

- 1 **Table 1S.** Precision of measurements ($n = 10$) for the different setup tested. A solution
2 containing $50 \mu\text{g L}^{-1}$ of each element was employed.

RSD, %			
Spectral line	Sample path length of 50 cm + 20 cm	Sample path length of 50 cm	Direct Introduction (without confluence)
Y 371.029	0.71	0.63	0.75
In 325.609	0.48	0.88	0.85
In 230.606	0.63	0.73	0.53
Ga 417.206	0.49	0.88	0.90
Ga 294.364	0.57	0.45	0.68

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4 **Table 2S.** Parameters of calibration curve. The concentration of calibration solutions ranged from 5 to 200 $\mu\text{g L}^{-1}$.

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Analyte	Spectral Lines used for Internal Standardization											
	External Calibration		In 230.606 nm		In 325.609 nm		Y 371.029 nm		Ga 417.206 nm		Ga 294.364 nm	
	Slope	R ²	Slope*	R ²	Slope*	R ²	Slope*	R ²	Slope*	R ²	Slope*	R ²
Ba 233.527	1226.5	0.9997	1164.3	0.9992	1495.9	0.9978	1181.8	0.9999	1221.8	0.9994	1220.9	0.9993 ₈
Cd 228.802	1043.2	0.9999	990.58	0.9986	1271.6	0.9989	1005.3	0.9998	1039.2	0.9999	1038.4	0.9998
Cd 214.440	258.65	0.9999	245.54	0.9986	315.47	0.9988	249.22	0.9999	257.65	0.9998	257.45	0.9998 ₉
Co 228.616	449.04	0.9999	426.57	0.9981	546.67	0.9992	432.83	0.9996	447.31	0.9999	446.97	0.9999
Cr 267.716	540.95	0.9999	513.7	0.9979	659.3	0.9993	521.32	0.9996	538.85	0.9999	538.43	0.9999 ₁₀
Cr 357.869	1549.3	0.9999	1471.3	0.9984	1887.9	0.999	1493.1	0.9998	1543.4	0.9999	1542.2	0.9998
V 292.464	239.11	0.9992	226.81	0.9998	291.97	0.9965	230.32	0.9997	238.22	0.9986	238.01	0.9988 ₁₁
V 290.880	737.2	0.9996	698.74	0.9995	903.58	0.9974	709.6	0.9999	724.41	0.9992	733.80	0.9989
Zn 206.200	105.92	0.9996	100.52	0.9969	129.79	0.9993	102.02	0.9993	105.56	0.9999	105.46	0.9999 ₁₂
Zn 213.857	576.26	0.9991	546.6	0.9958	705.66	0.9994	554.88	0.9987	573.94	0.9998	573.43	0.9999
Pb 220.353	33.452	0.9993	31.755	0.9959	40.871	0.9998	32.221	0.9987	33.321	0.9998	33.290	0.9999 ₁₃
Pb 217.000	5.5367	0.999	5.2541	0.9964	6.7621	0.9989	5.3352	0.9986	5.5162	0.9992	5.5110	0.9992
Sr 407.771	84749	0.9999	80489	0.9988	103238	0.9986	81681	0.9999	84426	0.9998	84362	0.9997 ₁₄
Cu 327.393	1773.7	0.9993	1684.7	0.9964	2162.2	0.9995	1709.4	0.9989	1766.8	0.9998	1765.3	0.9999 ₁₅
Cu 224.700	183.41	0.9982	174.15	0.9938	223.92	0.9996	176.71	0.9974	182.67	0.9992	182.51	0.9993
Mn 257.610	7970.6	0.9999	7569.4	0.9979	9714.4	0.9993	7681.1	0.9996	7939.6	0.9999	7933.4	0.9999 ₁₆
Ni 231.604	219.18	0.9999	208.01	0.9981	267.36	0.9992	211.18	0.9997	218.33	0.9999	218.16	0.9999
Ni 232.003	94.813	0.9999	90.051	0.9978	115.51	0.9993	91.383	0.9995	94.451	0.9999	94.370	0.9999 ₁₇

18 * Correspondent to external calibration

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22 **Table 3S.** Element concentration (in $\mu\text{g g}^{-1}$) found in certified tomato leaves ($n = 3$, mean \pm standard deviation). Values in bold agree with those
 23 certified at 95% confidence level.

Spectral Lines of Internal Standard Elements, nm							
Analyte Line	Certified Value	External Calibration	In 230.606 (II)	In 325.609 (I)	Y 371.029 (II)	Ga 417.206 (I)	Ga 294.364 (I)
Ba 233.527 (II)	-	23 \pm 1	48.3 \pm 1.8	26.8 \pm 1.0	55.4 \pm 2.5	52.1 \pm 1.5	47 \pm 2
Cd 228.802 (I)	(3)	1.0 \pm 0.1	2.3 \pm 0.1	1.06 \pm 0.01	2.6 \pm 0.10	2.7 \pm 0.10	2.4 \pm 0.1
Cd 214.440 (II)	(3)	1.08 \pm 0.02	2.5 \pm 0.1	1.15 \pm 0.02	2.85 \pm 0.08	2.95 \pm 0.05	2.6 \pm 0.1
Co 228.616 (II)	(0.6)	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
Cr 267.716 (II)	4.5 \pm 0.5	1.48 \pm 0.04	3.36 \pm 0.16	1.63 \pm 0.05	4.0 \pm 0.1	3.93 \pm 0.10	3.5 \pm 0.1
Cr 357.869 (I)	4.5 \pm 0.5	1.44 \pm 0.12	3.26 \pm 0.31	1.61 \pm 0.13	3.8 \pm 0.3	3.9 \pm 0.3	3.3 \pm 0.2
V 292.464 (II)	-	0.44 \pm 0.04	1.20 \pm 0.10	0.41 \pm 0.06	1.40 \pm 0.14	1.58 \pm 0.11	1.30 \pm 0.1
V 290.880 (II)	-	0.68 \pm 0.07	2.24 \pm 0.20	0.71 \pm 0.07	2.65 \pm 0.10	2.83 \pm 0.15	2.33 \pm 0.15
Zn 206.200 (II)	62 \pm 6	25 \pm 1	52 \pm 1	29.0 \pm 0.5	61.4 \pm 1.7	57 \pm 1	52 \pm 1
Zn 213.857 (I)	62 \pm 6	23 \pm 0.5	49 \pm 1	27.3 \pm 0.4	59 \pm 1	54 \pm 1	49 \pm 1
Pb 220.353 (II)	6.3 \pm 0.3	2.41 \pm 0.15	6.22 \pm 0.34	2.77 \pm 0.12	7.39 \pm 0.20	7 \pm 0.1	6.3 \pm 0.3
Pb 217.000 (I)	6.3 \pm 0.3	2.80 \pm 0.17	5.26 \pm 0.30	3.10 \pm 0.20	6.04 \pm 0.30	5.8 \pm 0.4	5.3 \pm 0.30
Sr 407.771 (II)	44.9 \pm 0.3	15 \pm 0.3	30.4 \pm 1.8	17.0 \pm 0.6	35.8 \pm 0.8	33.3 \pm 1.4	31 \pm 2
Cu 327.393 (I)	11 \pm 1	4.17 \pm 0.05	8.7 \pm 0.1	4.8 \pm 0.1	10.2 \pm 0.36	9.8 \pm 0.2	9 \pm 1
Cu 224.700 (II)	11 \pm 1	4.16 \pm 0.12	9.6 \pm 0.4	4.8 \pm 0.1	11.4 \pm 0.13	10.9 \pm 0.25	10.3 \pm 0.5
Mn 257.610 (II)	238 \pm 7	145 \pm 3	194 \pm 4	93.5 \pm 3.5	230 \pm 9	210 \pm 7	164 \pm 6
Ni 231.604 (II)	-	0.24 \pm 0.05	0.73 \pm 0.09	0.18 \pm 0.05	0.88 \pm 0.13	1.13 \pm 0.11	0.88 \pm 0.10
Ni 232.003 (II)	-	0.396 \pm 0.053	1.11 \pm 0.11	0.36 \pm 0.05	1.34 \pm 0.10	1.56 \pm 0.11	1.26 \pm 0.11

24 Indicative values in parenthesis. n.q. (not quantified)

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26 **Table 4S.** Element concentration (in $\mu\text{g g}^{-1}$) found in certified orchard leaves ($n = 3$, mean \pm standard deviation). Values in bold agree with those
 27 certified at 95% confidence level.

Spectral Lines of Internal Standard Elements, nm							
Analyte Line	Certified Value	External Calibration	In 230.606 (II)	In 325.609 (I)	Y 371.029 (II)	Ga 417.206 (I)	Ga 294.364 (I)
Ba 233.527 (II)	(44)	20.5 \pm 0.5	37.5 \pm 0.3	29.3 \pm 1.9	42 \pm 2	37.5 \pm 2	38 \pm 0.20
Cd 228.802 (I)	0.11 \pm 0.01	0.06 \pm 0.02	0.10 \pm 0.03	0.07 \pm 0.02	0.12 \pm 0.03	0.12 \pm 0.04	0.50 \pm .05
Cd 214.440 (II)	0.11 \pm 0.01	0.05 \pm 0.01	0.09 \pm 0.02	0.06 \pm 0.01	0.11 \pm 0.04	0.12 \pm 0.03	0.47 \pm 0.03
Co 228.616 (II)	(0.2)	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
Cr 267.716 (II)	2.6 \pm 0.3	1.37 \pm 0.30	2.77 \pm 0.4	1.95 \pm 0.30	2.42 \pm 0.20	2.47 \pm 0.88	2.3 \pm 0.3
Cr 357.869 (I)	2.6 \pm 0.3	1.38 \pm 0.25	2.76 \pm 0.3	1.95 \pm 0.25	2.37 \pm 0.20	2.45 \pm 0.31	2.3 \pm 0.1
V 292.464 (II)	-	0.17 \pm 0.02	0.55 \pm 0.04	0.18 \pm 0.04	0.56 \pm 0.06	0.81 \pm 0.06	0.65 \pm 0.05
V 290.880 (II)	-	0.44 \pm 0.02	1.48 \pm 0.03	0.76 \pm 0.05	1.63 \pm 0.05	2.0 \pm 0.30	1.6 \pm 0.1
Zn 206.200 (II)	25 \pm 3	13 \pm 3	24.6 \pm 1.5	19.3 \pm 3.0	23 \pm 1	25 \pm 2	25 \pm 2
Zn 213.857 (I)	25 \pm 3	12.5 \pm 3.2	24 \pm 3	18.54 \pm 2.3	22 \pm 1	24 \pm 1	24 \pm 2
Pb 220.353 (II)	45 \pm 3	19.3 \pm 1.0	36 \pm 2	28.5 \pm 2.1	41 \pm 2	36 \pm 4	36.5 \pm 1.5
Pb 217.000 (I)	45 \pm 3	18.0 \pm 1.3	33 \pm 2	26 \pm 2.4	37 \pm 2	33 \pm 4	33 \pm 2
Sr 407.771 (II)	37 \pm 1	14 \pm 0.5	27 \pm 3	21 \pm 0.7	29 \pm 1	26 \pm 2	26 \pm 1
Cu 327.393 (I)	12 \pm 1	5.3 \pm 0.1	9.9 \pm 0.2	7.64 \pm 0.37	11 \pm 0.4	10 \pm 0.6	10 \pm 0.2
Cu 224.700 (II)	12 \pm 1	5.3 \pm 0.15	10.6 \pm 0.2	7.92 \pm 0.52	11.8 \pm 0.6	10.7 \pm 1	10.7 \pm 0.2
Mn 257.610 (II)	91 \pm 4	41 \pm 1	86 \pm 2	51 \pm 1.0	89 \pm 1	85 \pm 4	82 \pm 2
Ni 231.604 (II)	1.3 \pm 0.2	0.37 \pm 0.05	0.86 \pm 0.10	0.49 \pm 0.09	0.99 \pm 0.13	1.17 \pm 0.12	1.1 \pm 0.1
Ni 232.003 (II)	1.3 \pm 0.2	0.43 \pm 0.11	1.02 \pm 0.21	0.59 \pm 0.10	1.16 \pm 0.23	1.33 \pm 0.20	1.2 \pm 0.2

28 Indicative values in parenthesis. N.q. (not quantified)

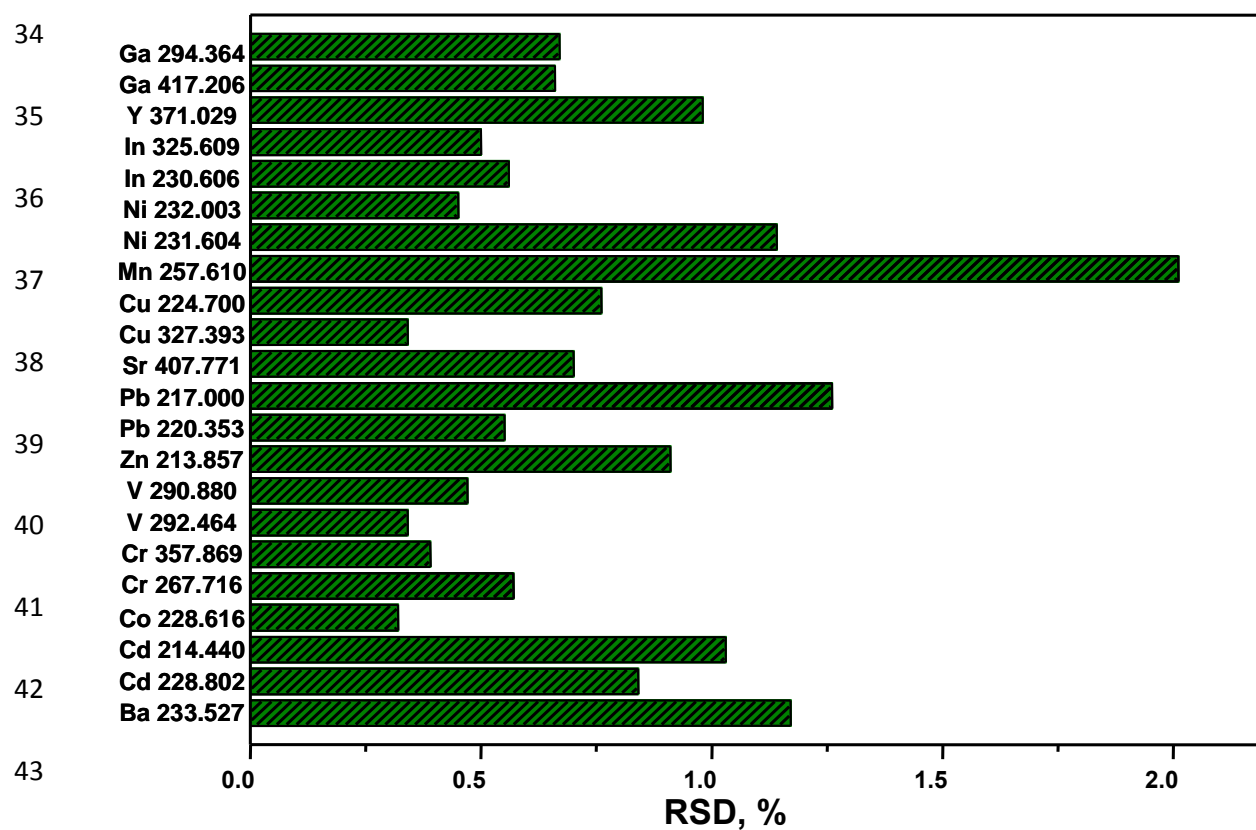
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30 **Table 5S.** Element concentration (in $\mu\text{g g}^{-1}$) found in certified bush branches and leaves ($n = 3$, mean \pm standard deviation). Values in bold agree
 31 with those certified at 95% confidence level.

Analyte Line	Certified Value	External Calibration	Spectral Lines of Internal Standard Elements, nm				
			In 230.606 (II)	In 325.609 (I)	Y 371.029 (II)	Ga 417.206 (I)	Ga 294.364 (I)
Ba 233.527 (II)	19 \pm 3	9 \pm 2	15.5 \pm 3	10 \pm 3	15 \pm 3	10.4 \pm 4.0	14 \pm 3
Cd 228.802 (I)	0.14 \pm 0.06	0.10 \pm 0.01	0.10 \pm 0.01	0.34 \pm 0.01	0.14 \pm 0.02	0.14 \pm 0.01	0.20 \pm 0.01
Cd 214.440 (II)	0.14 \pm 0.06	0.12 \pm 0.01	0.13 \pm 0.02	0.36 \pm 0.01	0.20 \pm 0.02	0.18 \pm 0.01	0.27 \pm 0.02
Co 228.616 (II)	0.39 \pm 0.05	0.15 \pm 0.02	0.20 \pm 0.02	0.37 \pm 0.02	0.20 \pm 0.02	0.20 \pm 0.02	0.30 \pm 0.04
Cr 267.716 (II)	2.3 \pm 0.3	1.3 \pm 0.2	1.6 \pm 0.2	1.2 \pm 0.1	1.6 \pm 0.2	1.2 \pm 0.1	1.5 \pm 0.2
Cr 357.869 (I)	2.3 \pm 0.3	1.2 \pm 0.1	1.8 \pm 0.3	1.3 \pm 0.1	1.8 \pm 0.3	1.4 \pm 0.2	1.7 \pm 0.2
V 292.464 (II)	2.4 \pm 0.3	0.7 \pm 0.1	1.2 \pm 0.2	0.9 \pm 0.1	1.2 \pm 0.2	0.8 \pm 0.1	1.2 \pm 0.1
V 290.880 (II)	2.4 \pm 0.3	1.8 \pm 0.2	3.3 \pm 0.2	2.0 \pm 0.2	3.0 \pm 0.3	2.2 \pm 0.2	2.8 \pm 0.3
Zn 206.200 (II)	20.6 \pm 2.2	12.1 \pm 0.4	20.3 \pm 1	11.7 \pm 0.3	19.6 \pm 0.6	14.1 \pm 0.5	18.5 \pm 1
Zn 213.857 (I)	20.6 \pm 2.2	12.2 \pm 0.5	20.1 \pm 1	11.6 \pm 0.2	19.7 \pm 0.9	14.2 \pm 0.5	18.2 \pm 0.8
Pb 220.353 (II)	7.1 \pm 1.1	4.0 \pm 0.2	7.0 \pm 0.2	4.1 \pm 0.3	6.6 \pm 0.4	4.7 \pm 0.3	6.2 \pm 0.5
Pb 217.000 (I)	7.1 \pm 1.1	4.4 \pm 0.2	7.7 \pm 0.3	4.4 \pm 0.3	7.2 \pm 0.4	5.2 \pm 0.2	6.7 \pm 0.4
Sr 407.771 (II)	345 \pm 11	145 \pm 5	256 \pm 4	151 \pm 4	338 \pm 9	274 \pm 3	315 \pm 6
Cu 327.393 (I)	5.2 \pm 0.5	2.5 \pm 0.1	4.3 \pm 0.2	2.6 \pm 0.1	4.1 \pm 0.2	3.0 \pm 0.1	3.8 \pm 0.2
Cu 224.700 (II)	5.2 \pm 0.5	2.4 \pm 0.1	4.2 \pm 0.2	2.5 \pm 0.1	4.0 \pm 0.2	2.9 \pm 0.1	3.7 \pm 0.2
Mn 257.610 (II)	58 \pm 6	28 \pm 2	50 \pm 1	27 \pm 2	54 \pm 2	33 \pm 2	45 \pm 3
Ni 231.604 (II)	1.7 \pm 0.4	0.75 \pm 0.05	1.2 \pm 0.1	0.96 \pm 0.06	1.3 \pm 0.1	0.9 \pm 0.1	1.3 \pm 0.1
Ni 232.003 (II)	1.7 \pm 0.4	0.98 \pm 0.05	1.6 \pm 0.1	1.17 \pm 0.06	1.5 \pm 0.1	1.2 \pm 0.1	1.5 \pm 0.05

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44 **Figure 1S.** Relative standard deviation (RSD) obtained for analyte ($100 \mu\text{g L}^{-1}$) and IS (50
45 $\mu\text{g L}^{-1}$) measurements ($n = 10$) using the on-line IS addition system (see Figure 1).