Solid Sampling Electrothermal Vaporization Inductively Coupled Plasma Optical Emission Spectrometry for the Analysis of Insects

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ABSTRACT: Alternative protein sources such as insects are of interest because of their many nutritional and ecological benefits compared to traditional animal-based proteins. As they may contain potentially toxic elements in addition to essential elements, their analysis is important to ensure their safety for human consumption. To avoid time-consuming acid digestion, which may lead to contamination or loss of analytes, the direct analysis of insects via solid sampling electrothermal vaporization coupled with inductively coupled plasma optical emission spectrometry (SS-ETV-ICPOES) was explored for the first time. Different approaches for the analysis of black soldier fly meal were evaluated, using CF_4, polytetrafluoroethylene (PTFE) powder pre-mixed with the sample, or PTFE pre-mixed with the sample and H_2 in the carrier gas as chemical modifier. Addition of N_2 as a sheathing gas around the ETV effluent to increase plasma robustness was also studied. The best results were obtained with the Ar-N_2 mixed-gas plasma, PTFE powder pre-mixed with samples, and H_2 in the carrier gas, allowing the accurate determination of Cd, Co, Fe, K, P, S, and Zn in black fly soldier meal in 100 s by external calibration with a dogfish muscle certified reference material (CRM) and internal standardization with Ar 404.442 nm to compensate for sample loading effects on the plasma. Application of this method to other insects resulted in accurate results for Co, Fe, and S in cricket flour as well as Co, Fe, P, S, and Zn in mealworm powder. Thus, SS-ETV-ICPOES shows promise as a screening method for insect analysis.

INTRODUCTION

Electrothermal vaporization (ETV) allows for the direct analysis of solid, liquid, and slurry samples by inductively coupled plasma (ICP) spectrometry.[1] However, ICP optical emission spectrometry (OES), which involves the passive measurement of emitted light, is inherently more robust than ICP mass spectrometry (MS), which requires physical extraction of ions from the ICP and is thus subject to solid deposition problems on the ion sampling interface during solid sampling ETV analysis. The direct analysis of solid samples is thus more straightforward using ETV-ICPOES. Other advantages of using ETV include the elimination of solvent (causing a reduction of oxide formation in the plasma), improved transport efficiency of 60-100%, and increased sensitivity compared to conventional nebulization from both the higher transport efficiency and the elimination of the dilution that is inherent to solid dissolution.[1]

A commercially available ETV system consists of a graphite furnace, into which a small graphite boat loaded with sample (1-5 mg of solids or 5-100 µL of liquids) is inserted.[1,2] The furnace is then heated in steps using a programmable temperature program that can range up to 3000°C. It may include a drying step to remove the solvent in addition to a pyrolysis step that ashes most of the matrix, and a vaporization step that removes any remaining matrices and volatilizes the analytes.[1] A cleaning step is also used to remove any residues.[1] The vapors are transported into the ICP by a continuous stream of Ar carrier gas through a transfer tube connecting the ETV system to the base of the torch.[1,2]

Chemical modifiers in gaseous, liquid, or solid form are often

used to increase analyte volatility and selectively remove matrix components during the pyrolysis step.[1,3] For example, nitric acid can be added to seawater to help remove Cl as volatile HCl during pyrolysis, thereby eliminating the $ArCl^+$ interference on As^+ in ICPMS.[1] Most commonly, high-purity gases, such as H_2, $CHClF_2$, $CHCl_3$, and CHF_3,[3-10] added to the carrier gas at a consistent rate, allow for good reproducibility.[5,6] This not only prevents the analyte from forming refractory carbides (with higher boiling points than the highest possible ETV temperature) but also promotes the vaporization and transport of the analytes through the formation of volatile species (halides, hydrides, etc.).[1,6,11,12] Notably, CCl_2F_2 (Freon R12) was widely used because of its ability to form volatile chlorides and fluorides; however, it is now banned in several countries because of its harmful environmental effects.[5,13,14] When gaseous modifiers are not available, an alternative fluorinating agent is polytetrafluoroethylene (PTFE) powder, which however requires more sample preparation, as it must be mixed with the sample.[9,15,16] Table S1 gives examples of ETV-ICPOES applications to the direct analysis of environmental samples, where a chemical modifier was used in most cases.

Solid sampling ETV-ICPOES (SS-ETV-ICPOES) avoids the digestion step and thus the use of acids, which simplifies sample preparation, and reduces potential contamination.[1] Furthermore, the pyrolysis step drastically reduces matrix effects and spectroscopic interferences as most of the matrix components are removed then.[1]

On the other hand, relative standard deviations (RSDs) of 10-30% (versus less than 3% for conventional nebulization) typically result from the inherent heterogeneity of real-life samples and low masses required.[5,9,17,18] Grinding the sample into a fine powder, increasing the number of replicates, or analyzing liquids may improve RSDs, but while concurrently decreasing the sample throughput. Memory effects may also result from incomplete analyte vaporization or aerosol deposition in the transfer tube.[1,5] Furthermore, the absence of water, or its removal during the desolvation step, decreases the excitation capability of the ICP.[19] To compensate for this, a mixed-gas plasma may be used. For instance, both N_2 and H_2 have a higher thermal conductivity and heat capacity than Ar and may thus increase the energy to the central channel when introduced through a sheathing device around the aerosol flow.[10]

This work will focus on a new application of ETV-ICPOES: direct analysis of insects. Considering that the world's population is expected to reach 9.7 billion by 2050, and a shortage of the current protein availability is anticipated,[20,21] alternative protein sources, such as insects, are growing in popularity. However, as the emergence of such products is still relatively new, information on their total elemental concentrations is required to assess if they are safe for human consumption. The aim of this work was to explore the possibility of using SS-ETV-ICPOES for the fast screening of insects. This included the implementation of different mixed-gas plasmas for increased plasma robustness. The goal was to develop an accurate method to directly analyze black soldier fly meal and then apply it to cricket flour and mealworm powder. As these three alternative proteins are certified reference materials (CRMs) produced by the National Research Council of Canada (NRC), the accuracy of the method could be verified through comparison of the measured concentrations to the certified ones. To the authors' knowledge, this is the first time that such a method was developed for the direct analysis of insects.

Fig. 1 ETV-ICPOES setup used for the addition of high purity N_2 as sheathing gas and H_2 in the carrier gas.

EXPERIMENTAL

Instrumentation. An ETV system (ETV 4000C, Spectral Systems, Fürstenfeldbruck, Germany) coupled to a lateral view ARCOS ICPOES instrument (SPECTRO Analytical Instruments, Kleve, Germany) was used. A pyrolytically coated graphite boat (Meinhard, Holden, CO, USA) held the sample and was manually placed into the ETV furnace using a pair of tweezers. A 1-m long, 5-mm internal diameter PTFE tube connected the base of the torch to the ETV outlet. This tubing length was required because of space constraints limiting where the ETV system could be located with respect to the ICPOES instrument. When a mixed-gas plasma was used, this PTFE tube connected the base of the sheathing device (connected to the ICP torch) to the ETV outlet (Fig. 1).

For mixed-gas plasmas, a mass flow controller (MCR-Series, Alicat Scientific, Tuscon, AZ, USA) was employed to regulate the flow of high purity N_2 gas into the plasma central channel through a sheathing device to increase plasma robustness. The addition of H_2 gas to the Ar carrier gas using a brass tee valve was also investigated to improve the volatility of the analytes and increase analyte uptake. Table 1 summarizes the operating conditions

Table 1. Instrumental operating conditions for ETV-ICPOES

Parameter	Ar ICP	Ar-N_2 ICP	Ar-N_2-H_2 ICP
Plasma power (kW)	1.400	1.400	1.400
Ar plasma gas flow rate (L min^{-1})	13.00	13.00	13.00
Ar auxiliary gas flow rate (L min^{-1})	2.00	2.00	2.00
N_2 sheath gas flow rate (mL min^{-1})	----------	45.00	45.00
Observation height (mm)	10	10	10
Signal scan mode	Transient	Transient	Transient
Sampling rate (Hz)	10.0	10.0	10.0
Integration time (ms)	10	10	10
Ar carrier gas flow rate (mL min^{-1})	300	300	300
H_2 gas flow rate (mL min^{-1})	---------	---------	30.00
Ar bypass gas flow rate (mL min^{-1})	400	400	400
Chemical modifier	5.00 mL min^{-1} CF_4	2 mg PTFE	2 mg PTFE
Elements and analytical lines (nm)	Ar (404.442), Cd II (226.502), Co II (238.892), Fe I (373.486), K I (766.491), Mg II (279.079), P I (178.287), S I (180.731), and Zn I (334.502)		
ETV temperature program	**Temperature (ºC)**		**Time (s)**
Step 1 (startup)	21		10
Step 2 (pyrolysis)	300		30
Step 3 (cool down)	No heating		10
Step 4 (vaporization)	2200		30
Step 5 (cool down)	No heating		20

with the different plasmas, along with the ETV temperature program that was used irrespectively of the plasma composition. The transient signals were obtained using the Smart Analyzer Vision software and the raw data were then exported to Excel for processing. Emission lines presenting maximum intensity with minimal spectroscopic interferences were monitored.

Reagents. Tetrafluoromethane (CF_4, MEGS Gases, Ottawa, ON, Canada) added to the carrier gas promoted analyte volatility for experiment with a conventional Ar plasma. Alternatively, PTFE powder (Sigma-Aldrich, Saint Louis, MO, USA) was used to promote the vaporization of analytes.[11] High purity Ar (99.996% purity, liquid in Dewar, MEGS Specialty Gases, Ottawa, ON, Canada) was used for the plasma, bypass, auxiliary, and carrier gases. Three solid, ground alternative proteins CRMs from NRC (National Research Council Canada, Ottawa, ON, Canada) were used as the samples: black soldier fly meal, BFLY-1, cricket flour, KRIK-1, and mealworm powder, VORM-1. For external calibration, NIST 1568b rice flour (National Institute of Standards and Technology, Gaithersburg, MD, USA) and DORM-5 fish protein from NRC were tested.

SS-ETV-ICPOES analysis procedure. With CF_4 as chemical modifier, an empty graphite boat served as blank and was analyzed ten times using the ETV temperature program in Table 1, prior to carrying out an external calibration using 1.0-5.0 mg of CRM increasing in 1 mg increments. Five 3.0 mg replicates of the samples were weighed directly in the graphite boats and inserted into the ETV furnace using tweezers.

With PTFE as chemical modifier, 2.0 mg of PTFE powder were added to the blanks, CRM, and samples as was done previously with soil and clay.[22] External calibration curves were obtained using pre-mixed ratios of 1:2, 2:2, 3:2, 4:2, and 5:2 DORM (fish protein) to PTFE powder (from 3.0 mg to 7.0 mg, increasing in 1.0 mg increments). A ratio of 3:2 solid sample to PTFE powder was pre-mixed for each sample. Five 5.0 mg replicates of each sample-PTFE mixture were weighed directly into graphite boats and inserted into the ETV furnace using a pair of tweezers. A grounding strap worn around the wrist may help to minimize static electricity while manipulating and mixing PTFE.

Data processing. The raw temporal profiles of signal (counts s^{-1} (cps)) versus time (s) generated by ETV-ICPOES were exported to Microsoft Excel for manual data processing. Point-by-point internal standardization with Ar 404.442 nm was used to compensate for sample loading effects on the ICP (Fig. 2), where the analyte/Ar signal ratio was computed for each point of the raw temporal profile from each blank, CRM, and sample to obtain the internally standardized temporal profile of signal (arbitrary units (a.u.)) versus time (s).[15,16] For each blank, CRM, and sample, the peak area of each analyte was then integrated during the vaporization step (50-80 s), except for S, which was integrated over both the pyrolysis and vaporization steps because vaporization also occurred during the pyrolysis step (Fig. 2). Blank subtraction was systematically performed, where the average integrated analyte peak area of the blank was subtracted from the analyte peak area of each CRM and sample.

The equation of the line of best fit from linear regression analysis of the peak area versus analyte mass (equal to the real mass of CRM multiplied by the certified mass fraction) external calibration curve allowed conversion of the peak area from samples into analyte mass, which was then divided by the real mass of sample to obtain analyte concentration in the sample. A Grubbs test was performed to identify any outlier in the experimentally obtained data, which was then removed from the replicates. A Student's *t-test* was performed at the 95% confidence level between the experimentally determined concentrations and the certified values to assess the accuracy of the results. The limit of detection (LOD) was calculated as three times the standard deviation corresponding to the average peak area from ten blanks divided by the slope of the calibration curve.

RESULTS AND DISCUSSION

Rationale for SS-ETV-ICPOES procedure. Fluoride formation

Fig. 2 SS-ETV-ICPOES temporal profile of P (178.287 nm) and S (180.731 nm) in BFLY-1 showing S vaporization during the pyrolysis and vaporization steps (10-40 s and 50-80 s, respectively). Suppression of Ar 404.442 nm emission line during pyrolysis and especially during vaporization is also shown.

Fig. 3 Average percent recovery for analytes in BFLY-1 by SS-ETV-ICPOES with CF_4 chemical modifier (± standard deviation, n=4 or 5) using NIST 1568b (rice flour, red bars) and DORM-5 (fish protein, blue bars) for external calibration compared to the certified values (yellow bars ± uncertainty).

using a F-containing chemical modifier allowed all analytes monitored in this work, except S (Fig. 2), to be exclusively vaporized during the vaporization step (Fig. S1). The analysis of solid samples with SS-ETV-ICPOES has a visible effect on the plasma, which is reflected in the intensity of Ar emission lines (Fig. 2). This effect being proportional to sample mass[22] enables the use of an Ar emission line as internal standard to compensate for sample loading effects on the plasma. Without internal standardization, 1-2 mg of solid sample at the most can be used to minimize the loading effect, which limits sensitivity and detection limit. Moreover, point-by-point internal standardization with an Ar emission line significantly increases the linearity of the calibration curve using up to 5 mg of solid sample with the ETV effluent being continuously directed into the ICP[17] or up to 13 mg solid if only the effluent during the vaporization step enters the ICP.[13] The insertion of a cooling step between the pyrolysis and vaporization steps significantly increased the vaporization peak for numerous analytes (Al, Ca, Fe, Hg, K, Mg, Mo, Na, P, Pb and Zn) without affecting that for As, Cu, Co, S and Se during the analysis of rice by ETV-ICPOES.[17] Such a beneficial effect was also observed during the analysis of soil and clay samples.[22] Given that point-by-point internal standardization with an Ar emission line and a cooling step between the pyrolysis and vaporization steps of the ETV temperature program were applied to the accurate analysis of a variety of environmental samples (Table S1), both approaches were adopted for this work.

Although ICPOES allows the simultaneous determination of numerous elements, eight elements were chosen for this study because they constitute a wide range of minor, major, potentially toxic, and essential elements. Cd is a potentially toxic element and can cause health risks at large and/or chronic doses.[23] K and Mg are major elements, with K being known for its role in kidney and heart regulations, muscle contraction, and nerve transmission,[24] whereas Mg helps maintain nerve and muscle contractions, blood pressure regulation, and bone development.[25] Co supports red cell production and the nervous system.[26] Fe plays a role in human growth and development, circulating oxygen throughout the body.[27] Zn is responsible for cellular metabolism, immune health, human growth and development.[28] S plays an essential role in human growth and development.[29] P plays a key role in gene transcription, enzyme activation, pH regulation, and energy storage.[30]

Analysis of black soldier fly meal with an Ar plasma and CF_4 chemical modifier. Fig. 3 summarizes the results for the analysis of BFLY-1 using two CRMs for external calibration (see Fig. S2 for examples of calibration curves for K, which were consistent among the other analytes, and Table S2 for concentrations). Based on a Student's *t-test* at the 95% confidence level, the measured concentrations for 3/8 elements (Co, Fe, and K) and 5/8 elements (Cd, Co, K, S, and Zn) agreed with the certified values when using NIST 1568b and DORM-5 for external calibration, respectively. Clearly, the fish protein CRM is a better match for the accurate analysis of this insect. The relative standard deviation (RSD) ranged from 1.5 to 38%, despite 3-mg aliquots being used instead of the 250 mg representative size specified

Table 2. Relative standard deviation (RSD) achieved using CF_4 or PTFE as chemical modifier during the replicate analysis of BFLY-1 by ETV-ICPOES using an Ar plasma and DORM-5 for external calibration (n=4 or 5)

Analyte	Certified concentration (mg kg^{-1})	RSD with CF_4	RSD with PTFE
Cd	0.521 ± 0.022	19	20
Co	0.135 ± 0.014	17	16
Fe	419 ± 18	1.5	5.7
K	15900 ± 400	3.0	5.0
Mg	4130 ± 140	4.5	1.4
P	9300 ± 200	2.6	6.2
S	4050 ± 360	8.6	2.5
Zn	134.5 ± 4.2	9.1	4.6

Fig. 4 Average percent recovery for analytes in KRIK-1 and VORM-1 by SS-ETV-ICPOES with CF_4 chemical modifier (± standard deviation, n=4 or 5) using DORM-5 for external calibration compared to the certified values (± uncertainty).

Fig. 5 Average percent recovery for analytes in BFLY-1 by SS-ETV-ICPOES (± standard deviation, n= 5) with pre-mixing of PTFE (red bars) or mixing PTFE with sample in the graphite boat (blue bars) using DORM-5 for external calibration compared to the certified values (yellow bars ± uncertainty).

Fig. 6 LOD (n=10) by ETV-ICPOES using DORM-5 for external calibration, with CF_4 (red bars) or pre-mixed PTFE (yellow bars) chemical modifier, or PTFE and N_2 sheathing gas (green bars), or PTFE and N_2 sheathing gas and H_2 additional chemical modifier (blue bars).

on the BFLY-1 certificate. The possibility of obtaining accurate results using as little as 1 mg, *i.e.*, much smaller amount than specified on the certificate, was reported previously for environmental CRMs.[31] The precision of replicate analyses (Table 2) clearly depends on analyte concentration, being poorest for Cd and Co, *i.e.*, the lowest concentration analytes.

As the proposed method accurately determined most of the studied elements in BFLY-1, it was applied to two other insect-based CRMs, KRIK-1 and VORM-1 (Table S3). The results were accurate for 5/8 elements (Cd, Co, Fe, K, and S) in KRIK-1 and 2/8 elements (Fe and Zn) in VORM-1 upon external calibration with DORM-5 (Fig. 4). The fact that, with the same method, most of the measured elements in VORM-1 did not agree with the certified values may be a result of VORM-1 being coarser than BFLY-1 and KRIK-1 (which were both similar in particle size). This may cause inconsistencies with analyte vaporization in the ETV furnace. To alleviate this, alternative chemical modifiers were tested.

Analysis of black soldier fly meal with PTFE chemical modifier. Based on previous work, 2.0 mg of PTFE powder and 3.0 mg of sample were used for analysis.[23] However, because the previous study did not specify if the PTFE powder and sample were mixed directly in the graphite boat or pre-mixed in lots prior to analysis, both methods were tested using BFLY-1 (Fig. 5). According to a Student's *t test* at the 95% confidence level, pre-mixing PTFE with the sample prior to putting an aliquot in the graphite boat provided concentrations in agreement with the certified values for 6/8 elements (Cd, Co, K, P, S, and Zn) (Table S4) whereas only Co, K and Zn had results in agreement when mixing in the graphite boat. Clearly, pre-mixing provided the best results in addition to being most convenient and less time-consuming. Indeed, a lot could be prepared prior to analysis, reducing the risk of contamination, loss of sample, and heterogeneity that was observed when mixing the PTFE powder and sample directly in the boat. This heterogeneity translated into a generally larger RSD than with pre-mixing. Given that an additional element, P, could be accurately determined using PTFE instead of CF_4 without a significant effect on the limit of detection (LOD) (Fig. 6) and that a similar precision was obtained for replicate analysis as when using CF_4 (Table 2), pre-mixing PTFE was adopted for the remainder of the work.

Analysis of black solder fly meal with a mixed-gas plasma and PTFE chemical modifier. N_2 as a sheathing gas was first tested because it was reported to increase plasma robustness more than H_2 and water vapour while not increasing the background as much as sensitivity.[10] In a separate experiment, H_2 in the carrier gas was tested, in addition to N_2 as a sheathing gas around the ETV effluent, to assess if it could act as a second chemical modifier to improve the vaporization of analytes. With both mixed-gas plasmas, external calibration was done using

DORM-5 (in addition to internal standardization with Ar 404.442 nm emission line). The results for BFLY-1 are summarized in Fig. 7. With N_2 sheathing (Table S5), the results for Cd, Co, Fe, K, S, and Zn (6/8 elements) agreed with the certified values based on Student's *t-test* (95% confidence). Also adding H_2 to the carrier gas (with N_2 sheathing gas) provided accurate results for Cd, Co, Fe, K, P, S, and Zn (*i.e.* 7/8 elements) (Table S6).

Based on the promising results obtained for BFLY-1, the method was applied to KRIK-1 and VORM-1 (Fig. 8). Accurate results were obtained for 3/8 elements (Co, Fe, and S) in KRIK-1 and 5/8 elements (Co, Fe, P, S, and Zn) in VORM-1 (Table S7). The fact that better results were obtained for VORM-1 than KRIK-1 under these different conditions, whereas 5 elements could be accurately determined in KRIK-1 and only 2 in VORM-1 with an Ar plasma using CF_4 as chemical modifier without H_2 added to the carrier gas flow, indicates that further optimization of the conditions may enable accurate analysis of a variety of insects using a single method. Indeed, the LODs were improved for Cd, Co, Fe and Zn but degraded for K, Mg, P and S under these conditions.

CONCLUSION

The aim of this preliminary study was to help fill the current lack of information in the literature on the elemental composition of protein alternatives by developing a quick and reliable method for the simultaneous multi-elemental analysis of black solder fly meal. The results demonstrate that SS-ETV-ICPOES is promising as a screening tool. Using an Ar plasma and gaseous CF_4 as chemical modifier, with internal standardization using an Ar emission line and external calibration using a dogfish muscle CRM, allowed the accurate determination of Cd, Co, K, S, and Zn, *i.e.*, 5 out of 8 elements monitored in black soldier fly meal. Replacing CF_4 by pre-mixing of solid PTFE powder with samples prior to placing aliquots of the mixtures into graphite boats enabled the accurate determination of an additional element, *i.e.*, Cd, Co, K, P, S, and Zn, without LOD degradation. Finally, using an Ar-N_2 mixed-gas plasma and H_2 in the carrier gas as an additional chemical modifier (in addition to pre-mixing PTFE) further increased the number of elements that could be accurately determined to 7, *i.e.* Cd, Co, Fe, K, P, S, and Zn.

As fewer elements could be accurately determined in cricket powder and mealworm powder than in black soldier fly meal, future work will include a detailed multivariate optimization of ETV and ICPOES operating conditions with the aim of obtaining one method suitable for the accurate analysis of a variety of insects. This will include studying the effect of using an insect CRM for external calibration, i.e. truly matrix-matched external calibration.

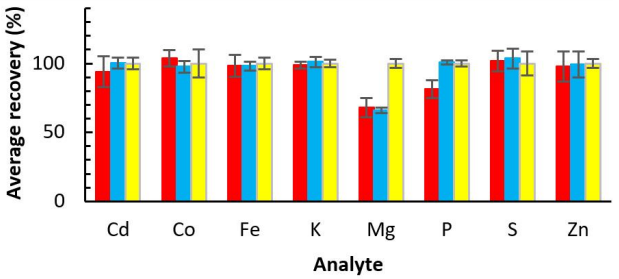

Fig. 7 Average percent recovery for analytes in BFLY-1 by ETV-ICPOES (± standard deviation, n=4 or 5) with pre-mixing of PTFE using DORM-5 for external calibration with N_2 sheathing gas (red bars) or N_2 sheathing gas and H_2 additional chemical modifier (blue bars) compared to the certified values (yellow bars ± uncertainty).

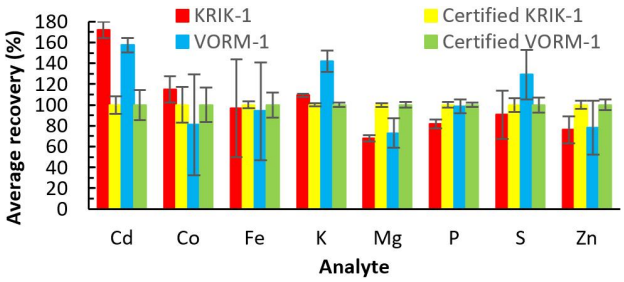

Fig. 8 Average percent recovery for analytes in KRIK-1 and VORM-1 by SS-ETV-ICPOES with pre-mixing of PTFE in combination with a mixed-gas plasma (± standard deviation, n=4 or 5) using DORM-5 for external calibration compared to the certified values (± uncertainty).

ASSOCIATED CONTENT

Supporting information (Figs S1-S2 and Tables S1-S7) is available at www.at-spectrosc.com/as/home

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Notes

The authors declare no competing financial interest.

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