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Direct element analysis of honeys by atmospheric pressure glow discharge generated in contact with flowing liquid cathode

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Abstract

Miniaturized atmospheric pressure glow discharge sustained in a compact discharge cell in contact with a flowing liquid cathode was used for element analysis of honeys by optical emission spectrometry. A simplified sample preparation procedure was proposed and samples of honeys were only dissolved in water and acidified with HCl to a concentration of 0.10 mol L⁻¹. Resulting 1.0% *m/V* in case of K and Na and 5.0% *m/V* in case of Ca, Cu, Fe, Li, Mg, Mn, Rb and Zn solutions of honeys were directly introduced into the discharge cell acting as the liquid cathode of the discharge. To eliminate matrix effects coming from fructose and glucose, a non-ionic surfactant (Triton X-405) was added to solutions and this resulted in improving signals of studied elements. For calibration, simple (for K and Na) and matrix-matching (for other elements) standard solutions were used. The method was proved to give reliable results and applied in analysis of 16 commercial white- to amber-colored honeys with limits of detection at level of 1.0 (Ca), 0.7 (Cu), 2.5 (Fe), 0.5 (K), 0.02 (Li), 0.2 (Mg), 1.8 (Mn), 0.04 (Na), 0.1 (Rb) and 0.2 (Zn) µg g⁻¹.

1. Introduction

Miniaturized low power direct (dc) or alternating current (ac) atmospheric pressure glow discharge (APGD) generated in contact with a flowing liquid cathode (FLC) has rapidly gained in popularity and significance, as evidenced by original works published in recent 2 years.¹⁻¹⁴ Important developments reported for this promising and original excitation source used in analytical optical emission spectrometry (OES) relied on replacing a solid metallic anode with a miniature flow Ar or He^{1,2} jets or more commonly by changing the chemical composition of FLC solutions³⁻¹⁰. In the latter case, it has been established that adding low molecular weight carboxylic acids, i.e., formic⁶⁻⁸ or acetic¹⁰ acids, to FLC solutions, it results in substantial enhancements of signals of some elements, e.g., 5-^{7,8} or 78-fold⁶ for Pb, 5-¹⁰ or 10-fold⁸ for Hg, 8-⁸ or 13-fold⁶ for Ag and 17-fold for Cd⁶. Responses of other elements, namely Ca, Co, Cu, Fe, Mg, Mn and Ni, were established to increase as well but enhancements observed for them were at level of 2.^{7,8} A similar effect was also achieved by adding non-ionic (Triton X-405, Triton X-114)^{4,5,9} or ionic (cetyltrimethylammonium chloride, CTAC)³ surfactants. The presence of these substances in FLC solutions was responsible for enhancements of signals of various elements in a magnitude similar to this reported in case of formic and acetic acids, i.e., 7-³ or 10-fold^{5,9} for Pb, 6-fold for Cu,^{5,9} 5-fold for Hg and Mn,^{3,5,9} and 2-4-fold for other elements (Ca, Cd, Co, Cr, Cs, Fe, Li, Mg, Ni, Rb, Sr, Zn)^{3,5,9}.

Aforementioned suitable signal enhancements were presumed to be a consequence of an increase in boiling point and a decrease in surface tension of FLC solutions.³⁻¹⁰ Alterations of physicochemical properties of these aqueous solutions possibly led to changes in rates of sputtering of analytes and vaporization of water.^{7,10} According to visual observations made by Schwartz et al.,¹² mentioned changes could promote formation of small solution droplets that were easily pulled from the surface of the FLC and increase an electrospray-like transport of analytes into the discharge. Indeed, as indicated by a spectroscopic diagnostic of dc-APGD generated in contact with FLC solutions containing non-ionic surfactants,⁹ the addition of these substances resulted in an expedient increase in the sputtering rate of elements and a decrease in the vaporization rate of water. In these conditions, APGD was stably operated in a less water vapor saturated atmosphere and hence, the electron number density in the near-cathode region of the discharge was higher. However, it appears that the mechanism of action of carboxylic acids and surfactants is not entirely the same. Apart from increases in signals of elements, surfactants present in FLC solutions led to a reduction of the background level in

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3 the vicinity of analytical lines of elements and its fluctuation.^{3-5,9} What is more, the
4 morphology of the background spectrum was simplified due to a substantial reduction of
5 intensities of emission bands of OH, NO and N₂ molecules.^{3-5,9} In a consequence, limits of
6 detections (LODs) of elements were much improved because of lower background
7 fluctuations and higher signals of their analytical lines. Unfortunately, in case of formic and
8 acetic acids added to solutions of the FLC, the morphology of background emission spectra
9 acquired in presence or absence of these acids in FLC solutions was practically the same and
10 thus, improvements of LODs of elements corresponded only to those noted for signals of
11 these elements.^{6-8,10}

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13 To the best of our knowledge, APGD generated in contact with the FLC, as an
14 alternative excitation source in OES, was applied so far in element analysis of different
15 environmental samples, tissues and food including tuna fish,¹⁰ aquatic plant,¹⁰ human hair,³
16 tea,¹⁴ stream sediments,³ coal fly ashes,⁴ soils,⁵ and spruce needles⁵, that were wet digested or
17 extracted. Direct element analysis with this method concerned only ground,⁴ tap,⁶ natural,⁶
18 mineral,¹⁴ and pond⁵ waters.

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20 The information about the element composition in honey is an important issue
21 considering quality, safety and nutritional value of this functional food product and nutrient.
22 Measurements of total concentrations of some selected major (Ca, K, Mg, Na) and minor (Cu,
23 Fe, Mn, Zn) elements help in assessing its geographical and/or botanical origins and
24 wholesomeness.^{15,16} Due to a high content of carbohydrates, direct element analysis of honey
25 encounters many problems related to heterogeneity of samples and matrix effects.^{17,18}
26 Possible chemical and physical interferences accompanying spectrochemical analysis of
27 honey are commonly eliminated by mineralizing samples using dry and wet ashing
28 procedures. Simplified analysis of honey, in which samples are only dissolved in water or
29 acidic solutions prior to measurements, is uncommon. Such analysis can certainly decrease
30 the time of the sample preparation and the risk related to losses of elements at high
31 temperature and/or contamination of analyzed samples. Considering the effect of non-ionic
32 and ionic surfactants in APGD generated in contact with the FLC on increasing recorded
33 signals of elements as well as reducing the background level and improving its stability,^{3-5,9} it
34 could be expected that these substances would particularly be desirable in element analysis of
35 undigested samples of honey, containing a rich in carbohydrates mainly organic matrix. Here,
36 due to a unique ability to extinguish molecular emission spectra and quench intensities of OH,
37 N₂, NO bands, the use of surfactants could simplify emission spectra of solutions of analyzed
38 samples.

To verify this research hypothesis, a suitability of dc-APGD sustained in a modified compact discharge cell in contact with a small-sized FLC for direct element analysis of honey was examined. To the best of our knowledge, no works on element analysis of honeys using OES with excitation in dc-APGD generated in contact with the FLC have been reported to date. Initially, the effect of a honey-like matrix on intensities of atomic emission lines of studied elements (Ca, Cu, Fe, K, Li, Mg, Mn, Na, Rb and Zn) was studied and established to be destructive on the performance of the system. As a remedy, a non-ionic surfactant (Triton X-405) was used as a modifier of the FLC, resulting in boosting intensities of analytical lines of studied elements and simplifying the morphology of emission spectra of dc-APGD fed with solutions of honey. The analytical performance of the developed dc-APGD-OES method, with the modified FLC by adding Triton X-405, was assessed. The method was used for analysis of 16 commercial weight- to amber-colored honeys on the content of Ca, Cu, Fe, K, Li, Mg, Mn, Na, Rb and Zn. Reliability of results was verified by using a recovery study as well as a reference method, i.e., flame atomic emission spectrometry (FAES) in case of K and Na, and another calibration strategy, i.e., standard solutions' additions in case of Ca, Mg, Mn, Rb and Zn.

2. Experimental

2.1. Reagents, solutions and samples

Doubly distilled water was used throughout. TraceCERT grade single-element 1000 mg L⁻¹ standard solutions of Ca, Cu, Fe, K, Li, Mg, Mn, Na, Rb and Zn were supplied by Sigma-Aldrich Chemie GmbH (Germany). A 70% *m/V* water solution of polyethylene glycol tert-octylphenyl ether (Triton X-405, C₁₄H₂₂O(C₂H₄O)₄₀) non-ionic surfactant was also provided by Sigma-Aldrich. J.T. Baker ACS grade reagents, meeting ACS reagent chemical requirements for trace element analysis, were used, i.e., solutions of 30% *m/m* H₂O₂, 37% *m/m* HCl and 65% *m/m* HNO₃. Analytical grade D-fructose (>98%) and D-glucose (>98%) were provided by Avantar Performance Materials (Poland).

Studying the effect of the honey-like matrix on the response of minor and trace elements of honey, i.e., Ca, Cu, Fe, Li, Mg, Mn, Rb and Zn, 5.0% *m/V* (g per 100 mL) solutions of this matrix were prepared, assuming that an average concentration of fructose and glucose in honeys is similar and equals in total to 80% *m/m*. Mentioned 5.0% *m/V* honey-like matrix solutions contained Ca, Cu, Fe, Li, Mg, Mn, Rb and Zn at a concentration of 0.5 mg L⁻¹

¹, fructose and glucose, each at a concentration of 20 g L⁻¹, and the sum of K and Na at a concentration increasing up to 100 mg L⁻¹ (the ratio of concentrations of K to Na was close to 10:1, which was derived from the data provided by initial analysis of studied honeys on the content of K and Na by FAES). Triton X-405 was added to solutions of standards and samples to a final concentration of 4.0 mmol L⁻¹ that corresponded to its 5 times critical micelle concentration (5×CMC), which was 0.81 mmol L⁻¹ as given by Hait and Moulik¹⁹. All solutions were acidified with concentrated HCl to a concentration of 0.1 mol L⁻¹.

Sixteen white- to amber-colored commercial honeys from 3 the greatest producers and/or distributors of bee products in Poland, i.e., CD Inc. (X), Huzar™ Ltd. (Y) and Sadecki Bartnik® (Z), were selected for the study and included acacia (A), buckwheat (B), heather (H), lime (L), multiflower (M) and rape (R) honeys.

2.2. dc-APGD-OES

A fully open-to-air discharge system of a simplified compact design (see Fig. 1) was used throughout for sustaining dc-APGD in contact with a FLC. The system was similar to the one reported in previous studies,^{5,9,14} but a couple of changes were introduced. Most notably, a W rod, which tip was sharpened, replaced a Mo rod with a rounded end. Such arrangement of the anode was found to give slightly higher intensities of analytical lines of all studied elements and higher values of signal to background ratios (SBRs) for these lines as compared to a former system. In addition, dancing and flickering of the discharge column, possible in case of the rounded tip, were eliminated. Using a 2-channel peristaltic pump, solutions of the FLC were delivered to the discharge system through a quartz capillary (ID 2.0 mm) at a flow rate of 1.8 mL min⁻¹. The capillary was inserted into a graphite tube (ID 4.0 mm) in such a way that its edge was 2.0 mm below the edge of the graphite tube. Overflowing liquid was collected in a cavity formed at the end of an outer glassy carbon tube, holding the graphite tube and housing the whole cathode compartment. Solutions treated by the discharge were drained out using another peristaltic pump. Both electrodes were vertically oriented. A gap between them, i.e., the anode tip and the surface of the FLC solution, was 5 mm. The discharge was maintained after applying to the graphite tube (the electric ground) and the W rod anode (the positive potential) a voltage of 1500 V from a dc power supply. This resulted in a current flow of 45 mA through electrodes, additionally stabilized by a 5 kΩ ballast resistor. The discharge could also be stably operated using lower (down to 0.6 mL min⁻¹) and higher (up to 3.0 mL min⁻¹) flow rates of solutions of the FLC.

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3 An achromatic UV lens was used to collect the radiation emitted from the near-
4 cathode region of the discharge. An unmagnified image of this region was focused on the
5 entrance slit (100 μm) of a 320 mm-focal length single 1200 grooves mm^{-1} holographic
6 grating monochromator Triax 320 (Horriba-Jobin Yvon). The exit slit of the monochromator
7 was 100 μm . The resolved radiation was detected by a Hamamatsu R-928 photomultiplier
8 biased at a voltage of -700 V. An output signal of the photomultiplier was amplified using a
9 single photon counting acquisition system SpectraAcq2 integrated with the monochromator.
10 A SpectraMax/32 for Windows software (Instruments SA, Inc.), version 3.2, was used to
11 control the operation of the monochromator, record profiles of emission lines of studied
12 elements and process the data, i.e., read out intensities of analytical lines and the background
13 in the vicinity of these lines. For the OES acquisition, an integration time of 500 ms was used.
14 Profiles of the most prominent and free from spectral interferences atomic emission lines of
15 studied elements, i.e., Zn at 213.9 nm, Fe at 248.3 nm, Mg at 285.2 nm, Cu at 324.8 nm, Mn
16 at 403.1 nm, Ca at 422.7 nm, Li at 670.8 nm, Na at 589.0 nm, K at 766.5 nm and Rb at 780.0
17 nm, were recorded with a resolution of 0.02 nm. For each element, profiles of its analytical
18 line were acquired 5 times while single intensities were averaged.
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31 2.3. FAES

32 A Perkin-Elmer (MA, USA) single-beam atomic absorption spectrometer, model 1100 B,
33 with a deuterium lamp for background correction was used as a reference method in
34 measurements of concentrations of K and Na by FAES. A fuel-lean air- C_2H_2 flame used was
35 maintained in a single-slot 10-cm burner head using a flow rate of air of 8.0 L min^{-1} and a
36 flow rate of C_2H_2 of 1.4 L min^{-1} . Solutions of standards and samples were introduced into the
37 flame using a stainless steel nebulizer mounted onto a burner/spray chamber, integrated with
38 an end-cup and a drain assemblage. No flow spoiler was used to increase sensitivity of
39 measurements. The instrument was operated under conditions recommended by a
40 manufacturer for K and Na and included the wavelength of 766.5 nm (K) and 589.0 nm (Na),
41 the spectral resolution of 0.4 nm (K) and 0.2 nm (Na) and the lamp current of 15 mA. For
42 calibration, 5 simple aqueous standard solutions were used with concentrations within 0.01-2
43 mg L^{-1} ranges. For each measurement cycle, 3 absorbance read-outs were made over a 3-s
44 integration time and averaged (a time-average integration mode).
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56 2.4. Procedures

Prior to FAES measurements of K and Na, samples of selected honeys, i.e., acacia honey from CD Inc. (XA) and heather honey from Sadecki Bartnik (ZH), were wet digested in the open-vessel system. Samples of honeys (2.0 g) were treated with 10.0 mL of concentrated HNO₃ and heated on a hot plate at 80-90 °C for 2 h to reduce the volume to about 1 mL. Aliquots left were reconstituted with water and diluted to 20.0 mL. Concentrations of K and Na in such prepared 5.0% *m/V* sample solutions were determined by FAES against simple standard solutions. Prior to measurements, sample solutions were appropriately diluted. For each honey, 3 parallel samples were prepared and analyzed in addition to respective blank samples.

In case of dc-APGD-OES, 1.0% *m/V* honey solutions of honeys were prepared by dissolving appropriate amounts of analyzed samples (1.0 g per 100 mL) and acidified with a concentrated HCl solution to a concentration of 0.1 mol L⁻¹. The addition of Triton X-405 was not necessary in this case. In such prepared sample solutions, concentrations of K and Na were determined using 5 simple standard solutions within concentration ranges of 0.5-40 mg L⁻¹ (K) and 0.1-10 mg L⁻¹ (Na). Other elements, i.e., Ca, Cu, Fe, Li, Mg, Mn, Rb and Zn, were determined in 5.0% *m/V* solutions of honey (5.0 g per 100 mL). As before, these solutions were acidified with HCl and Triton X-405 at a concentration of 4.0 mmol L⁻¹ (its 5×CMC) was added to modify the FLC solution. For quantification, 5 matrix-matching standard additions, containing 40 g L⁻¹ of total glucose and fructose and 30 mg L⁻¹ of total K and Na, were used. For each honey, 3 independent samples were prepared and measured in addition to analysis of respective blank samples.

3. Results and discussion

Honey is a complex sample with the matrix rich in the organic matter. Multi-element analysis of honey samples by inductively coupled plasma optical emission spectrometry (ICP-OES) is commonly preceded by their calcinations using wet or dry ashings.^{20,21} Simplified sample preparation of honey prior to its spectrochemical analysis, e.g., by dissolving respective samples in water only and acidifying, is infrequently reported,¹⁸ although has certainly a special significance in view of analysis simplicity. As previously reported, the concentration of honey in solutions prepared by dissolving respective samples in water is limited since a high organic content, i.e., >2-5% *m/V*, may substantially increase viscosity of solutions and markedly affect sensitivity of measurements, primary due to formation of C-containing

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3 compounds.^{14,20} Even when analyzed solutions contain dissolved honey in amount of 1-2%
4 m/V , intense matrix effects could be present and hence, simple standard calibration cannot be
5 used.²⁰
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3.1. Effect of the honey-like matrix on the response of elements

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10 To evaluate suitability of dc-APGD-OES for determining Ca, Cu, Fe, Li, Mg, Mn, Rb and Zn
11 in solutions of honey samples dissolved only in water (without any pre-digestion), the effect
12 of a honey-like matrix, containing fructose and glucose, was examined at first. Both simple
13 carbohydrates are almost equally present in honey at an average concentration of 0.80 g g^{-1} .²²
14 Therefore, a 5.0% m/V solution of such honey-like matrix should contain 20 g L^{-1} of fructose
15 and 20 g L^{-1} of glucose (40 g L^{-1} in total). The effect of such 5.0% m/V honey-like matrix,
16 present in solutions of Ca, Cu, Fe, Li, Mg, Mn, Rb and Zn, was studied on the background
17 corrected (net) intensities of analytical lines of these elements versus an increasing
18 concentration of total K and Na (present in solutions at ratio 10:1) up to 100 mg L^{-1} . A blank
19 used for this experiment was a solution containing the honey-like matrix but no elements. For
20 comparison purposes, the effect of the increasing concentration of total K and Na on the
21 response of Ca, Cu, Fe, Li, Mg, Mn, Rb and Zn was also studied in conditions with an added
22 modifier of the FLC, i.e., non-ionic surfactant Triton X-405 at a concentration of its $5 \times \text{CMC}$,
23 and with or without the mentioned 5.0% m/V honey-like matrix in solutions. Net intensities of
24 analytical lines of Ca, Cu, Fe, Li, Mg, Mn, Rb and Zn were measured for 3 independently
25 prepared solutions and averaged. Blanks for this experiment were a solution containing Triton
26 X-405 only or a solution with both the surfactant and the honey-like matrix but with no
27 elements. For simplicity, for each analytical line measured in different experimental
28 conditions, its net intensities were related to the net intensity acquired for a solution without
29 the honey-like matrix, K with Na and Triton X-405, and expressed as the relative intensity.
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45 As can be seen from Fig. 2, the presence of fructose and glucose results in decreasing
46 net intensities of analytical lines of studied elements by 50% (Cu, Fe, Mg, Zn), 35% (Li, Mn),
47 25% (Ca) and 15% (Rb) as compared to net intensities recorded in conditions without the
48 5.0% m/V honey-like matrix. SBR values for these analytical lines of studied elements were
49 either decreased by 20-40% (Cu, Fe, Li, Mn), 120-140% (Mg, Zn) or remained unchanged
50 (Ca, Rb) (see Fig. 3a). Changes in the response of studied elements versus the concentration
51 of total K and Na increasing up to 100 mg L^{-1} were rather slight (see Fig. 2). Both, with and
52 without the honey-like matrix in solutions, relative net intensities of analytical lines of studied
53 elements were maximally, i.e., at a concentration of total K and Na of 100 mg L^{-1} , decreased
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3 by 10-15% (Ca, Fe, Mg, Mn, Zn) or less than 10% (Cu, Li). An exception was Rb, for which
4 the mentioned increase in the concentration of total K and Na up to 100 mg L⁻¹ led to a rise of
5 the relative net intensity by about 10 or 20%, respectively, in case of the presence or the
6 absence of the honey-like matrix in solutions.
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10 It was also verified that when the concentration of the honey-like matrix in solutions
11 of studied elements was 2.5 or 10% *m/V*, which corresponds to the presence of fructose and
12 glucose at a concentration of 40 or 160 g L⁻¹ in total, a decrease in net intensities of analytical
13 lines of studied elements was, correspondingly, about 2 times lower or 2 times higher than
14 this noted for the 5.0% *m/V* honey-like matrix. This indicated that the suppression of signals
15 of studied elements observed for dc-APGD generated in contact with FLC solutions
16 containing fructose with glucose was strictly related to an increase in viscosity of these
17 solutions. Considering the morphology of emission spectra of dc-APGD loaded with 2.0, 5.0
18 and 10% *m/V* solutions of the honey-like matrix, no emission bands of molecules containing
19 C atoms were identified.
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28 **3.2. The effect of the addition of Triton X-405**

29 The addition of Triton X-405 at a concentration of its 5×CMC to solutions of studied
30 elements, but without the 5.0% *m/V* honey-like matrix, was quite beneficial because caused an
31 increase in net intensities of analytical lines of studied elements by 1.4- (Zn), 1.5- (Fe), 1.6-
32 (Li), 1.7- (Mg, Mn), 1.9- (Ca), 2.2- (Cu) and 2.7-fold (Rb) as compared to net intensities
33 acquired in conditions with no non-ionic surfactant added to FLC solutions. Observed
34 enhancements well corresponded to those recently reported,⁵ however, it should be borne in
35 mind that the design of the present discharge system is changed.
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41 Surprisingly, the addition of Triton X-405 (at its 5×CMC) to solutions containing the
42 5.0% *m/V* honey-like matrix led to much higher enhancements of net intensities of analytical
43 lines of studied elements than without it. Accordingly, relative net intensities were equal to
44 1.8 (Zn), 2.5 (Li), 3.0 (Fe, Mg), 3.4 (Mn), 3.8 (Cu), 3.9 (Ca) and 4.3 (Rb). As can be seen
45 from Fig 3a, SBR values are also increased in these conditions correspondingly by about 3
46 (Fe), 4 (Ca, Cu, Li, Mn, Rb), and 5 times (Mg, Zn). When Triton X-405 was added to 5.0%
47 *m/V* honey-like matrix solutions at lower concentrations, i.e., 1×CMC or 2×CMC, observed
48 enhancements of net intensities of analytical lines of studied elements were lower. At present,
49 the mechanism of a synergistic effect observed for fructose with glucose and the added non-
50 ionic surfactant is difficult to explain, however, it appears that the addition of Triton X-405 to
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3 5.0% *m/V* honey-like matrix solutions results in gainfully increasing the efficiency of
4 transportation of elements to phases of the discharge. As a result, net intensities of analytical
5 lines of studied elements were enhanced more than 7 (Cu), 6 (Fe, Mg, Mn), 5 (Ca, Rb) and 4
6 times (Li and Zn) as compared to those recorded in conditions when FLC solutions contained
7 only the 5.0% *m/V* honey-like matrix, suppressing the response of studied elements.
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11 As can be seen from Fig. 2, an increase in the concentration of total K and Na in
12 solutions to 30 mg L⁻¹ causes a slight enhancement of relative net intensities of analytical
13 lines of all elements except for Zn. Above this concentration, a gradual fall in the response of
14 all elements can be noted. The behavior of SBR values was quite corresponding. Fig. 3b gives
15 SBRs for analytical lines of studied elements for conditions when 30 mg L⁻¹ of total K and Na
16 was present in the 5.0% *m/V* honey-like matrix solution along with the added Triton X-405
17 modifier. It is evident that the presence of K with Na leads to a slight increase in SBR values,
18 i.e., by about 7% (Fe) to 14% (Rb). At concentrations of total K and Na higher than 30 mg L⁻¹,
19 relative net intensities and SBRs were established to gradually deplete.
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23 Concluding, it appears that the use of Triton X-405 would enable to determine studied
24 elements in 5.0% *m/V* solutions of honeys using external calibration with matrix-matching
25 standard solutions. Considering the morphology of emission spectra of dc-APGD loaded with
26 5.0% *m/V* solutions of the honey-like matrix with and without added Triton X-405 (see Fig.
27 4), it was found that the use of the non-ionic surfactant was responsible for extinguishing
28 emission bands of NO, OH and N₂ molecules. Interestingly, in the presence of 10% *m/V*
29 solutions of the honey-like matrix, the addition of Triton X-405 at its 5×CMC also resulted in
30 enhancing net intensities of analytical lines of studied elements. Accordingly, relative net
31 intensities of these lines were by about 30-40% higher than those acquired for solutions
32 containing the 5.0% *m/V* honey-like matrix, however, the handling of such viscous solutions
33 was rather inconvenient. Therefore, in further experiments, Ca, Cu, Fe, Li, Mg, Mn, Rb and
34 Zn were determined in analyzed honeys using their 5.0% *m/V* solutions.
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47 3.3. Determination of K and Na

48 Due to relatively high concentrations of K and Na in analyzed white- to amber-colored
49 honeys as well as sensitivities of analytical lines of K and Na, assessed when measuring 0.5
50 and 1.0% *m/V* solutions of the honey-like matrix, the use of more concentrated solutions and
51 Triton X-405 as the FLC modifier was not necessary. Indeed, it was verified that the presence
52 of 1.0% *m/V* honey-like and honey matrices had no effect on sensitivities of analytical lines of
53 both elements. Slopes of calibration curves (in a. u. per μg L⁻¹) determined for simple water
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standard solutions, e.g., 27.1 ± 0.2 for the K I 766.5 nm line and 420 ± 12 for the Na I 589.0 nm line, did not statistically differ from slopes of calibration curves obtained for 1.0% *m/V* solutions of the honey-like matrix and 1.0% *m/V* solutions of the honey matrices (acacia XA and heather ZH honeys). However, linearity ranges for both elements were different. In case of K, calibration curves were linear up to 100 mg L^{-1} ($R^2=0.9986-0.9999$, depending on the matrix), while in case of Na, the upper linearity range was 40 mg L^{-1} , while coefficients of determination (R^2) for different matrices were varied within 0.9945-0.9967.

By cause of this, it was decided that 1.0% *m/V* solutions of analyzed honeys would be prepared for the quantification of their K and Na contents by dc-APGD-OES using simple standard solutions for calibration. To confirm reliability of results obtained with this methodology, two honeys were selected, i.e., acacia XA and heather ZH, and their samples were analyzed by dc-APGD-OES (after simple water dissolution and acidification with HCl to 0.1 mol L^{-1}) and FAES (after wet oxidative digestion). Results of both analyses are given in Table 1. They well correspond to results obtained in other Polish honeys.^{18,23,24} As it can be seen, a good agreement between results obtained with both methods was achieved. Standard errors between concentrations of K and Na determined by both methods were within -6.8 to 2.4% . In addition, a recovery study was carried out. Accordingly, K and Na were added to both selected honeys to double their original concentrations and then, respective samples were prepared and resulting solutions measured by dc-APGD-OES against simple standard solutions. Recoveries of added K and Na for both honeys were found quantitative, confirming that results of measurements of K and Na concentrations with the proposed methodology are reliable. Precision was also good since RSDs were in the range from 0.4 to 4.9% in case of K and from 0.5 to 4.5% in case of Na. Capability of the method was also evaluated through determining LODs for K and K. In this case, 1.0% *m/V* solutions of the honey-like matrix were used.

A complete set of validation parameters evaluated for dc-APGD-OES, as the alternative method of analysis of honey without necessity of its mineralization, is given in Table 2.

3.4. Determination of Ca, Cu, Fe, Li, Mg, Mn, Rb and Zn

Concentrations of Ca, Cu, Fe, Li, Mg, Mn, Rb and Zn were measured in analyzed honeys using standard solutions with the matrix matching in relation to an average amount of fructose and glucose (40 g L^{-1} in total) and an average concentration of total K and Na (30 mg L^{-1}) in 5.0% *m/V* solutions of honeys. Results of this analysis are given in Table 1 (Ca and Mg) and

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3 Table 3 (Cu, Fe, Li, Mn, Rb and Zn) and they well correspond to those reported for other
4 Polish honeys.^{18,23,24} Concentrations of Cu and Li in examined honeys were established to be
5 lower than respective LODs of these elements, i.e., 0.7 and 0.02 $\mu\text{g g}^{-1}$. Precision (as the
6 RSD) of measurements was satisfactorily good and varied in majority cases in the following
7 ranges: 0.3-8.7% (Ca), 6.7-12% (Fe), 0.7-6.9% (Mg), 5.2-6.3% (Mn), 1.8-8.2% (Rb), and 0.8-
8 8.7% (Zn). Occasionally, in case of 1 to 3 honeys out of 16, these vales were higher, i.e.,
9 within 11-18%.

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11 To verify validity of results achieved with the proposed methodology, the recovery
12 study was carried out for acacia XA and heather ZH honeys. Samples were spiked with
13 standard solutions of studied elements to roughly double their original concentrations, then,
14 respective 5.0% *m/V* sample solutions were prepared and analyzed by dc-APGD-OES against
15 matrix-matching standard solutions. Recoveries found for acacia XA honey were in the range
16 from 92.5% (Zn) to 102% (Cu, Fe). In case of heather ZH honey, except for Li and Rb,
17 recoveries changed from 96.0% (Mg) to 109 \pm 2% (Cu). Higher recoveries were established for
18 Li (140%) and Rb (145%), however, heather ZH honey contains the highest concentration of
19 total K and Na out of all studied honeys. In these conditions, the matrix matching used was
20 inadequate and, likely due to an ionization buffering effect, intensities of atomic emission
21 lines of Li and Rb were enhanced by about 40% (Li) and 45% (Rb). Additionally,
22 concentrations of Ca, Mg, Rb and Zn in acacia XA honey as well as Ca, Mg, Mn, Rb and Zn
23 in heather ZH honey were determined by dc-APGD-OES and the developed methodology but
24 using 3 standard solutions' additions for calibration (results are given in Tables 1 and 3). As it
25 can be seen, both calibration strategies give comparable concentrations of studied elements in
26 both honeys. This proves that results of analysis of 5.0% *m/V* solutions of honeys, resulted
27 from dissolution of their samples in water only and acidification with HCl, and made by dc-
28 APGD-OES in conditions of Triton X-405 added to them, are dependable. As was expected,
29 the only exception was the content of Rb in heather ZH honey, which was by about 45%
30 lower as compared to this determined when matrix-matching standard solutions were used.
31 This was due to the mentioned ionization buffering, and hence, concentrations of Rb in lime
32 XL, YL and ZL honeys, where concentrations of total K and Na in their 5.0% *m/V* solutions
33 were higher than 30 mg L^{-1} , were determined by the method of 3 standard solutions'
34 additions. In addition to this calibration method, a higher concentration of total K and Na in
35 matrix-matching solutions or a separate ionization buffer, i.e., CsCl as in flame atomic
36 absorption spectrometry (FAAS), could be used as well, give accurate results.

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3 Other figures of merit of dc-APGD-OES for Ca, Cu, Fe, Li, Mg, Mn, Rb and Zn are
4 given in Table 2. They demonstrate a good analytical performance of the method proposed in
5 reference to LODs, changing from 0.8 $\mu\text{g g}^{-1}$ for Li to 125 $\mu\text{g g}^{-1}$ for Fe, and precision,
6 changing from 0.7% for Mn to 4.8% for Zn.
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10 11 12 13 **4. Conclusions**

14 This work demonstrated a compact discharge system for miniaturized dc-APGD generated in
15 contact with the FLC for simplified OES element analysis of honey. Using Triton X-405 as a
16 modifier of the FLC, the described dc-APGD excitation source along with the OES detection
17 was successfully used for the direct determination of Ca, Cu, Fe, K, Li, Mg, Mn, Na, Rb and
18 Zn in solutions only prepared by dissolving appropriate samples of honeys in water and
19 acidifying with HCl to a concentration as required for electrical conductivity of the FLC. The
20 methodology proposed enabled to measure all studied elements with relatively high
21 sensitivity, good precision and fair limits of detection. Giving dependable results in element
22 analysis of the complex honey matrix, the developed method could also be used a viable
23 alternative for fast and convenient analysis of other sugar-rich samples, i.e., syrups, nectars
24 and juices.
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Captions for figures

Fig. 1 A schematic diagram of a compact discharge cell for dc-APGD generated in contact with a small-sized flowing liquid cathode (FLC).

Fig. 2 The effect of the presence of the honey-like matrix, the increasing concentration of total K and Na (10: 1) and Triton X-405 (5×CMC) in the FLC solution on relative net intensities of analytical lines of Ca, Cu, Fe, Li, Mg, Mn, Rb and Zn.

Fig. 3 The effect of the presence of the honey-like matrix and Triton X-405 (5×CMC) in the FLC solution on signal to background ratios of analytical lines of Ca, Cu, Fe, Li, Mg, Mn, Rb and Zn in conditions of the presence of a) no and b) 30 mg L⁻¹ of K and Na (10: 1).

Fig. 4 The effect of the addition of Triton X-405 (5×CMC) to the FLC on the morphology of the emission spectrum of dc-APGD loaded with a solution containing 40 g L⁻¹ of fructose and glucose in total.

Table 1. Concentrations of Ca, K, Mg and Na determined in white- to amber-colored commercial honeys by dc-APGD-OES against external calibration with simple (K, Na) and matrix-matching standard solutions (Ca, Mg). The concentration of honey in sample solutions: 1.0% *m/V* for K and Na, 5.0% *m/V* for Ca and Mg. The concentration of added Triton X-405: 4.0 mmol L⁻¹ (5×CMC) only in case of Ca and Mg

| Honey | Concentration, $\mu\text{g g}^{-1}$ | | | |
|-----------------|-------------------------------------|----------|-----------|-----------|
| | Ca | K | Mg | Na |
| XA | 36.0±1.5 | 184±8 | 11.2±0.6 | 9.29±0.24 |
| XA ^a | 37.2±1.9 | 180±4 | 11.5±0.3 | 8.92±0.18 |
| XA ^b | 96.5±3.5 | 101±6 | 96.5±5.5 | 104±9 |
| XB1 | 27.0±3.9 | 91.7±1.5 | 9.26±0.38 | 269±4 |
| XB2 | 43.3±0.5 | 242±10 | 13.1±0.9 | 11.2±0.1 |
| XH | 58.4±1.7 | 564±27 | 22.2±1.1 | 38.7±0.7 |
| XL | 61.8±1.0 | 633±14 | 17.9±0.3 | 96.1±0.5 |
| XM | 63.7±0.2 | 334±76 | 16.6±1.9 | 69.8±1.9 |
| YA | 15.0±0.2 | 225±7 | 6.00±0.15 | 23.2±0.6 |
| YB | 45.6±0.2 | 224±4 | 13.8±1.5 | 25.4±0.3 |
| YL | 74.5±0.4 | 873±22 | 21.4±0.3 | 25.2±0.6 |
| YM | 67.4±0.8 | 412±10 | 16.9±0.3 | 20.4±0.5 |
| ZA | 16.8±1.9 | 195±1 | 6.54±0.29 | 5.50±0.22 |
| ZB | 29.9±0.7 | 334±8 | 14.5±0.1 | 9.95±0.45 |
| ZH | 51.7±3.1 | 1066±26 | 19.4±0.7 | 19.7±0.8 |
| ZH ^a | 52.9±1.2 | 1040±15 | 20.7±1.6 | 21.1±0.3 |
| ZH ^b | 99.0±4.0 | 94.9±4.8 | 96.0±7.0 | 108±5 |
| ZL | 58.7±3.3 | 767±23 | 17.8±0.4 | 9.32±0.39 |
| ZM | 50.2±2.3 | 476±9 | 19.5±0.8 | 12.3±0.3 |
| ZR | 54.3±4.7 | 208±8 | 17.1±0.3 | 9.05±0.13 |

Average value (n=3) ± standard deviation.

^a Results obtained analyzing dissolved samples by dc-APGD-OES with calibration by 3 standard solutions' additions (Ca and Mg) and digested samples by FAES with calibration by simple standard solutions (K and Na).

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3 ^b Recoveries (in %). XA: 35.0, 200, 10.0 and 10.0 $\mu\text{g g}^{-1}$ of Ca, K, Mg and Na, respectively,
4 were added. ZH: 50.0, 1000, 10.0 and 20.0 $\mu\text{g g}^{-1}$ of Ca, K, Mg and Na, respectively, were
5 added.
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Table 2. Analytical characteristics of dc-APGD-OES for analysis of honey samples

| Element | Sensitivity, a. u. per μg L^{-1} | Upper linearity range, mg L^{-1} | R^2 | Limit of detection (3σ), μg L^{-1} | Limit of detection, ^a μg g^{-1} | Precision ^b , % |
|-----------------|--|---|--------|---|--|-------------------------------|
| Ca ^c | 5.18 | 10 | 0.9993 | 49 | 0.98 | 2.0 |
| Cu ^c | 85.4 | 10 | 0.9973 | 33 | 0.66 | 3.2 |
| Fe ^c | 1.77 | 10 | 0.9991 | 125 | 2.5 | 3.4 |
| K ^d | 27.1 | 100 | 0.9990 | 4.6 | 0.46 | 3.7 |
| Li ^c | 220 | 10 | 0.9969 | 0.75 | 0.015 | 1.7 |
| Mg ^c | 324 | 10 | 0.9974 | 7.8 | 0.16 | 1.8 |
| Mn ^c | 4.13 | 10 | 0.9989 | 88 | 1.8 | 0.7 |
| Na ^d | 420 | 40 | 0.9999 | 0.37 | 0.037 | 2.8 |
| Rb ^c | 25.6 | 10 | 0.9956 | 5.2 | 0.10 | 3.9 |
| Zn ^c | 32.8 | 5.0 | 0.9959 | 8.0 | 0.16 | 4.8 |

^a Calculated for 1.0 g (K, Na) or 5.0 g (Ca, Cu, Fe, Li, Mg, Mn, Rb and Zn) of honey dissolved in 100 mL of water.

^b As relative standard deviation ($n=3$) for solutions containing 1.0 mg L^{-1} of studied elements.

^c Assessed using 5.0% m/V honey-like matrix-matching standard solutions (40 g L^{-1} of total glucose and fructose, 30 mg L^{-1} of total K and Na).

^d Assessed using 1.0% m/V honey-like matrix-matching standard solutions (8.0 g L^{-1} of total glucose and fructose).

Table 3. Concentrations of Fe, Mn, Rb and Zn determined in white- to amber-colored commercial honeys by dc-APGD-OES against external calibration with matrix-matching standard solutions. The concentration of honey in sample solutions: 5.0 *m/V*. The concentration of added Triton X-405: 4.0 mmol L⁻¹ (5×CMC)

| Honey | Concentration, $\mu\text{g g}^{-1}$ | | | | | |
|-----------------|-------------------------------------|-----------|-------|-----------|------------------------|-----------|
| | Cu | Fe | Li | Mn | Rb | Zn |
| XA | <0.7 | <2.5 | <0.02 | <1.8 | 0.37±0.02 | 8.36±0.38 |
| XA ^a | NA | NA | NA | NA | 0.35±0.03 | 8.86±0.20 |
| XA ^b | 102±3 | 102±3 | 100±4 | 98.5±3.5 | 100±2 | 92.5±1.5 |
| XB1 | <0.7 | 32.9±2.2 | <0.02 | <1.8 | 0.43±0.02 | 7.15±0.17 |
| XB2 | <0.7 | 9.81±1.16 | <0.02 | <1.8 | 1.04±0.03 | 3.90±0.23 |
| XH | <0.7 | <2.5 | <0.02 | 5.38±0.34 | 5.45±0.27 | 6.02±0.27 |
| XL | <0.7 | <2.5 | <0.02 | <1.8 | 0.92±0.03 ^a | 4.04±0.35 |
| XM | <0.7 | <2.5 | <0.02 | <1.8 | <0.10 | 2.97±0.11 |
| YA | <0.7 | <2.5 | <0.02 | <1.8 | 0.36±0.04 | 0.63±0.03 |
| YB | <0.7 | 8.04±1.33 | <0.02 | <1.8 | 0.39±0.07 | 1.36±0.02 |
| YL | <0.7 | <2.5 | <0.02 | <1.8 | 1.06±0.05 ^a | 1.24±0.09 |
| YM | <0.7 | <2.5 | <0.02 | <1.8 | <0.10 | 1.26±0.01 |
| ZA | <0.7 | <2.5 | <0.02 | <1.8 | 0.31±0.01 | 1.51±0.23 |
| ZB | <0.7 | <2.5 | <0.02 | <1.8 | 0.85±0.07 | 19.0±0.8 |
| ZH | <0.7 | <2.5 | <0.02 | 6.90±0.36 | 13.8±1.9 | 0.98±0.12 |
| ZH ^a | NA | NA | NA | 6.80±1.03 | 9.47±0.88 | 0.97±0.06 |
| ZH ^b | 109±4 | 105±1 | 140±2 | 102±2 | 145±6 | 102±2 |
| ZL | <0.7 | <2.5 | <0.02 | <1.8 | 0.92±0.02 ^a | 2.66±0.21 |
| ZM | <0.7 | <2.5 | <0.02 | <1.8 | 0.57±0.01 | 10.8±0.2 |
| ZR | <0.7 | <2.5 | <0.02 | <1.8 | <0.10 | 1.23±0.06 |

Average value (n=3) ± standard deviation.

^a Results obtained analyzing dissolved samples by dc-APGD-OES with calibration by 3 standard solutions' additions.

^b Recoveries (in %). XA: 2.0, 5.0, 1.0, 5.0, 1.0 and 10.0 $\mu\text{g g}^{-1}$ of Cu, Fe, Li, Mn, Rb and Zn, respectively, were added. ZH: 2.0, 5.0, 1.0, 5.0, 10.0 and 1.0 $\mu\text{g g}^{-1}$ of Cu, Fe, Li, Mn, Rb and Zn, respectively, were added.

NA Not analyzed.

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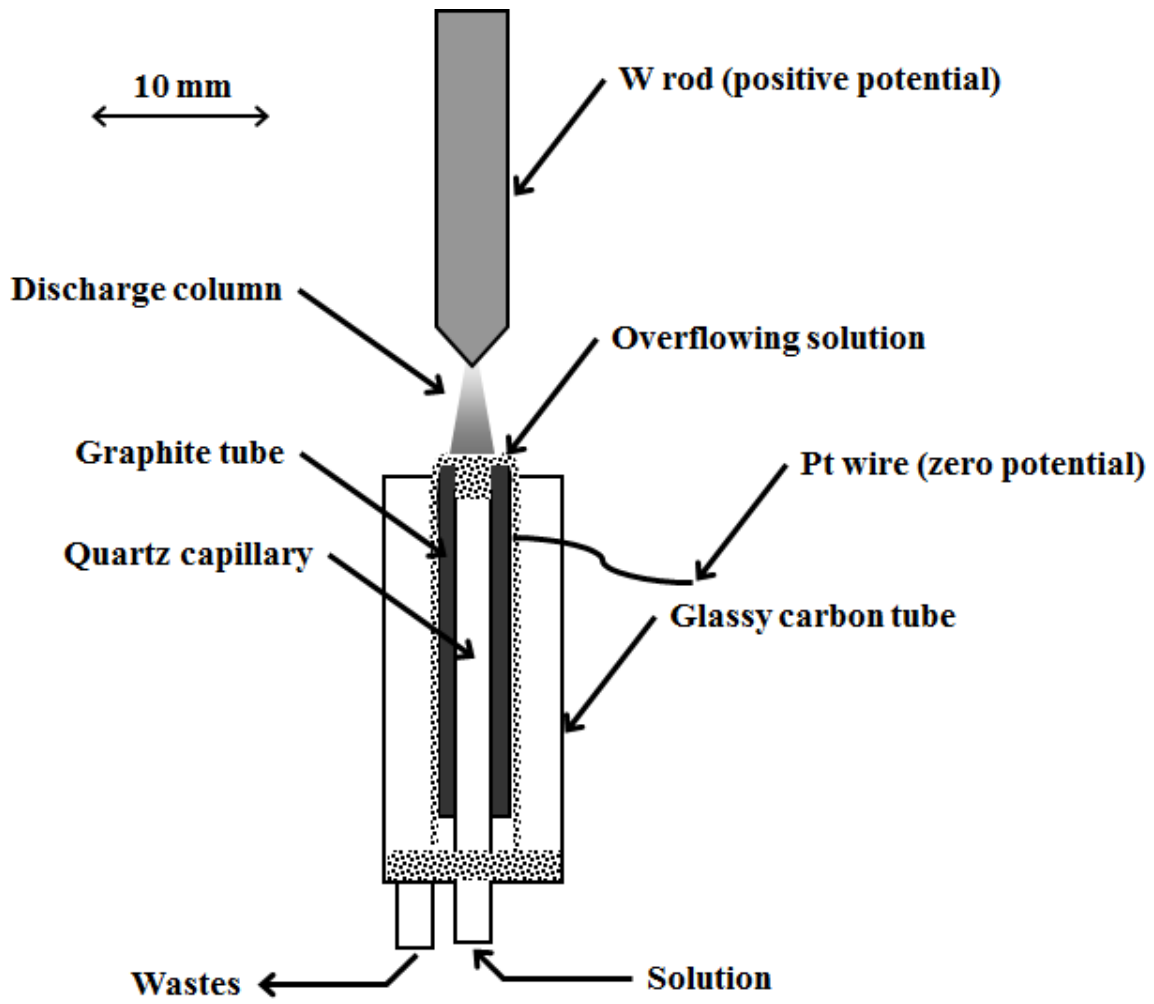


Fig. 1.

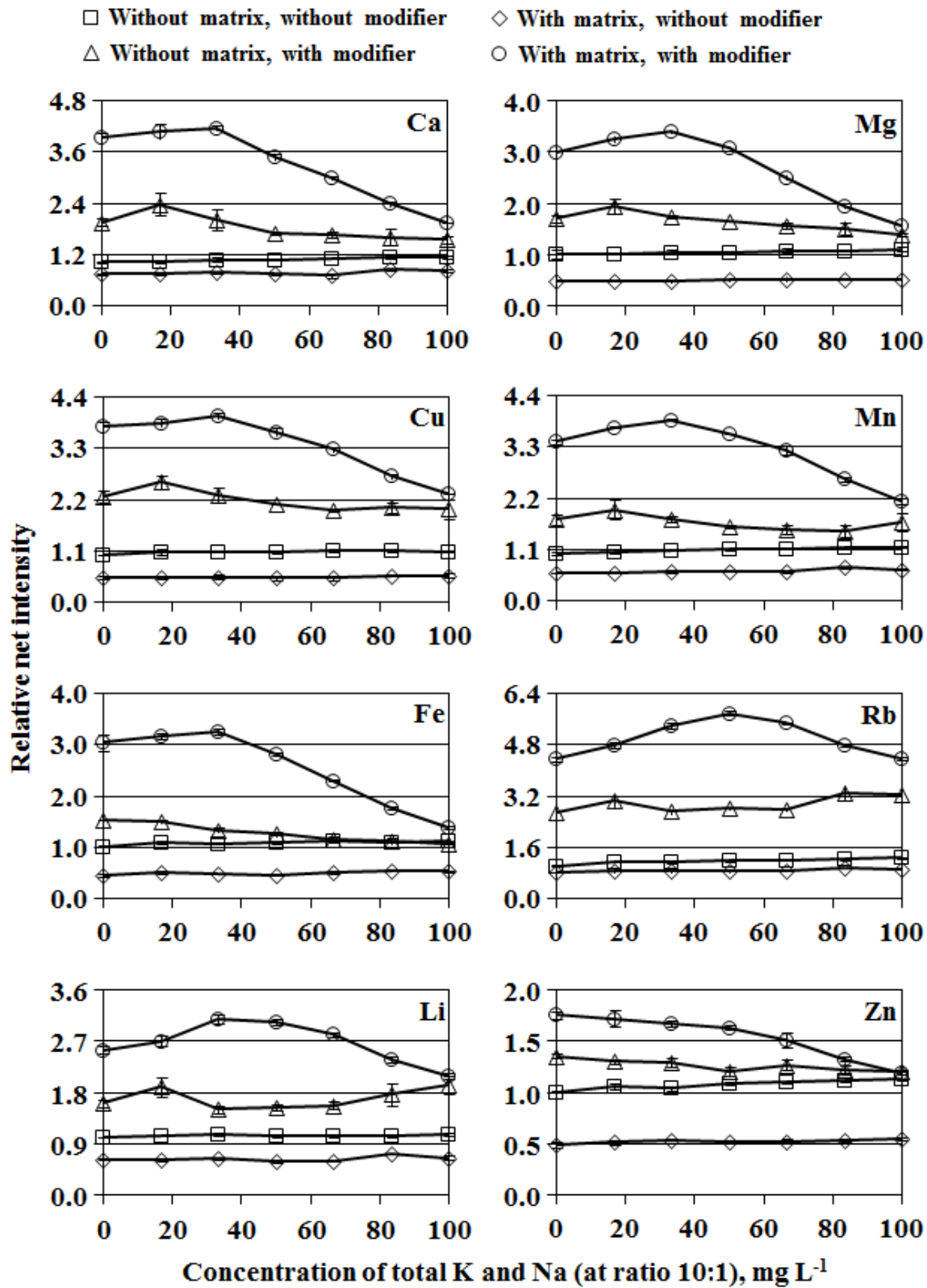


Fig. 2.

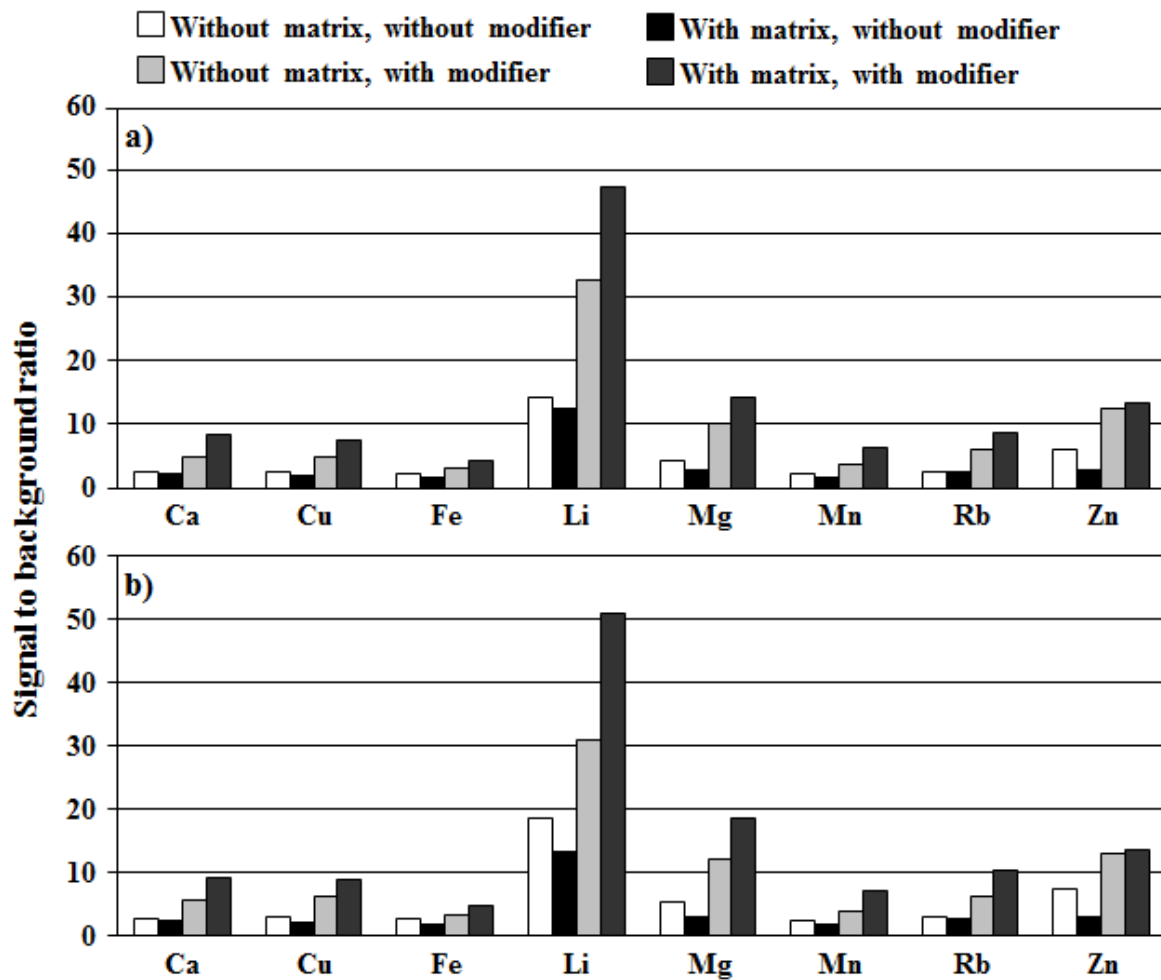


Fig. 3.

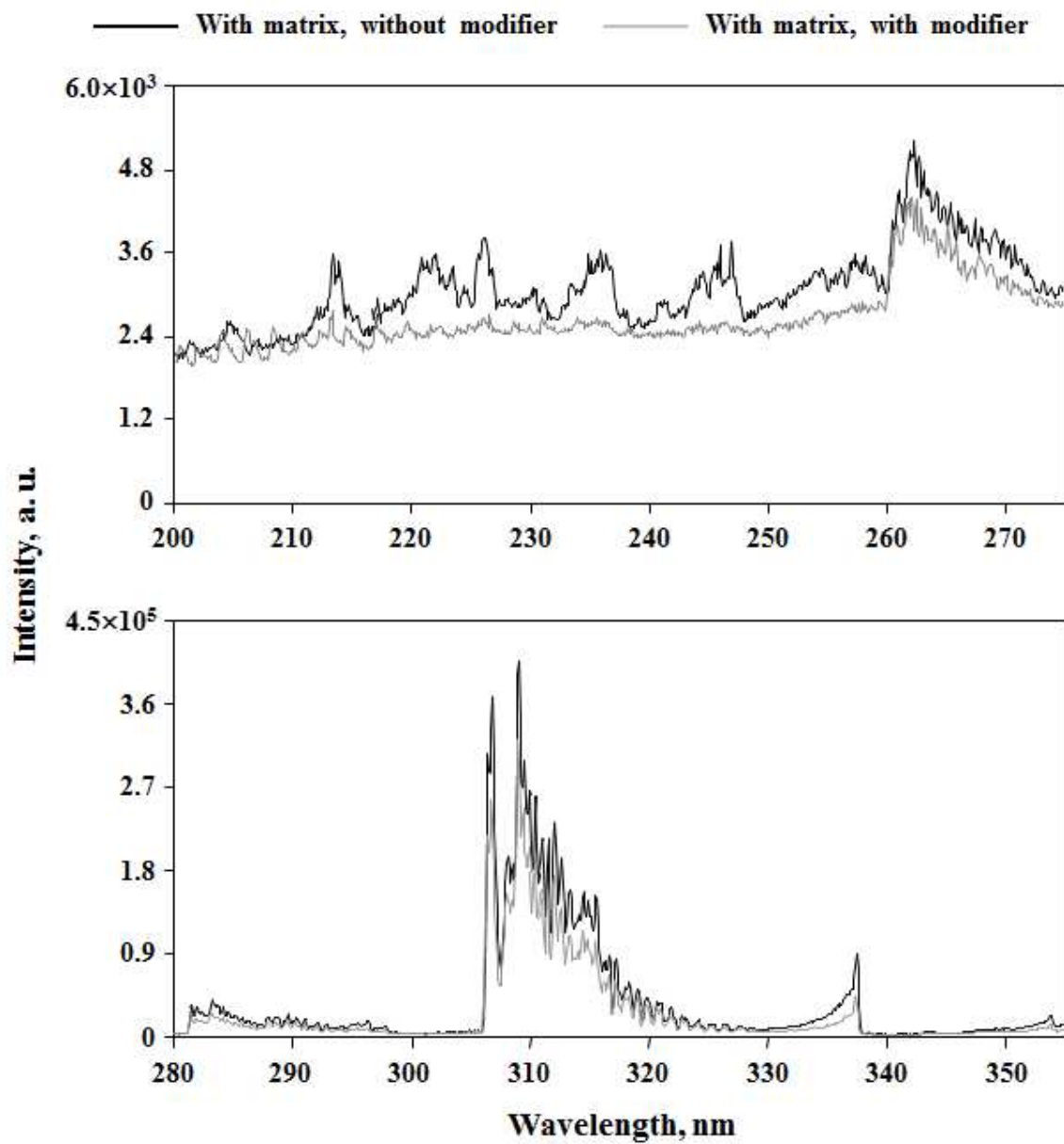


Fig. 4.