TECHNICAL DETAILS FOR USERS OF INDIANA ZINC

Different types of Indiana Zinc

We offer zinc with chemical properties that best match a variety of analytical demands. 2H/1H data from any batch of zinc should always be calibrated using water isotope standards with known $^{2}H/^{1}H$ ratios relative to VSMOW2 and SLAP2. Proper calibration makes $^{2}H/^{1}H$ data directly comparable, regardless of the type of Indiana Zinc used. Without proper calibration relative to VSMOW2 and SLAP2, $^{2}H/^{1}H$ data can only be directly compared within the same batch of zinc because different batches of zinc typically differ in the amount of their hydrogen blank.

All batches of Indiana Zinc manufactured after 1999 have their hydrogen blanks quantified in our laboratory to better serve the analytical needs of the research community.

Batches of zinc differ in their composition as expressed in their hydrogen blank ("amount effect"; see paper by Attila Démeny, 1995). Some batches of 'traditional Indiana Zinc' have medium to high hydrogen blanks. The 'traditional formula' has proven reliability for laboratories that can maintain a constant zinc: water weight ratio, for example in hydrogeological and clinical applications where sample size is usually not restricted. Users who want to react physiological fluids (serum, urine, etc.) without prior distillation are advised to specifically request 'traditional zinc' because waters containing dissolved salts sometimes react poorly with low-blank zinc. Low- to ultra-low blank zinc formulas are available upon request for researchers who have limited amounts of water available, or who cannot control the zinc: water weight ratio within a narrow range, for example in studies on fluid inclusions.

All batches of zinc are thoroughly quality-controlled at Indiana University in multiple tests using VSMOW and SLAP waters, to ensure quantitative conversion of water to elemental hydrogen and reproducibility of stable isotope ratios. For best results, we recommend adherence to our analytical guidelines (see below).

Please inquire with us if you are unsure which type of zinc is best suited for your application. Before ordering zinc you may request a small free sample for testing (international shipping charges may apply).

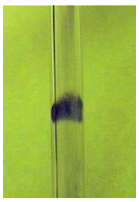
Storage of Indiana Zinc

Indiana Zinc is shipped in evacuated and sealed Pyrex® bulbs or ampoules. Indiana Zinc has an unlimited shelf life when properly sealed under vacuum. Indiana Zinc will deteriorate when in contact with moist air. Vacuum desiccators are preferred for short-term storage, provided that acids (droplets from sulfuric acid or dust from phosphorous pentoxide desiccant), vacuum grease, DryeriteTM dust, and other particulates or corrosive vapors cannot contaminate the zinc. Never store Indiana Zinc at elevated temperature in a drying oven.

Recommended analytical procedures:

(a) Loading of zinc: Because stopcocks cannot be adequately heated and outgassed, stopcock vessels are less suited than Pyrex® or Kimax® glass ampules that are flame-sealed after loading with zinc and water. The stopcock part will always be a 'cold spot' in the reactor. Also, hydrogen gas may diffuse through O-rings and through Teflon parts of stopcocks, which may lead to fractionation of the remaining elemental hydrogen pool. We prefer the use of 6 mm outer diameter glass tubes for safe, efficient, and cheap batch processing of water samples to hydrogen gas. Ampules can be reliably marked by engraving. Ampules should be pre-baked at 500ºC to burn off organic contaminants.

We recommend to load 100 mg of Indiana Zinc in a Pyrex® or Kimax® glass ampoule with an outer diameter of 6 mm and a length of approximately 20 cm. 100 milligrams of Indiana Zinc are sufficient for complete reaction with 2 microliters of water (i.e. 2 mg).



After pre-heating of Indiana Zinc in vacuum at 350 ºC for at least five minutes, a metallic mirror of sublimated zinc should have precipitated inside of the glass tube above the heated zone. Failure to notice this mirror indicates either poor vacuum or low temperature, or both. Insufficient pre-heating may cause an increased hydrogen blank.

We suggest to load 100 mg of zinc for reaction with every 2 mg of water. Avoid mixing of batches of Indiana Zinc because different batches may have different hydrogen blanks. The ampule containing zinc can be connected to a vacuum line with an Ultra-Torr® fitting. The apparatus is designed to admit water from a syringe. Other setups for admission of water are required for certain applications, such as work on fluid inclusions in minerals or work on water that is derived from combustion of organic hydrogen.

The vacuum line connects via Ultra-Torr® fitting to the top left. From the right side, the syringe pierces through a septum (see also picture below). Another Ultra-Torr® connection at the bottom holds the 6mm o.d. glass ampule containing zinc. This setup is specialized for the injection of liquid water with a syringe. Other arrangements are necessary if water is derived from fluid inclusions or from combusted organic matter.

We recommend to inject water at a ratio of 2 microliter of water (= 2 mg) for each 100 mg of Indiana Zinc.

(b) Pre-heating of Indiana Zinc under vacuum: Indiana Zinc contains some adsorbed atmospheric moisture and some chemisorbed hydrogen, probably in form of hydroxy-groups. It is recommended to heat the loaded zinc under a good vacuum for at least 5 minutes at 350ºC, to reduce the hydrogen blank. Heating with a torch is not recommended because open flames offer little temperature control. Overheating needs to be avoided because zinc would excessively sublimate and may lose its reactivity. Consistency in the technique is important to achieve good reproducibility. A small, lightweight heating block or heating sleeve (= coil of electrically insulated heating tape around a small copper tube with ca. 7 to 8 mm inner diameter; apply additional external thermal insulation for easy handling; an integrated thermocouple should permit monitoring of core temperature) can be built to slip over the bottom of the ampule, to enclose the end of the zinc-containing glass ampule. The sleeve is fed a constant voltage from a variac transformer to hold a core temperature of 350ºC. After 5 minutes, a faint metallic mirror should have sublimated onto the interior glass surface just above the heated zone. Absence of this mirror indicates insufficient temperature and/or poor vacuum. A gas torch can be used to briefly flame and outgas the ampule above the heating sleeve.

(c) Loading of water: Most analytical applications provide enough water to use a syringe for injection through a septum. We suggest the use of a 10 microliter gastight syringe that injects 2 microliter of water for each 100 mg of Indiana Zinc. The septum interface should be located near the Ultra-Torr® fitting, with as little internal surface and as few stopcocks as possible. Before injection, the zinc-containing part of the ampule must be under good vacuum and at the temperature of liquid nitrogen. Any leak in the system would admit incondensible nitrogen, oxygen, etc. and would provide a diffusion barrier that prevents water from quantitatively collecting at the bottom of the ampule. The complete freeze-down of injected water should occur within five minutes. Following (i) visual confirmation that no liquid phase is left in the syringe and (ii) monitoring of a sufficiently low pressure in the system, the ampule is flame-sealed off with a small glassblowing torch. Fully loaded and properly sealed ampules can be stored for long periods of time without danger of isotope fractionation. Water will not readily diffuse through glass walls. Every batch of water analyses should use the same batch of zinc and should include internal laboratory water isotope standards and/or VSMOW and SLAP for proper normalization of isotopic results relative to VSMOW (zero permil) and SLAP (-428 permil). A syringe can carry water from one injection to the next, thus causing a memory effect. According to a suggestion by Dr. Gilles St-Jean (ISOGEOCHEM list, 9 Dec 2003), a syringe can be thoroughly dried between injections as follows:

- If clean water is to be analyzed, use 3 rinses with acetone, then insert needle through the septum to expose the barrel for 60 seconds to vacuum, while pumping the plunger once every 20 seconds.
- For saline or urine samples, rinse the syringe 3 times with deionized water, followed by 3 rinses with acetone, and 60 seconds of vacuum drying while pumping the plunger once every 20 seconds.

(d) Generation of hydrogen: The reaction of water with Indiana Zinc occurs quantitatively at 500ºC over 30 minutes. Temperature ramp-up time does not count. We recommend the following options:

(i) Spread the zinc over the entire length of a glass ampule and place the ampule horizontally into a 500ºC oven. It is important to place a reliable thermocouple very close to where the zinc is located. Some ovens without forced convection have strong thermal stratification. Improper heating conditions may result in incomplete reaction.

(ii) With the zinc at the bottom of the ampule, place the ampule vertically into a heating block that is at 500ºC. The upper part of the ampule, which sticks out of the heating block, should be at about 300ºC. Convection of water vapor and hydrogen gas will cause rapid conversion of water to elemental hydrogen.

Before any heating, glass ampules can be conveniently engraved using a diamond-coated engraving tool. During heating at 500 ºC for 30 minutes, Indiana Zinc reacts quantitatively with water. The zinc surface becomes oxidized and turns gray and dull.

(e) Mass-spectrometry: Following reaction to elemental hydrogen, the ampules can be scored with a glass knife and directly fitted to an interface at the mass-spectrometer in manual dual-inlet mode. Indiana Zinc does not produce much zinc oxide dust, but as a precaution a small safety screen should be placed at the inlet system to protect valve seats from particulates.

(f) Disposal of Indiana Zinc: Indiana Zinc cannot be regenerated after use. The 'recycling' via leaching in nitric acid will not yield satisfactory results. After use, Indiana Zinc should be disposed in the same way as required for regular zinc shavings.