Stability of selenium sources reviewed

Sodium selenate is stable in premixes during storage, stable in feeds during manufacture and more biologically available to most species than sodium selenite.

By David Eisenberg, Nikolay Barashkov, Zachary Eisenberg and Thomas May*

Sodium selenate is a chemically stable compound, whereas sodium selenite is chemically unstable. This superior stability of sodium selenate over selenite has been previously demonstrated in animal feed premixes (Eisenberg, 2007).

Although both compounds are permitted as animal feed additives in the U.S. and internationally, the current article provides additional research supporting sodium selenate over sodium selenite as a lower cost option than selenium yeast as a feed additive.

Background

Selenium is an essential element for most animal species, including humans, and its functions include serving as a cofactor in protein synthesis and metabolism, stimulating the production of antibodies and aiding in male fertility.

However, selenium is toxic in excess concentrations, with an LD50 (lethal dose for 50% of test animals if fed continuously) of between 5 and 7 parts per million for most species.

Because many formula feeds are deficient in selenium, the Food & Drug Administration allowed selenium additions to feed beginning in 1974, in recognition of these and other dietary benefits. This regulation permitted the addition of a maximum of 0.1 ppm selenium as sodium selenite or as sodium selenate to chicken and pig feeds and at 0.2 ppm to turkey feeds under strict manufacturing controls that precluded any toxicity while incorporating the nutritional benefits.

Over the years, these limits were carefully expanded to 0.3 ppm for all species. In addition, the allowable concentration of premixes was increased, the requirements that premixes be analyzed was eliminated and additives via salt/mineral mixes and organo-selenium (e.g., selenomethionine) in the form of yeasts were permitted.

While sodium selenite, sodium selenate and selenium yeast are all legally permitted feed additives in the U.S., virtually all inorganic selenium is added as the selenite form, as it is about 30% less expensive than selenate. Elemental selenium and volatile selenium compounds are not considered bioavailable and are, therefore, not used.

Metabolism of selenite, selenate and selenium yeast are different, but all are accepted by FDA as being bioavailable. However, numerous published research studies indicate that sodium selenite is 20-30% more bioavailable than sodium selenate (Whanger, 2002; Ammerman et al., 1995; Borshel et al., 1993), which could indicate that higher costs of selenate are worthwhile considering the nutritional losses that may occur due to the greater instability of sodium selenite. Selenate may be more efficiently metabolized than selenite or significant amounts of selenate may be lost due to its greater chemical instability in premixes and from chemical oxidation during feed manufacturing. While this difference may not seem economically significant, because the sodium selenite is more expensive than the sodium selenate, it may be very significant when one considers the total added selenium is limited to 0.3 ppm and the positive benefit of adding the maximum permitted amount may be substantial.

Currently, various companies are supplying selenium yeast containing 50% or more selenomethionine for feeds at a far higher cost than the cost of the sodium selenite or sodium selenate. Formulated at 0.5 ppm, the cost for sodium selenite or sodium selenate is about $5.0 or 6.5 cents per ton of feed, respectively (assuming a current price of $80/kg for sodium selenite). The cost for selenium yeast is $1/ton or more.

The organic selenium compounds are being added to feeds because they apparently provide more biological benefit than the selenite or the selenate. If a significant part of the advantage of organo-selenium compounds is due to chemical instability of selenite, then selenate may be a useful alternative to selenite and provide a significant economic benefit to the feed industry.

Storage stability

It is impossible today to speciate selenium compounds in complex feed premixes. It is, however, possible to speciate possible chemical transformations of sodium selenite in premixes.

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*David A. Eisenberg, Dr. Nikolay Barashkov and Zachary Eisenberg are with Micro-Tracers Inc. and Dr. Thomas May is with the U.S. Geological Survey in Columbia, Mo. Mostafa Raisa El-Fenni and Anastasia Banita of Micro-Tracers contributed to the article.

selenium in water extracts of such pre-mixes.

Micro-Tracers Inc. obtained samples of 10 feed premixes (Attachment A) as well as a sample of fish-grade molasses. Selenium was added at a rate of 1,000 ppm as sodium selenate, as “unprotected” sodium selenite (ACS grade) and as “protected” selenite (proprietary mixture of sand, sodium selenite and soybean oil) to three sets of each of the 10 feed premixes, to molasses and to molasses with 1% added phosphoric acid (typical in molasses-based liquid feeds).

A total of 108 samples were prepared—12 samples x 3 selenium sources x 3 sets. One set of 36 samples was immediately frozen. The second set was incubated at 45°C for one week and frozen. The third set was incubated for three weeks at 45°C and frozen.

Water extracts of the 108 samples were made and preserved by adding nitric acid (pH 2.0); refrigerated samples were then shipped to the U.S. Geological Survey Laboratory at Columbia, Mo., for specified selenium analysis (May et al. 2009). Results are listed in Table 1.

Anresco Laboratory (associated with Micro-Tracers) analyzed four samples of the premixes to which “unprotected” sodium selenite had been added after water extraction (Table 2). For these samples, the residual selenium in the wet premix, when added to the water-soluble selenium, approximated 100% of the formulated level. The non-water-soluble sodium selenite in these premixes was probably reduced to mostly elemental selenium and not transformed into volatile compounds.

**Interpretation**

In evaluating our analytical findings, it was assumed that the sum of sodium selenite plus sodium selenate equated to recovery of selenium.

The results are best interpreted in three groups as follows:

- Three premixes containing ferrous sulfate where selenium degraded nearly totally and immediately in water extracts of two samples and where it degraded gradually over time in the third;
- The two molasses mixes, and
- The remaining seven dry premixes where the sodium selenite and “protected” selenite both degraded 20% plus initially but were then stable over time.

The sodium selenate appeared reasonably stable in all 12 premixes, including molasses and molasses plus phosphoric acid, at all times tested (at preparation of the samples and after incubation of one and three weeks) with an average recovery of 88.9%, with no result lower than 74.1%.

Sodium selenite and “protected” selenite degraded almost totally and immediately in water extracts of two premixes (4011 and 1202), both containing ferrous sulfate. The unprotected sodium selenite degraded more slowly in one premix (1598) that contained ferric ammonium citrate (an oxidizing compound) in addition to ferrous sulfate, whereas the “protected” selenite in this premix appeared

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**1. Effects of time on percent selenium source in feed premix extracts**

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**Averages**

- All: 52.2
- Time = 0 weeks: 60.2
- Time = 1 week: 51.9
- Time = 3 weeks: 44.6

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stable over time (Table 1). Recovery from premix 1598 for unprotected sodium selenite was 77.2% at preparation of the samples, 68.4% after one week incubation and 44.2% after three weeks of incubation. Recovery of "protected" sodium selenite was 55.5% at preparation of the samples, 88.2% after one week and 85.3% after three weeks, indicating analytical error in the testing process.

The average recoveries of sodium selenite, "protected" selenite and selenate from the remaining seven dry premixes are shown in Table 3.

In these premixes, the selenite appeared stable, while both the selenite and the "protected" selenite lost more than 20% during sample preparation and then seemingly achieved stability.

In the molasses and molasses-plus-phosphoric-acid premixes, significant percentages of selenite and "protected" selenite degraded to the selenate form. The incubated samples apparently lost a substantial portion of the selenite to gaseous compounds. The applicable chemical reactions are explained in the Figure.

The average total recovery of the bioavailable selenium (selenite plus selenate) from the two molasses premixes after three weeks of incubation was 51.9% for sodium selenite, 83.5% for "protected" selenite and 86.9% for sodium selenate.

Besides oxidation into selenate and reduction to elemental selenium, selenites can be converted into two volatile products: selenium dioxide (through intermediate formation of selenious acid following by its thermo-degradation) and hydrogen selenide. Reduction of selenites to hydrogen selenide requires the presence of very strong reducing agents and, therefore, loss of selenium to hydrogen selenide in premixes is less likely than loss to selenium dioxide.

During manufacturing
In a trial with a simulated corn/soybean meal-based poultry feed manufactured at the Oceanic Institute in Hawaii, 1,000 ppm selenium was added to two batches of feed, one batch as sodium selenite and a second batch as sodium selenate. Four samples were taken from each batch at each of three locations, mash, after conditioning and after pelleting.

The recovery of selenium from water extracts of the mash feed was 90.5% of the conditioned feed was 74.5% and of the pelleted feed was 69.5% based on analyses of all samples by Micro-Tracers using the Norris-Fay titration method. Results from the samples with added selenate were meaningless due to false high results from the method.

In a trial with a corn/soybean meal-based poultry mash feed, Micro-Tracers added 1,000 ppm selenium as either sodium selenite or as sodium selenate, incubated them for two weeks at 40°C, made water extracts from them and sen; the extracts and the residual wet premixes to the University of California-Davis for speciated selenium analysis by LC-ICPMS.

The recovery of selenium from the water extract was 76.3% and from the selenate was 99.5%. The additional recovery of total selenium from analysis of the wet premix formulated with sodium selenite was 20.3% and from the wet premix formulated with sodium selenate 4.3%. The selenium from the wet premix analyses was probably elemental selenium.

Sodium selenate appeared stable in the corn/soybean meal poultry mash feed whereas sodium selenite degraded by 25.5% in the fist trial and by 23.7% in the second trial. It appears likely the sodium selenite degrades when feed is conditioned and pelleted or merely incubated.

During digestion
Dr. P.D. Whanger of Oregon State University (2002) reported that ruminant microbes reduce sodium selenite to insoluble forms. Whanger further reported that the uptake and retention by sucking rat pups was most rapid for selenomethionine (70%), followed by selenite (51%) and least for selenite (29%). He also reported that the transfer of selenium as selenomethionine and selenate to vascular effluents was respectively 2.4-fold and 1.5-fold greater than the transfer of selenite-based selenium.

These data suggest that selenomethionine (and therefore, selenium yeast) is preferable to sodium selenite and that sodium selenite is preferable to sodium selenite as a feed additive.

Bioavailability
The summary data reported in "Bioavailability of Nutrients for Animals," by Ammerman et al. (1995; no newer summary data was found) indicates that sodium selenate, selenium yeast and selenomethionine are more bioavailable than sodium selenite (Table 4).

In that book, the term bioavailability is defined as "the degree to which an ingested nutrient in a particular source is absorbed in a form that can be utilized..."
in metabolism by the animal. ... For some nutrients, measurement is extremely difficult."

One can reasonably conclude that sodium selenite is stable in premixes during storage, stable in feeds during manufacture and more biologically available to most species than sodium selenate. It is probably less bioavailable for some species than selenium yeast containing selenomethionine, but it costs far less and should be seriously considered as a feed additive.

One may also reasonably conclude that sodium selenite may be particularly unstable in premixes containing ferrous sulfate, vitamin C or other compounds, and it may also degrade during the pelleting of formula feeds and during digestion in the rumen of cattle.

References

Attachment A

List of Premixes Used

**Code 4011** — Dairy — Ingredients: vitamin A supplement, D-activated animal sterol (source of vitamin D3), DL-alpha tocopherol acetate, iron sulfate, iron carbonate, zinc methionine, zinc sulfate, zinc oxide, manganese methionine, manganese sulfate, manganese oxide, copper lysine, copper sulfate, cobalt glucoheptonate, cobalt carbonate, EDDI, sodium selenite, calcium carbonate, mineral oil, ethoxyquin.

**Code 1202** — Swine — Ingredients: ferrous sulfate, zinc sulfate, manganese sulfate, copper sulfate, cobalt sulfate, EDDI, sodium selenite, calcium carbonate, mineral oil.

**Code 1590** — Swine — Ingredients: ferrous sulfate, ferrous fumarate, ferrous gluconate, iron ammonium citrate, iron amino acid complex, zinc oxide, manganese oxide, copper sulfate, cobalt carbonate, EDDI, calcium carbonate, mineral oil.

**Code 170** — All species — Ingredients: D-biotin, roughage products, calcium carbonate, mineral oil.

**Code 1819** — Swine — Ingredients: vitamin A acetate, vitamin D3, vitamin E, vitamin B12, riboflavin, D-calcium pantothenate, niacin, choline chloride, vitamin E-MSBC, calcium carbonate, corn dried distillers grains plus solubles (DDGS), mineral oil.

**Code 1910** — Beef — Ingredients: vitamin B12, riboflavin, D-calcium pantothenate, niacin, choline chloride, vitamin K-MSBC, pyridoxine hydrochloride, thiamine monohydrate, folic acid, D-biotin, calcium carbonate, corn DDGs, roughage products, natural mixed tocopherols, citric acid, rosemary extract.

**Code 199** — All species — Ingredients: EDDI, salt, calcium carbonate, iron oxide and mineral oil.

**Code 1548** — Swine — Ingredients: vitamin A acetate, vitamin D3, vitamin E, vitamin B12, vitamin K-MSBC, riboflavin, D-calcium pantothenate, niacin, choline chloride, pyridoxine hydrochloride, folic acid, thiamine monohydrate, D-biotin, ethoxyquin, roughage products.

**Code 1703** — Swine — Ingredients: vitamin A acetate, vitamin D3, vitamin E, vitamin B12, riboflavin, D-calcium pantothenate, niacin, vitamin K-MSBC, Aspergillus oryzae, calcium carbonate, roughage products, mineral oil.

**Code 1815** — Swine — Ingredients: vitamin A acetate, vitamin D3, vitamin E, calcium carbonate, DDGs, mineral oil.
23 July 2012

MEMORANDUM

TO: Feedstuffs

FROM: David Eisenberg

RE: Response to Feedstuffs letter to the Editor of Mr. Jon D. Nelson, Executive Vice President, Southeastern Minerals, published in Feedstuffs 9 July 2012.

I read with great interest Mr. Nelson’s Letter to the Editor as referenced. I am pleased to respond with comments as follows.

Mr. Nelson states that since the water solubility of sodium selenite is not much greater than for sodium selenate (85 grams/100 ml as compared with 82 grams/100 ml) there should not be much difference in their stability in feeds.

He did not consider that “water activity” not solubility in water is what determines if a feed material will pickup or lose moisture. The water activity for feed grade sodium selenite averaged 0.68 and for sodium selenate 0.73 (S. Eisenberg, JAOAC March 2007) again seemingly a small difference. But the difference had major consequences. After 23 days incubated storage petri dishes containing sodium selenite picked up 78.1% and 80.0% moisture becoming wet slurries while sodium selenate picked up 0.85% moisture and was visually unchanged. Most chemical reactions require water so this difference is huge.

Further, sodium selenite is an inherently reactive compound whereas sodium selenate is inherently stable as outlined in the June 18th Feedstuffs article..

Mr. Nelson also states sodium selenate for feed use has 5% or more contamination by selenite. This is untrue. Micro-Tracers analyzed a sample of feed grade sodium selenate supplied by Pacific Rare Metals, The Philippines and it was 99.46% pure with 0.54% selenite.

Sodium selenate is more expensive by 20-30% per unit selenium than selenite but it is also more stable and more bioavailable and certainly should be considered as a superior alternative to sodium selenite.

With best wishes,
David A. Eisenberg, President, Micro-Tracers, Inc.
Our food safety system isn’t failing

A NYONIC paying attention to the thousands of food safety-related headlines that appeared each year would likely have reason to trust our food system.

Increased media coverage has led the public to believe that foodborne illnesses are increasing at an alarming rate, but the number of foodborne illnesses has actually decreased by more than 25% in the last decade. This reduction is caused in large part by the substantial increase in coverage of foodborne illness outbreaks and food recalls, a symptom of the changes in global media, the rise of the internet and shorter news cycles.

Media coverage of food recalls related to illnesses dropped by 15% in the past five years and by more than 22% in the past 10 years, while actual laboratory-confirmed illnesses have dropped 25% in the past five years and by more than 22% in the past 10 years.

The media has ample coverage of food safety issues, and the public is aware of the risks, but the public is not aware of the much larger risk of death and disability from foodborne illnesses. The risk of death from foodborne illnesses is much higher than the risk of death from other causes, such as accidents, cancer, or heart disease.

Food companies can do this by adopting a 360-degree approach to food safety communications that proactively builds confidence, responds to questions and concerns, and restores trust among the public.

The average foodborne illness outbreak has increased by more than 15%, while the number of foodborne illness outbreaks has dropped 15% in the past five years and by more than 22% in the past 10 years.

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Food companies can do this by adopting a 360-degree approach to food safety communications that proactively builds confidence, responds to questions and concerns, and restores trust among the public.

Average incidence of foodborne illnesses linked to Listeria, E.coli and campylobacter

Selenium review questioned

Dear Editor:

I read with interest the recent article in the June 28 issue of Foodasts, entitled “Selenium deficiency increases risk of cancer,” by David Eisenberg of Micro-met Research Inc., along with two of his staff and Dr. Thomas May of the U.S. Geological Survey.

I was interested to read the statement of your readers that the use of selenium is not necessary because the role of selenium in the prevention of cancer is not well established.

Some readers also pointed out that although the use of selenium is not necessary, the use of selenium is not contraindicated.

It is extremely doubtful that the 3.6% difference in selenium concentration in the blood of the two groups of patients who received selenium or placebo is statistically significant.

It is also very difficult and expensive to create a selenium product that is 100% selenium. Usually, the product is manufactured and then designated as a dietary supplement, which is a blend of 25% selenium and 75% sodium. A selenium supplement product can be created, but not with significant advantage. Essentially, this opens up a nightmare for the Association of American Feed Control Officials and would require a redefinition of selenium based on the selenium content.

Respectfully submitted:

Joel D. Nelson
Executive Vice President, Nutrition & Quality Assurance
Southeastern Minerals Inc.