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Original article

Evaluating soluble and insoluble ash, alkalinity of soluble and insoluble ash and total alkalinity of ash in honey using electrical conductivity measurements at 20 °C

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Summary — In 30 samples of Basque Country (Spain) honey, relations were established between electrical conductivity measured at 20 °C in solutions of 10 g of honey in 75 ml of water, and soluble and insoluble ash contents, total alkalinity, and alkalinity of the soluble and insoluble ash. Correlations for these relations were best for total alkalinity of ash, soluble ash and its alkalinity; these values could be predicted from electrical conductivity at 20 °C. Poorer correlations (r = 0.58) were found for the relations involving the insoluble ash but these were expected since amounts of this type of ash were very small, and determination involves several more steps than for soluble ash determination.

honey / electrical conductivity / soluble ash / insoluble ash / ash alkalinity

INTRODUCTION

Relative amounts of soluble and insoluble ash, the alkalinity of these fractions and total alkalinity of ash in honey are very important factors in the determination of ash content. Oxide alkalines or alkaline-terreus are measured in soluble ash. Insoluble ash is a measure of siliceous matter present in ash (*Manuel Suisse des Denrées Alimentaires*, 1969).

Alkalinity of ash is a measure of presence of combined cations with organic acids. By ignition, organic acids become alkaline or alkaline-terreous carbonates or in alkaline-terreous oxides which can be measured by a titrimetric method (*Manuel Suisse des Denrées Alimentaires*, 1969).

The importance of the content of the soluble and insoluble ash, and the alkalinity of the soluble and insoluble ash and total alkalinity of ash in honey has been corroborated by including all these determinations (Leach and Winton, 1920; *Association of Official Analytical Chemists* (AOAC), 1990).

In the literature there are no data on soluble and insoluble ash and alkalinity of the soluble, insoluble and total ash of hon-

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eys. Determining these parameters is laborious and time-consuming. In honey, a very good correlation (r = 0.9998) was found between the electrical conductivity of 20% honey solutions expressed from the honey dry weight (Vorwohl, 1964a, b; Louveaux *et al,* 1973) and the electrical conductivity measured in solutions of 10 g of honey in 75 ml of water (Sancho *et al,* 1991a).

A correlation was found between total ash content and electrical conductivity of 20% honey solutions expressed from honey dry weight (Accorti *et al,* 1986, 1987). Sancho *et al* (1991b) found a relation between the total ash and sulphated ash content and the electrical conductivity of 10 g honey dissolved in 75 ml water (White, 1962; AOAC 962.19, 1990).

This study examines the possible relationship between the electrical conductivity of honey and soluble and insoluble ash, specifically the alkalinity of soluble, insoluble and total ash.

MATERIALS AND METHODS

Samples

The samples consisted of 30 honeys from the Basque Country (Spain) harvested in the autumn of 1987 and described in Sancho *et al* (1991b).

Reagents

The following reagents were used:

– 0.1 N HCl, prepared from concentrated HCl (Probus), d = 1.19 and concentration = 38%, normalized with 0.1 N sodium carbonate solution prepared from anhydrous sodium carbonate pa, specified as an evaluation standard (Merck Art 6394);

– 0.1 N NaOH, prepared from Probus reagent and normalized with potassium pthallic acid pa, specified as an evaluation standard (Merck Art 4876);

– 10% H_2SO_4 (p/p), prepared from 95–97% sulphuric acid pa (Merck Art 732).

Electrical conductivity

Electrical conductivity was measured at 20 °C in solutions of 10 g honey in 75 ml of water (Sancho *et al,* 1991a).

Ash and ash alkalinity

Total ash was determined according to the method of White *et al* (1962), which is the Official Final Action method in the AOAC (32.120, 1984; 920.181A, 1990).

Soluble ash and its alkalinity were determined according to the method of Leach and Winton (1920), which is the AOAC Official Final Action method for honey (920.181B and 920.181C, 1990). Insoluble ash and its alkalinity were determined according to method of Leach and Winton (1920), which is the AOAC Official Final Action method for honey (900.02D and 900.02F, 1990) as regards sugar and sugar products. 80x 30 mm containers and a 250 W Tungsram infrared lamp (used in place of the 375 W lamp specified by the AOAC (1990), which is not available in Spain) were used.

In the determinations of alkalinity of insoluble and soluble ash, the titration end-point was established by measuring the pH and calculating the second derivative, which gives a more certain end-point prediction than using methyl orange.

The total alkalinity of the ash is the sum of the alkalinities of the soluble and insoluble ash.

All alkalinity values were expressed in ml of 1 N acid per 100 g of sample.

RESULTS AND DISCUSSION

Table I presents the experimental electrical conductivity values measured in solu-

Table I. Electrical conductivity at 20 °C and measured ash values in Basque Country honeys.

Sample No	*Electrical conductivity (10^{-4} S cm^{-1})*		*Ash (%)*			*Alkalinity of ash (ml of 1 N acid/100 g of honey)*		
	Dry matter [1]	*Humid matter* [2]	*Total*	*Soluble*	*Insoluble*	*Soluble*	*Insoluble*	*Total*
1	9.5	6.3	0.50	0.41	0.09	5.93	1.44	7.37
2	5.7	3.8	0.22	0.14	0.08	2.04	1.20	3.24
3	4.0	2.7	0.14	0.11	0.03	1.75	0.73	2.48
4	5.5	3.7	0.19	0.13	0.06	1.93	1.14	3.07
5	4.6	3.1	0.17	0.10	0.07	1.17	0.86	2.03
6	7.5	5.0	0.26	0.17	0.09	2.21	1.82	4.03
7	6.5	4.3	0.21	0.16	0.05	1.76	1.25	3.01
8	5.6	3.7	0.19	0.14	0.05	1.56	0.89	2.45
9	5.0	3.3	0.20	0.15	0.05	1.92	0.61	2.53
10	5.4	3.6	0.23	0.19	0.04	2.34	0.52	2.86
11	5.0	3.3	0.18	0.12	0.06	1.69	0.75	2.44
12	3.4	2.3	0.11	0.06	0.05	1.11	0.44	1.55
13	5.0	3.3	0.17	0.12	0.05	1.57	0.58	2.15
14	4.8	3.2	0.14	0.09	0.05	1.18	0.51	1.69
15	2.5	1.7	0.05	0.04	0.01	0.46	0.17	0.63
16	6.0	4.0	0.24	0.18	0.06	2.13	0.63	2.76
17	8.0	5.3	0.38	0.34	0.04	4.38	0.75	5.13
18	3.8	2.5	0.15	0.11	0.04	1.40	0.53	1.93
19	6.0	4.0	0.26	0.21	0.05	2.15	0.80	2.95
20	4.9	3.3	0.16	0.09	0.07	1.08	1.91	1.99
21	5.1	3.4	0.21	0.16	0.05	2.33	0.65	2.98
22	9.1	6.1	0.45	0.38	0.07	4.57	1.12	5.69
23	5.4	3.6	0.18	0.14	0.04	2.17	0.69	2.86
24	10.0	6.7	0.45	0.40	0.05	5.28	0.79	6.07
25	6.7	4.5	0.32	0.25	0.07	1.91	0.67	2.58
26	5.5	3.7	0.22	0.19	0.03	3.35	0.60	3.95
27	9.0	6.0	0.35	0.22	0.13	2.77	1.38	4.15
28	6.6	4.4	0.26	0.12	0.14	1.61	1.87	3.48
29	3.0	2.0	0.08	0.06	0.02	0.88	0.30	1.18
30	9.2	6.1	0.41	0.32	0.09	3.55	2.14	5.69

[1] Measured in solutions of 20% dry matter (Vorwohl, 1964a,b). [2] Measured in solutions containing 10 g honey in 75 ml of water (Sancho *et al*, 1991a).

Table II. Relationships between the electrical conductivity (10^{-4} S cm^{-1}) measured in solutions containing 10 g honey in 75 ml of water (Sancho *et al*, 1991a) and soluble and insoluble ash (%) and the alkalinity of the soluble, insoluble and total alkalinity of ash (ml 1 N acid/100 g of honey).

		r	Q
% Soluble ash	= 0.070 x electrical conductivity –0.102	0.91	0.79–0.96
% Insoluble ash	= 0.0126 x electrical conductivity +0.0092	0.58	0.36–0.79
Alkalinity of soluble ash	= 0.85 x electrical conductivity –1.11	0.85	0.67–0.93
Alkalinity of insoluble ash	= 0.225 x electrical conductivity +0.0315	0.58	0.36–0.79
Total alkalinity of ash	= 1.093 x electrical conductivity –1.167	0.93	0.84–0.96

N = 30; *r* = correlation coefficient; *Q* = significance level of correlation for a 95% confidence interval (David, 1938).

Table III. Student's *t*-test applied to the differences between value pairs (predicted values and experimental values) of the different types of ash and alkalinity of ash contents in honey.

	Ash (%)		*Alkalinity of ash (ml of 1 N acid/100 g of honey)*		
	Soluble	*Insoluble*	*Soluble*	*Insoluble*	*Total*
DM	–0.017	–0.0080	–0.234	–0.189	–0.393
STD dev	0.1519	0.0275	1.849	0.5534	2.268
SEM	0.0277	0.0050	0.338	0.1010	0.4140
DF	29	29	29	29	29
t-value	–0.60	–1.60	–0.69	–1.87	–0.95

$t = 2.045$ for $P < 0.05$; DM: Difference between means; STD dev: Standard deviation; SEM: Standard error of the mean (S/√N); DF: Degrees of freedom.

tions of 20% dry matter (Vorwohl, 1964a, b) and in solutions containing 10 g of honey in 75 ml of water (Sancho *et al*, 1991a), the experimental values of total ash, soluble and insoluble ash content, alkalinity of soluble and insoluble ash and total alkalinity of ash.

The mean soluble ash content (with the real values) was 0.18% (0.04–0.41%) and its mean alkalinity was 2.21 ml of 1 N acid/ 100 g honey (0.46–5.93). The mean insoluble ash content was 0.06% (0.01–0.14) and its alkalinity was 0.92 ml of 1 N acid/ 100 g honey (0.17–1.91). Total ash alkalinity varied between 0.63–7.37 ml of 1 N acid/100 g honey and the mean value was 3.16 ml of 1 N acid/100 g honey.

Linear regression indicated that linear relationships existed between electrical conductivity measured at 20 °C in solutions containing 10 g of honey in 75 ml of water paired with the soluble and insoluble ash contents, total alkalinity and alkalinity of the soluble and insoluble ash (table II).

Student's *t*-test was applied to the differences between value pairs (predicted and experimental values), and did not reveal significant differences at the $P < 0.05$ significance level for soluble and insoluble ash and their alkalinity, or for total alkalinity of the ash (table III). This shows that a quick and easy method of measurement such as that of electrical conductivity at 20 °C can be used to predict values of these parameters in honey.

For the honeys analyzed, the soluble and insoluble ash contents, total alkalinity, and alkalinity of the soluble and insoluble ash can be estimated from the values of electrical conductivity at 20 °C measured in solutions of 10 g honey in 75 ml water.

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Résumé — Évaluation de la teneur en cendres solubles et en cendres insolubles, de leur alcalinité et de l'alcalinité totale des cendres dans les miels à l'aide de la conductibilité électrique mesurée à 20 °C. Trente échantillons de miel provenant du Pays Basque ont été récoltés à l'automne 1987. Les cendres solubles *(cs)* et leur alcalinité, de même que les cendres insolubles *(ci)* et leur alcalinité, ont été déterminées selon les méthodes de Leach et Winton (1920), reconnues comme méthodes officielles par l'Association of Official Analytical Chemists (AOAC) respectivement pour l'analyse des miels (930.181B et 920.181C, 1990) et pour l'analyse des sucres et des produits sucrés (900.02D et 900.02F, 1990). Lors de la détermination de l'alcalinité des *cs* et des *ci*, le point final de la titration a été fixé en mesurant le pH et en calculant le second dérivé, ce qui fournit une prévision du point final plus sûre qu'avec le méthylorange. L'alcalinité totale des cendres est la somme des alcalinités des *cs* et des *ci*. La conductivité électrique a été mesurée à 20 °C dans des solutions de 10 g de miel dans 75 ml d'eau (Sancho *et al*, 1991a). Le tableau I donne les valeurs de la conductibilité électrique, les valeurs expérimentales de la teneur en cendres totales, en *cs* et en *ci* et l'alcalinité de chacunes d'entre elles. La régression linéaire indique qu'il existe des relations linéaires entre la conductivité électrique mesurée à 20 °C et les teneurs en *cs* et en *ci*, l'alcalinité totale et l'alcalinité des *cs* et des *ci* (tableau II). Le test *t* de Student a été appliqué aux différences entre les couples de valeurs (valeur prédite et valeur expérimentale). Il n'a pas montré de différence significative au seuil $P < 0{,}05$ pour les *cs*, les *ci* et leur alcalinité respective, ni pour l'alcalinité totale des cendres (tableau III). Ceci montre qu'une mesure rapide et facile telle que la conductibilité électrique à 20 °C peut être utilisée pour prédire les valeurs de ces paramètres.

miel / conductibilité électrique / cendres solubles / cendres insolubles / alcalinité

Zusammenfassung — Berechnung der löslichen und unlöslichen Asche, der Alkalität der löslichen und unlöslichen Asche und der Gesamtalkalität der Asche von Honigen durch Messung der elektrischen Leitfähigkeit bei 20 °C. In dieser Studie werden die möglichen Beziehungen zwischen der elektrischen Leitfä-

higkeit des Honigs (die schnell und einfach zu messen ist) und der löslichen und unlöslichen Asche sowie der Alkalität der löslichen, unlöslichen Asche und der Gesamtalkalität untersucht. Untersucht wurden 30 Honigproben aus der Herbsternte 1987 des Baskenlandes, Spanien. Die lösliche Asche und ihre Alkalität wurden nach den Leach und Winton-Methoden (1920) untersucht, die in den AOAC-Untersuchungsmethoden für Honig offiziell anerkannt sind (920.1818 und 920.181C, 1990). Die unlösliche Asche und ihre Alkalität wurden ebenfalls nach den Leach und Winton-Methoden (1920) untersucht, die nach AOAC (900.02D und 900.02F) offizielle Methoden für Zucker und Zuckerprodukte. Bei der Bestimmung der Alkalität der unlöslichen und löslichen Asche wurde der Endpunkt der Titration durch Messung des pH und Berechnung des zweiten Derivats festgesetzt, wodurch eine präzisere Voraussage des Endpunkts gewonnen wird als durch Methylorange. Die Gesamtalkalität der Asche ist die Summe aus den Alkalitäten von gelöster und ungelöster Asche. Die elektrische Leitfähigkeit wurde bei 20 °C in einer Lösung von 10.00 g Honig in 75 ml Wasser gemessen (Sancho *et al,* 1991a). Tabelle I gibt die Werte der elektrischen Leitfähigkeit, die experimentellen Werte der Gesamtasche, des löslichen und unlöslichen Aschegehalts, der Alkalität der löslichen und der unlöslichen Asche und der Gesamtalkalität der Asche. Die lineare Regression weist auf eine lineare Beziehung zwischen elektrischer Leitfähigkeit gemessen bei 20 °C und des löslichen wie des unlöslichen Aschegehalts, der Gesamtalkalität und der Alkalität der löslichen und der unlöslichen Asche (Tabelle II). Die Unterschiede zwischen den Datenpaaren (vorausgesagter Wert und experimenteller Wert) wurden mit Student's *t*-test geprüft; es ergaben sich weder für die lösliche und unlösliche Asche und ihre Alklalität, noch für die Gesamtalkalität der Asche signifikante Unterschiede für den Vertrauensbereich $P < 0.05$ (Tabelle III). Dies zeigt, daß eine rasche und einfache Meßmethode wie die Bestimmung der elektrischen Leitfähigkeit bei 20 °C zur Schätzung dieser Parameter im Honig benutzt werden kann.

Honig / Leitfähigkeit / löslichen Asche / unlöslichen Asche / Asche Alkalität

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