

Feature

Element of the Month

Cerium

Named after the asteroid, Ceres, the element is the most common of the rare earths. With 58 protons in its nucleus it falls within the group of elements called Lanthanides, and has found important usage in modern technology... and some other ingenious applications.

Rare earth metals are the elements in row 6 of the Periodic Table, and are not really all that rare as the name implies. In fact, cerium ranks about 26th in abundance among the elements in the Earth's crust, making up about 0.0046% of

its weight, which is more abundant than the better-known and more widely used tin and lead, and almost as abundant as copper and zinc. Though not found free in nature, it is found in a number of minerals including cerite, allanite, monazite,

hydroxylbastnasite, and bastnasite, though it also occurs as a trace impurity in numerous other minerals in which cerium is not an essential element. Monazite and bastnasite are the two most important sources, of which there are large deposits found in India, Brazil and the USA.



Unlike the base metals, which were known and used since antiquity, cerium had no usage in the early 1800s when it was first studied by chemists Jons Berzelius and Wilhelm Hisinger in Sweden, and independently by German chemist

Martin Heinrich Klaproth around the same time. However, these scientists did not discover the pure element, but cerium combined with oxygen and other elements. They merely determined that the rock sample they were studying contained a new element.

Pure cerium was not produced for another 70 years. In 1839, cerium was isolated by Swedish chemist Carl Mosander. It was Mosander who named the new element *cerium* (in honor of the asteroid Ceres that had been discovered in 1801) just two years before the elemental metal was finally obtained by William Hillebrand and

Thomas Norton by passing an electric current through molten cerium chloride. Thus, it would be incorrect to say that any one or the other of these scientists was the actual discover of cerium.

The process for isolating cerium has been honed over decades of experimentation, but is not significantly different than Hillebrand and Norton's original technique.

Commercially, it is obtained by heating bastnaesite (for example) to convert the ore to cerium oxide, then treating with hydrochloric acid to produce cerium chloride. The metal can then be extracted by electrolysis of the molten chloride in a graphite cell which acts as the cathode, and using graphite as the anode, producing chlorine gas as a by-product. It can also be obtained by reduction of the fused fluoride with calcium. In bulk, it is relatively inexpensive—\$1.20 per 100 grams—but pure cerium comes in at nearly \$400 for the same quantity!

Fortunately, cerium metal is available commercially so it's not normally necessary to make it in the laboratory, which is just as well as it is difficult to isolate as the pure metal since many other lanthanides usually reside in the raw material, are thus included in the refined products, and react

similarly. For many purposes it is not particularly necessary to separate the metals, but if separation into individual metals is required, the process is quite complex. Initially, the metals are obtained as salts from the ores by extraction with sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and sodium hydroxide (NaOH). The ceric ion, Ce(IV) is more



easily hydrolysed than the lanthanide (III) ions and therefore precipitates as a salt upon treatment with an oxidizing agent such as KMnO_4 .

Cerium is the second most active lanthanide after europium. Lanthanides are the elements with atomic numbers 58 through 71. Considered to be moderately toxic, cerium is a reactive, soft, gray, lustrous metal with a melting point of 795°C ($1,460^\circ\text{F}$) and a boiling point of $3,257^\circ\text{C}$ ($5,895^\circ\text{F}$). It is malleable and ductile, but little



Half-inch rod recovered from
a used cigarette lighter

used, because it tarnishes easily in moist air, and burns when heated. It also reacts with cold water (slowly) and hot water (rapidly) to form cerium hydroxide and hydrogen gas, is attacked by all alkali solutions (bases) and acids, and combines readily with other metals. Because it is so active, it must be handled with caution!

However, an interesting characteristic of cerium is that, because it reacts so readily with oxygen in the air, the metal can ignite simply by scratching its surface with a knife! This quality has been put to good use in modern times. Cerium, predominantly alloyed with iron (with small amounts of lanthanum and neodymium as well), is called *misch metal*, which is used as the 'flint' for cigarette and gas lighters.

Naturally occurring cerium is a mixture of four isotopes: non-radioactive cerium-136, cerium-138, and cerium-140, and radioactive cerium-142, though 30 isotopes are known from laboratory experiments with mass numbers ranging from 123 to 152. Isotopes are two or more forms of an element, differing from each other according to their mass number, which is the number of protons plus neutrons in the nucleus of an atom of the element. The number of *protons*

determines the element, but the number of *neutrons* in the atom of any one element can vary, each variation being an isotope. A radioactive isotope is one that breaks apart due to instability and gives off some form of radiation.

The element has a variable electronic structure: the energy of the inner 4f level is nearly the same as that of the 6s level, allowing variable occupancy of these two levels. When present in compounds, it exists in two oxidation states, tetravalent (Ce^{4+} , ceric) yielding *colorless* salts; the other, trivalent (Ce^{3+} , cerous) yielding *yellow to red* salts, which has found usefulness in the production of many kinds of specialty glass and ceramics, and in the chemical industry.

Added to glass and ceramics, cerium and its compounds add color (yellow), remove unwanted color (by keeping iron in its ferrous state), make glass sensitive to certain forms of radiation, and add special optical (light) qualities to glass. Cerium sulfide is a non-toxic compound that has a rich red color used as a pigment.

Cerium compounds are substantial components of certain phosphors, materials that shine when struck by electrons. The color of the phosphor depends on the elements of which it is made. Phosphors that contain cerium compounds produce a red or orange light when struck by electrons, a handy property used in flat-screen TVs.

Although none of the radioactive isotopes of cerium have any commercial relevance, its properties have led to other interesting and significant usages, such as in low-energy light bulbs and floodlights, and carbon-arc lighting (especially in the motion picture industry). It is used to strengthen certain kinds of dental materials, eliminate free oxygen and sulfur during the manufacturing of steel, and is utilized in the inside walls of self-cleaning ovens to prevent the build-up of cooking residues.



VII 140 D

Lanthanite-Ce
Columbium Mine
Quebec, Canada
1.6 x 1.9 inches



VII 138 D

Ancylite-Ce
Dark Star Claim
Ravalli Co. Montana
1.2 x 1.25 inches

All specimens from the G. Miles Lehman Collection



XVII 14 C

Cerite-Ce

Mountain Pass Mine
San Bernardino Co., CA
5 x 2.9 inches



VII 35 D

Bastnaesite-Ce

Mountain Pass Mine
San Bernardino Co., CA
2.5 x 1.75 inches

All specimens from the G. Miles Lehman Collection

Cerium oxide is also used as an abrasive, replacing the former abrasive known as rouge for polishing specialized glass. It is considered to be the most efficient glass polishing agent for precision optical polishing, such as for telescope mirrors.

In the medical field, flammacerium (cerium nitrate-silver sulphadiazine) is a cream that treats and prevents infections in extensive burn wounds. The cerium nitrate component reduces the occurrence of immunosuppression.

Important new applications are being found for cerium lasers. A laser is a device that produces light of a single frequency or color. Cerium lasers contain a crystal made of lithium, strontium, aluminum, and fluorine, to which a small amount of cerium is added. A cerium laser produces light in the ultraviolet region. Ultraviolet radiation is not visible, but it is very similar to the blue and violet light our eyes can see. Cerium lasers are used to search for ozone and sulfur dioxide, two air pollutants in the atmosphere.

Arguably its most important use, cerium (in the form of cerium oxide) finds employment as a catalyst, which is a substance used to speed up or slow down a chemical reaction without undergoing any change itself during the reaction. In the automotive industry, it finds extensive environmental notoriety. Exploited by catalytic converters, cerium oxide helps reduce carbon monoxide emissions in exhaust fumes by acting as a stabilizer for the high surface area alumina, is a promoter of the water-gas shift reaction, and functions as an oxygen storage component.



VII 94 D

Parisite-Ce

Snowbird Mine; Montana

1.25 x .75 inches



VII 130 D

Bastnaesite-Ce

Zagi Mtn; Pakistan

1.5 x 1 inches

All specimens from the G. Miles Lehman Collection

Compounds of cerium help break down complex chemicals found in petroleum into simpler forms that work better as fuels, adding their contribution in regard to environmental concerns. Cerium oxide, as a nanopowder, is added to diesel fuel to reduce sooty fumes and improve engine performance. For internal combustion engines, adding the oxide to the fuel helps it burn more cleanly, producing fewer pollutants.

As the demands of technological advancement progress, there is little doubt that cerium and its compounds will find additional employment in sophisticated applications well into the future.

Tests for Cerium

Testing for most lanthanides and actinides (the rare earth elements) with conclusive results is generally beyond the means of average amateur at-home chemists. Of the two methods that follow, the first is the easiest and could produce the best results. The second is an industrial method that could produce good results for those with experience in qualitative analysis.

Borax Bead Test: Fuse a small splinter of test specimen in a borax bead. When heated in the oxidizing portion of the flame (near the tip), the bead will be *red* when hot, turning *yellow to orange* when cold. In the reducing flame (near the interior of the flame), the bead will be colorless both hot and cold.

Note: Iron will give similar results in an oxidizing flame, but can be distinguished from Ce when heated in the reducing flame, by which the bead will be *green* hot or cold if it is saturated. If not saturated, the bead will be colorless when cold.

Precipitation from acid solutions: The sample is crushed, ground, and treated with hot concentrated sulfuric acid to produce water-soluble sulfates of rare earths. The acidic filtrates are partially neutralized with sodium hydroxide to pH 3–4. Thorium precipitates out of solution as a hydroxide and is removed. After that the solution is treated with ammonium oxalate to convert rare earths into their insoluble oxalates. The oxalates are converted to oxides by annealing. The oxides are dissolved in nitric acid that excludes one of the main components, cerium, whose salts are insoluble in nitric acid.

Note: Metallic cerium is prepared by metallothermic reduction techniques, such as by reducing cerium fluoride or chloride with calcium, or by electrolysis of molten cerous chloride or other cerous halides. The metallothermic technique is used to produce high-purity cerium.

Lime-light effect: Infusible minerals containing cerium will glow with exaggerated incandescence when heated in a flame. However, since Sr, Mg, Zr, Zn, and Ca will do likewise, this test is insufficient when performed alone, but can be considered confirmatory if the above tests indicated the presence of Ce.