

Supporting information for

Novel solid sampling electrothermal vaporization atomic absorption spectrometry for fast detection of cadmium in grain samples

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1. Blank test

In analysis process, the sample boat without sample can be considered as blank. Considering heating the integrated tube by the vaporization/detection procedure in reducing atmosphere, there is hardly any cold area in the ETV and transportation tube. In our experiment, after one aliquot measurement according to the proposed method, no residual Cd was detected in the second and third measurements. When the sample boat was first used, it has to be heated by the proposed testing method (Table 1) to remove possible Cd residue.

Table S-1. Heating programs of graphite furnace atomic absorption spectrometer

Program	Temperature (°C)	Heating time (s)	Holding time (s)	Ar flow rate (mL/min)
1	110	1	30	250
2	130	15	30	250
3	350	10	20	250
4	1500	0	3	0
5	2450	1	3	250

Table S-2. Microwave digestion program

Program	Temperature (°C)	Holding time (s)
1	110	5
2	150	15
3	190	15

Table S-3. Peak height and area of Cd atomic absorbance at different furnace temperatures. (n = 4)

Furnace temperature (°C)	Peak height	RSD (%)	Peak area	RSD (%)
600	0.028	10.3	1.15	22.4
650	0.044	7.6	2.68	9.7
700	0.071	2.4	3.68	2.0
750	0.101	6.0	3.83	4.4
800	0.159	2.6	3.94	1.1
850	0.246	2.3	3.81	1.1

Table S-4 Comparison of solid sampling atomic spectrometric methods for Cd analysis

Analytical techniques ^a	Sample matrices	Instrumental LODs (pg)	Method LODs (ng/g) ^b	Carrier gas supply	Instrumental analysis time (s)	Maximum sample size (mg)	References
DSS-HR-CS-GFAAS	Cosmetic	0.56 pg	1.86	Ar	64	0.3	12
ETV-TC-AFS	Food	0.3 pg	0.015	Ar+H ₂	151	20	18
ETV-ICP-MS	Food	0.16 pg	0.005	Ar	142.5	30	19
DSS-ETV-AAS	Wheat flour	0.8 pg	0.3	Ar	137	3	36
DSS-HR-CS-GFAAS	Vegetables	0.42 pg	0.5	Ar	53	0.8	24
ETV-TC-AFS	Food	0.5 pg	0.02	Ar+H ₂	186.5	30	39
ETV-AAS	Grain	30 pg	0.15	Air+water	125	200	This work

^a DSS: direct solid sampling; HR: high resolution.

^b This method LOD is calculated based on the instrumental LOD and maximum sample size in the literatures.

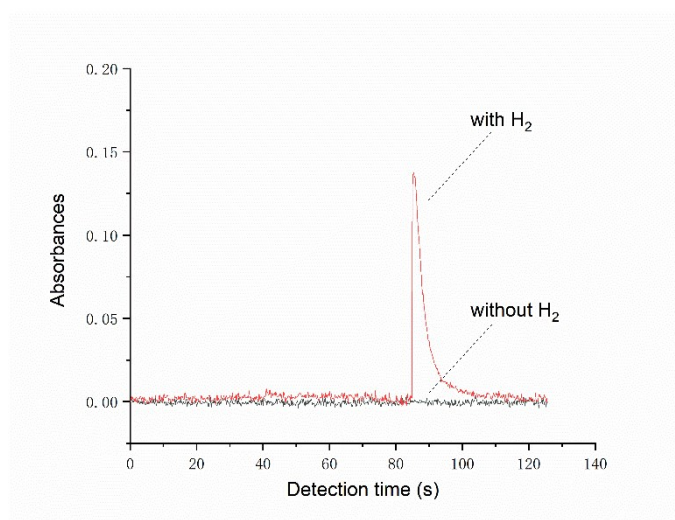


Figure S-1. Comparison of Cd signal under O₂-rich atmosphere and N₂/H₂ by solid sampling ETV-AAS.

The other parameters are in accordance with Table 1. The origin on the X-axis starting time of sample drying.

A rice sample (60 mg DM-4 rice sample for each, Cd = 418 ± 3 ng/g) was evaporated and detected with H₂ (350 mL/min) or without H₂ input (air only), respectively.

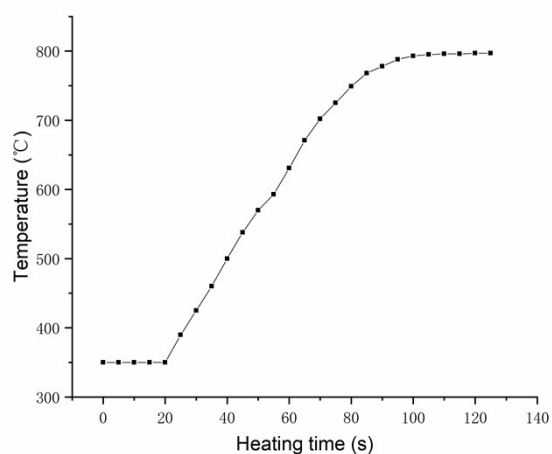


Figure S-2. The vaporization temperature curve of the ETV unit. A proportion integration differentiation (Changsha Kaiyuan Hongsheng Technology Co., Ltd, Changsha, China) device was employed to control the temperature with time increase. From 0 – 20 s, the temperature was set as 350°C for sample drying. From 20 s, the ETV temperature was increased and then kept stable at ~800°C (100 s).

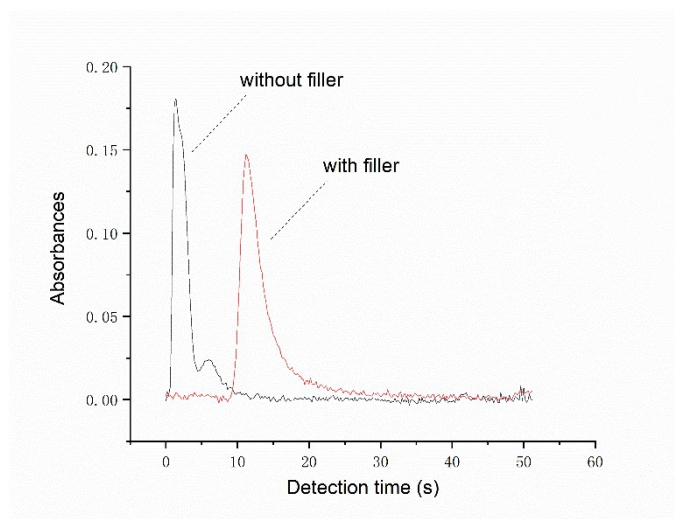


Figure S-3. Cd signals with or without filler by solid sampling ETV-AAS. No filler: filler was moved out from the quartz tube, and other experimental conditions were in accordance with that with filler according to Table 1. A rice sample (60 mg DM-4 rice sample for each, Cd = 418 ± 3 ng/g) was employed here. The origin of X-axis corresponds to the starting time of H₂ introduction.

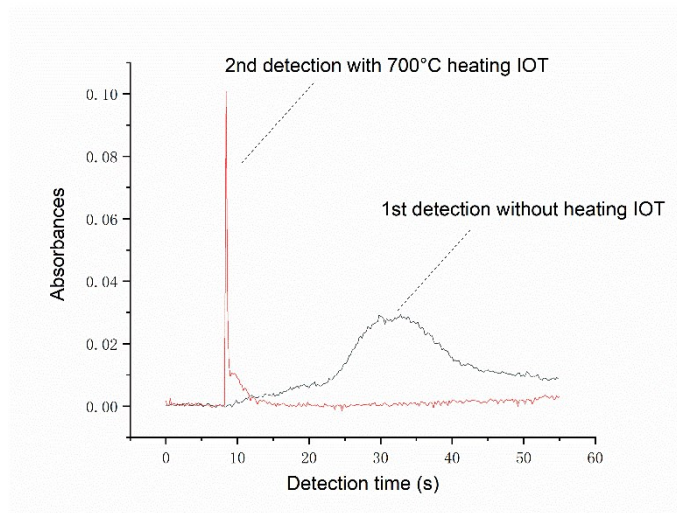


Figure S-4. Effect of the IOT without heating on the Cd signal. Black line: the first detection was performed without heating the IOT, and other ETV-AAS conditions are in accordance with Table 1. Red line: after the first detection, blank detection was performed with IOT heated at 700°C; so, the signal was considered to be Cd residual in the IOT. A rice sample (60 mg DM-4 rice sample for each, Cd = 418 ± 3 ng/g) was analyzed here. The origin of X-axis corresponds to the starting time of H₂ introduction.

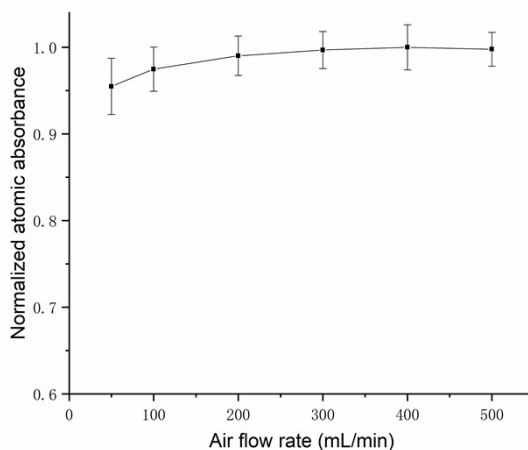


Figure S-5. Optimization of air flow rate for Cd during ashing process. Cd signal at 400 mL/min was set to be 1; other results were normalized to this value. DM-4 rice sample (100 mg) was employed here. The normalized atomic absorbance indicates the integrated absorbance (peak area).

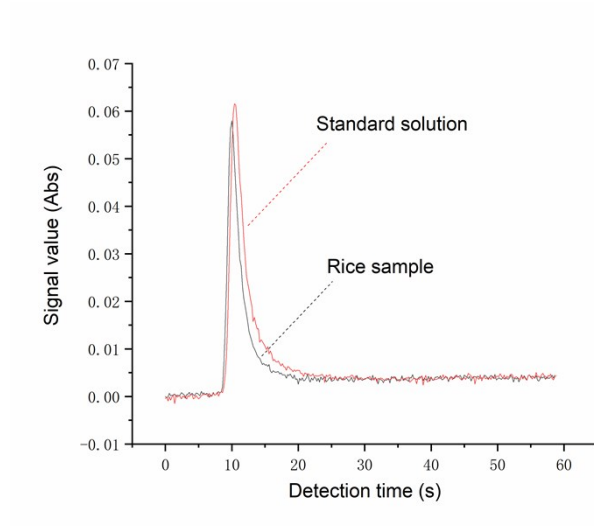


Figure S-6. Comparison of real rice sample and corresponding Cd standards. A rice sample (DM-1, Cd = 51 ± 2 ng/g, 100 mg) and 100 μ L of 51 ng/L Cd standard were employed here.

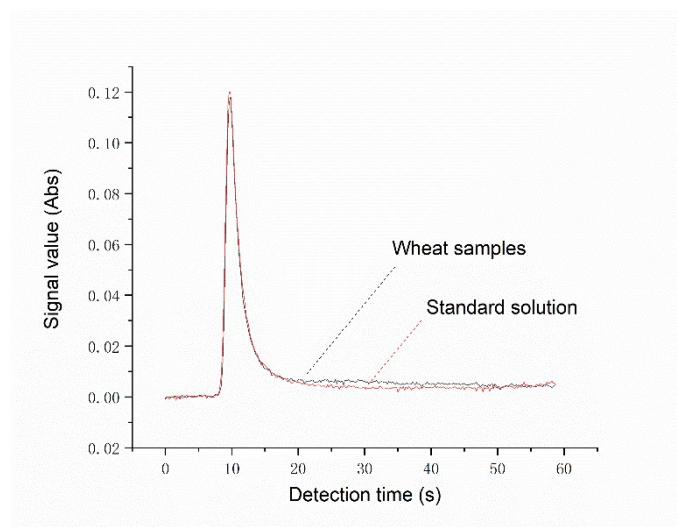


Figure S-7. Comparison of real wheat sample and corresponding Cd standards. A wheat sample (XM-1, Cd = 150 ± 4 ng/g, 100 mg) and 100 μ L of 150 ng/L Cd standard were employed here.

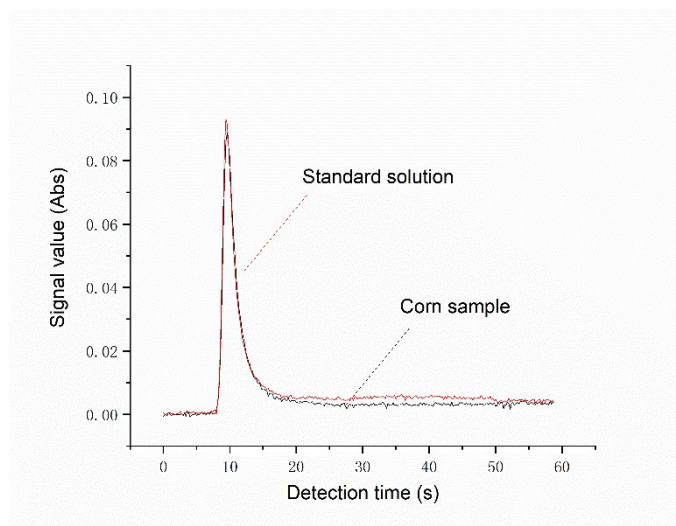


Figure S-8. Comparison of real corn sample and corresponding Cd standards. A corn sample (GBW(E)100498, Cd = 110 ± 10 ng/g, 100 mg) and 100 μ L of 110 ng/L Cd standard were employed here.

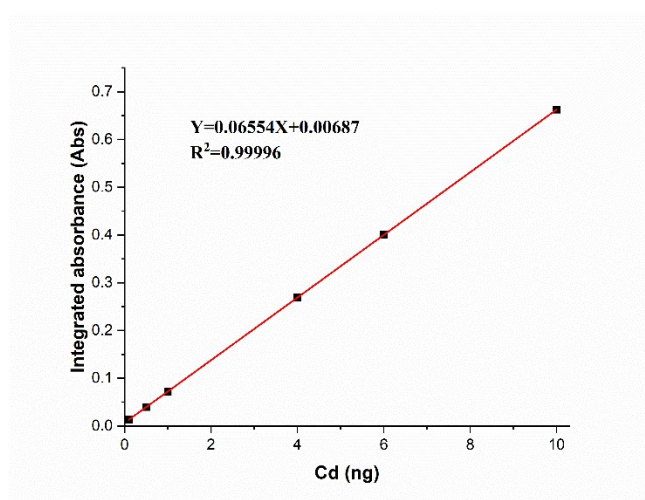


Figure S-9. Standard curve of Cd ranging from 0.1 ng to 10 ng. A group of 100 μ L Cd standards containing 1 ng/mL to 100 ng/mL were measured under 850°C pyrolysis temperature, and other parameters are performed according to Table 1.

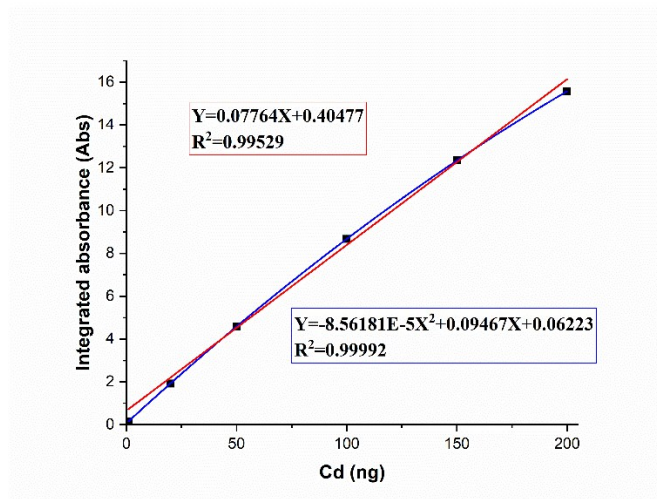


Figure S-10. Standard curve of Cd ranging from 1 ng to 200 ng. A group of 100 μ L Cd standards containing 10 ng/mL to 2000 ng/mL were measured under 700°C pyrolysis temperature, and other parameters are performed according to Table 1. In Fig. S-7, if simple equation (red line) was employed, R^2 reaches 0.9953 due to the saturation trend of atomic absorbance at high Cd level. However, considering the deviation at low level, the simple equation is not suitable for accurate quantification especially for low Cd concentration in grain sample. When quadratic equation (blue line) was used, R^2 reaches 0.9999 and the quantification is accurate at low Cd concentration. As a result, the quadratic equation was employed to establish the standard curve ranging from 1 ng to 200 ng Cd.

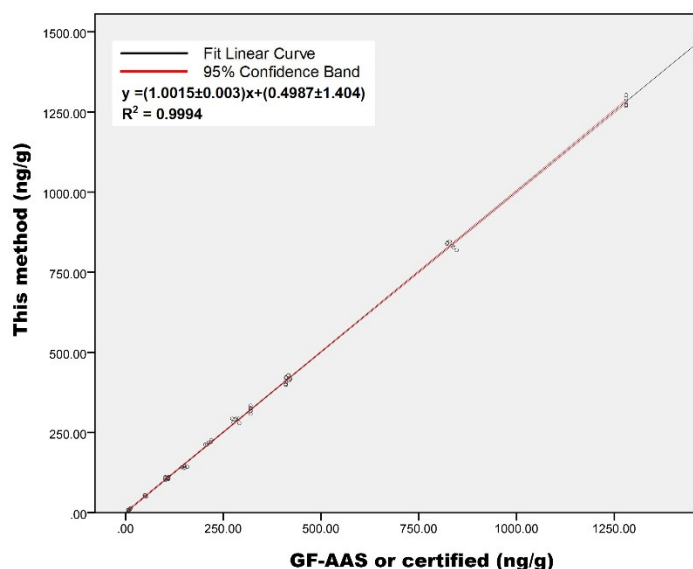


Figure S-11. Comparison of the proposed method with GF-AAS or CRMs. The X axis means Cd concentration (ng/g) measured by GF-AAS or certified value of CRMs from Table 4; the Y axis indicates Cd concentration (ng/g) measured by the proposed solid sampling Cd analytical method from Table 4.