards and Technology, Gaithersburg, MD) and bovine liver with a certified value of 0.27 ± 0.04 μg/g (NIST 1577) were analyzed to evaluate the bias of the proposed method. At least six independent portions of ±0.4 g from each of them were taken for digestion. The sample preparation procedure is as mentioned above except for the bovine liver digests, which were diluted to 20 mL.

RESULTS AND DISCUSSION

1. Optimization of Experimental Conditions. Cd is a volatile element, which is evaporated at an ashing temperature of 300 °C in GFAAS. In our previous work (Smeyers-Verbeke et al., 1990), a mixture of 6 μg of Pd and 500 μg of NH_4NO_3 was found to be suitable as a matrix modifier for the analysis of urine, blood, and milk. This modifier allowed an increase in ashing temperature up to 700 °C and, as a result, matrix interferences were greatly reduced. The benefit of using NH_4NO_3 as one of the components in the matrix modifier is that the determination can tolerate high concentrations of salts such as NaCl. This is due to the fact that a chemical reaction occurs between NaCl and NH_4NO_3 and yields volatile $NaNO_3$ and NH_4Cl, which evaporate at lower temperature before the Cd atomization. However, it is seen in Figure 1 that, for total diet digest, a significant loss of Cd occurs at an ashing temperature of 700 °C with this modifier. When the Pd amounts are increased, the maximum ashing temperature is reached at 800 °C. Moreover, compared with the temperature program for urine, blood, and milk (Smeyers-Verbeke et al., 1990), it was found necessary to increase the drying ramp time from 30 to 60 s and the ashing ramp time from 15 to 30 s to allow the excess of acid in the measurement solution to evaporate and to avoid sputtering of the solution. Furthermore, it was observed that the deformation of the Cd signal, which occasionally occurred, could be avoided when the volume of matrix modifier injected was increased from 10 to 15 μL.

As seen in Figure 2, with the modifier containing 27 μg of Pd and 750 μg of NH_4NO_3, the maximum ashing

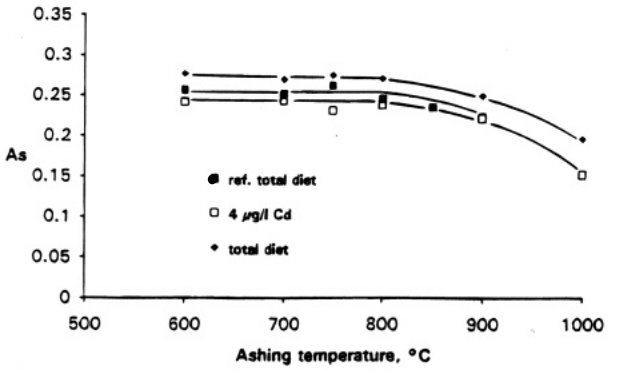

Figure 2. Thermal pretreatment curves for Cd in the total diet reference material spiked with 40 pg of Cd, a standard solution containing 4 µg/L Cd, and a real total diet sample. Matrix modifier: 27 µg of Pd + 750 µg of NH_4NO_3. Other experimental conditions are listed in Table 1.

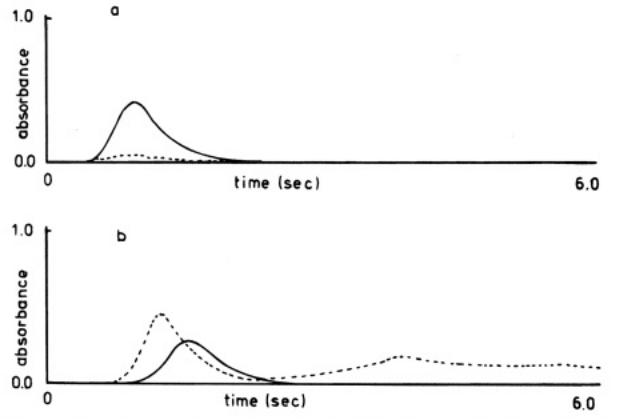

Figure 3. Atomization signal of Cd (full line) (broken line is the background signal) obtained from (a) the reference total diet spiked with 40 pg of Cd and (b) a total diet sample. Matrix modifier: 27 µg of Pd + 750 µg of NH_4NO_3. Experimental conditions are listed in Table 1.

temperature of 800 °C is applicable for a standard solution containing 4 µg/L Cd, the reference total diet spiked with 40 pg of Cd, and a real total diet sample digest. Finally, 750 °C was selected for the following experiments. The optimized temperature program is summarised in Table 1.

Figure 3 shows the atomization signal obtained for the spiked total diet reference material digest and for a total diet sample digest, both measured in the presence of a mixture of 27 µg of Pd and 750 µg of NH_4NO_3. From a preliminary recovery experiment (using digests spiked with Cd) a Cd recovery of 95−104% was obtained for the total diet reference material digests and total diet sample digests. It was therefore decided to validate the whole method.

2. Method Validation. *2.1. Linearity Test for the Calibration Line.* Six series of standard solutions containing 0, 1, 2, 4, 6, 8, and 10 µg/L Cd were prepared. For each series, new intermediate solutions containing 10 mg/L and 100 µg/L were prepared from the commercial concentrate of 1000 mg/L Cd. The variance of the peak areas (As) at the different concentration levels is shown in Figure 4. The variances at 1 and 10 µg/L are compared using an F-test (one-tailed, $\alpha = 0.05$). As the calculated F value is smaller than the critical one, the variances can be considered to be homogeneous, and therefore linear ordinary least-squares regression was applied. Subsequently, an ANOVA lack-of-fit test (Massart, 1988) was applied to check the linearity of the calibration line. The mean squares due to lack-of-fit and

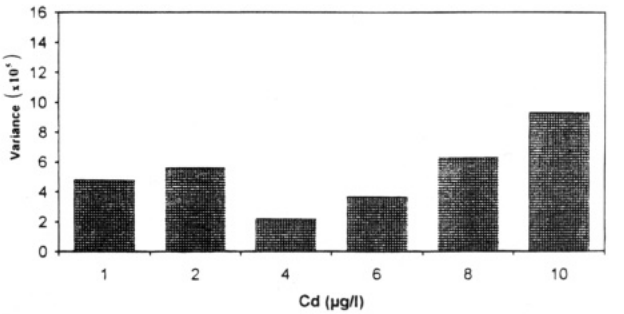

Figure 4. Estimated variance of the measurements as a function of the Cd concentration.

Table 3. Cd Recovery from Spiked Total Diet Samples

	mean concn (µg/L)	Cd found (µg/L)	recovery (%)
sample ($n^a = 6$)	1.72		
sample + 1 µg/L Cd	2.67	0.94 ± 0.06	94 ± 6
sample + 4 µg/L Cd	5.58	3.86 ± 0.21	97 ± 5
sample + 7 µg/L Cd	8.74	7.07 ± 0.26	101 ± 4

[a] n is the number of independent sample digestions.

due to the pure experimental error are compared by an F test. The results indicate no significant lack of fit: the straight line model is adequate and the calibration line is linear up to a Cd concentration of 10 µg/L. The regression equation is $y = 0.0813x + 0.0068$, with y representing the peak area and x the Cd concentration in micrograms per liter.

2.2. Detection of Matrix Effects. The slopes of a standard calibration line and a standard addition line were compared to detect possible matrix effects. The method of standard additions was performed on the reference total diet and total diet samples collected on the first, second, and seventh days at the Royal Military School in Brussels. The ratios of the slopes for the standard addition line and calibration line were 1.00, 1.07, 1.10, and 0.97, respectively, which are considered acceptable. A t test (two-tailed, $\alpha = 0.05$) (Massart, 1989) was also performed to compare the slopes and pointed to the absence of significant matrix interferences that introduce relative systematic errors. Therefore, the direct calibration with standard solutions will be used in the sample analysis.

2.3. Bias. The bias is determined by recovery experiments and the analysis of reference materials. The recovery experiments were performed on a diet sample (sample b collected on the second day at the Barrack Major Houssiau in Peutie), that was spiked with three different Cd concentration levels. At each level, six independent aliquots were spiked. The addition of Cd was performed by, respectively, pipetting 1 or 4 mL of a 10 µg/L Cd solution and 0.7 mL of a 100 µg/L Cd solution to ±0.4 g samples in the digestion vessels. The samples were then digested as previously described, and the digests were diluted to 10 mL in quartz volumetric flasks. As seen in Table 3, the Cd recoveries obtained from these samples are 94 ± 6%, 97 ± 5%, and 101 ± 4%, which are acceptable.

A more effective method for the detection of the method bias is the analysis of reference materials. In our work, a total diet reference material (NIST 1548) and a bovine liver reference material (NIST 1577) were analyzed. For the total diet, the Cd concentration obtained from 12 digests was 0.030 ± 0.004 µg/g, which is in good agreement with the certified value (0.028 ± 0.004 µg/g). The Cd concentration obtained from six

Table 4. Cd in 24-h Diets (Belgium)

day	subsample	Cd in dry meal (μg/g) digestion 1	Cd in dry meal (μg/g) digestion 2	Cd in fresh meal (μg/100 g) digestion 1	Cd in fresh meal (μg/100 g) digestion 2	Cd in fresh meal (μg/100 g) mean	Cd in fresh meal (μg/100 g) day mean	μg/day	total sample wt (g)	water (%)
				A. Sample Source: Royal Military School in Brussels						
1	a	0.050	0.056	0.91	1.02	0.96	1.00	24.4	2445	81.8
	b	0.061	0.052	1.11	0.95	1.03				81.7
2	a	0.034	0.036	0.63	0.67	0.65	0.79	20.6	2620	81.5
	b	0.050	0.050	0.92	0.92	0.92				81.5
3	a	0.076	0.058	1.38	1.05	1.22	1.19	32.3	2723	81.8
	b	0.062	0.065	1.13	1.18	1.15				81.8
4	a	0.078	0.072	1.24	1.14	1.19	1.19	23.2	1959	84.1
	b	0.075	0.074	1.19	1.17	1.18				84.1
5	a	0.048	0.047	0.93	0.91	0.92	0.93	23.9	2570	80.6
	b	0.046	0.050	0.90	0.98	0.94				80.4
6	a	0.040	0.040	1.12	1.12	1.12	1.11	23.1	2081	72.0
	b	0.039	0.040	1.09	1.12	1.10				72.0
7	a	0.055	0.066	1.06	1.28	1.17	1.14	29.5	2594	80.7
	b	0.056	0.058	1.08	1.12	1.10				80.7
		weekly Cd intake (μg) 177.0							mean 2427	
		av daily Cd intake (μg) 25.3 ± 4.1[a]								mean 80.4
				B. Sample Source: University Hospital in Liège						
1	a	0.040	0.037	0.81	0.75	0.78	0.78	15.4	1968	79.8
	b	0.039	0.039	0.79	0.79	0.79				79.9
2	a	0.034	0.036	0.75	0.80	0.78	0.80	14.9	1865	77.8
	b	0.037	0.035	0.85	0.80	0.82				77.2
3	a	0.041	0.040	0.80	0.78	0.79	0.76	14.9	1967	80.6
	b	0.037	0.038	0.72	0.74	0.73				80.6
4	a	0.041	0.044	0.82	0.88	0.85	0.85	18.2	2148	80.0
	b	0.043	0.042	0.86	0.84	0.85				80.1
5	a	0.041	0.042	0.82	0.84	0.83	0.84	17.4	2074	80.1
	b	0.044	0.041	0.88	0.82	0.85				80.1
6	a	0.033	0.030	0.67	0.61	0.64	0.65	12.6	1945	79.6
	b	0.033	0.031	0.67	0.63	0.65				79.6
7	a	0.038	0.036	0.75	0.71	0.73	0.64	12.3	1903	80.1
	b	0.030	0.026	0.59	0.52	0.55				80.2
		weekly Cd intake (μg) 105.7							mean 1981	
		av daily Cd intake (μg) 15.1 ± 2.2[a]								mean 79.7
				C. Sample Source: University Hospital in Antwerp						
1	a	0.029	0.026	0.79	0.71	0.75	0.74	14.0	2202	80.8
	b	0.025	0.029	0.68	0.79	0.74				80.8
2	a	0.058	0.055	1.24	1.18	1.21	1.22	14.7	2118	81.3
	b	0.058	0.057	1.24	1.22	1.23				81.3
3	a	0.041	0.043	0.92	0.97	0.95	0.97	9.3	2228	81.1
	b	0.044	0.045	0.99	1.01	1.00				81.1
4	a	0.037	0.036	1.18	1.15	1.17	1.13	11.2	2126	80.7
	b	0.034	0.035	1.09	1.12	1.10				80.8
5	a	0.019	0.022	0.54	0.63	0.59	0.63	17.7	2176	80.1
	b	0.027	0.020	0.77	0.57	0.67				80.1
6	a	0.033	0.029	0.89	0.78	0.83	0.83	13.3	2033	78.4
	b	0.028	0.034	0.75	0.91	0.83				78.4
7	a	0.041	0.041	0.90	0.90	0.90	0.90	12.7	1923	80.4
	b	0.042	0.040	0.92	0.88	0.90				80.4
		weekly Cd intake (μg) 92.9							mean 2115	
		av daily Cd intake (μg) 13.3 ± 2.7[a]								mean 80.4
				D. Sample Source: Barrack Major Houssiau						
1	a	0.029	0.0 26	0.79	0.71	0.75	0.74	14.8	1996	72.7
	b	0.025	0.029	0.68	0.79	0.74				72.7
2	a	0.058	0.055	1.24	1.18	1.21	1.22	28.9	2368	78.6
	b	0.058	0.057	1.24	1.22	1.23				78.6
3	a	0.041	0.043	0.92	0.97	0.95	0.97	22.2	2280	77.5
	b	0.044	0.045	0.99	1.01	1.00				77.5
4	a	0.037	0.036	1.18	1.15	1.17	1.13	24.4	2150	68.1
	b	0.034	0.035	1.09	1.12	1.10				68.0
5	a	0.019	0.022	0.54	0.63	0.59	0.63	12.2	1940	71.4
	b	0.027	0.020	0.77	0.57	0.67				71.4
6	a	0.033	0.029	0.89	0.78	0.83	0.83	17.3	2072	73.1
	b	0.028	0.034	0.75	0.91	0.83				73.1
7	a	0.041	0.041	0.90	0.90	0.90	0.90	20.3	2260	78.1
	b	0.042	0.040	0.92	0.88	0.90				78.1
		weekly Cd intake (μg) 140.1							mean 2152	
		av daily Cd intake (μg) 20.0 ± 5.7[a]								mean 74.2

[a] Mean ± SD.

digests of the bovine liver samples was 0.297 ± 0.018 μg/g, which again agrees well with the certified value (0.27 ± 0.04 μg/g). It is therefore concluded that the method is accurate.

2.4. Limit of Detection and Limit of Quantification. The limit of detection (LOD) in solution is defined as 3 times the standard deviation of the blank absorbance divided by the slope of the calibration line (IUPAC, 1978). The standard deviation was obtained from the analysis of 15 digestion blanks which were prepared and measured independently. The limit of detection in solution calculated in this way is 0.140 μg/L. When the sample weight used (±0.4 g) and the dilution (10 mL) are taken into account, the LOD in the dry product is 0.004 μg/g.

The limit of quantification (LOQ) is defined as the concentration level at which the measurement precision is satisfactory for the quantitative determination (IUPAC, 1978). This was obtained by taking 10 times the standard deviation of the blank absorbances (Long and Winefordner, 1983), from which an LOQ equal to 0.012 μg/g was obtained.

As seen in Table 4, the daily average amount of food consumed is about 2.2 kg (wet weight), which, when the water content (±80%)is taken into account, corresponds to a dry weight of approximately 0.5 kg. As mentioned earlier, the ADI for Cd is 60 μg. Therefore, the maximum concentration of Cd that is allowable in the total diet is about 0.12 μg/g. This value is much higher than the LOD (0.004 μg/g) and LOQ (0.012 μg/g); it is concluded that the method is suitable for the monitoring of Cd in total diets.

2.5. Precision. Precision is evaluated as both repeatability (within-run variation) and within-laboratory reproducibility (between-day variation). The repeatability was determined from six independent digests prepared and measured the same day. For the reproducibility, each day during six days a digest was prepared and measured. The relative repeatability standard deviation at a Cd concentration of about 0.050 μg/g is found to be 1.6% and the relative reproducibility standard deviation 7.3%.

3. Sample Analysis and the Estimation of Daily Cd Dietary Intake. The Cd concentration in each diet subsample was obtained from the mean of two digestions, each of which was injected twice. The results for the different locations are given in Table 4A–D. The daily Cd intake was calculated as the mean of the two subsamples. For each location, an average daily Cd intake was then obtained. From all results the daily Cd dietary intake in Belgium was estimated to be 18.4 ± 6.0 μg (mean ± standard deviation). The intake is considerably lower than the ADI. In addition, this estimate is comparable with an estimate of 18 μg/day reported from the latest survey in 1983 (Buchet et al., 1983). It thus seems that there is no trend that the Cd intake in Belgium is increasing. The intake is ranked at the lower levels compared to the average intakes in 21 countries over the period of 1980–1988 (Galal-Gorchev, 1993).

It is also seen from Table 4 that the Cd daily intakes in the two military schools are relatively higher than in other locations. A similar trend was also reported for Cr, Zn, and Fe in these samples (Penninckx et al., 1994). However, no individual diet samples were found to contain high concentrations of Cd.

The Cd concentrations in all samples are above the LOQ specified value.

4. Conclusions. The proposed method is considered to be adequate for the trace Cd determination in total diets

The daily Cd dietary intake estimated from this study is far below the ADI. Therefore, Cd dietary intake in Belgium seems not to constitute a risk to human health. No trend was found that the Cd intake has increased compared with the intake reported in 1983. However, to reach a final conclusion, more locations have to be included in the study.

ACKNOWLEDGMENT

We thank A. Vander Straeten for technical assistance. We gratefully acknowledge the four locations (the University Hospital in Liège, the Royal Military School in Brussels, the University Hospital in Antwerp, and the Barrack Major Houssiau in Peutie) for providing the total diets in this study. We also thank the "Diensten voor Programmatie van het Wetenschapsbeleid" for financial support.

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Received for review April 18, 1995. Accepted July 21, 1995.[⊗]

JF9502257

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1995.