Fast and High Sensitive Analysis of Lead in Human Blood by Direct Sampling Hydride Generation Coupled with in situ Dielectric Barrier Discharge Trap

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A direct sampling hydride generation (HG) system based on modified gas liquid separator (GLS) coupled with in situ dielectric barrier discharge (DBD) to replace the original atomizer of atomic fluorescence spectrometry (AFS) to satisfy the in situ preconcentration. After 40-fold dilution, foams generated from protein in a blood sample can be eliminated via the double-GLS set; and lead in a blood sample were generated as plumbane under 3.5% HNO3 (v:v) and 30 g/L NaOH with 8 g/L KBH4, 10 g/L H3BO3, and 5 g/L K2[Fe(CN)6]. Then, lead analyte was trapped on the DBD quartz surface by 9 kV discharging at 50 mL/min air; and subsequently released by 12 kV discharging at 110 mL/min H2. The absolute detection limit (LOD) for Pb was 8 pg (injection volume = 2 mL), and the linearity (R2 > 0.997) range was 0.05 – 50 μg/L. The results were in good agreement with that of blood certified reference materials (CRM), and spiked recoveries for real blood samples were 95 – 104% within a relative standard deviation of 5% (RSD).

Keywords Lead, blood, direct sampling, dielectric barrier discharge trap, gas phase enrichment, atomic fluorescence spectrometry

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Introduction
Chronic exposures to toxic trace metals give rise to hazardous effects on human health, of which lead (Pb) is well-known for the high and chronic toxicity to children. As such, the Pb level in human blood is the most widely employed indicator for clinical diagnosis and public health surveillance.1–3 According to the Pb poisoning standard set by the US Centers for Disease Control in 1991, the normal range of Pb concentration in blood was <100 ng/mL at I level, while >100 ng/mL was considered Pb poisoning.4 To monitor Pb in blood, a variety of analytical methods are available, including electrochemistry, inductively coupled plasma mass spectrometry (ICP-MS), graphite furnace atomic absorption spectrometry (GF-AAS), and hydride generation atomic fluorescence spectrometry (HG-AFS).5–13 Among them, GF-AAS is the most commonly used in laboratories, but is accompanied by problems such as linear range, analytical sensitivity and matrix interference. In comparison, HG-AFS is a favorable alternative because of its higher sensitivity, wider linearity and better matrix separation, and it is also low-cost and popular in Chinese laboratories.14 However, GF-AAS and HG-AFS are both not comparable to ICP-MS regarding the analytical sensitivity. On the other hand, considering the complicated matrix in blood, existing atomic spectrometry commonly requires a tedious digestion process, which could yield extra operational error, trace elemental loss and more labor/time inputs.

For blood samples, direct sampling (DS) without digestion, such as electrothermal vaporization (ETV) or slurry sampling (SLS), is a fast and effective approach of sample introduction for atomic spectrometric analysis. Due to the simplified sample preparation procedures, potential experimental error and elemental pollution can be minimized as much as possible. In comparison, slurry sampling takes full advantage of the original liquid sampling system commonly used in atomic spectrometers, rather than replacing it with a new one. However, both ETV and SLS techniques still suffer from the biggest bottleneck problem, namely matrix interference.16 The use of a matrix modifier, and standard addition, matrix matching calibrations, and background correction17–20 are frequently performed to address the limitations derived from the matrix effect. However, these are remedial strategies, and thus do not completely eliminate the effect. So, direct dilution might be the simplest
scheme. If the dilution ratio is enhanced enough to decrease interferent below threshold level, interference-free measurement can be accomplished. However, another problem, insufficient analytical sensitivity, must also be addressed. In a word, direct sampling for Pb analysis in blood remains a dilemma concerning matrix interference and analytical sensitivity.

To solve these problems, gas phase enrichment (GPE) has been proven to be an effective separation and preconcentration method for elemental analysis with the advantages of efficiency, simplicity, and low cost, compared with liquid–liquid extraction, solid phase extraction or co-precipitation. The traditional GPE techniques derived from quartz tube, graphite furnace and metal traps were in need of high temperature, which limits its applicability due to the heating/cooling device, larger size/ power, and adverse thermal effects. Dielectric barrier discharge (DBD), as a low temperature microplasma, has shown to be a competitive alternative to preconcentrate elemental analyte that quartz trap made of planar plates or coaxial tubes. Due to the ambient temperature plasma, DBD has been frequently utilized as atomizer, atomic emission or chemical vapor generation excitation, solid ablation sampling, etc. for elemental analysis.

As for the use of DBD atomizers for plumbane excitation, solid ablation sampling, as atomizer, atomic emission or chemical vapor generation, ambient temperature plasma, DBD has been frequently utilized power, and adverse thermal effects. Dielectric barrier discharge (DBD) following DBD reactor and even to plasma extinguishing.46

To fulfil the direct sampling of lead in a blood sample via hydride generation, massive foams caused by protein in acid medium must be eliminated firstly. Because foams might overflow from the hydride generator, they could contaminate the following DBD reactor and even lead to plasma extinguishing.46 According to the previous studies, protein precipitation or defoamer is available to avoid forming foams when introducing a blood sample directly into the HG system. However, the former one requires an extra sample preparation; by contrast, defoamer can be fixed into the instrumental device without additional operation. So, if DBD can be applied to enhance the analytical sensitivity of Pb, the multi-fold dilution is helpful to alleviate the foaming effect; then, larger size and double gas liquid separators (GLS) design is capable of reducing the foam interference below the threshold level. So, a set of homemade foam breaker of double GLSs was fabricated to couple with the peristaltic pump to introduce blood sample directly.

In this study, a direct sampling method of Pb in a blood sample via DBD preconcentration was first rendered, of which double larger GLSs set was chosen as a foam breaker to eliminate foam interference. Here, the HG conditions of Pb and DBD discharging, and working gas conditions for GPE were investigated to fulfil the direct sampling analysis. Without digestion, lead in blood can be measured by the DS-HG-DBDT-AFS method quickly, accurately, sensitively and free of interference.

Experimental

Reagents and chemicals

All chemicals were guarantee reagent grade and purchased from Sinopharm Chemical Reagent (Beijing, China) unless otherwise stated. Ultrapure water (18.25 MΩcm, 24°C) was prepared from a Milli-Q integral water purification system (Millipore, Billerica, MA, USA) for the following experiments. HNO₃ was used as the acid medium to mix with KBH₄, H₃BO₃, H₂O₂, K₂[Fe(CN)₆], and NaOH for the subsequent hydride generation. Working standard solutions of Pb were prepared daily by step-wise dilution of the 1000 mg/L stock solution (GBS-04-1742-2004, National Nonferrous Metals and Electronic Materials Analysis and Testing Center, Beijing, China) with 3.5% HNO₃ (v:v). A certified reference material (CRM) of freeze-dried bovine blood (GBW09139, 111 ± 15 μg/L Pb), used for the method verification, was purchased from the National Research Center for Certified Reference Materials (NRCCRM) (Beijing, China). Before using GBW09139, 2 mL deionized water was added to each bottle and then kept for 60 min standing; after that, the bottles were sealed and mixed well until no blood clotted; finally, the CRM samples were stored in bottles at −20°C immediately after use.

Apparatus

The schematic diagram of the DS-HG-DBDT-AFS setup used in the experiment is depicted in Fig. 1. For the DS-HG process, a blood sample was directly introduced into a new design double GLS set by a peristaltic pump (PP) after multiple dilution. The GLS set (in Fig. 1) comprised two enlarged GLS vessels (volume ~36 mL), of which the first one (2.3 × 9.0 cm, ~37 mL) is responsible for hydride generation and the second one (a modified 50 mL centrifuge tube), namely foam breaker, for foam elimination. Then, plumbane was generated from mixing analyte with HNO₃ and reductant, in which foams generation can be eliminated to the greatest extent. Thereafter, the generated plumbane was transported to the DBD reactor by the carrier gas (Ar, 99.9999%, v:v) mixed with air (from air pump) or H₂ (from hydrogen generator) for trapping or releasing; finally, detection by AFS was carried out with a solar blind PMT (AFS 9130, Beijing Titan Instrument Co. Ltd, Beijing, China). The cylindrical configuration of DBD reactor was employed as before: the inner quartz tube (o.d. 3.00 mm/i.d. 1.00 × 69 mm), and the middle tube (o.d. 6.85 mm/i.d. 5.60 × 72 mm). An aluminum foil was used as the ground electrode that wrapped outside the middle tube, and a copper bar inserted in the center of the inner tube served as the high voltage electrode, in which the inner and middle quartz tubes acted as dielectric barriers. The shielding gas passed between the middle and outer (o.d. 12 mm/ i.d. 10 × 64 mm) quartz tubes to isolate the target element with air outside. A high voltage power supplier (Mev 40 kV, Beijing Ability Technology, Beijing, China) was used to supply 35 kHz sinusoidal voltage for the DBD reactor. All gas circuits were...
controlled by separate gas mass flow controllers (Beijing Horiba Metron Instruments, Beijing, China). Herein, air or H₂ could be switched to the upstream or downstream GLS via three-way valves. Emitted fluorescence of Pb by hollow cathode lamp (HCL, Beijing General Research Institute for Nonferrous Metals, Beijing, China) was monitored by a photomultiplier tube (PMT) embedded in the AFS instrument. The operation conditions of HG-AFS are listed in Table 1.

Sample preparation

For real samples of whole blood, five obtained venous blood samples (No. 1 to 5 in Table 4) were added into anticoagulant vessels, and mixed thoroughly; then, stored at 4°C for transportation and preserved under –80°C before use. Auto Kjeldahl analysis equipment (Foss Kjeltec 2300, Denmark) was used to determine the protein content of the model blood, whose mean level is 19.37% (n = 2). Considering the inaccessibility to children’s finger blood, a 0.05-mL aliquot or less blood sample was added into 0.5 mL 3.5% HNO₃ (v:v) in a 15-mL centrifuge tube; next, a high speed tissue disperser (Model OSE-Y50, Tiangen Biotech (Beijing) Co. Ltd., Beijing, China) was operated for 2 min to disrupt and break the cell in blood; finally, 3.5% HNO₃ (v:v) was employed to wash the disperser to obtain 2 mL for the following measurement.

Table 1 HG-AFS experimental parameters

| Unit         | Parameter | Value |
|--------------|-----------|-------|
| HG           | Acid medium | 3.5% HNO₃ |
|              | Reducing agent | 30 g/L NaOH, 8 g/L KBH₄, 10 g/L H₃BO₃, and 5 g/L K₃[Fe(CN)₆] |
|              | Low pressure mercury discharge lamp (LPML) | 19 W for on-line digestion via ultraviolet irradiation |
| AFS          | Lamp current (total/main) | 80/40 mA |
|              | Voltage of PMT | 270 V |
|              | Wavelength | 283.3 nm |
|              | Carrier gas | 600 mL/min (Ar) |
|              | PP speed | 130 rpm |

Analytical procedures

DS-HG-DBDT-AFS. As depicted in Fig. 1, a 2-mL prepared blood aliquot was injected into the GLS mixed with the 1.4 mL reductant (30 g/L NaOH, 8 g/L KBH₄, 10 g/L H₃BO₃, and 5 g/L K₃[Fe(CN)₆]). The generated plumbane was transported to the DBD reactor; then, 9 kV discharging was carried out for Pb trapping under 50 mL/min air admixed with Ar carrier; then, 190 s Ar carrier sweeping eliminated the moisture interference; next, 12 kV discharging under 110 mL/min H₂ with Ar was exerted for Pb release. The released Pb was irradiated by HCL and emitted for AF detection, in which the peak area was employed for Pb signal calculation.

Microwave digestion ICP-MS for method verification

To 0.5 mL blood sample, HNO₃ (3 mL) and H₂O₂ (2 mL) were added for microwave digestion using the Model TOPEX system (PreeKem Scientific Instruments Co., Ltd., Shanghai, China). Digestion was performed as follows: step 1, increasing to 80°C within 5 min; step 2, 80 to 120°C within 5 min; step 3, 120 to 190°C within 5 min and keeping for 20 min; step 4, cooling to room temperature. After the microwave digestion step, the aliquot was heated to remove acid to 1 mL solution residual and then was diluted to 10 mL with deionized water. The analyte solution was measured (standard calibration curve method) by ICP-MS (EXPEC 7000, Focused Photonics (Hangzhou), Inc., Hangzhou, China), and its instrumental conditions are listed in Table S1 (Supporting Information).

Results and Discussion

Sample preparation

To fulfil the direct sampling of Pb in blood samples, the HG reaction condition such as KBH₄ or HNO₃ is crucial to generate plumbane in such complicated matrix, and other conditions such as H₃BO₃ and K₃[Fe(CN)₆] were consistent with the previous report. The pH value of the waste liquid after the reaction of lead hydride was 8 as detected by pH test paper. KBH₄ is a reducing agent commonly used in HG, and it was thus controlled by separate gas mass flow controllers (Beijing Horiba Metron Instruments, Beijing, China). Herein, air or H₂ could be switched to the upstream or downstream GLS via three-way valves. Emitted fluorescence of Pb by hollow cathode lamp (HCL, Beijing General Research Institute for Nonferrous Metals, Beijing, China) was monitored by a photomultiplier tube (PMT) embedded in the AFS instrument. The operation conditions of HG-AFS are listed in Table 1.

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investigated using blood sample No. 5 (Pb = 10.3 ± 0.3 ng/mL measured by microwave digestion ICP-MS) in this work. As depicted in Fig. 2, Pb intensity increases with KBH₄ concentration in the range of 2 to 8 g/L; then, a plateau is reached. The increase of KBH₄ concentration does not necessarily lead to more plumbane generation for AFS detection considering finite concentrations of HNO₃ and Pb in solution; on the other hand, excessive H₂ produced from the HG process could interfere with the trap process of Pb in the DBD quartz tube. As a result, Pb intensity did not increase with an increase of KBH₄ after 8 g/L, as shown in Fig. S2 (Supporting Information). So, 8 g/L KBH₄ is capable of supporting the reduction reaction. In addition, HNO₃ is also optimized here considering acid medium for HG reaction, and the results are shown in Fig. S3. With the increase in HNO₃ concentration, the Pb signal goes up until 3.5% because more acid assists the generation of H radicals; and then declines obviously due to the dilution effect caused by more H₂ generation. Based on the above, 8 g/L KBH₄ and 3.5% HNO₃ were chosen for the following experiments.

If the detection is sensitive enough, dilution is a simple and available approach to reduce possible interferent below the threshold level, including foam and other matrices interference. However, the previous GLS unit is not enough to eliminate all foams so that they would overflow into the DBD tube. So, it is indispensable to modify the GLS design. According to the previous study, a double-GLS set with larger size comprising the first GLS and foam breaker was employed to defoam the HG-DBD. Defoaming reagents like n-octanol were used to eliminate foams, but additional toxic reagents and operational procedures are indispensable. By comparison, the foam breaker as a small size component was simpler and greener than the previous defoaming methods. To match the re-designed GLS set, the dilution factor was investigated using 0.05 mL blood sample No. 5, and the results are shown in Fig. 2. From 10 to 40 times dilution, Pb intensity increases steeply because the smaller size of the blood sample introduced into the GLS reduces foam overflow; after reaching 40, a signal platform begins to appear, in which the fluctuation might be due to excessive dilution. Considering the analytical sensitivity, 40-fold dilution was thus selected for the subsequent experiments.

**Effect of carrier gas**

Argon carrier determines the analyte transportation and detection sensitivity, so it was optimized using a real blood sample (No. 5). As illustrated in Fig. S4, Pb intensity increases significantly with Ar flow rate from 300 to 600 mL/min due to Ar carrying more gaseous analyte into the DBD and detector; meanwhile, a flow rate above 800 mL/min shows a decline because of possible dilution effect of a higher Ar flow rate decreasing the analyte residence time in the DBD microplasma. Thus, the optimal Ar flow rate was chosen as 600 mL/min for the next experiment.

**Trapping Pb by DBD**

In our previous report, the optimized discharge distance and structure design of in situ DBD were obtained, and were also utilized here. This is the first time to utilize DBD to preconcentrate Pb for the direct sampling analysis of Pb in blood, for which carrier gas and discharge voltage as the most crucial factors must be optimized. For working gas of trapping, 10 – 60 mL/min air was mixed with the carrier Ar mentioned above and the results are shown in Fig. 3A. Considering atomic fluorescence quenching, the released Pb signal was measured to illustrate the trapping efficiency. With an increase in air flow rate, AF signals go up rapidly and then reach a plateau in the range of 50 – 60 mL/min due to more Pb trapped on the DBD quartz surface. So, 50 mL/min was chosen considering the highest response with reasonable RSD. For another, discharging voltage was investigated in Fig. 3B. With an increase in voltage, the released Pb rises until 9 kV; and shows an insignificant decline at 10 kV presumably due to discharging turbulence caused by too high voltage. Thus, 9 kV discharging under 50 mL/min air was the optimum condition for Pb trapping. In addition, based on the previous report, the binding energy (139.65 eV) and sputtering information obtained by XPS indicated that lead can be trapped on the surface of the quartz tube discharge area in the form of lead oxide.

**Releasing Pb by DBD**

Excessive moisture generated from the HG is detrimental to DBD plasma, which could be removed by desiccant, however suffering from short life and inconvenience. Sweeping by carrier gas is a simple alternative to eliminate moisture effectively. So, Ar was employed to blow the DBD tube for different lengths of times; the results are shown in Fig. S5. The signal increases obviously before 100 s, then keeps an approximate plateau from 150 to 270 s. Although 230 s is the highest response, 190 s shows an excellent RSD. To reduce the analytical time as much as possible, 190 s sweeping was chosen to eliminate moisture interference in this work.

H₂-containing working gas and discharging voltage govern the performance of DBD release, considering hydrogen radicals excited by discharging for the atomization of Pb trapped on the quartz surface. Herein, the above factors were both investigated using a real blood sample (No. 5). As shown in Fig. 4A, the Pb intensity indicates a plateau from 110 to 120 mL/min H₂ with reasonable RSDs; in Fig. 4B, the highest Pb intensity appears under 12 kV discharging. Thus, 110 mL/min H₂ and 12 kV discharging voltage was accepted for the release of Pb. According to Fig. 5, the comparison of peak area between preconcentration and without preconcentration (the area ratio is 1) proves that it is a complete release process for lead by in situ DBD. For another, the lead atoms were released from the quartz surface by discharging under H₂-containing Ar working gas, and transported in the form of Pb atom for the AFS detection.
Interference study

To verify the potential interferences, Se, Bi, As, Hg, Cd (considered as hydride/cold vapor forming elements), Cu, Zn, Fe, Co, Ni (transition metals), and K, Ca, Na, and Mg (macro/micro elements) were investigated under different spiking levels. In Table 2, the Pb (10 μg/L) recoveries were in the range of 88 - 108%, indicating no significant interference. Among these, 5 mg/L Cu resulted in 88% recovery. Although more than 85% is considered acceptable for testing, the results indicated an interference to some extent caused by Cu as a transition metal possibly influencing the HG process of lead. The normal level of Cu in blood is usually about 1 mg/L. If the Cu level exceeds 5 mg/L, or Cu poisoning level for the human body, the analyte

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Table 2: The effect of possible coexisting substances on the spiked recovery of Pb

| Interfering element | Concentration/μg mL⁻¹ | Recovery, % | Recovery after dilution, % |
|---------------------|-----------------------|-------------|----------------------------|
| Na                  | 1.0 × 10⁴             | 95          | —                          |
| K                   | 1.0 × 10⁴             | 102         | —                          |
| Ca                  | 1.0 × 10⁴             | 100         | —                          |
| Mg                  | 1.0 × 10⁴             | 105         | —                          |
| S                   | 1.0 × 10⁴             | 92          | —                          |
| Fe                  | 50                    | 108         | —                          |
| Zn                  | 50                    | 98          | —                          |
| Co                  | 50                    | 96          | —                          |
| As                  | 10                    | 103         | —                          |
| Se                  | 10                    | 99          | —                          |
| Cd                  | 10                    | 93          | —                          |
| Cu                  | 5                     | 88          | 95 (diluted by 5 times)    |
| Hg                  | 5                     | 94          | —                          |
| Bi                  | 5                     | 97          | —                          |
solution can be diluted as we need to consider the excellent the LOD of this proposed method. For example, 5-fold dilution fulfills the tolerance of 25 mg/L Cu at 1.6 μg/L Pb LOD, which is acceptable for the real sample analysis. Therefore, sufficient capability of anti-interference was verified for the proposed DS-HG-DBDT-AFS.

Analytical performance of the proposed method

Under the optimized conditions, the analytical performance of the proposed DS-HG-DBDT-AFS was evaluated. The time in Table 3 indicates the overall time, including the time for sample preparation and instrument testing. The analysis with the proposed method could be performed within 10 min, which is significantly better than other methods. The instrumental LOD (calculated from 3 times the blank standard deviation divided by the slope of the calibration curve) was 8 pg (2 mL injection), which was obviously lower than that in the conventional HG atomic spectrometric methods reported previously, as well as in line with the LOD of ICP-MS (in Table 3); for direct sampling of 0.05 mL blood sample via 40-fold dilution (2 mL injection), the method LOD was 0.16 μg/L, fulfilling the blood lead criterion. Furthermore, the larger the volume of sample introduced for GPE, the lower the method fulfills the tolerance of 25 mg/L Cu at 1.6 μg/L Pb LOD, which is acceptable for the real sample analysis. Therefore, sufficient capability of anti-interference was verified for the proposed DS-HG-DBDT-AFS.

Table 3 Detection limits of the proposed method and other reported methods

| Method          | Method LOD/μg mL⁻¹ | Absolute LOD/ng | Time/ min | Accuracy (recovery, %) | RSD, % | Ref. |
|-----------------|--------------------|-----------------|-----------|------------------------|--------|------|
| HG-AES          | 1.0                | 5               | >40       | —                      | 1.2    | 5    |
| HG-AAS          | 0.56               | 1.68            | —         | —                      | 4.5    | 49   |
| HG-AFS          | 0.014              | 0.042           | >50       | 100                    | 0.7    | 50   |
| Direct sample ETAAS | 15              | 0.18            | —         | 80                     | 6 - 14 | 10   |
| GFAAS           | 0.2                | 0.04            | Acid digestion, 10 | — | 6.4 - 7.5 | 51 |
| ICP-MS          | —                  | 0.008           | >25       | —                      | —      | 52   |
| HG-DBD-AFS      | 0.27               | 0.14            | >20       | —                      | —      | 40   |
| HG-DBD-AAS      | 2.3                | —               | —         | —                      | —      | 41   |
| DS-HG-DBDT-AFS  | 0.16               | 0.008           | <10       | 95 - 104               | 5      | This method |

Table 4 Extraction efficiency, spiked recoveries and lead presence in real blood samples (n = 3)

| Sample   | ICP-MS or certified value/ng mL⁻¹ | The proposed method/ng mL⁻¹ | Extraction efficiency, % | Added/ ng mL⁻¹ | Found/ ng mL⁻¹ | Recovery, % |
|----------|----------------------------------|-----------------------------|--------------------------|----------------|----------------|-------------|
| 1        | 5.2 ± 0.4                        | 5.6 ± 0.3                   | 108                      | 10             | 15.5 ± 0.4     | 99          |
| 2        | 30.7 ± 0.7                       | 29.6 ± 0.4                  | 96                       | 30             | 60.2 ± 0.6     | 102         |
| 3        | 36.5 ± 0.3                       | 36.8 ± 0.5                  | 101                      | 30             | 65.3 ± 0.5     | 95          |
| 4        | 7.2 ± 0.4                        | 7.5 ± 0.3                   | 104                      | 10             | 17.4 ± 0.3     | 99          |
| 5        | 10.3 ± 0.3                       | 10.1 ± 0.5                  | 98                       | 10             | 20.5 ± 0.3     | 104         |
| GBW09139 | 111 ± 15                         | 103 ± 5                     |                          |                |                |             |

a. Extraction efficiency is the ratio of the found values by the proposed method to that by microwave digestion ICP-MS.

Conclusions

In conclusion, a novel direct sampling HG system coupled with DBD preconcentration was first utilized to perform the fast analysis of Pb in blood samples. The proposed GLS-DBD apparatus is effectively capable of eliminating foam generated from protein in blood. On the basis of high sensitivity, the established method can measure 0.16 μg/L lead in blood samples within 10 min including sample preparation and dilution procedures. Compared with the conventional atomic spectrometry, the established method demonstrates quickness, sensitivity, and simplicity without requiring digestion for the determination of Pb in blood samples. Due to the preconcentration, the DBD-GPE approach plays a crucial role for matrix interference elimination and sensitivity enhancement. Thus, the proposed DS-HG-DBDT-AFS method has a promising future for monitoring lead in blood to protect humans, especially children’s health.

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Supporting Information

The Supporting Information is available free of charge on the website. The sizes of the DBD tube. Effect of different KBr concentrations on the direct sampling analysis of Pb in the preconcentration mode. Effect of different HNO3 contents on the direct sampling analysis of Pb in the preconcentration mode. The effect of Ar flow rate on DBD preconcentration of Pb. The effect of Ar sweeping on eliminating moisture interference from the hydride generator. Instrumental conditions of ICP-MS.

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