Tecaliman
Center of expertise for a sustainable feed business

i'Tec_H12
May 2005

Keywords: Homogenisation, Homogeneity, Plant, Tracer.

Conformity and distribution trends in two tracers during plant manufacture of animal feeds

This test was designed to compare homogeneity and conformity trends at four sampling locations at a given industrial site, both before and after pelleting, and using two tracers: Chlortetracycline (CTC) and the RF-Blue Lake microtracer (MT).

1. Principle

The two tracers were incorporated together via a single premix that was injected into the standard additives incorporation circuit. Two feed batches containing the tracers were produced in series. These two batches were then sampled:

- at the mixer output (SM)
- at the entry to the silo bin upstream of the press (EB)
- at the press conditioner output (SB)
- at the entrance to finished products bins (EC)

These samples were used to evaluate the changes in tracer conformity and distribution in two successive batches.

2. Equipment and apparatus

2.1. Tracers

The two tracers (Table 1) were incorporated into the final feed product via a premix at 0.8% or 8 kg/ton. The dosage of microtracer and chlortetracycline was 25 250 ppm and 800 ppm respectively.

	MT	CTC premix
Bulk density (g/cm^3)	2.976	493.7
D50 (Sieving) (µm)	65.1	217.2
Standard geometric deviation	*1.47*	*1.59*
Angle of repose (flow) (°)	29.6	70.6

Table 1: Tracers - physical properties

2.2. Feedstuff

Two 2.5-ton batches of medicated pig feed with a liquid content of approx. 1% were used (Table 2 - Figure 1).

	L1	L2
Bulk density (g/l)	630.6	641.9
D50 (Sieving) (µm)	436.0	410.3
Standard geometric deviation	*2.16*	*2.15*
Angle of repose (flow) (°)	64.5	62.6

Table 2: Physical properties of the animal meal

L1 – SM **L2 – SM**

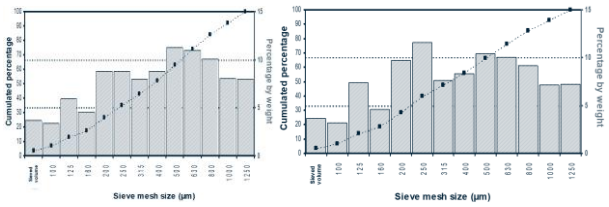

Figure 1: Animal meal particle size spectra

2.3. Circuit

The following equipment was set up between the various sampling stations:

Premix incorporation point
Weighing bin
2 Hatches
Hopper
Lock
Pneumatic conveyor belt
Cyclone
Lock
2 Hatches
Hopper above the mixer
Mixer
Hopper below the mixer
Chain conveyor

Mixer output (SM)
Elevator
3 distribution boxes
Chain conveyor
Bin
Screw
Molasser
Elevator

Entry to the silo bin upstream of the press (EB)
Distribution boxes
Silo bin upstream of the press
Hopper
Feed screw
Press conditioner

Press input (SB)
Press
Cooler
Elevator
Chain conveyor

Entry to the loading bin (EC)

2.4. Mixer

The reverse pitch double screw mixer has the following characteristics:

- Internal length 4.0 m
- External blade diameter 1.4 m
- Blade rotation speed 19 rpm
- Linear speed 1.37 m/s
- Design capacity 6.0 m^3
- Shaft diameter 0.15 m
- Number of hatches 1
- Opening mode Integrated

3. Method

3.1. Testing

The premix containing the tracers was added to the two batches. Data was collected both on weighings taken during batch manufacture and on pelleting conditions, and then used to interpret the results.
Sampling points were chosen so as to ensure that they were located in passing flows. The aim was to collect around 40 samples, sampling all batches and all 4 sampling points.
Sampling times ranged from 5.5 seconds to 37 seconds depending on the sampling station. At mixer output, samples were taken using an on-site cross-sampler. At the entries to the silo bin and the finished products bin the samples were taken directly in sampling pots. At the entry to the press (silo bin output), the samples were taken using a plastic hand and poured directly into the pots.

3.2. Processing the samples

Homogeneity trends in batch L1 were tracked by performing duplicate microtracer analyses on approx. every other sample. Ten samples taken from across the whole batch were selected for a single chlortetracycline analysis.
Homogeneity trends in batch L2 were tracked by performing microtracer and chlortetracycline analyses on approx. every other sample. The analyses on the two tracers were duplicated. A few samples from each batch were used to measure physical properties.
The microtracers were extracted magnetically based on the protocol described in **i'Tec_H17**; optical density was determined following solubilization. Tracer quantity was calculated by means of its linear relationship with an optical density of 629 nm.
Chlortetracycline underwent HPLC-analysis based on a protocol that enables detection up to a threshold of 0.2 ppm.

3.3. Processing the data

The data were processed according to the guidelines given in the technical rules in **i'Tec_H1**.

4. Results

4.1. Conditions governing batch manufacture

The weighing record shows expected concentrations of active ingredient that were close to the projected values (Table 3).
Mixing times were approx. 5 minutes in all, while the mixing time following the injection of liquids was closer to 4 minutes (Table 4). The mixer was cleaned months before the test.

Batches	Total weights (kg)	Expected conc. of microtracer (ppm)	Expected conc. of chlortetracycline (ppm)
L1	2520.5	248.0	793.5
L2	2525.5	247.5	791.9

Table 3: Record of weighings taken on the industrial site

Events	L1	L2
Opening of the weighing bins	0	0
Closing of the weighing bins	34'' 07	33'' 64
Start of liquid injection	55'' 93	56'' 28
End of liquid injection	1' 06'' 72	1' 05'' 70
Opening of the mixer	4' 56'' 61	4' 54'' 46

Table 4: Breakdown of mixing time for the two batches

The die was less than one month old, and therefore in the first quarter of its lifetime. The die had a thickness of 58 mm and was pierced with 6,720 4-mm diameter holes giving a compression index of 14.5. The two rollers had a honeycomb structure. Pelleting conditions were recorded (Tableau 5). The first batch had a difficult start due to jamming. The other batch pelleting operations proceeded smoothly.

	L1	L2	L3	L4
Débit (t/h)	5.2	6.6	6.5	6.5
Tpt sortie conditionneur (°)	58	64	64	64

Tableau 5 : Conditions de granulation

Moisture content analyses were carried out on aggregate samples made up from each batch at all 4 sampling stations. The results demonstrated minor fluctuations in moisture content. These fluctuations were corrected in order to be able to track changes in tracer concentrations at constant moisture content.
Batch durability and the percentage of fines were determined (Eurotest) post-test using aggregate samples made up from the first two batches. The result revealed a slight variance in the percentage of fines but gave similar figures for durability.

	% de fines	Durabilité
L1	0.9	90.4
L2	1.6	90.3

Table 6: Percentage of fines and durability for the first two batches

4.2. Conformity trend

The mean concentrations of the two batches were determined based on the analyses performed on 10 or 20 samples, depending on which tracer or batch was involved.
These concentrations were scaled to the expected concentration for each tracer, calculated based on the on-site weighings in order to determine the recovery rates (Table 7).

	Batch 1		Batch 2	
	MT	CTC	MT	CTC
Mixer output	93.1	96.9	74.0	88.3
Silo bin input	90.4	95.2	90.3	85.7
Silo bin output	68.9	88.3	78.5	81.5
Bin input	51.5	80.0	49.8	74.5

Table 7: Recovery rates for both tracers according to sampling location

These calculations were first used to validate all the tests based on the acceptance criteria listed in the technical rules (70 – 110%), excluding the microtracer results obtained post-pelleting.
During circuit throughput of batch L1, it was observed that the recovery rate for both tracers decreased as the distance travelled increased (Figure 2).

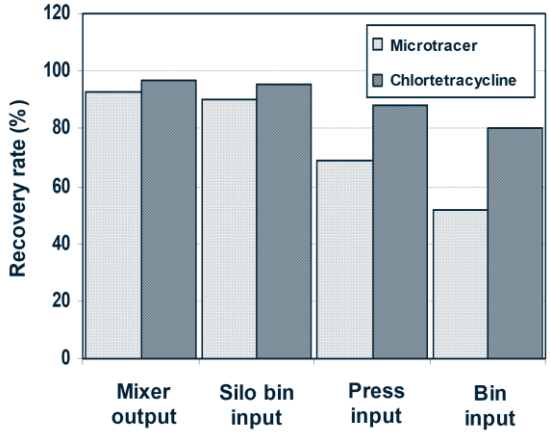

Figure 2: Changes in the recovery rate for batch L1 samples according to sampling location

At each sampling station, microtracer recovery rates were systematically lower than those for chlortetracycline. However, while the rates were equivalent at the first two sampling stations, the gap between the two tracers increased before and after the pelleting treatment.
This trend would seem to indicate three hypothetical phenomena:

- Widespread carry-over at the facility that disseminates the two traced products as the feedstuff travels through the circuits
- Higher microtracer carry-over rates result in a lower residual concentration
- The effects of pelleting on the two tracers, with the microtracer showing a higher sensitivity

Batch L2 gave slightly different results (Figure 3). The microtracer recovery rate at mixer output was lower than that recorded in the first batch while, logically, it should be higher due to this batch being contaminated by carry-over from the previous batch. The same applies to the chlortetracycline, but to a lesser degree.
Conversely, at the entry to the silo bin upstream of the press, the microtracer recovery rate regained the value recorded in the first batch, in contrast to the chlortetracycline which, for the first time, recorded lower recovery rates than the microtracer.

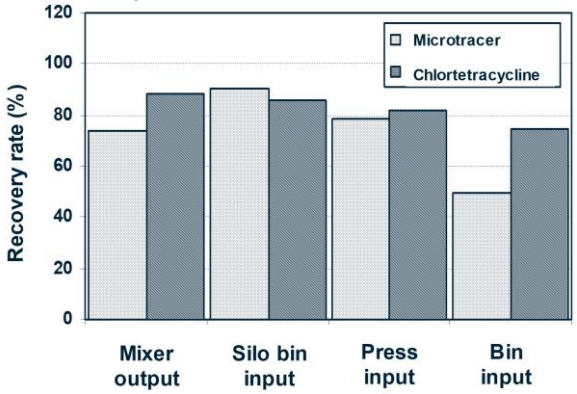

Figure 3: Recovery rate trend for batch L2 samples according to sampling location

While both tracers showed slightly lower concentrations at the press input, microtracer loss was less than in batch 1. After pelleting, however, the difference in recovery rates between the two tracers observed in batch 1 reappeared.
The most surprising feature of the batch 2 results is that, excluding the microtracer at the entry to the silo bin, both tracers showed lower recovery rates than those observed in batch 1 at the same locations, while reason states that they should be higher due to carry-over.
Despite this, overall recovery rates for both tracers were again seen to decrease from one sampling station to the next. This suggests that while the phenomena observed after throughput of batch 1 were confirmed by batch 2, understanding them is a little more complicated.
It has already been confirmed that the microtracer is damaged during heat treatment; it would now appear that the chlortetracycline also suffers partial damage.

4.3. Homogeneity trend

4.3.1. Batch L1

In contrast to the guidelines in the technical rules, microtracer analysis was performed on the first sample collected at the beginning of batch throughput. Including this sample in the variance analysis could lead to overestimating batch heterogeneity (Table 8). The size of the overestimate would increase in line with increasing dilution of the initial sample due to higher carry-over levels. The variance between the concentration of this sample and that of the batch mean is illustrated on the left-hand graphs in Figure 5. This reveals that for this batch and this production line, the variance is low at mixer output, rises at the entrance to the silo bin, and peaks on exiting the silo bin.

	CV $_{Homogeneity}$ (with Spl. 1)	CV $_{Homogeneity}$ (without Spl. 1)	"Variance"
SM	5.9	5.8	+ 0.1
EB	11.0	9.3	+ 1.7
SB	25.5	16.7	+ 8.8
EC	22.0	19.6	+ 2.4

Table 8: Microtracer coefficient of variation values for batch 1 according to sampling location - with or without the initial sample

If this sample is ignored, the homogeneity trend in batch 1 can be compared using the two tracers (Table 9). This comparison can only be made on this batch if using total coefficients of variation.
Based on the industry's current targets (CV < 5%), mixer performance would be considered acceptable for chlortetracycline, but not for the microtracer.
Figure 4 illustrates the increase in the coefficient of variation for microtracer distribution between sampling locations. Microtracer coefficients of variation are always higher than those of chlortetracycline.

	MT	CTC
SM	6.4	4.2
EB	9.4	8.1
SB	16.9	6.2
EC	19.8	5.2

Table 9: Coefficient of variation values for batch 1 for both tracers according to sampling location

While the values for chlortetracycline increased between the mixer output and the entrance to the silo bin upstream of the press, this was no longer observed in following samples - with the distribution even showing a slight tendency to improve. This difference in behaviour is clearly evident as from transfer between the silo bin's input and output locations. This increase in heterogeneity could be attributed to the lower microtracer concentration observed at the press input. However, adding 50 ppm artificially to the concentrations recorded at silo bin output in order to scale them up to the level of the

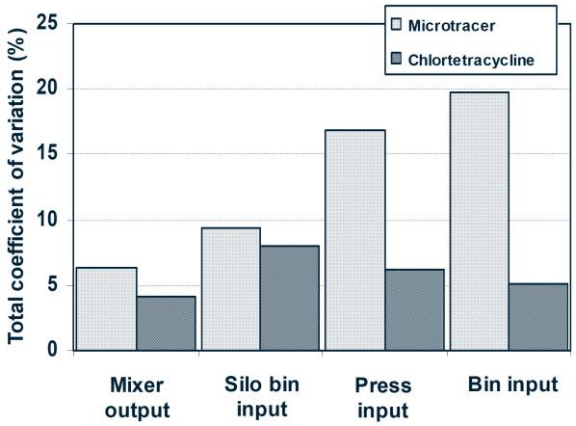

Figure 4: Change in total coefficient of variation values for batch 1 for both tracers according to sampling location

Comparing concentration trends during batch throughput at each sampling station (Figure 5 next page) can provide insight into the mechanism driving this difference in behaviour.
At mixer output, fluctuations from one sample to the next are clearly greater for the microtracer. Rather than a continuous variation in concentration, both tracers showed rapid fluctuations around the mean. This type of configuration argues that the mixer has distributed the products in question to the best of its capability.
At the entrance to the silo bin upstream of the press, there is evidence of a fluctuation in concentration for both products, but this is more marked for the microtracer. The concentration rises gradually during the first two thirds of batch throughput, then falls slightly before finally rising sharply at the end of the batch. This concentration trend profile indicates that the batch is starting to segregate, which could be explained by its transfer through various equipment (2 elevators, chain conveyor, molasser, feed screw) and the feedstuff's relatively broad particle size spectrum.
At the silo bin output, while the coefficient of variation is different, the fluctuation in concentration is visible with both tracers in the form of two successive peaks. The microtracer showed a greater range of variation.
After pelleting, concentration trends diverge significantly.
As with previous tests, it would appear that the microtracer amplifies the observed segregation phenomena.
The trend profiles and coefficient of variation follow a similar direction at the first two sampling stations but, on exiting the press conditioner, while the trends remain parallel the coefficient of variation values start to diverge. Lastly, the correlation becomes practically non-existent after pelleting. As the disturbance is clearly linked to the steam injection phase (decrease in microtracer concentration, change in variation of coefficient), it would not be unreasonable to assume that the heat treatment is driving the gap between the two tracers, even if the

treatment was only moderately applied in this test.

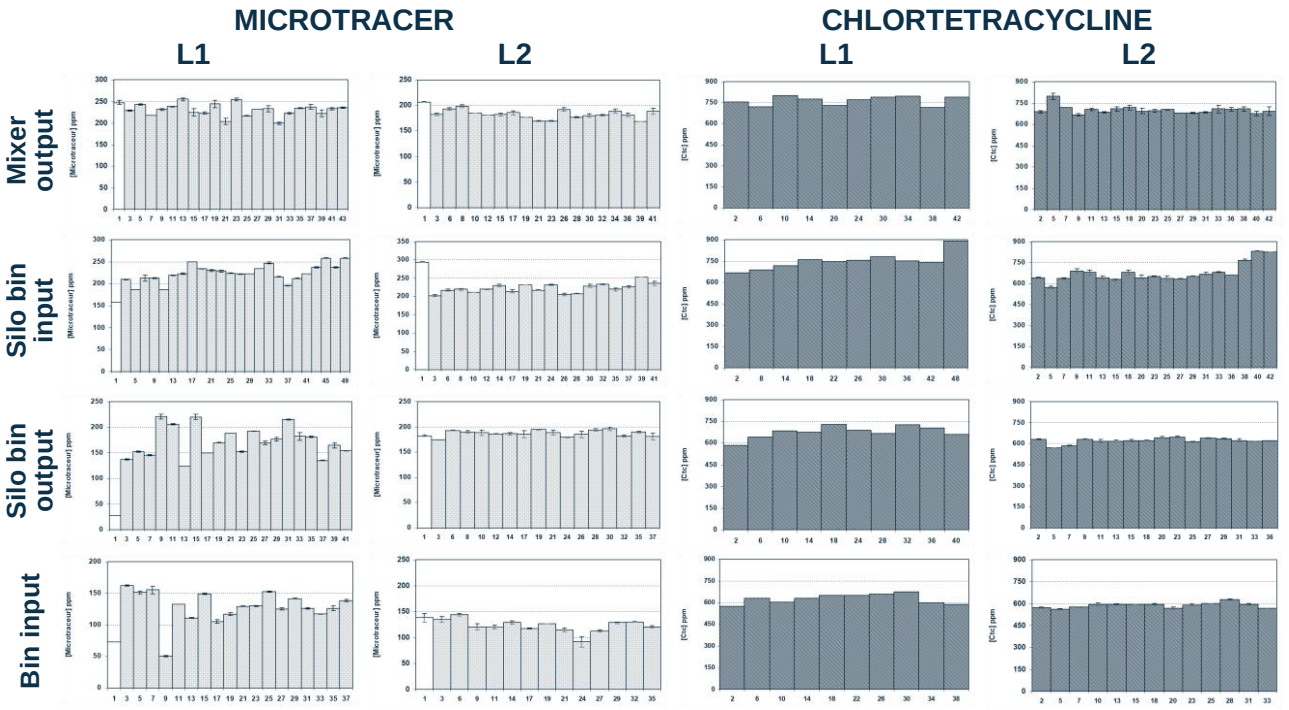

Figure 5: Concentration trend for both tracers according to throughput of the two batches at each sampling point

4.3.2. Batch L2

In contrast to batch 1, including the initial sample taken at the beginning of batch throughput in the assessment did not generate any significant deviation between the batch 2 coefficients of variation (Table 10).

	CV Homogeneity (with Spl. 1)	CV Homogeneity (without Spl. 1)	"Variance"
SM	5.1	4.3	+ 0.8
EB	8.8	5.1	+ 3.7
SB	2.5	2.5	+ 0.0
EC	9.8	9.8	+ 0.0

Table 10: Microtracer coefficient of variation values for batch 2 according to sampling location - with or without the initial sample

This result can be explained by the existence of carry-over between these two successive batches. This interpretation was confirmed by comparing concentrations between the initial sample and the rest of the batch. While the concentrations of the initial samples were lower in the first batch, they were higher in this second batch. The clearest result was observed at the entrance to the silo bin where batch 1 finished with an increase in microtracer concentration, while batch 2 started with a decrease (Figure 5). This suggests that fines with a high tracer content remain in the transfer circuit at the end of the first batch, and are then picked up at the start of the second batch.
Duplicating the analyses for both tracers on a large number of samples enabled a more reliable comparison of their behaviour based on $CV_{homogeneity}$.
As other tests have shown, while $CV_{homogeneity}$ values at mixer output were lower for batch L2 than for batch L1, the ranking between the two tracers remained the same (Table 11). The most likely interpretation is that this phenomenon is an illustration of the impact of carry-over on homogeneity.

	MT	CTC
SM	4.3	3.2
EB	5.1	7.9
SB	2.5	3.1
EC	9.8	2.8

Table 11: Homogeneity coefficient of variation values for batch 2 for both tracers according to sampling location

Batch transfer in the circuit between the mixer and the entrance to the silo bin upstream of the press again resulted in segregation of the two tracers (Figure 6). However, in this second batch, the segregation was more marked for chlortetracycline than for the microtracer. This reversal of the ratio between the tracers was observed both in recovery rate and in homogeneity.

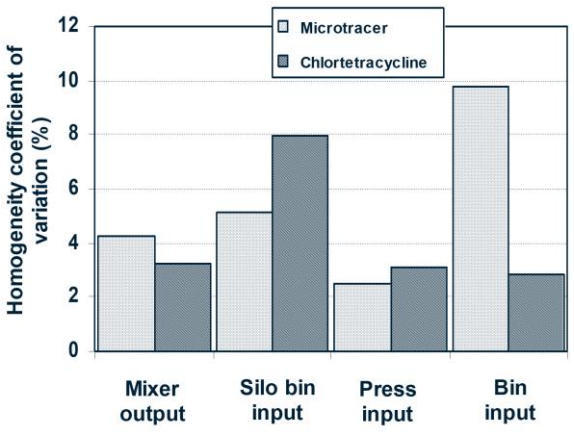

Figure 6 : Change in homogeneity coefficients of variation in batch 2 for both tracers according to sampling location

In batch 1, after passing through the silo bin upstream of the press, the chlortetracycline was distributed more effectively than the microtracer. In batch 2, however, a significant improvement was observed in the distribution of both tracers. As at the silo bin input, the distribution of microtracer was better than that of the chlortetracycline. Lastly, while chlortetracycline distribution remained stable after pelleting, microtracer distribution showed a clear deterioration.
Comparing concentration trends during throughput of batch 2 (Figure 5) does not fully explain the reversal in tracer rankings observed at silo bin input and output. Conversely, there was a reappearance of previously observed phenomena:

- Segregation that occurred between the mixer and the entrance to the silo bin upstream of the press, indicated by the tracers migrating towards the end of the batch. One possible explanation for this migration could again relate to feedstuff fines due to the feed's particle size distribution.
- Significant microtracer damage during pelleting, although concentration trends are fairly similar over most of the batch with, in particular, a fall in concentration in both tracers seen around sample 20.

5. Conclusion

Tracking the conformity of tracer batches during this test led to the unexpected observation that tracer concentrations decreased between the first and second batches while, following this, the presence of carry-over was effectively demonstrated by the decrease in recovery rates from one sampling station to the next.
This test nevertheless made it possible to demonstrate that using the RF-blue lake microtracer based on its latest dosing procedure provided reasoned insight into homogeneity status up to entry into the press. While obviously, in certain respects, the microtracer behaves differently to an internal tracer such as chlortetracycline, these differences may be considered fairly minor in terms of the differences in the products' physical properties.
Concerning homogeneity, as noted during previous industrial trials, the microtracer appears to amplify segregation phenomena. Therefore, while both tracers reveal additive transfer towards the end of the batches at the entrance to the silo bin upstream of the press, this transfer is more marked in the microtracer.
Conversely, despite the moderate pelleting conditions applied at this plant, some damage to the microtracer and/or the colorant it contains was observed following pelleting.

6. Bibliography

i'Tec_H1: Règles techniques pour l'évaluation du niveau d'homogénéisation. Fev. 2000.

i'Tec_T9: Nouvelle technique d'extraction du microtaceur RF Bleu lake et son évaluation. Jul. 2004.