International Fishmeal & Oil Manufacturers Association

COMPARISON BETWEEN KJELFOSS AND LECO TECHNIQUES FOR MEASURING PROTEIN CONTENT OF FISH MEALS

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EXECUTIVE SUMMARY

The LECO Corporation of St Joseph, Michigan, USA offers laboratories a technique for measuring the protein content in feed stuffs which is claimed to be faster, safer and cheaper than the traditional Kjeldahl or automated Kjelfoss process.

The Kjeldahl method takes from one to several hours to complete and can be summarised in three steps:

- acid digestion with a heavy metal catalyst
- caustic dilution
- titration

Each analytical step poses a potential health risk to the operator exposed to toxic fumes and acid/caustic solutions.

The LECO system is based on total combustion of the sample in an atmosphere of oxygen followed by analysis of the volatile nitrogen gases. Samples can be analysed in 5 minutes.

Courtesy of Corpesca in Chile, twenty Chilean fish meal samples were analysed by Kjelfoss and the LECO method. There was a small difference between the two sets of analysis (Table 2). LECO employed a correction factor resulting in figures shown in Table 3 and plotted in Figure 2. Close agreement was obtained.

INTRODUCTION

Reproduced below is an introduction to the LECO method prepared by the LECO Company:

Today, LECO Corp. of St. Joseph, Michigan offers laboratories a technology to conduct faster, safer and cheaper analysis. the company developed a device that uses a combustion system without the hazards associated with earlier models.

In the past, the classical method for nitrogen determination has been the Kjeldahl method, developed more than 100 years ago. The Kjeldahl method takes from one to several hours to complete and can be summarised in three steps:

1) Acid digestion with a heavy metal catalyst.
2) Caustic dilution.
3) Titration.

This method can be hazardous. Each analysis poses a potential health risk to the operator exposed to its toxic fumes, acid or caustic solutions.

For this method, laboratories must safely vent fumes into the environment and pay for proper disposal of spent chemicals. The costs have been accepted because no viable alternative existed.

Later, a combustion system was developed for nitrogen determination. This principle is still used today but it has been improved by LECO Corp.

For the combustion method, a sample is combusted in an oxygen atmosphere and the nitrogen in the sample is isolated and detected. The positive aspects of this method include faster analysis and elimination of hazardous chemicals. the samples can be analysed in five minutes with no need for acids, caustics or heavy metal catalyst.

In the past 10 years, LECO corp. has taken the combustion method to new levels for the feed industry. The company improved its system and laboratories are embracing the method.

With a focus on expanding the method, LECO first designed an instrument that could test 1 g. of sample routinely. The product line grew to include a determinator to handle up to 4 g. Analysing these larger samples, comparable to the Kjeldahl method, eliminates precision problems due to heterogeneity.

To use LECO's combustion analyser, 1 to 4 g. of sample is placed in a reusable ceramic boat on a 49-position autoloader. The best automatically moves into a furnace where it combusts in a pure oxygen atmosphere.

Moisture is removed from the combustion gases via a thermoelectric cooler before being routed into a ballast. The gases are given time to equilibrate before an aliquot is taken. Interfering gases are removed and nitrogen is detected by thermal conductivity. The analysis takes three to five minutes.

Two parts of the analytical hardware display innovative development: the combustion schematic design; and use of a ballast system.

One of the most important aspects of the combustion schematic is employing a horizontal furnace. The combustion tube is mounted horizontally and made concentric. This allows combustion gases to flow to one end of the combustion tube and back through the outer sleeve of the tube. The effective hot zone is doubled, which helps guarantee complete oxidation of the combustion gases.

another benefit of the furnace design is the use of pure oxygen as the carrier gas. using pure oxygen ensures that the entire sample is combusted and that no nitrogen remains in the ash. Older systems rely on oxygen dosing and hazardous oxide materials that are unsatisfactory for larger sample weights.

Another feature in the combustion schematic is a lance to help transport oxygen to the sample as fast as possible. Three grams of solid material combust rapidly. To ensure that the sample does not starve itself of oxygen, a lance was added.

Oxygen may be introduced on top of the sample instead of relying only on flow from the front of the combustion tube. This feature has optimised the combustion process. A sample that burns rapidly can be analysed immediately before or after a sample that burns slowly.

The second innovation is the ballast. The ballast volume expands to collect combustion gases during analysis. This eliminates any high pressure chemistry from occurring and allows all gases to form a homogeneous mixture.

When a sample combusts, not all the nitrogen is released immediately. Some nitrogen burns off quickly while the rest may evolve out slowly. Without a ballast, gases would continuously pass through the detector, which could lead to multiple and broad peaks. This could cause problems during the separation and detection.

By collecting gases in the ballast for a specified length of time, gases are allowed to form a homogeneous mixture. After that, a 10 cc aliquot sample is taken from the ballast scrubbed of impurities and detected for total nitrogen.

There are two major benefits of taking an aliquot instead of analysing the entire ballast. One is that 10 cc of gas are passed through the detector for a faster response.

The cost per analysis is around US $0.75. This value does not include labour and energy costs and is dependent on oxygen and helium price that can vary according to local suppliers.

The combustion-based method has eliminated the Kjeldahl method from hundreds of laboratories. It has also gained accreditation from several associations including the Association of Official Analytical Chemists, American Oil Chemist's Society and American Association of Cereal Chemists.

METHOD

Corpesca, Chile, selected 20 samples of Chilean fish meal and analysed them using the Kjelfoss technique.

A sub-set of these samples were sent to the LECO laboratory in Chile for analysis.

Results

Table 1 shows the analysis of protein by the LECO technique in the 20 fish meal samples with some estimate of repeatability of the method on individual samples.

Table 2 shows a comparison of the results from the LECO laboratory with those of Corpesca using the Kjelfoss technique and estimates of differences. These results are plotted in Figure 1.

LECO then proposed applying a correction to each of its samples resulting in the figures in Table 3 and Figure 2.

CONCLUSION

Protein determination in the 20 samples of Chilean fish meal ranging from 66% - 73% protein were satisfactorily close between the Kjelfoss and LECO techniques once the correction factor had been applied.

TABLE 1

RESULTS OF ANALYSIS

Analysis:	% Protein
Requested by:	Corpesca S.A.
Samples:	Fish meal
Date:	23/04/98

PARAMETERS

Instrument	Analysis of nitrogen LECO FP-528L
Sample weight	0.25 grammes approx.
Analysis time	250 seconds
Standard used	EDTA p.a. 9.56% of nitrogen
Results	In duplicate and triplicate

	Analysis 1	Analysis 2	Analysis 3	Average	S.D.
1	69.3	68.8	68.8	69.0	0.3
2	68.0	68.2		68.1	0.1
3	67.4	67.4		67.4	0.0
4	67.0	67.8		67.4	0.5
5	66.3	66.4		66.4	0.1
6	66.7	67.2		67.0	0.4
7	66.7	65.9		66.3	0.6
8	66.7	67.3		67.0	0.6
9	66.5	66.2		66.4	0.2
10	73.9	73.2		73.6	0.5
11	74.1	74.1		74.1	0.0
12	72.1	72.3		72.2	0.1
13	71.9	71.8		71.9	0.1
14	71.7	72.5		72.1	0.6
15	72.0	71.9		72.0	0.1
16	72.3	72.6		72.4	0.2
17	72.6	73.1		72.9	0.4
18	72.3	72.8		72.6	0.4
19	72.2	72.8		72.5	0.4
20	72.2	71.9		72.1	0.2

TABLE 2

COMPARISON OF RESULTS
CORPESCA VERSUS FP-528L

	LECO (FP-528L)	CORPESCA (Kjelfoss)	DIF
1	69.0	68.2	0.8
2	68.1	67.4	0.7
3	67.4	66.4	1.0
4	67.4	67.5	-0.1
5	66.4	65.3	1.1
6	67.0	66.4	0.6
7	66.3	65.8	0.5
8	67.0	66.3	0.7
9	66.4	66.1	0.3
10	73.6	72.9	0.7
11	74.1	72.2	1.9
12	72.2	71.3	0.9
13	71.9	71.0	0.9
14	72.1	70.9	1.2
15	72.0	71.3	0.7
16	72.5	72.1	0.4
17	72.9	71.7	1.2
18	72.6	73.1	-0.5
19	72.5	72.3	0.2
20	72.1	72.0	0.1

TABLE 3

COMPARISON OF RESULTS USING CORRECTED VALUES OF THE EQUIPMENT 528L

	CORPESCA (Kjelfoss)	LECO FP-528L	DIF
1	68.2	68.3	0.1
2	67.4	67.5	0.1
3	66.4	66.8	0.4
4	67.5	66.8	-0.7
5	65.3	65.8	0.5
6	66.4	66.4	0.0
7	65.8	65.7	-0.1
8	66.3	66.4	0.1
9	66.1	65.8	-0.3
10	72.9	72.9	0.0
11	72.2	73.4	1.2
12	71.3	71.5	0.2
13	71.0	71.2	0.2
14	70.9	71.4	0.5
15	71.3	71.3	0.0
16	72.1	71.8	-0.3
17	71.7	72.2	0.5
18	73.1	71.9	-1.2
19	72.3	71.8	-0.5
20	72.0	71.4	-0.6

Correction Factor: 0.9905
Correlation Coefficient 0.9830

Correction Factor: $\frac{\text{Sum of results of Corpesca}}{\text{Sum of results of FP - 528L}}$

G. BUSCH & CIA. LTDA.

EQUIPOS PARA LABORATORIOS QUIMICOS , DE ALIMENTOS Y METALOGRAFICOS

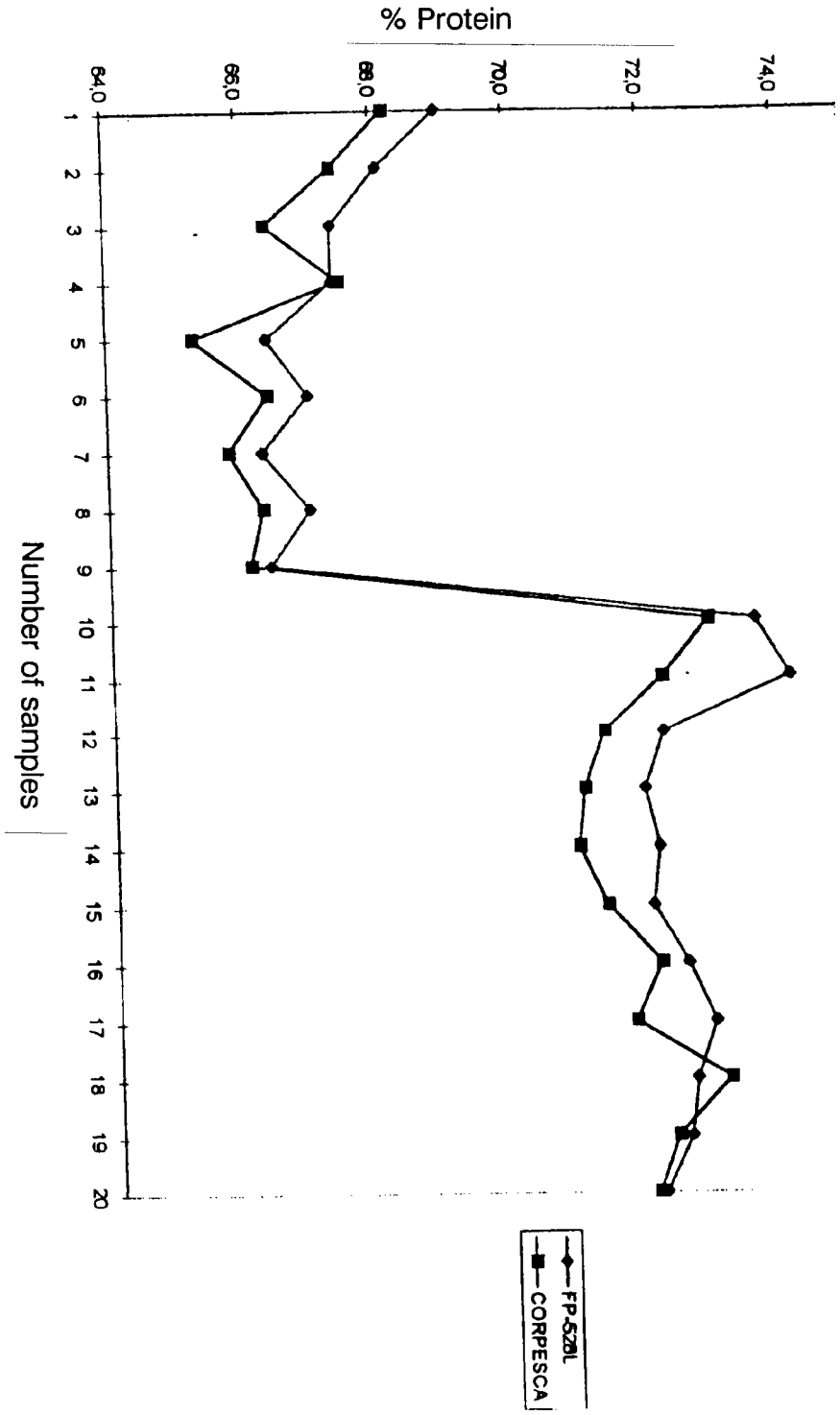

Figure 1 COMPARISION CORPESCA VERSUS FP528L

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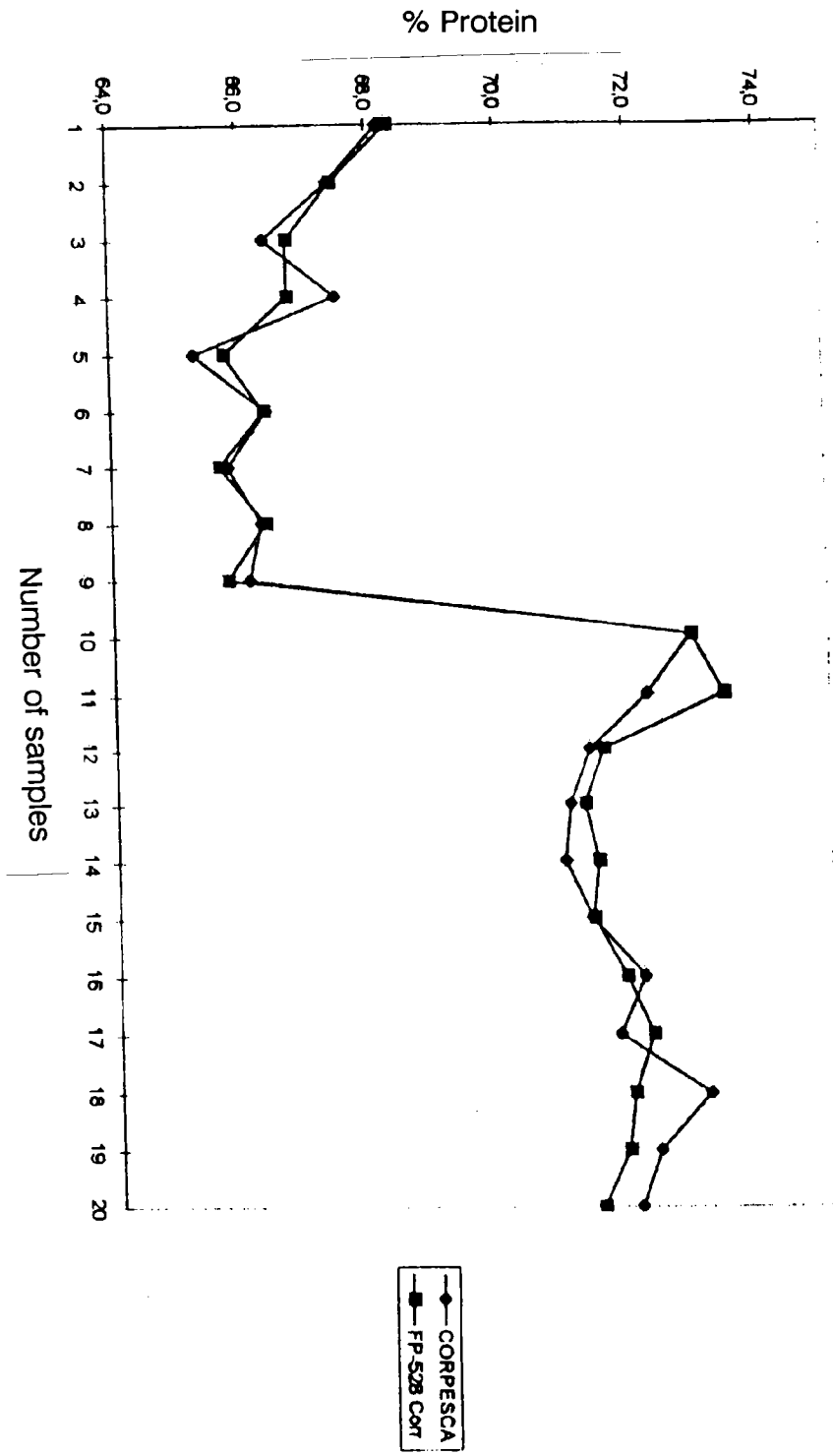

Figure 2 COMPARISION CORPESCA VERSUS FP528L (Corrected)