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Dissolution of copper, tin, and iron from sintered tungsten–bronze spheres in a simulated avian gizzard, and an assessment of their potential toxicity to birds

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ABSTRACT

The rates of dissolution of copper, tin, and iron from sintered tungsten–bronze spheres (51.1%W, 44.4%Cu, 3.9%Sn, 0.6%Fe, by mass) were measured in an *in vitro* simulated avian gizzard at pH 2.0, and 42C. Most of the spheres had disintegrated completely to a fine powder by day 14. Dissolution of copper, tin, and iron from the spheres was linear over time; all $r > 0.974$; all $P < 0.001$. The mean rate of release of copper, tin, and iron was 30.4 mg, 2.74 mg, and 0.38 mg per g tungsten–bronze per day, respectively. These rates of metal release were compared to those in published studies to determine whether the simultaneous ingestion of eight spheres of 3.48 mm diameter would pose a toxic risk to birds. The potential absorption rates of iron and tin (0.54 mg Fe/day, and 3.89 mg Sn/day) from eight tungsten–bronze spheres of total mass 1.42 g would not prove toxic, based on empirical studies of tin and iron ingestion in waterfowl. The release of 43.17 mg copper/day from eight tungsten–bronze spheres, while exceeding the daily copper requirements of domesticated birds, is far below the levels of copper known to cause copper toxicosis in birds. We conclude that sintered tungsten–bronze material made into gunshot, fishing weights, or wheel balance weights, would not pose a toxic risk to wild birds when ingested.

1. Introduction

The extent of fatal lead poisoning of birds from the ingestion of discharged lead shot has led to an ever-growing list of nations regulating bans on the use of lead shot (Beintema, 2001; Thomas and Guitart, 2005). This, in turn, has induced the development of diverse lead substitutes containing iron, tungsten, bismuth, tin, and copper in different proprietary combinations (USFWS, 2006). In Canada and the USA it is mandatory that such lead substitutes pass a rigorous toxicological screening before being approved for use (USFWS, 1997; Thomas, 2003), but no other countries require such an evaluation.

The need to regulate lead in shot is being extended to other applications of lead, as in fishing weights (Perry, 1994; Scheuhammer et al., 2003), but in this case, no nation requires mandatory toxicological screening of lead substitutes (Thomas and Guitart, 2003). Sintered tungsten–bronze is a new material devised and approved, initially, for shot (USFWS, 2004), but has physical and manufacturing properties that dispose it to use in fishing weights and automotive wheel balance weights.

In both recreational shooting and angling it is inevitable that discharged shot and lost fishing weights will be ingested by waterfowl and other aquatic avian species (Perry, 1994; Twiss and Thomas, 2003). In situations where birds have been wounded by gunfire, and then fall prey to both avian and mammalian

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Table 1 – Chemical composition of tungsten–bronze spheres used in dissolution tests

Sample replicate	Mass (mg)	Copper %	Tin %	Iron %	Tungsten %
Mean ± standard deviation	177.7 ± 2.9	44.4 ± 0.55	3.9 ± 0.12	0.60 ± 0.016	51.1 ± 0.56

The values are % by mass, based on five randomly-selected batches. The level of tungsten was measured by difference.

predators and carrion feeders, shot in the tissues will enter the gut of the animal, and may prove toxic (Kramer and Redig, 1997; Fisher et al., 2006). Lead balance weights are lost from vehicle wheels, pollute roadside habitats, and increase the lead loading of human urban environments (Root, 2000). Thus, there needs to be a process to evaluate the potential toxicity of ingested candidate lead substitutes to animals, especially outside of the USA and Canada. The passage of the European Directive on Chemicals in the Environment in 2007 (CEC, 2006) means that every new chemical material that may be released to the European environment must be assessed in terms of its potential toxicity.

The release of copper from sintered tungsten–bronze spheres under different pH conditions was measured by Thomas et al. (2007a), and shown to pose no toxic risks to even the most sensitive aquatic organisms. Determination of the non-toxicity of any substitute for lead shot and sinkers also requires that the release of metal salts under the prevailing pH in waterfowl gizzards be measured and compared with known levels that pose toxic risks to birds. This *in vitro* study was designed to simulate the chemical dissolution that ingested tungsten–bronze spheres would experience inside an avian gizzard. The amount of copper, tin, and iron liberated from the spheres was measured over time and related to their potential toxicity to birds. The only metals of potential concern in this study are copper and tin, since tungsten and iron have already been shown to be non-toxic to waterbirds when ingested (Mitchell et al., 2001a,b,c). Nonetheless, a discussion of the potential dissolution and absorption of tungsten salts from the tungsten–bronze spheres is provided in light of the findings of Mitchell et al. (2001a,b,c).

2. Materials and methods

Both physical and chemical break-up of ingested materials occurs in the highly acid medium of the gizzard (ventriculus). Kimball and Munir (1971) established an *in vitro* protocol to measure the dissolution of metals in simulated waterfowl gizzards. This protocol was used to measure the actual rates of release of aqueous copper, iron, and tin from tungsten–bronze spheres into the synthetic medium. The experimental work was performed in the laboratories of the International Tin Research Institute, UK. The digestive medium was 1 M sodium chloride solution containing 20 g/l of Pepsin A, and the pH of the solution was adjusted to 2.0 using hydrochloric acid (Kimball and Munir, 1971). All reagents were of analytical grade (Merck), whether used in the dissolution medium or for subsequent ICPOES metal analyses.

The experiment comprised an experimental treatment using tungsten–bronze spheres (3.48 mm diameter), a glass bead (3 mm diameter) control, a pure copper sphere (3.4 mm) control, a tin sphere (3.3 mm diameter) control, and an iron sphere (3.3 mm diameter) control. The composition of the tungsten–bronze sphere was 51.1% tungsten, 44.4% copper, 3.9% tin, and 0.6% iron (Table 1). The trace elemental composition of the sphere, and the particle size distribution of the bronze and tungsten components are given in Thomas et al. (2007a). The presence of iron in the formula serves as a densifier of the material, and also serves to render the material magnetic, as per the legal requirements of the USFWS (2006).

There were five replicates within each control and experimental treatment. A single tungsten–bronze sphere was weighed and placed in a 100-ml Pyrex bottle fitted with a loose screw-top closure. One hundred ml of the acid medium was added, together with a Teflon magnetic stirring bar. The same procedure was used for the glass bead, tin, iron, and copper sphere controls. The bottles were placed on magnetic stirrers inside a thermostatically-controlled oven set at 42 °C, and the samples were stirred continuously for 14 days. Each bottle allowed air to equilibrate with the dissolution medium for the entire 14-day period. This time period was selected because it was consistent with the known time taken for tungsten–bronze spheres to disintegrate, completely, in the simulated gizzard (Table 2). A third experimental treatment was used to measure the impact of the presence of iron in the tungsten–bronze formula on the physical integrity of the spheres and potential dissolution rates of copper and tin by the acid medium. In this case, the tungsten–bronze pellet did not contain 0.6% iron, but had the composition 3.9% tin, 44.4% copper, and 51.7% tungsten. This experimental treatment was subjected to the same dissolution conditions as the tungsten–bronze spheres containing iron.

Table 2 – The mass of individual tungsten–bronze spheres before and after 14 days of immersion in the dissolution medium (A), and (B), the mass of individual tungsten–bronze spheres (containing 0% iron) before and after dissolution in the acid medium for 14 days

A	Tungsten–bronze spheres (0.6% iron)			
	Mass before test mg	Mass after test mg	Loss of mass mg	%
Mean value ± 1 SD	173.7 ± 4.8	1.96[a] ± 2.9	171.7 ± 4.2	98.9 ± 1.6
B	**Tungsten–bronze spheres (0% iron)**			
	Mass before test mg	Mass after test mg	Loss of mass mg	%
Mean ± 1 SD	125.74 ± 1.76	98.97 ± 9.61	26.77 ± 9.15	21.31 ± 6.00

N = 5 for each mean value.
[a] Denotes that no measurable pieces were in three of the five reaction bottles.