Applying of non-destructive analysis methods in determination of whey solids*

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Summary

Possibility of applying non-destructive methods in determination of whey solids was investigated.

The non-destructive methods used were : infrared spectroscopy, cryoscopy, conductometry and gravimetric method as a referent method.

With statistical interpretation of results the stochastic relation of variable between independent variable (investigated method) and dependent variable (referent method) was established. The stochastic relation showed satisfactory dependency of variables with linear equation: $\hat{Y} = b_0x_0 + b_1x_1 + \varepsilon$.

Determination coefficient verified model's efficacy.

Infrared spectroscopy and cryoscopy were successful methods for determination of whey solids. Less precise were conductometry results.

Additional index words: whey, dry matter of whey, infrared spectroscopy, cryoscopy, conductometry.

Introduction

Whey has been considered for a long time as waste product of dairy industry, its main use was in cattle - feeding (Posavec, 1992). At present it is regarded as a product of wide-ranging application potentials (Baković & Tratnik, 1972; Grba et all., 1988; Nickerson & Vujičić, 1977; Marošević & Peraković 1981). Assessment of whey solids is as important as its alternative quality parameters.

An assay method should meet the requirements of rapidity and precision and also it should be nondestructive. The objective of the present paper was to compare three methods, i.e., infrared spectroscopy (method 2) (De Vilder & Bossuyt 1983; Golc - Teger 1989; Leray 1989; Lynch & Barbano 1990; Mendehall & Brown 1990.), cryoscopy (method 3) (Black & Van Leeuwen, 1985.) and electroconductivity (method 4) to gravimertic method (method 1) as a reference.

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Material and methods

From the batches of Zdenka DD.'s semi-hard cheeses produced at PPI Veliki Zdenci 40 samples of sweet whey were collected immediately or the very last an hour after its separation and processing. Three methods, i. e. infrared spectroscopy - Milko Scan 133B (De Vilder & Bossuyt, 1983; Golc-Teger, 1989.), cryoscopy using Krioskop 4D2 device (Black & Van Leeuwen, 1985.), and electroconductivity measurement with an MA 5964 conductometer accompained by sample drying to constant mass (105°C) were used to determine the level of solids in whey.

Samples acidity ranged from pH 6.2 to 6.5, titration acidity varied from 4.0 to 5.5°SH.

The results were analyzed statistically on a PC.

For individual components Milko Scan 133B was gauged using classic methods:Kjeldahl's (A O A C, 1990.a) for proteins, polarimetric (A O A C, 1990.b) for lactose, and Gerber's (I S O, 1984.) for milk fat, and adding a constant of 0.65% for mineral content.

Results and discussion

To determine solids levels in 40 whey samples methods 2, 3 and 4, were used respectively infrared spectroscopy, cryoscopy and electroconductivity. The results were compared to those obtained using standard method of drying to constant mass (105° C) (method 1). Table 1 shows the results obtained using these methods and Table 2 gives the basic statistical indicators.

Whereas the solids assay, emploing drying to constant mass, gave the lowest relative dispersion (2.75%), the electroconductivity method produced the highest relative dispersion (4.34%).

Positive correlation between methods 1-2 (r=0.96) and for methods 1-4 (r=0.82) was high and significant ($p < 0.05$) high and significant negative correlation between methods 1-3 (r= -0.94). There was a slightly lower correlation coefficient in electroconductivity measurement, due to inequality of samples milk fat content. Because the electroconductivity metdoh is incapable of measuring milk fat, this has caused larger deviations.

Correlation coefficients showed high qualitative interrelation among individual methods, and the scatter diagram show a linear relationship between the gravimetric and other methods (Figs. 1-3).

This may thus be expressed by a linear regression equation of the type:

$$\hat{Y} = b_0x_0 + b_1x_1 + \varepsilon$$

where:

$b_0 = (\Sigma y)^2/n$

b_1 = linear regression coefficient

ε = random error

Table 1 Experimental data for used methods
Tablica 1. Eksperimentalni podaci provedenih mjerenja

Solids/suha tvar (%) Method 1/Metoda 1	Solids/suha tvar (%) Method 2/Metoda 2	Freezing point/Točka smrzavanja (°C) Method 3/Metoda 3	Conductivity/Elektropro -vodljivost (mS/cm) Method 4/Metoda 4
5.36	5.40	-0.412	4.965
5.57	5.56	-0.435	5.136
5.64	5.65	-0.444	5.215
5.65	5.62	-0.441	5.330
5.65	5.68	-0.449	5.141
5.67	5.66	-0.447	5.230
5.69	5.68	-0.446	5.200
5.70	5.70	-0.448	5.188
5.71	5.68	-0.456	5.242
5.71	5.71	-0.454	5.207
5.72	5.66	-0.444	5.255
5.72	5.70	-0.457	5.407
5.72	5.73	-0.448	5.230
5.75	5.75	-0.454	5.246
5.76	5.76	-0.456	5.256
5.76	5.79	-0.440	5.176
5.77	5.75	-0.465	5.456
5.77	5.77	-0.454	5.194
5.78	5.75	-0.458	5.154
5.80	5.82	-0.463	5.302
5.81	5.83	-0.462	5.101
5.82	5.81	-0.450	5.397
5.82	5.89	-0.472	5.580
5.85	5.81	-0.465	5.318
5.85	5.89	-0.468	5.320
5.85	5.92	-0.471	5.403
5.85	5.92	-0.477	5.661
5.88	5.88	-0.472	5.655
5.89	5.99	-0.481	5.457
5.90	5.92	-0.474	5.653
5.91	6.04	-0.480	5.553
5.95	6.01	-0.468	5.632
5.97	6.03	-0.481	5.465
6.00	5.96	-0.483	5.436
6.01	5.98	-0.482	5.382
6.02	6.03	-0.475	5.452
6.04	5.95	-0.477	5.372
6.06	6.15	-0.492	5.887
6.10	6.13	-0.488	5.387
6.20	6.18	-0.505	5.506

Methods / Metode:

1. Solids (%) - using gravimetry / Suha tvar (%) - gravimetrijski
2. Solids (%) - using Milko Scan 133 B / Suha tvar (%) - s Milko scan-om 133B
3. Freezing point (°C) - using Advanced 4D2 cryoscope / Točka smrzavanja - s Advanced 4D2 krioskopom
4. Conductivity (mS/cm) - using MA5964 conductometer / Elektroprovodljivost s konduktometrom MA5964

Table 2 Basic statistical indicators
Tablica 2. Osnovni statistički pokazatelji

Method Metode	Mean Srednja vrijednost $\bar{x}$	Standard deviation Standardna devijacija (s)	Coefficient of variation Koeficijent varijacije % (V)
1	5.82	0.16	2.75
2	5.83	0.17	2.92
3	-0.462	0.02	3.91
4	5.43	0.24	4.34

Methods / Metode:
1. Solids (%) - by gravimetry / Suha tvar (%) - gravimetrijski
2. Solids (%) - using Milko Scan 133B / Suha tvar (%) - s Milko Scan-om 133B
3. Freezing point (°C) - using Advanced 4D2 cryoscope / Točka smrzavanja (°C) - s Advanced 4D2 krioskopom
4. Conductivity (mS/cm) - using MA5964 conductometer / Elektroprovodljivost - s konduktometrom MA5964

Figure 1 Scatter diagram (methods 1-2)
Slika 1. Dijagram rasipanja podataka (metode 1-2)

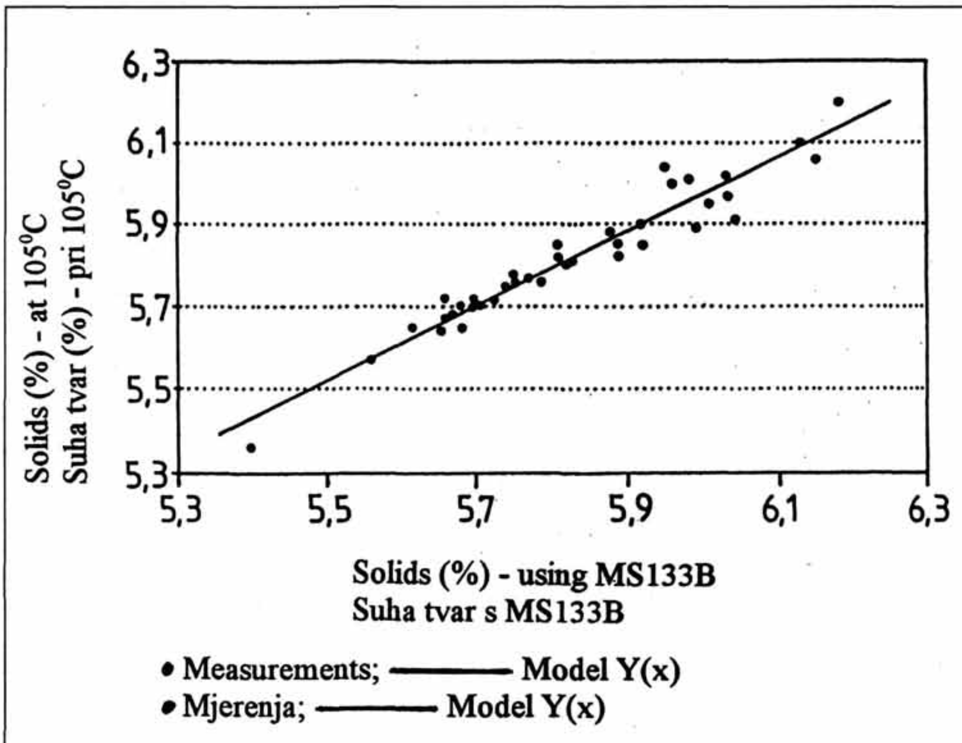


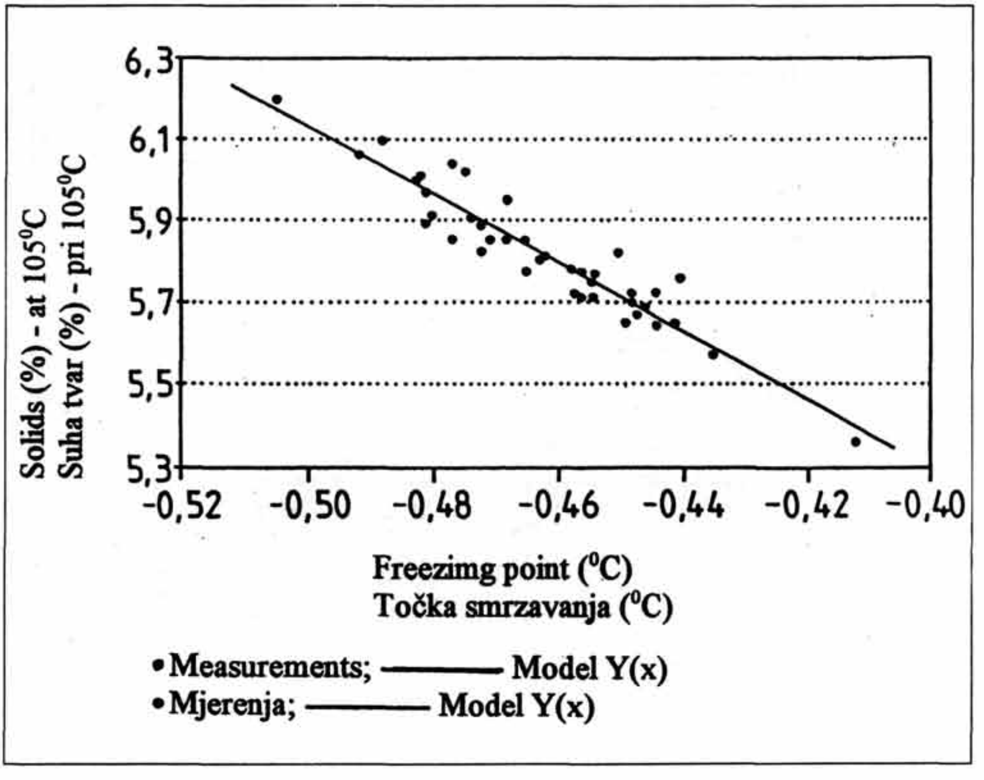
Table 3 Equations of linear regresion Y(x)
Tablica 3. Jednadžbe linearne regresije Y(x)

Methods Metode	Linear regression Linearna regresija
1 - 2	Y = 0.547778 + 0.904044 x
1 - 3	Y = 1.964223 - 8.333030 x
1 - 4	Y = 2.788193 + 0.557771 x

Methods / Metode:

1. Solids (%) - using gravimetry / Suha tvar (%) - gravimetrijski
2. Solids (%) - using Milko Scan 133B / Suha tvar (%) - s Milko Scan-om 133B
3. Freezing point (°C) - using Advanced 4D2 cryoscope / Točka smrzavanja (°C) - s Advanced 4D2 krioskopom
4. Conductivity (mS/cm) - using MA5964 conductometer / Elektroprovodljivost - s konduktometrom MA5964

Figure 2 Scatter diagram (methods 1-3)
Slika 2. Dijagram rasipanja podataka (metode 1-3)



The calculation of linear regression was done with least square technique (Dawies, 1964.). Equations of linear regression Y(x) appears in Table 3. A PC using ABDO software computed the linear model's coefficients (Coob, 1988.). The confidence limits of methods 1-2, 1-3 and 1-4 are $\hat{Y}\pm0.09$, $\hat{Y}\pm0.11$ and $\hat{Y}\pm0.19$, respectively.

Verification of relationships between regresion models (1-2, 1-3, 1-4) was done with conventional methods of mathematical statistic (Tables 4, 5 and 6).

The efficiency of the above methods was assessed as follows (Diagram 1):

1. Dry substance level using the MS 133B technique	93.09%
2. Dry substance level by cryoscopy	88.93%
3. Dry substance level measured using electroconductivity	67.80%

Figure 3 Scatter diagram (methods 1-4)
Slika 3. Dijagram rasipanja podataka (metode 1-4)

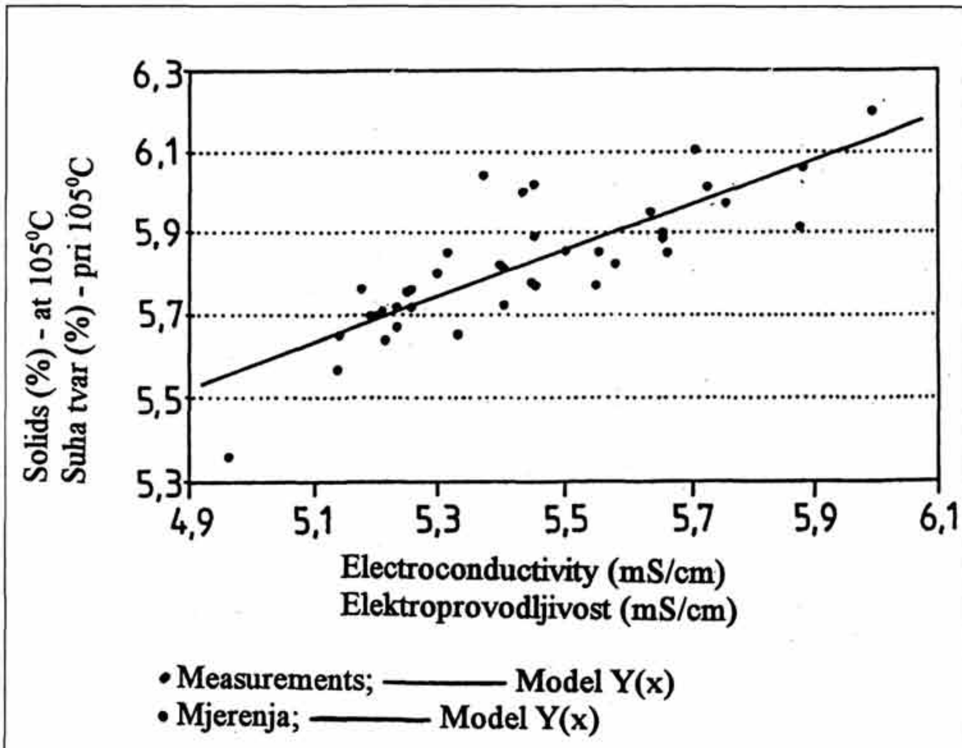


Table 4 Analysis of variance for regression model 1-2
Tablica 4. Analiza varijance modela regresije 1-2

Source of variation Izvor varijacija	SS	Degrees of freedom Stupnjevi slobode	MS	F_0
Total Ukupno	1354.494	40		
b_0 b_0	1353.500	1		
Total (corr.) Ukupno (korig.)	0.994	39		
Model b_1 Model b_1	0.926	1	0.926	512.2097***
Residual Ostatak	0.068	38	0.00181	
$F_{0.01}$ (1/38) = 7.35	p<<0.001			

Efficiency of model SS (b_1) / SS (total corr.) x 100 = 93.09%
Efikasnost modela SS (b_1) / SS (ukupno korig.) x 100 = 93.09%
Not explained by model 6.91%
Nije objašnjeno modelom 6.91%

Methods / Metode:
1. Solids (%) - using gravimetry / Suha tvar (%) - gravimetrijski
2. Solids (%) - using Milko Scan 133B / Suha tvar (%) - s Milko Scan-om 133B

Table 5 Analysis of variance for regression model 1-3
Tablica 5. Analiza varijance modela regresije 1-3

Source of variation Izvor varijacija	SS	Degrees of freedom Stupnjevi slobode	MS	F_0
Total Ukupno	1354.494	40		
b_0 b_0	1353.500	1		
Total (corr.) Ukupno (korig.)	0.994	39		
Model b_1 Model b_1	0.884	1	0.884	305.1534***
Residual Ostatak	0.110	38	0.002898	
$F_{0.01}$ (1/38) = 7.35	p<<0.001			

Efficiency of model SS (b1) / SS (total corr.) x 100 = 88.93%
Efikasnost modela SS (b1) / SS (ukupno korig.) x 100 = 88.93%
Not explained by model 11.07%
Nije objašnjeno modelom 11.07%

Methods / Metode:
1. Solids (%) - using gravimetry / Suha tvar (%) - gravimetrijski
2. Freezing point (°C) - using Advanced 4D2 cryoscope / Točka smrzavanja (°C) - s Advanced 4D2 krioskopom

Table 6 Analysis of variance for regression model 1-4
Tabica 6. Analiza varijance modela regresije 1-4

Source of variation Izvor varijacija	SS	Degrees of freedom Stupnjevi slobode	MS	F_0
Total Ukupno	1354.494	40		
b_0 b_0	1353.500	1		
Total (corr.) Ukupno (korig.)	0.994	39		
Model b_1 Model b_1	0.674	1	0.674	80.03907***
Residual Ostatak	0.320	38	0.008425	

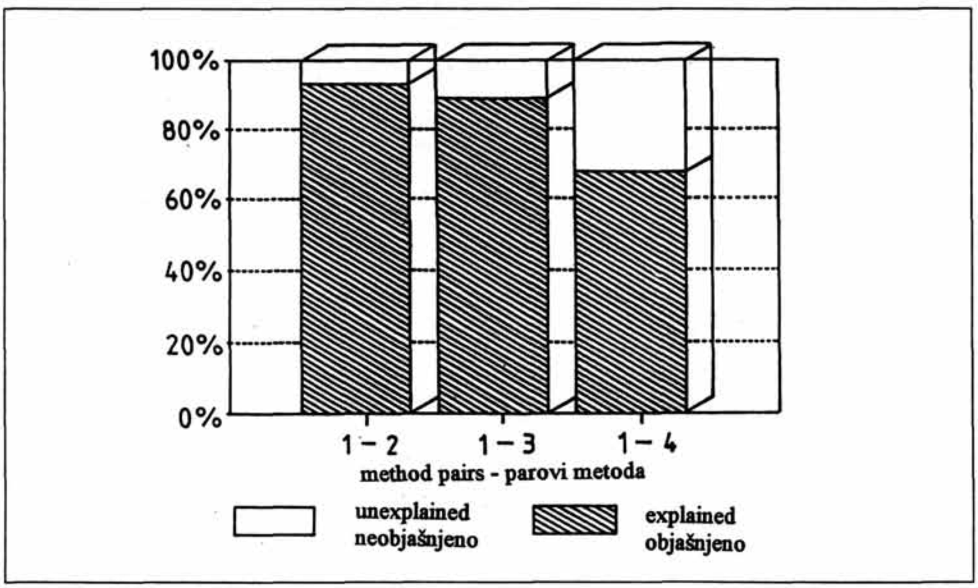
$F_{0.01}$ (1/38) = 7.35 p<<0.001

Efficiency of model SS (b_1) / SS (total corr.) x 100 = 67.80%
Efikasnost modela SS (b_1) / SS (ukupno korig.) x 100 = 67.80%
Not explained by model 32.20%
Nije objašnjeno modelom 32.20%

Methods / Metode:

1. Solids (%) - using gravimetry / Suha tvar (%) - gravimetrijski
2. Conductivity (mS/cm) - using MA5964 conductometer / Elektroprovodljivost - s konduktometrom MA5964

Diagram 1 Efficiency of the regression model
Dijagram 1. Efikasnost modela regresije



Conclusion

Results suggest that the Milko Scan (infrared spectroscopy) method is suitable for determination of whey solids in dairy industry laboratories.

The cryoscopy method, method for whey the freezing point determination was also reliable and could be recommended for laboratory use. Electroconductivity, between three methods, affords the lowest precision when used to measure the level of whey solids.

PRIMJENA NEDESTRUKTIVNIH METODA ANALIZE U ODREĐIVANJU SUHE TVARI SIRUTKE

Sažetak

U radu je istražena mogućnost primjene nedestruktivnih metoda za određivanje suhe tvari sirutke.

Korištene su slijedeće nedestruktivne metode: infracrvena spektroskopija, krioskopija i mjerenje elektroprovodljivosti, a kao referentna korištena je gravimetrijska metoda.

Statističkom obradom rezultata utvrđen je stohastički odnos između nezavisne varijable (provjeravana metoda) i zavisne varijable (referentna metoda). Stohastički odnos pokazao je zadovljavajuću ovisnost varijabli linearnom funkcijom oblika $\hat{Y} = b_0x_0 + b_1x_1 + \varepsilon$.

Efikasnost modela je provjerena koeficijentom determinacije.

Infracrvena spektroskopija i krioskopija bile su uspješne metode za određivanje suhe tvari sirutke. Rezultati dobiveni mjerenjem elektroprovodljivosti manje su precizni.

Riječi natuknice: sirutka, suha tvar sirutke, infracrvena spektroskopija, krioskopija, mjerenje elektroprovodljivosti.

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