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Supplementary Information

Determination of iron in plant samples using isotope dilution inductively coupled plasma mass spectrometry with a quadrupole ICP-MS operated in a He/H_2 cell mode

Experimental

Instrumentation

The ICP-MS used was an Agilent 7500c Octopole Reaction System (Agilent Technologies, Japan). Liquid argon (Hong Kong Oxygen & Acetylene Co. Ltd., Ar ≥ 99.999 % (v/v), $O_2 \leq 2$ vpm, $H_2O \leq 3$ vpm, $N_2 \leq 3$ vpm) and ultra-high purity grade helium (Hong Kong Oxygen & Acetylene Co. Ltd., $O_2 \leq 5$ vpm, $H_2O \leq 5$ vpm) were used for analysis. Hydrogen was generated by a hydrogen generator (Packard, model number: 8200) and was purified by passing through a gas purifier (Agilent Technologies, part number: 5182-3467) to remove oxygen, moisture and hydrocarbons. The standard daily optimization procedure recommended by the manufacturer was applied to determine the nebulizer gas flow rate and the ion lens voltage. The detector was set in dual mode. Optimum conditions for ICP-MS analysis are shown in Table 1. The freeze-drying system for drying of sample materials before analysis consisted of Dura-Top™ Microprocessor Control Bulk Tray Dryer and Dura-Dry™ Microprocessor Control Corrosion Resistance Freeze-Dryer (FTSSYSTEMS™, USA). The closed vessel microwave digestion system was MARS X (CEM Corporation, USA), which is equipped with a turntable of 12 vessels (vessel type: XP-1500 Plus). Muffle furnace (Thermolyne 30400, Barnstead/Thermolyne, Dubuque, IA) was used for dry ashing.

Reagents and Samples

All reagents were of analytical reagent grade. High-purity water (18 MΩ cm) was prepared by a deionized water purification system (Milli-Q Plus, Millipore, USA) and was used throughout the work. Concentrated nitric acid (69 %, Tracemetal grade, TEDIA), concentrated hydrochloric acid (35 %, Tracemetal grade, TEDIA), concentrated hydrofluoric acid (47 %, Tracemetal grade, TEDIA) and hydrogen peroxide (30 %, Suprapur®, Merck) were used in sample decomposition. The primary assay standard of iron and the enriched ^{57}Fe spike solution were NIST SRM 3126a (certified value of iron: 9.97 mg g^{-1} ± 0.02 mg g^{-1}) and Certipur® Reference Material Spike Solution 10 mg/kg Fe-57 (certified value of iron: 10.05 mg ^{57}Fe kg^{-1} ± 0.17 mg ^{57}Fe kg^{-1}; isotopic composition:- ^{54}Fe: 0.0294%, ^{56}Fe: 0.82%, ^{57}Fe: 96.10%, and ^{58}Fe: 3.06%) respectively. Two certified reference materials (CRMs) employed for method validation were IAEA-359 (cabbage) and NIST SRM 1515 (apple leaves). The reference material of NIST RM 8412 (corn stalk) was also examined. The three plant samples were freeze-dried for about 18 hours before use. All solutions prepared from dilution of the primary assay standard and the enriched ^{57}Fe spike were stored in perfluoralkoxy bottles, which were pre-cleaned with 5 % (v/v) nitric acid and water before use. The solutions prepared were kept in zipped bags to minimize evaporative loss. Ion exchange cartridges (MAXI-CLEAN cartridges, 1.5 mL bed volume, IC-Chelate, part number: 30265, Alltech) and ammonium acetate buffer solution (2.0 M, pH 5.4 ± 0.1, part number: 033440, Dionex) were used in ion-exchange chromatographic cleanup.

Sample preparation

Microwave-assisted digestion with HNO_3-H_2O_2-HF:[2]
To a microwave digestion vessel, 0.25 g – 0.5 g of sample and a suitable amount of the enriched ^{57}Fe spike solution were accurately weighed and added. The isotope ratio of $^{56}Fe/^{57}Fe$ was about 3:1. Then, 10 mL of concentrated nitric acid, 6 mL of hydrogen peroxide, and 1 mL of concentrated hydrofluoric acid were added. The sample mixture was left at room temperature for 16 hours. Microwave-assisted acid digestion was performed according to the program shown in Table 2. Upon completion of digestion, microwave-assisted evaporation of acids was carried out until about 2 mL of the digested sample solution was left. The digested sample solution was transferred to a screw-capped 50-mL polyethylene tube. The resulting sample blend was diluted with water to approximately 50 mL. Blank spikes were prepared at the same analytical run.

Ion-exchange chromatographic (IC) cleanup procedure:
The ion-exchange cartridge was cleaned with sufficient amount of 1 M HNO_3 until the eluate was free from the analyte when examined by ICP-MS. The cartridge was rinsed with 10 mL of water followed by 5 mL of 0.2 M ammonium acetate buffer solution.

10 mL of the sample blend was first buffered by addition of 10 mL of 0.2 M ammonium acetate buffer solution. The buffered sample blend solution was loaded onto the pre-cleaned ion exchange cartridge. The cartridge was washed with 15 mL of 0.2 M ammonium acetate buffer solution followed by 20 mL of water. 11 mL of 1 M HNO_3 was added to the cartridge to elute the analyte. The first 1 mL of eluate was discarded and the remaining 10 mL of eluate was collected for ICP-MS analysis.

Dry ashing:
To a ceramic dish, 0.25 g – 0.5 g of sample and a suitable amount of the enriched ^{57}Fe spike solution were accurately weighed and added. The isotope ratio of $^{56}Fe/^{57}Fe$ was about 3:1. Then, 10 mL of concentrated nitric acid was added. The ceramic dish was heated on a hot plate for 1 hour. Nitric acid was slowly evaporated. The sample was gradually charred by increasing the temperature of the hot plate. Ashing of the charred sample was carried out in a muffle furnace set at 500 °C for 8 hours. 20 mL of 1 M HCl was added to the ashed sample. The ceramic dish was gently heated on a hot plate until about 5 mL of sample solution was left. The sample solution was transferred to a screw-capped 50-mL polyethylene tube. The ceramic dish was rinsed with about 15 mL of 1 M HCl. Then, 1 mL of concentrated hydrofluoric acid was added. The polyethylene tube was placed in a boiling water bath for at least 2 hours. The resulting sample blend was diluted with water to approximately 50 mL. Blank spikes were prepared at the same analytical run.

Preparation of calibration blend

To a screw-capped 50-mL polyethylene tube, 0.25 – 0.5 g of the primary assay standard of iron at a concentration similar to the sample being analyzed and a suitable amount of the enriched ^{57}Fe spike solution were accurately weighed and added. The isotope ratio of $^{56}Fe/^{57}Fe$ was about 3:1. Then, 2.5 mL of concentrated HNO_3 was added. The resulting calibration blend was diluted with water to approximately 50 mL.

Analytical conditions

Prior to ICP-MS analysis, all isotopic blends were further diluted with water to achieve reasonable signal intensity for the isotope ^{57}Fe, for example at least 10000 counts s^{-1} in our instrument. Isotope signal intensities were corrected for detector dead time effect.[6] The detector dead time calibration was performed according to the procedure recommended by the manufacturer.

To establish mass bias, a primary assay standard solution of iron (300 μg L^{-1}) was analyzed before and after each measurement of isotopic blends. The mass bias correction factor, K was calculated using the equation (1).[1]

$$K = R_{true}/R_{measured} \qquad (1)$$

where R_{true} = true ratio of the isotope amount fractions calculated from the IUPAC composition data for natural iron;[7] $R_{measured}$ = experimental ratio of the isotope amount fractions measured by ICP-MS.

Data evaluation

The element amount concentration in a sample was calculated from the concentration of primary assay standard solution using isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS). For the calculation of the mass fraction of iron in the sample, the element amount concentration was multiplied by the atomic mass of iron.[7] Details about equations employed for quantification purposes can be found elsewhere.[8] The uncertainty estimation in the measurement of the mass fraction of Fe was calculated following the numerical method reported by Kragten.[9] The expanded uncertainty, *U* (expressed as CV%), was calculated by multiplying the combined standard uncertainty with a coverage factor *k* of 2, which gives a level of confidence of approximately 95%.

Table S1 Optimum conditions for ICP-MS analysis

Sample introduction and plasma	
ICP-MS	Agilent 7500c
Nebulizer	Babington
Spray chamber	Quartz, Scott double pass, chilled to 2 °C
Torch	Quartz, 2.5 mm ID
Sampling depth	8 mm
Sampler and skimmer cones	Nickel, 1 and 0.4 mm ID respectively
RF power	1490 W
Plasma gas flow rate	15 L min^{-1}
Carrier gas flow rate	1.0 L min^{-1}
Makeup gas flow rate	0.1 L min^{-1}
Data acquisition	
Acquisition mode	Isotope analysis
Acquired mass	54 (Fe), 56 (Fe), 57 (Fe)
Integration time (sec) / point	1
Integration time (sec) / mass	3
Number of points per mass	3
Detector dead time	38.4 ns
Cell mode	He/H_2
Cell gas flow rate	He: 4.0 mL min^{-1}; H_2: 1.5 mL min^{-1}
Octopole bias	– 20 to –19 V
Quadrupole bias	– 18 to –17 V

Table S2 Microwave-assisted acid digestion program

Stage	Max power (W)	% Power (%)	Ramp (Minute)	Temperature (°C)	Hold (Minute)
1	1200	100	05:00	80	10:00
2	1200	100	10:00	120	10:00
3	1200	100	10:00	180	40:00