Optimization of food sample digestion by oxygen flask combustion for metals determination by capacitive-coupled microplasma optical emission spectrometry with electrothermal vaporization from a Rh filament (SSETV-μCCP-OES)

(Activity 1.1, CO-UBB)

The digestion of food samples by oxygen flask combustion for the subsequent determination of elements by capacitively coupled microplasma optical emission spectrometry using electrothermal evaporation from a Rh filament (OFC-SSETV-μCCP-OES) was optimized with respect to: (i) the volume of oxygen used for combustion, by employing flasks of different capacities; (ii) the amount of sample subjected to combustion; and (iii) the volume and concentration of the diluted HNO_3 absorbing solution used for capturing the elements released during combustion. The optimization was performed using both certified food reference materials (CRMs) and real food samples with matrices similar to those of the CRM materials.

a) Optimization of food sample combustion

The combustion of food samples was carried out in Schöniger-type quartz Erlenmeyer flasks with volumes of 250, 500, and 1000 mL, manufactured by Exeter Analytical (Coventry, UK), equipped with a platinum sample holder basket (20 × 7 mm) produced by Elemental Microanalysis Ltd. (Okehampton, Devon, UK). The schematic representation of the SSETV-μCCP-OES experimental setup used for method development at TRL4 level is shown in Figure 1.

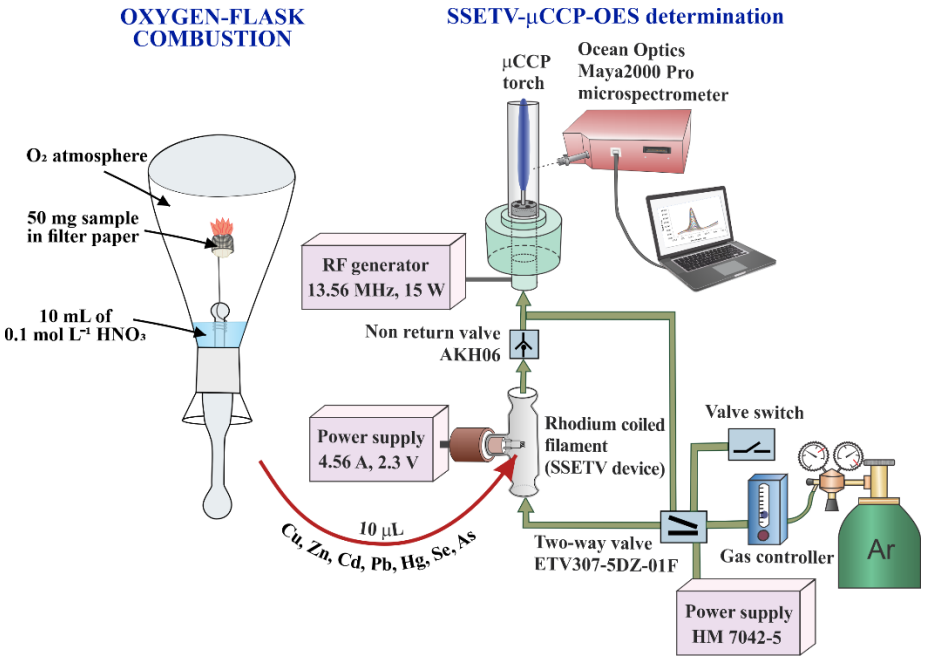

Figure 1. Schematic representation of oxygen flask combustion assisted digestion of samples for the determination of Cu, Zn, Cd, Pb, Hg, Se, and As by (OFC)-SSETV-μCCP-OES. (AC. Mot, A.-I. Dudu, T. Frentiu, D. Petreus, E.-A. Levei, Z. Stupar, M. Frentiu, E. Covaci. *J. Anal. Atom. Spectrom.*, 2025, Advance article, DOI:10.1039/D5JA00297D)

The optimization was carried out by combusting 50 mg of CRM samples and freeze-dried, ground, and homogenized food samples, weighed directly onto 3 cm × 2 cm ashless Whatman® Grade 542 filter paper supports. The samples were then wrapped and placed in the platinum basket attached to the stopper of the Erlenmeyer flask. The sample mass of 50 mg and the flask volumes selected for optimization were chosen according to the combustion capacity of the system, which depends on the amount of oxygen required for efficient combustion of carbon-rich matrices such as food samples. A volume of 10 mL of 0.1 mol L^{-1} HNO_3 absorbing solution was introduced into the flask to retain the gases generated during combustion. The flask was subsequently purged with 5.0 grade oxygen for 5 minutes at a flow rate of 1 L min^{-1}. The filter paper containing the sample was manually ignited and immediately inserted into the Erlenmeyer flask through the stopper, which allowed airtight sealing of the vessel. Combustion was carried out with the flask positioned upside down to prevent gas losses. The resulting gases were absorbed for 10 minutes into the nitric acid solution by manually swirling the flask every 2 minutes. In parallel, a blank sample was prepared under identical combustion conditions by burning a filter paper of the same dimensions without sample material.

The combustion efficiency was evaluated based on the mass balance of the total organic carbon (TOC) fraction in the solid sample and the residual fraction present in the absorbing solution, as well as any remaining residue after combustion. For this purpose, the total carbon (TC), TOC fraction, and total inorganic carbon (TIC) fraction were determined in the solid aliquot and in the solution/suspension obtained after combustion and gas absorption. Experimental determinations of TC, TOC, and TIC were performed using a Multi N/C 2100S Analyzer (Analytik Jena, Jena, Germany), in accordance with ISO 20236:2024. Total carbon in the solid was measured directly by combustion of the sample at 1100 °C, while the TOC fraction was determined after removing the TIC fraction by treating the solid samples with 0.1 mL of 1 mol L^{-1} HCl for 30 minutes directly in the ceramic boats. In liquid samples potentially containing suspended particulate matter, the determinations were performed by catalytic oxidation at 800 °C. Initially, the samples were homogenized by vortexing for 2 minutes, followed by continuous stirring in the vial during measurement. The combustion efficiency (CE, %) was calculated according to relation (1).

$$EC = \frac{m_{TOC\ food\ sample} - m_{TOC\ suspension}}{m_{TOC\ food\ sample}} \times 100 \quad (1)$$

The results obtained for various CRM and food samples, presented in Table 1 and Figure 2, indicate that the TOC fraction was predominant, ranging from 49% to 99%, with lower proportions observed in dietary supplements. In the absorbing solution, the TOC concentration ranged between 8.2 and 50.2 µg mL^{-1}, while the TIC fraction accounted for the largest proportion (39–89%), due to CO_2 absorbed into the solution after combustion. This observation is supported by the fact that, in solutions purged with nitrogen, the TIC fraction was below the method detection limit of 1 mg L^{-1}, and only the dissolved TOC fraction was quantified. The combustion efficiency for a 50 mg sample combusted in a 250 mL vessel was 96.3 ± 7.2% for Tort-3 (lobster hepatopancreas) and 90.1 ± 7.3% for GBW 10011 (wheat flour), indicating incomplete combustion based on the residual material remaining on the platinum basket. Consequently, the flask volume was increased to 500 and 1000 mL, resulting in combustion efficiencies of 98.1 ± 6.8% and 99.9 ± 6.7% for Tort-3, and 99.6 ± 6.2% and 99.9 ± 7.1% for GBW 10011, with residual masses of 0.2–20 mg on the platinum basket, containing TOC below the detection limit of the method. Although no unburned residue was observed when using the 1000 mL vessel, the 500 mL flask was selected for subsequent determinations, as it provided an average combustion efficiency of 99.7 ± 5.7%, considered complete for the food samples investigated in this study.

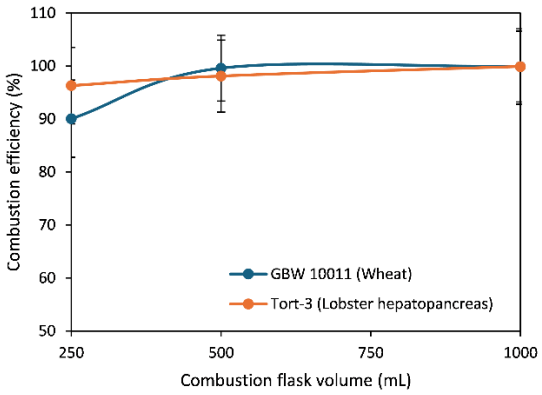

Figure 2. Combustion efficiency (%) for 50 mg of GBW 10011 (Wheat flour) and Tort-3 (Lobster hepatopancreas) using 250, 500, and 1000 mL flasks. Error bars represent the relative standard deviation for n = 3 repeated measurements. (AC. Mot, A.-I. Dudu, T. Frentiu, D. Petreus, E.-A. Levei, Z. Stupar, M. Frentiu, E. Covaci. *J. Anal. At. Spectrom.*, 2025, Advance article, DOI:10.1039/D5JA00297D)

b) Optimization of environmental samples combustion

In the case of environmental samples, the combustion procedure was optimized for soil matrices. To this end, the effects of the sample mass subjected to combustion (50, 100, and 150 mg), the volume (10, 20, and 30 mL) and concentration of HNO_3 in the absorbing solution (0.05, 0.1, and 0.3 mol L^{-1}) were investigated with respect to the recoveries (%) obtained using the SSETV-μCCP-OES method from the CRM SQC001-30G Metals in Soil (Sigma Aldrich, Laramie, USA). Experimental determinations were carried out using the TRL4 level (OFC)-SSETV-μCCP-OES setup shown in Figure 1. Combustion was performed using the 500 mL flask. Multielement determinations were conducted directly in the absorbing solution after centrifugation at 3000 rpm for 10 minutes to remove suspended particulates. The SSETV-μCCP-OES experimental system consists of a capacitively coupled plasma microtorch (Babeș-Bolyai University, Cluj-Napoca), operated at 15 W and 150 mL min^{-1} Ar, powered by a miniaturized 13.56 MHz radiofrequency generator (Technical University of Cluj-Napoca), and interfaced with a Maya2000 Pro microspectrometer (Ocean Optics, Dunedin, USA), purged with 6.0 grade argon and covering the 165–309 nm spectral range with a resolution of 0.35 nm. A 10 μL microsample was evaporated using the miniaturized SSETV device (Babeș-Bolyai University, Cluj-Napoca) from a Rh microfilament with a diameter of 250 μm and 99.9% purity (Goodfellow, Cambridge, UK). The microfilament was heated using a Tenma 72-13360 programmable power supply (Tenma, China) at 80 °C (0.25 V and 1.93 A) for 180 s for sample drying, and at 1500 °C (2.3 V and 4.56 A) for 10 s for sample vaporization. Spectroscopic observation for recording the three-dimensional episodic spectra (signal – wavelength – time), with an integration time of 100 ms per spectrum, was achieved using a 10 mm focal length collimating lens without optical fiber, positioned at a height of 0.8 mm above the Mo tip microelectrode.

Table 1. Total carbon (TC), total inorganic carbon (TIC), and total organic carbon (TOC) concentrations in food samples and in the absorbing solution/suspension for CRMs and real food samples (AC. Mot, A.-I. Dudu, T. Frentiu, D. Petreus, E.-A. Levei, Z. Stupar, M. Frentiu, E. Covaci. *J. Anal. At. Spectrom.*, 2025, Advance article, DOI:10.1039/D5JA00297D)

Sample	Carbon fractions in food samples ± SD[a] (μg mg^{-1})			Carbon fractions in the sample solution/suspension obtained after combustion (μg mL^{-1})			Combustion efficiency (%)[b]
	TC	TIC	TOC	TC	TIC	TOC	
Certified reference materials (CRMs)							
Tort-3 (Lobster hepatopancreas)	482 ± 15	158 ± 27	324 ± 22	50.2 ± 0.9	19.7 ± 3.0	30.5 ± 3.1	98.1 ± 6.8
CE278k (Mussel tissue)	436 ± 27	66 ± 32	370 ± 17	9.8 ± 0.5	7.3 ± 1.0	2.5 ± 1.1	99.9 ± 4.6
CS-M-3 (Dried mushroom powder)	445 ± 25	19 ± 31	426 ± 19	8.7 ± 0.2	6.2 ± 0.5	2.5 ± 0.5	99.9 ± 4.5
GBW 10011 (Wheat flower)	395 ± 25	25 ± 34	370 ± 23	10.6 ± 0.9	8.0 ± 0.8	2.6 ± 1.2	99.6 ± 6.2
SRM 3280 (Multivitamin tablets)	129 ± 7	3 ± 9	126 ± 6	15.9 ± 0.9	13.2 ± 0.8	2.7 ± 1.2	99.6 ± 4.8
Food samples and dietary supplements							
Fish muscle 1	537 ± 33	175 ± 39	362 ± 21	20.3 ± 1.3	14.0 ± 1.5	6.3 ± 2.0	99.7 ± 5.8
Fish muscle 2	495 ± 24	177 ± 31	318 ± 19	18.4 ± 1.1	13.1 ± 0.8	5.3 ± 1.4	99.7 ± 6.0
Mushroom 1	409 ± 27	2 ± 37	407 ± 26	8.2 ± 0.9	6.2 ± 0.6	2.0 ± 1.1	99.9 ± 6.4
Mushroom 2	464 ± 30	67 ± 41	397 ± 28	19.3 ± 0.8	16.7 ± 0.9	2.6 ± 1.2	99.9 ± 7.1
Mushroom 3	438 ± 31	34 ± 40	404 ± 25	24.3 ± 1.1	20.2 ± 0.8	4.1 ± 1.4	99.8 ± 6.2
Mushroom 4	451 ± 29	38 ± 38	413 ± 24	15.9 ± 0.8	14.2 ± 0.5	1.7 ± 0.9	99.9 ± 5.8
Dietary supplement 1	693 ± 51	353 ± 53	340 ± 16	9.2 ± 0.8	6.0 ± 0.9	3.2 ± 1.2	99.8 ± 4.7
Dietary supplement 2	636 ± 43	346 ± 46	290 ± 16	8.7 ± 1.1	5.8 ± 0.8	2.9 ± 1.4	99.8 ± 5.5
Dietary supplement 3	164 ± 7	68 ± 8	96 ± 4	8.3 ± 0.6	6.1 ± 0.6	2.2 ± 0.9	99.5 ± 4.2
Mean combustion efficiency (%)							99.7 ± 5.7

[a]SD is the standard deviation for n = 3 repeated measurements;

[b]Combustion efficicency (%) was calculated using the relation $\frac{m_{TOC\ food\ sample} - m_{TOC\ suspension}}{m_{TOC\ food\ sample}} \times 100$ for 50 mg sample and combustion in 500 mL flask

The recoveries obtained by the (OFC)-SSETV-μCCP-OES method, summarized in Table 2, indicated that under the tested conditions recovery values ranged between 90 ± 13% and 111 ± 11%. For subsequent studies, a sample mass of 50 mg, an absorbing solution volume of 10 mL, and an HNO_3 concentration of 0.1 mol L^{-1} were selected, as these conditions enable the development of attractive methods aligned with green analytical chemistry principles regarding reagent and sample consumption, as well as the amount of waste generated.

Table 2. Recovery degrees (%) obtained by the OFC-SSETV-μCCP-OES method for the CRM sample SQC001 Metals in Soil under different combustion conditions

Certified values (mg kg^{-1})			Hg	Cd	Cu	Pb	Zn	Se
			2,86 ± 0,1C	118 ± 2	330 ± 4	144 ± 2	874 ± 11	154 ± 3
Sample combustion conditions			Recovery degrees ± U_{lab} (%)					
Sample mass (mg)	Absorbing solution volume (mL)	HNO_3 concentration (mol L^{-1})						
50	10	0,05	94 ± 17	90 ± 9	100 ± 13	108 ± 8	100 ± 7	102 ± 9
50	20	0,3	105 ± 12	106 ± 12	111 ± 11	90 ± 13	107 ± 13	94 ± 10
50	30	0,1	108 ± 10	101 ± 14	100 ± 9	109 ± 12	92 ± 12	89 ± 13
100	10	0,3	106 ± 17	95 ± 6	107 ± 10	104 ± 12	96 ± 7	97 ± 12
100	20	0,1	104 ± 17	98 ± 11	102 ± 9	95 ± 6	107 ± 9	95 ± 14
100	30	0,05	90 ± 18	94 ± 15	106 ± 8	106 ± 8	110 ± 8	101 ± 11
150	10	0,1	93 ± 16	90 ± 15	95 ± 7	104 ± 10	109 ± 9	94 ± 13
150	20	0,05	103 ± 10	108 ± 7	107 ± 11	97 ± 11	102 ± 12	103 ± 12
150	30	0,3	92 ± 16	99 ± 15	106 ± 8	103 ± 13	104 ± 9	98 ± 12

Rezults: Oxygen flask combustion assisted digestion optimized for the determination of Cd, Pb, Cu, Zn, Hg, and Se by SSETV-μCCP-OES.