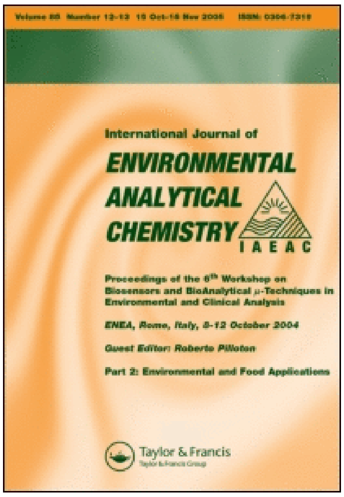

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MULTI-ELEMENT ANALYSIS OF DRY-ASHED HONEY SAMPLES BY THICK-TARGET PIXE

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Honey samples were dry ashed at 550°C and the ashes were directly analysed with the Thick-Target Particle Induced X-ray Emission (TTPIXE) technique. The elements P, K, Ca, Mn, Fe, Ni, Cu, Zn, Pb, Rb and Sr, were analysed quantitatively. The method allowed the determination of concentrations well below 100 ng/g for most of the elements studied. The ash content can be used for characterization of a honey sample. The samples were collected from two areas in Finland and from the Prague region in the Czech Republic. A Cu-Ni smelter, documented as a source of heavy-metal emission, is situated in one of the areas in Finland. A comparison of metal concentrations in ashes of honey samples proved to be useful for environmental monitoring.

Keywords: Honey; dry ashing; PIXE; multi-element analysis; heavy metals

INTRODUCTION

Honey consists to about 80% of sugars, mainly glucose and fructose. Water contents of 13-27% have been reported.[1–4] Koivistoinen found 18% of water in Finnish honey samples.[5] Honey also contains minute amounts of mineral elements which originate in the plants, and hence vary in different honeys.[1–3] Potassium is reported to be the mineral element of highest concentration in honey. The ash content of a nectar honey is typically about 0.1% but can be up to 1% in a honey-dew honey.[1–3] The ash content is a measure of the amount of inorganic components in a biological material.

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Honey is produced mainly from nectar and honey dew, which the bees collect, process and store in their combs. Both nectar and honey dew originate from the phloem sap of higher plants. Honey dew is produced by certain plant-sucking insects belonging to the order *Rhynchota*. Unlike bees these insects have mouth-parts to pierce plant surfaces and can thus use phloem sap as their food. The insects excrete small drops of a sugar containing substance, called honey dew, which is found on the surface of leaves and twigs and is collected by bees and other insects.[1–3]

Because bees sample large areas there has been some interest towards the use of honey as an indicator of environmental pollution. In the studies of honey for monitoring heavy metal emission, only a few metals have generally been analysed. The wet-chemical methods of analyses in these studies include a digestion procedure to bring the sample into solution. Atomic absorption spectrometry (AAS) has been mostly used to analyse the solutions. Jones[6] used graphite furnace AAS (GFAAS) to analyse Ag, Cd, Cu and Pb in honey samples collected through the UK. The same technique was used by Stein and Umland[7] to analyse Pb, Cd and Mn in honey samples collected in Germany. Cimino *et al.* also used GFAAS in their study of the impact of volcanic activity on the chemical composition of honey.[8] Bohacenko *et al.*[9] determined Pb, Cd, Zn and Cu in honey by polarography.

With the Particle Induced X-ray Emission (PIXE) technique solid samples can be directly analysed. The PIXE-technique was introduced at the beginning of the 70s[10] and has since then found its place as a well-established analytical technique.[11] We have used Thick-target PIXE (TTPIXE) for environmental monitoring in earlier studies.[12,13] TTPIXE is a sensitive technique compared with other methods enabling direct analyses of solid materials. The detection limit for heavy metals is 1–10 μg/g. The technique cannot be directly applied in the analyses of honey due to an impressive swelling of the honey sample during the irradiation causing an unstable geometry and thereby disabling a reliable quantification. However, ashes of honey can be easily analysed with TTPIXE.

Due to the low ash content of honey high enrichment factors can be achieved by dry-ashing. Good geometrical stability and high sensitivity are gained in the direct analyses of ashes with TTPIXE. A method has been earlier evaluated for the calibration of the analyses of ashed biological materials using ashes of certified reference materials (CRMs). It was shown that analytical errors due to matrix effects are negligible when ashes of biological materials are analysed with PIXE.[14] In this work the method is utilized for evaluating honey as an indicator of heavy-metal emission, a serious environmental problem today and far in the future. Because honey is a food agent a knowledge of its elemental

FIGURE 1 Map showing the locations of the sampling areas in Finland.

content is also of interest. The ashes of honey collected from three regions were studied. In one of the areas in Finland a Cu-Ni smelter is situated. The other area is relatively unpolluted. The samples from the Czech Republic represented a different type of honey.

EXPERIMENTAL SECTION

Sample Collection and Treatment

Honey samples were collected during the first two weeks of July 1992 from areas around Harjavalta and Mikkeli. Both areas are situated at the same latitude in southern Finland, Harjavalta in the west and Mikkeli in the east (Figure 1). Honey samples were also collected from the Prague region in the Czech Republic.

A copper-nickel smelter is situated in Harjavalta. It started its activity in 1945. The smelter is well documented as the largest point source of emission of these two metals in Finland.[15] Samples from the Harjavalta region were collected at different distances from the smelter. The Mikkeli region on the other hand is known to be relatively unpolluted.

The honey samples were collected from beekeepers. Pieces of honey with wax were cut out from the frames. The honey was separated from the wax by placing the samples in a plastic funnel on the top of a polyethene bottle. The funnel with the sample and the bottle were placed in a warming cupboard at 40–50 °C. At this temperature the honey was liquefied and could be collected into the bottle. The bottle was sealed and stored until the ashing of the honey. All laboratory vessels used (funnels, bottles, crucibles, glass rods etc.) were acid washed using concentrated hydrochloric acid (analytical reagent grade) and deionised water.

Ashing of the Honey Samples

The following procedure was developed for the ashing of honey samples to avoid problems caused by foaming of the honey at the beginning of the heating.[16] Five to ten grams of honey was weighed to a porcelain crucible and placed in an electric oven. The temperature was increased at a rate of about 1°C/min to 250 °C and then kept stable until the samples were fully carbonized. The voluminous material was crushed with a glass rod before slowly increasing the temperature to 550 °C. The honey samples were kept in the oven at this temperature overnight. After cooling in a desiccator the crucible with the remaining ashes was weighed. This enabled the determination of the ash content of the samples. The ashed samples were stored in the desiccator until the target preparation.

Target Preparation

The targets were prepared with a slightly modified version of an earlier procedure.[14] A pelletizing device was used. A pellet of spectroscopically pure graphite was made using low pressure. The plug of the pelletizing device was removed and a small cavity was made in the graphite surface by rotating a glass rod. The ashes were placed in the depression at the center of the pellet. A metal disc was placed on the top of the material. The plug was replaced and the final pellet pressed using a higher pressure. The small cavity minimized the risk of the ashes falling of the pellet surface. The pellet amended with ashes on the front surface was placed in a plastic sample holder and stored in a desiccator until analysed.

Instrumental

A proton beam of 3 MeV from the Åbo Akademi MGC-20 cyclotron was used to generate X-rays in the sample. The proton beam exiting the accelerator vacuum and hitting the sample was collimated to a diameter of 1 mm. The X-rays were detected with an Intrinsic Germanium Planar (IGP) detector (Figure 2).

The areas of individual peaks, representing specific elements, in the X-ray spectrum are proportional to the concentrations of the elements in the sample,

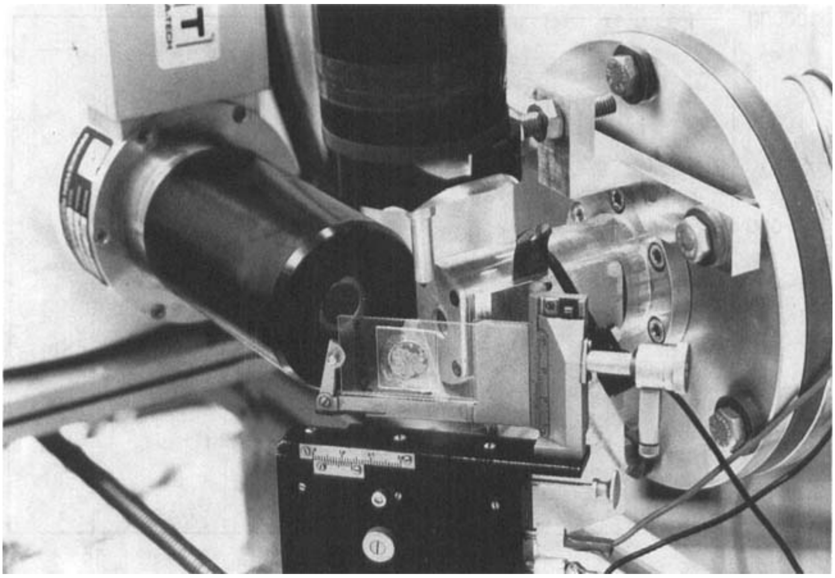

FIGURE 2 The PIXE-setup with pellet-target (front), IGP detector (left), PM-tube (up) and exit window for particle beam out of cyclotron-vacuum system (right).

the irradiation time and the intensity of the proton beam. Therefore it is necessary to normalize the peak areas with respect to the number of protons incident on the sample material during irradiation (the integrated charge).

The integrated charge is indirectly measured utilizing the light emission in air during irradiation. After exiting the cyclotron vacuum through a 7.5 μm thick Kapton foil the proton beam induces light emission in air in the beam path. The beam path in air can be seen, by the naked eye, as a blue line. A photomultiplier (PM) tube is used for measuring the intensity of the light induced by the proton beam.[17] The PM-tube current is integrated over the time of irradiation of the sample. This integrated value, proportional to the number of protons incident on the sample material, is used for the normalization of the recorded X-ray peak areas.

During the analyses an absorber, a so called funny filter, placed in front of the detector window, was used. This filter consists of 3 mm thick polycarbonate with a 0.5 mm diameter drilled hole in the center. Using this filter we obtained PIXE spectra in which the high yields of low energy X-rays, from lighter main elements, were suppressed relative to the yields from heavier elements. This increased the analytical sensitivity for the heavy metals which were of interest

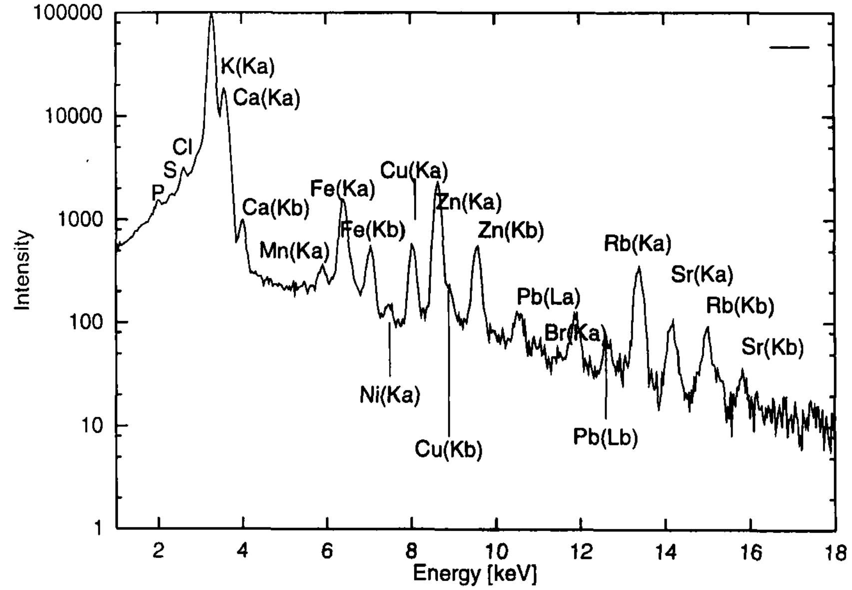

FIGURE 3 PIXE-spectrum obtained from ashed honey from the Prague region. A funny filter in front of the detector window was used to improve the analytical sensitivity for heavier elements.

in this study. An X-ray spectrum of honey ashes is shown in Figure 3. Further information about the instrumentation can be found elsewhere.[14,17]

Calibration

The ashes of the standard reference material (SRM) Tomato Leaves 1573 from the National Institute of Science and Technology (NIST), Gaithersburg, MA, USA, were used for calibration of the analyses. The concentration of nickel was not certified for this SRM. Therefore a sample of Pine Needles 1575 (NIST) was ashed and used for the quantification of the nickel peaks in the X-ray spectra. Both the SRMs used for calibration and the samples were irradiated for 10 minutes each, changing irradiation spot every second minute.

RESULTS AND DISCUSSION

In studies on the use of honey as a bioindicator material the elemental concentrations have been given for fresh honey i.e. on wet-weight basis. This is convenient due to the hygroscopic nature of honey. In the present work the mean water content of Finnish honey samples was 18.6 % (SD = 0.9 for n = 5).

TABLE I Results of three analyses of a honey sample (three ashings and PIXE analyses of each ash). The mean concentrations in ashes and fresh honey with corresponding deviations are given.

Element	*Energy [keV]*	*Ashed honey*		*Fresh honey*	
		Conc. [‰]	*RSD [%]*	*Conc. [μg/g]*	*RSD [%]*
Ash [%]				*0.123*	*8*
P	2.01	24	15	23	21
K	3.32	256	9	318	12
Ca	4.02	19.7	10	23.5	13
Mn	5.89	1.01	5	1.25	9
Fe	7.01	1.90	18	2.31	13
Ni	7.48	0.28	12	0.34	4
Cu	8.05	0.46	25	0.56	22
Zn	8.64	0.43	15	0.52	10
Pb	10.55	0.055	18	0.067	11
Rb	13.38	0.50	12	0.61	14
Sr	14.15	0.082	10	0.101	10

The concentrations of eleven elements were determined in the honey samples. In addition to these elements, Ba and Ti were detected in some of the samples. Bromine was detected in all of the samples. Fluorine (gamma line at 109.89 keV) as well as S and Cl were also detected in many of the samples although the setup was not optimized for the determination of these elements. It must be mentioned that halogenides and sulfur can be partly lost during ashing. The extent of loss depends on the composition of the material studied.[14]

In Table I the results from PIXE-analyses of three different ashes obtained from the same honey sample are given both as concentrations in ash and as concentrations in honey. The elemental concentrations in the honey were calculated from the respective ash contents. These results give an estimate of the reproducibility of the whole analytical procedure. Heavy metals can be detected at levels well below 100 ng/g in honey by the method used.

The RSD value given for the ash percentages in Table I indicates the practical problems related to dry ashing of honey. For dry ashing of other biological materials, e. g. plants, RSD values in the range 0.5–2 % have been obtained.[14] However, RSD values below 10% can be considered satisfactory for practical environmental analysis.

The results of the PIXE analyses of honey samples, collected from the polluted area around Harjavalta, are presented in Table II. Samples from locations at five different distances, 3–48 km from the Cu-Ni smelter were studied. Three samples, each from a separate hive at each location, were analysed. The mean values and corresponding relative standard deviations are presented in Table II. The elemental concentrations for each fresh honey sample were calculated using its ash content. Lead was detected in only one of the samples from site 2 and

TABLE II.1 Analyses of 15 samples collected at 5 sites around the Harjavalta metal-smelter. Each pair of columns represent the result of analyses of three samples collected from the same locality (three different hives), except site 4. Both concentrations for ashes (Table II.1, in mg/g) and fresh honey (Table II.2, in μg/g) are given.

Element	*Site 1*		*Site 2*		*Site 3*		*Site 4*		*Site 5*	
	Conc.	*RSD [%]*	*Conc.*	*RSD [%]*	*Conc.*	*RSD [%]*	*Conc.*	*RSD [%]*	*Conc.*	*RSD [%]*
P	16	33	54	34	18	47	11	55	29	
K	364	21	274	23	271	33	308	15	351	1
Ca	26	17	55.8	25	27.8	32	33	47	24.6	23
Mn	1.19	34	1.05	6	0.79	27	1.87	27	1.06	28
Fe	1.09	55	1.7	31	1.47	33	1.40	18	2.3	94
Ni	0.151	60	0.114	21	0.084	26	0.040	55	0.078	80
Cu	0.46	39	0.56	43	0.35	59	0.23	13	0.39	34
Zn	0.31	23	0.55	13	0.37	27	0.40	26	0.35	26
Pb	0.029	7	0.021		0.025		0.043	49	0.062	60
Rb	0.71	22	0.27	61	0.32		0.46	26	1.17	29
Sr	0.076	8	0.087	26	0.086	18	0.093	31	0.076	56

Table II.2

Element	Site 1		Site 2		Site 3		Site 4		Site 5	
	Conc.	RSD [%]	Conc.	RSD [%]	Conc.	RSD [%]	Conc.	RSD [%]	Conc.	RSD [%]
Ash [%]	*0.17*	*31*	*0.11*	*30*	*0.14*	*33*	*0.12*	*40*	*0.17*	*33*
P	28	49	61	56	22	19	11	43	61	
K	669	8	278	17	359	27	391	1	672	6
Ca	47.2	45	58	27	36.1	2	33.5	7	40.5	34
Mn	1.95	28	1.17	22	1.02	12	2.03	12	1.92	58
Fe	1.72	39	1.74	26	2.20	62	1.59	25	2.74	57
Ni	0.23	37	0.12	24	0.11	27	0.04	50	0.08	63
Cu	0.86	6	0.56	38	0.44	40	0.27	38	0.44	34
Zn	0.51	9	0.57	12	0.49	22	0.41	12	0.63	56
Pb	0.051	33	0.029		0.043		0.042	19	0.063	47
Rb	1.31	49	0.27	57	0.48		0.59	62	2.16	50
Sr	0.13	33	0.09	6	0.12	45	0.10	6	0.11	15

Site 1. 3 km north of the smelter.
Site 2. 5 km northwest of the smelter.
Site 3. 10 km southeast of the smelter.
Site 4. 3 different locations 16–26 km south of the smelter.
Site 5. 48 km south of the smelter.

in two samples from site 3. The corresponding relative standard deviations have not been calculated in these and in similar cases. The mean ash contents varied from 0.11 % to 0.17 % for the different locations. The highest concentrations of copper and nickel were found in samples collected closest to the metal-smelter. For other metals no clear trend could be found, e.g. the zinc concentrations were quite constant for all five locations.

A summary of the analytical data obtained in this work for honey samples from all three areas studied is given in Table III. The comparison shows that the ash contents of Finnish honey samples - from Harjavalta and Mikkeli - are of the same level, but for samples from Prague the level of ash content is almost three times higher. The honey samples from the Prague region were dark in color which is typical for honey-dew honey.[2–4] The mean ash contents in Table III also indicate that the honey samples from the Prague region represent a different type of honey.

Potassium, the predominant mineral element in honey samples, was found at concentrations of 400–1500 μg/g in our samples. Other main elements are phosphorus and calcium. Mn, Fe, Rb, Cu and Zn occurred in concentrations close to 1 μg/g. Two main elements in honey,[1–3] Mg and Na, could not be determined with the instrumental setup used in this work.

The nickel concentrations were higher in all honey samples from the Harjavalta region than in any sample from Mikkeli. Higher concentrations of copper were also found in all but one of the locations from the area around the metal smelter in Harjavalta, compared to the levels at Mikkeli. The similar comparison of concentrations in ashes shows higher levels of both Ni and Cu for all locations in the Harjavalta area. These results show the same pattern as the results from the European study of metal emission to the environment using mosses as bioindicators.[15] The moss study showed distinctly higher concentrations of both nickel and copper in samples taken from an area around Harjavalta.

The last columns in Table III give the results of the analyses of Czech honey. The general metal content was high in honey samples from the Prague region. As mentioned earlier, honey from different areas can be of different type which complicates an estimation of pollution based on analytical data for fresh honey samples. For environmental monitoring of heavy metal pollution a comparison of elemental concentrations in ashes could be more useful. In this way a normalization is automatically obtained with respect to the total content of inorganic components in the honey sample. This is visualized in Figure 4, where the relative mean concentrations for the K, Ni, and Cu concentrations in honey and honey ashes are plotted for the samples from the Harjavalta, Mikkeli and Prague areas. For graphical reasons the concentrations of these elements for samples from the Harjavalta region are scaled to 100%. For fresh honey the Prague area shows clearly the highest concentrations of both K, Ni, and Cu. However, in the ashes we have the highest concentrations of Ni and Cu in samples from Harjavalta followed by Prague and Mikkeli. Concentrations of potassium, the dominating inorganic component in honey,[1–3] in ashes of honey samples were almost the same for the three areas studied. By comparing the concentrations of Ni and Cu in honey ashes it can be concluded that Harjavalta is the most polluted

TABLE III Analyses of 5 honey samples from different locations in the Mikkeli and Prague regions, respectively. The mean values from analyses of 15 samples from Harjavalta and its surroundings are also included (Table II)

Element	*Harjavalta (n = 15)*				*Mikkeli (n = 5)*				*Prague (n = 5)*			
	Ashed [‰]	*RSD [%]*	*Fresh [µg/g]*	*RSD [%]*	*Ashed [‰]*	*RSD [%]*	*Fresh [µg/g]*	*RSD [%]*	*Ashed [‰]*	*RSD [%]*	*Fresh [µg/g]*	*RSD [%]*
Ash [%]			*0.143*	*38*			*0.158*	*34*			*0.409*	*48*
P	25.7	76	36.6	80	27.6	46	44.8	48	26	25	111	66
K	314	27	474	62	375	36	642	62	349	9	1443	50
Ca	33.4	46	43.1	38	17.3	47	23.2	21	16.4	23	64.3	46
Mn	1.19	41	1.62	45	1.25	97	1.69	70	0.42	98	2.29	116
Fe	1.59	71	2.00	55	0.74	58	1.04	40	2.05	12	8.21	48
Ni	0.094	45	0.12	67	0.018	45	0.029	58	0.050	22	0.21	55
Cu	0.40	52	0.51	69	0.16	35	0.27	24	0.29	63	0.97	43
Zn	0.40	30	0.52	36	0.27	39	0.31	43	0.42	33	1.49	30
Pb	0.039	67	0.048	48	0.044		0.074		0.040	39	0.17	74
Rb	0.60	64	1.00	94	0.85	31	1.36	46	0.31	35	1.31	65
Sr	0.084	33	0.11	34	0.10	38	0.14	21	0.061	13	0.24	48

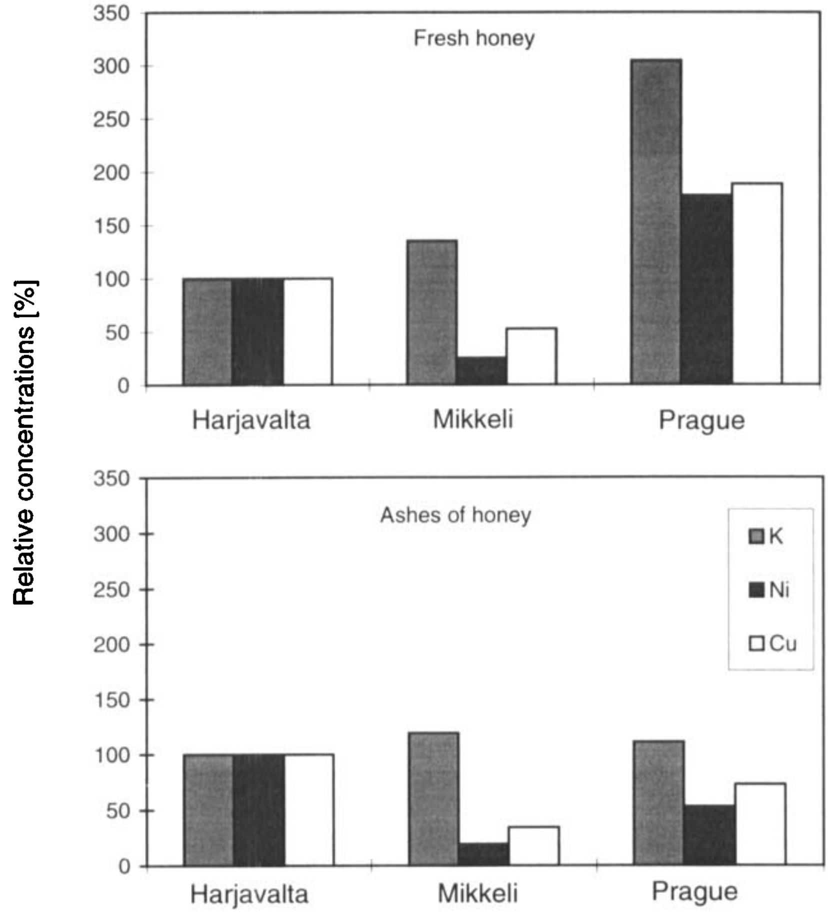

FIGURE 4 Relative concentrations of nickel, copper and potassium in (a) honey samples and (b) in ashes of honey samples. The elemental concentrations of samples from the Mikkeli and Prague regions are compared with the levels found in samples from the Harjavalta area.

area and Mikkeli the purest one. This order of pollution is in good agreement with the data given for Cu and Ni in the European moss study.[15]

As was mentioned earlier there has been some interest in using honey as an indicator of metal emission. Bohacenko *et al.*[9] analysed honey samples from 5 different regions in the Czech Republic. The regions were classified as differing in environmental quality. However, no correlation was found between concentrations of the heavy metals (Pb, Cd, Zn and Cu) and the environmental load. Stein and Umland[7] analysed Pb, Cd and Mn in honey samples collected at different times during a season from the same colonies of bees. For these samples from urban areas they noted that the concentrations of Pb increased as the year progressed. Jones[6] analysed Ag, Cd, Cu and Pb in honey samples collected in the UK. The conclusion drawn was that honey seemed to be largely insensitive to spatial differences in contaminant emissions. Jones pointed out inherent differences between types of honey as a source UUUUUUUUUUUUU interpretation of the results. Our results show that it can be recommended to normalize elemental concentrations with respect to the concentration of potassium if heavy metal analyses of honey have been performed with wet-chemical methods.

CONCLUSIONS

The results obtained by combining dry ashing and thick-target PIXE spectrometry and applying the method to analyses of honey samples were at least satisfactory. The analysis of fresh honey with TTPIXE is problematic due to the impressive swelling of the sample. By dry ashing a preconcentration factor of about 100–1000 can be obtained due to the low ash content of honey. A detection limit of well below 0.1 μg/g is thus obtainable for most heavy metals. Besides an increased sensitivity, the geometrical stability necessary in PIXE analyses is gained by the relative inertness of ashes to beam damages. As 5–10 g of honey was ashed, a statistically representative amount of the original sample was analysed. The ash percentage can be used for characterization of honey. The main drawback of the ashing procedure is that volatile elements like halogenides will be partly lost.

The elemental concentrations in honey depend both on natural biological and geochemical parameters as well as man-made environmental pollution. This complicates the interpretation of analytical data for honey. In the present work, comparisons of the elemental concentrations in ashed honey samples has demonstrated the feasibility of using honey as a bioindicator of environmental pollution.

As might have been expected, the most highly contaminated honey samples were from the Harjavalta region, where a Cu-Ni smelter is situated. In this area the highest copper and nickel concentrations were found in the samples collected closest to the smelter. The described analytical method could be of use in many fields of environmental research where concentrations of metals and other elements in biological material are of interest. The method enables fast and reliable monitoring of many elements at low concentrations.

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