

Vitamin Stability in Premixes and Feeds A Practical Approach in Ruminant Diets

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Introduction

Vitamins are essential organic elements which cattle must obtain from their environment or rumen as they cannot themselves produce adequate quantities. Their discovery and the understanding of their function in preventing classical deficiency diseases are among the most important achievements of the century. Vitamins are essential for growth, health, reproduction and survival. They are involved in over 30 metabolic reactions in cellular metabolism and critical to the efficiency of the Krebs/Citric Acid cycle (Marks, 1979). Vitamins are present in most common feedstuffs in minute amounts and because they are necessary for normal metabolism, cause a specific deficiency disease if absent from the diet. Today all industrial cattle feeds are fortified with vitamins. To satisfy cattle's nutrient requirements, industrially produced vitamins are added to supplement the natural vitamin content of food ingredients. Vitamins provide many essential metabolic functions. Table 1 summarizes the major functions and deficiencies of essential vitamins in cattle.

Table 1. Major vitamin functions and deficiencies in cattle

Nutrient	Major Function	Major Deficiency
Vitamin A	Vision, mucous tissue integrity, immunity	Blindness, night blindness, xerophthalmia, ataxia, tissue keratinization, polyneuritis, hind legs paralysis, defective bone shape, elevated cerebro-spinal fluid pressure, skin edema, papilloedema, lacrimation, depressed immune system, reduced fertility.
Vitamin D3	Calcium and phosphorus metabolism, bone calcification, immunity	Rickets, osteomalacia, parturient paresis
Vitamin E	Intracellular respiration, antioxidant, membrane protection, immunity	Encephalomalacia, depressed immune status, myopathy, skin edema, liver necrosis, anemia, erythrocyte hemolysis, muscular dystrophy, fetal death, reduced fertility.
Vitamin K	Blood coagulation	Prolonged blood clotting time, low prothrombin, intramuscular bleeding, general hemorrhage, hemorrhage under the skin, anemia.

Table 1. Major Vitamin function and deficiencies in cattle (cont.)

Nutrient	Major Function	Major Deficiency
Thiamine	Metabolism of carbohydrates and proteins, nervous system	Loss appetite, polyneuritis, polio-encephalomalacia, skin edema, lacrimation, fatty liver, fatty heart, convulsions, cyanosis, gastrointestinal hemorrhage, diarrhea.
Riboflavin	Antioxidant, H-transfer, ligament integrity	Poor growth, shortened bones, fused ribs, dermatitis, lesions in corner of mouth, poor hair coat, photophobia, cataracts, anemia, stiff crooked legs, fetal death, reduced fertility, diarrhea, anal mucosa inflammation.
Pantothenic	Conversion of amino acids groups as coenzyme A, skin integrity	Dermatitis in feet and mouth, blindness, demyelination of spinal cord, depressed immune system, decreased milk production, diarrhea, GI ulceration, fatty liver.
Niacin	Metabolism of carbohydrates, proteins and fats, H carrying enzymes NAD and NADP, skin integrity	Bowed legs, diarrhea, general dermatitis, dermatitis of feet and mouth, anorexia, hind legs paralysis, GI ulceration
Pyridoxine	Metabolism of proteins	Dermatitis around the eyes, fatty liver, ataxia, convulsions, diarrhea, vomiting, depressed immune system.
Choline	Methyl donor group, phospholipids	Poor growth, fatty liver, perosis, enlarged spleen, abnormal gait, demyelination of peripheral nerves, depressed immune system, puppy spraddle legs, reduced fertility, kidney damage
Vitamin B ₁₂	Protein metabolism, transport of methyl groups	Anemia, poor growth, poor hair coat, fatty kidney, kidney damage, ataxia, uncoordinated hind legs, impaired thyroid, diarrhea
Folic Acid	Transfer of single carbon units in activated form for methylation reactions involving methyl donors such as methionine and choline, immunity	Poor growth, anemia, poor skin condition, reduced fertility

Table 1. Major Vitamin function and deficiencies in cattle (cont.)

Biotin	metabolism of fats, carbohydrates and proteins as coenzyme for CO ₂ fixation and transcarboxylation, collagen maintenance.	General dermatitis, dermatitis on feet, mouth and eyes, poor hoof integrity, poor collagen integrity, fertility, poor hair coat, spasms in hind legs, stiff gait, reduced fertility
Vitamin C	Antioxidant, hormone synthesis, conversion of vitamin D ₃ to Calcitriol, essential for bone calcification	Poor hair coat, depressed immune system, hemorrhage, prolonged clothing time, delayed wound healing, degenerated-enlarged adrenal.

Ruminant vitamin requirements

Ruminant vitamin requirements have not been as intensely studied as vitamin requirement of monogastrics. Research on vitamin E has demonstrated increased benefits on meat quality (Faustman et al., 1989) and reproduction (Weiss, 1998). Recent research on biotin demonstrating increased milk and protein yields (Zimmerly and Weiss, 2001), begs the obvious question of why do ruminants with a functional rumen may see a benefit of a B-vitamin such as biotin?. Although a dairy cow may produce B-vitamins in the rumen, the rapid changes in feeding and management (much higher milk production, less pasture and more total confinement) have led to a much faster rate of passage and reduced ruminal function. Increased milk production, faster rate of passage and lower ruminal function has created a different animal from the vitamin requirement standpoint. A high producing dairy cow under these conditions, has a B-vitamin requirement that can not be met by the rumen microorganism and therefore requires vitamin supplementation that more resembles a monogastric animal. A recent feeding trial with high producing dairy cows documented the effect of a composite B-vitamin formulation fed between 0-75 days post calving on milk production. The composite B-vitamin formulation was supplemented at 0, 25, 50, 75 and 100% of formulation detailed in table 2.

Table 2. Composite B-vitamin supplementation for milking dairy cows.

Vitamin	mg/head/day
Biotin	20
Niacin	2000
Riboflavin	250
Pantothenic acid	50
Thiamin	200
B ₁₂	2

Milk production linearly increased with composite B-complex supplementation (39.4, 40.9, 42.0, 43.1 and 43.4 kg/d) for 0, 25, 50, 75 and 100% of formulation. Composite B-complex supplementation did not affect milk fat, but increased true protein yield.

Vitamin stability

Vitamins, as biologically active biochemicals, generally are quite sensitive to their physical and chemical environment (Vitamin stability in premixes and feeds: a practical approach, KC 9138, 6th revised edition, 1999).

Feed processes tend to improve the distribution of nutrients (premixing) and the digestibility of carbohydrates (pelleting, extrusion). However, these processes are harmful to labile nutrients, such as vitamins, that can be easily oxidized (Gadient, 1986; Schneider, 1986).

Vitamin Intrinsic Factors

Vitamin A

Several vitamins contain unsaturated carbon atoms or have double bonds, both highly susceptible to oxidation. For example, vitamin A retinol has both a free hydroxy group and 5 double bonds. The esterification of retinol with acetic acid produces retinyl acetate which has the hydroxy group protected, but still has 5 double bonds susceptible to oxidation. For this reason, even pure retinyl acetate oil has to be emulsified in gelatin and sugars, and processed into a beadlet containing an antioxidant.

New technology has further improved vitamin A and D₃ stability by a crosslinking process, such as the reaction between the gelatin and the sugar, that makes the beadlet insoluble in water, giving it a more resistant coating that can sustain higher pressure, friction, temperature and humidity.

Vitamin E

Vitamin E, as d,l-alpha-tocopherol, is an antioxidant by itself and, therefore, if applied directly to feeds, is consumed rapidly. The free phenolic hydroxy group in this molecule is responsible for the antioxidant activity. When the hydroxy group is protected by formation of an ester, as in tocopheryl acetate, the compound obtained is resistant to oxygen, since it has no double bonds and free hydroxy groups. Vitamin E acetate is stable in feeds with neutral or slightly acidic pH. However, even slightly alkaline conditions may affect the stability, such as when limestone carrier is used or in the presence of large quantities of magnesium oxide (Basemixes). Under these conditions, some of the protective acetate groups split off and free tocopherol is formed, which can be rapidly oxidized.

Vitamin K

Menadione, pure vitamin K₃, is a crystalline yellow powder that is unstable and irritating to skin and mucous membranes. It is not utilized in pure form, but is formulated with sodium bisulfite and derivatives thereof. The most common menadione compounds used in the industry are menadione sodium bisulfite (MSB), menadione sodium bisulfite (MSBC), menadione dimethyl pyrimidinol bisulfate (MPB); and the most recent compound introduced into the market is menadione nicotinamide bisulfite (MNB). Since vitamin K is one of the most unstable vitamins, there are significant differences in vitamin K stability among the above compounds. MSB is the most unstable formulation followed by MSBC,

MPB, MSB coated and finally the most stable is MNB. Recent reports by Huyghebaert (1991) and Stoppani Labs (1981) determined the stability of different vitamin K formulations in a multivitamin, choline chloride and trace mineral premix at room temperature. At the end of 4 months, MSB retained 33%, MPB 57%, MSB coated 62% and MNB retained 83%.

B-Vitamins Stability

B-vitamins are also unstable to a certain extent. Vitamin B₁ and B₆ are more stable under acidic conditions, while pantothenic and folic acids are most stable in a slightly alkaline environment. pH of the medium is far less important than the aggressiveness of moisture and trace elements. Thiamine hydrochloride is destroyed rapidly in a choline/trace mineral premix (high moisture, pH 4-5) while it is fairly stable in a basemix (low moisture, pH 7-8). Thiamine mononitrate also degrades rapidly in a trace mineral/choline premix. Vitamin solubility in water is inversely correlated to stability. Thiamine mononitrate with a solubility of 10g/100ml, is significantly more stable in premixes than thiamine hydrochloride with a solubility of 100 g/100 ml (Adams, 1982). Vitamin B₆ is more rapidly destroyed in a choline chloride/trace mineral premix (high moisture) than in a basemix (low moisture). Calcium D-pantothenate is quite stable. Losses occur only after prolonged storage at acidic pH. Riboflavin is stable in all premixes and also under climatic stress.

Vitamin B₁₂ and choline are very stable compounds, but B₁₂ is sensitive to strong acid, alkali, reduction, light, ascorbic acid and ferrous sulfate.

Folic acid is stable to heat and air, but unstable in acid and alkaline solutions. It is light sensitive, slightly sensitive to moisture and sensitive to oxidation and reducing agents.

Vitamin C, or ascorbic acid, is extremely difficult to maintain in premixes or feeds since it is susceptible to destruction by so many environmental factors, especially oxidation. Phosphorylation of ascorbic acid (Ascorbyl phosphate) produces a highly stable product.

Adams (1982) reported the stability of pyridoxine and thiamine in premixes without and with trace minerals. After storage for 3 months under stressful conditions, pyridoxine retained 100% and 45%, respectively. After 21 days under stressful conditions, thiamine hydrochloride retained 48% and thiamine mononitrate, 95%. BASF, 1986, compared the stability of crystalline ascorbic acid and ethyl cellulose coated ascorbic acid through pelleting. Crystalline retained 85% and ethyl cellulose, 82%. A follow up study determined the stability of ascorbyl-phosphate. This compound not only is very stable, but also maintains the bioavailability. Ascorbyl phosphate and crystalline ascorbic acid retained through extrusion 95% and 55%, respectively. After four weeks storage, ascorbyl phosphate and crystalline ascorbic acid retained 85% and 30%.

Vitamin Formulation Processes

Vitamin formulations vary significantly in complexity and cost. Cost is a very important factor because the vitamin manufacturing costs are passed on to the consumer. Manufacturing processes should not only be evaluated based on physico-chemical properties of the vitamin, but also need to further process the vitamin to improve handling properties and stability through feed processing. The crystalline form is the easiest and least expensive to manufacture, followed by silica adsorbing, ethylcellulose coating, fat coating, drum drying, spray drying, spray congealing and finally, the most expensive, cross-linked spray congealing.

Vitamins, such as thiamine mononitrate and pyridoxine Hcl, that have good handling properties and stability in the crystalline form, should be sold as such without any need for further processing. Silica adsorbing should be reserved for highly stable liquid vitamins, such as vitamin E and choline chloride. Ethylcellulose coating was developed for the pharmaceutical industry, to allow tableting of ascorbic acid. Ethylcellulose coating is produced by dispersing ethylcellulose fibers and ascorbic acid crystals in an alcohol medium, evaporating the alcohol while the fiber sticks to the crystals. The only benefit of ethylcellulose coating is increasing the adherence of particles to each other. In the feed industry, ethylcellulose coating drastically decreases the flowability without improving the stability or any other physico-chemical property of importance to the feed industry.

Fat coating was also developed for the food industry to improve the crystalline ascorbic acid stability. However, any high temperature process (pelleting, extrusion, cooking) melts down the fat, and the crystal is again completely exposed to oxidation. The fat can also oxidize, which in turn will oxidize the vitamins by autoxidation and propagation. Drum drying is a very old process that dries the vitamin emulsion at very high temperatures into a very thin sheet, which is subsequently crushed into small flakes. These crushed flakes have a very poor flowability and are highly exposed to oxidation since they don't have a continuous protection surrounding the vitamin molecules. The drum drying process also offers no benefit to the feed industry. Spray drying, a process also developed for the pharmaceutical industry to allow tableting of several vitamins, is quite expensive. The vitamin emulsion is sprayed in a tower and dried with cold air. Usually, it contains starch to improve the adhesion of particles in the tableting process. Starch containing spray dried products, such as vitamin E 50% SD, are highly hygroscopic and tend to cake and form lumps. Poor flowability decreases the throughput in a premix or feed plant and lumping decreases the distribution throughout the feed. However, spray granulation, where non-starch containing emulsions are sprayed and granulated to a higher particle size, can be a benefit to vitamins with very poor flowability and high electrostaticity such as riboflavin and folic acid.

Finally, spray congealing, the most expensive of all formulation processes should be reserved for highly unstable vitamins such as vitamin A and D. In this process, the emulsion, containing gelatin and sugars, is sprayed in a tower and slowly dried with cold air, starch and silica.

Vitamin Stress Factors

Several factors can influence vitamin stability in premixes pelleting and storage, including temperature, humidity, conditioning time, reduction and oxidation (redox) reactions and light. Heat, pressure, humidity, friction and redox reaction vary drastically among the different ways feed can be processed (Table 3). Vitamin oxidation can also be due to propagation of autooxidation of fats, Fenton type induced oxidation by trace minerals, hydrolytic induced oxidation and microbial induced oxidation.

Therefore, it is critical to calculate the vitamin stability at each stage of processing: straights, premixes, pelleting, and feed storage, because vitamins incur losses that vary from process to process. Tables 4 through 13 reflect average industry vitamin stability through different processes. This data is an average from a broad set of data from vitamin manufacturers' laboratories, industry and academic research, and different conditions of processing and storage. The data does not reflect any specific vitamin manufacturer.

Premix Stress Factors

In vitamin/trace mineral premixes, the dominant effect exerted on vitamins is redox reactions by trace minerals (Table 5). Trace minerals also vary in redox potential. The type of trace mineral molecular structure, with copper, zinc and iron being the most reactive and manganese and selenium the least reactive, has a significant impact on vitamin stability. Free metal ion is the most reactive (metal filings) followed by sulfate, carbonate, oxide and the least reactive form is chelated. Chelated forms become incapable of initiating formation of free radicals. Friction is also an important factor because it erodes the coating that protects several vitamins and reduces vitamin crystals to a smaller particle size.

In fat-soluble vitamins, esters are significantly more stable than alcohols. The hydroxy group of alcohols is extremely sensitive to oxidation. The five double bonds in retinyl acetate still make the compound sensitive to oxidations. Vitamin A is significantly more stable in vitamin premixes than in vitamin-trace mineral premixes because trace minerals catalyze oxidation of the five double bonds (Tables 4 through 9). Christian, 1983, determined the stability of vitamin A in a basemix. After 3 months' storage, the vitamin A retention was 88% under low temperature and humidity, 86% under high temperature and low humidity and 2% under high temperature and high humidity. He concluded that humidity was significantly more stressful than temperature.

Pelleting Stress Factors

In pelleting, the most important factors are friction (abrasion), pressure, heat, humidity and conditioning time (Tables 4, 11 and 12). Friction and pressure expose more vitamin molecules to chemical destruction. Heat and humidity accelerate most chemical reactions.

Conditioning time prolongs redox and other chemical reactions. Shields et al., 1982, measured the stability of vitamin A in mash and pelleted feeds. After 3 months storage, vitamin A retention varied from 50% at low temperature to 39% at high temperature in mash feed and 65% at low temperature and 20% at high temperature in pelleted feeds.

Extrusion Stress Factors

In extrusion, the dominant effects are pressure, heat, humidity and redox reactions. Extrusion is considered the most aggressive process against vitamins due to the high temperatures (100-150°C), pressure (400-1000 PSI), and moisture (30%) (Tables 4, 10 and 12).

Practical Applications

The vitamin stability data presented in Tables 4 through 12 follow the several steps used in feed manufacturing. Based on specific conditions, one can estimate each vitamin retention from time of purchasing, until it is absorbed by the animal. Tables 13 consolidates the data for a specific process conditions. In each case, the vitamin retentions for each manufacturing step are multiplied, producing the total vitamin retention from time of purchasing to time of feeding. The continued increase in pelleting temperature and conditioning time is destroying vitamins at a higher rate. Since 1980, the average pelleting temperature has increased by 20°C.

Methods of Correcting for Vitamin Losses Caused by Processing

The high losses experienced by some vitamins through pelleting have led to a constant search for ways to reduce these losses. The option most commonly proposed is vitamin application after pelleting and extrusion. No matter how careful the application (usually spraying) is, it presents insurmountable obstacles. (1) Difficulty in maintaining vitamins in solution. (2) Vitamin forms in a liquid medium have no protection. (3) Vitamin solutions will only coat the outside of the pellet (spraying hot pellets does increase penetration but will also increase vitamin losses). (4) The vitamin distribution throughout the feed is very poor, with a coefficient variation, c.v., of 15-40%, which is unacceptable for small to medium size animals (poultry and swine). Poor distribution of nutrients leads to variable performance throughout a flock. (5) Storage time of 2 to 6 weeks for vitamin-coated feed will lead to very high vitamin losses, since these vitamins will be overly exposed to environmental stresses without any protection.

Another method to correct for vitamin losses caused by processing is to reduce the very same factors that increase vitamin losses through processing. This would include (1) separate trace minerals from vitamins, (2) reduce premix storage time, (3) reduce pelleting temperature and conditioning time and (4) reduce feed storage time. However, several other factors determine premix storage time and pelleting conditions that take precedence over vitamin stability, such as, pellet quality, microbial contamination, etc. Therefore, the industry is left with the most commonly used option which is to compensate for the vitamin losses through overages added into the vitamin supplementation. Knowing the vitamin retention from time of purchase until consumption by the animal, one can easily calculate the overage required to compensate for those losses.

Economics of Vitamin Stability

Although vitamin stability is an important factor in selecting vitamins, other factors should be taken into consideration such as price and potency of the product.

In the final analysis, what should be relevant to the petfood manufacturer is the cost/retained unit, and not stability alone or cost alone. Cost/retained unit gives the cost of each active unit after processing.

$$\text{Cost/Retained unit} = \text{Price/ Kg/ (\% active X \% retained)}$$

Table 3. Level of Vitamin Stress in Different Feed Processes

	Vitamin Premix	Choline/ Trace Mineral Premixes	Basemixes	Pelleting	Extrusion
Heat	low	low	Low	High	very high
Pressure	low	low	Low	high	very high
Humidity	low	high	Low	high	very high
Redox reactions	low	high	High	high	very high
Friction	low	high	High	very high	low

Table 4. Average Industry Vitamin Stability in Vitamin (W/O Choline) Premixes (Blends)

VITAMIN	VITAMIN RETENTION %								% AVG. LOSS/MONTH
	MONTH								
	0.25	0.5	1	2	3	4	5	6	
A beadlet, cross-linked	100	99	99	98	96	96	94	95	0.9
A beadlet Non Spray Cong. Non-cross link	99	97	95	93	91	87	84	80	2.9
D ₃ beadlet (A/D ₃) corss-linked	100	99	99	98	98	97	97	96	0.6
D ₃ Spray Congealed (SC)	100	99	99	98	98	97	97	96	0.6
D ₃ Spray dried (SD)	100	99	98	96	95	94	92	91	1.6
D ₃ Drum Dried	100	98	97	95	94	93	91	90	1.8
E acetate 50%	100	99	99	99	98	98	98	98	0.2
E alcohol, Natural	90	80	64	36	21	13	7	0	35.0
MSBC	100	99	99	98	98	97	97	96	0.6
MSB coated	100	100	100	100	99	99	99	99	0.04
MSB	100	99	99	98	97	96	95	94	1.0
MNB	100	100	100	100	99	99	99	99	0.04
MPB	100	100	100	100	99	99	99	99	0.04
Thiamine HCL	100	99	98	98	97	96	96	95	0.7
Thiamine Mono	100	100	100	100	99	98	98	99	0.04
Riboflavin	100	100	100	100	99	99	99	99	0.04
Pyridoxine	100	100	100	100	99	99	99	99	0.04
B ₁₂	100	100	100	100	99	99	99	99	0.04
Calcium Pantothenate	100	100	100	100	99	99	99	99	0.04
Folic Acid	100	100	100	100	99	99	99	99	0.04
Biotin	100	100	100	100	100	99	99	99	0.04
Niacin	100	100	100	100	100	99	99	99	0.04
Niacinamide	100	100	100	99	99	99	98	98	0.08
Ascorbic Acid	100	98	97	95	94	93	91	90	1.8
Ethyl Cellulose Coated Ascorbic	100	98	97	95	94	93	91	90	1.8

Fat Coated Ascorbic	100	99	98	97	96	96	95	95	0.9
Ascorbyl Phosphate	100	99	99	98	98	97	97	99	0.6

TABLE 5. Effect Of Trace Element Source On Average Industry Vitamin Stability In Premixes

VITAMIN	TRACE ELEMENT SOURCE	VITAMIN RETENTION % MONTH								% AVG LOSS/MONTH
		0.25	0.5	1	2	3	4	5	6	
A beadlet	chelated	99	97	93	89	85	81	76	74	4.0
	oxide	98	96	92	87	82	78	73	71	5.0
	carbonate	97	95	89	83	89	70	66	62	7.0
	sulfate	95	93	86	74	65	57	53	47	11.0
	free metal	94	92	83	71	62	54	50	43	12.0
E acetate 50%	chelated	100	99	97	96	95	93	92	90	2.0
	oxide	99	98	96	95	94	92	90	88	2.3
	carbonate	99	98	96	95	93	91	89	87	2.4
	sulfate	98	97	95	92	88	86	83	80	3.0
	free metal	97	96	94	91	86	84	80	77	3.4
MSBC	chelated	95	87	73	63	55	47	38	32	15.0
	oxide	93	85	68	59	50	42	32	25	20.0
	carbonate	90	82	65	57	48	39	29	20	25.0
	sulfate	85	75	55	30	20	10	5	0	45.0
	free metal	82	72	54	26	15	5	0	0	60.0
Thiamine Mono	chelated	100	98	92	83	77	70	65	59	6.0
	oxide	98	96	90	79	72	64	59	52	9.0
	carbonate	96	94	86	74	64	55	50	42	12.0
	sulfate	96	93	84	72	61	52	46	37	14.0
	free metal	95	91	82	69	57	48	42	32	20.0
Biotin	chelated	99	98	97	89	84	76	71	68	5.2
	oxide	98	97	96	88	82	74	68	65	6.0
	carbonate	98	97	95	87	80	70	64	61	7.0
	sulfate	97	95	88	76	66	58	53	47	11.0

	free metal	96	95	87	75	64	56	51	44	12.0
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Table 6. Average Industry Vitamin Stability in Vitamin (W/Choline) Premixes

VITAMIN	VITAMIN RETENTION %								% AVG. LOSS/MONTH
	MONTH								
	0.25	0.5	1	2	3	4	5	6	
A beadlet cross-linked	99	98	97	96	95	94	92	90	2.0
A beadlet Non-Spray Cong. non-XL	98	96	90	86	80	74	68	60	8.1
D ₃ beadlet (A/D ₃) X-Link	100	99	98	97	96	95	94	93	1.1
D ₃ Spray Congealed.	100	99	98	97	96	95	94	93	1.1
D ₃ Spray dried (SD)	99	98	96	95	93	92	91	90	2.0
D ₃ Drum Dried	98	97	94	93	90	87	84	80	2.9
E acetate 50%	100	100	99	99	99	98	98	98	0.3
E alcohol, Natural	89	77	52	30	18	10	5	1	40.0
MSBC	97	95	87	80	73	65	58	50	9.0
MSB coated	99	97	92	86	80	76	73	68	5.4
MSB	97	93	84	75	66	58	49	40	13.0
MNB	99	98	93	87	81	77	75	70	5.0
MPB	98	96	90	83	76	68	64	56	8.0
Thiamine HCL	98	94	87	81	74	68	63	57	8.0
Thiamine Mono	99	97	93	90	87	83	79	73	4.0
Riboflavin	100	99	98	96	94	91	89	85	2.6
Pyridoxine	99	99	98	95	93	90	87	83	3.0
B ₁₂	100	100	100	99	99	99	98	98	0.3
Calcium Pantothenate	100	99	98	96	95	92	89	86	2.4
Folic Acid	98	96	95	92	88	85	81	78	3.6
Biotin	100	99	98	97	95	93	89	87	1.5
Niacin	100	99	98	97	95	93	88	85	2.2
Niacinamide	98	96	95	94	91	88	84	81	3.0
Ascorbic Acid	93	88	75	68	60	55	50	45	11.0
Ethyl Cellulose Coated Ascorbic	94	89	76	70	62	58	53	46	10.0
Fat Coated Ascorbic	98	97	94	93	90	87	84	80	2.9

Ascorbyl Phosphate	100	99	98	97	96	95	94	92	1.2
Choline	100	100	100	99	99	99	98	98	0.2

Table 7. Average Industry Vitamin Stability in Vitamin (W/O Choline) Trace Mineral Premixes

VITAMIN	VITAMIN RETENTION % MONTH								AVG. LOSS/MONTH (%)
	0.25	0.5	1	2	3	4	5	6	
A beadlet cross-linked	98	97	94	93	90	87	84	80	2.9
A beadlet Non-S.Cong. non-XL	97	94	90	86	80	74	68	60	8.1
D ₃ beadlet (A/D ₃) X-Link	99	98	96	95	93	90	87	84	2.5
D ₃ Spray Congealed	99	98	96	95	93	90	87	84	2.5
D ₃ Spray dried (SD)	100	97	95	92	89	85	82	78	3.5
D ₃ Drum Dried	98	96	94	90	84	80	76	72	4.8
E acetate 50%	99	98	96	95	93	90	87	84	2.7
E alcohol, Nat	90	78	50	28	14	7	4	0	46.0
MSBC	97	93	89	83	75	70	65	62	6.4
MSB Coated	99	98	95	87	81	77	72	70	2.9
MSB	97	95	87	80	73	65	58	50	9.0
MNB	99	98	95	87	81	77	72	70	2.9
MPB	99	97	92	87	79	75	71	67	5.5
Thiamine HCL	97	93	83	78	72	65	60	55	9.0
Thiamine Mono	99	97	94	93	90	87	84	80	2.9
Riboflavin	100	98	97	94	92	89	87	83	2.6
Pyridoxine	99	97	96	93	91	88	85	81	2.8
B ₁₂	100	99	99	98	98	97	97	96	0.6
Calcium Pantothenate	100	100	99	98	96	94	91	88	2.2
Folic Acid	98	97	94	93	90	87	84	80	2.9
Biotin	99	97	95	94	92	91	88	85	2.6
Niacin	99	96	94	92	90	89	86	83	2.7
Niacinamide	98	95	93	92	89	86	81	79	3.0
Ascorbic Acid	94	92	82	70	59	50	44	35	17.0
Ethyl Cellulose Coated Ascorbic	95	93	84	72	62	53	48	40	13.0

Fat coated Ascorbic	97	95	90	86	80	74	68	60	8.1
Ascorbyl Phosphate	99	98	95	92	90	86	84	82	2.9

Table 8. Average Industry Vitamin Stability in Vitamin (W/ Choline) Trace Mineral Premixes

VITAMIN	VITAMIN RETENTION % MONTH								AVG. LOSS/MONTH (%)
	0.25	0.5	1	2	3	4	5	6	
A beadlet cross-linked	98	96	94	90	84	79	75	70	3.9
A beadlet Non-S.Cong. non-XL	94	85	68	59	50	42	32	25	20.0
D ₃ beadlet (A/D ₃) X-Link	100	97	95	91	86	82	78	73	2.9
D ₃ Spray Congealed.	100	97	95	91	86	82	78	73	2.9
D ₃ Spray dried (SD)	98	95	90	84	78	73	70	66	4.0
D ₃ Drum Dried	97	93	88	81	75	69	66	62	6.4
E acetate 50%	99	98	96	92	88	85	81	77	2.4
E alcohol, Nat	85	76	35	20	7	0	0	0	57.0
MSBC	95	93	84	72	61	52	46	37	15.0
MSB Coated	97	95	87	80	73	65	58	50	9.0
MSB	92	81	63	47	34	25	17	10	35.0
MNB	97	92	84	72	61	53	47	45	10.0
MPB	96	91	76	69	62	53	46	40	13.0
Thiamine HCL	94	89	73	64	57	44	34	20	18.0
Thiamine Mono	95	90	84	77	70	62	55	48	9.0
Riboflavin	99	96	95	91	85	80	76	71	3.8
Pyridoxine	98	95	93	89	83	78	74	68	4.5
B ₁₂	100	99	97	96	95	74	92	90	2.0
Calcium Pantothenate	99	97	92	87	79	75	71	67	5.5
Folic Acid	99	96	94	84	77	69	64	58	8.5
Biotin	98	95	93	89	83	78	74	68	4.5
Niacin	98	96	94	90	85	80	75	70	4.0
Niacinamide	99	96	92	82	74	64	60	64	5.0
Ascorbic Acid	94	93	82	70	58	36	26	17	25.0
Ethyl Cellulose Coated Ascorbic	95	94	85	73	62	39	29	20	20.0
Fat coated Ascorbic	96	95	87	76	65	50	45	35	13.0

Ascorbyl Phosphate	99	97	95	91	86	83	79	75	4.2
Choline chloride	100	99	99	98	97	95	93	91	2.0

Table 9. Average Industry Vitamin Stability in Basemixes (w/choline and magnesium)

VITAMIN	VITAMIN RETENTION % MONTH								AVG. LOSS/MONTH (%)
	0.25	0.5	1	2	3	4	5	6	
A beadlet Cross-Linked	99	97	95	90	86	82	79	75	4.2
A beadlet Non S. Cong. non-XL	96	94	86	74	63	40	30	21	20.0
D ₃ beadlet (A/D ₃) X-Link	99	98	95	92	88	86	83	80	3.3
D ₃ Spray Congealed.	99	98	95	92	88	86	83	80	3.3
D ₃ Spray dried (SD)	98	96	92	86	82	78	73	71	5.0
D ₃ Drum Dried	97	94	90	83	78	74	68	65	7.0
E acetate 50%	99	98	96	92	88	86	81	77	4.0
E alcohol, Nat	85	70	30	10	5	0	0	0	70.0
MSBC	95	90	82	69	59	49	43	30	17.0
MSB coated	97	94	87	80	73	65	58	50	9.0
MSB	90	78	60	42	30	20	10	5	35.0
MNB	96	92	84	72	61	53	47	45	10.0
MPB	96	91	76	69	62	52	45	39	13.0
Thiamine HCL	95	91	82	70	59	52	44	37	14.2
Thiamine Mono	97	93	86	80	72	66	60	55	9.0
Riboflavin	99	97	92	81	74	66	61	54	9.0
Pyridoxine	99	97	95	85	78	70	65	59	8.2
B ₁₂	98	96	92	86	82	78	73	70	4.2
Calcium Pantothenate	100	98	97	94	90	88	85	82	3.0
Folic Acid	98	95	92	80	73	65	60	53	9.2
Biotin	99	97	93	88	84	80	76	72	4.7
Niacin	99	97	94	91	87	85	82	79	3.5
Niacinamide	98	96	94	90	85	80	75	70	4.0
Ascorbic Acid	94	93	82	70	58	36	26	17	25.0
Ethyl Cellulose Coated Ascorbic	95	94	85	73	62	39	29	20	20.0
Fat Coated Ascorbic	96	95	87	76	65	50	45	35	13.0

Ascorbyl Phosphate	99	98	95	92	88	86	83	80	3.3
Choline	99	98	97	95	93	92	91	90	2.0

TABLE 10. AVERAGE INDUSTRY VITAMIN STABILITY THROUGH EXTRUSION

Vitamin Retention % Extrusion Temperature C											
Vitamin	91-95	96-100	101-105	106-110	111-115	116-120	121-125	126-130	131-135	136-140	141-145
A beadlet Cross-Linked	90	88	86	84	81	77	75	72	69	65	62
A beadlet Non Spray Congealed, Non X-Linked	85	84	82	75	70	66	61	55	51	46	40
A acetate oil	81	80	75	67	60	55	48	41	35	30	25
D ₃ beadlet (A/D ₃) X-Linked	96	95	94	93	92	91	90	89	88	87	86
D ₃ Spray Congealed Beadlet	95	94	93	92	91	89	87	86	85	84	83
D ₃ Spray Dried (SD)	92	90	89	85	82	78	74	70	66	62	57
D ₃ Drum Dried	92	90	89	86	84	82	78	76	73	70	66
E acetate 50%	95	94	93	92	91	90	88	86	84	83	81
E alcohol	65	60	55	50	45	39	33	22	15	10	5
MSBC	70	65	60	55	50	45	40	35	30	25	20
MSB Coated	74	70	68	62	59	54	51	47	46	40	36
MSB	60	55	50	44	39	34	28	23	18	12	7
MNB	75	71	70	64	61	56	53	49	48	42	38
MPB	72	68	65	59	56	50	46	42	38	34	30
Thiamine HCL	89	87	83	80	76	72	66	62	55	50	45
Thiamine Mono	93	91	88	86	84	82	81	77	74	71	66
Riboflavin	98	96	95	94	94	93	93	85	92	91	91
Pyridoxine	93	92	90	88	86	85	84	81	79	78	73
B ₁₂	97	96	95	94	93	92	91	90	89	87	86
Calcium Pantothenate.	94	93	91	89	87	86	85	83	81	79	75
Folic acid	93	92	90	88	86	77	76	71	70	67	64
Biotin	93	92	90	88	86	77	76	72	69	66	63
Niacin	92	91	89	87	85	77	76	72	70	68	64
Niacinamide	90	88	87	85	82	74	72	69	66	64	60
Ascorbic acid	57	53	47	42	37	31	25	20	15	10	5
Ethyl Cellulose Coated ascorbic	59	55	49	45	40	34	29	25	21	15	10
Fat Coated Ascorbic	80	76	75	72	68	65	63	60	50	43	38

Vitamin Retention % Extrusion Temperature C											
Vitamin	91-95	96-100	101-105	106-110	111-115	116-120	121-125	126-130	131-135	136-140	141-145
Ascorbyl phosphate	96	95	94	93	92	91	89	87	85	84	83
Choline	99	98	98	97	97	97	96	96	95	95	94

Table 11. Average Industry Vitamin Stability Pelleting

VITAMIN	VITAMIN RETENTION % Pelleting Temperature °C ^a										
	66-70	71-75	76-80	81-85	86-90	91-95	96-100	101-105	106-110	111-115	116-120
A beadlet cross-linked	98	97	96	95	94	91	88	86	83	80	76
A beadlet Non S. Cong. non X-L	87	85	81	78	73	69	64	60	57	55	52
A acetate oil	80	75	70	65	60	55	50	45	40	36	33
D ₃ beadlet (A/D ₃) X-Link	97	96	95	94	93	92	91	90	89	87	84
D ₃ Spray Congealed Beadlet	96	95	94	93	91	89	86	84	83	81	78
D ₃ Mineral stable., SD	95	94	92	91	88	86	82	80	77	75	74
D ₃ Drum Dried	94	93	90	88	85	82	78	76	73	71	69
E acetate 50%	97	96	95	94	93	92	91	90	88	86	84
E alcohol, Nat	75	70	65	60	54	49	43	30	23	21	17
MSBC	80	76	72	70	65	60	56	51	44	42	39
MSB Coated	85	83	81	77	75	72	70	67	60	58	55
MSB	70	66	62	59	53	48	44	39	31	29	26
MNB	86	84	82	80	78	75	72	69	62	60	57
MPB	82	79	77	75	72	68	65	62	55	53	50
Thiamine HCL	92	88	87	84	80	75	70	64	58	54	50
Thiamine Mono	96	93	92	88	86	85	82	77	74	71	66
Riboflavin	95	94	93	91	89	87	84	80	78	76	73
Pyridoxine	94	93	92	90	87	85	82	78	75	72	69
B ₁₂	99	98	97	97	96	96	95	95	94	93	91
Calcium Pantothenate	95	94	93	91	89	87	84	80	78	76	74
Folic acid	95	94	93	90	89	87	84	80	77	75	72
Biotin	95	94	93	90	89	87	84	80	77	75	72
Niacin	96	95	94	91	90	89	86	82	80	78	84
Niacinamide	94	93	91	88	87	86	82	78	76	76	72
Ascorbic acid	65	60	55	50	45	40	35	30	25	20	15
Ethyl Cellulose Coated Ascorbic	67	62	57	53	47	44	39	34	30	25	20
Fat Coated Ascorbic	85	83	81	77	75	72	70	67	60	45	37
Ascorbyl phosphate	97	96	95	94	93	92	91	90	89	87	85

Choline	99	99	98	98	97	97	96	96	95	94	92
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Table 12. Average Industry Vitamin Stability in Pelleted and Extruded Feed

VITAMIN	VITAMIN RETENTION %												AVG. LOSS/MONTH (%)
	1	2	3	4	5	6	7	8	9	10	11	12	
A beadlet cross-linked	97	93	88	82	76	72	67	63	57	55	45	40	8.0
A beadlet Non-S.Cong. non-XL	95	90	73	58	44	37	30	25	20	15	7	0	30.0
A acetate oil	93	85	65	48	30	25	15	10	5	0	0	0	35.0
D ₃ beadlet (A/D3) X-Link	98	94	90	84	79	75	70	65	60	55	50	45	4.0
D ₃ Spray Congealed Beadlet	97	94	90	84	79	75	70	65	60	55	50	45	4.0
D ₃ Spray dried (SD)	97	92	84	75	60	54	50	46	42	38	34	30	12.0
D ₃ Drum Dried	96	91	82	73	58	51	47	44	41	37	33	29	16.0
E acetate 50%	99	98	95	93	90	87	84	81	77	74	71	67	2.9
E alcohol, Nat	90	78	59	33	20	11	5	0	0	0	0	0	40.0
MSBC	93	85	75	61	52	44	37	30	23	15	11	5	17.0
MSB Coated	96	91	82	75	60	55	50	45	40	35	30	25	11.0
MSB	92	90	80	70	60	48	37	27	17	7	0	0	23.0
MNB	96	92	83	76	61	56	51	47	43	39	35	31	10.5
MPB	95	91	81	74	59	54	48	42	36	32	28	24	12.0
Thiamine HCL	97	93	88	82	75	72	65	60	55	50	45	39	4.0
Thiamine Mono	98	94	89	84	81	77	74	71	66	62	56	50	4.5
Riboflavin	99	98	95	94	92	90	88	86	84	82	80	78	2.0
Pyridoxine	99	97	95	93	91	87	84	81	78	74	71	67	2.9
B ₁₂	99	97	95	93	91	87	84	81	78	74	71	67	2.9
Calcium Pantothenate	99	98	97	95	94	93	91	89	87	85	83	81	1.8
Folic Acid	98	95	90	86	83	80	77	73	70	67	63	58	4.5
Biotin	99	97	94	93	89	87	86	85	84	83	82	81	2.4
Niacin	98	97	94	92	89	88	86	85	84	83	82	81	2.4
Niacinamide	98	97	92	88	86	83	81	79	77	75	73	71	4.2
Ascorbic Acid	90	80	64	45	31	22	15	7	0	0	0	0	37.0
Ethyl Cellulose Coated Ascorbic	92	82	67	48	35	27	20	15	5	0	0	0	30.0
Fat coated Ascorbic	95	92	82	70	59	50	44	40	35	30	24	17	17.0

Ascorbyl Phosphate	98	95	90	86	83	80	77	74	71	68	65	62	4.5
Choline chloride	100	99	99	99	98	98	97	96	95	94	93	92	1.0

Table 13. Vitamin stability in ruminant premixes and feeds

	1	2	3	4
	Vitamin Premix (TABLE 8)	Pelleting Temperature (TABLE 11)	Feed Storage Time (TABLE 10)	Total Vitamin Retention %
	2 Months	96°C	2 Weeks	1x2x3
A Beadlet	90	88	98	78
D ₃ Beadlet	91	91	99	82
E Acetate 50%	92	91	99	83
Thiamine Mono	77	82	99	63
Riboflavin	91	84	99	76
B ₁₂	96	95	100	90
Calcium Pantothenate	87	84	99	72
Biotin	89	84	99	74
Niacin	90	86	99	77

Summary:

Vitamins, like any other sensitive biochemical nutrient, must be managed properly in order for ruminants to obtain the proper vitamin nutrition. Several factors can influence vitamin stability in premixes pelleting and storage, including temperature, humidity, conditioning time, reduction and oxidation (redox) reactions and light. Changes in processes such as higher pelleting temperature and conditioning time, longer drying time, replacement of ethoxyquin with natural antioxidants, and longer shelf time, lead to higher vitamin degradation. On average, after 1 month feed storage, vitamin retention varied between 63% for thiamine mononitrate to 90% for B12.

The high losses experienced by some vitamins through pelleting has led to a constant search for ways to reduce these losses. The option most commonly proposed is vitamin application after pelleting and extrusion. No matter how careful the application (usually spraying) is, it presents insurmountable obstacles. (1) Difficulty in maintaining vitamins in solution. (2) Vitamin forms in a liquid medium have no protection. (3) Vitamin solutions will only coat the outside of the pellet (spraying hot pellets does increase penetration but will also increase vitamin losses). (4) The vitamin distribution throughout the feed is very poor, with a coefficient variation, c.v., of 15-40%, which is unacceptable for small to medium size animals (poultry and swine). Poor distribution of nutrients leads to variable performance throughout a flock. (5) Storage time of 2 to 6 weeks for vitamin-coated feed will lead to very high vitamin losses, since these vitamins will be overly exposed to environmental stresses without any protection.

Another method to correct for vitamin losses caused by processing is to reduce the very same factors that increase vitamin losses through processing. This would include (1) separate trace minerals from vitamins, (2) reduce premix storage time, (3) reduce pelleting temperature and conditioning time and (4) reduce feed storage time. However, several other factors determine premix storage time and pelleting conditions that take precedence over vitamin stability, such as, pellet quality, microbial contamination, etc. Therefore, the industry is left with the most commonly used option which is to compensate for the vitamin losses through overages added into the vitamin supplementation. Knowing the vitamin retention from time of purchase until consumption by the animal, one can easily calculate the overage required to compensate for those losses.

Literature Cited

- Adams, C.R., 1982. Folic acid, thiamine and pyridoxine. *Vitamins - The Life Essentials*. National Feed Ingredient Institute. NFIA. Ames, Iowa.
- BASF, 1986. Effect of pelleting on crystal and ethyl cellulose-coated ascorbic acid assay levels of poultry feed. BASF Animal Nutrition Research. RA873. BASF Corporation, Mount Olive, New Jersey.

- BASF, 1999, Vitamins, one of the most important discoveries of the century, 6th revised ed., BASF Corporation, Mount Olive, New Jersey
- BASF, 1999. Vitamin Stability in Premixes and Feeds: A Practical Approach. BASF Keeping Current KC 9138, 6th ed., BASF Corporation, Mount Olive, New Jersey.
- Christian, L.D., 1983. Vitamin stability in mineral mixes formulated with different calcium phosphates stored at two temperatures and relative humidities. Proceedings AFIA Nutrition Council. p. 22.
- Coelho, M. 1991. Fate of Vitamins in Premixes and Feeds: Vitamin Stability. Feed Management, 42(October):24.
- Dove, C.R. and R.C. Ewan, 1986. The effect of diet composition on the stability of natural and supplemental vitamin E. Swine Research Report AS-580-J. Iowa State University. Ames, Iowa.
- Faustman, C. R.G Cassens, D.M. Schaefer, D.R. Buege, S.N. Williams and K.K. Scheller, 1989. Vitamin E supplementation of Holstein steer diets improves sirloin steak color. J. Food Sci. 54(2):485.
- Gadiant, M. 1986. Effect of pelleting on nutritional quality of feed. Maryland Nutrition Conference. p. 73.
- Huyghebaert, A. 1991. Stability of vitamin K₃ in a mineral premix. World Poultry. 7:71.
- Machlin, L.J. 1993. Antioxidant Vitamins: Petfood Industry, November issue, p. 4.
- Marks, J., 1979. A guide to the vitamins: their role in health and disease. Published by MTP, Medical and Technical Publishing Co., Ltd., England.
- Schlude, M. 1987. The Stability of vitamins in extrusion cooking. Extrusion Communique. Jan-March.
- Schneider, J., 1986. Synthesis; formulation and stability of vitamins. Proceedings of the Twenty-second Annual Nutrition Conference for Feed Manufacturers. p. 18.
- Schneider, J., 1988. Technical service internal reports, BASF AG Animal Nutrition, Ludwigshafen, Germany.
- Weiss, W.P., 1998. Requirements of fat-soluble vitamins for dairy cows: A review. J. Dairy Sci, 81:2493.
- Zimmerly, C.A. and W. P Weiss, 2001. Effects of supplemental dietary biotin on performance of Holstein cows during early lactation. J. Dairy Sci, 84:498.

Vitamin stability in ruminant diets-ruminant nutrition, Univ. Florida02