

# Examination of packaging materials in bakery products 

A validated method for detection and quantification

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Cover: oil paint impression of remnants of packaging materials.

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## Summary

Methods for the detection and quantification of packaging materials in feed materials are necessary for the control of the prohibition of these materials according to Regulation (EC) $767 / 2009$. A method has been developed and validated at RIKILT for bakery products, including sweet bread and raisin bread. This choice is based on the situation that this category of former food products has the highest volume for re-use as feed ingredient.

The method of analysis can briefly be summarised as: 1) visual selection of undesired ingredients which can be identified as remnants of packaging materials, 2 ) weighing of the selected materials, 3) defatting, 4) dehydration, 5) final weighing, 6) reporting of weight and percentage. In all cases the total amount of the sample material was investigated, which is usually 500 grams. This procedure prevents inhomogeneity of the sample to be a problem.

The method for establishing the level of contamination with remnants of packaging materials in bakery products intended for animal feeding has been validated successfully at RIKILT with a quantification limit of $0.01 \% \mathrm{w} / \mathrm{w}$ and an average recovery of $95.5 \%$ at a contamination level of $0.15 \% \mathrm{w} / \mathrm{w}$. The standard deviation of the intra-laboratory reproducibility was $\mathrm{S}_{\mathrm{w}, 0.15}=0.012 \%$ $\mathrm{w} / \mathrm{w}$. The repeatability of the method could not be established because of the semi-destructive nature of the method. The method is accredited in 2010 by the Dutch Board for Accreditation (RvA).

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## 1 Introduction

In the current practice of food production, proper packaging of materials is provided for assuring quality maintenance during transport and storage. Article 6 of Regulation (EC) 767/2009 of the European Parliament and of the Council of 13 July 2009, states that: "Feed shall not contain or consist of materials whose placing on the market or use for animal nutritional purposes is restricted or prohibited". In Annex III of this Regulation, packaging from the use of products from the agri-food industry, and parts thereof, are mentioned as prohibited for placing on the market or use for animal nutritional purposes.

The main or at least one of the main categories of former food products intended for feeding purposes (FFPs) is bakery products. This category includes dried and ground meal from bread and biscuit products. Biscuit meal comprises sweet bread, raisin bread, biscuits, treacle waffles, chocolate bread (not confectionary), gingerbread, breakfast cereals, crisps, nuts, a.o. The estimated volume of recycling in the Netherlands is approx. 150,000 metric ton (MT). Approximately an identical volume is imported from surrounding countries, especially Germany, which means that an estimated amount of 300,000 MT of bakery products are processed in the Netherlands to yield animal feed. The processed bread is predominantly packaged, while the majority of the biscuit products is processed unpacked (ca. 80\%) (van Raamsdonk et al., 2011). The importance of the share of bakery products is also indicated in previous studies (Kamphues, 2005).

From 2005 on, the Netherlands Food and Consumer Product Safety Authority (NVWA) has conducted the official control of remains of packaging materials in FFPs that are intended to be used as feed material. RIKILT Institute of Food Safety has carried out the analyses in the framework of this monitoring program. The majority of these samples (160 out of 243 as analysed between 2005 and 2010) consisted of dried and ground bakery products (bread and biscuit meal). Some other categories are sweets (in the form of syrups), chocolate products, and dairy products (predominantly milk and whey powders). A remainder category consists of a diversity of products, ranging from vegetable products, potato products, dough for baking, to starch products (van Raamsdonk et al., 2011).

In the framework of the Dutch monitoring program a method for detection and quantification of packaging materials in bakery products intended as feed material has been developed and validated. The scope of the method excludes the detection of remnants of packaging materials in processed (e.g. pelleted) matrices. This report presents the method and the parameters of its performance.

## 2 Method development

### 2.1 Background

The type of packaging materials is not easy to establish. For food products relevant for reclaiming and re-use in feed production, mainly plastics, and paper and board packaging materials are used. Principally, the following types of materials can be present:

- polyolefins (PO, including polypropylene (PP) and polyethylene (PE); [1]),
- polyethylene terephthalate and its copolymers (PET; [2]),
- polystyrene (PS; [3]),
- rigid polyvinylchloride (PVC; [4]),
- regenerated cellulose (RC; [5]),
- paper and board [6],
- aluminium foil [7].

In general, in processed FFP fibres (representing paper and board), plastic (including PP, PE, PET, PS, PVC, RC), aluminium (aluminium foil as well aluminium coated paper that is usually used as wrapping of sweets a.o.), and metal (clips) can be recognised. RC should not be classified as plastic, but distinction is not feasible.

### 2.2 Method development

The original material is usually fractionated by the factory in a mill with 2 to 4 mm mesh size. Therefore, the method applies to ground and dried meal from bread and biscuit products. Biscuit meal comprises sweet bread, raisin bread, biscuits, treacle waffles, chocolate bread (not confectionary), gingerbread, breakfast cereals, crisps, nuts, a.o. No further processing in the laboratory, such as grinding, is applied to the samples before analysis.

The basic principle is to select and separate every particle that is not native to the matrix by bare eye examination. It is necessary for a proper selection procedure to have particles of approximately the same size. Furthermore, the difficulty of recognising and picking up of particles depends on their size. Particles smaller than 1 mm are very difficult to handle. The effect of sieving was tested by examination of eight samples from practice.

Table 1. Description of samples used for the method development.

| RIKILT nr | matrix | Type packaging material |
| :--- | :--- | :--- |
| RIK208913 | Bread meal | Fibres, plastic, aluminium coated paper |
| RIK210280 | Bread meal | Fibres, plastic |
| RIK215359 | Bread meal | Fibres, plastic |
| RIK210282 | Bread meal | Fibres, plastic |
| RIK211732 | Bread meal | Fibres, plastic |
| RIK211735 | Biscuit | Fibres, plastic, aluminium coated paper |
| RIK211733 | Biscuit | Fibres, plastic, aluminium coated paper |
| RIK214297 | Biscuit | Fibres, aluminium coated paper |

The samples listed in Table 1 were sieved with sieves of mesh sizes of $4.75 \mathrm{~mm}, 2.0 \mathrm{~mm}, 1.0 \mathrm{~mm}$ and 0.5 mm , resulting in five fractions. Of every fraction, the non-native particles were selected and weighted separately. The resulting amounts of the fractions and of the selected portions were presented in Figures 1 and 2.


Figure 1. Share of material of five size fractions of bakery products. $X$-axis: size limits of the particles of each fraction. $Y$-axis: cumulative amount $(g)$ of the fractions.


Figure 2. Share of amount of remnants of packaging material in five size fractions of bakery products. $X$ axis: size limits of the particles of each fraction. $Y$-axis: cumulative amount $(g)$ of the remnants.

The contribution of the fraction with particles larger than 4.75 mm to the total amount of material in the samples was negligible (Figure 1). The share of other fractions differed between the samples, but in all cases their contribution was significant. The major share of fragments of packaging material was recovered from the three fractions with the larger particles ( $>1 \mathrm{~mm}$ ). The other two fractions did not contribute to the final amount of packaging materials (Figure 2). It was concluded that it is not necessary to separate the fraction with the largest particles ( $>4.75 \mathrm{~mm}$ )
and the fraction with the smallest particles ( $<0.5 \mathrm{~mm}$ ). Only sieves of mesh sizes of 2.0 mm and 1.0 mm need to be applied, resulting in three fractions.

The remaining fragments of packaging materials can absorb a certain amount of fat or grease, and of water, depending on the type of matrix. In order to establish this effect and to assure that the selected portion of fragments is a net amount, defatting and dehydrating experiments were carried out. Four samples of 400 grams were contaminated artificially with 0.6 grams of fragments of packaging materials $(0.15 \% \mathrm{w} / \mathrm{w})$ and placed at room temperature for a week. The four samples were sieved, all fragments were selected from the several fractions and weighted (gross weight). The fragments were defatted in tetrachloroethylene (TCE) for four hours, the remaining TCE was decanted and the remaining portion was dried at $60^{\circ} \mathrm{C}$ for at least four hours. The remaining material was weighted again (net weight). The fragments were put back in the matrix, thoroughly shuffled, and kept at room temperature for seven days. After that a second procedure was started by sieving the sample, selecting the fragments, weighting, defatting, drying and weighting again. The results are presented in Table 2.

Table 2. Results of two experiments using the same set of four samples for establishing the effect of defatting and of drying on the remnants of packaging materials in feed.

|  | EXPERIMENT |  |  | EXPERIMENT |  |  |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Sample | Gross weight <br> of fragments <br> before <br> defatting and <br> drying | Net weight of <br> fragments <br> after <br> defatting and <br> drying | Percentage <br> recovered | Gross weight <br> of fragments <br> before <br> defatting and <br> drying | Net weight of <br> fragments <br> after <br> defatting and <br> drying | Percentage <br> recovered |
| Bread <br> meal 1 | 1.22 g | 0.7250 g | $120.8 \%$ | 0.82 g | 0.7210 g | $120.2 \%$ |
| Bread <br> meal 2 | 3.22 g | 0.6107 g | $101.7 \%$ | 2.79 g | 0.5750 g | $95.8 \%$ |
| Biscuit <br> meal 1 | 1.66 g | 0.7107 g | $118.5 \%$ | 1.14 g | 0.6490 g | $108.2 \%$ |
| Biscuit <br> meal 2 | 1.22 g | 0.6343 g | $105.7 \%$ | 1.08 g | 0.6654 g | $110.9 \%$ |

The difference in gross weight between the fragments in the first experiment and the second experiment is obvious. Apparently the fragments could not absorb the same amount of fat and/or water. Although the net weights of both experiments show a good reproducibility, the recovered amounts were between $95 \%$ and $121 \%$ of the original amount of contaminating material.

The method was improved by decanting over a sieve with a mesh size identical to the fraction (either 1 mm or 2 mm ). The result was that small grains of the matrix, originally adhering to the fragments of packaging material but released during the defatting process, could be removed together with the TCE. The clean fragments of packaging material were then collected on top of the sieve and dried. Several periods of time for the defatting and drying steps were tested, resulting in an optimization of the method.

### 2.3 Method description

The description of the method of analysis is:

1. Principally approx. 500 grams of material (former food product) is taken for investigation, without further pre-treatment. The entire sample is weighted. The material is sieved at mesh sizes of 2 mm and 1 mm . The fraction with particles larger than 2 mm , the fraction with particles between 1 and 2 mm and the fraction with particles less than 1 mm are all weighted individually. The two largest fractions ( $>2 \mathrm{~mm}$ and $1-2 \mathrm{~mm}$ ) are investigated separately for remnants of presumed packaging materials in a large plate with upright borders. All particles that are not native to the matrix are selected and kept apart in two separate portions. The selected particles are picked up by a pair of tweezers. If necessary, a large magnifying glass can be used. These two portions of remnants of presumed packaging materials are kept separately for the entire process.
2. The two portions of selected material are weighted (gross weight).
3. Defatting: the two portions each are placed in a beaker together with 50 ml of tetrachloroethylene (TCE) for 10 min . The TCE is decanted over a sieve of the appropriate mesh size ( 2 mm or 1 mm , respectively). The remnants are each placed in a sieve tray for drying overnight.
4. Dehydration: the two portions in the sieve trays are placed in an oven at 60 degrees Celsius for 4 hours.
5. The two portions are weighted for establishing the final amount (net weight). The amounts, together with the results of step 1), are used to calculate the percentage (w/w) of the amount of remnants of presumed packaging materials per fraction and for the entire sample.
6. If necessary and depending on the nature of the sample, selected portions of 1 gram can be taken from the third fraction with particles smaller than 1 mm for a further investigation under the microscope for the presence of remnants of presumed packaging materials. Quantification of these small particles is at least time consuming to get a rough estimate at the best. During the validation study it was concluded that if any small particles are present in this third fraction, the share in the total weight is insignificant. If desired the nature of the remnants found can be established (e.g. paper, board, plastic aluminium, foil etc.).
7. Reporting of net weight and percentage (w/w).

## 3 Results

### 3.1 Method validation

Validation of a method of analysis at RIKILT is implemented according to the Dutch guidelines NEN 7777 and NEN 7779. For a newly developed method it is requested to establish the values for the parameters reproducibility, accuracy, limit of detection, selectivity and robustness. The repeatability was not examined due to the situation that the full samples are investigated and that the method as described is semi-destructive. Duplicate samples and, hence, duplicate results were therefore not available.

The measuring range chosen is $0.02-0.15 \% \mathrm{w} / \mathrm{w}$. The $0.15 \%$ contamination level was based on unofficial proposals for a reasonable tolerance limit (Kamphues 2005; van Raamsdonk et al., 2011). The $0.02 \%$ level was the assumed limit of detection. The procedure chosen was an intralaboratory validation, which means that only the intra-laboratory reproducibility was established.

### 3.1.1 Description of the experiments

The mentioned guidelines request a series of experiments to be carried out:

- Experiment A: Eight samples from practice (four bread meals, two biscuit meals, two other matrices within the scope, all contaminated with an unknown amount of packaging materials) are measured twice for establishing the intra-laboratory reproducibility. The selected fragments of packaging material were replaced in the sample after the first examination. The waiting time between the two examinations was one week in order to allow the fragments of packaging materials to re-assimilate fat and moist from the sample.
- Experiment B: Eight laboratory samples (four bread meals, four biscuit meals) were artificially contaminated with $0.15 \%$ of fragments of relevant packaging materials. The results were used to establish the accuracy.
- Experiment C: Eight laboratory samples (four bread meals, four biscuit meals) were artificially contaminated with $0.02 \%$ of fragments of relevant packaging materials for determining the limit of detection.
- Experiment D: Two samples of bread meal were contaminated with $0.15 \%$ of fragments of packaging materials together with $0.15 \%$ of chocolate sprinkles, and two biscuit meals with $0.15 \%$ of fragments of packaging materials together with $0.15 \%$ of raisin fragments. These samples were used to examine the selectivity.
- Experiments E1 and E2: Two samples of bread meal contaminated with $0.15 \%$ of fragments of packaging materials were defatted in TCE at a shorter time ( 5 minutes instead of 10 minutes), and two samples of bread meal contaminated with $0.15 \%$ of fragments of packaging materials were dehydrated during a shorter period ( 3 hours instead of 4 hours). These experiments were used to establish the robustness.

Experiments B, C, D and E are based on artificially made matrices without remnants of packaging materials, produced by RIKILT. Adulteration was carried out according to the descriptions of the experiments. All experiments were carried out during the months November and December 2009.

### 3.1.2 A-priori set limits for performance parameters

The criteria used for approving the performance of each of the parameters are a-priori set based on the guidelines or on internal RIKILT standards. The guidelines and standards are originally developed for chemical method of analysis. Modification is applied when necessary since the current method is based on visual inspection with a semi-destructive nature. The latter implied that the parameter repeatability could not be established.

The Dutch guidelines NEN 7777 and NEN 7779 provide equations for calculating whether performance parameters are within limits, but does not provide the actual values for these limits. EU legislation provides guidelines (EC, 2002) for setting limits for performance parameters. A working group of the European Commission developed guidelines for pesticide analysis, including criteria for performance parameters (EC, 2009b). In addition, International Standard ISO 5725 (ISO, 1994) has been used to approve further the strategy chosen in this study for fixing the parameters limits. The result of the justification of the chosen a-priori parameter limits based on these literature sources is presented in Table 3.

The minimal limits which can be chosen for accuracy or recovery differ for different circumstances. The range is wider for screening methods (60-140\%) than for confirmation methods (70-120\%; EC, 2009b). In addition, for lower levels of contamination modified ranges might be used (EC, 2002). RIKILT, based on EC (2002), applies as common procedure to apply a range of $80-110 \%$. This range was set as a-priori criterion for the accuracy.

The intralaboratory reproducibility can be defined in relation to the level of contamination (EC, 2002). The given examples range from $1 \mu \mathrm{~g} / \mathrm{kg}$ to $1000 \mu \mathrm{~g} / \mathrm{kg}$, which is a factor of 1000 below the levels in the current study. The reproducibility is defined in EU (2009b) as precision (RSD ${ }_{w R}$ ) and should be lower than or equal to $20 \%$. This statement, which is applicable for chemical analysis, cannot clearly be transformed to semi-destructive visual methods of analysis. In the current study the second analysis of a sample was applied on a version of the test sample that was restored as good as possible (re-integration of the remnants of the packaging materials in the total sample, storage for one week to allow assimilation of fat and moist). Under these circumstances a limit of $S_{w}=0.02$ has been used.

The level of quantification is defined (EC, 2009b) as the level where quantified results can be achieved complying to the criteria for accuracy ( $70-120 \%$ ) and precision ( RSD $_{\mathrm{wR}}<=20 \%$ ). It was chosen in the current validation study to use a contamination level of $0.02 \%$ as presumed level of detection. The experimental results will show if this limit can be validated as level of quantification.

For robustness two aspects of the method have been altered. The experimental results are expected to maintain within the limits for accuracy (80-110\%).

### 3.2 Results of the validation experiments

The full data of the five experiments are presented in Annex I. The summary of the results of the validation experiments with the performance parameters of the method is shown in Table 3.

The standard deviation of the intra-laboratory reproducibility was $\mathrm{S}_{\mathrm{w}, 0.15}=0.012 \% \mathrm{w} / \mathrm{w}$. The relative deviation between the duplicate analyses of each sample was $R_{\text {REL }}=32.75 \%$. These
results comply with the a-priori set criterion, and are acceptable considering the qualification of the method as semi-destructive. The relative deviation of the accuracy for the eight samples at the contamination level of $0.15 \% \mathrm{w} / \mathrm{w}$ was $\mathrm{d}_{\mathrm{T}, \text { rel }}=-4.48$, indicating that more than $95 \% \mathrm{w} / \mathrm{w}$ of the contaminated material was recovered. The recovery in seven out of eight samples was between $92.7 \%$ and $102.1 \% \mathrm{w} / \mathrm{w}$. The eighth sample showed a lower recovery ( $86.2 \% \mathrm{w} / \mathrm{w}$ ). Notwithstanding this result, the recovery is well within the set limits. Also at the level of contamination of $0.02 \% \mathrm{w} / \mathrm{w}$ the relative deviation and the precision are within the set limits, although the deviation was slightly larger than at the level of $0.15 \%$.

Table 3. Performance parameters of the method for quantification of remnants of packaging materials in bakery products.

| Parameter | Result | Criterion |
| :--- | :--- | :--- |
| Intra-lab reproducibility | $R_{\text {rel }}=32.75 \%, \mathrm{~S}_{\mathrm{W}, 0.15}=0.012 \% \mathrm{w} / \mathrm{w}$ | $\mathrm{S}_{\mathrm{W}}=0.02 \% \mathrm{~W} / \mathrm{w}$ |
| Accuracy $0.15 \%$ | $\mathrm{~J}=95.5 \%(86.2 \%-102.1 \%), \mathrm{d}_{\mathrm{T}, \mathrm{rel}}=-4.48$ | $80-110 \% \mathrm{w} / \mathrm{w}$ |
| Accuracy $0.02 \%$ | $\mathrm{~J}=94.3 \%(85.0 \%-105.5 \%), \mathrm{d}_{\mathrm{T}, \mathrm{rel}}=-5.73$ | $80-110 \% \mathrm{~W} / \mathrm{w}$ |
| Quantification limit | $\mathrm{S}_{\mathrm{AG}}=0.001246, \mathrm{AG}_{\mathrm{W}}=0.004 \% \mathrm{w} / \mathrm{w}$ | $\mathrm{AG}_{\mathrm{W}}=0.02 \% \mathrm{~W} / \mathrm{w}$ |
| Selectivity (chocolate, raisins) | $\mathrm{RA}=-2.99 \%, \mathrm{RA}=-0.57 \%$ | $5 \% *$ |
| Robustness (defatting, drying) | $\mathrm{RA}=-0.552 \%, \mathrm{RA}=0.734 \%$ | $5 \% *$ |

*: based on: 86.2\% (lowest recovery percentage) - 5\% > 80\%; 102.1\% (highest recovery percentage) + 5\% < 110\%

The calculation of the limit of detection was based on the analysis of eight samples contaminated at a level of $0.02 \% \mathrm{w} / \mathrm{w}$. Because of the semi-destructive nature of the method it was impossible to comply to the guideline by analysing the same sample at a series of subsequent days. The standard deviation of the eight results was $S_{A G}=0.001246$, resulting in a detection limit of $A G_{w}=3 * S_{A G}=0.004 \% \mathrm{w} / \mathrm{w}$ (calculation according to NEN 7777). As shown, the accuracy at the $0.02 \%$ level is within the set limits, which allows the conclusion that a reliable quantification is sufficiently reached at this level. Since the method as presented excludes the quantification of particles in the smallest fraction (particles $<1 \mathrm{~mm}$ ), it is reasonable to adjust the limit of quantification to $A G_{w}=0.01 \% \mathrm{w} / \mathrm{w}$. RIKILT applies the rule for the limit of quantification as $\mathrm{BG}_{w}=6 * \mathrm{~S}_{\mathrm{AG}}$. In the current practice of a visual method, however, it can be argued that every fragment of the contaminant that is detected will add to the final amount. In any case, the limit of quantification is well below the criterion of $0.02 \% \mathrm{w} / \mathrm{w}$ (see Table 3).

The relative deviations after adding confusing materials (chocolate sprinkles and ground raisins) for determining selectivity and after changing some method parameters (shorter drying time and shorter defatting time) for determining robustness are low in all cases (table 3). Because of the exclusive nature of the presented method parameters, setting criteria is difficult. A deviation of $5 \% \mathrm{w} / \mathrm{w}$ is set as criterion, since this value limits the results including the deviations between the range for recovery of $80-110 \% \mathrm{w} / \mathrm{w}$. The results for selectivity and robustness are well within this criterion.

## 4 Discussion en conclusions

The proposed method for detection and quantification of remnants of packaging materials in bakery products intended as feed ingredient is a non-chemical and semi-destructive method. Guidelines or standard procedures for validation of these methods are currently not available. It is also important to stretch that European guidelines for intralaboratory validation are not available as well. As a next best approach the Dutch guidelines NEN 7777 and NEN 7779 are applied and modified when necessary. In addition, guidelines for setting a-priori limits or performance parameters have been consulted.

The method is developed in line with other visual methods (see IAG section Microscopy for examples [8]). Nevertheless, modifications appeared to be necessary with respect e.g. to the fraction of the matrix with particles smaller than 1 mm and to the cleaning of the particles of the contaminant. Fibres of paper and board, fragments of plastic, aluminium foil and metal, chips of plastic clips and metal wires are the types of materials that can be recovered from the samples. These types are indicated along the way of appearance. The indication "plastic" refer to several types of packaging materials with each a different chemical background and application (van Raamsdonk et al., 2011).

The method for establishing the level of contamination with remnants of packaging materials in bakery products intended for animal feeding has been validated successfully at RIKILT with a quantification limit of $0.01 \% \mathrm{w} / \mathrm{w}$ and an average recovery of $95.5 \%$ at a level of $0.15 \% \mathrm{w} / \mathrm{w}$. The standard deviation of the intra-laboratory reproducibility was $\mathrm{S}_{\mathrm{w}, 0.15}=0.012 \% \mathrm{w} / \mathrm{w}$. The repeatability of the method was not established because of the semi-destructive nature of the method. The method is accredited in 2010 by the Dutch Board for Accreditation (RvA).

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## Internet links

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[2] http://en.wikipedia.org/wiki/Polyethylene_terephthalate (26 Jan 2011)
[3] http://en.wikipedia.org/wiki/Polystyrene (26 Jan 2011)
[4] http://en.wikipedia.org/wiki/PVC (26 Jan 2011)
[5] http://en.wikipedia.org/wiki/Cellophane (26 Jan 2011)
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[7] http://en.wikipedia.org/wiki/Aluminium_foil (26 Jan 2011)
[8] http://www.iag-micro.org/ (7 Dec 2011)
Annex I
Raw data validation experiments
Experiment A: Intralaboratory reproducibility

| sample type | Sample nr. | day 1 | day 2 | day 3 | day 4 | day 5 | day 8 | day 9 | day 10 | day 11 | day 12 | day 15 | day 16 | day 17 | day 18 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| bread meal | 1-217774 | 0.055\% |  |  |  |  | 0.057\% |  |  |  |  |  |  |  |  |
| bread meal | 2-230626 |  | 0.123\% |  |  |  |  | 0.111\% |  |  |  |  |  |  |  |
| bread meal | 3-229078 |  |  |  |  |  | 0.022\% |  |  |  |  | 0.025\% |  |  |  |
| bread meal | 4-232700 |  |  |  |  |  |  | 0.053\% |  |  |  |  | 0.052\% |  |  |
| biscuit meal | 5-233622 |  |  | 0.042\% |  |  |  |  | 0.051\% |  |  |  |  |  |  |
| biscuit meal | 6-227212 |  |  |  |  |  |  |  | 0.027\% |  |  |  |  | 0.037\% |  |
| other | 7-227211 |  |  |  | 0.084\% |  |  |  |  | 0.067\% |  |  |  |  |  |
| other | 8-217778 |  |  |  |  |  |  |  |  | 0.640\% |  |  |  |  | 0.598\% |

Experiment B: Accuracy

| sample type | Sample nr. | day 1 | day 2 | day 3 | day 4 | day 5 | day 8 | day 9 | day 10 | day 11 | day 12 | day15 | day 16 | day 17 | day 18 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| bread meal | B1 |  | 0.143\% |  |  |  |  |  |  |  |  |  |  |  |  |
| bread meal | B2 |  |  |  |  | 0.144\% |  |  |  |  |  |  |  |  |  |
| bread meal | B3 |  |  |  |  |  |  | 0.141\% |  |  |  |  |  |  |  |
| bread meal | B4 |  |  |  |  |  |  |  |  |  |  | 0.129\% |  |  |  |
| biscuit meal | K1 |  |  | 0.147\% |  |  |  |  |  |  |  |  |  |  |  |
| biscuit meal | K2 |  |  |  |  |  | 0.153\% |  |  |  |  |  |  |  |  |
| biscuit meal | K3 |  |  |  |  |  |  |  |  | 0.148\% |  |  |  |  |  |
| biscuit meal | K4 |  |  |  |  |  |  |  |  |  |  |  | 0.139\% |  |  |

Experiment C: Quantification limit

| sample type | Sample nr. | day 1 | day 2 | day 3 | day 4 | day 5 | day 8 | day 9 | day 10 | day 11 | day 12 | day15 | day 16 | day 17 | day 18 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| bread meal | B5 | 0.018\% |  |  |  |  |  |  |  |  |  |  |  |  |  |
| bread meal | B6 |  |  |  | 0.019\% |  |  |  |  |  |  |  |  |  |  |
| bread meal | B7 |  |  |  |  |  | 0.019\% |  |  |  |  |  |  |  |  |
| bread meal | B8 |  |  |  |  |  |  |  |  | 0.019\% |  |  |  |  |  |
| biscuit meal | K5 |  |  |  |  | 0.018\% |  |  |  |  |  |  |  |  |  |
| biscuit meal | K6 |  |  |  |  |  |  | 0.021\% |  |  |  |  |  |  |  |
| biscuit meal | K7 |  |  |  |  |  |  |  | 0.017\% |  |  |  |  |  |  |
| biscuit meal | K8 |  |  |  |  |  |  |  |  |  |  |  |  |  | 0.020\% |


| sample type | Sample nr. | day 1 | day 2 | day 3 | day 4 | day 5 | day 8 | day 9 | day 10 | day 11 | day 12 | day15 | day 16 | day 17 | day 18 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| bread meal* | B1 |  | 0.143\% |  |  |  |  |  |  |  |  |  |  |  |  |
| bread meal* | B3 |  |  |  |  |  |  | 0.141\% |  |  |  |  |  |  |  |
| bread meal | B9 |  | 0.143\% |  |  |  |  |  |  |  |  |  |  |  |  |
| bread meal | B10 |  |  |  |  |  |  | 0.143\% |  |  |  |  |  |  |  |
| biscuit meal* | K1 |  |  | 0.147\% |  |  |  |  |  |  |  |  |  |  |  |
| biscuit meal* | K4 |  |  |  |  |  |  |  |  |  |  |  | 0.139\% |  |  |
| biscuit meal | K9 |  |  | 0.147\% |  |  |  |  |  |  |  |  |  |  |  |
| biscuit meal | K10 |  |  |  |  |  |  |  |  |  |  |  | 0.151\% |  |  |

Experiments E1 and E2: Robustness

| sample type | Sample nr. | day 1 | day 2 | day 3 | day 4 | day 5 <br> (5'TCE) | day 8 <br> (3 hrs drying) | day 9 | day 10 | day 11 <br> (5'TCE) | day 12 | day 15 | day 16 | day 17 <br> (3 hrs <br> drying) | day 18 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| bread meal | B11 |  |  |  |  | 0.144\% |  |  |  |  |  |  |  |  |  |
| bread meal | B12 |  |  |  |  |  |  |  |  | 0.144\% |  |  |  |  |  |
| bread meal | B13 |  |  |  |  |  | 0.153\% |  |  |  |  |  |  |  |  |
| bread meal | B14 |  |  |  |  |  |  |  |  |  |  |  |  | 0.151\% |  |

RIKILT - Institute of Food Safety is part of the international knowledge organisation Wageningen UR (University \& Research centre). RIKILT conducts independent research into the safety and quality of food. The institute is specialised in detecting and identifying substances in food and animal feed and determining the functionality and effect of those substances.

RIKILT advises national and international governments on establishing standards and methods of analysis. RIKILT is available 24 hours a day and seven days a week in cases of incidents and food crises.

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RIKILT is a member of various national and international expertise centres and networks. Most of our work is commissioned by the Dutch Ministry of Economic Affairs, Agriculture and Innovation and the new Dutch Food and Consumer Product Safety Authority. Other parties commissioning our work include the European Union, the European Food Safety Authority (EFSA), foreign governments, social organisations, and businesses.

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