Solid sampling electrothermal vaporization inductively coupled plasma optical emission spectrometry for direct determination of total oxygen in coal

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Supporting Information

Table S-1. Operating conditions for ETV-ICP OES

Instrument	Parameter		Value
ETV	Carrier gas flow rate [L · min^{-1}] (Ar)		0.130
	Bypass gas flow rate [L · min^{-1}] (Ar)		0.400
	Reaction gas flow rate [L · min^{-1}] (CCl_2F_2)		3
ICP OES	Plasma RF power [W]		1650
	Coolant-gas flow rate [L · min^{-1}] (Ar)		17
	Auxilary gas flow rate [L · min^{-1}] (Ar)		1.6
	Inner diameter of injector tube (mm)		2.5
	View configuration		axial
	Wavelengths [nm]	O	130.603
		Ar	425.118
		Ca	300.686
	Integration range [s]	O	12,5 - 180

Table S-2. Operating conditions for oxygen analyzer

Parameter	Value
Carrier gas flow rate [L · min^{-1}] (He)	1.0
Temperature [°C]	2400
Sample mass [mg]	1-4

Table S-3. Temperature profile of the ETV-furnace

Step	Program	
	t [s]	T [°C]
Preheating	5	100
	20	135
First evaporation	70	1100
Second evaporation	25	2350
Third evaporation	15	2400

Table S-4. Temperature profile of the oxygen analyzer-furnace

Step	Program	
	t [s]	T [°C]
Purging	30	1100
Heating	5	2400
Pyrolysis	65	2400

Table S-5. Obtained contents on dry basis for FNAA (literature), ETV-ICP OES and oxygen analyzer experiments, relative standard deviations (RSD's) and percent recoveries (R) of ETV-ICP OES vs. FNAA or OA vs. FNAA

Samples	FNAA	ETV-ICP OES vs. FNAA			Oxygen analyzer vs. FNAA		
	Content [%]	Content [%]	RSD [%]	R [%]	Content [%]	RSD [%]	R [%]
POC		3.97	3.34	94.12	4.24	7.85	100.43
UF		8.61	1.35	96.46	8.79	8.05	98.46
PITT		10.12	0.50	92.80	10.53	8.73	96.56
1632d		11.61	1.18	96.77	10.56	7.85	87.96
UT		11.78	1.31	94.21	13.26	7.27	106.07
IL		13.81	1.70	92.66	15.28	6.09	102.58
WV		15.36	2.85	93.11	15.73	5.29	95.32
WY		19.87	2.46	95.97	21.35	3.19	103.15
ND		22.59	0.37	96.96	22.92	4.26	98.37

Table S-6. t-Test for ETV vs. FNAA and OA vs. FNAA with α = 0.05

$$t = \frac{|\bar{x} - \mu|}{s}\sqrt{n}$$

$\bar{x}$ = average content ETV/OA; μ = content FNAA; n = 3;
s = standard deviation ETV/OA values

Samples	ETV-ICP OES vs. FNAA			Oxygen analyzer vs. FNAA		
	s [%]	t	t_{krit}	s [%]	t	t_{krit}
POC	0.1326	3.24	4.303	0.7078	0.34	4.303
UF	0.1163	*4.71*	4.303	0.9310	0.71	4.303
PITT	0.0507	*26.79*	4.303	0.9193	0.71	4.303
1632d	0.1372	*4.89*	4.303	0.3326	0.09	4.303
UT	0.1546	*8.11*	4.303	0.9637	1.36	4.303
IL	0.2343	*8.08*	4.303	0.8314	1.61	4.303
WV	0.4380	*4.50*	4.303	0.9758	0.67	4.303
WY	0.4895	2.95	4.303	0.6819	1.65	4.303
ND	0.0843	*14.56*	4.303	0.8289	3.02	4.303

F-Test and t-Test for ETV vs. OA with α = 0.05

$$F_{calc} = \frac{{s_1}^2}{{s_2}^2}$$

$$s_{pooled} = \sqrt{\frac{s_1^2\,(n_1-1) + s_2^2\,(n_2-1)}{n_1 + n_2 - 2}}$$

$$t = \frac{|\bar{x}_{ETV} - \bar{x}_{OA}|}{s_{pooled}} \cdot \sqrt{\frac{n_1 \cdot n_2}{n_1 + n_2}}$$

Samples	ETV-ICP OES vs. OA					
	s_1 (ETV) [%]	s_2 (OA) [%]	F_{calc}	s_{pooled}	t	t_{krit}
POC	0.1326	0.7078	0.1589	0.2532	1.29	4.303
UF	0.1163	0.9310	0.0270	0.5072	0.43	4.303
PITT	0.0507	0.9193	0.0030	0.6511	0.77	4.303
1632d	0.1372	0.3326	0.0274	0.5941	2.18	4.303
UT	0.1546	0.9637	0.0257	0.6902	2.63	4.303
IL	0.2343	0.8314	0.0633	0.6789	2.66	4.303
WV	0.4380	0.9758	0.2775	0.6645	0.67	4.303
WY	0.4895	0.6819	0.5152	0.5935	3.07	4.303
ND	0.0843	0.8289	0.0075	0.6925	0.58	4.303

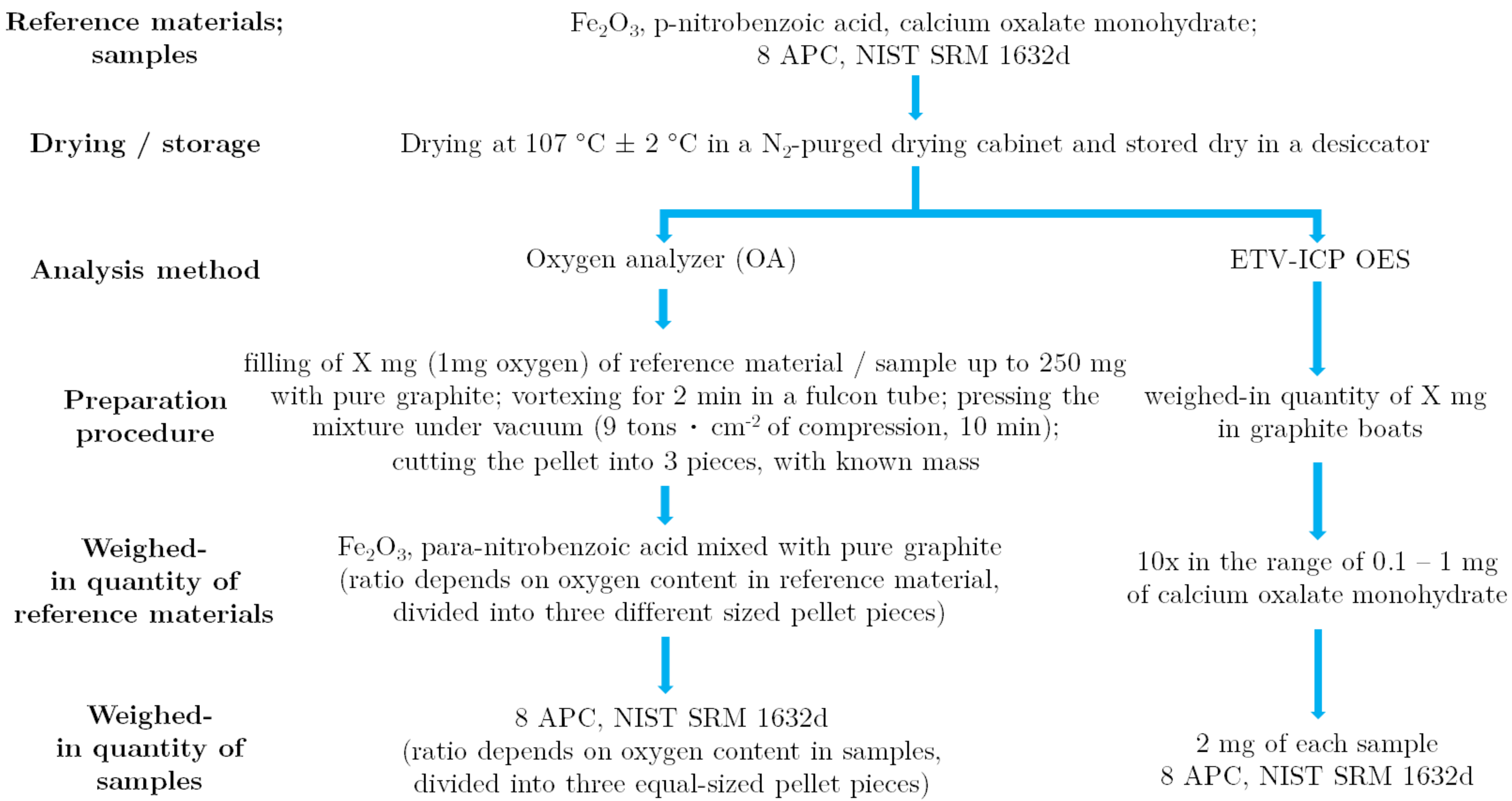

Figure S-1. Overview of the sample preparation

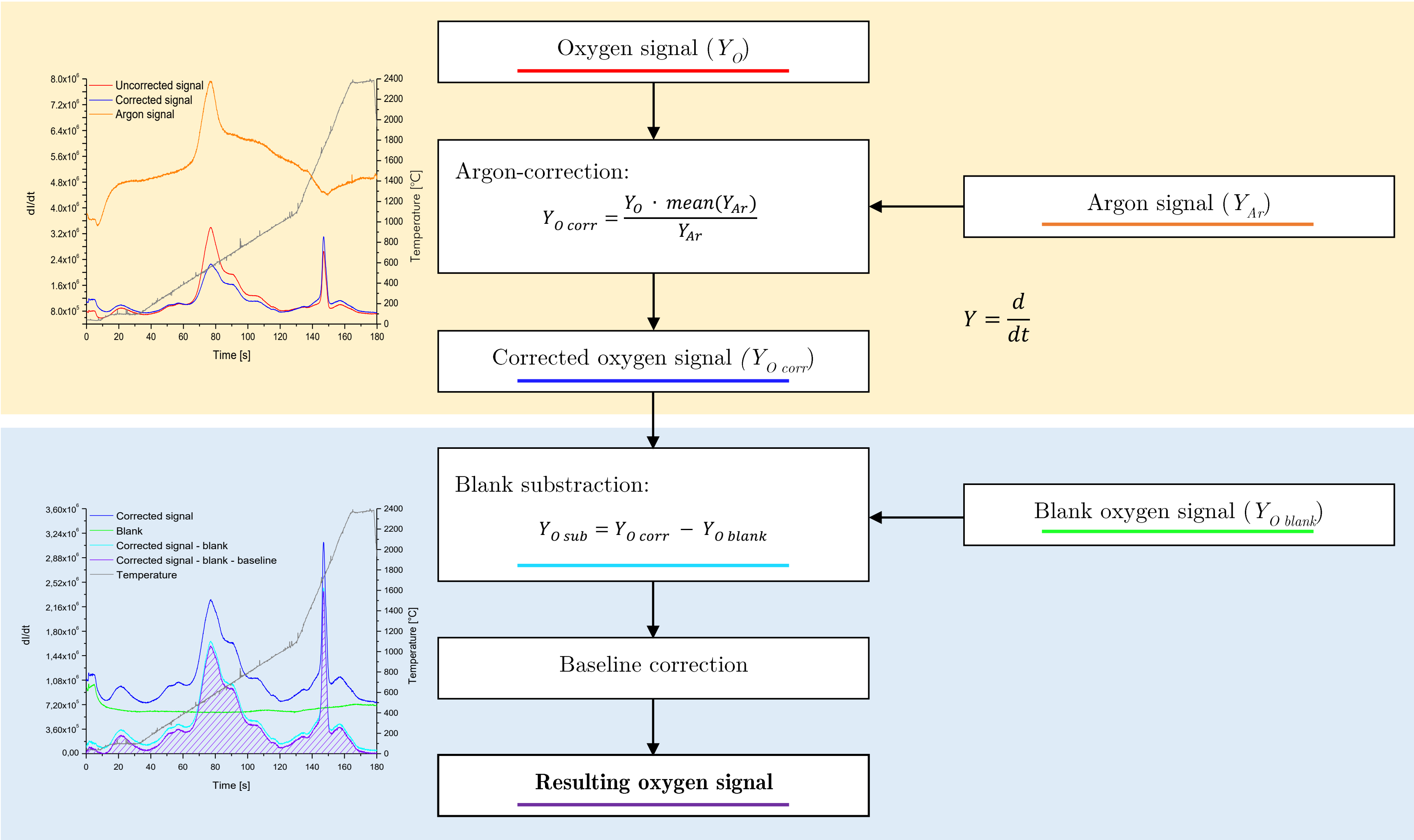

Figure S-2. Scheme of data processing and correction of the oxygen signal

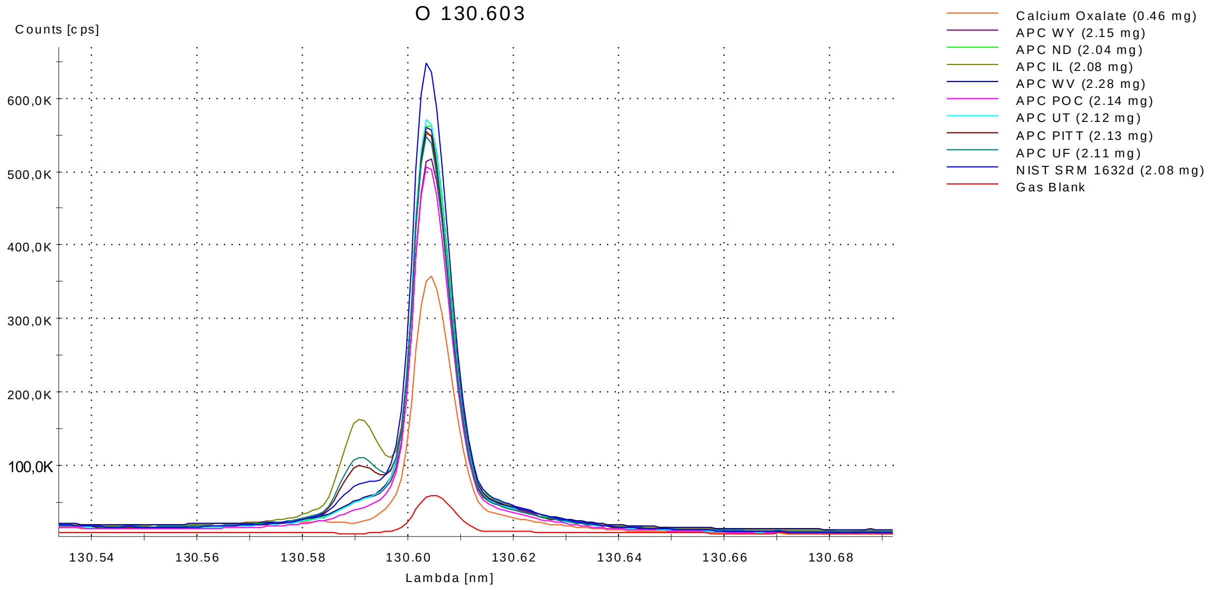

Figure S-3. Excerpt of the full spectra (130.5 – 130.7 nm) from the gas blank, all eight APC, NIST SRM 1632d and the calibration material calcium oxalate monohydrate

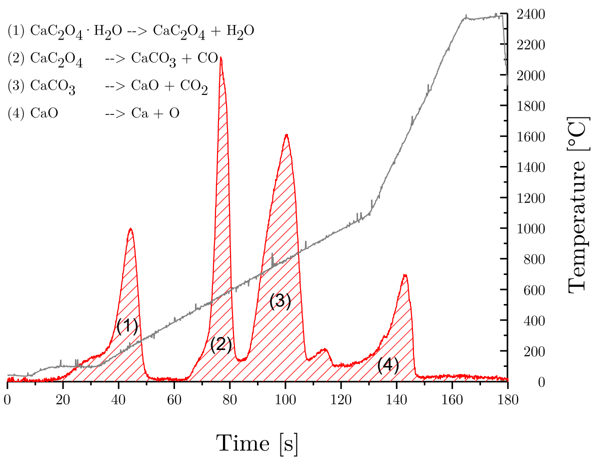

Figure S-4. Detailed explanation of the stepwise decomposition process of calcium oxalate monohydrate by means of ETV-ICP OES – oxygen release (red line); temperature profile (black line)

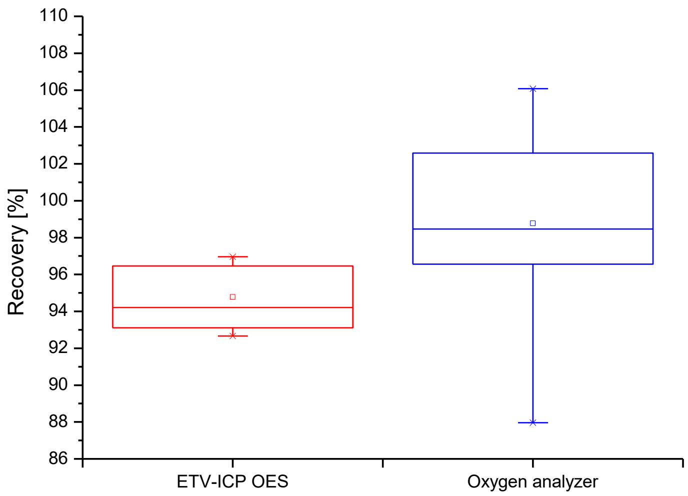

Figure S-5. Box-and-Whisker plots of recovery of oxygen from APC and NIST SRM 1632d for both analysis techniques

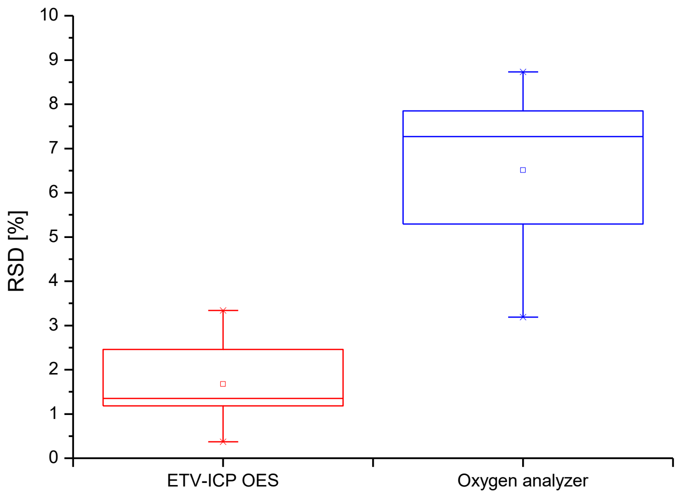

Figure S-6. Box-and-Whisker plots of RSD's of oxygen from all APC and NIST SRM 1632d for both analysis techniques