Electronic supplementary information

1. Proof of the linear relationship between the particle density D (in cm^{-3}) and the concentration C (in ppm) of the element. When the uptake rate η is 1 mL/min, the working gas flow rate γ is 1 SLM, the nebulizer efficiency β is 3%, the pressure P=101 kPa, and the plasma gas temperature T$_{gas}$ is 5000 K. The matrix is water. The mapping between the concentration of the element Li and the theoretically calculated particle density is shown in Fig. S1.
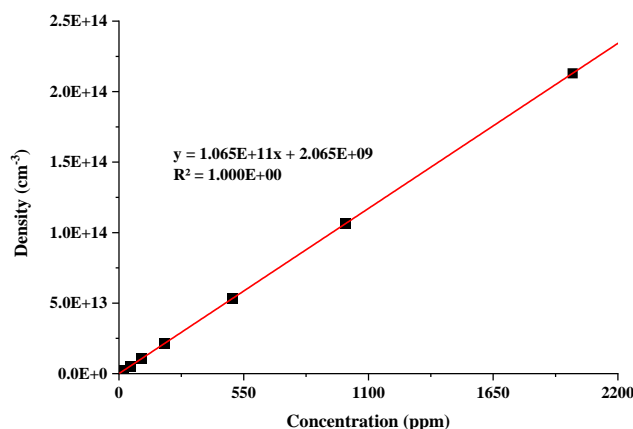

Fig. S1 Relationship between the concentration of Li in solution and the particle density of Li in plasma.

The calculation process is as follows:

Firstly, the total density of particles n in the plasma is determined by solving the ideal gas equation. The effect of electrons on the gas pressure is not considered.

$$n = P/k_B T_{gas} = 1.47 \times 10^{24} \tag{S1}$$

Next, assuming that the concentration of Li is C. Then, the respective fluxes of Ar, O, H, and Li in the plasma are calculated under the above conditions as follows.

$$
\begin{aligned}
Q(Ar) &= n \cdot \gamma = 2.69 \times 10^{22} \\
Q(H) &= \frac{2 \cdot \beta \cdot \eta \cdot NA}{M(H_2O)} = 2.01 \times 10^{21} \\
Q(O) &= \frac{\beta \cdot \eta \cdot NA}{M(H_2O)} = 1.00 \times 10^{21} \\
Q(Li_{sam}) &= \frac{\beta \cdot \eta \cdot C^x \cdot NA}{M(element_{Sam}^x)} = 2.60 \times 10^{15} \cdot C
\end{aligned}
\tag{S2}
$$

Finally, the particle density of each element in the steady state plasma is calculated.

$$
\begin{aligned}
D(Ar) &= \frac{Q(Ar)}{\sum_{i=1}^{v+3} Q^x} \cdot n \\
D(H) &= \frac{Q(H)}{\sum_{i=1}^{v+3} Q^x} \cdot n \\
D(O) &= \frac{Q(O)}{\sum_{i=1}^{v+3} Q^x} \cdot n \\
D(Li) &= \frac{Q(Li)}{\sum_{i=1}^{v+3} Q^x} \cdot n = \frac{Q(Li) \cdot n}{Q(Ar) + Q(H) + Q(O) + Q(Li)} \\
&= \frac{n \cdot 2.60 \times 10^{15} \cdot C}{2.69 \times 10^{22} + 2.01 \times 10^{21} + 1.00 \times 10^{21} + 2.60 \times 10^{15} \cdot C}
\end{aligned}
\tag{S3}
$$

According to Eq. (S3), the particle density D(Li) is not absolutely linear with the concentration C(Li) since the change in Li concentration affects the denominator ($\sum_{i=1}^{v+3} Q^x$), i.e., $R^2 \neq 1$ for the fitted curve in Fig. S1. However, the R^2 for the fitted curve in Fig. S1 is still approximated to be 1 due to the large proportion of the remaining three elements (Ar, H, and O) in the plasma.

2. Eq. 8 in the paper can be converted to a one-element higher-order equation by eliminating unknowns. For each additional n elements, the corresponding higher-order equations will be increased to the n+1th power. Taking the 4-element model as an example, the higher-order equations with the electron number density n_e as the unknown are as follows:

$$A^5 n_e{}^5 + A^4 n_e{}^4 + A^3 n_e{}^3 + A^2 n_e{}^2 + A^1 n_e + A^0 = 0$$

The significance of the coefficients in the above equation is as follows.

$$A^5 = 1$$
$$A^4 = \sum C_4^1(S) = \sum_{i=1}^{4} S_i$$
$$A^3 = \sum C_4^2(S) - \sum C_4^1(Sn)$$
$$A^2 = \sum C_4^3(S) - \sum \left(C_4^1(Sn) \cdot \sum C_3^1(S) \right)$$
$$A^1 = C_4^4(S) - \sum \left(C_4^1(Sn) \cdot \sum C_3^2(S) \right)$$
$$A^0 = -C_4^4(S) \cdot \sum C_4^1(n)$$

The meaning of the number of combinations in each equation is explained below. In addition, the symbols S and n represent the Saha coefficients and particle densities of each element, respectively.

$$C_4^4(S) = S_1 S_2 S_3 S_4,$$
$$\sum C_4^1(Sn) = \sum_{i=1}^{4} S_i n_i,$$
$$\sum \left(C_4^1(Sn) \cdot \sum C_3^1(S) \right) = \sum_{i=1}^{4} \left(S_i n_i \cdot \sum_{k \neq i} S_k \right),$$
$$\sum \left(C_4^1(Sn) \cdot \sum C_3^2(S) \right) = \sum_{i=1}^{4} \left(S_i n_i \cdot \sum_{k \neq i, \ j \neq i} S_k S_j \right).$$

3. Experimental conditions for comparative tests (Effect of matrix K on analyte Na)

Table S1 Experimental parameters for comparative tests (Effect of matrix K on analyte Na).

Instrumental parameter	Operating condition
Microwave power (kW)	0.55
Integration time (s)	0.5
Gain	2600
Gas purity	99.999%
Observation mode	Side-on
Oxygen shielding gas (SLM)	1.8
Argon maintenance gas (SLM)	0.54
Argon carrier gas (SLM)	0.40
Injection rate (mL/min)	1

The experimental group is referred to as group 1 and the control group is referred to as group 2. Changes in the instrumental response of the analyte Na at concentrations of 4, 5, 6, 7, and 8 ppm were observed after a gradual increase in the concentration of matrix K (2.5, 5, 10, 20, and 40 ppm) in group 1 and the concentration of matrix K (5 ppm) in group 2. All samples were made by diluting standard samples of 1000 ppm with 3% HNO_3 and configuring the mix.

4. Effect of plasma temperature on the density distribution of elemental particles

The following figures are drawn from the software computational simulation to illustrate the important role of temperature parameters in influencing the model. The x-axis of the graph shows the concentration of Li in ppm. y-axis corresponds to the density of each type of particle calculated by the software in m^{-3}.
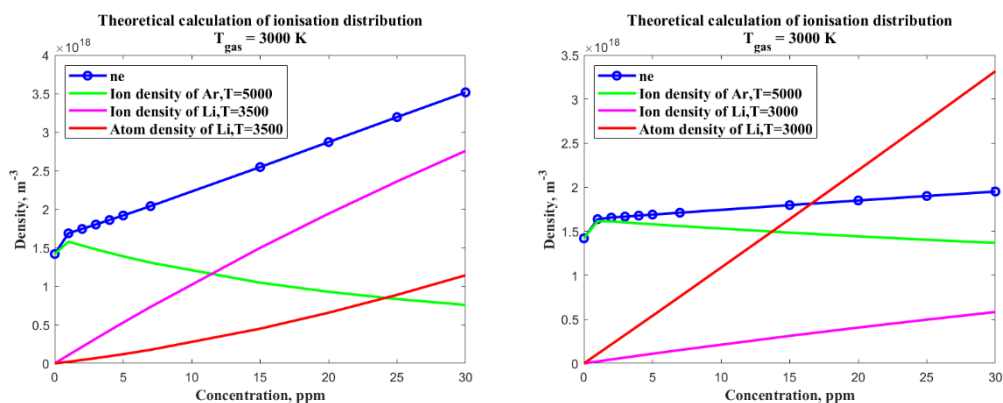
Fig. S2 The influence of plasma temperature on the density of various particles in the model.

5. Experimental conditions for artificial seawater sample BWR3030-2016

A summary of the experimental parameter information is shown in the table below. Spectral data were collected for two gain conditions because of the different sensitivities of the detector in response to different analysis line intensities.

Table S2 Experimental parameters for sample BWR3030-2016.

Instrumental parameter	Operating condition
Microwave power (kW)	0.5
Integration time (s)	0.3
Gain	2380, 2800
Gas purity	99.999%
Observation mode	Side-on
Oxygen shielding gas (SLM)	1.35
Argon maintenance gas (SLM)	0.54
Argon carrier gas (SLM)	0.40
Injection rate (mL/min)	1

6. Experimental conditions for brine samples

A summary of the experimental parameter information is shown in Table S3.

Table S3 Experimental parameters for brine samples

Instrumental parameter	Operating condition
Microwave power (kW)	0.5
Integration time (s)	0.2
Gain	2400, 2800
Gas purity	99.999%
Observation mode	Side-on
Oxygen shielding gas (SLM)	1.5
Argon maintenance gas (SLM)	0.54
Argon carrier gas (SLM)	0.45
Injection rate (mL/min)	1

7. Information on the standard spiked concentrations of different elements in the spiked recovery experiments for brine samples is shown in the table below.

Table S4 Spiked concentration information table.

Element	K^+	Na^+	Ca^{2+}	Mg^{2+}	Li^+	B^{3+}
Unit	mg/L (ppm)	mg/L (ppm)	mg/L (ppm)	mg/L (ppm)	mg/L (ppm)	mg/L (ppm)
Circulating mother liquor	20	30	1	30	3	3
Raw ore brine	20	30	1	400	3	3
Mineralized brine	20	30	1	400	3	3
Lithium ore brine	20	30	1	400	3	3

8. The procedure for spiking recovery is to take two equal quantities of the sample to be tested, one of which is spiked to a standard of a certain amount of the component to be tested. Both samples are then analysed following the same process. The results obtained from the spiked one will be subtracted from the results obtained from the unspiked one, and the recovery rate is the ratio of the difference to the spiked concentrations.

9. Operational procedures of Saha IESC

Experimental data

Begin

Configure 3–6 standard samples (Contains the major matrix elements of the sample to be tested and the element to be measured);

Collection of spectral line intensities of analytes in standard samples and samples to be measured;

Modelling and parameter optimisation

Inputs: information about the analysed elements (χ, g, A, E, etc.), spectral intensity I, Concentration C of standard samples, experimental parameters (P, η, β, γ);

Set the initial temperature T_0 , iteration stopping conditions, new solution generation rules. References can be made to the results of the Boltzmann plot method or to the results reported in the literature.

Referring to Eq. (2), calculate the Saha coefficient S for each element[a].

Calculate the total particle density n in the equilibrium plasma at the air pressure at which the laboratory is located referring to Eq. (3).

Referring to Eqs. (4–5), the particle density of each element (denoted by the symbol D) in plasma is calculated based on the total particle density n as well as the information of experimental parameters (β, η, γ, and C).

Referring to the Eqs. (8–10), numerical iterations are applied to calculate the densities of various types of particles (n_e、 n_{ion} 、 n_{atom})

Referring to Eq. (11), fitting the Saha-IESC correction curve (n_{atom}-I) for each element, and calculate the sum of R^2 .

Compare and record the maximum sum of R^2 .

Generate new solutions ← No — Whether to stop the iteration[b]? — Yes

Quantification and calibration

Calculation of n_e , n_{ion} , n_{atom} of each standard sample under optimal temperature conditions .

Calculate the atomic density of each element in the sample to be measured referring to Eq. (11)

Determine the concentration of the sample to be measured referring to Eq. (12).

Correction of the intensity of the analysis line can be achieved by selecting any one of the electron densities of the standard samples as the reference electron density (n_e^{ref}) and analysing all the samples standardised to the n_e^{ref} with reference to Eq. (13).

END

a. The relevant parameters (including wavelength λ, excitation energy E_j, ionisation energy χ, and statistical weights g_j) can be obtained from the NIST.
b. Iteration termination condition: a preset number of iterations is reached or the difference between the results of two neighbouring iterations is less than the error tolerance.
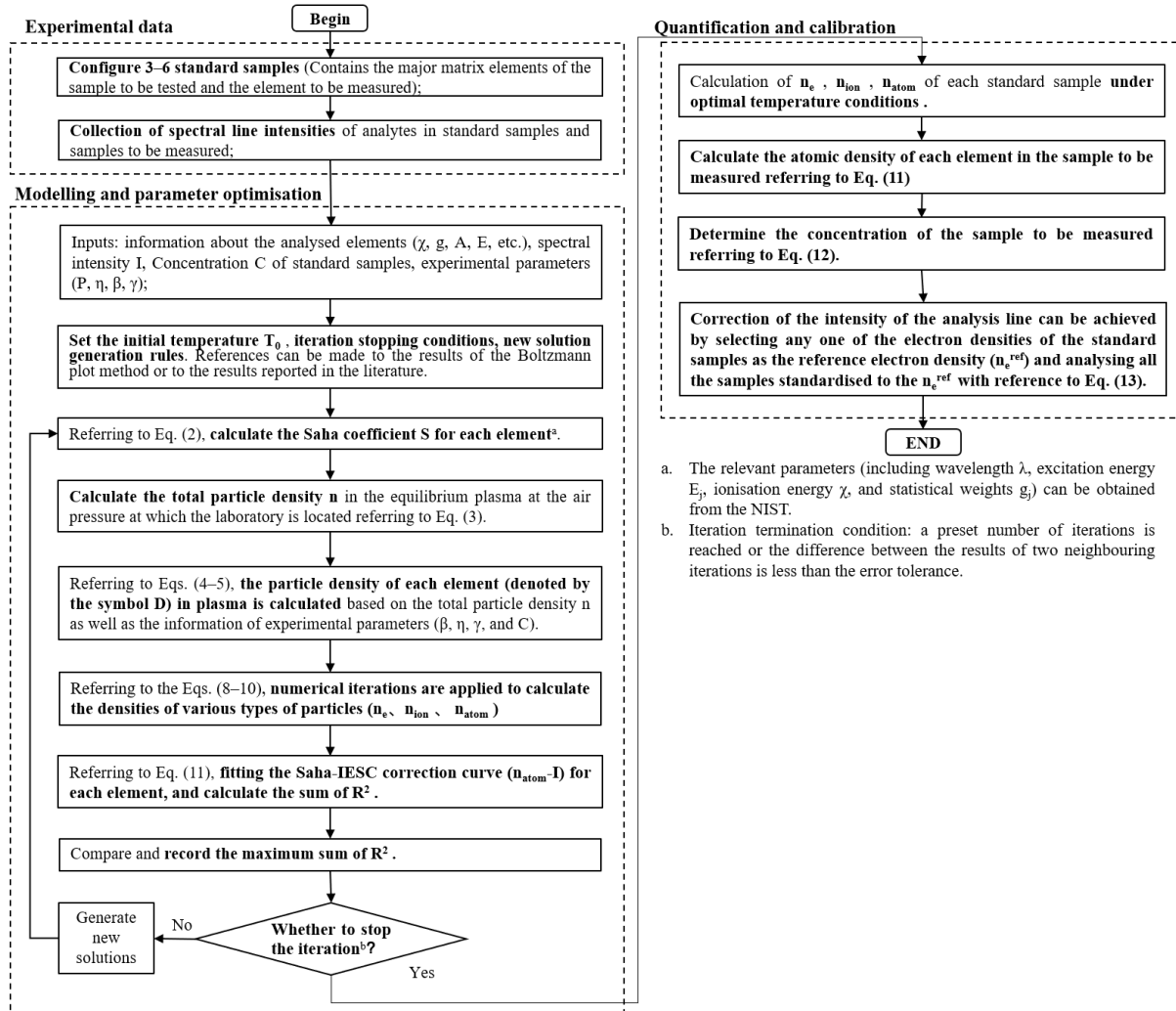
Fig. S3 Saha-IESC Operating Procedure

10. Particle Swarm Optimisation (PSO)

PSO is a heuristic computing technique. Derived from the behavioral study of bird feeding in flocks, it finds optimal solutions through collaboration and information sharing between individuals in a group. It is easy to implement and does not have many parameters to regulate. Particles have only two properties: velocity and position. Velocity represents the magnitude of the change in position; position represents the direction of motion and is also a viable solution.

The control parameters of PSO include: population size, inertia weight, acceleration constant c1 and c2, maximum velocity, stopping criterion, constraint range, boundary condition processing strategy, etc. Among them, the population size indicates the number of calculations of the objective function in a iteration. The inertia weights indicate the amount of inheritance of the particle to the current velocity, which is generally a fixed value. When the inertia weight is large, it is more capable of global optimisation; when the inertia capacity is small, it is more capable of local optimisation. The two acceleration constants are used to regulate the maximum step size for individual position and group position flights, respectively, reflecting the exchange of information between the particle swarms. The particles have a maximum velocity in each dimension, which is used to limit the particle speed. The

maximum velocity is used to determine the strength of the spatial search. The stopping criterion can generally be set as the maximum number of iterations, the maximum number of stopping steps for optimal solution or computational accuracy. When the position or velocity of a dimension exceeds the set value, boundary condition processing can limit the position of the particle to the solution space limited by the constraints, avoiding population dispersion and blind search of the particle.

The brief process is:

Step 1. Generate a set of initial solutions (including initial positions and velocities of particles) as the current population (current feasible solution set);

Step 2. Calculate the objective function value of each feasible solution in the current population (current solution set);

Step 3. The objective value of each particle is compared with the current optimal solution (individual optimal vs. population optimal) and the individual optimal and population optimal solutions are updated.

Step 4. Population position update: Update the velocity of each particle before updating the position. Firstly, update the velocity of each particle by using the acceleration constant, inertia weight, current optimal position of individual and group. Then update the particle position (feasible solution) by using the updated velocity.

Step 5. Calculate the fitness (objective function value) of each solution in the current population (current solution set).

Step 6. Update the individual optimal solution and the population optimal solution.

Step 8. Determine whether the iteration termination condition is met. If so, execute Step 9, otherwise, return to Step 3.

Step 9. Output the optimal solution.