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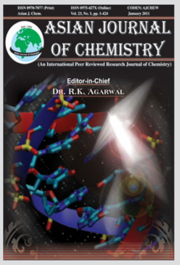

Simple Multi-Element Solid Phase Extraction Procedure to Determine Some Heavy Trace Metals in Honey by Flame Atomic Absorption Spectrometry

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A multi-element solid phase extraction procedure on C_{18}ec and C_6H_5 modified silica cartridges and flame atomic absorption spectrometric determination of some heavy metals in honey samples is proposed. Manufacturing of a simple handmade solid phase extraction stand has also been illustrated in this work. The influences of analytical parameters including pH, eluent composition and sample volume, *etc*., on the recoveries of copper, iron, manganese, nickel and zinc were investigated. The interfering effects of some common coexisting cations on the retentions of the analytes were also examined. The recoveries of analytes were generally higher than 95 % for both phases. The developed methods were applied to the determination of metal ions in 25 Syrian honey samples from different botanical and geographical areas. The accuracy of samples' results was compared by GF-AAS determination.

Key Words: Honey, SPE, C_{18}ec modified silica phase, Phenyl modified silica phase, FAAS.

INTRODUCTION

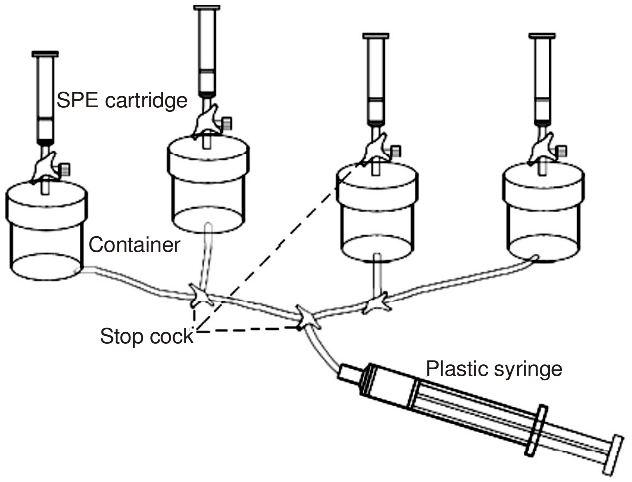
Honey contains a variety of metals. Major metals are primarily derived from soil and nectar-producing plants, but consideration also needs to be given to environmental pollution or other human activities. Metals in honey, especially Cd, Cr, Cu, Fe, Ni, Pb and Zn, may be a hazard to human health and adversely affect the quality and the safety of honey[1,2]. Direct instrumental analysis of these samples is difficult because of complex formation and significant matrices, which invariably influence normal instrumental analysis[3]. In addition, some metals have low concentrations, which are near or below the limit of detection of the instrument, therefore a preconcentration method is required[4,5]. Solid-phase extraction would be the preferred preconcentration method on account of the fast, simple and direct application in micro liters without any sample loss; a higher preconcentration factor; rapid phase separation and time and cost savings[6]. Various solid phase extractants including activated carbon[7,8], modified silica gel[9], microcrystalline naphthalene[10], modified ODS[11], Amberlite XAD resins[12], alumina[13], TiO_2 nanotubes[14] and polyurethane foam[15], *etc*., have been used for the separation and preconcentration of traces of heavy metal ions from environmental and food samples. According to the literature review, the extraction procedures of studied ions with 8-hydroxyquinoline have good recoveries[16], as do those with sodium diethyldithiocarbamate[17,18].

The aim of this work is to develop a highly sensitive and rapid simple method for extraction, concentration and determination of very low levels of Fe(III), Cu(II), Mn(II), Ni(II) and Zn(II) in aqueous solution using C_{18}ec modified silica phase with 8-hydroxyquinoline (8-HQ) as a ligand and phenyl modified silica phase with sodium diethyldithiocarbamate (NaDDTC) as a ligand, as well as the optimum condition of these elements determination by FAAS, with a methanol-water mixture with a volume ratio 90:10 in the final extracted solution. The developed method was applied to determine these elements in 25 Syrian honey samples taken from different botanical and geographical areas. The relation between obtained results and geographical origin was also studied. A simple manufacturing of a handmade manual solid phase extraction stand was illustrated in this work.

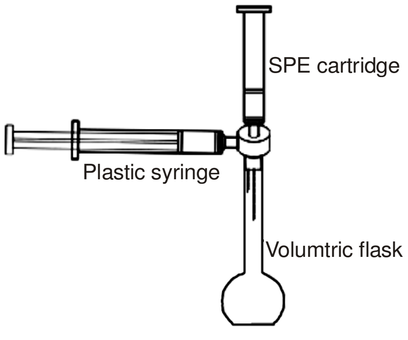
EXPERIMENTAL

Honey samples: Twenty-five natural honey samples were collected from different geographical areas in Syria stationed in the coastal, central and northern regions. The honey was made by traditional procedures in the producing region and collected into PVC (200 mL) containers which were washed twice by R.O. water. None of these samples underwent any process that could alter their composition. The samples were stored at room temperature until analysis.

The measurements of Fe(III), Cu(II), Mn(II), Ni(II) and Zn(II) metal ions were performed with a Hitachi Z-2000 polarized Zeeman atomic absorption spectrometer equipped with single element hollow cathode lamps at respective wavelengths using an air-acetylene flame. The instrumental parameters were studied and arranged in Table-1. A Metrohm 691 pH/ion meter with a combined glass-calomel electrode was used for adjustment of test solution pH. The solid phase extraction stand used was handmade and consisted of two units which are a sorption unit and an elution unit. The sorption unit consist of container, 3-way stop cock with 10 cm tubing and pump plastic syringe (50 mL) which are fixed together as shown in Fig. (1a). The elution unit consists of a plastic stopper of a volumetric flask which is pricked at the center, with two syringe needles passed through the hole. The first needle is plastic for the elution, while the other is metallic for evacuating by a plastic syringe as shown in Fig. (1b).



(a) Sorption unit



(b) Elution unit

Fig. 1. Solid phase extraction handmade stand

All chemicals were analytical reagent-grade (Merck and POCh) and all solutions were prepared in distilled/RO water. C_{18}ec and phenyl modified silica cartridges were purchased from MN (Germany). Stock solutions of all metals (Merck) with a concentration 1000 mg/L in 0.5 mol/L HNO_3 were used. The model and the standard solutions of the metals were prepared by diluting from the stock solutions using suitable ratios. Then, 0.5 mL of model solution (Cu, Mn, Ni, Zn = 1 μg, Fe = 2 μg) was diluted to 25 mL with suitable buffer solution and was used for all studies. Acetate and ammonia buffer solutions were prepared by mixing of appropriate volumes of 0.1M acetic acid and 0.1M ammonia for pH = 4-9.

Sample preparation: Honey was subjected to wet-acid digestion to disrupt the organic substances and release metals from the complex sample matrix into solution. A safety reflux wet acid digestion with HNO_3 and $HClO_4$ was performed in semi-enclosed system which consisted of a condenser attached to a round bottom flask. This method overcomes the traditional wet acid digestion by avoiding losses of metal species by sample spattering and foaming and reduces chances of sample contamination. An additional advantage of this procedure is the reduction of nitric acid losses by re-condensing its vapour. This method also overcomes microwave-oven digestion through the relatively huge sample quantity that can be digested. In general the disadvantage of this procedure is the quantities of reagents and the long digestion time.

Digestion procedure: A 5 g quantity of honey placed in a round bottom flask with 20 mL of concentrated HNO_3, 3 mL of $HClO_4$ and 10 mL of R.O. water. The round bottom flask heated and stirred at 100 ºC under reflux inside a fume hood for *ca.* 2 h until the end of NO_2 gas emission. The digestion procedure is continued by transforming the flask content into a beaker and washing the flask twice by RO water. The beaker content is evaporated to near dryness. If the colour of the reacting mixture (after the nitric acid and the water are completely evaporated) begins to dim, 0.5 mL of concentrated nitric acid is added until the final resulting solution is clearly colourless. The resulting solution is diluted with R.O. water to about 25 mL. Blank was prepared as illustrated above without adding of honey.

Preconcentration procedure

Cartridges conditioning: The column was washed with one column volume methanol, then two column volumes of ammonia buffer, which was adjusted with ammonia solution to pH = 7.5 for C_{18}ec cartridges and to pH = 8 for C_6H_5 M.S. cartridges.

Sorption on C_{18}ec cartridge: First, 150 μL of concentrated CH_3COOH and 250 μL of 0.5 % 8-hydroxyquinoline

TABLE-1
FAAS INSTRUMENTAL PARAMETERS USED TO DETERMINE METAL IONS (WITH 90 % METHANOL RATIO)

	Wavelength (nm)	Lamp current (mA)	Lamp max. current (mA)	Slit width (nm)	C_2H_2 flow (L/min)	Air flow (L/min)	Burner height (mm)
Cu	324.3	4.0	5.0	1.3	1.0	15	5.0
Fe	248.3	8.0	15	0.2	1.4	15	5.0
Mn	279.5	7.5	12	0.4	1.2	15	5.0
Ni	232.0	8.5	15	0.2	1.2	15	5.0
Zn	213.9	6.5	10	1.3	1.0	15	5.0

solution in 0.5M HCl were added by micropipette to the diluted digested honey solution. The resultant solution was adjusted to pH = 7.5 by ammonia solution and passed completely through the activated cartridge. The beaker was rinsed twice with 2 mL of ammonia buffer and added to the cartridge; then the cartridge was relatively dried.

Sorption on C_6H_5 M.S. cartridge: First, 150 µL of concentrated CH_3COOH and 400 µL of 1 % aqueous sodium diethyldithiocarbamate solution were added by micropipette to the diluted digested honey solution. The resultant solution was adjusted to pH = 8 by ammonia solution and passed completely through the activated cartridge, the beaker was rinsed twice with 2 mL of ammonia buffer and added to the cartridge; then the cartridge was relatively dried.

Elution: After transferring the sample into the cartridge (C_{18}ec or C_6H_5 M.S.), the retained species (metal-ligand) on the modified silica was eluted directly into 5 mL volumetric flask by the following eluents: 2 mL of methanol, 0.5 mL of 1M HNO_3, 2.5 mL of methanol successively. Finally the solution was analyzed by FAAS. After elution, both cartridges were washed by 5 mL of methanol and dried for using them in the next analysis.

RESULTS AND DISCUSSION

Effect of pH on the metals recovery: The influences of pH on the recoveries of analyte ions on C_{18}ec and C_6H_5 M.S. were investigated in the pH range 4-9. The change of recovery of metals with pH is shown in Fig. 2a-b. The analyte ions were quantitatively recovered in the pH range of 7.5-8.0. According to the results, the optimum pH for all the analytes was determined as 7.5 for C_{18}ec cartridges and 8 for C_6H_5 M.S. cartridges.

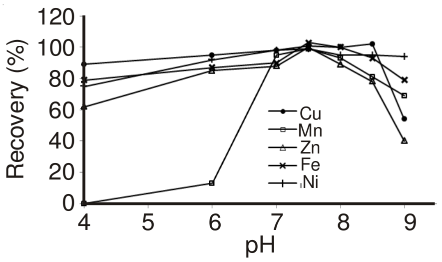


Fig. 2. (a) Effects of pH on the recoveries of metal ions-8-HQ complexes on C_{18}ec. Eluent: 2 mL MeOH + 0.5 mL HNO_3 1M + 2.5 mL MeOH, N = 4

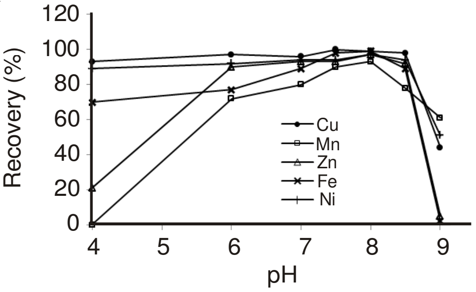


Fig. 2. (b) Effects of pH on the recoveries of metal ions-DDTC complexes on C_6H_5 M.S. Eluent: 2 mL MeOH + 0.5 mL HNO_3 1M + 2.5 mL MeOH, N = 4

Effect of ligand concentration: The effects of 8-HQ and NaDDTC concentration on the adsorption of studied metals on the C_{18}ec and C_6H_5 M.S. were investigated by using the model solution. It was found that, the recoveries of the metal ions increase with increasing concentrations of 8-HQ and NaDDTC added and reach a constant value (96-100 %) with at least 120 µL of 0.5 % 8-HQ for C_{18}ec cartridges and 200 µL of 1 % NaDDTC for C_6H_5-M.S. cartridges. After this point the recoveries became constant. In all further studies 250 µL of 0.5 % 8-HQ and 400 µL of 1 % NaDDTC were used to ensure that the optimum recoveries of all studied metals in different honey samples were obtained.

Desorption studies (eluent type and volume): The desorption of the retained metal-8-HQ and metal-DDTC chelates on the C_{18}ec and C_6H_5 M.S. cartridges, respectively, were tested by using model solution at pH 7.5 for C_{18}ec and pH = 8 for C_6H_5 M.S. Various methanol and nitric acid mixtures were used to identify the best elution. The results are summarized in Table-2. The preferred eluent for both phases was found to be (2 mL of MeOH + 0.5 mL of 1M HNO_3 + 2.5 mL of MeOH) where the recoveries were (> 95 %) for all metal ions, (except Mn with phenyl cartridge which reached 92 %). Also the high ratio (90 %) of methanol in the eluted solution increased the sensitivity of FAAS determination Fig. 3.

The volume of eluent is important for the high concentration factor. The smallest volume of the chosen eluent mixture for the quantitative elution was found to be as 5 mL for both phases in the range of the studied metal concentrations.

Sample and eluent flow rates: The proposed SPE stand flow rate can be controlled by the pulling strength of the scalar plastic syringe. The optimum sample and eluent flow rates were found to be 2-5 mL/min for both cartridges.

TABLE-2
EFFECT OF ELUENT TYPE ON THE RECOVERY OF THE INVESTIGATED IONS
(pH = 7 FOR C_{18}ec AND pH = 8 FOR C_6H_5 M.S., SAMPLE VOLUME: 25 mL, N = 3)

Eluent	Cu		Mn		Zn		Fe		Ni	
	C_{18}ec	C_6H_5	C_{18}ec	C_6H_5	C_{18}ec	C_6H_5	C_{18}ec	C_6H_5	C_{18}ec	C_6H_5
0.5M HNO_3	100 ± 5	> 5	96 ± 2	85 ± 3	73 ± 3	13	98 ± 6	> 5	100 ± 4	> 5
1M HNO_3	96 ± 4	> 5	84 ± 3	87 ± 5	70 ± 4	23	100 ± 6	> 5	100 ± 3	> 5
2 mL MeOH + 0.5 mL $HNO_3$1M + 2.5mL MeOH	100 ± 2	98 ± 3	98 ± 2	92 ± 4	100 ± 1	96 ± 3	99 ± 1	97 ± 2	100 ± 1	97 ± 3
2 mL MeOH + 1 mL HNO_3 1M + 2 mL MeOH	98 ± 3	98 ± 2	92 ± 1	84 ± 3	99 ± 1	97 ± 1	87 ± 4	84 ± 5	97 ± 3	88 ± 3
4.5 mL of 0.5M HNO_3 in MeOH	99 ± 1	90 ± 2	96 ± 1	82 ± 2	96 ± 4	90 ± 3	94 ± 2	95 ± 1	95 ± 2	82 ± 2
4.5 ml of MeOH*	96 ± 2	92 ± 3	76 ± 2	> 5	63 ± 5	> 5	88 ± 4	45	98 ± 4	90 ± 2

*50 µL of concentrated HNO_3 was added to the eluted solution before FAAS measurement.

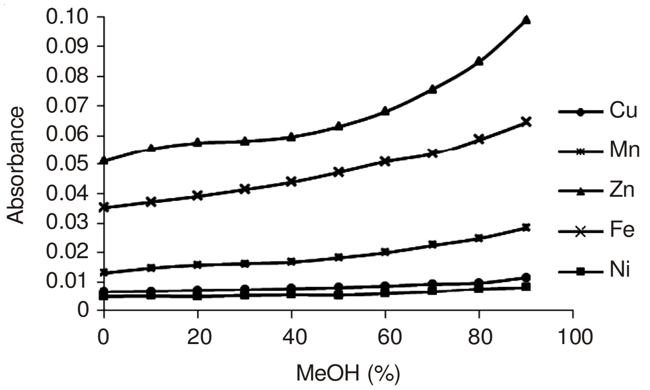


Fig. 3. Effect of methanol ratio in the solution on the absorbance of analytes

Sample volume: Due to the low concentrations of trace metals in real samples, the sample volume is one of the most important parameters for obtaining high preconcentration factors. Therefore the effect of sample volume on the retention behaviour of the analytes was examined in the 5-300 mL range. The recoveries of the analytes were quantitative in the studied range for C_{18}ec phase, but for C_6H_5 M.S. phase the recoveries of the analytes were quantitative until 250 mL and decreased especially for Mn and Cu at higher volumes.

Effect of diverse ions on recovery: The effect of some foreign ions which interfere with the determination of metal ions by the proposed methods and often accompanied analyte ions in various real samples, was examined. The results are summarized in Table-3. As it is seen, a number of studied cations have no considerable effect on the determination of analyte ions. Hence, the presented method can be applied to honey.

Analytical performance: The detection limit was calculated as *sb* + 3*s*, where *sb* is the average signal of 10 blank injections (absolute value) and *s* is the standard deviation. The quantification limit was calculated as *sb* + 10*s*. The detection limits for Cu(II), Mn(II), Zn(II), Fe(III) and Ni(II) were found as 5.70, 0.10, 0.88, 5.73 and 7.54 µg/L respectively. The quantification limits for last cations were found to be 14.80, 6.20, 1.97, 17.59 and 24, 29 µg/L, respectively.

The calibration curves for analyte ions were drawn after setting various parameters of FAAS including wavelength, slit width, lamp current at an optimum level (Table-1). The optimum concentration ranges and regression equations for analytes were given in Table-4. The precision of the method was investigated by using solutions containing the elements on the optimal conditions of the method (Table-4).

To estimate the recovery by standard addition method, different amounts of the investigated metal ions were mixed with 5 g of honey and subjected to the procedure given in Experimental section. The results were given in Table-5. The recovery percentages of analyte ions were evaluated and the results showed that the real sample matrixes did not affect the recovery of the trace metals (Table-5).

Application of the method on honey samples: The method was applied to natural honey samples collected from three locations in Syria. The results are shown in Table-6.

Conclusion

The good features of the proposed methods showed that they are convenient and low cost. Instead of the use of fresh solvent as an extracting phase for each sample, the reusability of C_{18}ec and C_6H_5 M.S. cartridges was as high as more than 40 cycles without any loss in their sorption behaviour. The possible interference of some alkaline and earth alkaline ions to the analysis were investigated and an important interference was not encountered. Comparison of C_{18}ec/8-HQ and C_6H_5 M.S./NaDDTC methods showed that C_{18}ec/8-HQ method has higher recoveries for the studied ions than C_6H_5 M.S./NaDDTC method. The result of analyzing 25 Syrian honey sample collected from different botanical and geographical areas showed that amounts of analyzed metals agree with those from Mediterranean region.

TABLE-3
MATRIX IONS AND THE RECOVERY OF THE METAL IONS (pH = 7 FOR C18ec AND pH = 8 FOR C_6H_5 M.S, SAMPLE VOLUME: 10 mL, N=3)

Cation	Conc. (ppm)	Cu		Mn		Zn		Fe		Ni	
		C_{18}ec	C_6H_5	C_{18}ec	C_6H_5	C_{18}ec	C_6H_5	C_{18}ec	C_6H_5	C_{18}ec	C_6H_5
Na^+	1000	102 ± 3	100 ± 4	94 ± 3	89 ± 5	98 ± 3	93 ± 5	85 ± 4	97 ± 2	100 ± 1	95 ± 2
Ca^{2+}	500	103 ± 2	99 ± 3	99 ± 2	79 ± 4	102 ± 2	100 ± 3	104 ± 2	93 ± 7	103 ± 3	103 ± 3
Mg^{2+}	1000	97 ± 4	99 ± 2	98 ± 2	92 ± 4	97 ± 4	95 ± 3	102 ± 5	104 ± 3	102 ± 2	101 ± 4
Cu^{2+}	1	–	–	101 ± 4	99 ± 2	87 ± 5	86 ± 6	100 ± 2	87 ± 4	100 ± 3	97 ± 2
Mn^{2+}	5	89 ± 2	100 ± 3	–	–	103 ± 2	101 ± 4	102 ± 3	89 ± 3	91 ± 2	85 ± 3
Zn^{2+}	5	83 ± 5	98 ± 3	102 ± 4	100 ± 3	–	–	90 ± 3	87 ± 2	100 ± 3	95 ± 2
Fe^{2+}	5	100 ± 3	96 ± 2	100 ± 3	98 ± 5	100 ± 3	96 ± 2	–	–	100 ± 2	94 ± 4
Ni^{2+}	2.5	93 ± 4	90 ± 6	100 ± 2	88 ± 5	103 ± 2	97 ± 4	93 ± 2	96 ± 3	–	–
NH_4^+	1000	99 ± 2	98 ± 3	97 ± 2	93 ± 2	99 ± 2	96 ± 3	100 ± 2	96 ± 4	99 ± 2	98 ± 2

TABLE-4
ANALYTICAL CHARACTERISTICS OF THE CALIBRATION CURVES OF THE ANALYTES (WITH 90 % METHANOL RATIO)

Analyte	Correlation coefficient	Linear range (mg/L)	Regression equation	RSD % (N = 5)
Cu	0.9998	0.10-4.00	A = 0.0568C + 0.0006	3.57
Mn	0.9999	0.05-2.20	A = 0.1391C + 0.0012	3.90
Zn	0.9997	0.01-0.54	A = 0.4594C + 0.0013	2.70
Fe	0.9998	0.10-3.00	A = 0.0786C - 0.0018	1.09
Ni	0.9999	0.05-2.60	A = 0.0871C + 0.0001	2.33

TABLE-5
ANALYSIS OF NATURAL HONEY SPIKED ANALYTE IONS
(pH = 7 FOR C_{18}ec AND pH = 8 FOR C_6H_5 M.S., SAMPLE VOLUME: 10 mL, N = 5)

Analyte	Added (μg)	Found (μg)*		Recovery (%)	
		C_{18}ec	C_6H_5	C_{18}ec	C_6H_5
Cu	0	–	–	–	–
	1	0.99 ± 0.02	0.97 ± 0.01	99	97
	2	1.97 ± 0.03	1.95 ± 0.03	99	98
Mn	0	–	–	–	–
	1	0.95 ± 0.03	0.90 ± 0.04	95	90
	2	1.96 ± 0.04	1.84 ± 0.09	98	92
Zn	0	–	–	–	–
	1	1.00 ± 0.01	0.93 ± 0.02	99	93
	2	1.94 ± 0.04	1.94 ± 0.08	97	97
Fe	0	–	–	–	–
	2	1.97 ± 0.03	1.93 ± 0.07	99	97
	4	4.03 ± 0.10	3.84 ± 0.16	101	96
Ni	0	–	–	–	–
	1	1.02 ± 0.03	0.97 ± 0.05	101	97
	2	1.94 ± 0.07	1,90 ± 0.09	97	95

*Values here are after the subtraction of metal amounts existed in the natural honey sample.

TABLE-6
APPLICATION OF PRESENTED METHODS AND GF-AAS IN 25 SYRIAN HONEY SAMPLES FOR CONTENTS OF ANALYTE IONS (N = 5), HONEY SAMPLES FOR GF-AAS MEASUREMENT WAS PREPARED WITHOUT MINERALIZATION BY APPROPRIATE HONEY DILUTION[1]

Sample's geographical and botanical origin	Element concentration (μg/g)$_{(honey)}$														
	Cu			Mn			Fe			Zn			Ni		
	C_{18}ec	C_6H_5	GF-AAS	C_{18}ec	C_6H_5	GF-AAS	C_{18}ec	C_6H_5	GF-AAS	C_{18}ec	C_6H_5	GF-AAS	C_{18}ec	C_6H_5	GF-AAS
Latakia (Alrdimia) Citrus	0.172 ± 0.005	0.170 ± 0.006	0.170 ± 0.007	0.540 ± 0.003	0.508 ± 0.005	0.543 ± 0.035	4.041 ± 0.029	4.015 ± 0.032	4.123 ± 0.154	4.311 ± 0.034	4.307 ± 0.061	4.347 ± 0.233	0.061 ± 0.002	0.060 ± 0.002	0.062 ± 0.007
Latakia (Alkurdaha) Citrus	0.296 ± 0.005	0.272 ± 0.006	0.293 ± 0.011	0.236 ± 0.004	0.217 ± 0.005	0.233 ± 0.011	10.664 ± 0.029	10.668 ± 0.017	10.766 ± 0.282	23.268 ± 1.064	21.777 ± 1.043	23.462 ± 0.079	0.052 ± 0.002	0.048 ± 0.002	0.050 ± 0.003
Latakia (vidio) Citrus	0.253 ± 0.006	0.247 ± 0.008	0.2532 ± 0.003	0.205 ± 0.003	0.201 ± 0.004	0.212 ± 0.015	3.748 ± 0.017	3.671 ± 0.012	3.836 ± 0.041	6.852 ± 0.058	6.3299 ± 0.073	6.994 ± 0.204	0.049 ± 0.003	0.046 ± 0.002	0.048 ± 0.004
Latakia Citrus	0.209 ± 0.006	0.199 ± 0.004	0.2043 ± 0.013	0.258 ± 0.004	0.239 ± 0.005	0.258 ± 0.003	1.966 ± 0.012	1.921 ± 0.019	1.983 ± 0.087	8.456 ± 0.080	8.3567 ± 0.135	8.502 ± 0.212	0.047 ± 0.002	0.045 ± 0.002	0.047 ± 0.003
Latakia (Basa) Citrus+ Coriander	0.446 ± 0.005	0.442 ± 0.006	0.449 ± 0.018	0.246 ± 0.004	0.230 ± 0.005	0.249 ± 0.005	2.055 ± 0.026	2.025 ± 0.039	2.064 ± 0.091	2.733 ± 0.044	2.715 ± 0.053	2.647 ± 0.141	0.066 ± 0.002	0.063 ± 0.002	0.066 ± 0.006
Latakia- Idleb Citrus	0.097 ± 0.005	0.097 ± 0.005	0.099 ± 0.001	0.220 ± 0.003	0.197 ± 0.007	0.221 ± 0.021	2.367 ± 0.013	2.283 ± 0.023	2.355 ± 0.059	4.625 ± 0.052	4.503 ± 0.064	4.842 ± 0.141	0.115 ± 0.002	0.108 ± 0.003	0.114 ± 0.007
Latakia-Citrus	0.150 ± 0.005	0.146 ± 0.007	0.146 ± 0.006	0.279 ± 0.004	0.261 ± 0.007	0.280 ± 0.013	3.109 ± 0.041	3.055 ± 0.040	3.158 ± 0.133	3.565 ± 0.036	3.511 ± 0.061	3.586 ± 0.023	0.058 ± 0.002	0.056 ± 0.002	0.057 ± 0.005
Latakia Citrus	0.101 ± 0.004	0.097 ± 0.005	0.102 ± 0.005	0.727 ± 0.003	0.670 ± 0.005	0.733 ± 0.003	2.591 ± 0.021	2.468 ± 0.026	2.595 ± 0.027	8.803 ± 0.097	8.755 ± 0.090	8.794 ± 0.120	0.127 ± 0.002	0.124 ± 0.003	0.127 ± 0.003
Latakia Citrus	0.127 ± 0.005	0.126 ± 0.005	0.127 ± 0.009	0.169 ± 0.004	0.154 ± 0.006	0.170 ± 0.014	4.735 ± 0.035	4.596 ± 0.066	4.743 ± 0.027	2.443 ± 0.022	2.290 ± 0.043	2.459 ± 0.092	0.049 ± 0.002	0.046 ± 0.002	0.047 ± 0.004
Idleb -Citrus+ Polychaetes	0.173 ± 0.005	0.167 ± 0.005	0.169 ± 0.001	0.199 ± 0.006	0.162 ± 0.006	0.182 ± 0.018	2.375 ± 0.027	2.316 ± 0.029	2.380 ± 0.062	4.009 ± 0.037	3.893 ± 0.067	4.029 ± 0.064	0.070 ± 0.002	0.068 ± 0.002	0.071 ± 0.006
Latakia-Citrus + mountainous wild plants	0.184 ± 0.005	0.181 ± 0.005	0.183 ± 0.015	0.370 ± 0.004	0.344 ± 0.004	0.376 ± 0.020	2.356 ± 0.026	2.314 ± 0.028	2.359 ± 0.130	3.140 ± 0.022	2.979 ± 0.055	3.146 ± 0.049	0.062 ± 0.002	0.060 ± 0.002	0.063 ± 0.005
Hama- Citrus+ Coriander+ Anise	0.187 ± 0.005	0.184 ± 0.006	0.184 ± 0.003	0.391 ± 0.003	0.361 ± 0.007	0.392 ± 0.031	2.313 ± 0.025	2.302 ± 0.039	2.337 ± 0.126	3.176 ± 0.057	3.017 ± 0.068	3.268 ± 0.066	0.107 ± 0.002	0.104 ± 0.002	0.107 ± 0.005
Idleb (Has) summer flowers	0.117 ± 0.004	0.115 ± 0.004	0.117 ± 0.008	0.540 ± 0.003	0.508 ± 0.005	0.543 ± 0.035	1.569 ± 0.015	1.585 ± 0.025	1.634 ± 0.026	4.172 ± 0.048	4.039 ± 0.038	4.188 ± 0.010	0.038 ± 0.002	0.037 ± 0.003	0.040 ± 0.005
Idleb (Has) Eucalyptus+ Elm	0.163 ± 0.005	0.156 ± 0.005	0.158 ± 0.005	0.236 ± 0.004	0.217 ± 0.005	0.233 ± 0.011	1.936 ± 0.027	1.879 ± 0.046	1.945 ± 0.050	2.933 ± 0.048	2.778 ± 0.064	2.923 ± 0.051	0.048 ± 0.002	0.048 ± 0.003	0.049 ± 0.002
Homs Anise	0.177 ± 0.003	0.169 ± 0.006	0.171 ± 0.015	0.205 ± 0.003	0.2012 ± 0.004	0.212 ± 0.015	2.673 ± 0.016	2.636 ± 0.025	2.725 ± 0.044	1.458 ± 0.022	1.309 ± 0.031	1.491 ± 0.007	0.043 ± 0.002	0.043 ± 0.003	0.044 ± 0.004
Homs-Coriander+ Polychaetes	0.199 ± 0.003	0.196 ± 0.004	0.202 ± 0.005	0.258 ± 0.004	0.239 ± 0.005	0.258 ± 0.003	4.294 ± 0.017	4.224 ± 0.014	4.329 ± 0.105	7.219 ± 0.062	6.969 ± 0.102	7.290 ± 0.037	0.048 ± 0.002	0.047 ± 0.003	0.048 ± 0.003
Homs -Coriander+ Polychaetes	0.322 ± 0.003	0.311 ± 0.003	0.320 ± 0.003	0.246 ± 0.004	0.230 ± 0.005	0.249 ± 0.005	6.629 ± 0.047	6.570 ± 0.014	6.657 ± 0.246	8.844 ± 0.051	8.541 ± 0.036	8.847 ± 0.414	0.055 ± 0.002	0.053 ± 0.002	0.056 ± 0.006
Homs Anise	1.529 ± 0.010	1.494 ± 0.022	1.522 ± 0.056	0.220 ± 0.003	0.197 ± 0.007	0.221 ± 0.021	3.641 ± 0.014	3.567 ± 0.025	3.686 ± 0.118	13.365 ± 0.197	13.103 ± 0.304	13.584 ± 0.051	0.165 ± 0.003	0.161 ± 0.003	0.167 ± 0.010
(Homs-Jablah-Idleb)-Citrus+ Coriander+ Anise	0.216 ± 0.006	0.209 ± 0.003	0.218 ± 0.015	0.279 ± 0.004	0.261 ± 0.007	0.280 ± 0.013	3.998 ± 0.015	3.858 ± 0.038	3.994 ± 0.031	1.633 ± 0.027	1.582 ± 0.060	1.642 ± 0.062	0.048 ± 0.002	0.048 ± 0.002	0.049 ± 0.003
Aleppo(Sphera) Cottons+sesame	0.341 ± 0.004	0.326 ± 0.006	0.333 ± 0.017	0.727 ± 0.003	0.670 ± 0.005	0.733 ± 0.003	3.449 ± 0.033	3.380 ± 0.060	3.495 ± 0.106	3.292 ± 0.060	3.136 ± 0.067	3.329 ± 0.049	0.048 ± 0.002	0.048 ± 0.002	0.049 ± 0.003
Idleb-euphorbia helioscopia+Camel thorn	0.282 ± 0.006	0.271 ± 0.008	0.276 ± 0.006	0.169 ± 0.004	0.154 ± 0.006	0.170 ± 0.014	4.526 ± 0.028	4.447 ± 0.043	4.577 ± 0.161	6.820 ± 0.066	6.705 ± 0.070	6.835 ± 0.062	0.066 ± 0.002	0.065 ± 0.002	0.065 ± 0.001
Idleb-Coriander+wild plants	0.159 ± 0.005	0.154 ± 0.005	0.158 ± 0.004	0.199 ± 0.006	0.162 ± 0.006	0.182 ± 0.018	2.985 ± 0.032	2.928 ± 0.077	3.059 ± 0.079	2.661 ± 0.038	2.660 ± 0.068	2.671 ± 0.027	0.044 ± 0.002	0.042 ± 0.003	0.046 ± 0.005
Idleb Mountainous honey	0.268 ± 0.006	0.261 ± 0.007	0.266 ± 0.019	0.370 ± 0.004	0.344 ± 0.004	0.376 ± 0.020	3.095 ± 0.019	3.012 ± 0.028	3.109 ± 0.110	5.429 ± 0.052	5.314 ± 0.073	5.418 ± 0.014	0.126 ± 0.002	0.122 ± 0.003	0.126 ± 0.005
Raka- Cotton+ wild plants	0.504 ± 0.004	0.493 ± 0.008	0.503 ± 0.012	0.391 ± 0.003	0.361 ± 0.007	0.392 ± 0.031	2.636 ± 0.039	2.559 ± 0.038	2.653 ± 0.094	3.772 ± 0.053	3.636 ± 0.069	3.761 ± 0.047	0.083 ± 0.002	0.082 ± 0.002	0.084 ± 0.003
Aleppo (Hayan) Regional plants	0.295 ± 0.005	0.290 ± 0.005	0.288 ± 0.019	0.540 ± 0.003	0.508 ± 0.005	0.543 ± 0.035	6.400 ± 0.018	6.228 ± 0.037	6.406 ± 0.176	7.991 ± 0.057	7.830 ± 0.086	7.994 ± 0.017	0.103 ± 0.002	0.102 ± 0.003	0.105 ± 0.010

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