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Low gas flow inductively coupled plasma optical emission spectrometry for the analysis of food samples after microwave digestion

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ABSTRACT

In this work, the recently introduced low flow inductively coupled plasma optical emission spectrometry (ICP-OES) with a total argon consumption below 0.7 L/min is applied for the first time to the field of food analysis. One goal is the investigation of the performance of this low flow plasma compared to a conventional ICP-OES system when non-aqueous samples with a certain matrix are introduced into the system. For this purpose, arsenic is determined in three different kinds of fish samples. In addition several nutrients (K, Na, Mg, Ca) and trace metals (Co, Cu, Mn, Cd, Pb, Zn, Fe, and Ni) are determined in honey samples (acacia) after microwave digestion. The precision of the measurements is characterized by relative standard deviations (RSD) and compared to the corresponding precision values achieved using the conventional Fassel-type torch of the ICP. To prove the accuracy of the low flow ICP-OES method, the obtained data from honey samples are validated by a conventional ICP-OES. For the measurements concerning arsenic in fish, the low flow ICP-OES values are validated by conventional Fassel-type ICP-OES. Furthermore, a certified reference material was investigated with the low gas flow setup. Limits of detection (LOD), according to the 3σ criterion, were determined to be in the low microgram per liter range for all analytes. Recovery rates in the range of 96–106% were observed for the determined trace metal elements. It was proven that the low gas flow ICP-OES leads to results that are comparable with those obtained with the Fassel-type torch for the analysis of food samples.

1. Introduction

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) has proven to be one of the most powerful tools for trace metal analysis in recent decades.

Unfortunately a total argon consumption of 14–20 L/min is normal when a conventional Fassel-type torch is used. This high argon consumption of the ICP-OES system currently is the main driving force for the development of alternative excitation sources. The major part of the argon consumption is reserved for the cooling of the torch, so alternatives were sought for already more than thirty years ago [1]. The miniaturization of the conventional torch as a means to minimize the argon consumption has been described by different working groups [2–4]. Another approach was to change the cooling technique from internal to external by using cheaper cooling media such as air [5,6] or water [7,8]. These investigations have led to the conclusion, that air was better suited than water as cooling media [9,10]. Dedicated assemblies for optimized gas flow lines were also one part of the investigations to reduce the argon consumption [11,12], as an alternative torch designs, which worked with reduced rf powers and lower argon flow rates [13]. The operation of an ICP-OES system below atmospheric pressure was another attempt to reduce the argon consumption [14,15]. One of the most recent constructive attempts was using a double featured gas inlet for argon and helium ICPs [16]. A new inductively coupled plasma torch was presented in 2005 with the Static High-Sensitivity ICP (SHIP) [17]. The analytical performance of this system with respect to its detection power is in general comparable with the state-of-the-art performance of the conventional setup in aqueous solution [18,19] and the system was successfully applied to the determination of rare earth elements in luminescent nanoparticles after microwave digestion and matched the state of the art of the conventional setup [20]. However, the system is less well characterized with respect to its

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application for samples with decisive matrix contents. The much lower argon consumption of the low-flow system leads to a higher sample and matrix concentration within the plasma. Also, the much lower argon flow rate and the bulb shaped design of the low flow torch lead to a higher residence time of the samples within the plasma compared to a Fassel-type torch, which can lead to devitrification and a rapid deterioration of the torch. Therefore it was our aim to investigate other matrices than aqueous samples with the low flow ICP-OES and to compare the results to those observed with the conventional setup. In order to investigate the robustness of the low-flow torch for the analysis of real-world samples with decisive matrix content we selected food samples. Therefore, arsenic was determined in plaice, haddock und catfish and several elements like potassium, sodium, magnesium, calcium, cobalt, copper, manganese, cadmium, lead, zinc, iron and nickel were determined in honey samples (acacia) after microwave digestion with the low flow ICP-OES.

2. Experimental

2.1. Instrumentation

2.1.1. ICP-OES/Low flow ICP-OES

For multielement determination, a Spectro CIROS^{CCD} ICP-OES (Spectro Analytical Instruments, Kleve, Germany) instrument with axial plasma viewing was used in two different operation modes. The gas flows were controlled by internal mass flow controllers. The free-running generator was operated at 27.12 MHz with a maximum output of 2 kW and the inner diameter of the load coil was 25 mm. In low flow ICP-OES mode, the conventional Fassel type torch was replaced by an externally air-cooled torch and the ICP was operated at significantly lower argon flow rates (<0.7 L/min). The torch design was preliminary characterized in detail [20,21]. For sample introduction of the low flow ICP-OES, a self aspirating PFA nebulizer with a double pass spray chamber (Scott type) was used (Fig. 1). For the Fassel mode (ca. 14 L/min argon consumption), a standard Fassel-type torch (No. 75160526, Spectro Analytical Instruments) was employed and the system's peristaltic pump with a cross flow nebulizer and a double-pass spray chamber (Scott type) was used for sample introduction. The wavelengths for potassium, cobalt, lead, calcium, sodium, iron, copper, magnesium, nickel, cadmium, arsenic, zinc and manganese were selected based on their highest sensitivity. The operating conditions for both ICP-OES measurements are shown in Table 1.

2.1.2. Microwave

Microwave sample digestion was carried out with a CEM Mars 5 (CEM Corporation, Mathews, NC, USA) instrument. Operational parameters for microwave digestion are shown in Table 2.

2.2. Reagents/Standards

2.2.1. Chemicals

Standards of arsenic, cadmium, calcium, cobalt, copper, iron, lead, magnesium, manganese, nickel, potassium sodium and zinc (1.000 mg/L for each element), nitric acid (suprapure grade) cesium chloride (per analysis) and lanthanum chloride (per analysis) were obtained from Merck KGaA (Darmstadt, Germany). Hydrogen peroxide, (per analysis) was purchased from ACROS Organics (Geel, Belgien). All chemicals were used in the highest quality available. Purified water (18.2 M Ω cm, TOC < 4 ppb, Milli-Q Gradient, Millipore GmbH, Schwalbach, Germany) was used for all experiments.

2.2.2. Standard and stock solutions

Volumetric flasks for ICP-OES measurements were pretreated with 2% suprapure HNO_3 and purified water to minimize adsorption effects. Calibration solutions (from 1.000 mg/L single element standard solutions) for ICP-OES and FAAS were prepared by diluting the

Table 1
Instrument parameters (Spectro CIROS^{CCD} ICP-OES, axial plasma viewing).

ICP-OES system	Low-flow ICP-OES	Conv. ICP-OES
Rf power (W)	1100	1400
Total argon flow (L/min)	0.66	14.05
Sample carrier gas (L/min)	0.36	1.05
Auxiliary plasma gas (L/min)	0.3	1.00
Outer plasma gas (L/min)	–	12.0
External air cooling (m/s)	60	–
Torch geometry	SHIP type[a]	Fassel type[b]
Torch injector tube i.d. (mm)	1	2.5
Nebulizer	PFA	CrossFlow
Sample uptake rate (mL/min)	0.27	2.00

[a] 24 mm o.d. SHIP-II torch[20].
[b] 19.5 mm o.d. conventional Fassel type torch.

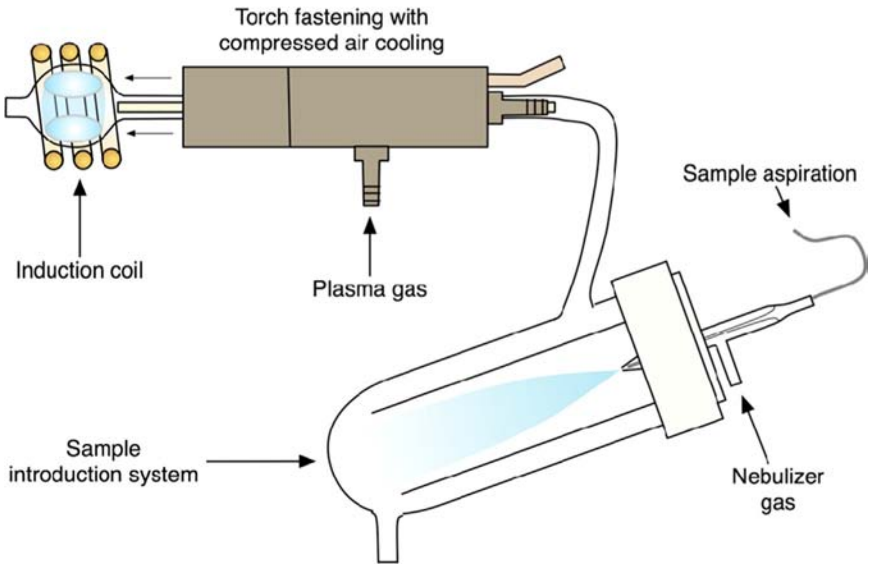

Fig. 1. Schematic sketch for the low flow ICP-OES.

Table 2
Instrument parameters (CEM Mars 5 microwave oven) for digestion of fish[a] and honey[b] samples.

Step	Power (W)[c]	Ramp time (min)	Temperature (°C)	Hold time (min)
1[a]	900	5	120	5
2[a]	900	5	160	5
3[a]	900	5	200	30
1[b]	300	5	50	15
2[b]	300	15	100	30

[c] The applied power is depending on the numbers of used PTFE vessels (1–3 vessels: 300 W, 3–6 vessels: 600 W and 7–9 vessels: 900 W).

specific single element ICP stock solutions with a 2% solution of nitric acid in purified water. The calibration range was, depending on the element and dilution factor, from 0.1 mg/L to 10 mg/L.

2.3. *Sample preparation*

2.3.1. *Preparation of honey samples*

Ca. 1 g of the honey was weighed into a PFTE vessel and mixed with each 2 mL of nitric acid and hydrogen peroxide. The PFTE vessels with the sample solution were left aside open for 10 min in order to evolve the reaction gases. Then, the vessels were closed and heated in the microwave oven in two steps. After cooling down to room temperature, the sample solutions were diluted with purified water to 50 mL for analysis.

2.3.2. *Preparation of fish samples (As)*

100 g of each fish sample were weighed in a cup made of aluminum and lyophilized by means of freeze-drying. Afterwards, approximately 1.5 g of each sample were weighed in PTFE vessels, mixed with 5 mL nitric acid and digested in the microwave oven. The closed vessels were then heated in the microwave oven in three steps. After cooling down to room temperature, the sample solutions were diluted with purified water to 50 mL for analysis.

2.3.3. *Optimization and operating conditions*

The analytes were determined with optimized operating parameters for multielement determination. By monitoring the signal to background ratio (SBR) and the successive calculation of the limit of detection for each element the optimal parameters for both setups were determined.

This was done by adjusting the observing position of the torch by vertical and horizontal variation of the torch box to the optimum position.

3. Results and discussion

3.1. *Figures of merit*

The limits of detection were determined, according to the 3σ-criterion for both setups, the low-flow ICP and the Fassel-type one, after the optimization of the observation position:

$$\mathrm{LOD}=\frac{3\mathrm{RSD}_{BG}I_{BG}c_{STND}}{100(I_{STND}-I_{BG})}$$

Table 3 presents the obtained results. The low-flow ICP provided limits of detection slightly better compared to conventional instrumentation for most of the analyzed elements.

3.2. *Analysis of fish samples (As)*

Table 3
Limits of detection for the conventional ICP-OES and low flow ICP-OES. Values in brackets show the LOD in dry mass (μg/kg).

Element	Wavelength[c] (nm)	Low-flow ICP-OES LOD (μg/L)	Conv. ICP-OES LOD (μg/L)
Arsenic	189.042 (I)	9.4 (0.141)	4.8 (0.072)
	192.262 (I)	18.5 (0.278)	8.2 (0.123)
	193.759 (I)	8.3 (0.125)	17.8 (0.267)
Potassium	766.491 (I)	1.4 (0.021)	3.8 (0.057)
Calcium	317.933 (II)	2.2 (0.033)	3.1 (0.047)
Magnesium	280.270 (II)	0.02 (0.001)	0.03 (0.001)
	285.213 (I)	0.3 (0.005)	0.4 (0.006)
Sodium	589.592 (I)	0.8 (0.012)	1.4 (0.021)
Cadmium	228.802 (I)	0.5 (0.008)	1.8 (0.027)
	214.438 (II)	0.2 (0.003)	0.4 (0.06)
Cobalt	228.616 (II)	1.6 (0.024)	1.7 (0.026)
Copper	324.754 (I)	1.5 (0.023)	0.8 (0.012)
	327.396 (I)	1.2 (0.018)	3.2 (0.048)
Iron	238.204 (II)	1.5 (0.023)	1.3 (0.012)
	259.940 (II)	1.4 (0.021)	1.7 (0.026)
Manganese	257.610 (II)	0.2 (0.003)	0.2 (0.003)
Nickel	232.003 (I)	8.1 (0.122)	9.7 (0.146)
	231.604 (II)	1.7 (0.026)	2.4 (0.036)
Lead	220.353 (II)	11.0 (0.165)	11.2 (0.168)
Zinc	213.856 (II)	1.3 (0.020)	1.3 (0.020)
	202.548 (II)	0.7 (0.011)	0.8 (0.012)
	206.191 (II)	2.0 (0.030)	2.5 (0.038)

[c] (I) Atomic emission lines and (II) ionic emission line.

Table 4
Determination of arsenic in three different kinds of fish samples by conventional ICP-OES and low flow ICP-OES.

Fish sample	Low flow ICP-OES (μg/g)	Conv. ICP-OES (μg/g)
Plaice-01	21.6 (± *0.3*)	21.5 (± *0.3*)
Plaice-02	16.3 (± *0.2*)	16.2 (± *0.1*)
Plaice-03	21.3 (± *0.4*)	19.9 (± *0.4*)
Haddock-01	9.7 (± *0.1*)	9.7 (± *0.1*)
Haddock-02	10.1 (± *0.1*)	9.5 (± *0.4*)
Haddock-03	10.0 (± *0.1*)	9.9 (± *0.1*)
Catfish-01	37.0 (± *0.4*)	37.9 (± *0.4*)

Using three different kinds of fish species (plaice, catfish, and haddock), the samples were analyzed for the total arsenic content by three individual measurements. The RSD and the recovery rates were also determined by these three measurements. Table 4 shows the results and the correlation between the low gas flow ICP-OES and the conventional setup. The results achieved with the ICP-OES and the SHIP-OES system are in very good agreement with recovery rates from 97% to 106%. In most cases, the comparison leads to a recovery rate of exactly 100%.

3.3. *Analysis of honey samples (trace metals)*

The honey samples (acacia) were analyzed for the total content of potassium, calcium, magnesium, sodium, cadmium, cobalt, copper, iron, manganese, nickel, lead and zinc. The RSDs were calculated by three replicate measurements of each element. In Table 5 the results are presented for the low flow ICP-OES and the conventional setup. The presented data for both systems are in very good agreement. The recovery rates range from 96% to 102%.

4. Conclusions

The low flow ICP-OES system was successfully applied for the determination of arsenic in three different kinds of fish samples and one honey sample after microwave digestion. A total argon consumption of only 0.66 L/min was used in contrast to 14 L/min normally used for the conventional ICP-OES system. Quantitative

Table 5
Analysis and comparison of the multielement determination in honey samples (acacia) by low flow ICP-OES and conventional setup.

Element	Low flow ICP-OES (mg/kg)	Conv. ICP-OES LOD (mg/kg)
Potassium	284.0 (± *2.1*)	286.0 (± *1.3*)
Calcium	17.6 (± *0.1*)	17.7 (± *0.2*)
Magnesium	6.4 (± *0.1*)	6.3 (± *0.2*)
Sodium	34.8 (± *0.1*)	34.5 (± *0.1*)
Cadmium	< 0.003	< 0.006
Cobalt	< 0.02	< 0.03
Copper	< 0.02	< 0.01
Iron	1.8 (± *0.1*)	1.8 (± *0.1*)
Manganese	< 0.003	< 0.003
Nickel	< 0.03	< 0.04
Lead	< 0.17	< 0.17
Zinc	1.7 (± *0.3*)	1.7 (± *0.2*)

information about the trace metals in both food samples was obtained with very good accuracy and low detection limits which are for most elements slightly better than the detection limits achievable with the Fassel-type ICP-OES. Furthermore, despite the higher matrix content which was introduced compared to earlier investigations, the torch of the low gas flow setup did not suffer from devitrification and could be used over the complete period of the investigation.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.06.045.

References

[1] J.L. Genna, R.M. Barnes, C.D. Allemand, Anal. Chem. 49 (1977) 1450.
[2] C.D. Allemand, R.M. Barnes, C.C. Wohlers, Anal. Chem. 51 (1979) 2392.
[3] R.N. Savage, G.M. Hieftje, Anal. Chem. 51 (1979) 408.
[4] G.M. Hieftje, Spectrochim. Acta 38B (1983) 1465–1481.
[5] P.A.M. Ripson, L. de Galan, Spectrochim. Acta 37B (1983) 707.
[6] P.A.M. Ripson, L. de Galan, J.W. de Ruiter, Spectrochim. Acta 37B (1982) 733.
[7] G.R. Kornblum, W. van der Waal, L. de Galan, Anal. Chem. 51 (1979) 2378.
[8] M.E. Bristke, J.S. Sukach, L.N. Filimonov, Zh. Prikl. Spectrosc. 25 (1976) 5.
[9] R.S. Houk, T. Hasan, N. Praphairaksit, Spectrochim. Acta 56B (2001) 409–418.
[10] P.W. Boumans, Inductively Coupled Plasma Emission Spectroscopy, John Wiley & Sons, New York, 1987 (Methology, Instrumentation and Performance).
[11] D.R. Demers, C.D. Allemand, Anal. Chem. 52 (1981) 1915.
[12] M.D. Lowe, Appl. Spectrosc. 36 (1981) 126.
[13] R. Rezaaiyaan, G.M. Hieftje, H. Anderson, H. Kaiser, B. Meddings, Appl. Spectrosc. 36 (1982) 627.
[14] C.J. Seliskar, D.K. Warner, Appl. Spectrosc. 39 (1985) 181–183.
[15] C.J. Seliskar, D.C. Miller, T.M. Davidson, Appl. Spectrosc. 39 (1985) 13–19.
[16] A. Okino, H. Yabuta, H. Miyahara, M. Watanabe, E. Hotta, J. Anal. At. Spectrom. 17 (2002) 1090–1095.
[17] A. Klostermeier, C. Engelhard, S. Evers, M. Sperling, W. Buscher, J. Anal. At. Spectrom. 20 (2005) 308–314.
[18] A. Scheffer, C. Engelhard, M. Sperling, W. Buscher, Anal. Bioanal. Chem. 388 (2007) 1605–1613.
[19] C. Engelhard, A. Scheffer, S. Nowak, T. Vielhaber, W. Buscher, Anal. Chim. Acta 583 (2007) 319–325.
[20] C. Engelhard, T. Vielhaber, A. Scheffer, M. Brocksieper, W. Buscher, U. Karst J. Anal. At. Spectrom. 23 (2008) 407–411.
[21] C. Engelhard, A. Scheffer, T. Maue, G.M. Hieftje, W. Buscher, Spectrochim. Acta, Part B 62 (10) (2007) 1161–1168.