



A review of isotope separation methods of importance to separation of silicon isotopes and isotopes of other light elements

By
Dag Øistein Eriksen,
Primus.inter.pares AS/Isosilicon AS

*November 1st, 2007. Revised September 2011 and June 2014
Version 3.7, March 2015*

Abstract

This literature review is based on published articles and patents on isotope separation with focus on light elements. Also included are isotope effects found in nature to show the ease, but also the difficulty with which isotopic separations occur. A survey of the use of isotopes is given together with a survey of isotope separation methods. For the most useful ones, reviews of published isotope separations are given.

Contents

Objective	3
Reasons for using silane, SiH ₄	3
Introduction	3
Naturally occurring isotope separation.....	3
Hydrology.....	3
Isotope effects in crystals	4
Use of isotopically pure substances	5
Isotope separation techniques.....	7
Diffusion.....	8
Thermal diffusion columns	9
Membrane separations.....	9
Distillation.....	10
Membrane distillation	10
Isotopic exchange.....	11
Chemical exchange	11
Centrifugation.....	12
Separation nozzle	12
Gas-jet centrifugation.....	12
Laser induced isotope separation	13
Chromatographic methods	13
Aqueous solution based separations.....	13
Gas-chromatographic processes	14
Theoretical considerations.....	14
Possible isotope separation methods for silicon using silane.....	15
References:	16

Objective

This review is aimed at giving a comprehensive presentation of technology for isotope separations published as articles or patents. This will be the basis for the work towards utilization of the patents owned by Isosilicon.

Reasons for using silane, SiH₄

Isosilicon's technology is based on the following ideas and considerations:

- The lighter the compounds to be separated are, the larger the differences in diffusion coefficient will be. There is no stable molecule lighter than SiH₄ among those involving gaseous Si. (MW is 32 for SiH₄ vs. 104 for SiF₄). The relative isotopic difference of mass between ²⁸Si and ²⁹Si is $1/32 = 0.03125$ in case of SiH₄ and $1/104 = 0.009615$ in case of SiF₄. This may have a major impact on the process' economy.
- While fluorine is monoisotopic the impact of ²H in natural hydrogen, i.e. 0,015%, will just add a small portion to the fractions of the heavier Si-isotopes.
- We know from the polysilicon industry that it is by far less economical to produce SiH₄ through SiF₄ than from chlorosilanes.
- SiH₄ is now (in spite of many potential hazards) widely used in the electronics and ceramics industry. Taylor made and certified equipment is currently available from the market place. SiF₄ is, as SiH₄, a very hazardous chemical and fluorine chemistry necessitates special equipment. Avoiding the conversion from SiF₄ to SiH₄ should therefore be a competitive advantage. However, with the implementation of know-how to perform the transformation of SiF₄ to SiH₄, Isosilicon is also in position of using SiF₄ for the isotope separation. This may give some technical advantages as SiF₄ is less reactive (e.g. self-igniting) than SiH₄.
- An advantage with silicon is that the suitable isotope ²⁸Si is by far the most abundant (92,23%). The other stable isotopes are ²⁹Si (4,67%) and ³⁰Si (3,10%). We may afford to "spoil" a large part of the feed of SiH₄ to increase the isotopic ratio. The remaining silane may still be used for purposes not requiring isotopically pure silane.

Introduction

Many physical processes are dependent on the molecule-mass, e.g. processes like diffusion, evaporation, precipitation, and some chemical reactions. Other processes such as isotope exchange, sedimentation, absorption and ion-exchange have also mass dependencies. There are even more sophisticated effects like coupling between the nuclear spin and the angular moment of valence electrons that may give isotopic effects (hyperfine couplings).

Naturally occurring isotope separation

Isotopic effects are also observed in nature. All involve the light elements and the effects are small, i.e. in the per mill range, but large enough for measurements with standard mass spectrometers. This chapter is included to show some of the possible mechanisms to use.

Hydrology

Water, H₂O, consists, in addition to the common molecule ¹H₂¹⁶O, also of ²H¹H¹⁶O and ¹H₂¹⁸O in addition to other minor mixes where in addition ³H and ¹⁷O are included.

Fractionation of the isotopic components of water is observed in precipitation, i.e. rain, snow etc., as a function of several parameters. Following Gonfiantini¹, these parameters are:

Confidential information

Must not be given to third parties without permission from Isosilicon

- i) the relative humidity and the temperature during the evaporation from the ocean, which is the main source of atmospheric vapour;
- ii) the temperature and the degree of condensation of atmospheric vapour;
- iii) the fraction and the nature of condensed phases, i.e. liquid water and ice, in clouds;
- iv) the contribution of re-evaporated fresh water;
- v) the evaporation during raindrop fall.

The main driving force is shown to be the temperature.

The content of ^2H and ^{18}O is usually only determined as intensities relative to a standard and referred to as $\delta^{\text{A}}\text{X}$ and is in the per mille range. The content of water molecules such as $^2\text{H}^1\text{H}^{16}\text{O}$ and $^1\text{H}_2^{18}\text{O}$ are correlated. It is shown that the correlation of ^2H and ^{18}O in precipitation can be expressed as $\delta^2\text{H} = 8 \delta^{18}\text{O} + 10\%$.² This formula may be explained by a Rayleigh evaporation model, but refined models are available. It is used extensively in measurements of recharge of groundwater reservoirs.

Other elements than H and O are also observed to have variable isotopic abundancies depending on environmental factors. For example, microbes have a preference for ^{12}C compared to ^{13}C , presumably due to faster mobility of the lighter isotope through the cell membrane. As a consequence, gas made by microbial degradation of longer chain hydrocarbons has a higher ratio of $^{12}\text{C}/^{13}\text{C}$ than gas made by thermal degradation. Also, a similar behaviour, but not as pronounced, can be seen on the $^{14}\text{N}/^{15}\text{N}$ -ratio. These effects are utilised in the study of petroleum reservoirs and in studies of trophic levels in biology. Isotopic separation has also been observed in the movement of chloride ions in sediment rock³.

Isotope effects in crystals

Plekhanov⁴ has made a comprehensive review on isotope effects on lattice dynamics in crystals. Isotope effects are a consequence of the zero-point vibration energy, which must be mass dependent. Isotope effects are manifested particularly in elastic- and thermal conductivity effects in addition to vibrational effects.

Thermal conductivity of germanium was proposed to be dependent on isotopes by Pomeranchuk⁵ in 1942, and proved by Geballe and Hull⁶ in 1958. In diamond the 1.07% content of ^{13}C reduces the thermal conductivity at room temperature with 30%⁷.

Bulanov et al.⁸ report the growth of a highly isotopic enriched (99.9%) ^{28}Si single crystal, but they do not report measurements of physical properties. Itoh et al. report preparation of crystals of all three silicon isotopes, 28, 29, and 30.⁹

Capinski et al.¹⁰, reported, on a 99.7% pure ^{28}Si -crystal made by liquid phase epitaxy an increase in thermal conductivity of at least 60% at 300K and 250% at 100K. These experiments have been repeated by several other research groups without the same high increase. Up till now it has been focused upon the increased thermal conductivity gained in transistors and microchips by using isotopically pure silicon. Today it is accepted that thermal conductivity is increased by $10 \pm 2\%$ for isotopic pure ^{28}Si compared to natural silicon (Haller¹¹; Kizilyalli et al.¹² including references; Kremer et al.¹³; Inyushkin¹⁴). Reduced electromagnetic noise, i.e. phonon-phonon- and electron-phonon interactions, as well as increased thermal conductivity makes the generated heat more rapidly removed in the more perfect crystal structure formed due to the absence of isotopic effects when using monoisotopic silicon.

Confidential information

Must not be given to third parties without permission from Isosilicon

Recently it has been proved¹⁵ that $^{28}\text{Si}^{12}\text{C}$ has approximately 25% higher thermal conductivity than $^{\text{nat}}\text{Si}^{\text{nat}}\text{C}$. SiC as semiconductor is very attractive for use in power electronics. Since the cost of raw materials is just a few per cent of the production cost, an increase in raw materials due to isotopic purity will not be harmful as it is for pure silicon.

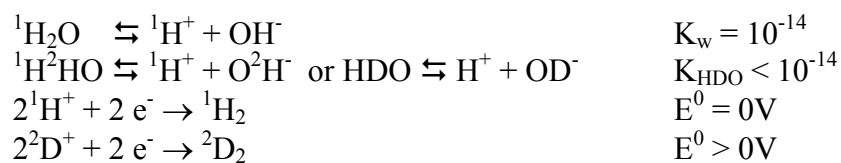
Use of isotopically pure substances

In many aspects of modern society isotopically pure substances are used. Some fields are listed below:

- ◆ In nuclear research isotopes are used in nuclear reactions both as targets and as projectiles. However, the amounts needed are small and the price is accordingly high in this market segment. The heavier calcium isotopes is here of particular interest.
- ◆ In organic chemistry the need for ^2H - and ^{13}C -labelled compounds is great due to use of NMR-spectroscopy. This need has also manifested itself in medicine where the increased use of MRI requires a large variety of isotopically doped compounds.
- ◆ As the use of NMR and MRI is increased, the need for other isotopes also increases. There is thus a market for ^{29}Si as this is the only isotope of silicon possessing nuclear spin.
- ◆ In nuclear medicine there is a need for special isotopes for specially designed compounds in both diagnostic and therapeutic work. The need is due to requirement of high specific activity of the final compound. The expanding use of PET requires use of target materials such as ^{18}O used in the production of ^{18}F .
- ◆ Use of tracers is an important part of many scientific and technological fields, e.g. biology, hydrology, residence time studies, process development, etc. Most often radioactive tracers are used, but non-radioactive, isotopically pure substances are also used. However, the price and availability of the latter have been limiting factors. In agriculture, additions of fertilizer with enhanced content of ^{15}N (0.365% natural abundance) is used to trace the uptake and mobility of the nitrogen.
- ◆ In electronics the use of pure ^{28}Si enhances thermal conductivity. This market segment is still in development and SiC seems to be the material of choice for isotopically pure materials. In this case also ^{12}C is needed.

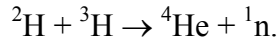
The most interesting isotopes are those of industrial importance, since the volumes and markets are much larger.

- ◆ Deuterium, i.e. ^2H - also denoted D, is produced from the electrolysis of water. Then the difference in the reduction potential of hydrogen-isotopes is used to produce heavy water, D_2O . The reduction potential is maintained at a level so that D_2 -gas is not formed.



Heavy water is used in nuclear power, i.e. CANDU reactors and research reactors as neutron moderators, and as a reagent in the synthesis of deuterated compounds. During the last 50 years the development of fusion energy (both the hydrogen bomb and peaceful fusion) has boosted a search for separation methods for ^2H and ^3H (D and T, tritium).

This is because these nuclides are key components in the fusion reaction:



- ◆ Fusion is also one of the reasons for interest in lithium. Using LiD instead of D₂ transforms a gas to a solid material. Moreover, ${}^6\text{Li} + {}^1_0\text{n} \rightarrow {}^4\text{He} + {}^3\text{H}$, thus producing tritium for further fusion. ${}^6\text{Li}$ (7.6%) can also be used as neutron absorbent. The most abundant Li-isotope, ${}^7\text{Li}$ (92.4%) has a very low absorption cross section for neutrons and is therefore used as a neutron reflector and for pH-adjustment in water cooled reactors, i.e. addition of ${}^7\text{LiOH}$. In the “molten salt reactors”, where the fuel is a eutectic mixture of fluorides, ${}^7\text{LiF}$ is one of the salts. Thus, both stable lithium isotopes have commercial value.
- ◆ Neutron detectors need absorbing materials with high affinity for neutrons and an easy detection of the resulting prompt radiation. Two gas detectors are dominating the market: ${}^3\text{He}$ and ${}^{10}\text{BF}_3$. The respective reactions are: ${}^3\text{He} + {}^1_0\text{n} \rightarrow {}^3\text{H} + {}^1_1\text{H}$, in which both product nuclei ionise the gas creating a recorded electrical discharge; ${}^{10}\text{B} + {}^1_0\text{n} \rightarrow {}^4\text{He} + {}^7\text{Li}$, where ${}^4\text{He}$ is the ionising species. Thus, there is a market for isotopically pure ${}^3\text{He}$ and ${}^{10}\text{B}$. ${}^3\text{He}$ is produced as decay product of ${}^3\text{H}$. Natural boron consists of two isotopes, ${}^{10}\text{B}$ (19.9%) and ${}^{11}\text{B}$ (80.1%). A novel design for neutron detectors based on the isotope ${}^{10}\text{B}$ has been suggested by the European Spallation Source (ESS), to overcome the very limited availability of ${}^3\text{He}$. In the detector design, very large area aluminum blades are coated with a thin film containing high amounts of ${}^{10}\text{B}$. ${}^{10}\text{B}_4\text{C}$ was chosen as the thin film material instead of pure ${}^{10}\text{B}$, since it is easier to handle in a deposition process and due to its high resistance towards oxidation and wear and also because B_4C has a higher electrical conductivity. As neutron shields, borides like ZrB_2 , HfB_2 , and MgB are proposed if ${}^{10}\text{B}$ is available.
Neutrons are used to detect hydrogen in industry. Thus, neutron sources and detectors are used to measure humidity in wood and paper, petroleum containing rock layers in oil wells, etc.
- ◆ Uranium is the most studied element when separation of isotopes is concerned. This is, of course, due to its use as nuclear fuel and in nuclear bombs. The fissile isotope is ${}^{235}\text{U}$ (natural abundance 0.720%) while ${}^{238}\text{U}$ is the most abundant isotope (99.275%). The isotopic separation is usually based on diffusion of UF_6 , a gas at temperatures above 56°C.
- ◆ In nuclear waste recovery the selective separation of ${}^1\text{H}^3\text{HO}$ from ${}^1\text{H}_2\text{O}$ is important since it reduces the amounts of radioactive water to dispose of.
- ◆ Also, the separation of transuranics, i.e. in particular plutonium, is another important topic in nuclear recycling of fuel and in waste recovery. In mixed oxide fuel (MOX) both ${}^{235}\text{U}$ and ${}^{239}\text{Pu}$ are used as fission sources. Thus it is important to control the amount of ${}^{238}\text{Pu}$ relative to ${}^{239}\text{Pu}$ since ${}^{238}\text{Pu}$ acts a neutron absorber, but producing ${}^{239}\text{Pu}$.
- ◆ As a future nuclear fuel a mixed nitride of uranium and plutonium is proposed. This nitride must contain pure ${}^{15}\text{N}$. Thus the future demand for ${}^{15}\text{N}$ is expected to increase drastically. Today’s main method for producing isotopically pure ${}^{15}\text{N}$ is based on isotopic exchange between the nitrogen oxides, NO and NO_2 , and nitric acid. This process, however, consumes huge amounts of sulfurous anhydride and produces sulfuric acid as a by-product. Russian scientists have published an improved method giving almost no waste.¹⁶
- ◆ The TRISO-fuel (triply coated ceramic particle fuel) uses silicides of the fuel elements to resist the high temperatures generated. It is therefore beneficial to use isotopically pure Si,

preferentially ^{28}Si as this isotope will need to capture two neutrons to be transmuted into phosphorous. Also improvements in the crystal properties are observed.

- ◆ Strong efforts are currently made in developing SiC as cladding (incapsulation) material. The temperature stability and other thermal properties makes SiC the probable future cladding material also for conventional fuel rods.
- ◆ Inside the cooling circuits of nuclear power plants, thin corrosive films develop on metal surfaces. One of these films contains cobalt from steel. This cobalt becomes easily irradiated and produces ^{60}Co , a nuclide with a half-life of 5.27 years and an emitter of high energy gamma rays. It is therefore desirable to remove it. Injecting zinc in the cooling circuit solution displaces the ^{60}Co from the film, reducing the amount of radioactive byproducts generated. In a reactor ^{64}Zn absorbs neutrons and transforms into ^{65}Zn , also long lived (244.3 days half-life) and with high energy gamma (1115 keV) emitted, thus negating the benefits achieved by adding zinc. The solution used therefore has to use zinc depleted in ^{64}Zn .
- ◆ Zirconium is used in nuclear reactors as cladding (encapsulation). It consists of five isotopes, ^{90}Zr (51.4%), ^{91}Zr (11.2%), ^{92}Zr (17.1%), ^{94}Zr (17.5%), and ^{96}Zr (2.8%). ^{91}Zr is the only isotope with a large absorption cross section for thermal neutrons. Using ^{90}Zr versus natural Zr results in a 7% increase in the produced energy, a 34% reduction in residual fissile material and a 20% reduction in volume of nuclear waste. At present the nuclear industry consumes 6 200 tons of Zr annually.¹⁷
- ◆ One of the future developments in electronics is expected to be the “quantum” computer in which nuclear spins are used as bits. As such ^{29}Si is interesting and also ^{28}Si as a separation means for keeping ^{29}Si -atoms apart.

Isotope separation techniques

There are several possible physical processes where mass-separation is observed. Some take place naturally, but to obtain large enhancements in mass ratios sophisticated processes have been developed. In the following a review of the most important processes is presented. The main processes studied are¹⁸:

- | | |
|---------------------|---------------------------------|
| • Diffusion based | • Centrifugation |
| • Membrane based | • Gas-jet centrifugation |
| • Distillation | • Selective excitation by laser |
| • Electrolysis | • Ion-mobility |
| • Electromagnetic | • Chemical exchange |
| • Separation nozzle | • Chromatography |

In most of the commercialized methods more than one of the above mentioned processes are used. For example are there methods developed utilising a combination of diffusion and membranes, distillation and membranes, diffusion and chromatography, etc.

According to Lederer¹⁹ the factors which dictate the choice of a process are dependent on the size of the production. In laboratories and small scale plants where flexibility and low capital cost are important the thermal diffusion column was the preferred method. For light elements,

distillation and chemical exchange are most economical at large scale, whereas for heavy elements gaseous diffusion and gas centrifugation are the most economical methods. Since the Isosilicon process is based on separation of silicon isotopes by chromatographic means, but also including diffusion and chemical exchange, the methods involved are given a more comprehensive presentation below.

Diffusion

“Diffusion is the process by which matter is transported from one part of a system to another as a result of random molecular motions.”²⁰ The basic concepts concerning diffusion based gas-separations are called convective flow, i.e. the fluid passes an opening by chance; Knudsen diffusion, i.e. some molecules pass more easily than others; and molecular sieving, i.e. only molecules small enough can pass. This partition is taken from Kirk-Othmer’s Encyclopaedia of Chemical Technology²¹.

The two governing laws of diffusion were first formulated by Fick in 1855. To his honour the laws carry his name. Fick’s first law, which is empirical, states that the flux through an area is proportional to the concentration gradient:

$$J_x = -D_x \frac{\partial c}{\partial x} \quad (1)$$

where J is the flux along the x-direction, c the concentration, and D_x the diffusion constant in x-direction. In three dimensions equation 1 becomes:

$$\vec{J} = -D\nabla c \quad (2)$$

Fick’s second law states that the time variation in concentration is proportional to the change in position.

For constant diffusion coefficient, which is a reasonable assumption for small concentration gradients, we have Fick’s second law on the usual form:

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} \quad (3)$$

In three dimensions equation 3 becomes:

$$\frac{\partial c}{\partial t} = D\nabla^2 c \quad (4)$$

Diffusion through a porous solid is slower than diffusion through an equal volume of homogeneous fluid because the molecules must travel greater distances to move around solid obstacles, and because diffusion can occur only through the pore fraction of the total cross-sectional area²². Thus, in porous media, an effective diffusion coefficient is usually introduced, D_{eff} .

The distributions of each isotope are smeared out as time evolves. Bell-shaped concentration profiles measured are identical to the Gaussian distribution of random errors employed in statistical sciences. This is a consequence of the random motions of diffusing molecules. It is shown that the standard deviation of the tracer profile, i.e. a measure of its width, is $(2Dt)^{1/2}$. From diffusion theory it can be shown that D is proportional to $m^{-1/2}$. This implies that the separation factor between two isotopes can be approximated by $(m_2/m_1)^{1/2}$.

However, for practical purposes we introduce a driving force making the mass transport moving towards one direction. We therefore have a mixture of convective flow and diffusion. The mass-transport equation is then governed by¹⁴

$$v \frac{\partial c}{\partial x} + \frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} \quad (5)$$

where v is the (linear) convective flow or phase velocity. In such situations we have dispersion in addition to diffusion. If the medium the molecules are diffusing through is

Confidential information

Must not be given to third parties without permission from Isosilicon

porous so that there is a concentration gradient also inside the medium, we must include an absorption term:

$$v \frac{\partial c}{\partial x} + F \frac{\partial Q}{\partial x} + \frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} \quad (6)$$

where Q is concentration in the medium the fluid is moving through, and F the ratio between the medium and the void volume. Equation 6 is a general expression for most kind of linear chromatographic methods, i.e. column based²³.

From equation 4 we deduce that the resultant concentration distribution is symmetric in position. However, if equations 5 or 6 apply this is no longer valid and an asymmetric distribution is observed.

In the equations above the gas concentration is used. Thermodynamically, the driving force in diffusion is the gradient of the chemical potential. This is reflected in Onsager's equation¹⁵:

$$J = -L_x \frac{\partial \mu}{\partial x} \quad (7)$$

where μ is the chemical potential and L_x the thermodynamic diffusion coefficient along the x -axis. L depends upon the mobility of the diffusing compound in the medium of interest, e.g. in gases with small (light) and large (heavy) molecules the small ones will have the largest mobility.

The diffusion coefficient D is related to L by

$$D = L \frac{\partial \mu}{\partial c} \quad (8)$$

When $\mu \approx c$ we see that $D \approx L$.

Thermal diffusion columns

Thermal diffusion arises when a mixture is subjected to a temperature gradient leading to partial separation of the components²⁴. The component with the lowest boiling point will tend to accumulate at the coldest zone. The method has received much theoretical and experimental attention and was the method employed for producing the enriched uranium used in the first nuclear bombs. At Oak Ridge National Laboratory (ORNL) in Tennessee, USA, they used 2100 columns each 15m long in this production. However, today the technology is not used industrially, but its principles can still be utilised also in other processes. At laboratory scale the method may still be in use for separation of minor quantities, e.g. hydrogen²⁵ and argon isotopes²⁶. Usually, in a thermal diffusion column a hot rod in the centre of the column is used instead of a hot wall. Such devices have been used for the separation of isotopes from gases like HCl, CH₄ and SiF₄, separating the isotopes ³⁵Cl/³⁷Cl, ¹²C/¹³C and ²⁸Si/²⁹Si/³⁰Si, respectively. Hoglund et al.²⁷ has a comprehensive list of isotope separations performed with thermal diffusion columns. In the separation of chlorine isotopes using HCl a column of 36m was needed to obtain 99.5% purity of the isotopes.

Membrane separations

Instead of letting gases diffuse through vapour like in the thermal diffusion column a more efficient separation may be obtained by using membranes. In addition, as a fourth diffusion method the solvation of molecules in membranes may also be included, in which case chemical effects are noticeable. When considering membranes the diffusion layer is always very thin. The flux across the membrane is given by:

$$J = \frac{D}{l} (c_0 - c_l) \quad (9)$$

where l is the membrane thickness, c_0 is the concentration at the feed side of the membrane and c_l is concentration at the permeate side.²⁸ To achieve a very thin effective layer it is mounted on a porous support. In isotopic separations only Knudsen diffusion apply in the thin membrane layer, and in the support the pores must be large enough to give convective flow.

Membrane separations are multi-stage processes since each membrane contactor or diffuser only can give enrichment according to the relative difference of the diffusion constants of the isotopes. In uranium separations the best possible separation factor for $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ is $(352/349)^{1/2} = 1.0043$. As $^{235}\text{UF}_6$ molecules are lighter than the $^{238}\text{UF}_6$ molecules they move faster and have a slightly better chance of passing through the pores in the membrane. The UF_6 which diffuses through the membrane is thus slightly enriched, while the gas which did not pass through is depleted in ^{235}U .

This process is repeated many times in a series of diffusion stages called a cascade. Each stage consists of a compressor, a diffuser and a heat exchanger to remove the heat of compression. The enriched UF_6 product is withdrawn from one end of the cascade and the depleted UF_6 is removed at the other end. The gas must be processed through some 1400 stages to obtain a product with a concentration of 3% to 4% ^{235}U .²⁹

On behalf of Scatec, the original sponsor for the isotope separation project, IsoPro International, represented by Dong and Byers³⁰, performed a calculation for a membrane based separation process giving 99.9% pure $^{28}\text{SiH}_4$. They concluded that 129 stages were needed for a meso- or macroporous membrane providing Knudsen-diffusion. However, they did not propose one or a group of membranes believed to work at the needed conditions.

Distillation

Already in 1922 Mulliken reported the separation of isotopes in distillation of mercury.³¹ In the distillation of a mixture which varies only in isotopic composition the lighter components tend to concentrate in the vapour phase. Distillation is used as the final refining step in production of heavy water. Cryogenic distillations of CO and NO for enrichment of ^{13}C and ^{15}N , respectively, have been performed by Los Alamos National Laboratory (LANL) at laboratory scale. For production of nitrogen isotopes a combination of distillation of NO and chemical exchange was developed at a pilot scale and operated for six years.³² LANL also designed and build a pilot plant for distillation of CO to produce ^{13}CO .^{33,34}

Mills report separation of sulphur and silicon isotopes by distillation.^{35,36} In the study of sulphur the following gaseous compounds were used: H_2S , SF_4 , SF_6 , COS , and CH_3SH . The separation factors ($^{32}\text{S}/^{34}\text{S}$) varied from 0.9978 for SF_4 to 1.0023 for H_2S . For silicon, Mills obtained a separation factor for $^{28}\text{Si}/^{30}\text{Si}$ of 0.9982. Referenced literature data by Mills are 1.00061 for SiH_4 and 0.99964 for SiCl_4 .

Cryogenic distillation was used for production scale separation of tritium from other hydrogen isotopes from 1967 to late 1990s³⁷ at Savannah River Laboratory. Today the method is replaced with a thermal cycling absorption process (TCAP) using palladium as absorbent.

Membrane distillation

The method, also called pervaporation, is combining distillation with diffusion through a membrane. It is a combination of three steps³⁸:

- Selective sorption of the components of the mixture into the membrane.

- Selective diffusion through the membrane
- Desorption into the vapour phase.

The method has been used for separating light and heavy water³⁹ and for chemical separation⁴⁰. So far the method seems to be only used in a laboratory scale.

Isotopic exchange

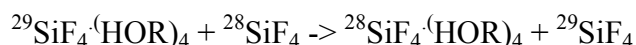
If equilibrium is established between a gas and a liquid which both contain the same element, e.g. H₂ and H₂O, the light isotopes of the element tend to concentrate in the gas phase. For example heavy water can be produced this way as ¹H₂ will dominate the gas phase and D₂O will concentrate in the liquid phase. Andreev et al.⁴¹ report results from a pilot operation for separation of hydrogen isotopes using catalytic isotopic exchange between H₂ and liquid water. Their set-up consisted mainly of a column of 5 m height and inner diameter 28 mm. Today's main method for producing isotopically pure ¹⁵N on an industrial scale is based on isotopic exchange between the nitrogen oxides, NO and NO₂, and nitric acid. This process, however, consumes huge amounts of sulfurous anhydride and produces sulfuric acid as a by-product. A non-polluting method using methane to first reduce sulphuric acid to SO₂ and further to sulfurous anhydride is published⁴².

Isotopic exchange also takes place between equal molecules but in different phases.

McCandless and Herbst have filed a US patent on isotope separation of boron using isotopic equilibrium between gaseous BF₃ and liquid BF₃⁴³ in exchange reactions with nitromethane. The exchange takes place in a countercurrent gas-liquid contactor at atmospheric pressure. Ownby⁴⁴ reports a study of separation of boron isotopes using BF₃ and nitromethane and explains the observed high separation factors in the Lewis acid-base conceptual framework. Prokhorov et al.⁴⁵ has filed a Russian patent on production of disilane, Si₂H₆, by letting silane, SiH₄, pass through an area of electric discharge creating disilane. The temperature must be kept below the boiling point of disilane (-19°C), but well above silane's (-112°C). They report two light and one heavy fraction of disilane comprising 85% ²⁸Si₂H₆, 8.7% ²⁸Si²⁹SiH₆, and 6.3% disilane of a mixture of all three Si-isotopes, respectively. In addition, the silane phase is enriched on ²⁸SiH₄. The observed distribution is the exact distribution expected from combining silane of natural composition. Thus, their claim contains no isotope enrichment.

Chemical exchange

A recent review of this method is published by Wang et al. in 2015⁴⁶. In this method the gas to be isotopically enriched is contacted with a Lewis acid or base depending on the compound in question. The major reaction can be described as the adduct formation between the silicon gas and an organic solvent like alcohol:



where ROH denotes an alcohol.

Eagle-Pitcher Industries, Inc., of Ohio, USA, has filed a patent on separation of Si- and Ge-isotopes by chemical exchange reactions⁴⁷. Their process utilises complexation with volatile organic solvents like methanol or solid phases like molecular sieves, silica gel and activated carbon. The preferred Si- and Ge-compounds are SiF₄ and GeF₄, respectively.

This technology has been studied further by Russian institutions and Khoroshilov et al.⁴⁸ showed that by using pentanol-1 as a complex forming agent the limiting stage of mass transfer during the separation of silicon isotopes was the exchange between SiF₄ and the SiF₄-2ROH complex. Razmadze and Tolmachev⁴⁹ have measured the height equivalent to a

theoretical stage (HETS) for SiF_4 complexed with aliphatic alcohols and have assessed the method. For isobutanol they measured an HETS of 34 mm.

Centrifugation

Like the diffusion process, the centrifuge process uses gas as its feed and makes use of the slight difference in masses between the isotopes. In a uranium plant the gas, i.e. UF_6 , is fed into a series of vacuum tubes, each containing a rotor about one to two metres long and 150-200 mm in diameter. To obtain efficient separation of the two isotopes the outer wall of the spinning cylinder must be moving at 400 to 500 m/s to give an acceleration of 10^6g . This acceleration corresponds to a rotation at 50 000 to 70 000 rpm. The heavier molecules increase in concentration towards the cylinder's outer edge. There is a corresponding increase in concentration of light molecules near the centre. These concentration changes are enhanced by forcing the gas to circulate axially within the cylinder. Wood et al.⁵⁰ has described a gas centrifuge in detail.

The enriched gas is drawn off and goes forward to further stages while the depleted gas may go back to a previous stage.

Although the capacity of a single centrifuge is much smaller than that of a single diffusion stage, its capability to separate isotopes is much greater. Centrifuge stages normally consist of a large number of centrifuges in parallel. Such stages are then arranged in cascades similarly to those for diffusion. In the centrifuge process, however, the number of stages may only be 10 to 20, instead of a thousand or more for diffusion.

Wood et al.⁴⁸ have developed a model for separating isotopes in elements where more than two isotopes are present. Their examples reported were, in addition to uranium, the separation of ^{50}Cr from natural chromium using the gas CrO_2F_2 . Kai and Hasegawa⁵¹ have modelled the isotope separation of sulphur using SF_6 .

Separation nozzle

In this method gas is fed into semi-spherical cavities and the centrifugal effect obtained makes a slight separation of isotopes. This concept has been developed further through gas-jet centrifugation methods.

Gas-jet centrifugation

In The Republic of South Africa (RSA) the aerodynamic separation process (ASP) developed by Klydon, formerly Scientific Development and Integration (SDI), was launched in 2006. The technology is developed from concepts originating from Europe named Rosegard Vortex Extraction and Wikdahl Vortex Separation, both from 1976, and developed further as the UCOR Vortex Process. Enrichment is achieved under pressurized conditions in stationary-wall centrifuges. Klydon is focusing on isotope separation processes for a number of isotopes using ASP and laser excitation.⁵² Klydon has presently stopped the development work and production of $^{28}\text{SiH}_4$ as the main customer was a project developing a high temperature nuclear reactor which was stopped due to the financial crisis from 2008 onwards.

Laser induced isotope separation

The concept of using laser excitation for separation of isotopes is based on the observation that non-zero nuclear spin is coupled to the electron spin thus creating slight changes in excitation levels. The conditions for laser separation of isotopes are⁵³:

1. There must be at least one absorption line of the isotope being separated that does not overlap any absorption lines of other isotopes in the mixture.
2. Laser radiation at the chosen frequency must be available with the characteristic power, duration, divergence, and monochromaticity necessary for the separation method chosen.
3. There must be a primary photophysical or photochemical process that permits easy separation of the excited species from the mixture.
4. The selectivity for the desired isotope must be maintained against all competing photophysical or photochemical processes.

So far laser induced isotope separation has been developed for uranium in which case ²³⁵U in metal vapour is selectively ionised and separated by an electric field. The CRISLA process⁵⁴ combines a nozzle concept with laser excitation. It is developed for separation of ²³⁵UF₆ from ²³⁸UF₆.

Ivanenko and Hering⁵⁵ report laser-induced isotope separation of ¹³C and ¹²C for industrial application. They used CHClF₂ which was dissociated into a product enriched in ¹³C, C₂F₂, and a rest enriched in ¹²C, CHClF₂. Another application is the photochemical dissociation of formaldehyde from which isotopes of H, C or O can be enriched⁵⁶. Also of interest may be the dissociation of SF₆ based on vibrational excitation. Here the rare ³⁶S (0.017% abundance) may be enriched to 70%. Freud et al.⁵⁷ have a patent on separating the carbon isotopes by exposing liquid CS₂ to UV-light. The photolytic decomposition of ¹³CS₂ is faster than the one for ¹²CS₂. Her monochromatic light is imperative, but laser is not needed.

Suslick⁵⁸ has patented a method where hydrogen is absorbed onto a solid surface, preferentially of porous silica glass, and then the selected isotopic molecules are evaporated by being exposed to infrared radiation with a laser.

Japanese groups^{59,60} have reported the separation of silicon isotopes using the splitting of Si₂F₆:



This splitting reaction is isotopically selective for molecules where one of the two silicon isotopes is different from ²⁸Si. Moreover the ^{29/30}SiF₂ can be further ionised with another laser to be separated from the rest of the molecular beam. Yokohama et al. have continued this line of development⁶¹ while Nomaru et al.⁶² have managed to separate isotopes of Si from SiF₄ by using an infrared field effect laser (IR FEL).

Pronko et al.⁶³ has filed a patent using two lasers. Firing of the first one creates a plasma of the desired element and the other one is then fired to spatially separate the ionized isotopic species. The inventors claim the method can be used for a number of elements and isotopes, but their examples are focused on boron.

Chromatographic methods

Aqueous solution based separations

Heumann and Lieser⁶⁴, and Heumann⁶⁵ have studied the ion-exchange of calcium-isotopes using both cation- and anion-exchange reactions. In both cases the heavier calcium isotopes were enriched in the solutions whereas the light ones were enriched in the solid (resin) phase. This is confirmed by Russel and Papanastassiou⁶⁶ studying isotope fractionation of calcium using Dowex 50W-X8. Jepson and Shockey⁶⁷ also used cation-exchange using BioRad AG-

50W-X4 and a solution of $\text{Ca}(\text{OH})_2$. Their separation factors were of the same magnitude as the former authors. Oi et al.⁶⁸, also studying calcium isotope effects, found that, for the alkali and alkaline earth metals, the magnitude of isotope effect per unit mass difference between isotopes accompanying pure ion exchange is nearly inversely proportional to the square of the atomic mass.

Kawada et al.⁶⁹ report aqueous separation of potassium isotopes by ion-exchange. They also report elements studied for isotope separation by ion-exchange to comprise Li, B, C, N, Mg, S, Ca, K, Rb, Zr, and U. In their present article separations using both weak and strong acidic ion-exchange resins are reported. The isotopic effects were pronounced at the edges of the elution band. The concentration of ^{41}K was increased by 6 – 10% at the back end. Also Gd has been studied for isotope separation by displacement ion exchange chromatography⁷⁰. Kim et al.⁷¹ have studied the isotope separation of Li by using a chelating cyclic diazo-compound. They obtained a separation factor of 1.024, but had previously obtained 1.053 using monobenzo-15-crown-5 ion-exchanger. Crown ether has also been tested by Nishizawa et al. who report enrichment of zinc isotopes by using a liquid membrane system comprising the crown ether dicyclohexano-18-crown-6.⁷²

A group at Tokyo Institute of Technology reported isotope separation of boron and uranium both by ion-exchange. For boron⁷³ a column of 620 m was needed to yield an enrichment of 98.43%. The uranium system developed⁷⁴ was based on differences in the reduction potentials of the isotopes.

Gas-chromatographic processes

Bruner et al.⁷⁵ separated isotopic methanes by gas chromatography. They obtained good separation between CH_4 and $\text{CH}_{4-x}\text{D}_x$, but less separation between $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$. They prepared columns of activated silica themselves. Lukac⁷⁶ also separated methane and deuterated methane by using commercial columns. The separations were not as good as reported by Bruner et al. While these authors report retention times of over 300 min, Berger et al.⁷⁷ have managed to separate $^{11}\text{CH}_4$ from $^{12}\text{CH}_4$ with a retention time of 65 min.

Andreev et al.⁷⁸ has developed a process based on the simulated moving bed (SMB) concept using palladium membrane or zeolites as the porous medium. They report separation of isotopes of the elements H, N, O, and Ar using the gases H_2 , N_2 , O_2 , and Ar, respectively. With Zeolite 13A they obtained separation factors of 1.020, 1.016, and 1.016 for $^{16}\text{O}_2/^{18}\text{O}^{16}\text{O}$, $^{14}\text{N}_2/^{14}\text{N}^{15}\text{N}$, and $^{40}\text{Ar}/^{36}\text{Ar}$, respectively. This process is similar to Isosilicon's improved process, covered by the second patent.

Kruglov et al.⁷⁹ report the separation of nitrogen isotopes by using ammonia (NH_3), aqueous cation-exchange columns on NH_4^+ -form and SMB. Fujiwara et al.⁸⁰ also used SMB for separation of hydrogen isotopes using columns packed with Pd-particles.

Cheh et al.⁸¹ have patented a method for low temperature gas chromatography particularly suitable for separation of hydrogen isotopes.

Common to all these studies is that the separation factors obtained are in the range of the ones quoted. These factors are comparable to other methods, i.e. diffusion based, and the advantage of chromatography versus the ones previously described is the cost of operation and investment. Also, the technology is usually well known.

Theoretical considerations

In chromatography, the fluid flow is through a porous medium. Thus, the mass flow is described by equation 6 or 7 depending on the concentration inside the medium. Instead of diffusion, dispersion is the main effect for broadening the mass distribution. In Isosilicon's initial method covered by the first patent, dispersion was eliminated by using mono-disperse particles as packing materials and a very low flow rate to enhance the diffusion effects.

Introducing the gas as a short peak of minute volume compared to the total column, the initial conditions can be approximated as a δ -function. Then a solution of equation 6 is given by:

$$c(x,t) = \frac{Ax}{2\sqrt{\pi D}(t-t_0)^{3/2}} \exp \left\{ - \left(\frac{v}{2\sqrt{D}} \sqrt{t-t_0} - \frac{x}{2\sqrt{D}} \frac{1}{\sqrt{t-t_0}} \right)^2 \right\} \quad (10)$$

where A is a normalizing constant and t_0 is the time of injection of the gas pulse. This can be least square fitted to the formula:

$$c(l,t) = a \exp \left\{ - \left(b\sqrt{t-t_0} - \frac{d}{\sqrt{t-t_0}} \right)^2 \right\} (t-t_0)^{-3/2} \quad (11)$$

$$a = \frac{AL}{2\sqrt{\pi D}}, b = \frac{v}{2\sqrt{D}}, d = \frac{L}{2\sqrt{D}}$$

Possible isotope separation methods for silicon using silane

From the preceding chapter we may conclude that a number of separation methods are available for the separation of silicon isotopes using silane. The following methods seem most promising:

- i) Thermal diffusion column. This method has been used for SiF₄, HCl and CH₄. Should therefore also be applicable for SiH₄. Isosilicon is now also in the position of employing SiF₄.
- ii) Membranes. Use of SiF₄ is reported in the press and at Internet. By proper choice of membranes this method should be feasible also for use of silane.
- iii) Membrane distillation. This method may utilise both the effect of membranes as well as the enrichment inherent in evaporation. For silane, it will be necessary to work at very low temperatures (bp. -112°C).
- iv) Centrifugation should work very well as the isotopic mass ratios for silane is much larger than in the case of UF₆.
- v) Laser induced separation has been shown to work on Si₂F₆. There is no reason that it should not be useful for disilane as well. However, laser methods seem to be still too complex with too low yield to be useful industrially. As mentioned, separation of SiF₄ is possible, and there has been also performed tests on SiH₄.⁸²
- vi) Isotopic exchange has been shown useful for separation of SiF₄.
- vii) Distillation has proved to work for SiF₄ as well as for SiH₄.
- viii) Chromatography has shown promising results for ionic compounds and for sorption/desorption of non-ionic compounds. The advantage of chromatography versus other methods (presumably except membranes) is low energy consumption and ease of operation.

Borisevich et al.⁸³ have compared a selection of promising methods for producing ²⁸Si and concluded that the most promising methods for production of large quantities are isotopic exchange and gas centrifuge. Distillation is the most expensive of the methods assessed.

References:

- ¹ Gonfiantini, R. "On the isotopic composition of precipitation" in Causse, C. and Gasse, F. (eds.) "Hydrology and isotope geochemistry" Editions de l'Orstom, Paris 1998
- ² Craig, H. Science 133, 1702 (1961) and Dansgaard, W. Tellus 6, 436 (1964)
- ³ Aranyosy, J.F., Coleman, M.L., Eggenkamp, H.M.S., "Determination of the Chlorine-37 profile in a 400m thick low permeability silty-clay formation" In Proc. Isotopes Techniques in Water Resources Development and Management", IAEA, 1999
- ⁴ Plekhanov, V.G., "Isotope effects on the lattice dynamics of crystals" Materials Science and Engineering R35 (2000) 139-237
- ⁵ Pomeranchuk, I., J.Phys. (Moscow) 6 (1942) 237
- ⁶ Geballe, T.H., and Hull, G., Phys.Rev. 110 (1958) 773
- ⁷ Anthony, T.R., Banholzer, W.F., Fleisher, J.F., Wei, L.-H., Kuo, P.K., Thomas, R.L., Phys. Rev. B 42 (1990) 1104 and Anthony, T.R., Banholzer, W.F., Diamond Relat. Mater. 1 (1992) 717
- ⁸ Bulanov, A.D., Devyatych, G.G., Gusev, A.V., Sennikov, P.G., Pohl, H.-J., Riemann, H., Schilling, H., Becker, P., "The Highly Isotopic Enriched (99.9%), High-Pure ²⁸Si Single Crystal" Cryst. Res. Technol. 35 (2000) 9, 1023-1026
- ⁹ Itoh KM, Kato J, Uemura M, Kaliteevski AK, Godisov ON, Devyatych GG, Bulanov AD, Gusev AV, Kovalev ID, Sennikov PG, Pohl HJ, Abrosimov NV, Riemann H: High purity isotopically enriched Si-29 and Si-30 single crystals: Isotope separation, purification, and growth JAPANESE JOURNAL OF APPLIED PHYSICS PART 1- 42 (10): 6248-6251, 2003
- ¹⁰ Capinski, W.S., Maris, H.J., Bauser, E., Silier, I., Asen-Palmer, M., Ruf, T., Cardona, M., Gmelin, E., (1997) Thermal conductivity of isotopically enriched Si, Appl. Phys. Lett. 71
- ¹¹ Haller, E. E., 2005, Isotopically controlled semiconductors; Solid State Communications, 133, p. 693-707
- ¹² Kizilyalli, I. C. et al., 2005, Power transistors fabricated using isotopically purified silicon (²⁸Si); IEEE Electron Device Letters, Vol. 26, No. 6
- ¹³ Kremer, R. K. et al., 2004, Thermal conductivity of isotopically enriched ²⁸Si: revisited; Solid State Communications, 131, p. 499-503
- ¹⁴ Inyushin, A. V., 2002, Thermal conductivity of isotopically modified silicon: Current status of research; Inorganic materials, Vol. 38, No. 5, pp. 427-433
- ¹⁵ O. Kordina, Private communication, September 2015
- ¹⁶ A.M. Tolmachev, E.N. Egorov, A.A. Razmadze, M.I. Godovikova "A physicochemical justification of a wasteless technology for separating nitrogen isotopes" Russian Journal of Physical Chemistry, Vol.74, No 12, 1955 – 1958 (2000)
- ¹⁷ http://www.sdi.co.za/isotopes_applications_nuclearrelated.htm
- ¹⁸ Lieser, K.H., „Einführung in die Kernchemie“, Verlag Chemie, Weinheim (1969)
- ¹⁹ Lederer, C.M., "Isotopes" Kirk-Othmer Encyclopedia of Chemical Technology, 3.ed. Vol.13, John Wiley & Sons, Inc. (2000)
- ²⁰ Crank, J., "The mathematics of diffusion" Clarendon Press, Oxford (1956).
- ²¹ Baker, R.W., "Membrane Technology" Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Inc. (2000)
- ²² Leaist, D.G. in McGraw-Hill Encyclopedia of Science and Technology, 8th edition (1997)266-272
- ²³ Katti, A.M., Guiochon, G.A., "Fundamentals of Nonlinear Chromatography: Prediction of Experimental Profiles and Band Separation"
- ²⁴ Høglund, R.L., Shacter, J., Von Halle, E., "Diffusion separation methods" in Kirk-Othmer Encyclopedia of Chemical Technology, Vol.7, John Wiley & Sons, Inc. (2000)
- ²⁵ Yamamoto, I., Makino, H., Kanagawa, A., "Optimum Feed Point for Isotope Separating Thermal Diffusion Column" J. Nucl. Sci. Tech., 32[3] (1995) 200-205
- ²⁶ Kobayashi, N., Shibata, A., Yamamoto, I., "Numerical Solution of Argon 36-38-40 Concentration within Thermal Diffusion Column" J. Nucl. Sci. Tech., 33 No.10 (1996) 781-786
- ²⁷ Høglund, R.L., Shacter, J., Von Halle, E., "Diffusion separation methods" in Kirk-Othmer Encyclopedia of Chemical Technology, Vol.7, John Wiley & Sons, Inc. (2000)
- ²⁸ Cussler, E.L., "Diffusion: Mass Transfer in Fluid Systems" 2.ed. (1985)
- ²⁹ World Nuclear Association, <http://www.world-nuclear.com/info/inf28print.htm>
- ³⁰ J. Dong and C.H. Byers. "Separation of Silicon Isotopes (Silanes) by membrane Methods – A Theoretical Analysis" Private communication, unpublished (2003)
- ³¹ R.S. Mulliken "The Separation of Isotopes by Distillation and Analogous Processes" 2387-2391(1922)
- ³² T.R. Mills, M.G. Garcia, R.C. Vandervoort, B.B. McInteer "A Chemical Exchange System for Isotopic Feed to a Nitrogen and Oxygen Isotope Separation Plant" Sep.Sci.& Tech. 24(5 & 6), 415-428, 1989

Confidential information

Must not be given to third parties without permission from Isosilicon

- ³³ D.E. Armstrong, A.C. Briesmeister, B.B. McInnter, R.M. Potter "A Carbon-13 Production Plant Using Carbon Monoxide Distillation" LA-4391, April 10, 1970
- ³⁴ B.B. McInnter "Isotope Separation by Distillation of a Carbon-13 Plant" Sep.Sci.and Techn. 15(3), 491-508 (1980)
- ³⁵ T.R. Mills "Practical Sulfur Isotope Separation by Distillation" Sep.Sci.& Tech. 25(13-15), 1919-1930 (1990)
- ³⁶ T.R. Mills "Silicon Isotope Separation by Distillation of Silicon Tetrafluoride" Sep.Sci.& Tech. 25(3), 335-345 (1990)
- ³⁷ Scogin, J.H., Poore, A. S., "Startup and operation of a metal hydride based isotope separation process" Proc.Fifth Topical Meeting on Tritium Technology in Fission, Fusion and Isotopic Applications, Lake Maggiore, Italy (1995)
- ³⁸ Chmielewski, A.G., Zakrzewska-Trznadel, G., Miljevic, N.R., v.Hook, A., "Investigation of the separation factor between light and heavy water in the liquid/vapor membrane permeation process" J. Membrane Sci. 55 (1991) 257-262
- ³⁹ Zakrzewska-Trznadel, G., Chmielewski, A.G., Miljevic, N.R."Separation of protium/deuterium and oxygen-16/oxygen-18 by membrane distillation" J. Membrane Sci. 113 (1996) 337-342
- ⁴⁰ Tanaka, K., Kita, H., Okamoto, K-i., Noble, R.D., Falconer, J.L., "Isotopic-transient permeation measurements in steady-state pervaporation through polymeric membranes" J. Membrane Sci. 197 (2002) 173-183
- ⁴¹ Anreev, B.M., Sakharovsky, Y.A., Rozenkevich, M.B., Magomedbekov, E.P., Park, Y.S., Uborskiy, V.V., Trenin, V.D., Alekeev, I.A., Fedorchenko, O.A., Karpov, S.P., Konoplev, K.A., "Installations for separation of hydrogen isotopes by the method of chemical isotopic exchange in the "water-hydrogen" system" Fusion Tech. Vol. 28 (1995) 515-518
- ⁴² Tolmachev, A.M., Egorov, E.N., Razmadze, A.A., Godovikova, M.I., "A Physicochemical Justification of a Wasteless Technology for Separating Nitrogen Isotopes" Russ. J. Phys. Chem. Vol.74, No.12 (2000) 1955
- ⁴³ McCandless, F.P., Herbst, R.S., "Separation of the isotopes of boron by chemical exchange reactions" US 5,419,887/A/ (1995)
- ⁴⁴ P.D. Ownby "The boron trifluoride nitromethane adduct" J.Solid State Chem. 177 (2004) 466-470
- ⁴⁵ Prokhorov, A.M., Petrov, G.N., Ljashchenko, B.G., Zueva, G.Ja., "Method of separating siliicon into fractions enriched with heavy and light isotopes" Russ.pat. No.: 2 170 609 C1 (2000)
- ⁴⁶ C. Wang, P. Bai and X. Guo "Advances in separation methods for large-scale production of silicon isotopes" J. Radioanal. Nucl. Chem. Published on-line 14 February 2015
- ⁴⁷ T.Abesadze, W.E. Saunders, M.Y. Wachs, D.K. Manning "Enrichment of silicon or germanium isotopes" US 6,146,601 Nov. 14, 2000
- ⁴⁸ A.V. Khoroshilov, S.A. Cherednichenko, A.V. Lizunov, S.N. Fedorova "Separation of Silicon Isotopes by Chemical Exchange between Silicon Tetrafluoride and Its Complex Compounds with Aliphatic Alcohols" Theor. Found. Chem. Eng. 44(4) 569-573 (2010)
- ⁴⁹ A.A. Razmadze and A.M. Tolmachev "Determination of Physicochemical Parameters of 28Si Isotope Enrichment in Countercurrent Column" Russ. J. Phys. Chem. A, 84(2) 304-306 (2010)
- ⁵⁰ Wood, H. G., Mason, T. C., Soubbaramayer "Multi-Isotope Separation in a Gas Centrifuge Using Onsager's Pancake Model" Sep. Sci. Tech. 31(9) (1996) 1185-1213
- ⁵¹ Kai, T., Hasegawa, K., "Numerical Calculation of Flow and Isotope Separation for SF6 Gas Centrifuge" J. Nucl. Sci. Tech. Vol. 37, No. 2, (2000) 153-165
- ⁵² Scientific Development and Integration. Private communication to Isosilicon. <http://www.sdi.co.za/>
- ⁵³ Letokhov, V.S., Moore, C.B., in C.B. Moore, ed., "Chemical and Biochemical Applications of Lasers", Vol. III, Academic Press, Inc., New York (1977) Chapt.1
- ⁵⁴ J.W. Eerkens, D.G. Garratt, B.C. Olson, K.J. Falk, J.H. Wang "CRISLA Process" US Patent 5,883,350 March 16, 1999 and patents referenced therein
- ⁵⁵ M. Ivanenko and P. Hering "laserinduzierte Stabil-Isotopentrennung von ¹³C und ¹²C für de industrielle Anwendung" Laser and Optoelektronik 30(6) 64-68/1998
- ⁵⁶ J. Marling "Isotope Separation of O-17, O-18, C-13, and Deuterium by ion-Laser Induced Formaldehyde" J. Chem. Phys. 66(9) 4200-4225 1977
- ⁵⁷ S.M. Freund, W.B. Maier II, R.F. Holland, and W.H. Beattie "Photolytic separation of isotopes in cryogenic solution" US Patent 4,554,060 November 19, 1985
- ⁵⁸ K.S. Suslick "Isotope separation by photochromatography" US Patent 4,010,100 March 1, 1977
- ⁵⁹ Okada, Y., Takeuchi, K., "Infrared Laser Isotope Separation of Silicon with Molecular Beam of Hexafluorodisilane" J. Nucl. Sci. Tech., Vol. 34, No. 4 (1997) 413-415 and references therein.
- ⁶⁰ H. Suzuki, H. Araki, and T. Noda "Enrichment of silicon isotopes by infrared laser irradiation" J. Jap. Inst. Metals Vol.61, No.2 (1997) 145-152
T. Noda, H. Suzuki, and H. Araki "Silicon isotope enrichment for low activation" Fusion Eng. Design 41 (1998) 173-179

Confidential information

Must not be given to third parties without permission from Isosilicon

-
- ⁶¹ A. Yokohama, H. Ohba, M. Hashimoto, K. Katsumata, H. Akagi, T. Ishii, A. Ohya, S. Arai "Silicon isotope separation utilizing infrared multiphoton dissociation of Si₂F₆ irradiated with two-frequency CO₂ laser lights" *Appl. Phys. B* 79, 883-889 (2004)
- ⁶² K. Nomaru, A.V. Chernyshev, A.K. Petrov, H. Kuroda "Novel process of isotope separation of silicon by use of IR FEL" *Nucl. Instr. Meth. Phys. Res. A* 507, 552-555 (2003)
- ⁶³ P.P. Pronko, P.A. Vanrompay, Z. Zhang "Method for laser induced isotope enrichment" US Patent 6,787,723 Sept. 7, 2004
- ⁶⁴ K.G. Heumann and K.H. Lieser "Untersuchungenvon Calciumisotopieffekten bei heterogenen Austaschgleichgewichten" *Z. Naturforsch.* 27b, 126-133 (1972)
- ⁶⁵ K.G. Heumann "Calciumisotopieffekte beim Ionenaustausch an Dowex A1" *Z. Naturforsch.* 27b, 492-497 (1972)
- ⁶⁶ W.A. Russel and D.A. Papanastassiou "Calcium Isotope Fractionation in Ion-Exchange Chromatography" *Anal. Chem.* Vol.50, No 8 (1978) 1151-1154
- ⁶⁷ B.E. Jepson and G.C. Shockey "Calcium Hydroxide Isotope Effect in Calcium Isotope enrichment by Ion Exchange" *Sep. Sci. Tech.* 19(2&3) 173-181, 1984
- ⁶⁸ T. Oi, N. Morioka, H. Ogino, H. Kakihana, and M. Hosoe "Fractionation of Calcium Isotopes in Cation-Exchange Chromatography" *Sep. Sci. Tech.* 28(11&12) 1971-1982, 1993
- ⁶⁹ Kawada, K., Oi, T., Hosoe, M., Kakihana, H., "Fractionation of potassium isotopes in cation-exchange chromatography" *J. Chrom.*, 538 (1991) 355-364 and references therein.
- ⁷⁰ Chen, J.R., Nomura, M., Fujii, Y., Kawakami, F., Okamoto, M., "Gadolinium isotope-separation by cation-exchange chromatography" *J. Nucl. Sci. Tech.*, Vol. 29, No. 11 (1992) 1086-1092
- ⁷¹ Kim, D. W., Park, S.R., Kim, S.J., Kim, Si J., Kim, H.J., "Separation of lithium isotope by NTOE compound" *J. Radioanal. Nucl. Chem.*, Vol. 229, Nos. 1-2 (1998) 165-168
- ⁷² Nishizawa, K., Miki, T., Satoyama, T., Fujii, T., Yamamoto, T., Nomura, M., "Enrichment of Zinc Isotopes by a Liquid Membrane System Using a Crown Ether" *Sep. Sci. Tech.* 33(7) (1998) 991-1002
- ⁷³ M. Aida, Y. Fujii, and M. Okamoto "Boron Isotope Separation by Using Weak Base Anion Exchange Resin" Presented at IEX'92, Cambridge, UK
- ⁷⁴ Y. Fujii, M. Higuchi, M. Nomura, M. Aida, M. Okamoto, and F. Kawakami "Uranium Isotope Separation by Ion Exchange Chromatography" Presented at IEX'92, Cambridge, UK
- ⁷⁵ F. Bruner, G.P. Cartoni, and M. Possanzini "Separation of Isotopic Methanes by Gas Chromatography" *Anal. Chem.* Vol.41 No.8, 1122-1124 (1969)
- ⁷⁶ S. Lukac "Separation of isotopic methanes by gas chromatography" *J. Chrom.* 166(1978) 287-289
- ⁷⁷ G. Bergen, C. Prenant, J. Sastre, and D. Comar "Separation of Isotopic Methanes by Capillary Gas Chromatography. Application to the Improvement of ¹¹CH₄ Specific Radioactivity" *Int. J. Appl. Radiat. Isot.* Vol.34, No. 11, 1525-1530, 1983
- ⁷⁸ Andreev, B.M., Kruglov, A.V., Selivanenko, Y.L., "Continuous Isotope Separation in Systems with Solid Phase. I. Gas-Phase Separation of Isotopes of the Light Elements" *Sep. Sci. Tech.* 30(16) (1995) 3211-3227
- ⁷⁹ A.V. Kruglov, B.M. Andreev and Y.E. Pojidaev "Continuous Isotope Separation in Systems with Solid Phase. II. Separation of Nitrogen Isotopes with Use of Ion-Exchange Resin" *Sep. Sci. Tech.* 31(4) 471-490 (1996)
- ⁸⁰ H. Fujiwara, S. Fukada, and M. Nishikawa "A study of a new hydrogen isotope separation system using a simulated moving bed" *Sep. Sci. Tech.* 36(3), 337-348 (2001)
- ⁸¹ C.H. Cheh, S.H. Hawthorne, R.E. Massey, O.K. Kveton, S.K. Sood "Low Temperature Preparative Gas Chromatography Apparatus" US Patent 4,780,116 Oct. 25, 1988
- ⁸² J. Marowe, O.V. Boyarkin, T.R. Rizzo "Isotopically Selective Infrared Multiphoton Dissociation of Vibrationally Excited SiH₄" *J. Phys. Chem. A* 106, 5221-5229 (2002)
- ⁸³ V.D. Borisevich, A.V. Khoroshilov, S.A. Cherednichenko "Thermal Conductivity of Silicon-28 and Separation Technology for Its Production" 5th Int. Conf. on Isotopes, Brussels, Belgium, April 25-29 2005