Electronic Supplementary Material (ESI) for Journal of Analytical Atomic Spectrometry.

Experimental evidence of water dissociation and spatial dependent charge-transfer reactions in a mix-gas inductively coupled plasma optical emission spectrometry

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Samples and Samples Preparation

The following certified reference materials were analyzed: Pine Needles (NIST 1575a), Bovine Liver (NIST 1577c), and Wheat Flour (NIST 1567a) from National Institute of Standards, and bush branches and leaves (NIM-GBW07602) from IGGE (Institute of Geophysical and Geochemical Exploration, China). 250 mg of sample were weighed and transferred to the vessel accompanying the microwave oven. Subsequently, 3 mL of HNO_3 and 1 mL of H_2O_2 were added to the sample in the flask. The flask was closed, adjusted in the rotor, and placed inside the microwave oven. The program informed in Table S1 was then run. A microwave oven (Berghof, Speedwave four, Eningen, Germany) was used to assist the samples decomposition The obtained solution was transferred to graduated vials and the volume adjusted to 25 mL by adding water.

Table S1 Microwave heating program applied to assist the certified reference material decomposition

Temperature (°C)	Pressure (bar)	Ramp (min.)	Holding (min.)	Pressure (%)
170	38	5	2	80
190	38	5	2	90
50	38	5	2	0
50	0	3	15	0
50	0	0	0	0

Table S2 Argon spectral lines that were monitored to study spatial dependence of charge transfer reactions in the ICP

Emission line (nm)	Excitation Energy (eV)	Emission line (nm)	Excitation Energy (eV)	Emission line (nm)	Excitation Energy (eV)
Ar 549.588	15.33	Ar 383.470	15.06	Ar 433.535	14.68
Ar 614.544	15.31	Ar 355.433	15.03	Ar 434.518	14.68
Ar 610.564	15.31	Ar 720.698	15.02	Ar 433.357	14.68
Ar 573.952	15.31	Ar 356.768	15.02	Ar 418.190	14.68
Ar 557.254	15.31	Ar 660.485	14.97	Ar 404.443	14.68
Ar 516.229	15.30	Ar 605.937	14.95	Ar 394.900	14.68
Ar 629.688	15.29	Ar 731.172	14.84	Ar 451.075	14.57
Ar 518.775	15.29	Ar 743.533	14.83	Ar 419.834	14.57
Ar 364.986	15.22	Ar 710.748	14.83	Ar 426.630	14.52
Ar 588.859	15.18	Ar 703.025	14.83	Ar 427.220	14.52
Ar 545.165	15.18	Ar 641.631	14.83	Ar 415.861	14.52
Ar 621.250	15.16	Ar 748.433	14.80	Ar 416.420	14.52
Ar 604.323	15.14	Ar 735.328	14.78	Ar 430.012	14.50
Ar 630.766	15.13	Ar 737.212	14.75	Ar 419.073	14.50
Ar 603.213	15.13	Ar 789.108	14.74	Ar 420.069	14.49
Ar 555.870	15.13	Ar 675.283	14.74	Ar 470.232	14.46
Ar 560.673	15.11	Ar 425.938	14.73	Ar 425.120	14.46
Ar 565.070	15.10	Ar 687.129	14.71	Ar 667.728	13.47
Ar 383.470	15.06	Ar 693.767	14.69	Ar 714.704	13.28

Table S3 Analysis of certified reference materials using pneumatic nebulization/aerosol desolvation - membrane desolvation (PN/DES-MD) for introducing the sample solution into the ICP. Emission signals were measured in Ar-N_2 ICP axially viewed

Element	GBW07602 (Bush branch and leaves)		NIST 1575a Pine Needles)		NIST 1577c (Bovine liver)		NIST 1567a (Wheat flour)	
	Certified	Found	Certified	Found	Certified	Found	Certified	Found
Pb	7.1 ± 1.1	7.3 ± 1.9	0.167 ± 0.015	< 0.25	0.0628 ± 0.001	< 0.25	< 0.020	< 0.25
Zn	20.6 ± 2.2	20.7 ± 0.8	38 ± 2	37 ± 1	181.1 ± 1.0	170.0 ± 9.0	11.6 ± 0.4	11.0 ± 0.4
Cd	0.14 ± 0.06	0.14 ± 0.01	0.233 ± 0.004	0.240 ± 0.010	0.097 ± 0.001	0.11 ± 0.01	0.026 ± 0.002	< 0.020
Fe	1020 ± 67	917 ± 21	46 ± 2	61.0 ± 0.2	197.94 ± 0.65	202 ± 6	14.1 ± 0.5	14.4 ± 0.8
Cr	2.3 ± 0.3	1.7 ± 0.9	0.3 - 0.5	0.31 ± 0.02	0.053 ± 0.014	< 0.020	-	< 0.020
Mn	58 ± 6	59 ± 2	488 ± 12	476 ± 13	10.46 ± 0.47	9.97 ± 0.40	9.4 ± 0.9	9.2 ± 0.1
Ni	1.7 ± 0.4	1.4 ± 0.1	-	1.80 ± 0.10	0.0445 ± 0.0092	< 0.023	-	< 0.023
Co	0.39 ± 0.05	0.35 ± 0.08	0.061 ± 0.002	< 0.023	0.300 ± 0.018	0.405 ± 0.140	0.006	< 0.023
Cu	5.2 ± 0.5	5.4 ± 0.4	2.8 ± 0.2	2.8 ± 0.2	275.2 ± 4.6	210.0 ± 7.5	2.1 ± 0.2	2.1 ± 0.1
V	2.4 ± 0.3	< 0.01	-	0.130 ± 0.003	0.00817 ± 0.00066	< 0.01	0.011	< 0.01
Mo	0.26 ± 0.04	0.28 ± 0.03	-	< 0.004	3.30 ± 0.13	2.80 ± 0.15	0.48 ± 0.03	0.41 ± 0.02