

Feature

Element of the Month

Arsenic

Known and utilized by the medieval alchemists in their pursuit of changing base metals into gold and to discover the elixir of perpetual youth, arsenic, a Group V metalloid with 33 protons in its nucleus, is the 53rd most abundant element in the Earth's crust.

In nature, small amounts of arsenic occur in the free form, but much of it is found in the form of sulfides—particularly realgar and orpiment (AsS and As_2S_3 respectively), which were at one time used as pigments for painting—arsenides and sulfarsenides of heavy metals, oxides, and arsenates. Minerals with the formula MAS and MAS_2 ($\text{M} = \text{Fe}, \text{Ni}, \text{Co}$) are the dominant commercial sources of arsenic; *Mispickel*, also known as arsenopyrite (FeAsS), is the most common arsenic-bearing mineral. Many minor minerals that contain small amounts of arsenic are known. Arsenic also occurs in various organic forms in the environment.

The element's natural occurrence in a positive oxidation state (3+) indicates the greater metallic character of arsenic compared to other members of the nitrogen group, including phosphorus, of which arsenic compounds resemble in some respects. Arsenic is less commonly observed in the pentavalent state, however. The most common oxidation states for arsenic include 3- in the arsenides, such as

alloy-like intermetallic compounds; and 3+ in the arsenites, arsenates, and most organoarsenic compounds. Arsenic also bonds readily to itself as seen in the square $\text{As}_3\text{-4}$ ions in the mineral skutterudite. In the 3+ oxidation state, arsenic is typically pyramidal owing to the influence of the lone pair of electrons.



Arsenic occurs in nature as one stable isotope, arsenic-75. As of 2003, at least 33 radioisotopes have also been synthesized, ranging in atomic mass from 60 to 92. The most stable of these is arsenic-73 with a half-life of 80.30 days. Most other isotopes have half-lives of under one day.

Isotopes that are lighter than the stable arsenic-75 tend to decay by α -decay; those that are heavier tend to decay by β -decay, with some exceptions.

Pure arsenic occurs in several allotropic forms, the most important of which are yellow arsenic (non-metallic-type lattice consisting of tetrahedral As_4) and metal-like gray arsenic (consisting of puckered six-membered rings within layers), which is the most stable. Several

oxides are known, the most important of which are As_2O_5 , and As_4O_6 , a white solid obtained by roasting As_2S_3 , an important reaction in testing for the presence of arsenic in unknown mineral samples (see page 23).

Arsenic sulfides (orpiment and realgar) and oxides have been known and used since ancient times. Zosimos (circa 300 AD) described roasting *sandarach* (realgar) to obtain *cloud of arsenic* (arsenous oxide), which he then reduced to metallic arsenic. During the Bronze Age, arsenic was often included in bronze (the so-called *arsenical bronze*), which made the alloy harder.

According to the *CRC Handbook of Chemistry and Physics 56th Edition 1975-76*, "it is believed that Albertus Magnus obtained the element in 1250" by heating soap together with arsenic trisulfide, and in 1649, "Schroeder published two methods of preparing the element." The oxide is then reduced with coke to produce elemental arsenic, As_4 . Elemental arsenic is also obtained by the thermal decomposition of arsenopyrite in the absence of air to produce iron sulfide and As_4 . The main use of metallic arsenic is for strengthening alloys of copper and especially lead (for example, in car batteries, and for hardening and improving the sphericity of shot). Arsenic is used in bronzing pyrotechny (used to boost color in

fireworks), and as a doping agent in solid-state devices, such as transistors. Gallium arsenide, the most common semiconductor in use after doped silicon, is used as a laser material to convert electricity directly into coherent light. Circuits made from GaAs are much faster (but also much more expensive) than those made out of silicon.

In 2005, China was the top producer of white arsenic with almost 50% world share, followed by Chile, Peru, and Morocco, according to the British Geological Survey and the USGS. Most operations in the US and Europe have closed for environmental reasons. The arsenic is recovered mainly as a side product from the purification of copper. Arsenic is part of the smelter dust from copper, gold, and lead smelters.

It should be no great leap of acumen to realize that *all* arsenic compounds are poisonous, and most of their former practical uses are now banned. As_2S_3 was used in matches; acidic copper arsenite, CuHAsO_3 (Scheele's green) served as a green paint pigment; lead arsenate, $\text{Pb}_3(\text{AsO}_4)_2$, and Paris green, $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{Cu}(\text{AsO}_2)_2$, were used as insecticides; sodium arsenite, Na_3AsO_3 , was effective as a weed killer; and calcium arsenate, $\text{Ca}_3(\text{AsO}_4)_2$, was used to kill the boll weevil. The maximum allowable concentration has been found to be only .5 mg/cubic meter of air, and

although only .1g ingested is lethal to humans, it has been discovered that trace amounts in the diet are essential for helping to stimulate production of red blood cells!

In an interesting historical note, as the symptoms of arsenic poisoning were for a long time somewhat ill-defined, it was frequently used for murder until the advent of the *Marsh test*, a sensitive chemical test for its presence. Owing to its use by the ruling class to murder one another, and its potency and discreetness, arsenic has been called the "poison of kings" and the "king of poisons."

In the Victorian era, arsenic (*white arsenic* or *arsenic trioxide*) was mixed with vinegar and chalk, then eaten by women to improve the complexion of their faces, making their skin paler to show they did not work in the fields! (Better to die a horrible death by arsenic poisoning than to let people think you had to actually work for a living!).

Ironically, arsenic finds use today in several medical applications, most commonly in the treatment of cancer, and in medications as diverse as *Fowler's solution* for the treatment of psoriasis. In 2000, the USDA approved this compound for the treatment of patients with *acute promyelocytic leukemia* that is resistant to all-trans retinoic acid.

Research has also been performed in locating tumors using arsenic-74

(continued on page 25)

A Collection of Arsenic Minerals



III 27 D

Tenanantite
Julcani Mine
Peru
1.75 x 1.5 inches



III 22 D

Proustite
Uchuccacua Mine
Peru
1.25 x 1.125 inches



III 05 D

Enargite
Mexico
4 x 3.5 inches



I 22 D

Arsenic
Bau, Sarawak
Malaysia
.75 x 1.25 inches



III 06 D

Proustite
Imiter Mine
Morocco
1.5 x .75 inches

*All specimens from the
G. Miles Lehman Collection*



II 27 D

Realgar
Getchell Mine
Nevada
3 x 3 inches



XIII 30 D

Roselite
Bou Azzer
Morocco
1.5 x 1.25 inches



XIII 37 D

Adamite
Mina Ojuela
Mexico
2.5 x 1.75 x 2.125 inches



XIII 35 S

Cuproadamite
Mina Ojuela
Mexico
2.58 x 1.88 inches



II 19 S

Orpiment
Getchell Mine
Nevada
.75 x 1 inch

*All specimens from the
G. Miles Lehman Collection*



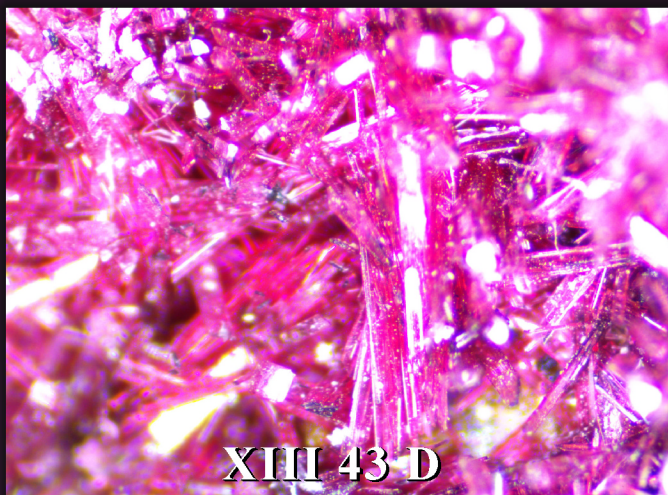
XIII 26 D

Arthurite

Getchell Mine

Nevada

2.5 x 1.5 inches



XIII 43 D

Erythrite

Bou Azzer, Morocco

1.5 x 1.06 inches



XIII 44 D

Annabergite

Km-3 Mine; Lavrion, Greece

1.3 x 1.125 inches

*All specimens from the
G. Miles Lehman Collection*

(a positron emitter). The advantages of using this isotope instead of the previously used iodine-124 is that the signal in the PET scan is clearer as the body tends to transport iodine to the thyroid gland producing signal noise.

Despite arsenic's deleterious reputation, arsenic-bearing minerals, in the form of the salts known as arsenates, are among the most attractive and sought-after of specimens. Their colorful appeal adds an immeasurable quality to any collection, and should not be neglected simply because of the poisonous nature of their headlining element.

Tests for Arsenic

Oxide Coating on Charcoal: When an arsenic mineral is heated in the oxidizing flame on charcoal, a volatile white coating of arsenious oxide, As_2O_3 , is deposited on the charcoal at a distance from the assay.

Garlic Odor: When an arsenic mineral is heated in the oxidizing flame on charcoal, a characteristic odor quite reminiscent of garlic is usually produced along with the white coating in the charcoal. Sometimes the odor can be produced simply by heating a splinter in a flame, sometimes also producing a pale blue flame color.

Sublimate on Plaster Tablet: When mixed with a mixture of potassium iodide and sulfur, then roasted in the oxidizing flame on a plaster tablet, arsenic minerals yield an orange-yellow coating of AsI .

Open Tube Test: When an arsenic mineral is *carefully* heated in an open tube, a white or colorless crystalline sublimate of arsenious oxide, As_2O_3 , forms a ring on the inner wall of the tube well above the assay.

Closed Tube Test: When heated in a closed tube, many arsenic minerals yield a metallic sublimate, known as the arsenic mirror. The sublimate appears as an amorphous black band above, and silver-gray band below.

Solution added to Magnesia Mixture: When magnesia mixture (a buffered aqueous solution of ammonia-ammonium chloride that contains magnesium chloride) is added to a solution containing arsenate ions, a white crystalline precipitate of magnesium ammonium arsenate, $\text{MgNH}_4\text{AsO}_4$, slowly forms, confirming the presence of As in the sample.

*The **garlic odor** emitted by roasted arsenic minerals is so characteristic and easily produced that further testing is rarely needed. This roasting of cuproadamite on charcoal produced a confirmatory and unmistakable white sublimate a short distance from, and around, the assay.*

