ELECTRONIC SUPPLEMENTARY MATERIAL

Boron elemental and isotopic determination via the BF diatomic molecule using high-resolution continuum source graphite furnace molecular absorption spectrometry

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Theoretical estimation of isotopic shifts

The theoretical isotopic shift can be derived from the equation available in the classic book of Herzberg[1] and reproduced below:

$$\Delta\nu = (1-\rho)\left[\omega'_e\left(\nu'+\frac{1}{2}\right)-\omega''_e\left(\nu''+\frac{1}{2}\right)\right] - (1-\rho^2)\left[\omega'_e x'_e\left(\nu'+\frac{1}{2}\right)^2-\omega''_e x''_e\left(\nu''+\frac{1}{2}\right)^2\right] + (1-\rho^3)\left[\omega'_e y'_e\left(\nu'+\frac{1}{2}\right)^3-\omega''_e y''_e\left(\nu''+\frac{1}{2}\right)^3\right]$$

where $\Delta\nu$ is the isotopic shift in cm^{-1}, ν is the vibrational quantum number, ω_e is the harmonic frequency, $\omega_e x_e$ and $\omega_e y_e$ are the first and second anharmonic constants, respectively; $\rho = (\mu/\mu^i)^{1/2}$, where μ is the reduced mass of the molecule and i corresponds to the heavier isotope. The number of apostrophes denotes the electronic levels (two for the lower one, and one for the upper one) involved in the electronic transition.

References

1 G. Herzberg, *Molecular Spectra and Molecule Structure. I. Spectra of Diatomic Molecules*, D. Van Nostrand Company, INC., Princeton, 2nd edn., 1950.

Table S1. Sequence for coating the graphite platform of a Graphite Furnace (GF) with W

1. Pipet 50 μL (integrated platform in GF for liquid samples), or 30 μL (platform for solid sample introduction) of a 1000 mg L^{-1} W standard solution onto the platform.
2. Run the following temperature program.

Step	Temperature (°C)	Ramp (°C s^{-1})	Hold (s)	Ar gas flow (L min^{-1})
Drying	120	24	25	2
Drying	150	15	60	2
Pyrolisis	600	30	10	2
Gas Adaptation	600	0	5	2
Atomization	1000	100	15	2

3. Repeat steps 1 and 2 either 3 times (integrated platform in GF for liquid samples) or 6 times (platform for solid sample introduction)
4. Pipet 50 μL (integrated platform in GF for liquid samples), or 25 μL (platform for solid sample introduction) of a 1000 mg L^{-1} W standard solution onto the platform.
5. Run the following temperature program, once for the integrated platform in GF for liquid samples and twice for the platform for solid sample introduction.

Step	Temperature (°C)	Ramp (°C s^{-1})	Hold (s)	Ar gas flow (L min^{-1})
Drying	120	24	25	2
Drying	150	3	60	2
Pyrolisis	600	18	10	2
Gas Adaptation	600	0	5	2
Atomization	1000	40	15	2
Clean	1400	40	5	2
Clean	2000	200	2	2

6. Run the following temperature program four times:

Step	Temperature (°C)	Ramp (°C s^{-1})	Hold (s)	Ar gas flow (L min^{-1})
Drying	150	150	10	2
Drying	600	35	10	2
Gas Adaptation	600	0	5	2
Atomization	1100	50	5	2
Clean	1400	30	10	2

7. Run the following temperature program four times.

Step	**Temperature (°C)**	**Ramp (°C s^{-1})**	**Hold (s)**	**Ar gas flow (L min^{-1})**
Drying	150	150	10	2
Drying	600	35	10	2
Gas Adaptation	600	0	5	2
Atomization	1100	50	5	2
Clean	1400	30	10	2
Clean	1500	34	5	2
Clean	1600	100	1	2
Clean	1700	100	1	2
Clean	1800	100	1	2
Clean	1900	100	1	2
Clean	2000	100	1	2

Table S2 . Software conditions introduced in the ContrAA 800G instrument to perform the temperature program included in **Table 1** for gas-phase fluorinating agents.

Step	Temperature (°C)	Ramp (°C s^{-1})	Hold (s)	Gas flow (L min^{-1})	
				Ar	Ar/CH_3F
Drying	80	6	20	MAX	STOP
Drying	110	5	40	MAX	STOP
Pyrolysis	850	300	20	MAX	STOP
Gas adaptation	850	0	5	STOP	MAX
Atomization	850	0	5	STOP	MAX
Cleaning	2500	1800	7	STOP	STOP
Cleaning	2700	3000	5	MAX	STOP

Table S3. Theoretical ($\Delta\lambda_{calc}$) and experimental ($\Delta\lambda_{exp}$) isotopic shifts for the BF molecule in the region 190-207 nm. Theoretical shifts, $\Delta\lambda_{calc}$, were calculated using the equation available on page 162 from reference 23, while experimental isotopic shifts were only included when detection in the ContrAA 800G was possible due to sensitivity constrictions.

Electronic transition: $X^1\Sigma - A^1\Pi$

λ [a]/ nm	λ_{exp}/ nm	ν', ν''	$\Delta\lambda_{calc}$/pm	$\Delta\lambda_{exp}$/pm
207.15	n.d.	1,3	338	n.d.
206.74	n.d.	0,2	333	n.d.
201.58	n.d.	1,2	184	n.d.
201.1	201.080	0,1	173	167
196.27	n.d.	1,1	25.4	n.d.
195.74	195.588	0,0	8.38	n.d.
191.10	n.d.	1,0	139	n.d.
186.78	n.d.	2,0	280	n.d.