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Ferromagnetic nanotracers based on Fe and Co oxides: synthesis and their role in assessing the quality of mixing liquid feeds

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Abstract

Ensuring homogeneity of the feed mixing is crucial for animal health and productivity. The growing complexity of feed formulations increases the need for uniform mixtures, particularly for young animals, where balanced feed significantly affects growth and consumption. Ferromagnetic microtracers, developed by MicroTracers Inc., are used to monitor mixing uniformity in dry feed production. These microtracers, including iron-based types, are effective due to their magnetic properties, facilitating detection, and separation. However, they are less suitable for liquid feeds, leading to the development of magnetic nanotracers based on the iron oxide for liquid feed applications. Nanoparticle Tracking Analysis (NTA) is used to measure the size and distribution of nanoparticles in liquid feeds, ensuring thus effective mixing. The stability and uniform distribution of magnetic nanoparticles are crucial, with various surfactants, such as dimethylamine salt of oleic acid (DMAOA) and ammonium oleate, influencing particle size and aggregation. DMAOA provides better dispersion and stability, essential for quality control in feed production. The concentration of cobalt in nanoparticles $Fe_xCo_yO_z$ was determined by a modified spectrophotometric method.

Keywords: homogeneity of the feed mixing; spectrophotometric determination of cobalt; magnetic nanotracers; nanoparticle tracking analysis; quality control.

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1. Introduction

The production of compound feed, both dry and liquid, is a critical component of the agricultural sector. With an annual production capacity exceeding 500 million tons worldwide, this industry plays a vital role in ensuring the health and productivity of livestock [1]. One of the most crucial aspects of compound feed production is the mixing process, which ensures homogeneity and balance of the feed. Recently, the formulation of compound feed has become much more complex, comprising more and more components [2]. This complexity increases the need for homogeneity of the feed mixture. Whether the ingredients are added directly to the mixer or as premixes, achieving a homogeneous mixture is essential. The process of mixing ingredients is fundamental for the production of complete and balanced feed [3]. This is especially important with the increasing use of low-grade ingredients such as industrial amino acids and other additives. These components, although used in small quantities, are vital for the nutritional value of feed [1]. Therefore, precise mixing is necessary to ensure even access of these nutrients to all animals. The efficiency of the mixing process has also significant economic and ethical implications. On one hand, over-mixing of feeds may lead to the degradation of vitamins and medications or cause the splitting of ingredients [4]. On the other hand, insufficient mixing may result in feed portions with incorrect nutrient levels, leading to economic losses for feed consumers and increased pharmaceutical residues in the food chain [5]. Thus, periodic scheduled tests of mixers are justified from both an economic and ethical view. Such testing ensures that all micronutrients are added correctly

and evenly, meeting regulatory standards and feed nutritional requirements.

Creating a completely homogeneous mixture is a key stage in the production of both dry and liquid feeds. A statistical approach to the distribution of particles is often used to assess the quality of mixing of multicomponent dry compound feed [6, 7]. This method assesses how well the ingredients are distributed in the mixture, ensuring that each portion of feed is uniform. The procedure for checking the homogeneity of dry feeds and premixes using methods such as microindicators was first presented in the Technical Specifications TS1.11 – Control of Residues & Homogeneity Version EN: 1 January 2022 GMP+BA2 Standard "Residue control". Currently, this is the Technical Specification TS1.11 – Control of Residues and Uniformity [8–10].

The works [11, 12] suggest several types of indicators that may be used as markers containing the following information:

a) designation of the type of crop, which refers to agricultural products;

b) a specific feature related to an agricultural product;

c) genetic content of an agricultural product.

Over the past 30 years, particles such as ferromagnetic indicators have been successfully used in practice. These indicators may be separated from the bulk mixture using magnetic separators much faster and easier than previous indicators.

There are some other works (Eisenberg 1979, 1980, 1987) [13–15] that describe the application of ferromagnetic microtracers (MT), which were patented and manufactured by the American company MicroTracers Inc., located in San Francisco, USA. These MTs consist of iron or stainless steel particles ranging in size from 150 to 350 microns with various food dyes adsorbed on their surface. The proposed method involves introducing these ferromagnetic microtracers into the mixing equipment as a microadditive, with a recommended dosage of 50–100 grams per ton of compound feed.

Three types of iron-based microindicators are currently available:

Microtracer F: Consists of iron grit containing approximately 25.000 particles per gram of tracer.

Microtracer FS: Made of stainless steel, containing approximately 50.000 particles per gram of tracer.

Microtracer RF: Consists of reduced iron powder, containing over 1.000.000 particles per gram of tracer.

When preparing vitamin, mineral or therapeutic premixes, the microtracer serves to indicate the presence of the premix in the finished feed, as well as to identify feed additives and feed containing such additives, which are patented. In quantitative analysis, Microtracers® may be used to document both the mixing efficiency and the adequacy of "cleaning" of mixers and other feed production equipment from batch to batch.

2. Research methods

According to the standards for compound feed, mixers shall be characterized by their ability to mix effectively.

For the production of all feed mixtures (with a mixing ability of 1:10000), the coefficient of variation shall be $\leqslant 15\%$. For the production of premixes (with a mixing ability of 1:100000), the coefficient of variation shall be $\leqslant 10\%$.

When determining the homogeneity by direct methods according to the requirements of the standard [8], the probability (p%) is estimated as follows: $-p \leqslant 1\%$: Not enough; significant deviation is probable; $-1\% < p < 5\%$: Probable significant deviation; it is not possible to make an unequivocal statement. The test shall be repeated; $-p \geqslant 5\%$: Accepted homogeneity.

The obtained measurement results were verified statistically to determine the coefficient of variation, which serves as a value for assessing the quality of the mixing process based on these criteria (see Table 1).

Table 1

The number of particles of microindicators in consecutive samples (by replicates) selected during unloading of the compound feed mixer

Number of Samples Analyzed, 20				Tracer Recovery	94.17
131	124	155	153	Mean	141.28
159	145	134	141	Standard deviation	13.39
143	112	**138**	161	Coefficient of variation (%)	10.18
134	148	162	146	Coefficient of variation-Poisson (%)	8.41
141	111	150	137	Chi-Square	27.84
Probability (%)					6.46
Conclusion: The change of Probability of more than 5% proves a complete mix for the red tracer					

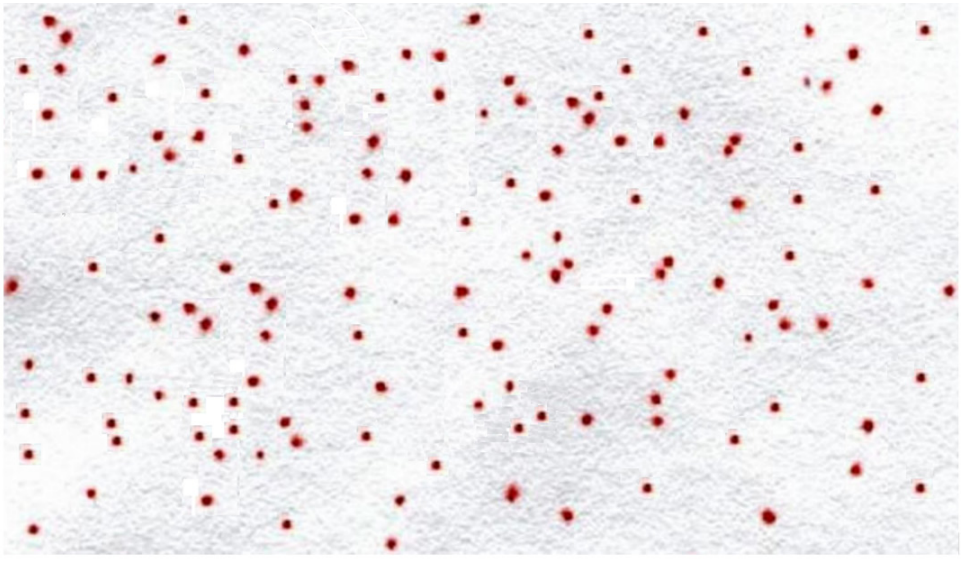

Fig. 1. Example of filter paper with microtracer particles used for quantitative microtracer testing

The number of particles (138 in Fig. 1) is obtained by counting the colored dots on the filter paper, either by eye or using a suitable computer system (such as the TraCo image evaluation and assessment system). To ensure accurate results, the statistical evaluation is performed according to the Poisson distribution.

It should be noted that iron-based microtracers are generally unsuitable for mixing liquid feeds and coding liquid additives such as enzymes and for assessing their distribution in premixes and finished feeds. To meet the growing demand for such liquid feeds, a magnetic pull-out nanotracer containing particles based on the iron oxide, which is a magnetic liquid, has been developed and tested [16]. Unlike microtracers, a nanotracer has a nanometer particle size, which ensures its high dispersity and uniformity of distribution in liquid media.

Typically, the process of obtaining a magnetic liquid consists of two main stages: obtaining magnetic particles of the required size and stabilizing them in the carrier liquid. Regarding the synthesis of magnetic nanoparticles, numerous papers and reviews have been published on this topic, as such particles are widely used not only in the preparation of magnetic nanoparticles but also in magnetic materials used in devices for magnetic recording and information storage, catalysis, electronics, electrical engineering, and other fields [17].

A review of the literature showed that one of the promising methods of obtaining ferromagnetic materials – magnetic nanoparticles (MNPs) – includes a two-stage process:

• First, ferromagnetic liquids (ferrofluids) are prepared [18];

• Dispersion of Ferrofluid Droplets: Ferrofluid Droplets are dispersed in an aqueous environment using a suitable surfactant. This process ensures the stabilization and uniform distribution of magnetic nanoparticles in liquid feeds, addressing the limitations of traditional iron-based microtracers [19].

Preparation of ferrofluid based on iron and cobalt oxides

Various methods have been developed to obtain nanoparticles, with chemical methods being among the most widespread ones. Co-precipitation from watersalt solutions with the addition of a base at room or higher temperature is usually used for the synthesis of magnetite [20].

The studies [21] evaluated the effect of salt mixtures: Fe^{2+}/Fe^{3+} $FeCl_2 \cdot 4H_2O$ – 5% (0.25 mmol/L); $FeCl_3 \cdot 6H_2O$ – 5% (0.17 mmol/L); $FeSO_4 \cdot 7H_2O$ – 2% (0.07 mmol/L); and Co^{2+} $CoCl_2 \cdot 2H_2O$ – 2% (0.12 mmol/L) for the process of biosynthesis of magnetic nanoparticles. MNPs obtained by the $FeCl_3/FeSO_4/CoCl_2$ mixture had a regular shape with little aggregation and were in the nanosize range (10–17 nm).

A modified technique [22] was used for the production of ferrofluid based on iron and cobalt oxides. For this, 0.44 M $FeCl_2 \cdot 4H_2O$, 0.95 M $FeCl_3 \cdot 6H_2O$ and 0.09 M $CoCl_2 \cdot 6H_2O$ were mixed in 1000 ml of water to obtain a homogeneous solution. Then, 350 ml of 28% aqueous ammonia solution and 350 ml of water were added to the resulting solution for 75 seconds. This led to the formation of magnetite in a colloidal state, which contains the cobalt oxide ($Fe_xCo_yO_z$). The magnetite solution was slowly heated to 90 °C with constant stirring.

To obtain a stable ferromagnetic liquid, a solution of oleic acid and heptane was prepared separately by mixing 40 ml of oleic acid and 460 ml of heptane and heating the mixture to 90 °C. The colloidal magnetite solutions and the oleic acid solution were mixed and stirred for 15 minutes, after which the upper organic layer was removed. The resulting stable ferromagnetic liquid had a saturation magnetization of 252 gauss, a density of 1.038 g/ml, and a viscosity of 4.3 cPz.

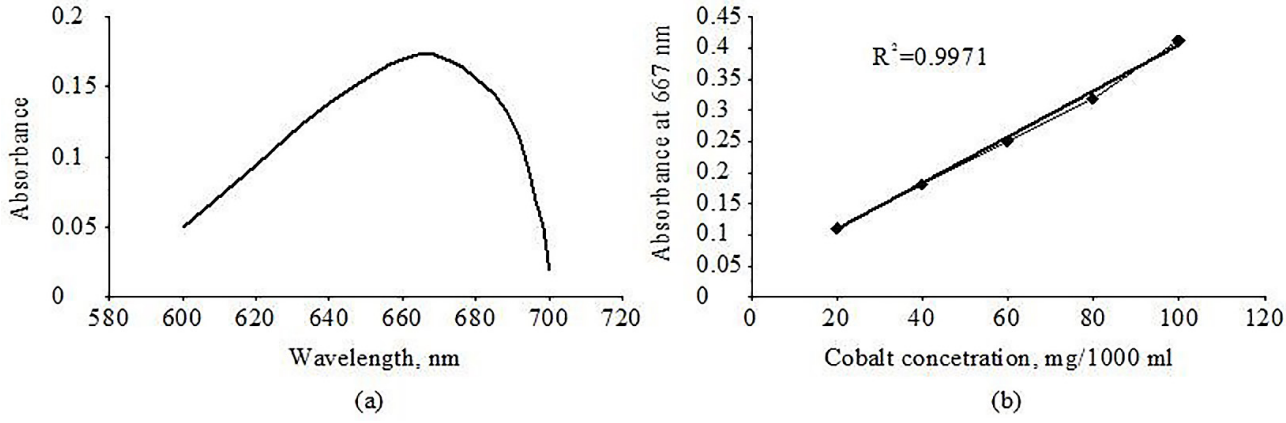

Fig. 2. a) – absorption spectrum of a complex containing cobalt thiocyanate and diethylamine in the DMSO solution; b) – calibration curve for determining the cobalt concentration in a suspension of $Fe_xCo_yO_z$ cobalt nanoparticles by the spectrophotometric method

The next stage was the dispersion of ferrofluid in a 0.5% aqueous solution of surfactant (ammonium oleate or dimethylamine salt of oleic acid (DMAOA)) in a mass ratio of ferrofluid: surfactant solution from 1:100 to 1:400. After that, the ferrofluid mixed with surfactant was filtered through Whatman filter paper with a pore size of 5 microns. The stable suspension was used both to determine the size of nanoparticles and to colorimetrically determine the content of cobalt in nanoparticles.

$Fe_xCo_yO_z$ suspension testing

One of possible ways of using the prepared stable suspension of ferromagnetic iron/cobalt oxide nanoparticles is:

- checking the quality of liquid feed mixing;
- coding of liquid additives, such as enzymes;
- assessment of the distribution of liquid additives in premixes and finished feeds.

The prepared stable suspension of $Fe_xCo_yO_z$ nanoparticles, which contains iron oxide (more than 95%) and cobalt oxide (less than 5%), was tested in laboratory and production tests, including checking the mixing quality of the liquid feed and coding of liquid additives.

In laboratory studies, a suspension of a nanotracer with a concentration of 100 ppm, which is mixed with a liquid enzyme (the concentration of the enzyme in the feed is 110 ppm), was added to dry feed with subsequent extraction of ferromagnetic nanoparticles. $Fe_xCo_yO_z$ nanoparticles were used as a magnetic marker and showed approximately 75% recovery in a laboratory test.

The cobalt concentration was determined by a modified spectrophotometric analysis of the complexes mentioned in several works. The maximum absorption spectrum of the complexes depends on the solvent and ranges from 615 to 625 nm in isobutyl methyl ketone, 623 nm in an n-butanol-dichloromethane, and 615 and 680 nm in dimethylsulfoxide and diethylsulfoxide with maxima at 619 and 676 nm [23].

We have done a spectrophotometric analysis of the blue complex formed by $CoCl_2$ (as a product of processing $Fe_xCo_yO_z$, extracted from an emulsion with hydrochloric acid), diethylamine, NH_4SCN, and ammonium acetate in a solution of dimethyl sulfoxide with an absorption maximum at 667 nm. Fig. 2a shows the absorption spectrum of a complex containing cobalt thiocyanate and diethylamine in the DMSO solution.

Depending on the amount of ferrofluid dispersed in an aqueous surfactant solution, the Co^{2+} concentration in the prepared emulsion may vary from 20 to 100 mg/1000 ml. Fig. 2b shows an example of a calibration curve for determining the cobalt concentration in a suspension of $Fe_xCo_yO_z$ nanoparticles using the spectrophotometric method.

Nanoparticle Tracking Analysis (NTA)

A major challenge in nanoparticle size determination is achieving precision, measurement accuracy, and true-to-value correspondence. According to [24], measurement accuracy is defined as "the closeness of the measurement result to the true value", which is affected by the occurrence of random and systematic errors [25]. Therefore, the measurement of such materials poses numerous metrological and mathematical problems [26], and this is especially true for the method of nanoparticle tracking analysis (NTA) [27]. Nanoparticle Tracking Analysis (NTA) is a modern method of direct visualization and analysis of nanoparticles [28, 29] in liquids in real-time. This method is based on a microscopic technique with laser illumination, which allows analyzing the Brownian motion of nanoparticles using a Charge-Coupled Device (CCD) camera in real time (Fig. 3). Each particle is simultaneously, but separately, visualized and tracked by a special image analysis program. The image analysis program enables NTA to:

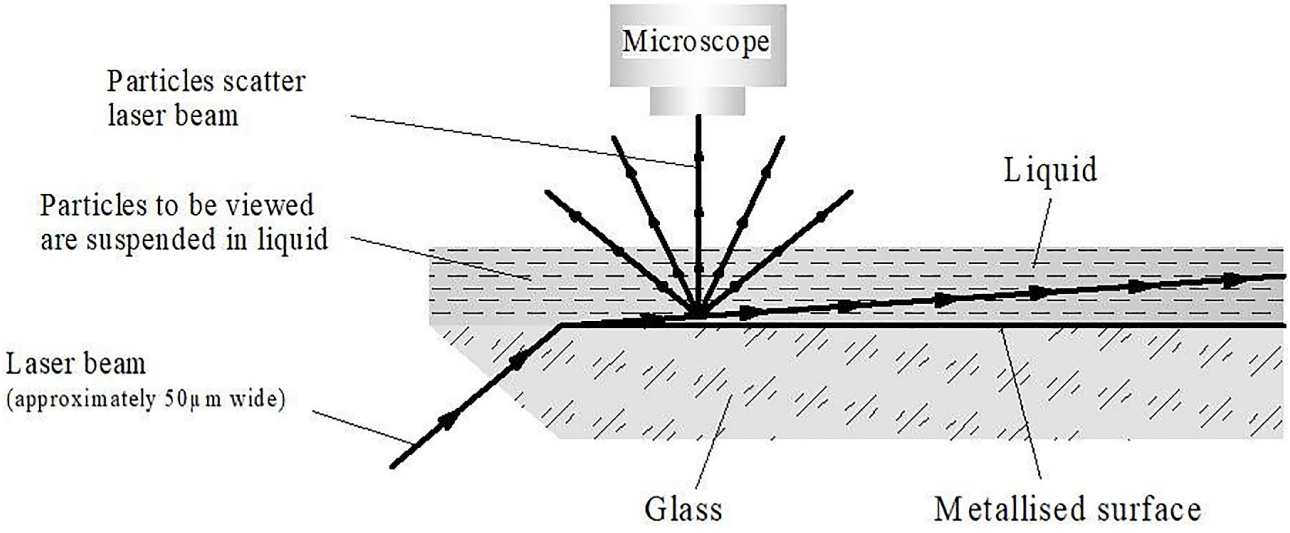

Fig. 3. Procedure of the NTA method [30]

- measure particle size and scattering intensity,
- separate heterogeneous mixtures of particles,
- directly assess particle concentration.

The NTA program simultaneously locates and tracks the centres of each particle frame by frame, automatically calculating the average distance each particle moves relative to the *x* and *y* axes of the image. This allows the particle diffusion coefficient D_t and hydrodynamic diameter (d_h) to be calculated using the Stokes-Einstein equation. Knowing the temperature of the test sample and the viscosity of the solvent, the particle size may be calculated. Achieving a statistically significant particle size distribution profile in samples requires a concentration of 10^7 to 10^9 particles/mL, which sometimes requires sample dilution.

Fig. 4 presents the results of the NTA analysis of the dispersion of the $Fe_xCo_yO_z$ nanotracer in a 0.5% aqueous solution of DMAOA, and Table 2 shows the results for two dispersions with different surfactants: DMAOA and ammonium oleate. The average size of nanotracer particles is from 90 to 120 nm.

When dispersed in solutions with two different surfactants, such as ammonium oleate and dimethylamine salt of oleic acid (DMAOA), the resulting particle size distribution provides insight into the effectiveness of each surfactant in stabilizing nanoparticles and preventing aggregation. Dimethylamine salt of oleic acid (DMAOA) has an average particle size of 90–120 nm. Ammonium oleate has an average particle size of 100–130 nm.

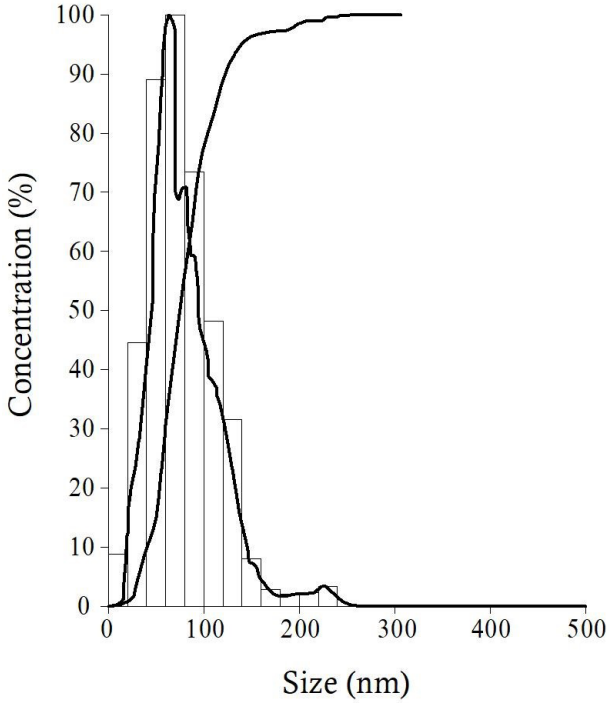

Fig. 4. Results of the NTA analysis of the dispersion of the $Fe_xCo_yO_z$ nanotracer in a 0.5% aqueous solution of the dimethylamine salt of oleic acid

Table 2

Particle size distribution in a suspension of $Fe_xCo_yO_z$ ferromagnetic nanoparticles dispersed in solutions with two different surfactants

D Values	D10 nm	D50 nm	D70 nm	D90 nm	Total number of analyzed particles
Sample A (0.5% DMAOA solution) number of particles in the sample	41	76	95	128	340
Found normalized to 100%	12.1	22.4	27.9	37.6	100%
Sample B (0.5% ammonium oleate solution) number of particles in the sample	76	118	142	210	546
Found normalized to 100%	13.9	21.6	26.0	38.5	100%

Ammonium oleate might result in a slightly broader particle size distribution compared to DMAOA. The nanoparticles in ammonium oleate solution show good stability, but not as high as in DMAOA. Ammonium Oleate, while effective, shows a slightly broader particle size distribution.

Conclusions

A method for obtaining the ferromagnetic nanotracer $Fe_xCo_yO_z$ based on iron and cobalt oxides has been developed, demonstrating the capability of forming a stable suspension of the nanotracer in aqueous solutions of surfactants.

The particle size of the nanotracer was determined using the NTA method, which relies on direct visualization and analysis of nanoparticles in aqueous media and includes two types of surfactants.

The potential of using the $Fe_xCo_yO_z$ nanotracer to evaluate the quality of liquid feed mixing in laboratory conditions has been demonstrated.

In choosing a surfactant for dispersing ferromagnetic nanoparticles in a suspension to determine the quality of mixed feed mixing, dimethylamine salt of oleic acid (DMAOA) is generally the better option due to the opportunity to produce a more uniform particle size distribution and greater stability, which is critical for accurate and reliable assessment of the feed mixing quality.

Феромагнітні нанотрейсери на основі оксидів Fe та Co: синтез та їхня роль в оцінці якості змішування рідких кормів

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Анотація

Забезпечення однорідності змішування кормів має важливе значення для здоров'я та продуктивності тварин. Зростаюча складність рецептур кормів підвищує потребу в однорідних сумішах, особливо для молодих особин, тому що збалансований корм суттєво впливає на ріст і споживання. Феромагнітні мікроіндикатори, розроблені MicroTracers Inc., використовуються для контролю рівномірності змішування при виробництві сухих кормів. Ці мікроіндикатори, розроблені на основі заліза, ефективні завдяки своїм магнітним властивостям, що полегшує їх виявлення та розділення. Однак ці мікроіндикатори менш придатні для рідких кормів, що призвело до розробки магнітних наноіндикаторів на основі оксиду заліза для рідких кормів. Розроблено метод отримання феромагнітного нанотрейсера $Fe_xCo_yO_z$ на основі оксидів заліза та кобальту, що демонструє можливість утворення стабільної суспензії наноіндикатора у водних розчинах поверхнево-активних речовин. Аналіз відстеження наночастинок (Nanoparticle Tracking Analysis) (NTA), який дає можливість прямої візуалізації й аналізу наночастинок у рідинах у реальному часі, використовується для вимірювання розміру та розподілу наночастинок у рідкому кормі, що забезпечує контроль ефективного змішування рідких кормів. Стабільність і рівномірний розподіл магнітних наночастинок є вирішальними, оскільки різні поверхнево-активні речовини, такі як диметиламін олеїнової кислоти (DMAOA) і олеат амонію, впливають на розмір частинок і їх агрегацію. Доведено утворення стабільної суспензії нанотрейсера $Fe_xCo_yO_z$ у водних розчинах цих поверхнево-активних речовин. Наведено порівняльний аналіз результатів дослідження нанотрейсера $Fe_xCo_yO_z$ методом NTA з різними поверхнево-активними речовинами. DMAOA забезпечує кращу дисперсію та стабільність, необхідну для контролю якості у виробництві кормів. Концентрацію вмісту кобальту в $Fe_xCo_yO_z$ визначали модифікованим спектрофотометричним методом. Нанотрейсер $Fe_xCo_yO_z$ перевірено в лабораторних і виробничих випробуваннях. Його може бути застосовано для контролю якості змішування рідких кормів (у лабораторних умовах і на виробництві); кодування рідких добавок (наприклад, ферментів); оцінки розподілу рідких добавок у готових кормах і premіксах.

Ключові слова: однорідність комбікормів; спектрофотометричне визначення кобальту; магнітні наноіндикатори; трекінг-аналіз наночастинок; контроль якості.

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