

## Supporting information

# **Potential Direct Mass Spectral Elemental Analysis of Solids by Microwave Plasma Torch Surface Release and Ionization**

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# Supporting Information

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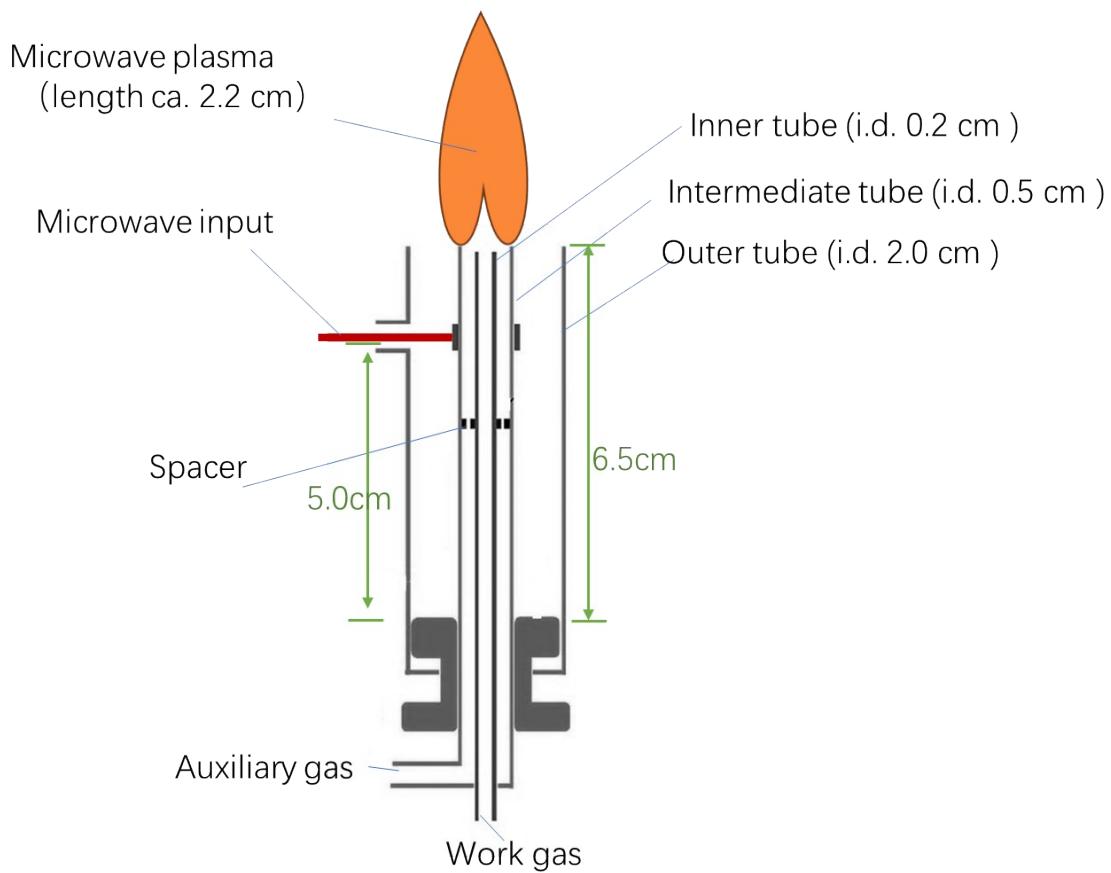
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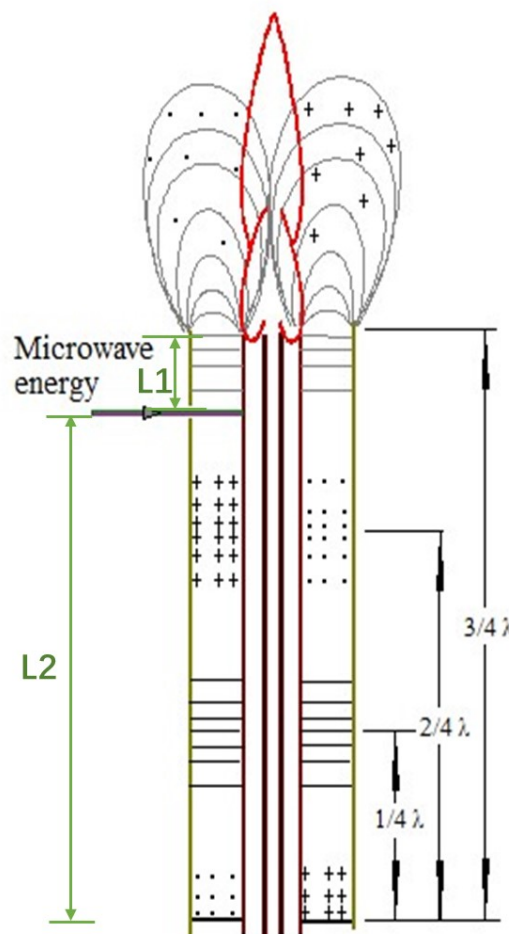
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## **1. Adsorption experiments**

Adsorption experiments were conducted under an initial pH of 6.5, with 50 mL polyethylene vials as reactors. 10 mg/L of As, Sb and Bi standards were reacted with 50 mg ferrihydrite. During adsorption process (48 hours), the tubes were capped tightly and shaken constantly on a shaker (HY-4A, Kexing, China). After adsorption, all the suspensions were filtered with a syringe filter (with a pore size of 0.25  $\mu\text{m}$ ). The obtained precipitates were dried under 65 °C and stored for direct analysis by MPT-MS. Similarly, for preparation of As, Sb, Ag, Pb, Te and Bi pre-adsorbed ferrihydrite, 50 mg/L of mixed standards reacted with 0.1g synthesized ferrihydrite. All the obtained ferrihydrite powder samples were simply pressed into tablet (4 mm diameter, 0.02g) for analysis, without any further pretreatment.

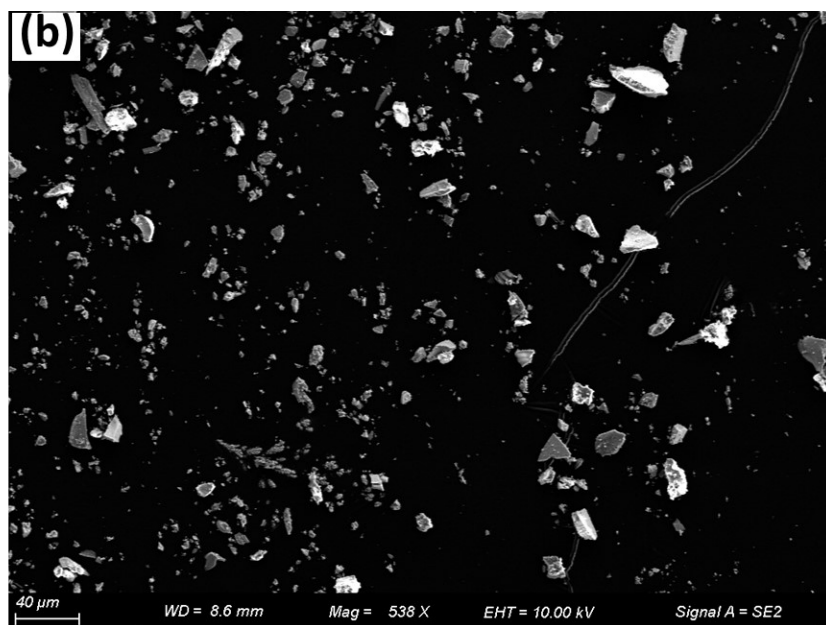
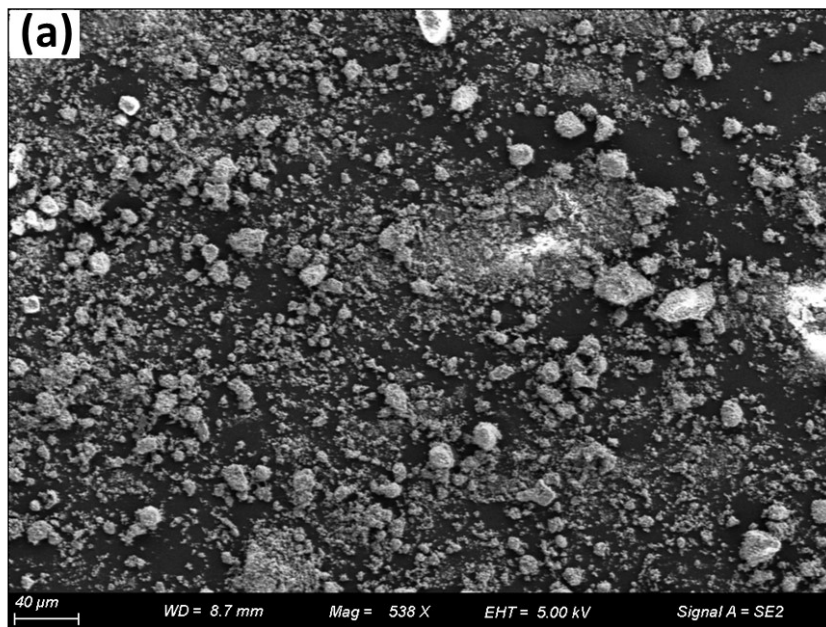


**Figure S1** Schematic diagram of the MPT.

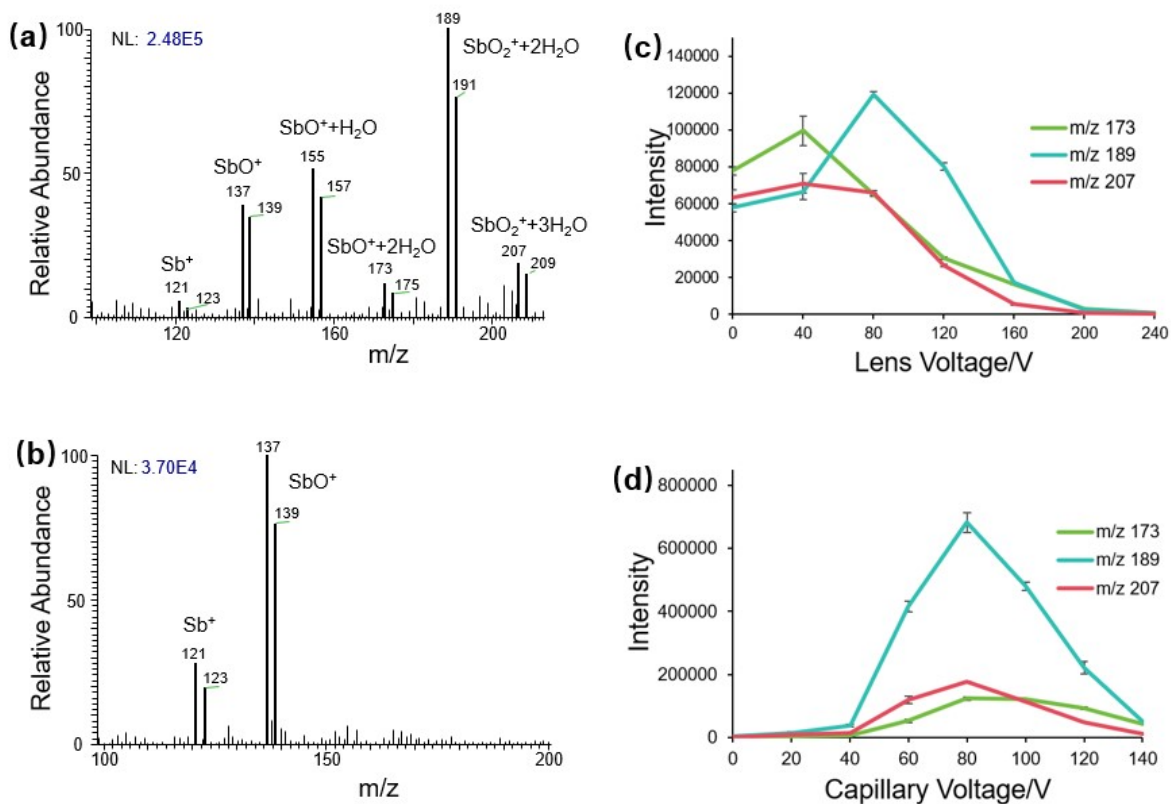


**Figure S2** Electric and magnetic field of MPT.

The microwave is directly coupled to the intermediate tube, and in the torch the microwave was divided into two directions with different distances of L1 and L2. By tuning the length of L1 and L2, a standing wave was formed inside the torch. The distance of L2 was  $\frac{3}{4} \lambda$ . The strongest electric field was found located 6-12 mm above the top of the torch, where the plasma core was formed. Detailed information can also be found in the following report. Yang, W.; Zhang, H.; Yu, A.; Jin, Q. Microwave Plasma Torch Analytical Atomic Spectrometry. *Microchem. J.* **2000**, 66 (1-3), 147-170. [https://doi.org/10.1016/S0026-265X\(00\)00057-6](https://doi.org/10.1016/S0026-265X(00)00057-6).

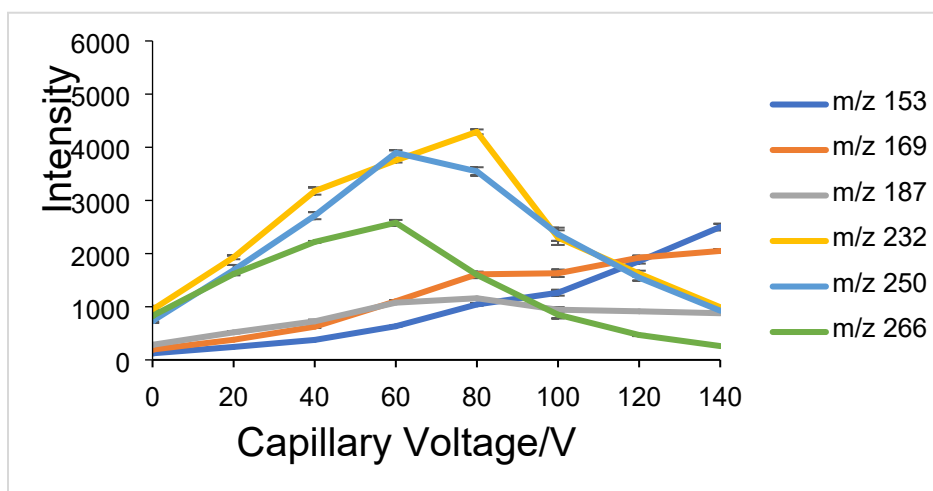
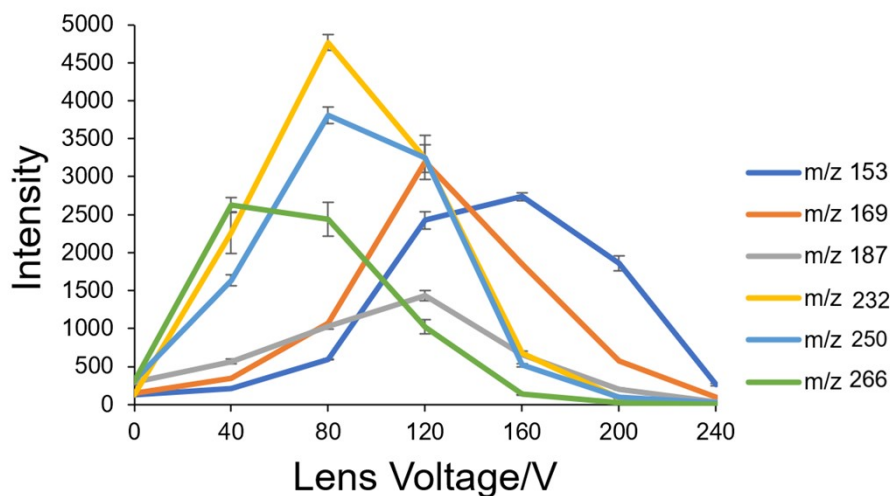


**Figure S3** The scanning electron microscope (SEM) images of soil standard sample (GBW07405) (a), and synthesized ferrihydrite (b).

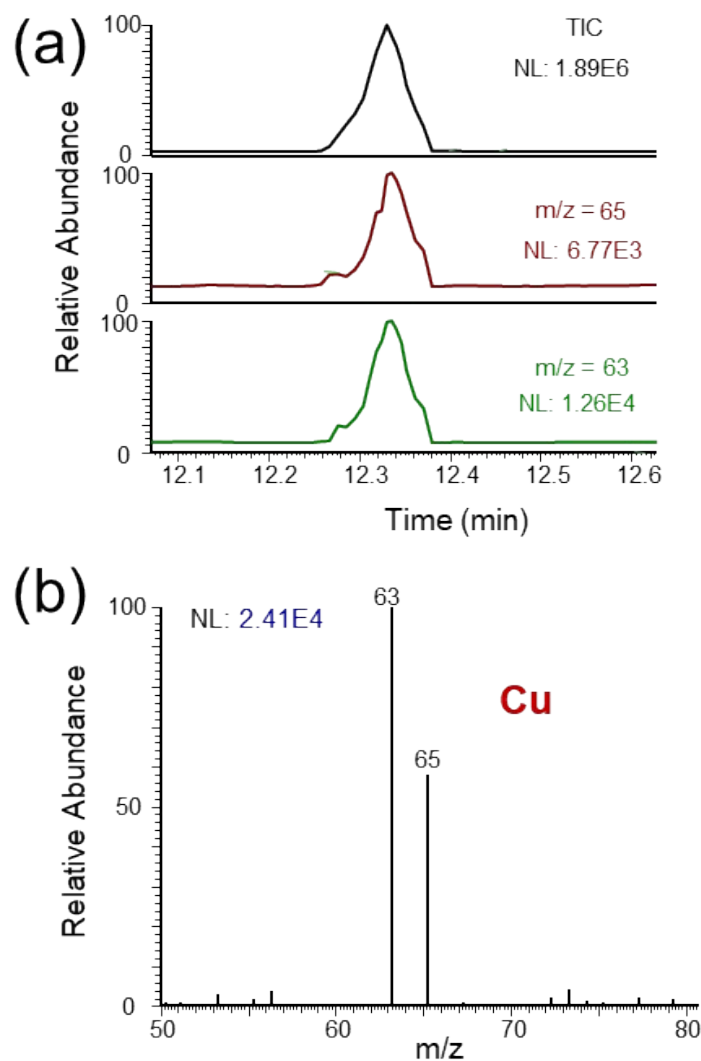


**Figure S4** (a) Sb mass spectrum by MPT-MS in positive ion mode with the capillary and tube lens voltages of 50 and 100V respectively; (b) Sb mass spectrum by MPT-MS in positive ion mode with the capillary and tube lens voltages of 80 and 240V respectively; (c)(d) Influence of tube lens voltage and capillary voltage on the signal intensity of Sb in stibnite by MPT-MS in positive ion mode. m/z 173, 189 and 207 were assigned to  $SbO^+ + 2H_2O$ ,  $SbO_2^+ + 2H_2O$  and  $SbO_2^+ + 3H_2O$  respectively. The relative intensity of each signal can be adjusted by tuning the capillary and tube lens voltages of mass spectrometer.

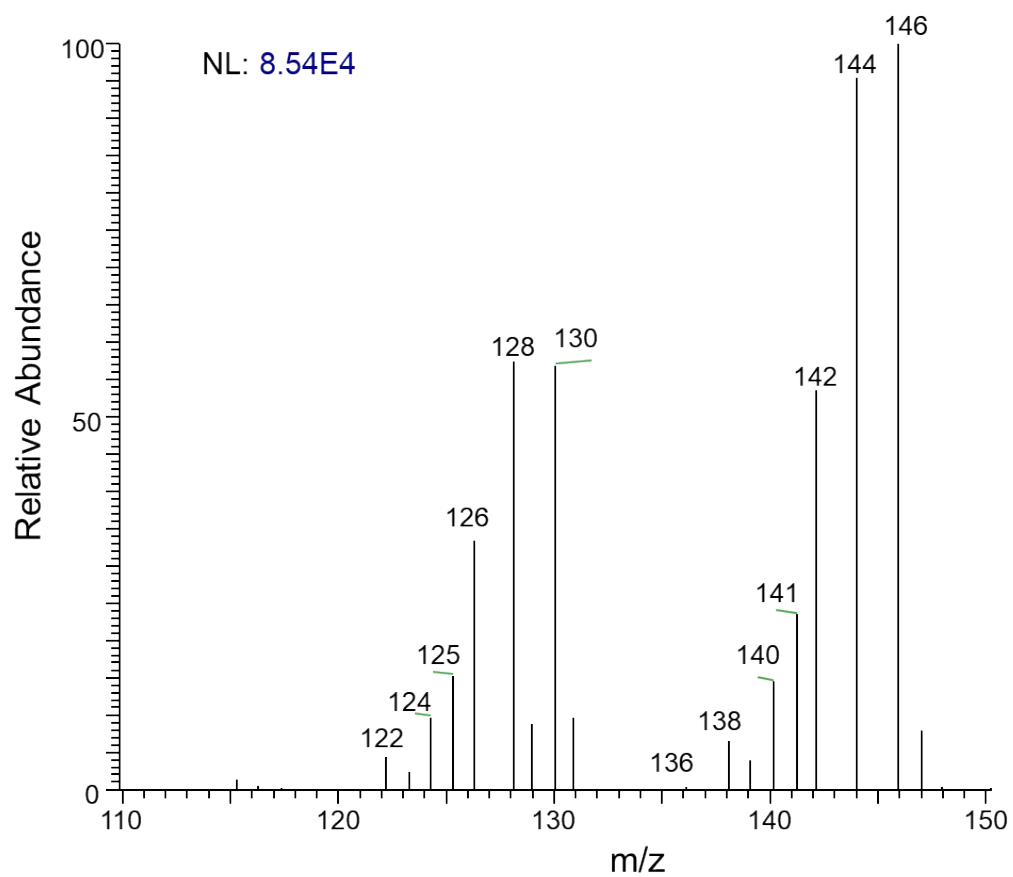




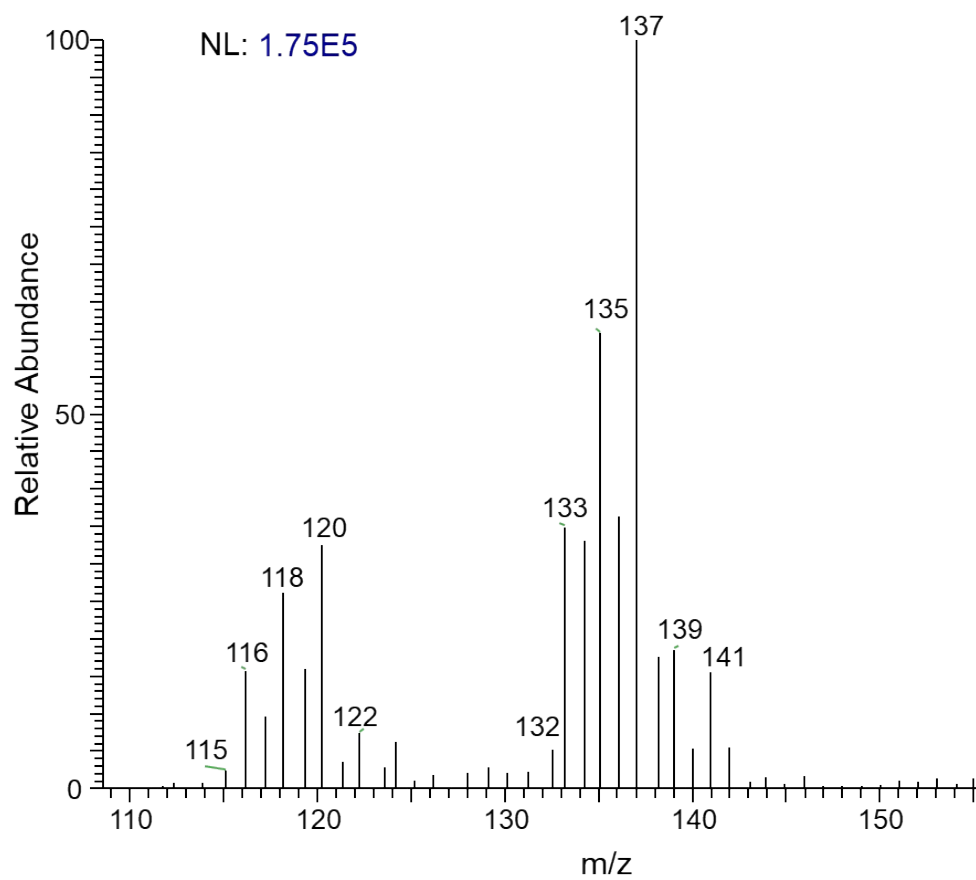
**Figure S5** Influence of tube lens voltage and capillary voltage on the signal intensity of Sb in stibnite by MPT-MS in negative ion mode. m/z 153, 169, 187, 233, 250 and 266 were assigned to  $\text{SbO}_2^-$ ,  $\text{SbO}_3^-$ ,  $\text{SbO}_3^- + \text{H}_2\text{O}$ ,  $\text{HSbO}_3 + \text{NO}_3^-$ ,  $\text{HSbO}_3 + \text{H}_2\text{O} + \text{NO}_3^-$  and  $\text{HSbO}_4 + \text{H}_2\text{O} + \text{NO}_3^-$  respectively.



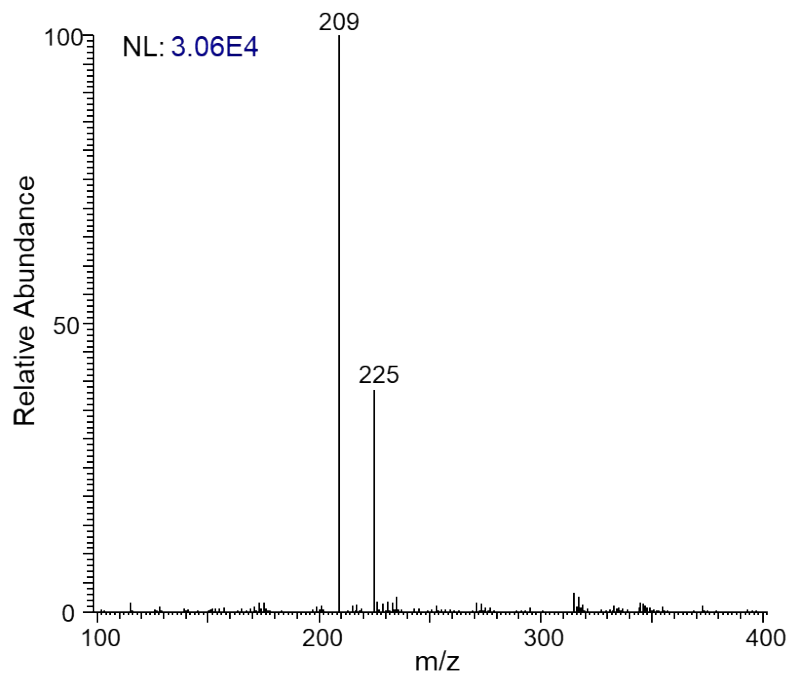
**Figure S6** Direct MPT-MS analysis of Cu from soil sample of GBW07406 in positive ion mode. (a) Total ion chromatogram (TIC) and extracted ion chromatogram (EIC) of Cu; (b) Mass spectrum of Cu. The detected isotopic ratio ( $^{65}\text{Cu}/^{63}\text{Cu} = 0.54$ ) was higher than that of the natural abundance ratio ( $^{65}\text{Cu}/^{63}\text{Cu} = 0.45$ ), which was probably due to isotopic interference from the background signal or sample matrices, considering the ambient working condition and the soft ionization property of MPT.



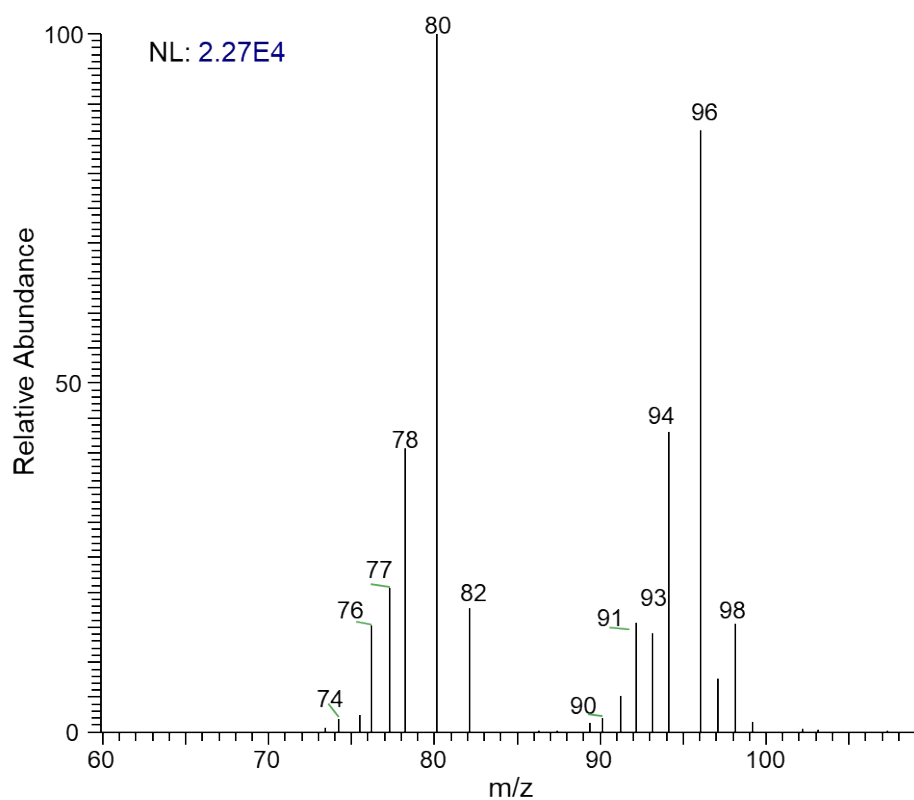
**Figure S7** Direct MPT-MS analysis of pure Te powder in positive ion mode. Te was detected as  $\text{Te}^+$  ( $m/z$  120-130) and  $\text{TeO}^+$  ( $m/z$  136-146). The capillary voltage and tube lens voltage were 100 and 200 V respectively, and the MPT power was 80W.



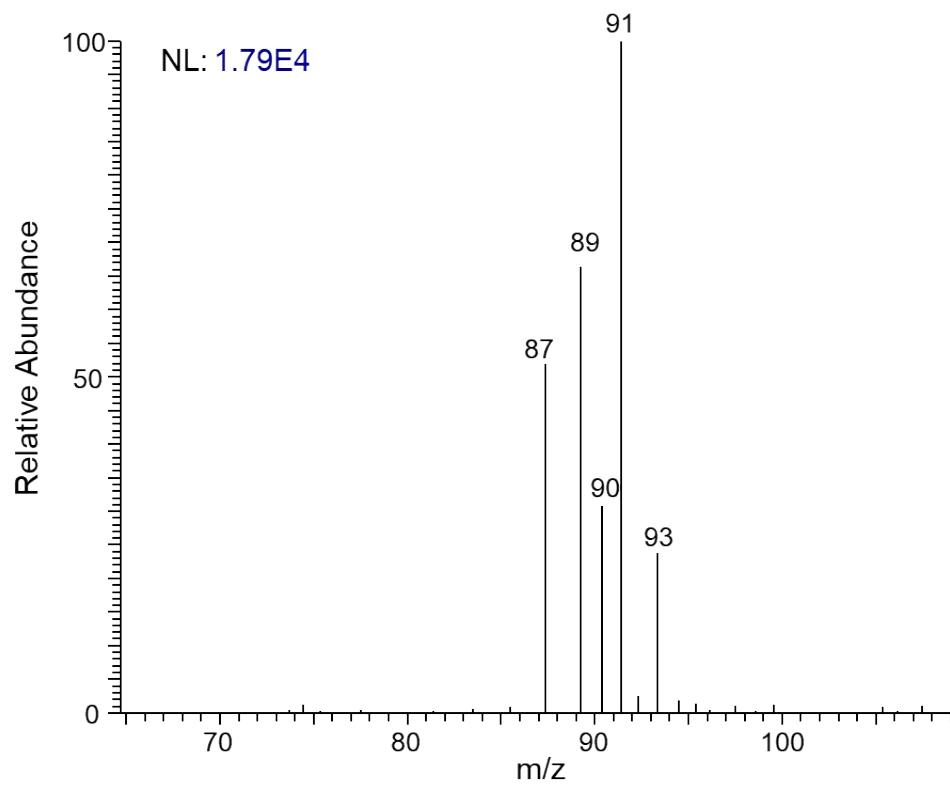
**Figure S8** Direct MPT-MS analysis of pure Sn powder in positive ion mode. Sn was detected as  $\text{Sn}^+$  ( $m/z$  112-124) and  $\text{SnOH}^+$  ( $m/z$  129-141). The capillary voltage and tube lens voltage were 100 and 200 V respectively, and the MPT power was 80W.



**Figure S9** Direct MPT-MS analysis of pure Bi powder in positive ion mode. Bi was detected as  $\text{Bi}^+$  ( $m/z$  209) and  $\text{BiO}^+$  ( $m/z$  225). The capillary voltage and tube lens voltage were 100 and 200 V respectively, and the MPT power was 80W.

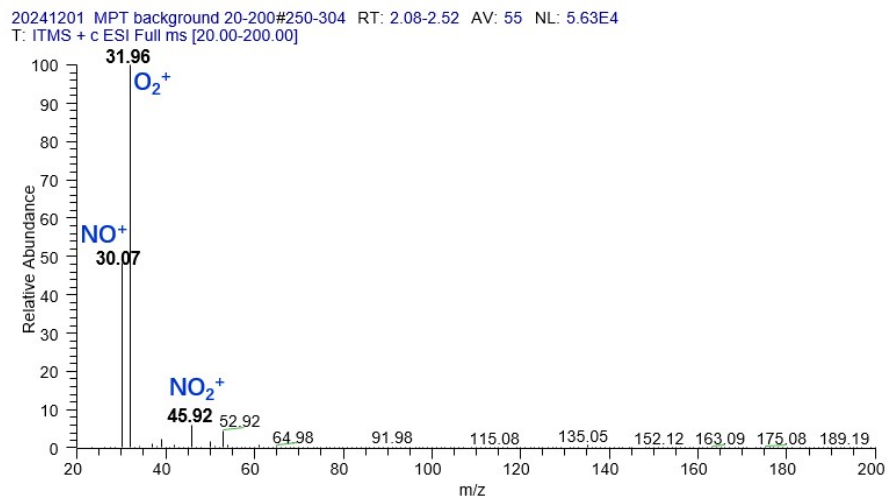


**Figure S10** Direct MPT-MS analysis of pure  $\text{SeO}_2$  powder in positive ion mode. Se was detected as  $\text{Se}^+$  (m/z 74-82) and  $\text{SeO}^+$  (m/z 90-98). The capillary voltage and tube lens voltage were 100 and 200 V respectively, and the MPT power was 80W.

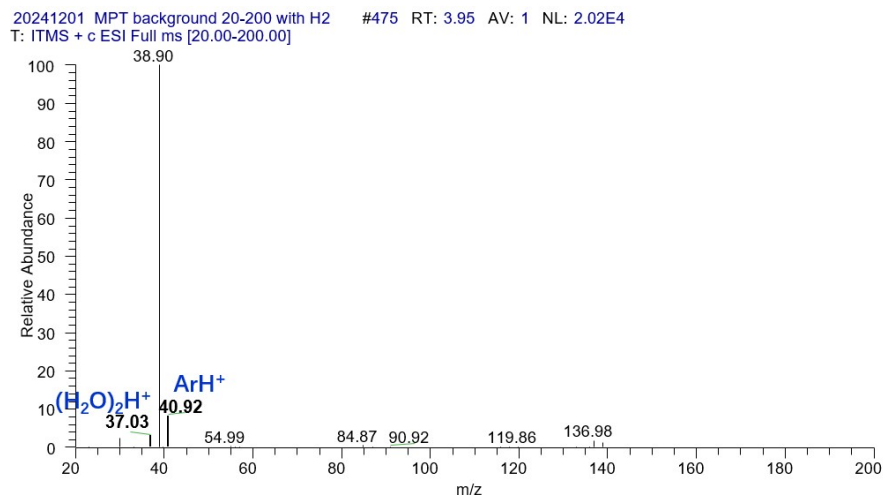


**Figure S11** Direct MPT-MS analysis of pure GeO<sub>2</sub> powder in positive ion mode. Ge was detected mainly as GeOH<sup>+</sup>(m/z 87-93). The capillary voltage and tube lens voltage were 100 and 200 V respectively, and the MPT power was 80W.

(a)



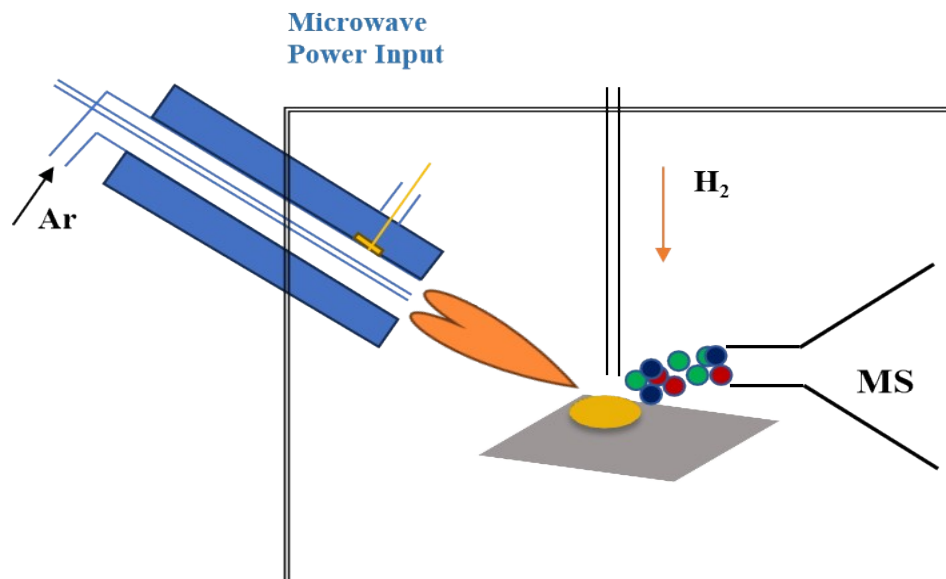
(b)



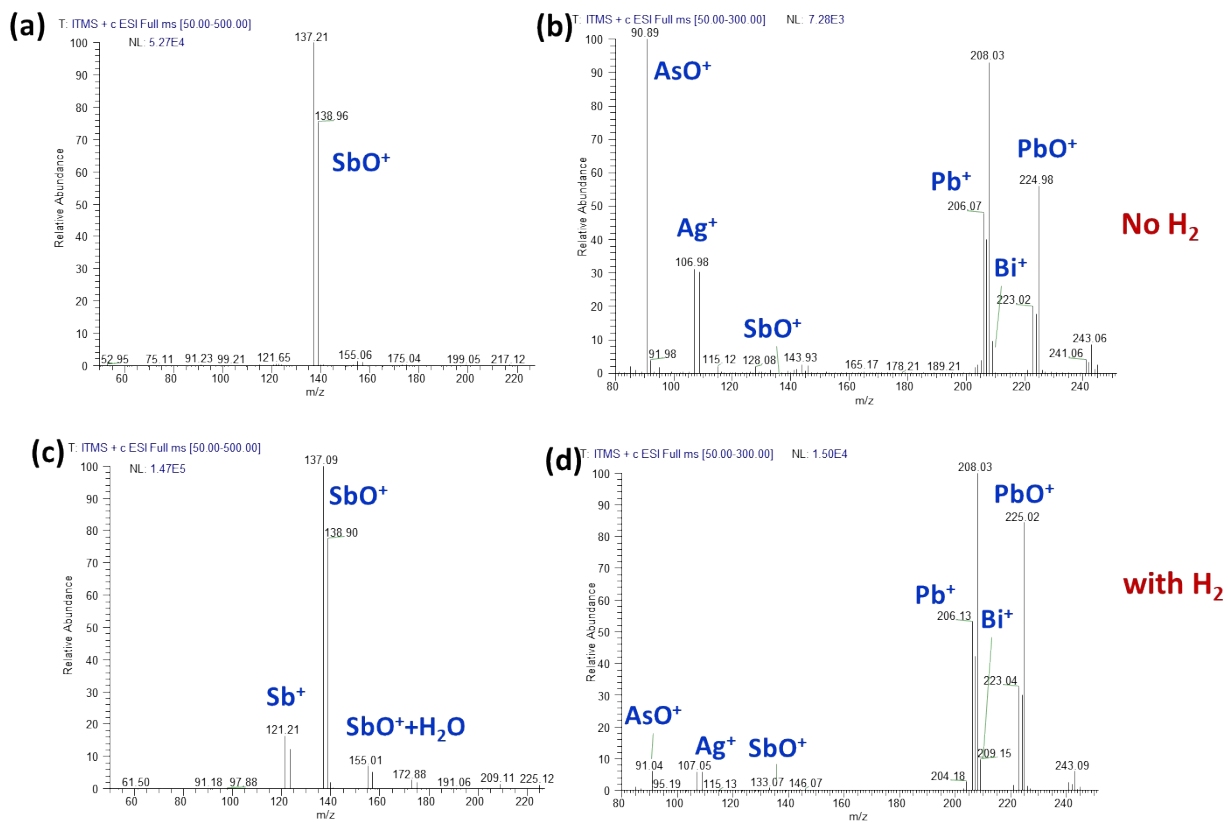
**Figure S12** Background mass spectrum signals of MPT without H<sub>2</sub> (a) and with addition of H<sub>2</sub> (b) in the mass range of 20-200 in positive ion mode with the capillary and tube lens voltages of 100 and 200V respectively.

The main ions in the background were m/z 30 (NO<sup>+</sup>), m/z 32 (O<sub>2</sub><sup>+</sup>) and m/z 46 (NO<sub>2</sub><sup>+</sup>) respectively (The first Figure). With addition of H<sub>2</sub>, the signal of m/z 41 (ArH<sup>+</sup>) emerged (the second Figure). In another work, signal of Ar<sup>+</sup>, ArH<sup>+</sup> and a small amount of Ar<sub>2</sub><sup>+</sup> were observed by MPT coupled to a time-of-flight mass spectrometer under a closed environment (Zuo, K.; Dai, J. X.; Zhao, Z. J.; Guo, X.; Duan, Y. X. Development and Applied Research on Elemental Detection of Microwave Plasma Torch Time-of-Flight Mass Spectrometer. J. Chinese Mass Spectrom. Soc. 2024, 45 (3), 343–353. <https://doi.org/10.7538/zpzb.2023.0115>).

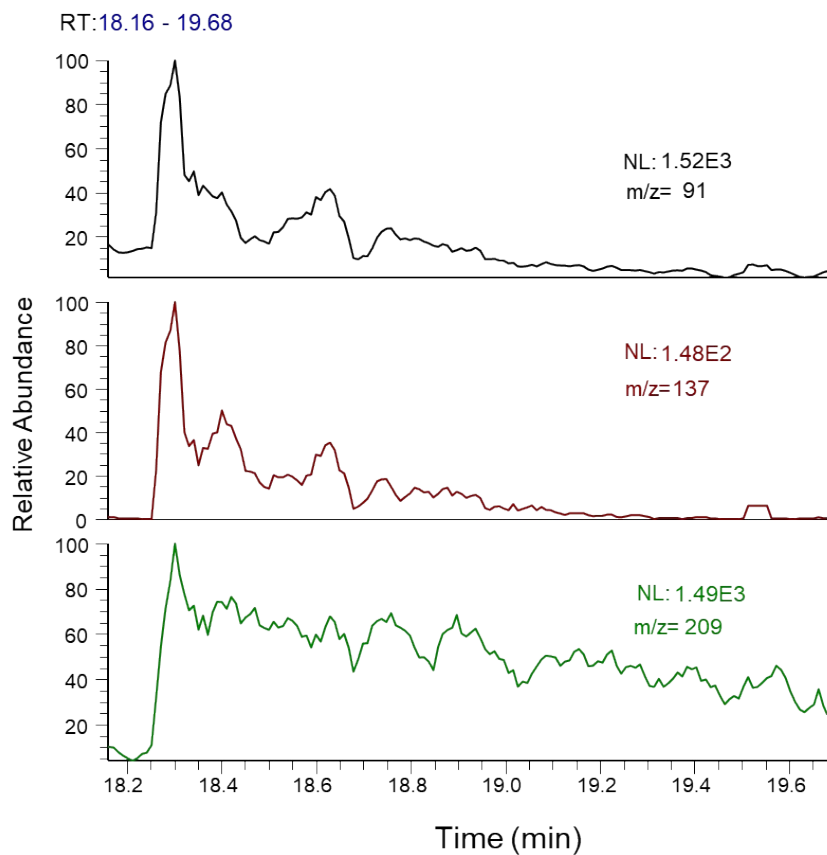




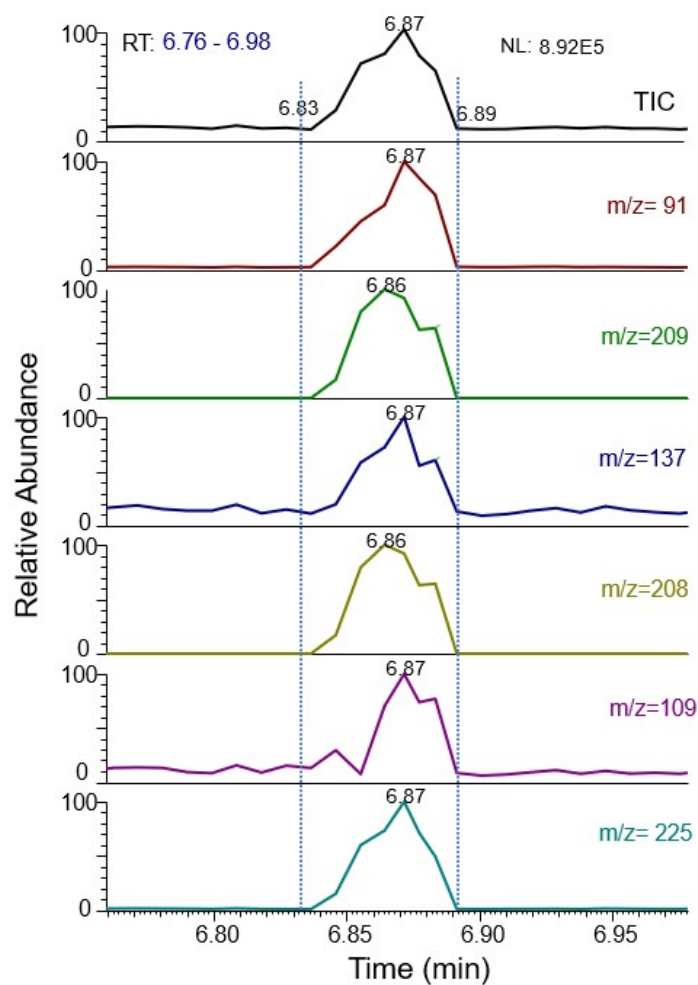
**Figure S13** Schematic of the experimental set up of MPT-MS for solid sample analysis with additional H<sub>2</sub> introduction.



**Figure S14** Direct MPT-MS analysis of solid stibnite (a, c) and soil standard of 7406 (b, d) with and without additional H<sub>2</sub> introduction. It can be seen that with additional H<sub>2</sub> introduction, the signals of various analytes were generally further enhanced by one order of magnitude.



**Figure S15** Extracted ion chromatography (EIC) of As ( $m/z$  91), Sb ( $m/z$  137) and Bi ( $m/z$  209) for direct MPT-MS analysis of soil standard of GBW07406 with additional  $H_2$  introduction. It can be seen that with additional  $H_2$  input obvious signal tailing was observed. One possible interpretation is that the application of  $H_2$  may lead to some continuous reactions between active hydrogen species and residual analytes in the ion trap of mass spectrometer.



**Figure S16** Total ion chromatogram (TIC) and extracted ion chromatogram (EIC) of As ( $\text{AsO}^+$ ,  $m/z$  91), Pb( $\text{Pb}^+$ ,  $m/z$  208), Bi( $\text{Bi}^+$ ,  $m/z$  209), Sb( $\text{SbO}^+$ ,  $m/z$  137), Ag( $\text{Ag}^+$ ,  $m/z$  109) and Te( $\text{TeO}^+$ ,  $m/z$  ) for the ferrihydrite pre-adsorbed with As, Sb, Ag, Te, Pb and Bi.  $t=6.83\text{min}$ : the sample contacted with plasma;  $t=6.89\text{min}$ : the sample was removed from plasma.

**Table S1** Analysis of pre-adsorbed ferrihydrite by direct MPT-MS. (n = 3)

	<b>As</b>	<b>Sb</b>
<b>Initial aqueous concentration (mg/L)</b>	50	50
<b>Residual aqueous concentration (mg/L)</b>	23.1±1.0	4.78±0.8
<b>Adsorbed (mg/L)</b>	26.9±1.0	45.2±0.8
<b>Adsorbed mass onto ferrihydrite (mg)</b>	1.34±0.05	2.26±0.04
<b>Detected concentration (mg)</b>	1.11±0.3	2.12±0.8

**Table S2** Other possible reactions involved in the MPT.

No.	Reaction equation	Reference
R1	$N_2 + e \rightarrow N_2^{*+} + 2e$	1,2
R2	$e + H_2O \rightarrow H_2O^+ + 2e$	3
R3	$e + H_2O \rightarrow H\cdot + OH$	
R4	$e + H_2O \rightarrow O\cdot + H_2$	
R5	$e + H_2 \rightarrow e + 2H$	4
R6	$e + H_2 \rightarrow 2e + H_2^+$	
R7	$e + H_2^+ \rightarrow e + H^+ + H$	
R8	$H_2 + H_2^+ \rightarrow H_3^+ + H$	

**Table S3** Analysis of As, Sb and Pb in two soil samples by MPT-MS and HG-AFS.

	<b>Detected element</b>	<b>MPT-MS (µg/g)</b>	<b>RSD (%)</b>	<b>HG-AFS (µg/g)</b>	<b>RSD (%)</b>
<b>Soil 1</b>	<b>As</b>	3.8±0.6	15.8	4.1±0.2	5.0
	<b>Sb</b>	1.1±0.2	18.2	0.9±0.08	8.9
	<b>Pb</b>	26.8±2.1	7.8	25.2±0.5	2.0
<b>Soil 2</b>	<b>As</b>	13.7±2.0	14.6	14.9±0.5	3.4
	<b>Sb</b>	1.7±0.5	29.4	2.0±0.2	10
	<b>Pb</b>	55.1±6.7	12.1	58.5±0.8	1.4

Note that:

#### **For HG-AFS analysis**

3mL HCl (12 mol/L) and 2 mL HNO<sub>3</sub> (16mol/L) was added into the PTEF digestion container preloaded with 1.0g soil sample powder. The digestion containers were then heated under 120 °C for 1 hour using a electric heating plate. Then, 3mL HF and 1mL HClO<sub>4</sub> was added into the container, and continue heating under 120 °C for 2 hours. Then increase the temperature to 130 °C and continue heating for another 2 hours. After that, heat the obtained digestion solution at 170 °C until close to dryness. Add 10mL deionized water into the container, filter and dilute the solution for analysis.

#### **For MPT-MS analysis**

The soil samples were firstly grinded and screened using a 200-mesh sieve. Then weighed 0.01g powder was pressed into tablet under controlled pressure of 15MPa for 1min. The obtained tablet was then analyzed by MPT-MS directly. For quantification, the soil powder with undetectable target analytes was used as blank. Different concentrations of As, Sb and Pb standard solutions were spiked into the 5 duplicate blanks (0.1g) respectively, generating a series of mix standards (1, 2, 5, 10, 20 µg/g for As; 1, 2, 5, 8, 10 µg/g for Sb and 10, 20, 50, 80, 100 µg/g for Pb, respectively). These standards were then dried under 65°C for 3 hours and grinded following the same procedure as sample pretreatment.

## References

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