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Correlation between the electrical conductivity of honey in humid and in dry matter

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Summary — For 115 honeys, comparing electrical conductivities at 20 °C in solutions containing 10.00 g of honey dissolved in 75 ml of water (x), used to determine pH and acidity type, and solutions containing 20% dry matter (y) revealed a linear relation represented by $y = 1.50x$ ($r = 0.9998$). On this basis, solution electrical conductivity, pH and acidity type can be measured without data on honey moisture content.

honey / electrical conductivity / water content

INTRODUCTION

Electrical conductivity measurements of honey give an indication regarding its origin (floral or honeydew) and the source of nectar, and can detect whether bees have been artificially fed with sugar (Vorwohl, 1964a, b). It has also been proposed as a measure of the suitability of the honey as a winter feed for bees (Kaat, 1961). Electrical conductivity is related to the content of mineral salts, organic acids, proteins and polyols of the honey (Crane, 1975).

Stitz and Szigvárt (1931) measured the electrical conductivity of various honey solutions at 50% dry matter and 20.5 °C and observed variations of this parameter with temperature and concentration, finding maximum electrical conductivity values with 30–35% dry matter. Vorwohl

(1964a, b), however, obtained maximum electrical conductivity values with solutions of 20–25% dry matter and proposed taking measurements with solutions of 20% dry matter. The measurement of the electrical conductivity of honey at this concentration has now become standard in many countries (Codex Alimentarius Commission, 1969), including Spain (Boletín Oficial del Estado, 1986).

A possible relation between the electrical conductivity of honey solution containing 10.00 g dissolved in 75 ml of water, used to determine pH and acidity type (White, 1962; Association of Official Analytical Chemists, 31.168, 1984), and that of a solution containing 20% dry matter (Vorwohl, 1964a, b) was investigated to simplify the determination of all these parameters by taking measurements in one solution.

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MATERIALS AND METHODS

The sample comprised 115 honeys from the Basque Country (a region in the north of Spain). To check the method, 10 additional honeys with moisture content > 20% from Galicia (a region in the north-west of Spain) and 9 honeys from the first sample, supercharged until they contained 25% moisture, were analysed.

Moisture content was determined by vacuum drying (White, 1969; Association of Official Analytical Chemists, 1984) with a vacuum oven and high vacuum pump.

A conductimeter was used with a 1.0 cm electrode (Radiometer Copenhagen Type CDM 2e No 187049 and Type CDC 104, respectively). Measurements were taken at 20 °C $\pm$ 0.1 °C.

The conductimeter was calibrated at 20 °C with a potassium chloride solution having an electrical conductivity which did not differ by more than 5.0×10^{-4} S cm⁻¹ from that expected for honey using a standard method (Boletín Oficial del Estado, 1986).

Honeys were dissolved in water, and two solutions were prepared:

Solution "x"

Ten g of honey exactly (humid matter) were dissolved in 75 ml of distilled water following the procedure of White (1962) for measuring pH and acidity type.

Solution "y"

Honey solutions containing 20% dry matter were prepared by dissolving 10.00 g in up to 50 ml of water (Vorwohl, 1964a, b).

In the 2 series of solutions ("x" and "y"), satisfactory coefficients of variation (0.86% for solution "x" and 0.57% for solution "y") were obtained from measurements of the electrical conductivity of 10 solutions of the same honey sample.

RESULTS AND DISCUSSION

Plotting the pairs of electrical conductivity measurements of solutions "x" and "y" for each sample gives (table I) a straight line that corresponds to the equation $y = 1.50x$ ($r = 0.9998$) (fig 1). The high level of correlation is surprising; 2 honeys with the same content of conducting substances but different moisture contents should have identical electrical conductivity values for the humid matter but different values for the dry matter, since different quantities of honey must be weighed and dissolved to prepare solutions of 20% dry matter. The explanation lies in considering the joint effects of 2 properties, *ie* effect of moisture content and effect of concentration.

Table I. Electrical conductivity (10^{-4} S cm⁻¹) in solution of wet matter "x", moisture content (% w/w), weight of 10.0 g of dry matter (DM) and electrical conductivity (10^{-4} S cm⁻¹) in solution of dry matter "y" for the 115 honeys analysed from the Basque Country (Spain).

	Electrical conductivity ("x")	Moisture content (%)	10 g honey (DM)	Electrical conductivity ("y")
$\bar{x}$	4.4	16.4	11.97	6.7
S_{n-1}	1.457	1.411	0.202	2.177
Min	1.7	12.4	11.42	2.5
Max	8.8	20.3	12.55	13.2

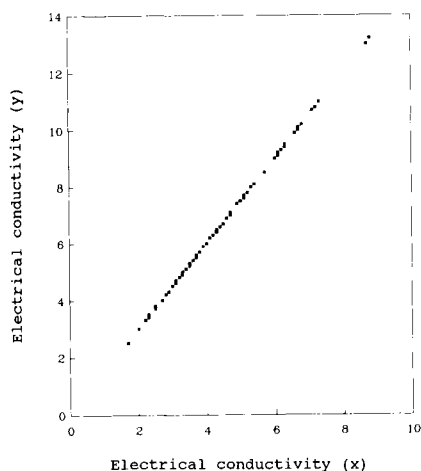


Fig 1. Graph of the relation between the electrical conductivities ($10^{-4} \text{ S cm}^{-1}$) of honey solutions in humid matter (x) and dry matter (y).

Effect of moisture content

The moisture content of the samples in this study varied between 12.4 and 20.3% (mean = 16.4, $S_{n-1} = 1.41$); the second value is 63.7% higher than the first. The effect of this on the electrical conductivity is much less noticeable; to prepare 50 ml of honey solution containing 20% dry matter 11.42 g is required for the honey containing 12.4% moisture, and 12.55 g for that containing 20.3%. In this case, the second value is only 9.9% higher (mean = 11.97 g, $S_{n-1} = 0.2024$ (table I).

This in itself does not justify the excellent correlation, since a 9.9% variation in the amount weighed would have some effect on the electrical conductivity.

Effect of concentration

The relation between the electrical conductivity and percentage dry matter for 3 honeys with different electrical conductivity values (low, medium and high), obeys a second order polynomial (table II). At $\approx 20\%$ dry matter, due to the increase in viscosity, there is a diminution of the ionic mobility and the curve becomes asymptotic (fig 2). Consequently, the effect of the amount weighed according to the moisture content of the sample has less influence on the electrical conductivity value.

The results of comparing the electrical conductivities of 3 solutions prepared by dissolving 11.50, 12.00 and 12.50 g of 10 honeys with different electrical conductivities and making them up to 50 ml (table III) show the influence of the 2 effects discussed. The maximum variation is $\pm 0.2 \times$

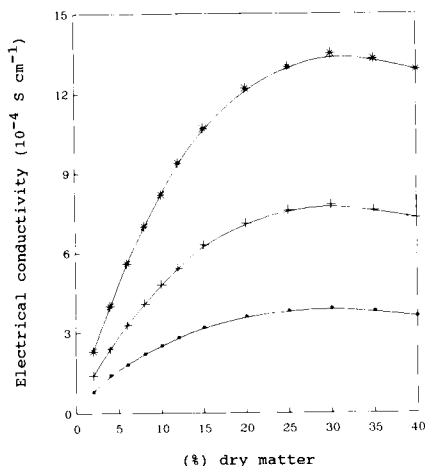


Fig 2. Graph of the relation between % of dry matter and electrical conductivity ($10^{-4} \text{ S cm}^{-1}$) in 3 honeys of low, medium and high electrical conductivity values.

Table II. Relation between the electrical conductivity (10^{-4} S cm^{-1}) and concentration of 3 honey solutions (%) of dry matter. Values in parentheses are theoretical values from the equation $y = a + bx + cx^2$.

% Dry matter (x)	Electrical conductivities of the honeys (y):		
	1	2	3
2	0.8 (0.9)	1.4 (1.6)	2.3 (2.6)
4	1.4 (1.4)	2.4 (2.5)	4.0 (4.1)
6	1.8 (1.8)	3.3 (3.3)	5.6 (5.5)
8	2.2 (2.1)	4.1 (4.0)	7.0 (6.8)
10	2.4 (2.4)	4.8 (4.7)	8.2 (8.0)
12	2.8 (2.7)	5.4 (5.3)	9.4 (9.1)
15	3.2 (3.1)	6.3 (6.1)	10.7 (10.5)
20	3.6 (3.6)	7.1 (7.1)	12.2 (12.3)
25	3.8 (3.9)	7.6 (7.7)	13.0 (13.3)
30	3.9 (4.0)	7.8 (7.9)	13.5 (13.8)
35	3.8 (3.8)	7.5 (7.7)	13.3 (13.5)
40	3.6 (3.5)	7.3 (7.1)	12.9 (12.5)
<i>r</i>	0.995	0.996	0.996
<i>a</i>	0.485	0.631	1.028
<i>b</i>	0.236	0.489	0.835
<i>c</i>	-0.004	-0.008	-0.014

10^{-4} S cm^{-1} for the value of electrical conductivity obtained for 16.7% dry matter.

The maximum permissible moisture content according to the Codex Alimentarius Commission (1969) is 20% except for the honey of *Calluna*, in which up to 23% is permitted. White, in McGregor (1979), indicates that moisture content may vary between 13–25%. Of the 91 samples that Huidobro and Simal analysed (1984), 10 honeys exceeded 23% moisture content and the maximum value obtained was 24.3%.

The electrical conductivities of "x" and "y" solutions of 10 immature honeys with moisture contents > 20% were measured

(table IV). The results do not show statistically significant variation from the values predicted using $y = 1.50x$ since $t_{\text{experimental}} < t_{\text{theoretical}}$.

Honeys with moisture contents ranging from 12.4–20.3% were supercharged until they contained 25% moisture (White; in McGregor, 1979; Huidobro and Simal, 1984) and the electrical conductivities were measured for "x" and "y" solutions. The results (table V) do not show statistically significant differences between the values of $y = 1.50x$ and the experimental "y" values.

From the above it follows that the electrical conductivity of honey solution containing 20% dry matter can be estimated by measuring the electrical conductivity of a solution of 10.00 g of honey in 75 ml of water (White, 1969; in AOAC 31.118, 1984) and multiplying it by 1.50. In this manner, electrical conductivity, pH and acidity type can be determined without prior knowledge of the moisture content of the honey.

Table III. Variation in electrical conductivity (10^{-4} S cm^{-1}) with the amount of honey required (g) to prepare 50 ml of solution with 20% dry matter, over the range of moisture contents of the honeys analysed from the Basque Country (Spain).

Amount weighed No of test	Electrical conductivity		
	11.50 g	12.00 g	12.50 g
1	2.4	2.4	2.4
2	3.9	4.0	4.0
3	5.2	5.3	5.4
4	5.6	5.7	5.8
5	6.4	6.5	6.6
6	7.4	7.6	7.8
7	8.4	8.5	8.6
8	9.5	9.6	9.7
9	10.4	10.5	10.6
10	11.5	11.6	11.7

Table IV. Electrical conductivity (10^{-4} S cm^{-1}) of "x" and "y" solutions of immature honeys with moisture content > 20%.

No	Moisture content (%)	Electrical conductivity		
		Solution "x" (x)	Predicted values ($y = 1.50x$)	Solution "y" (y)
1	20.7	4.5	(6.8)	6.6
2	20.7	7.6	(11.4)	11.4
3	20.9	4.8	(7.2)	7.3
4	20.9	6.9	(10.4)	10.4
5	21.0	5.0	(7.5)	7.4
6	22.3	6.5	(9.8)	9.8
7	22.4	5.5	(8.3)	8.0
8	23.0	3.8	(5.7)	5.5
9	23.8	5.2	(7.8)	7.6
10	24.3	6.1	(9.2)	9.1
$\bar{x}$			(8.4)	8.3
S_{n-1}			(1.77)	1.83

At the 95% probability level: $t_{\text{experimental}} = 0.125$; $t_{\text{theoretical}} = 2.101$; $t_{\text{experimental}} < t_{\text{theoretical}}$.

Table V. Electrical conductivity (10^{-4} S cm^{-1}) of "x" and "y" solutions of honeys supercharged up to 25% moisture content.

No	Moisture (%)		Electrical conductivity		
	Initial	Final	Solution "x" (x)	Predicted values ($y = 1.50x$)	Solution "y" (y)
1	12.4	25	3.4	(5.1)	5.3
2	13.0	25	7.3	(11.0)	11.0
3	14.0	25	5.3	(8.0)	8.1
4	15.0	25	2.5	(3.8)	3.8
5	16.0	25	4.0	(6.0)	6.0
6	17.0	25	7.0	(10.5)	10.8
7	18.0	25	6.3	(9.5)	9.4
8	19.0	25	5.0	(7.5)	7.8
9	20.3	25	6.1	(9.2)	9.1
$\bar{x}$				(7.8)	7.9
S_{n-1}				(2.48)	2.47

At the 95% probability level: $t_{\text{experimental}} = 0.090$; $t_{\text{theoretical}} = 2.1201$; $t_{\text{experimental}} < t_{\text{theoretical}}$.

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Résumé — Corrélation entre la conductibilité électrique du miel et la teneur en matière humide et en matière sèche.

Les mesures de la conductibilité électrique du miel servent à donner des informations sur son origine et à détecter si des abeilles ont été artificiellement nourries au sucre. On a recherché une éventuelle relation entre 2 méthodes différentes de mesure de la conductibilité électrique : dans une solution de 10 g de miel dans 75 ml d'eau, utilisée pour déterminer le pH et le type d'acidité (White, 1962; AOAC, 1984) et dans une solution à 20% de matière sèche (Vorwohl, 1964a, b). La comparaison visait à simplifier les procédures en faisant les mesures sur une même solution. Les mesures ont porté sur 115 miels.

Il existe une relation linéaire représentée par $y = 1,50x$ ($r = 0,9998$) (tableau I, fig 1). Cette forte corrélation est surprenante. Elle s'explique si l'on considère les effets communs des 2 propriétés : effet moindre de la teneur en eau parce que les différences dans les quantités pesées ne sont pas aussi grandes que celles attendues (tableau I) et effet de la concentration, qui obéit à une répartition polynomiale de deuxième ordre, puisque la courbe devient asymptotique à 20% de matière sèche environ (tableau II et fig 2). Le tableau III montre l'influence des 2 effets. La variation maximale de la conductibilité

électrique n'est pas significative. La corrélation de la teneur en eau dans un large domaine de valeurs a été comparée en mesurant 10 miels ayant une teneur en eau supérieure à 20% (tableau IV) et 9 miels surchargés en eau (jusqu'à 25%) (tableau V).

Il ressort des résultats que la conductibilité électrique d'une solution de miel à 20% de matière sèche peut être estimée en mesurant la conductibilité électrique d'une solution de 10 g de miel dans 75 ml d'eau et en multipliant la valeur par 1,50. Ainsi la conductibilité électrique, le pH et le type d'acidité peuvent être déterminés sans connaissance préalable de teneur en eau.

miel / conductibilité électrique / teneur en eau

Zusammenfassung — Korrelation der elektrischen Leitfähigkeit des Honigs in Flüssig- und Trockenzustand. Messungen der elektrischen Leitfähigkeit von Honigen können eine Vorstellung von seiner Herkunft geben und zur Feststellung beitragen, ob die Bienen künstlich mit Zucker gefüttert worden sind.

Es wurde nach möglichen Beziehungen zwischen zwei verschiedenen Meßverfahren der elektrischen Leitfähigkeit gesucht: Messung in einer Honiglösung von 10,00 g gelöst in 75 ml Wasser, wie sie zur Bestimmung des pH und des Säuregrades benutzt wird (White 1962, und in dem AOAC 31.168, 1984), und Messung in einer Lösung von 20% Trockensubstanz (Vorwohl 1964a, b). Die Messungen, vorgenommen zur Vereinfachung des Verfahrens durch Bestimmung aller Werte in einer einzigen Lösung, wurden an 115 Honigen durchgeführt. Es ergab sich eine lineare Beziehung ausgedrückt durch $y = 1,50 \times x$ ($r = 0,9998$) (tab I und fig 1).

Diese hohe Korrelation ist überraschend. Als Erklärung kann das Zusammenwirken von zwei Eigenschaften angenommen werden: Ein geringer Effekt des Wassergehalts, weil die Unterschiede in den gewogenen Mengen nicht so groß sind als erwartet (tab I), und ein Effekt der Konzentration, der einer Polynomialverteilung zweiter Ordnung gehorcht, indem die Kurve etwa bei 20% Trockensubstanz asymptotisch wird (tab II und fig 2). In tab III wird der Einfluß der beiden Effekte dargestellt. Die maximale Variation der elektrischen Leitfähigkeit ist nicht signifikant.

Die Korrelation des Wassergehalts über einen weiten Bereich wurde verglichen durch Messungen von 10 Honigen mit einem Wassergehalt über 20% (tab IV), und durch Messungen von 9 mit Wasser (bis 25%) überladenen Honigen (tab V).

Aus obigen Ergebnissen geht hervor, daß die elektrische Leitfähigkeit einer Honiglösung mit 20% Trockensubstanz durch Messung der elektrischen Leitfähigkeit einer Lösung von 10.00 g Honig in 75 ml Wasser (AOAC 31.168, 1984) und Multiplikation des Wertes mit 1.50 geschätzt werden kann. Auf diese Weise können elektrische Leitfähigkeit, pH und Aziditätstyp ohne vorherige Kenntnis des Wassergehalts des Honigs bestimmt werden.

Honig / elektrische Leitfähigkeit / Wassergehalt

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