

# A Novel Strategy of Anti-interference for Solid Dilution in Elemental Analysis Using Spontaneous Surface Dispersion Theory

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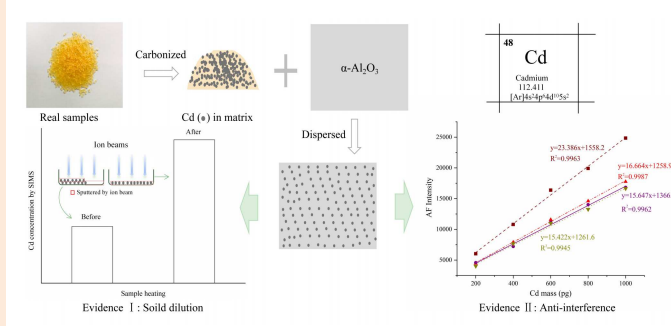
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**ABSTRACT:** A novel idea of anti-interference via solid dilution driven by spontaneous surface dispersion (SSD) is herewith first rendered for elemental analysis to determine trace cadmium in a solid sample, which is similar to the spontaneous monolayer dispersion theory originally applied to heterogeneous catalysts at the percentage level. After pre-ashing with agitation, Cd in a solid sample can be efficiently and quickly diluted via SSD on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support by heating at 600-700 °C for 30-40 min, thus leading to >180-fold dilution. Secondary ion mass spectrometry (SIMS) proved that the surface concentration of Cd on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support significantly increased, indicating that SSD occurred to Cd. The mechanism was thereby confirmed and then deduced. In essence, the proposed SSD is a dilution process for solid samples on the support's surface near Tammann temperature, where homogeneous monolayer or sub-monolayer coverage forms to reduce and even avoid contact of the target elements with interferent. The anti-interference effect has been completely verified via the matrix interference evaluation for Cd in a rice sample. In addition, SSD solid dilution consumes very little  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> for solid sample analysis after ashing, and shows reliability, precision, simplicity, and is green chemistry. This SSD approach opens a novel horizon for anti-interference research in the elemental field of analytical chemistry.



## INTRODUCTION

In analytical instrument design, it is ideal to measure analyte concentrations ranging from the lowest level to 100%, and obtain accurate and precise results without interference. However, in the real world, an analytical instrument is lacking due to multiple factors. For example, L'vov first utilized a graphite crucible in 1957 to fulfill electrothermal vaporization (ETV) of NaCl for atomic absorption spectrometry (AAS).<sup>1</sup> In fact, it is the rudiment of modern graphite furnace AAS (GF-AAS) derived from the Massmann furnace design. From then on, due to high sampling

efficiency and versatility, ETV has been employed as the solid sampling approach to couple with various atomic spectrometric techniques, such as ETV-AAS,<sup>2,3</sup> ETV-atomic fluorescence spectrometry (ETV-AFS),<sup>4,5</sup> ETV-inductively coupled plasma optical emission spectrometry (ICP-OES),<sup>6,7</sup> and ETV-inductively coupled plasma mass spectrometry (ICP-MS).<sup>8-10</sup> For real sample analysis, solid sampling became simple and rapid without requiring acid digestion. However, the use of liquid sampling with atomic spectrometric instruments still predominates today. Why does solid sampling analysis not win favor from researchers and

users in laboratories? To discuss this problem in depth, in this study Cd was chosen as the analyte considering the contamination severity found today in terms of food safety and quality of electronic products<sup>11,12</sup> in China. By using a liquid sampling atomic spectrometer, such as GF-AAS to measure Cd, acid digestion removes the organics in the analyte and homogeneously dilutes Cd in a liquid medium, then chemical modifiers<sup>13,14</sup> such as Pd(NO<sub>3</sub>)<sub>2</sub> and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> can further eliminate elemental interference, and finally apply background correction<sup>15,16</sup> like the Zeeman effect<sup>17-19</sup> which serves to diminish spectral interference. Among them, the dilution effect caused by the acid digestion process<sup>20,21</sup> is always ignored, where the interferent concentration would be decreased to weaken the matrix effect to some extent. Moreover, if the dilution ratio is enhanced enough to decrease the interferent below the threshold level, interference-free measurement can be obtained. So, the above-mentioned interference eliminations are all based on the diluted liquid with the analyte and interferent at low levels. Once meeting the interferent with several orders of magnitude higher than before, the existing anti-interference approaches would become invalid, like the problems generally observed with solid sampling analysis.

In recent years, attempts were frequently made to address the limitations derived from matrix effects, such as matrix modifier,<sup>22,23</sup> standard addition,<sup>24</sup> matrix matching calibrations,<sup>25</sup> background correction,<sup>15,16,26</sup> and so on. But their complete elimination is still not possible. Among them, matrix matching is one of the most effective means, but there is a lack of serial certified reference materials (CRMs) with different concentration levels of the analyte(s).<sup>4,5,27</sup> To improve matrix matching, analyte fusion with borate or glass, embedding the analyte in a polymer resin, preparation of a pressed disk in the presence of a binder, solid/solution mixture with spiking/drying, *etc.*,<sup>27-29</sup> was reported. However, these methods are still laborious, tedious, not suitable for other matrices, such as foods, and have unknown homogeneity, which compromises the precision of the analysis.<sup>30</sup> To the best of our knowledge, dilution is still performed in liquid or gas phases only to warrant analyte homogeneity in the diluted media rather than in the solid phase. Therefore, the accuracy and stability of the solid sampling techniques are always in doubt.<sup>31,32</sup> If solid phase dilution is achievable with a liquid medium, it might be a novel feasible solution for anti-interference. However, it is unfortunate that quantitative dilution of a solid sample remains a dilemma.

Why is it so difficult to dilute solid phase? As we know, the interparticle force of a solid is much higher than for a liquid, thus its bulk diffusion coefficient is so low that components in a solid cannot be homogenized as a liquid. For this reason, what is usually done is to grind or break the solid sample and medium into micro particles to mix sufficiently with each other. However, single homogenization cannot reach the desired effect. In previous studies on the synthesis and preparation of heterogeneous catalysts,<sup>33,34</sup> the spontaneous dispersion theory demonstrated an

excellent capacity of surface dispersion for components at the percentage level.<sup>35,36</sup> Though catalyst synthesis seems completely irrelevant with our theme, spontaneous dispersion is essentially a physicochemical phenomenon by which substances tend to evenly disperse on a support surface with increased entropy at an adequate temperature after a sufficient time lapse.

Xie and Tang<sup>37,38</sup> first applied the spontaneous dispersion theory to elucidate the synthesis process of heterogeneous catalysts. In their study,<sup>37,38</sup> when solid compounds such as oxides or salts were mixed with a support with a high melting point, such as SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, the former dispersed spontaneously on the support surface until a thermodynamically stable and homogeneous monolayer or sub-monolayer coverage formed after sufficient heat treatment.<sup>39-41</sup> In essence, this homogenization is a dilution process of solid compounds on the surface of the supports due to the higher surface diffusion speed at a certain temperature; in addition, the formation of homogeneous monolayer coverage is able to decrease and even cut off contacts of target elements with a concomitant matrix component so as to eliminate the matrix effect.<sup>37-42</sup>

The two phenomena occurring during the spontaneous dispersion process gave us an inspiration for problems demanding prompt solution in analytical chemistry: matrix interference and solid dilution. Until now, as a novel research field, the spontaneous dispersion theory has not been reported to directly apply to anti-interference and solid dilution. In this work, plastics and rice were chosen as model samples to investigate the solid dilution and anti-matrix effect. Based on the spontaneous surface dispersion (SSD) principle, if Cd-containing compounds in rice or plastic samples were ashed and then heated to spontaneously disperse on the support surface, it can accomplish physical separation of the Cd species from concomitant matrices during vaporization. We undertook SSD of Cd in solid rice and plastic samples using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder as the support. After optimization, quantitative elemental dilution of the solid sample and interference-free solid sampling analysis were successfully achieved. With reliability, precision, simplicity, and green chemistry, such an SSD approach opens a novel way of anti-interference in the inorganic element field of analytical chemistry.

## EXPERIMENTAL

**Instrumentation.** The solid sampling device (Model DCD-200, Beijing Titan Instruments Co. Ltd, Beijing, P. R. China) comprises an ashing furnace, ETV, tungsten coil trap (TCT), and a sample boat of porous carbon (SANYE Carbon Materials Factory, Shandong, P. R. China); the latter has been described in our previous studies.<sup>43,44</sup> A 10% H<sub>2</sub>-in-Ar (v/v) mixture was chosen as the carrier. The ETV programs for Cd analysis are slightly modified from previously reported conditions.<sup>4,5</sup> The AFS (Model AFS-8230, Beijing Titan Instruments, Beijing, P.R. China) was equipped with a 228.8 nm Cd-boostered hollow cathode lamp (HCL,

Beijing Research Institute of Nonferrous Metals, Beijing, P.R. China). The parameters are also listed in detail in Table S1. A vacuum/atmosphere tubular resistance furnace (Model LG0612K, Tianjin Laboratory Instrument, Tianjin, P.R. China), a box-type resistance furnace (Model SX2-10-12, Tianjin Zhonghuan Furnace, Tianjin, P.R. China) and a homogenization workstation (Model SiO-6512, Beijing Ability Technique, Beijing, P.R. China) were used in the SSD process of sample preparation. Secondary ion mass spectrometry (SIMS), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) were employed for studying the mechanism. SIMS (TOF-SIMS 5-100, ION-TOF GmbH, Münster, Germany) was used to measure the Cd concentration on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support surface; all of the parameters are listed in Table S2. The XRD (D8 Advance, Bruker Optics, Germany) was used to observe the crystal phase changes after high-temperature treatment; XPS (ESCALAB 250Xi, ThermoFisher, USA) was used to measure the bonding energy of Cd dispersed on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support surface; selection of its excitation source was dependent on the Al K $\alpha$  (2 keV) X-ray radiation. The ICP-MS (Model EXPEC-7000, Focused Photonics Inc., Hangzhou, P. R. China) was employed for the method verification. The detailed operating parameters of the ICP-MS were as follows: incident RF power, 1600 W; cooling argon gas flow rate, 13.0 L/min; nebulizer argon gas, 0.85 L/min; auxiliary argon gas, 0.80 L/min; the sampling depth was 5 mm with an inside diameter of 0.02 mm, and the peristaltic pump rate was 30 rpm. As for monitoring the isotope, <sup>114</sup>Cd was selected using standard mode.

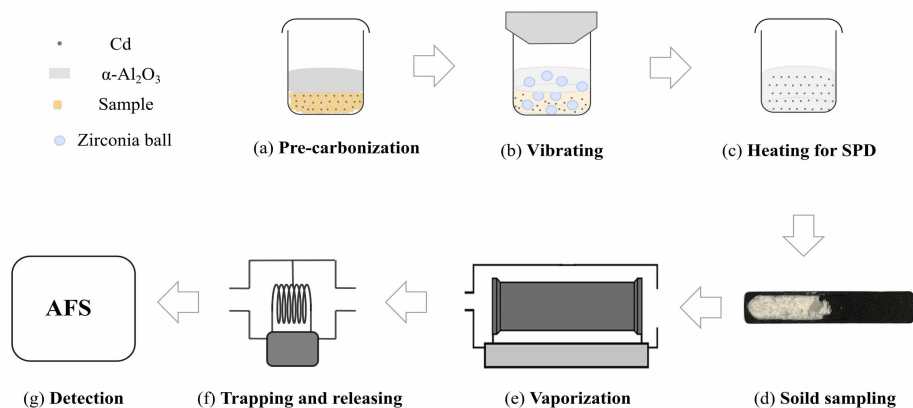
**Materials and Reagents.** Stock standards of Cd, Ca, Na, Al, As, Cr, and Pb (1000 mg/L), Fe, Cu, Mn, and Mg (100 mg/L) and rice, plastic CRMs (GBW100360, GBW100351, GBW100357, GBW10043, GBW10044, GBW08404, GBW08405, and GBW08406) were purchased from the National Research Center for Certified Reference Materials of China (Beijing, P. R. China). The working standard solutions were obtained by stepwise dilution of the stock standards with deionized water, which was prepared using the Milli-Q integral water purification system (Millipore Corporation, USA). All chemicals were of reagent grade and purchased from Sinopharm Chemical Reagent (Beijing,

P. R. China), unless otherwise stated. Powdered  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was used as supports for SSD.<sup>45</sup> Before use, the powdered  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was heated at 1000 °C for 10 h in a vacuum/atmosphere tubular resistance furnace in a 10% H<sub>2</sub>-in-Ar atmosphere to vaporize possible Cd residue in order to eliminate background interference. Zirconia balls ( $\phi$  3 mm, Saint-Gobain, Handan, P. R. China) were used to mix the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder with powdered rice or plastic samples using ethanol medium; if necessary, the Cd standards were diluted in ethanol. Rice samples were purchased from a local supermarket and milled into powder to pass through a 100-mesh sieve.

**Sample preparation for SSD using Cd solution.** To facilitate Cd dispersion on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports, a stepwise premixing process was performed as follows: (1) Cd standard solution was introduced into a centrifuging tube with ~18 g  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>; (2) 15 mL alcohol and several zirconia balls were added, then agitated at 1200 cycles per minute (cpm) for 3 min using a homogenization workstation; (3) the content was dried at 100 °C for 30 min; and finally, (4) the mixture was heated at 700 °C in the crucible in the box-type resistance furnace for SSD study.

**Rice sample preparation and analytical procedures.** The schematic diagram of the SSD-based sample preparation and Cd analysis is shown in Fig. 1. The step-by-step procedures were: (1) 100 mg rice sample and 0.5 g  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports were mixed with 1.5 mL of alcohol and several zirconia balls, then agitated in advance; (2) the sample was then heated at high temperature and the dispersed sample was introduced into the ETV to vaporize Cd in the homogenization workstation, *vide supra*; (3) the sample was pre-ashed at 300 °C for 30 min to remove the water and organics under an Ar/H<sub>2</sub> atmosphere; the Cd vapor was subsequently to evenly disperse Cd on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> surface; (4) a 5 mg dispersed sample was introduced into the ETV to vaporize Cd under an Ar/H<sub>2</sub> atmosphere; the Cd vapor was subsequently trapped by a TCT in the trapping chamber; (5) the TCT was heated to release Cd at an Ar/H<sub>2</sub> flow of 600 mL/min for AFS measurement.

**Plastic sample preparation and analytical procedures.** The procedures were: (1) ~100 mg plastic sample and ~18 g  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>



**Fig. 1** The schematic diagram of solid sampling analysis of Cd in real sample coupled based on spontaneous dispersion.

supports were mixed, placed into a quartz crucible and heated at 300 °C for 1 h to carbonize the organic substances; (2) the ash was mixed with 15 mL of alcohol and several added zirconia balls, then agitated, *vide supra*; (3) the content was equally divided into several aliquots, one of which was then heated at high temperature to evenly disperse Cd on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> surface; (4) the testing procedure was performed, *vide supra*.

## RESULTS AND DISCUSSION

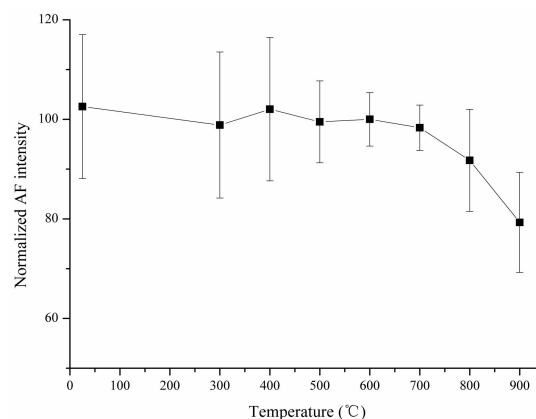
**Premixing for Cd SSD.** For SSD, in addition to the properties and structures of the solid compound-support pair, the temperature is the critical factor to achieve spontaneous dispersion. At a so-called critical dispersion temperature (T<sub>c</sub>, near Tammann temperature), the entropy effect becomes the governing factor, and the surface diffusion velocity approaches that in the solution media. Thus, the solid compounds disperse on the support surface at an appreciable rate. However, an ultrahigh temperature could lead to solid-support inter-reaction. According to the spontaneous dispersion theory,<sup>37,38</sup> the substances that disperse spontaneously as described are almost ionic or molecular crystalline compounds, while in ashed rice or plastic samples, the elements of interest usually exist as metallic oxides or salts dispersed on the support surface. As target elements disperse on a support surface into a homogeneous state, this virtually causes multi-fold dilution due to the large specific surface area of the supports.

To verify the occurrence of SSD, Cd standards were used on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> surface prior to testing a real sample. First, manual grinding was carried out to mix the Cd standard with the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports. Unfortunately, grinding for more than 1 h failed to sufficiently homogenize Cd as was evidenced by >45% RSD (each sampling took place from a random point in the mixed sample). Furthermore, the RSD of a ground sample was not significantly reduced after heating at 700 °C for 4 h. In theory, the long-range move of an analyte in liquid medium mainly relies on convection during homogenization; while short-range dispersion depends on analyte diffusion, which can be quickly reached *via* SSD. However, lack of analyte convection in a solid render it difficult to move an analyte as fast over a long range than over a short range. Thus, it is impossible to disperse Cd within several hours by relying only on thermal drive. In order to help an analyte to move to long range quickly, premixing must be employed to assist Cd homogenization on the support before SSD. An alternative is to dip the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports in 15 mL ethanol containing Cd and with several zirconia balls, place them into a centrifuging tube, and then agitate the mixture using a homogenization workstation at 1200 cpm. The ethanol medium not only promotes the convection in long range, but also volatilizes rapidly after agitation. After optimization, the RSDs were reduced to <15% with 3 min agitation, demonstrating better dispersion of

Cd on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support. As a result, agitation was included for the study of thermal treatment based on SSD, *vide infra*.

**Critical dispersion temperature for Cd SSD.** Temperature is of utmost importance to SSD; T<sub>c</sub> plays a crucial role in initiation of SSD. To investigate SSD dependence on temperature, 3.6  $\mu$ g Cd (0.36 mL standard solution) was mixed with 18 g  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports as mentioned, and one aliquot was heated for 4 h (in excess to ensure a sufficient dispersion) under varied temperatures (300 °C to 900 °C). Then, 5 mg dispersed sample was measured for Cd by random sampling. As shown in Fig. 2, the average Cd intensities remained constant at <700 °C and significantly decreased at >800 °C. On the other hand, the RSD without heat treatment exceeded 14%; heating below 400 °C did not improve the RSD either. On the other hand, heating up to 600 °C significantly reduced the RSD to <5%, indicating that SSD took place between 600 and 700 °C. Therefore, T<sub>c</sub> should be in this range. At >800 °C, the RSD rose likely due to the worsened heterogeneity caused by uneven Cd loss, and followed the trend of declining Cd concentration (Fig. 2). Reduced RSD implied that SSD occurred to Cd on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support. In addition, Fig. S1 shows that 30 min heating at 700 °C can reach the optimal Cd diffusion with ~5% RSD. Nevertheless, direct evidence employing surface analysis is still needed.

**Evidence of SSD occurrence to Cd on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support.** In previous studies on heterogeneous catalysis, XPS and XRD were utilized to prove SSD occurrence based on the binding energy and crystal phase of the support surface.<sup>37,46,47</sup> We thereby applied XPS and XRD to obtain evidence of SSD occurrence to Cd on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support. Before heating, the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports were dipped into 15 mL ethanol containing Cd and adding several zirconia balls; the mixture was dried following the above-mentioned protocol to attain samples spiked with Cd at 0, 0.5, 1, and 10  $\mu$ g/g. Then, the prepared mixtures were heated for SSD under 600 °C for 30 min. XRD and XPS measurements revealed no Cd, probably due to ultralow surface Cd concentration. In the previous XRD and XPS



**Fig. 2** Effect of temperatures on Cd dispersion on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports using standard solution (n=3). AF intensity of Cd at 600 °C is set as 100, and others are normalized.



**Table 1. Cd/Al on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> Support's Surface Measured by SIMS**

Sample preparation	Cd/Al <sup>a</sup>
Before heating	0.5
After heating	1.2

<sup>a</sup> Cd/Al means the ratio of Cd signal to that of Al by SIMS

studies, SSD occurred on supports at high concentrations;<sup>37,46,47</sup> however, such high elemental concentrations were not suited for real sample analysis. Thus, we employed SIMS to measure Cd on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support using a prepared sample spiked at 5  $\mu$ g/g Cd. Considering the mutual incomparability of Cd and Al SIMS signals, peak area ratio Cd/Al was employed to evaluate Cd dispersion, which was proportional to the Cd concentration on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> surface. From Table 1, the Cd/Al value after 600 °C heating was significantly higher than that without thermal treatment, indicating an increase in Cd concentration on the shallow  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support surface.

Prior to heating, Cd exists probably on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support as multi-layers or aggregates. Because SIMS only detects atoms on a very shallow surface with an ion beam, the average signal from the projected area covering Cd aggregates and the blank surface (no Cd occupation) should be lower than that from an even Cd monolayer. So, the increase of Cd/Al ratio is probably due to the formation of a Cd monolayer on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support. This can be considered as a direct evidence of Cd SSD that occurred only at an adequately high temperature. Furthermore, a reduced RSD aligned with the SIMS results supported SSD occurrence. Considering the relatively low Cd concentration dispersed on the support in real matrices, SIMS could not provide adequate signals. As a result, for real samples, a decreased RSD was selected as the proper evidence of SSD in the following experiment.

**Solid dilution study.** The above results showed a promising quantitative solid dilution *via* SSD. Taking real plastic samples (CRMs) as model analyte, solid particles made of organic polymeric materials are hardly mixable with the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports. As usual, ashing-acid digestion especially for plastics is time-consuming and requires toxic reagents prior to atomic spectrometric analysis. Moreover, Cd in plastics is apt to be lost at high temperatures during a direct ashing process due to rich organic substances. Thus, plastic sample analysis prefers solid dilution to replace acid digestion.

To obtain fine particulates for homogenization, organic components must be decomposed or completely removed prior to SSD. Therefore, it is indispensable to ash plastic samples to convert Cd to oxides or salts. Thereby, a mixture of plastic sample and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support was ashed in a quartz crucible. After optimization, 300 °C heating in a box-type resistance furnace for 1 h was able to achieve preliminary carbonization without Cd loss. Similar to the case using standard solutions, high temperature alone failed to disperse Cd on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support for real samples taking long-range SSD into account. The ash together with several zirconia balls was agitated at 1000 cpm for 3 min in 15 mL ethanol.

Based on the above-mentioned preparation protocol, the combination of ashing and agitation reduced the RSD to 27% before plastic SSD heating.

To verify SSD occurrence to Cd in real samples, 96.6 mg of CRM GBW08405 Plastic was mixed with 17.836 g of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> based on the above-mentioned protocol. One aliquot of the mixed sample was heated for 4 h at varied temperatures (300 °C to 800 °C); then, ~3 mg sample was measured for Cd presence. As shown in Fig. 3a, 600 °C is the turning point of Cd content decline. The RSD of 27% was reached without heating, but reduced to 8% at 600 °C. It was also indicative of effective dispersion on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support. On the other hand, worse RSD and a declining value were observed at >700°C, which could be attributed to carbides burning at high temperature. Here, carbides burning off caused a significant rise in temperature and accelerated Cd loss.<sup>48</sup> As a result, 600 °C was set for the following dynamic study for plastic sample with SSD.

Based on the above study, Cd from real plastic samples underwent SSD with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support well below T<sub>c</sub> at 600 °C. To investigate the dynamic conditions of Cd during SSD, as shown in Fig. 3b, 103.4 mg of CRM GBW08405 Plastic was mixed with 19.085 g  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and set at 600 °C, based on the protocols mentioned above; one aliquot was heated at different time durations (10 to 60 min). Next, ~3 mg dispersed sample was measured for Cd presence. The average Cd content *vs.* heating time from 20 to 60 min revealed no significant difference, indicating no loss of Cd under 600 °C. The RSD was 23% without heating, but reduced to a minimum of 9% after 30 min heating with a plateau of Cd presence. Homogeneous dispersion of Cd from the real plastic sample onto the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support was fulfilled using 600 °C heating for more than 30 min. Thus, 600 °C and 30 min were set as the optimal SSD conditions for solid dilution of plastic samples resulting in ~180-fold favorable homogeneity.

**Thermodynamic conditions and dynamic conditions of SSD for Cd in rice sample.** To overcome long-range SSD, the rice powder and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support were mixed, zirconia balls added, then agitated in ethanol medium and homogenization at 1200 cpm for 3 min. After optimization, 300 °C carbonization in a box-type resistance furnace for 30 min achieved complete carbonization without Cd loss. Based on the above-mentioned preparation protocol, the combination of agitation and ashing reduced the RSD to <20% before SSD heating of rice. To verify SSD of Cd in real samples, 100 mg of CRM GBW10045 Rice was mixed with 0.5 g  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and the above-mentioned protocol followed. One aliquot of the mixed sample was heated for 4 h at various temperatures (200 °C to 700 °C); then ~5 mg sample was measured for Cd. As shown in Fig. 3c, 400 °C is the turning point at which the Cd concentration plateaued. The RSD reached 18% without heating, but reduced to 1.7% at 700 °C. It was also indicative of effective dispersion on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support. As a result, 700 °C was set for the following dynamic study on rice analysis using SSD.

**Fig. 3** a) Thermodynamic conditions of Cd dispersion on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports using real plastic samples (n=3); b) Dynamic conditions of Cd dispersion on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports using real plastic samples (n=3); c) Thermodynamic conditions of Cd dispersion on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports using real rice samples (n=3); d) Dynamic conditions of Cd dispersion on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports using real rice samples (n=3). The solid red line and the solid brown line are the certified value of Cd in plastic sample (CRM, GBW08405) and rice sample (CRM, GBW10045), respectively. The blue broken lines are the lower and upper limits in the uncertainty ranges, respectively.

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**Fig. 4** Effect of different calibration strategies on matrix interference. Blank points and line show standard curve; green shows standard +  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>; red shows rice CRM; blue shows CRM +  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

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Based on the above study on Al<sub>2</sub>O<sub>3</sub>, Cd from a real rice sample underwent SSD on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support well below T<sub>c</sub> at 700 °C. To investigate the dynamic conditions of Cd during SSD, as shown in Fig. 3d, 100 mg of CRM GBW10045 Rice was mixed with 0.5 g  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at 700 °C, based on the protocols mentioned above; one

aliquot was heated using different time durations (10 to 60 min). Next, 5 mg dispersed sample was measured for Cd. The average Cd content vs. heating time revealed no obvious difference from 0 to 20 min, indicating no loss of Cd at 600 °C. The RSD was 21% without heating; but reduced to a minimum of 6% using 40 min heating, and then plateaued. Homogeneous dispersion of Cd from a real rice sample onto the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support was completed by heating at 700 °C for more than 40 min. However, the main aim of this investigation is not for solid dilution of a model rice sample, but rather than for its anti-interference effect. Thus, 700 °C and 40 min were considered as the optimal SSD conditions to investigate the matrix interference.

**Interference study.** Due to complicated concomitant interference during vaporization, the previous solid sampling method cannot obtain interference-free measurement of Cd in the rice sample. In practice, matrix matching calibration is time-consuming, inconvenient and frequently lacks availability of proper CRMs. To investigate the anti-interference effect, different calibration curves are shown in Fig. 4, including standard solution, standards +  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (SSD), CRM GBW10045 Rice, and rice CRM +  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>

**Table 2. Measured Cd Presence and Recoveries in Real Samples (ng/g, n = 3)**

Samples	Certified or ICP-MS	Previous method <sup>a</sup>	Proposed method <sup>b</sup>	Corrective ratio (%) <sup>c</sup>
Rice 1	11.9 ± 0.1	13.3±2.7	10.9±1.9	-18
Rice 2	6.0 ± 0.7	7.0±0.6	5.9±0.1	-15.7
Rice (GBW(E)100360)	220 ± 20	241±14	214±17	-11.2
Rice (GBW(E)100351)	420 ± 20	448±4	417±10	-6.9
Rice (GBW(E)100357)	216 ± 16	233±6	216±12	-7.3
Rice (GBW10043)	12 ± 3	15±1	11±1.6	-26.7
Rice (GBW10044)	18 ± 2	20.9±0.5	17.5±1.6	-16.3
Plastic (GBW08404)	9.26 ± 0.22	—	9.1 ± 0.3	—
Plastic (GBW08406)	36.2 ± 0.7	—	37.0 ± 2.0	—
Plastic (GBW08405)	92.3 ± 1.7	—	91.2 ± 4.5	—

<sup>a</sup> Measured value by ETV-TCT-AFS without SSD; <sup>b</sup> Measured value by the proposed SSD method; <sup>c</sup> Indicates (b-a)/a×100% according to the mean value from a and b, *vide supra*.

**Table 3. Effect of Possible Inorganic Elements**

Elements	Added (mg/L)	Recoveries (%)
Ca	100	105
Fe	10	102
Cu	10	88
Mn	10	91
Na	1000	97
Mg	200	99
Al	200	103
As	10	115
Cr	10	110
Pb	10	95

(SSD). First, the calibration curves of standard and standard +  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> are almost overlapped, indicating no extra influence from the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as support. However, the matrix matching calibration curve, namely the rice CRM curve, obviously deviates from the standard and standard +  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> calibrations. Here, matrix interference proved to exist again. So, it would lead to a positive-going deviation, yielding higher results than the true values as listed in Table 2. On the other hand, the rice CRM +  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> curve, namely SSD treatment, is very close to the standard and standard +  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> calibrations, demonstrating no significant interference. The measured Cd by the solid sampling analysis method using the standard solution strategy is within the certified values of the CRMs. Thus, the matrix interference can be corrected *via the* SSD protocol, where the corrective ratios range from -6.9% to -26.7% as compared without SSD. In other words, the solid dilution *via* SSD results in the complete elimination of matrix interference in the model solid sample used for this study.

To investigate a potential interference by other elements to Cd determination based on the proposed method, Ca, Fe, Cu, Mn, Na, Mg, Al, As, Cr, and Pb with 10 mg/L to 1000 mg/L levels were added to real samples (GBW10045) and then were dried at 40 °C using a drying oven. In Table 3, 88-115% Cd recoveries indicate absence of interference, which can be attributed in part to the intrinsic advantage of SSD.

## CONCLUSIONS

A novel solid dilution method for anti-matrix interference was first rendered and verified based on the SSD principle originally applied to the synthesis of heterogeneous catalysts. After pre-ashing and assistant agitation, Cd in the solid sample can be efficiently and quickly diluted *via* SSD on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support at critical temperature (600-700°C) for 30-40 min, in which >180-fold dilution was achieved and the mechanism confirmed and deduced. In essence, the proposed SSD is a solid dilution process on the support's surface near Tammann temperature where homogeneous monolayer coverage forms in order to reduce and even to avoid contact of the target elements with interferents. Thus, the anti-interference effect has been completely verified *via* matrix interference evaluation for Cd in the model rice sample. Moreover, the SSD solid dilution process requiring only low cost  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> for SSD and solid sampling analysis after ashing, offers the advantages of reliability, precision, simplicity, and green chemistry. The SSD theory is revolutionary for the dilution of solids and thoroughly different from the previous anti-interference technical routines. Though the mechanism of this SSD approach needs to be further explored for more elements, it potentially will lead to a novel theory for anti-interference research.

## ASSOCIATED CONTENT

Please contact the corresponding author for the Supporting Information (Table S1 and Table S2).

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### Notes

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