EVALUATION OF THE MPA™ INFRARED ANALYSER

The MPA™ is a near infrared TF spectrophotometer manufactured by Bruker Optik (Germany, Bruker Group Corporation) and commercialised in France by Bruker Optics. It is used for the determination of the principal components in milk and in liquid (retentate, serum, cream, milk-based drinks…) and solid (powder, cheese, butter, yoghurt…) dairy products.
The near infrared analyzer (MPA Multi Purpose Analyzer) from Bruker Optics (FT-NIR) can be customized and equipped with different sampling modules for optimal NIR measurement of different sample types:
1- Sample compartment for transmission measurements to analyze liquid samples in a with an InGaAs detector cooled thermo-electrically (range 12800 - 4000cm-1)
2- Transmission module for solid and paste like samples with a Si detector at room temperature (range 15500 - 9000cm-1)
3- Reflection module with integrating sphere for solid and paste like samples with a PbS detector (range 12800-3600cm-1).
Fiber optic probes can also be installed.
The heart of the instrument is a Rocksolid® permanent alignment interferometer (Bruker Patent) with gold mirrors.
The apparatus is computer controlled with Opus software, which ensures the signal treatment and the PLS calibrations.

The tests:

The evaluation tests were performed in Actilait-Cecalait's physico-chemistry laboratory (reference and instrumental analyses) from July to October 2010. After satisfactory preliminary stability tests performed for fat (MG), dry matter (MS) and crude protein (MAT) on a set of 3 samples of whole, semi-skimmed and skimmed homogenised milk, the following criteria were evaluated:

- evaluation of repeatability and accuracy on homogenised milk: fat, dry matter and crude protein parameters;
- evaluation of repeatability and accuracy evaluation on whey: fat and crude protein parameters;
- evaluation of repeatability and accuracy evaluation on cheese: fat and dry matter parameters;
- complementary tests of repeatability and accuracy on cheese: crude protein parameter.

The calibrations used have been developed by the supplier thanks the Opus software

The calculation parameters are in relation with the ISO 21543/IDF 201 standard.

A- HOMOGENISED MILK

A.1- Samples

The tests were performed on 30 samples of homogenised milk. The samples were prepared by mixing whole, semi-skimmed and skimmed milk from shops. Bronopol was added to the samples to give a final concentration of 0.02%.

A.2- Procedure

The repeatability and the accuracy of the instrument for fat, dry matter and crude protein were evaluated using all the milk samples. The infrared quantitative analysis of each sample was carried out in consecutive duplicate using a "skimmed milk" and "whole milk" model carried out by the manufacturer, optimised by the integration of 9 specific samples.

The following reference methods were used:

- fat: Röse-Gottlieb method according to ISO 1211 and ISO 7208 (single tests);
- dry matter: drying method according to ISO 6731 (single tests);
- crude protein: Kjeldahl method according to ISO 8968 (single tests), conversion crude protein = total nitrogen x 6.38

A.3- Results

The table and figures below summarise the results obtained:

	n	min	max	M	Sx	Sr	Sr (%)	r
FAT (g/kg) skimmed milk	7	1.45	4.85	3.09	1.27	0.04	1.22	0.10
FAT (g/kg) whole milk	14	9.90	34.00	23.11	9.10	0.03	0.14	0.09
DRY MATTER (g/kg)	21	8.86	12.21	10.59	1.14	0.01	0.14	0.04
CRUDE PROTEIN (g/kg)	21	33.80	37.60	34.79	0.84	0.05	0.15	0.15

Table 1: MPA repeatability criteria for fat, dry matter and crude protein on homogenised milk

n: number of results; min and max: minimum and maximum value; M and Sx: mean and standard deviation of deviations; Sr and Sr%: absolute and relative standard deviation of repeatability; r: maximal deviation of repeatability in 95% of cases.

	n	min	max	Y	Sy	d	Sd	Sy,x	Sy,x %	b	a
FAT (g/kg) skimmed milk	7	1.97	5.16	3.51	1.21	-0.42	0.08	0.054	1.75	0.952	0.57
FAT (g/kg) whole milk	13	13.98	32.97	23.82	8.25	0.31	0.40	0.175	0.73	0.958	0.70
DRY MATTER (g/100g)	20	9.33	12.21	10.66	1.10	0.02	0.04	0.041	0.38	0.996	0.02
CRUDE PROTEIN (g/kg)	20	33.99	35.24	34.63	0.46	0.02	0.17	0.132	0.38	0.806	6.69

Table 2: MPA accuracy criteria for fat, dry matter and crude protein on homogenised milk samples

n, min, max: number of results; minimum and maximum value; Y: mean results using the reference and instrumental methods; Sy: standard deviation of the results from the reference method; d, Sd: mean and standard deviation of deviations; Sy,x and Sy,x%: absolute and relative standard deviation; b, a: slope and intercept of the linear regression.

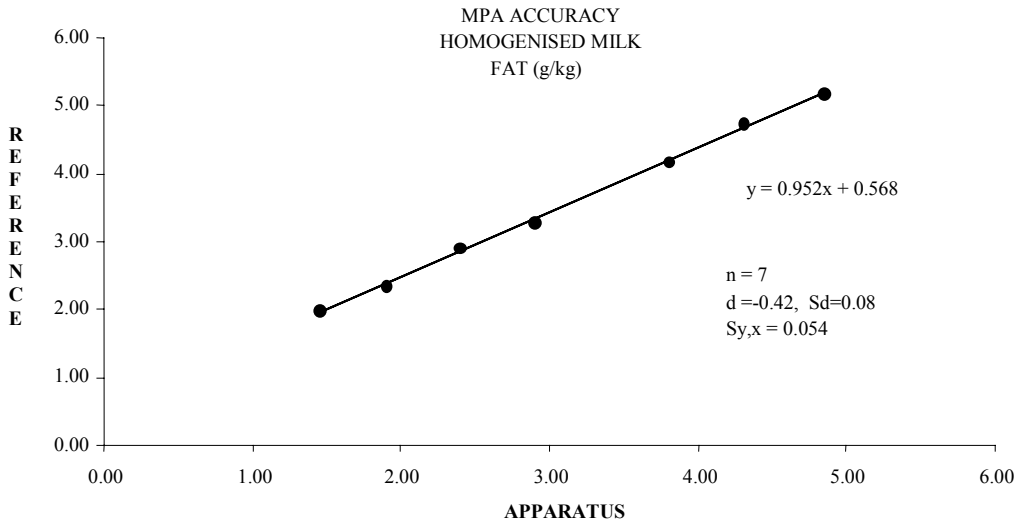

Figure 1: Relationship between the MPA and the reference results for fat on skimmed milk samples

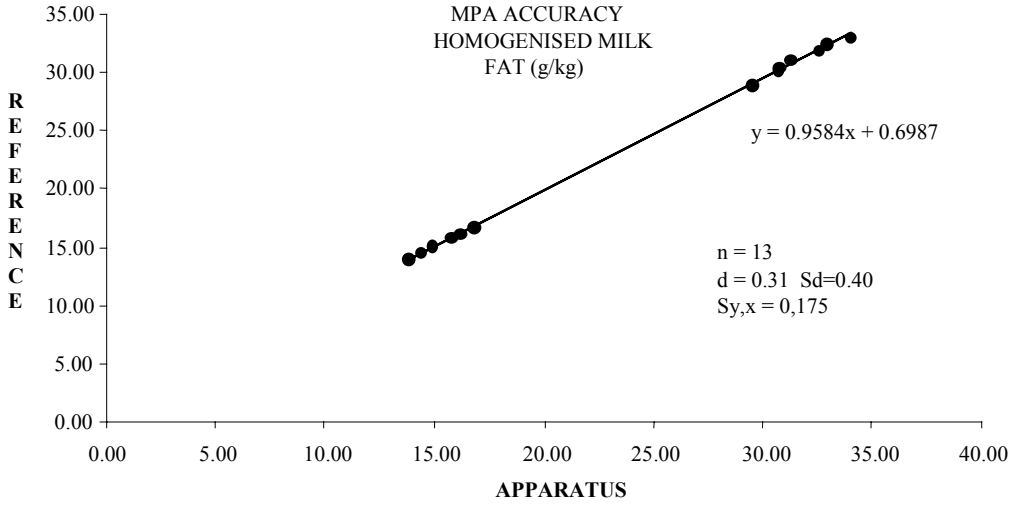

Figure 2: Relationship between the MPA and the reference results for fat on whole and semi-skimmed milk

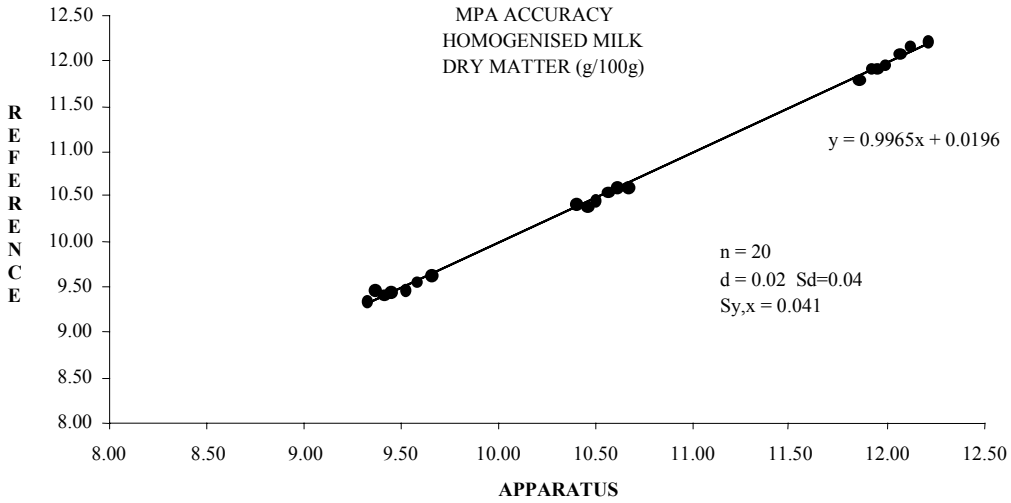

Figure 3: Relationship between the MPA and the reference results for dry matter on milk samples

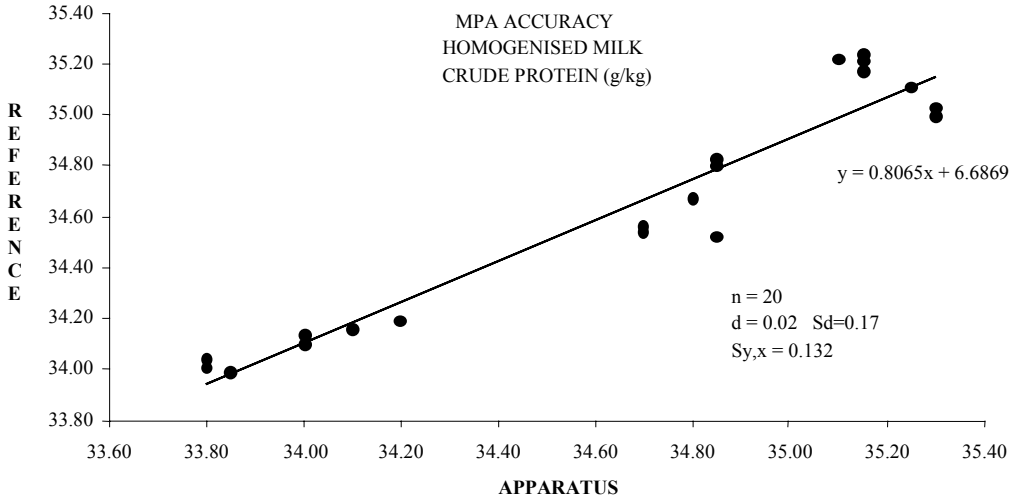

Figure 4: Relationship between the MPA and the reference results for crude protein on milk samples

It can be noted that:

- For fat, the relative residual standard deviations vary between 0.73% and 1.75% according to the rate of fat. For skimmed milk, the regression line is equal to 0.952 and is significantly different from 1 (P = 5%). For whole and semi-skimmed milk, the regression line is equal to 0.958 and is significantly different from 1 (P = 1%).
- For dry matter, the relative residual standard deviation is equal to 0.38 %. The regression line is equal to 0.996 and is not significantly differently from de 1 (P = 5%).
- -For crude protein, the relative residual standard deviation is equal to 0.38 %. The regression line is equal to 0.806 and is significantly different from 1 (P = 1%).

A.4- Conclusion

With no standard criteria, it can be noted that the relative standard deviations of repeatability vary between 0.14 and 1.22%. The values obtained are in compliance with the recommendations of ISO 9622/IDF 141 standard concerning the performances of the infrared analysers, which fixes a maximum limit of 0.14 g/l for non-homogenised whole milk. The residual standard deviations of regression observed enable the following relative accuracy of estimation (equal to ±2.Sy,x at 5% risk):
- For fat: ±3.5% (skimmed milk) and 1,5% (whole and semi-skimmed milk); - For dry matter: ±0,8%; - For crude protein: ±0,8%.

B- WHEY

B. 1- Samples

The tests were performed on 10 samples of whey. The samples were prepared by mixing filtrated wheys drainage of soft and hard cheese from a producing department. Bronopol was added to the samples to give a final concentration of 0.02%.

B.2- Procedure

The repeatability and the accuracy of the instrument for fat and crude protein were evaluated using all the samples. The infrared quantitative analysis of each samples was carried out in consecutive duplicate using the "whey" model carried out by the manufacturer, optimised by integration of 3 specific samples.

The following reference methods were used:
- Fat: Röse-Gottlieb method according to ISO 7208 (single tests);
- Crude protein: Kjeldahl method according to ISO 8968 (single tests.)

B.3- Results

The following tables and figures present the results obtained:

	n	min	max	M	Sx	Sr	Sr (%)	R
FAT (g/kg)	7	0.96	8.61	5.76	2.71	0.08	1.35	0.21
CRUDE PROTEIN (g/kg)	7	7.53	10.06	8.99	0.93	0.17	1.94	0.48

Table 3: MPA repeatability criteria for fat and crude protein on whey samples
n: number of results; min and max: minimum and maximum value; M and Sx: mean and standard deviation of the results; Sr and Sr%: absolute and relative standard deviation of repeatability; R: maximum deviation of repeatability in 95% of cases.

	n	min	max	Y	Sy	d	Sd	Sy,x	Sy,x %	b	a
FAT (g/kg) skimmed milk	7	0.69	9.32	5.90	3.05	-0.14	0.38	0.198	3.43	1.124	-0.57
CRUDE PROTEIN (g/kg) whole milk	7	7.52	10.08	8.95	0.92	0.04	0.08	0.086	0.96	0.989	0.06

Table 4: MPA accuracy criteria for fat and crude protein on whey samples
n, min, max: number of results, minimum and maximum values; Y,X: mean results using the reference and instrumental methods; Sy: standard deviation of the results from the reference method; d, Sd: mean and standard deviation of deviations; Sy,x and Sy,x%: absolute and relative residual standard deviation; b, a: slope and intercept of the linear regression

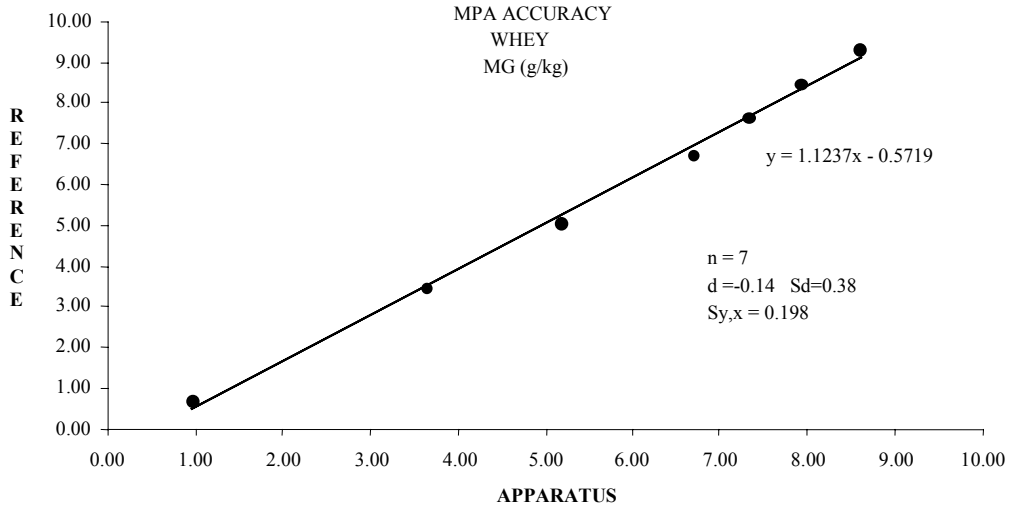

Figure 5: Relationship between the MPA and the reference results for fat on whey samples

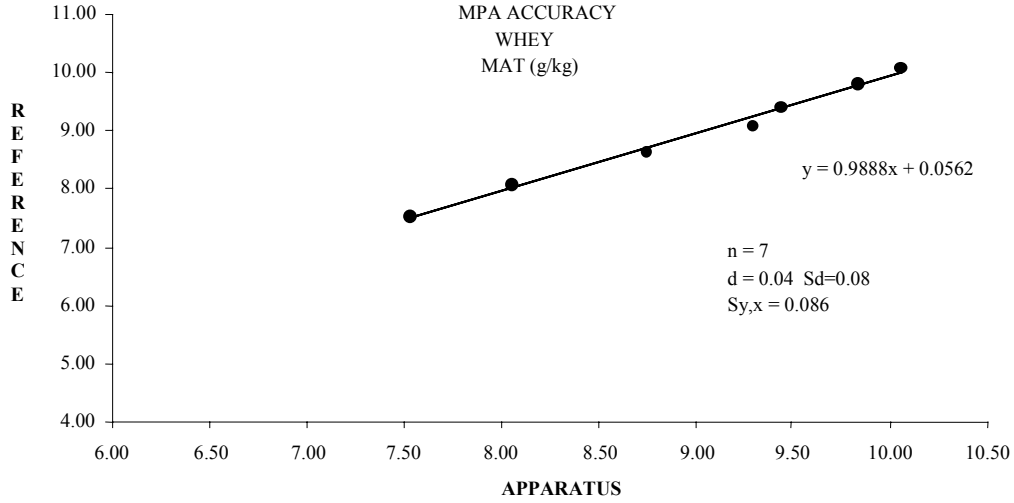

Figure 6: Relationship between the MPA and the reference results for crude protein on whey samples

It can be noted that:

- For fat, the relative residual standard deviation is equal to 3.43%. The slope is equal to 1.124 and is significantly different from 1 (P = 1%).
- For crude protein, the relative residual standard deviation is equal to 0,96 %. The slope is equal to 0.89 and is not significantly different from 1 (P = 5%).

B.4- Conclusion

With no standard criteria, it can be noted that the relative standard deviation of repeatability obtained is equal to 1.35% (fat) and 1.94% (crude protein). The residual standard deviation of regression observed enable the following relative accuracy of estimation (equal to 2.Sy,x at 5% risk):

- For fat: ± 6.9%;
- For crude protein: ±1.9%.

C- CHEESE

C.1- Samples

The tests were performed on 40 samples of cheese sold in supermarkets and hypermarkets: 20 samples of soft cheese and 20 samples of hard cheese. The samples were analysed after removing the rind and mixing or grinding according the type of cheese.

C.2- Procedure

The repeatability and the accuracy of the instrument were evaluated for dry matter and fat using all the cheese samples. The infrared quantitative analyses were performed for each sample in consecutive duplicate using the "soft cheese" and a "hard cheese" models carried out by the manufacturer, optimised by the integration of 12 specific samples. The measures were realised in transmission through polystyrene petri dishes.

The following reference methods were used:

- Dry matter using drying method according to ISO 5534 (single tests);
- Fat using SBR extraction method according to ISO 1735 (single tests).

C.3- Results

The results obtained are presented in the following tables and figures:

	n	min	max	M	Sx	Sr	Sr (%)	R
Dry matter (g/100g) soft cheese	14	36.84	53.30	47.24	4.16	0.17	0.35	0.46
Dry matter (g/100g) hard cheese	14	52.73	69.63	61.61	5.16	0.13	0.21	0.36
Fat (g/100g) soft cheese	14	11.37	30.29	25.68	4.67	0.07	0.28	0.20
Fat (g/100g) hard cheese	14	26.45	34.81	30.67	2.75	0.11	0.35	0.30

Table 5: MPA repeatability criteria for fat and dry matter on cheese samples

n: number of results; min and max: minimum and maximum value; M and Sx: mean and standard deviation of the results ; Sr and Sr%: absolute and relative standard deviation of repeatability; R: maximum deviation of repeatability in 95% of cases.

	n	min	max	Y	Sy	d	Sd	Sy,x	Sy,x %	RMSEP	RMSEP %	b	a
DRY MATTER (g/100g) Soft cheese	14	35.96	53.61	46.73	4.38	0.51	0.59	0.579	1.23	0.761	1.63	1.046	-2.69
DRY MATTER (g/100g) Hard cheese	14	52.57	69.52	61.05	5.30	0.56	0.42	0.414	0.67	0.692	1.13	1.024	-2.02
FAT (g/100g) Soft cheese	13	11.05	29.51	25.05	4.78	0.58	0.28	0.282	1.10	0.644	2.57	0.983	-0.14
FAT (g/100g) Hard cheese	14	25.98	36.28	30.67	3.48	0.00	0.84	0.474	1.55	0.809	2.64	1.256	-7.86

Table 6: MPA accuracy criteria for dry matter and fat on cheese samples

n, min, max: number of results, minimum and maximum value; Y,X: mean results using the reference and the instrumental methods; Sy: standard deviation of the results from the reference method; d, Sd: mean and standard deviation of deviations; Sy,x and Sy,x %: absolute and relative residual standard deviation; b, a: slope and intercept of the linear regression; RMSEP and RMSEP %: absolute and relative quadratic mean error of prediction.

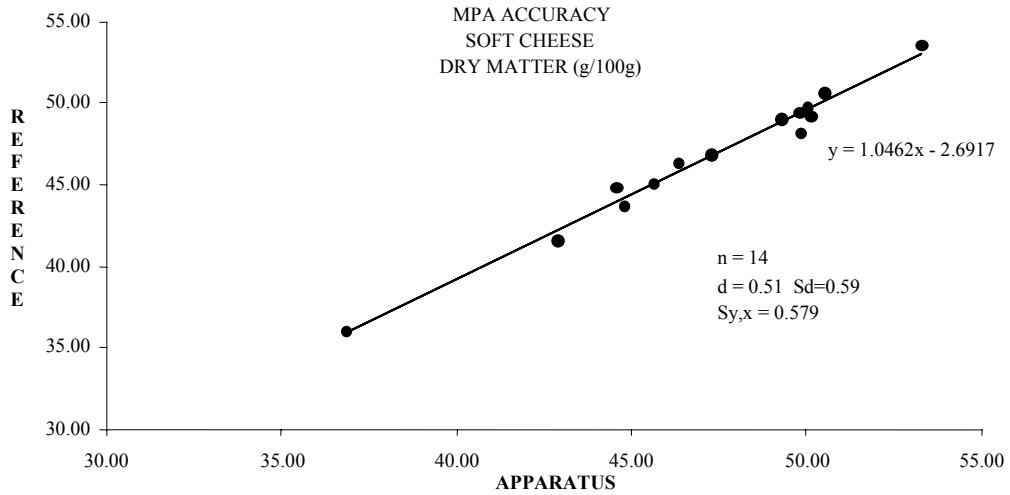

Figure 7: Relationship between the MPA and the reference results for dry matter on soft cheese samples

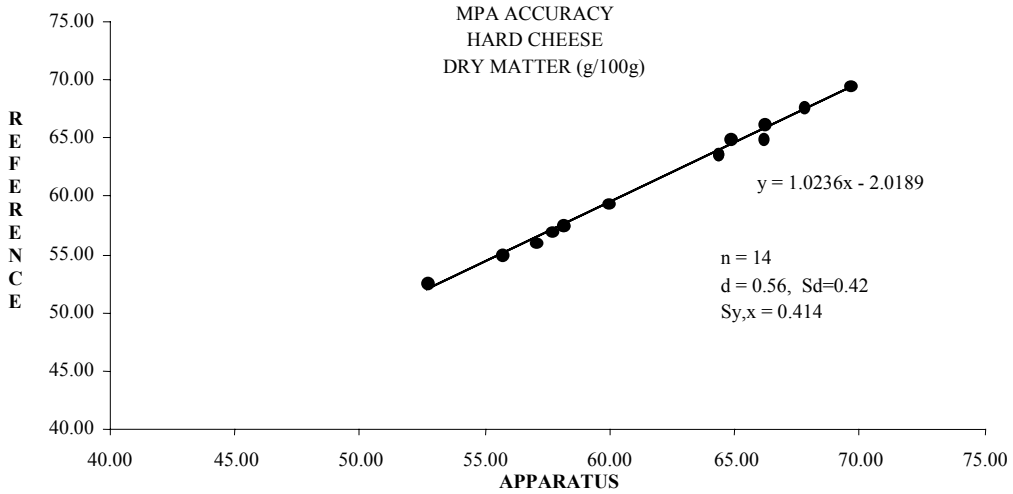

Figure 8: Relationship between the MPA and the reference results for dry matter on hard cheese samples

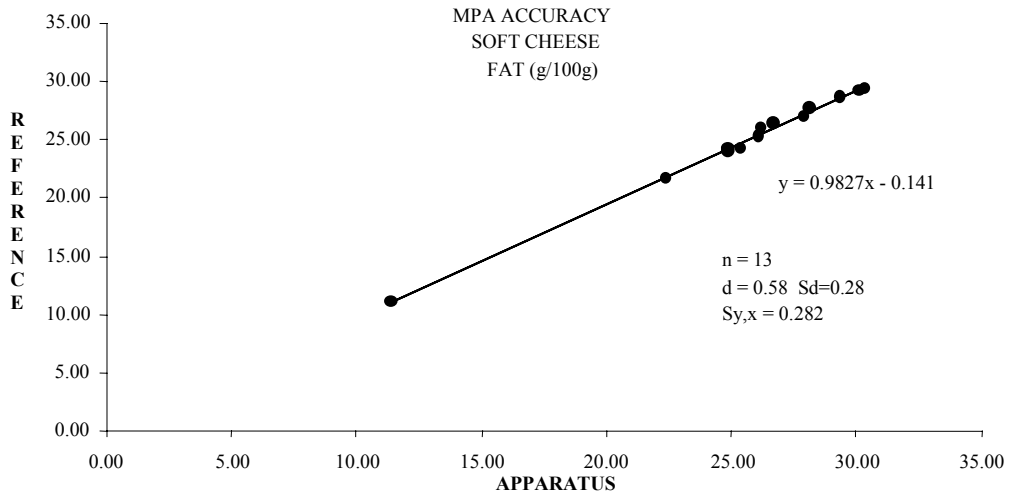

Figure 9: Relationship between the MPA and the reference results for fat on soft cheese samples

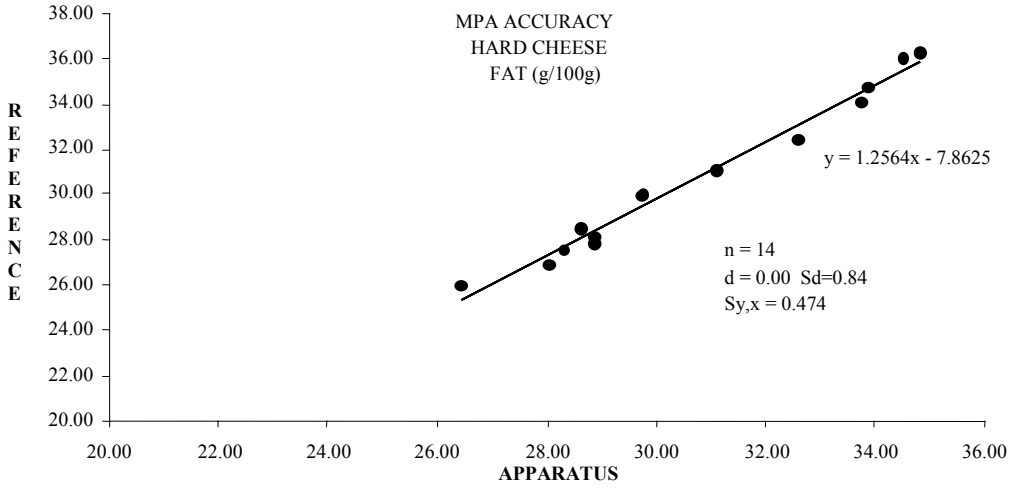

Figure 10: Relationship between the MPA and the reference results for fat on hard cheese samples

It can be noted that:

- For dry matter,
  - ❖ soft cheese: - the relative residual standard deviation is equal to 1.23%;
    - the slope is equal to 1.046, not significantly different from 1 (P = 5%);
    - the relative errors of prediction are equal to 1.63%.
  - ❖ hard cheese: - the relative residual standard deviation is equal to 0.67% ;
    - the slope is equal to 1.024, not significantly different from 1 (P = 5%) ;
    - the relative errors of prediction are equal to 2.57%.

- For fat,
  - ❖ soft cheese: * the relative residual standard deviation is equal to 1.10% ;
    * the slope is equal to 0.983, not significantly different from 1 (P = 5%) ;
    * the relative errors of prediction are equal to 1.63%.
  - ❖ hard cheese: * the relative residual standard deviation is equal to 1.55% ;
    * the slope is equal to 1.256, the slope is equal to 1 (P = 1) ;
    * the relative errors of prediction are equal to 2.64%.

C.4- Conclusion

With no standard criteria, it can be noted that the relative standard deviations of repeatability vary between 0.28 and 0.35% for the soft cheese samples, and between 0.21 andt 0.35% for the hard cheese samples. The values observed enable the following relative accuracy of estimation (equal to 2.RMSEP % at 5% risk):
- For dry matter: +/- 2.7% for soft cheese and +/- 2.3% for hard cheese;
- For fat: +/- 3.1% for soft cheese and +/- 3.3% for hard cheese.

C.5- Complementary tests

Complementary tests were performed on the previous samples to predict the crude protein value. The repeatability and accuracy of the instrument were evaluated using all the samples. The quantitative analyses were performed for each sample in consecutive duplicate. The instrumental values are from "soft cheese" and "hard cheese" calibrations carried out by the manufacturer, built by integration of 12 specific samples. The measures were realised in transmission through polystyrene petri dishes. The reference method used was the Kjeldahl method according to ISO 8968 (single test) with conversion by the following calculation: Crude protein = Total nitrogen x 6,38.

The results are summarised in the tables and figures below:

	n	min	max	M	Sx	Sr	Sr (%)	r
Crude protein (g/100g) soft cheese	14	14.09	23.07	19.31	2.37	0.15	0.76	0.41
Crude protein (g/100g) hard cheese	14	20.35	30.26	25.76	2.87	0.29	1.13	0.80

Table 7: MPA repeatability criteria for crude protein on cheese samples

n: number of results; min and max: minimum and maximum value; M and Sx: mean and standard deviation of the results; Sr and Sr%: absolute and relative standard deviation of repeatability; r: maximum deviation of repeatability in 95% of cases.

	n	min	max	Y	Sy	d	Sd	Sy,x	Sy,x %	RMSEP	RMSEP %	b	a
Crude protein (g/100g) Soft cheese	14	13.61	23.44	19.19	2.61	0.12	0.75	0.767	3.97	0.730	3.81	1.054	-1.16
Crude protein (g/100g) Hard cheese	12	21.26	30.25	25.76	2.57	-0.07	0.73	0.622	2.42	0.707	2.74	0.853	3.86

Table 8: MPA accuracy criteria for crude protein on cheese samples

n, min, max: number of results, minimum and maximum value; Y,X: mean results using the reference and instrumental methods; Sy: standard deviation of the results from the reference method; d, Sd: mean and standard deviation of deviations; Sy,x and Sy,x %: absolute and relative residual standard deviation; b, a: slope and intercept of the linear regression; RMSEP and RMSEP %: absolute and relative quadratic mean error of prediction.

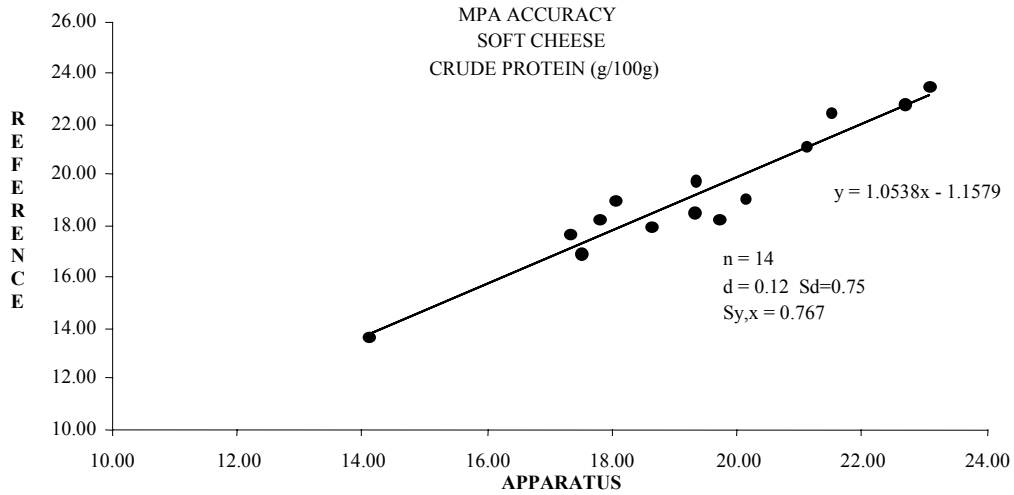

Figure 11: Relationship between the MPA and the reference results for crude protein on soft cheese samples

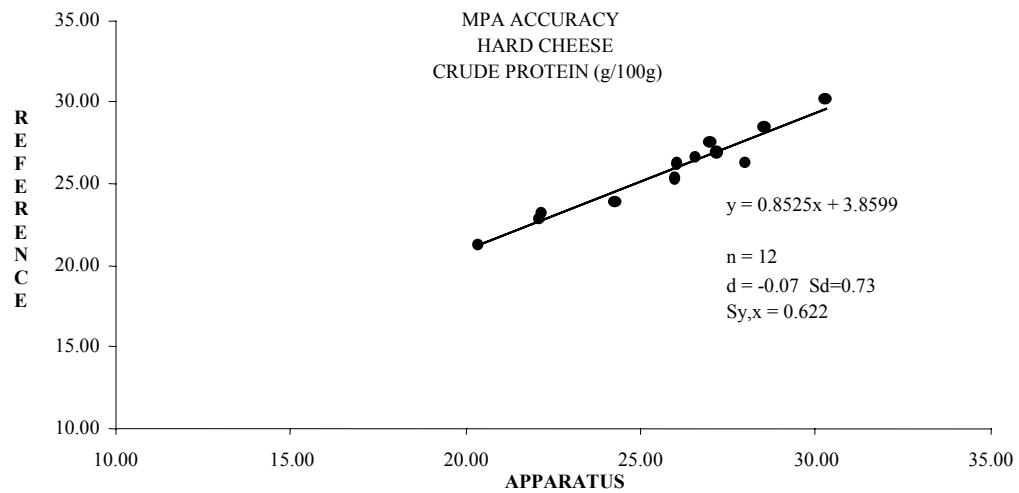

Figure 12: Relationship between the MPA and the reference results for crude protein on hard cheese samples

It can be noted that:

- For soft cheese: - the relative standard deviation of repeatability obtained is equal to 0.76%;
  - the relative residual standard deviation of regression is equal to 3.97%;
  - the slope is equal to 1.053;
  - the relative errors of prediction are equal to 3.81%.

- For hard cheese: - the relative standard deviation of repeatability obtained is equal to 1.13%;
  - the relative residual standard deviation of regression is equal to 2.42%;
  - the slope is equal to 0.852;
  - the relative errors of prediction are equal to 2.74%.

As no standard criteria exists, these values from a calibration built with some samples are perfectible. However they enable the setting up of a satisfactory constructor calibration..

CONCLUSION

The MPA repeatability performances on the liquid products tested (homogenised milk and whey) are in accordance with the recommendations of the ISO 9622 standard dedicated to the mid infrared analysers (for fat and crude protein on raw milk). Concerning the accuracy, the performances of the instrument vary according to the matrixes and the parameters. They must be studied according to the analytical objectives wished.
In general, for the evaluation on cheese, with no standard criteria ,the results cannot be precisely interpreted. However, as the evaluations were performed on various products in comparison with general manufacturer's calibrations, the repeatability and accuracy values observed are most probably maximums. The performances on specific products with dedicated calibrations would be best.

Thank to ENILBIO Poligny(39, France) for the supplying of whey samples

According to the evaluation report of the MPA ™ infrared analyser – X. QUERVEL and Ph. TROSSAT – Actilait/Cecalait – March 2011