Development of a Novel Tungsten-Based Electrothermal Vaporization Unit with Removable Crucible for the Direct Determination of Heavy Metals in Organic Matrices by ICP-OES and ICP-MS

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Abstract: This paper presents an innovative electrothermal vaporization unit with a heatable W coil (W-ETV) that enables the direct and digestion-free introduction of solid samples with a complex matrix in inductively coupled plasma mass spectrometry (ICP-MS). Thanks to a removable W crucible, the design allows the sample to be weighed directly on a balance and transferred to the vaporization cell without any further aids. The entire design is kept simple and cost-effective and, due to its compact dimensions, opens up the possibility of miniaturization. The performance of this system was demonstrated by determining the toxic heavy metals Cd, Tl and Pb in green tea. Satisfactory recovery rates of between 87% and 116% were achieved using reference samples. Detection limits of (0.101±0.042) µg/kg for Cd, (0.178±0.060) µg/kg for Tl and (1.05±0.47) µg/kg for Pb were obtained, which were sufficiently low to detect potentially harmful metal concentrations in green tea[1, 2, 3].

Experimental setup

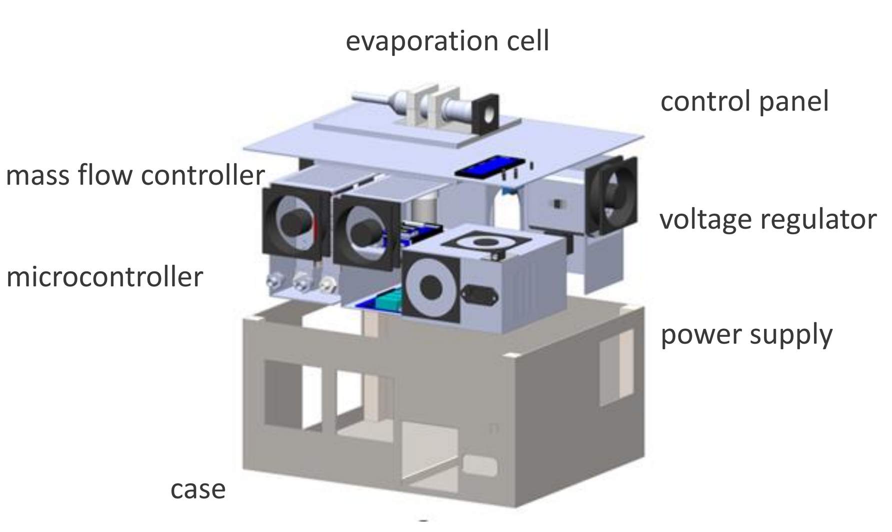

Fig. 1: Compact W-ETV system.

- **Transportable system** consisting of an evaporation cell with coil and **removable crucible**, power supply, control unit and mass flow controllers.
- Standard 700-watt **computer power supply unit.**
- ATmega2560 **microcontroller** consisting of processor, memory and various interfaces for semi-automatic control of the analysis process.
- **Metal Oxide Semiconductor Field-Effect Transistor** (**MOSFET**) for power control.
- **Mass flow controller.**
- Combination of two mechanically operated **valves** to vent the cell from pyrolysis gases.
- Flexible combination with **ICP-MS** or **ICP-OES.**

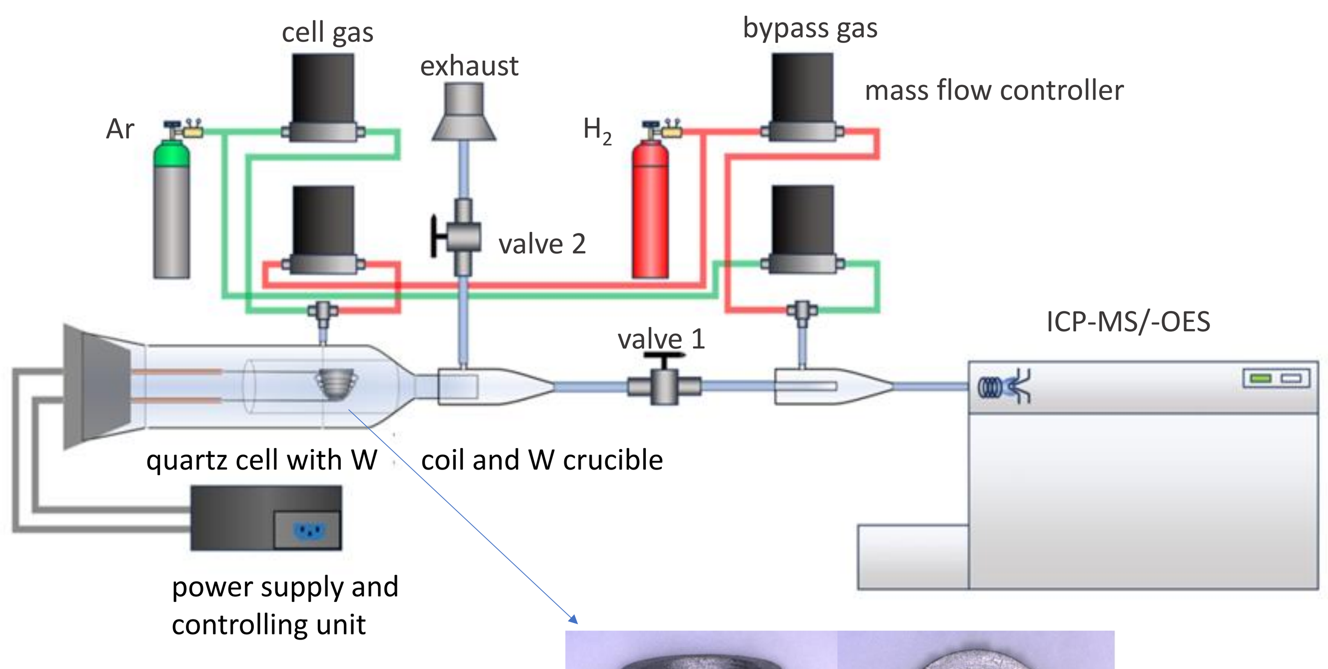

Fig. 2: Schematic overview.

Fig. 3: Images of the W crucibles.

Temperature regulation

- **Resistance heating** through applied voltage.
- Application of the **microcontroller** for **pulse width modulation (PWM).**
  - Fast pulse frequency (980 Hz).
  - Constant period duration, variable pulse length with 8-bit resolution.
  - Duty cycle: percentage "On".
  - System supplies **time-averaged signal** to W-coil.
    → "Quasi-analog" signal.

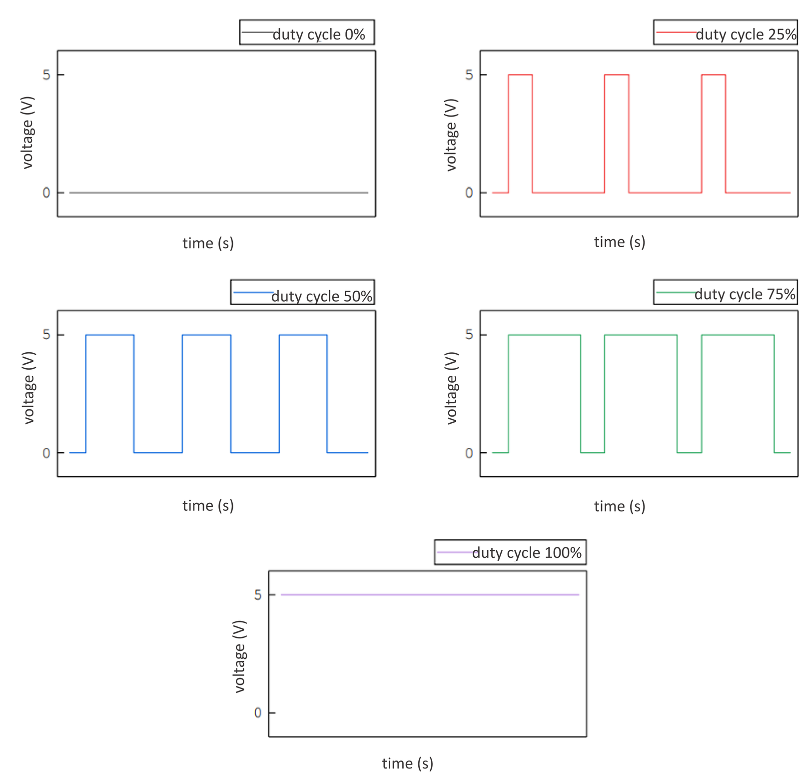

Fig. 4: Resistance heating via pulse width modulation (PWM).

Tungsten coil and removable crucible

- **Tungsten evaporators:**
  - High thermal stability (Mp. 3420°C).
  - High chemical resistance.
  - The addition of hydrogen enables evaporation in a reductive atmosphere to limit the formation of tungsten oxides.
  - High flexibility of the evaporator (coils, filaments, boats and furnaces).
- **Evaporator cell:**
  - Thermally resilient materials with low thermal expansion (quartz).
  - Low turbulence analyte transport with low dead volume.

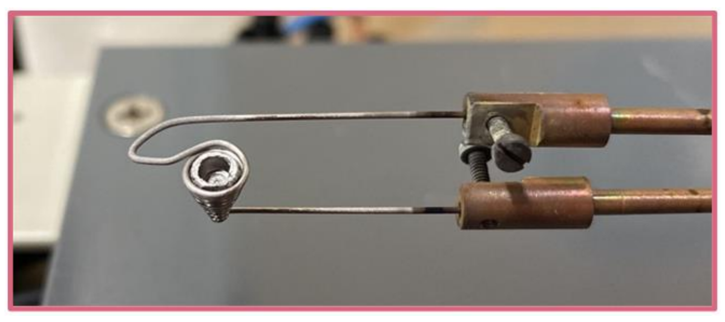

Fig. 5: Basket-shaped W-wire with crucible insert.

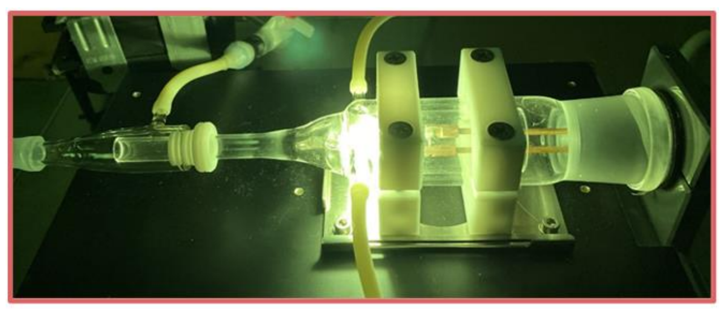

Fig. 6: W-ETV evaporation cell made of silica glass.

Method development and validation

Development of a digestion-free method using a tungsten electrothermal vaporization (W-ETV) unit coupled with ICP-MS for direct determination of toxic heavy metals (Cd, Tl, Pb) in green tea.

- **Sample Preparation**:
  - Green tea samples were ground, homogenized, and sieved (<180 µm).
  - 1.25 mg of the prepared sample was weighed directly into a tungsten crucible.
  - For calibration, 1.5 mg cellulose powder was spiked with 3 µL of calibration solution (2 % HNO_3).
    → **Matrix-Matched Calibration** (MMC) to simulate the carbon matrix.
- **Method Optimization** with respect to maximal Signal-To-Noise Ratio:
  - **Optimum WETV Parameters**:
    - **Total flow rate:** 1.7 L/min; **Argon cell gas flow rate:** 0.7 L/min; **Hydrogen content**: 15 %; **Argon bypass gas flow rate:** 0.8 L/min.
    - **Pyrolysis temperature**: 330 °C; **Vaporization temperature**: approximately 1350 °C.
  - **Optimum ICP-MS Parameters**:
    - **RF power** 1600 W; **sampling depth** 10.0 mm.
- **Validation** and analytical performance:
  - Validated with CRM Green Tea NIST 3254-standard (Cd, Pb) and real sample (Tl).

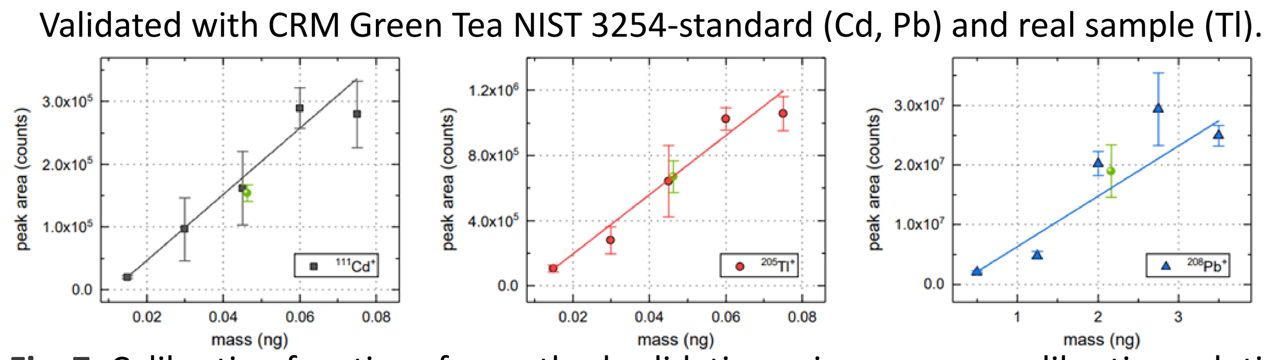

Fig. 7: Calibration functions for method validation using aqueous calibration solutions and a matrix-matched calibration approach. The NIST 3254-standard (Cd, Pb) and real tea sample (Tl) served as samples. The green sphere marks the signal area of the sample at the target value.

Tab. 1: Concentrations found in comparison to certified concentrations as part of the method validation. Data as mean value ± standard deviation. The values marked with an asterisk (*) were obtained from a real sample of green tea

Analyte	w ($\mu g\,kg^{-1}$)	RSD (%)	w (Ref., $\mu g\,kg^{-1}$)	WFR (%)
$^{111}Cd^+$	32.3 ± 2.0	6.1	37	87
$^{205}Tl^+$	26.04 ± 0.81*	3.1*	25.23*	103*
$^{208}Pb^+$	2000 ± 410	20.5	1730	116

- **Analysis of a real green tea sample**:
  - Cd (33.5 ± 1.4 µg/kg), Tl (26.04 ± 0.81 µg/kg), Pb (2760 ± 440 µg/kg).

Detection limits in the lower µg/kg range: The method is suitable for identifying harmful heavy metal concentrations in green tea[2, 3].

Summary

The performance of the W-ETV unit was evaluated by determining toxic heavy metals (Cd, Tl, and Pb) in green tea. The method demonstrated satisfactory recovery rates of 87% to 116% and detection limits were found to be (0.101±0.042) µg/kg for Cd, (0.178±0.060) µg/kg for Tl, and (1.05±0.47) µg/kg for Pb. These values are sufficiently low to assess potentially harmful metal concentrations in green tea, showing a comparable or superior analytical sensitivity relative to existing literature methods for food safety control[2, 3].

Outlook

- So far temperature up to 1500°C accessible.
  - **Integration of a new power supply unit:**
    - Higher efficiency with respect to the evaporation of refractory compounds
- **Use of Hydrogen most likely indispensable.**
  - Hydrogen reduces the spontaneous formation of tungsten oxides (solvents, samples).
- **New design of the evaporation cell.**
  - Simulation studies to improve aerosol transport.
  - Pyrometer for better temperature control.

References

[1] N. H. Bings, Z. Stefánka, *J. Anal. At. Spectrom.* **2003**, 18, 1088-1096
[2] C. Reilly, *Metal Contamination of Food: Its Significance for Food Quality and Human Health*, John Wiley & Sons, Hoboken, 3. Aufl., **2008**.
[3] Europäische Kommisssion, *Verordnung (EU) 2023/915 der Kommission über Höchstgehalte für bestimmte Kontaminanten in Lebensmitteln.*