United States Patent [19]

Pressman

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[54] **METHOD AND APPARATUS FOR MASS SEPARATION EMPLOYING PHOTO ENHANCED SURFACE IONIZATION**

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[52] **U.S. Cl.** ..... **250/41.9 SE,** 250/49.5 TI, 250/84, 313/63

[51] **Int. Cl.** **H01j 39/34**

[58] **Field of Search** ..... 250/41.3, 41.9 SE, 250/49.5 TI, 84; 313/63

[56] **References Cited**

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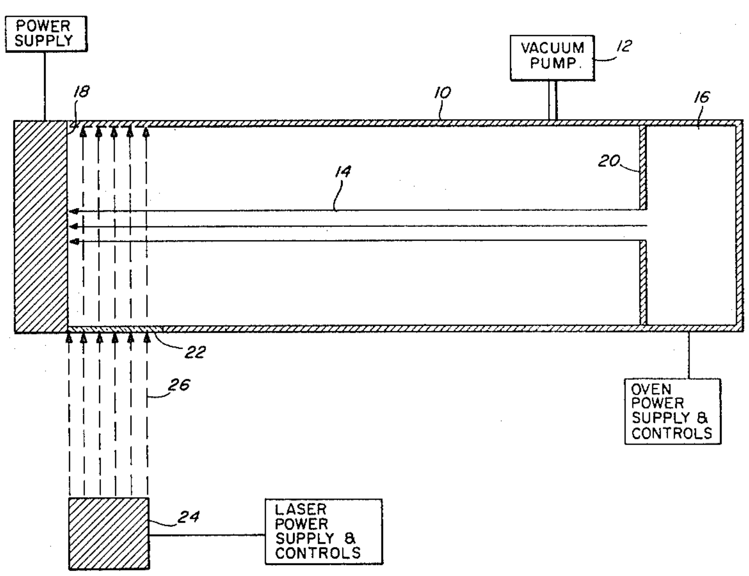
[57] **ABSTRACT**

Photo-assisted surface ionization techniques are employed for the separation of isotopes and the purification of materials, the formation of relatively pure and intense ion beams and plasmas and the detection of minor constituents, pollutants and leaks. A species intermingled with other constituents in an atomic or molecular beam or in a gas, for example, is selectively excited by irradiation at a resonance frequency in close proximity to an ionizing surface. The selected species, while still in the excited level, interacts with the surface and is ionized. The specimen is excited by the radiation to a level such that the energy required to ionize the atom is less than the work function of the solid surface.

20 Claims, 7 Drawing Figures



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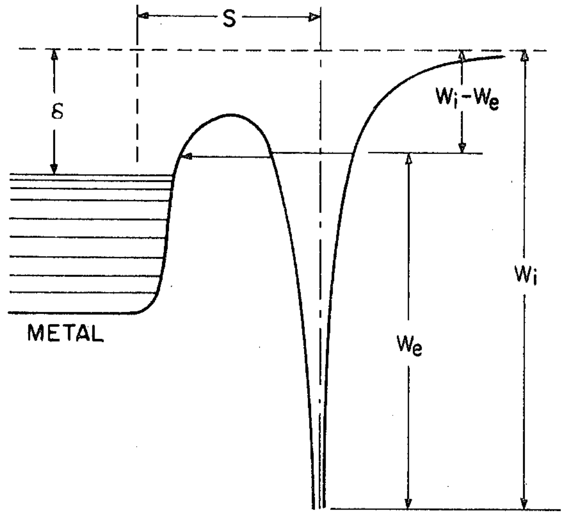
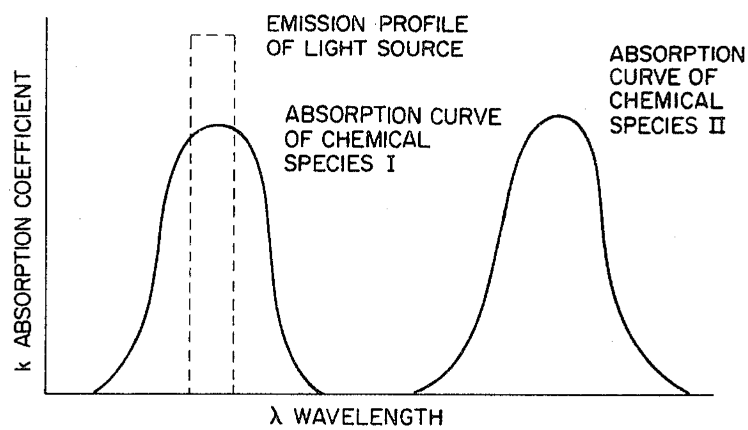


FIG. 1

FIG. 3



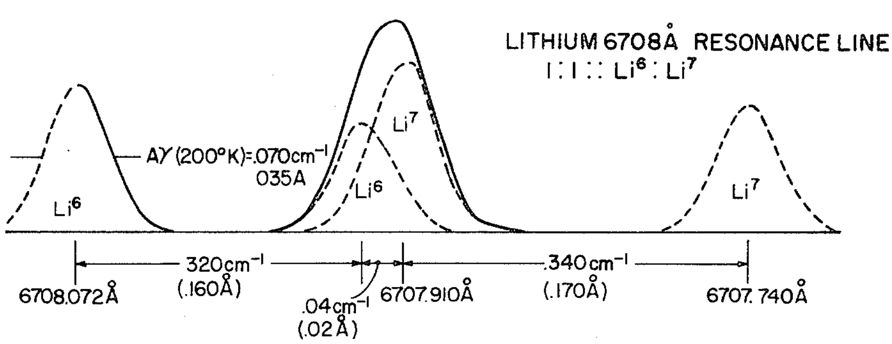


FIG. 7

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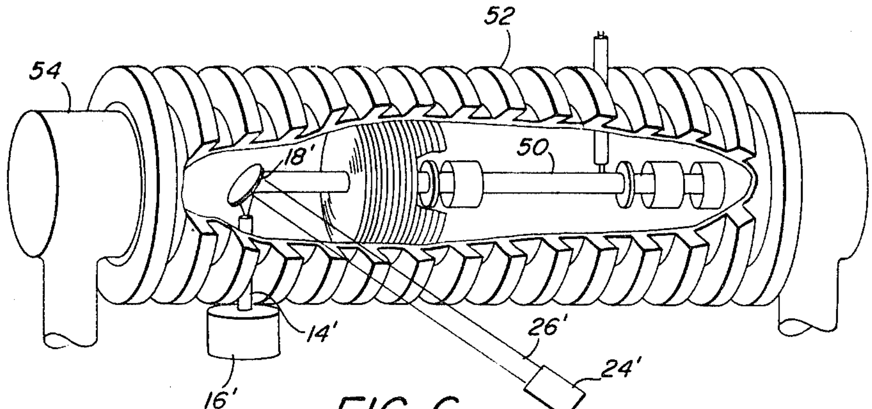

FIG. 6

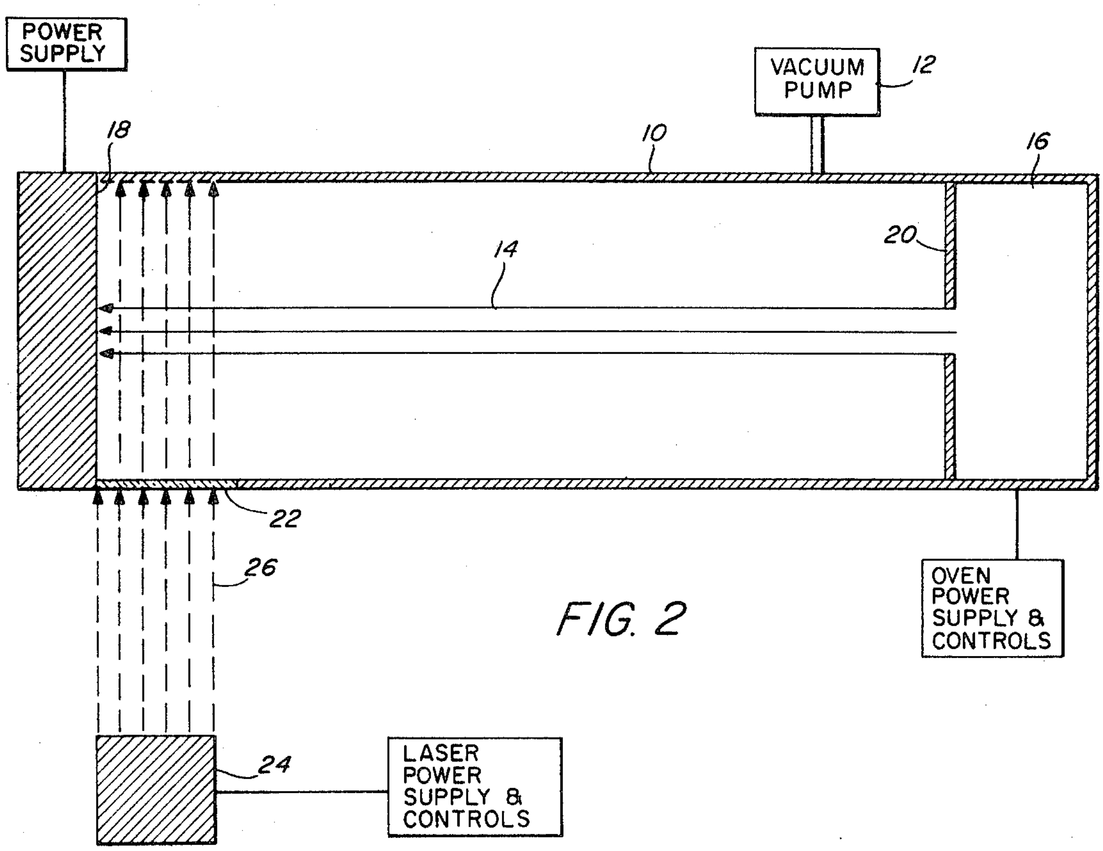

FIG. 2

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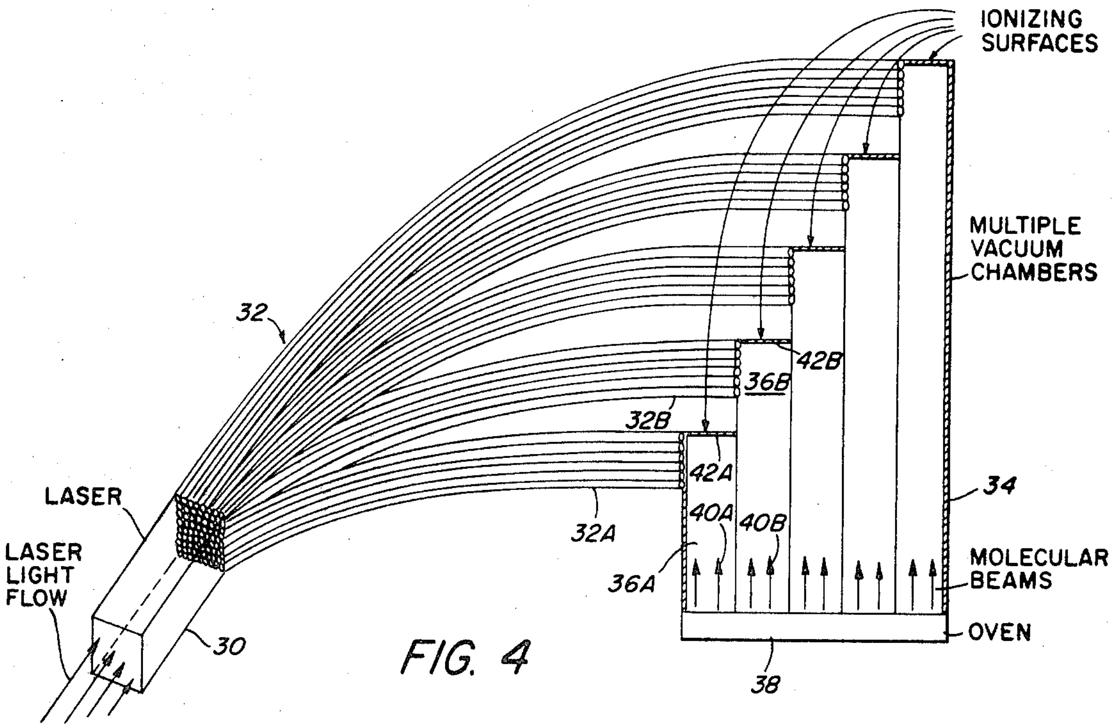

FIG. 4

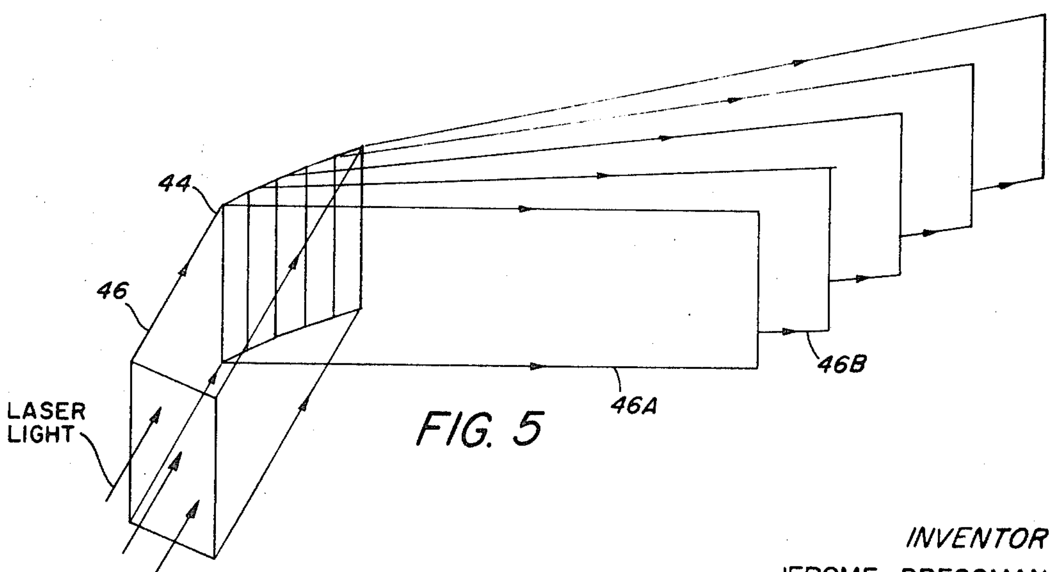

FIG. 5

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METHOD AND APPARATUS FOR MASS SEPARATION EMPLOYING PHOTO ENHANCED SURFACE IONIZATION

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates generally to a novel method and associated apparatus for separating isotopes and purifying materials, forming ion beams and plasmas and for detecting chemical species.

2. Summary of the Prior Art

The separation of isotopes heretofore has been carried out by using techniques and equipment which have been relatively inefficient and expensive. One such technique involves a mass spectrometer in which a plasma moves through a magnetic field. Another technique makes use of photophysical acceleration, while another employs thermal diffusion principles. These techniques and their related equipment generally required the use of large quantities of power and have been relatively limited with respect to range of operation and productivity.

It is an object of the present invention to provide improvements in mass separation techniques and equipment. A further object of this invention is to provide a new and improved method and apparatus for forming ion beams and plasmas as well as to improve the detection of selected chemical species.

SUMMARY OF THE INVENTION

This invention features the method of separating masses, forming beams and detecting chemical species comprising the steps of directing a diffuse mixture of particles towards an ionizing surface having a work function related to the ionization potential of the selected species, and irradiating the diffuse mixture with a beam of an electro-magnetic energy in close parallel proximity to the surface, the frequency of the beam being resonant only with the selected species to excite the species to a level where it may be surface ionized with a high degree of probability. The technique may be used to advantage in the separation of isotopes, purification of materials as well as the formation of relatively pure and intense ion beams, plasmas as well as the detection of minor constituents, pollutants and leaks.

This invention also features apparatus for separating a selected atomic or molecular species from a mass including an ionizing surface, means for directing the mass against the surface and a source of electro-magnetic energy adapted to radiate the mass in an area adjacent the surface and at a frequency resonant with the selected species for raising the species to an excited level to exclusively enhance surface ionization of the species.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagram illustrating resonance ionization of an excited atom at a surface,

FIG. 2 is a sectional view in side elevation, somewhat schematic, of a photo-assisted surface ionization apparatus made according to the invention,

FIG. 3 is a diagram of selective chemical species excitation by special light source,

FIG. 4 is a schematic representation showing a modification of the invention,

FIG. 5 is a schematic representation showing a further modification of the invention,

FIG. 6 is a perspective view, partially broken away and somewhat schematic, showing an apparatus for material purification or isotope separation made according to the invention, and,

FIG. 7 is a diagram showing the natural resonant lines of Lithium 6 and 7.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

This invention relates to a novel method and associated apparatus for achieving photo-assisted surface ionization useful in the separation of isotopes and the purification of materials, the formation of relatively pure and intense ion beams and plasmas and the detection of minor constituents, pollutants and leaks. The terms "photo assisted surface ionization" as employed herein are used to refer to a surface ionization which is made selective and enhanced by radiating the desired atomic or molecular species with electro-magnetic energy, typically light, at a selected frequency which is resonant with the species to raise the species to an excited level. While still in the excited state, the species impinges a selected ionizing surface and interacts with it to be ionized.

By way of background, surface ionization is the phenomenon in which atoms or molecules are adsorbed on a heated surface and then quickly evaporated in an ionic state. Both positive and negative ions may be formed in this fashion. The atom or molecule striking the surface gives up to or acquires an electron from the surface and evaporates as a positive or negative ion. Theoretically, if the ionization potential of an electropositive atom incident on a hot surface is less than the surface work function, then it is probable that the atom will be adsorbed on the surface and lose an electron to the surface material. Depending upon the temperature of the surface, the ion may remain adsorbed or evaporate as a positive ion or as a neutral atom.

Referring now to FIG. 1 there is graphically illustrated the energy levels of an atom or molecule that has been raised by radiation of a frequency $h\nu = W_e$, to an excited level W_e, such that the energy required to ionize the atom $(W_i - W_e)$ is less than the work function (δ) of an impinged solid surface where W_i is the atom's ionization potential. This is represented by the following equation:

$$\delta > W_i - W_e \tag{1}$$

The ability to raise an atom to an excited level then permits that the atom to be surface ionized with a high degree of probability, assuming equation (1) is satisfied, whereas in the ground state the probability of surface ionization may be almost zero. The theoretical fraction of a species which will be contact ionized is given by f_A where

$$f_A = [1 + \exp(W_i/V_{TH} - \delta/V_{TH})]^{-1} \tag{2}$$

Where T equals temperature, $V_{TH} = kt/e$, where k equals Boltzmann's constant and e equals electronic charge.

For an excited atom (at level W_e,) W_i in equation (2) must be replaced by $W_i - W_e$ and equation (2) becomes

$$f_X = [1 + \exp\{1/V_{TH}(W_i - W_e - \delta)\}]^{-1} \quad (3)$$

The theoretical separation factor for excited isotope raised to level W_e over a non-excited isotope is then

$$\int = f_X/f_A \quad (4)$$

Similarly from equations (2) and (3) it may be seen that for any given chemical species which can be excited substantially, this species can then be given in a suitable arrangement with an appropriate a preferential ionization. This preferential ionization can then be used for species separation, beam or plasma formation or detection purposes.

Essentially, the technique of photo-assisted surface ionization disclosed herein may be considered as the selective pseudo-lowering of the ionization potential of a species or isotope by means of photon absorption. This condition thus enhances the surface ionization for that species or isotope. Alternatively, the technique may be viewed as the pseudo-raising of the work function of a surface for one particular species or isotope.

Referring now to FIG. 2 of the drawings, there is illustrated somewhat schematically a system useful in the purification of materials or for separating isotopes, there being no fundamental differences between the different applications. In FIG. 2 the apparatus is generally organized about a housing **10** to which is connected a vacuum pump **12** adapted to produce an evacuated chamber within the housing for the formation of a molecular beam **14** generated by means of an oven **16** at one end of the housing and directed against an ionizing surface **18** at the opposite end of the housing. The oven **16** is separated from the evacuated chamber by means of an apertured wall **20** through which the beam is focussed. At the end of the housing and adjacent the ionizing surface **18** a window **22** is provided to pass a beam **26** from a laser **24** mounted exterior to the chamber and positioned to direct its beam along a path parallel to the ionizing surface **18** and perpendicular to the molecular beam **14.** The laser beam **26** intersects the molecular or atomic beam **14** in close proximity to the surface **18** whereby a selected species within the beam **14** will be excited as close as possible to the surface **18** to insure that the optimum number of selectively excited species contact the surface **18** still in the excited state for surface ionization.

Optical considerations

The system to be used is that of an atomic or molecular beam being illuminated near and hitting a suitable ionizing surface such as the surface **18.** A source of electro-magnetic energy, preferably the laser **24,** is tuned to the resonance level of the desired species in the beam **14** and raises that species only to the excited level when it is close to the surface **18** which normally would be a selected metal. This permits the excited species to be optimally ionized subject to equation (3) above.

The use of relatively high powers (0–1–10 watts) is advantageous in that it makes possible large populations of excited species At powers P_o given by:

$$P_o = 1/T_r k_o, \quad (5)$$

where T_r = the life time of the excited state and k_o = absorption at line center, approximately one-third of the species in the beam **14** will be excited. For example, for $T_r = 10^{-8}$ seconds and $k_o \approx 10^{-11}$ cm$^2 \approx P_o$ is $\approx 10^{19}$ photons/second, or on the order of a watt. For $P > P_o$ the ratios of the excited species to the ground state approaches equality. The time required for absorption or a deexcitation by stimulated emission T_{ss}, from the excited state is given by:

$$T_A = T_{ss} = 1/k_o P \quad (6)$$

For example, for $k_o = 10^{-11}$ cm^2 and $P = 10^{21}$ photons/sec cm^2, an atom in the field of the laser beam **26** is oscillating between the excited state and the ground state every 10^{-10} seconds. If its velocity is μ cm/sec then the distance it moves on the average in the excited or ground state, X_{cr} is given by:

If $\mu = 10^4$ cm/sec then for the values above

$$X_{cr} = 10^4 \times 10^{-10} = 10^{-6} \text{ cm} = 10^2 \text{ A} \quad (7)$$

For $T_A = 10^{-8}$ sec $X_{cr} = 10^{-4}$ cm $= 1\mu$

In terms of the surface ionization the behavior of the atom away from the surface is irrelevant. Consequently, this fact dictates that the interaction zone of the resonance radiation be adjusted so that it parallels the surface and is X_{cr} wide, subject to the practicalities of achieving this kind of flat thin beam. Under the circumstances, half of the desired species would be ionized and separated out at the surface and, ideally, only one photon would be required for each atom. Consequently, the efficiency of the process would be high. A major advantage of the process is that because of the above-described efficiency the throughput of the system can be greatly improved by slicing the light bean **26,** which typically might be 1 cm by 1 cm in area, into separate sections and using each section to operate in conjunction with different ionizing surface areas. If for example, $X_{cr} = 1\mu = 10^{-4}$ cm then the throughput can be increased by a factor of 10^4 as suggested in FIG. 4.

Referring now to FIG. 4 of the drawings, there is illustrated a modification of the invention in this embodiment a laser beam **32** is sliced or divided in such a fashion that a single laser **30** may intersect a plurality of different molecular beams. In FIG. 4, the laser **30** is optically coupled to a bundle of optical fibers **32,** the bundle being divided into different groups **32A** and **32B,** etc. Each group is connected to a housing **34** formed with a plurality of vacuum chambers **36A, 36B,** etc., with each chamber connected to an oven **38** adapted to produce separate molecular beams **40A, 40B,** etc., directed against individual ionizing surfaces **42A, 42B,** etc. The number of different beams corresponds with the number of fiber groups **32A,** etc., and each fiber group is positioned to direct a laser beam perpendicularly with respect to the molecular flow and in close proximity to the ionizing surfaces **42A,** etc. Thus a single laser may service a number of molecular beams and a corresponding number of ionizing surfaces. While five such beams and fiber groups are illustrated, obviously the number may be increased or decreased as desired.

Referring now to FIG. 5 of the drawings, there is illustrated a modification of the optical beam-slicing system and, in this embodiment, a plurality of individual mirrors **44** or the like arranged in a bank are employed in the path of a laser light beam **46** with each individual mirror being tilted at a different angle causing the beam **46** to be broken up into a plurality of beams **46A**, **46B**, etc., depending upon the number of mirrors. Each separate beam **46A**, **46B**, etc., is directed into a different molecular beam system and ionizing surface such as suggested in the FIG. 4 embodiment.

In the preferred form of the invention, the optical light source is a laser tuned to the resonance frequency of the selected atom which is to be separated or detected. Suitable laser devices which may be employed in this invention include continuous wave as well as pulse type dye lasers, parametrically tuned lasers and semiconductor lasers, depending upon the wave length range of the laser and the chemical species involved. Where the process is to be employed to separate isotopes or detect a particular substance in addition to the many laser fine tuning techniques available such as diffractive gratings, etc., an absorption cell may be used external to the molecular beam in which the undesired isotope absorb out their components of the radiation before the light beam enters the molecular beam apparatus.

Purification of Materials & Isotopes Separation

In the system illustrated in FIG. **2**, materials may be purified or isotopes separated insofar as both processes are essentially the same. For purifying materials, the light source **24** must be tuned to the resonance frequency of the desired species in the beam **14** and, in this regard, reference is made to the absorption characteristic curves shown in FIG. **3** with respect to two different species. Also, the ionizing surface **18** must be selected from a material that will cause only the selectively excited species to ionize to the exclusion of other species in the ground state. While it is known that preferential contact ionization has been proposed for material purification, the method disclosed herein extends preferential contact ionization of chemical species by the pseudo-reduction of the ionization potential, thus creating new possibilities for surface ionization, viz., for elements or compounds of higher ionization potential than would otherwise be considered for this technique.

Once the photo-assisted surface ionization technique has preferentially created the unique desired ionic species, any one of numerous techniques available may be employed to remove the ionized species. For example, there is illustrated in FIG. **6** a magnetoplasma device in which the separation is achieved through a plasma **50** moving parallel to a magnetic field generated by coils **52** about an evacuated housing **54**. The plasma moves through an orifice and deposits on perpendicular or transverse plates. Alternatively, ion beam pullout can be achieved and the desired atoms or molecules can be removed from the ionizing surface in the form of ions. The specific nature of removable process is not critical in the present invention insofar as a variety of possible arrangements of electrical electrodes and/or magnetic fields used in conventional surface ionization devices may be employed for this purpose.

The method and apparatus utilized for photo-assisted surface ionization involved in the separation of isotopes is similar to that employed in the purification of materials. The only exception is that the light source must be tuned to the resonance frequency of one of the isotopes and not to that of the others. The isotope in the excited state is then preferentially ionized in accordance with equations (1) through (4). This technique is dependent upon the fact that the optical spectra of isotopes are different. By way of illustration, in FIG. **7** there are shown the resonance lines of Lithium 6 and 7. While these atomic isotopic lines have a small shift, presently available light sources, such as tuned lasers, monoisotopic lasers, use of depleted isotope absorption cells, etc., are able to resolve this difference. Molecular isotopic shifts are considerably larger, being on the order of one part in one hundred in comparison with atomic shifts on the order of one part in one thousand.

By way of example, there is described herein the parameters relating to the separation of Uranium 235 (U_{235}). To separate this isotope an apparatus such as shown in FIG. **2** is employed and, in this instance, the ionizing surface **18** is fabricated from Tungsten whose work function, δ, is 4.54 electron volts. This surface is heated and serves to do the ionizing. The surface is operated at a typical temperature, T, such that $V_{Th} = 0.2$ volts. The laser **24** is tuned to the Uranium 235 line at 4153A where the isotopic shift is 0.7A, this being much larger than the uranium line width. An alternative possibility is another Uranium 235 resonance line at 5027A. It has been shown that these lines have small hyperfine structures (M. Deringer, Compt. Rendu. 250 (1960) 828. As a result, a minimum amount of interference should develop between Uranium 235 and its related isotopes and neighboring lines of uranium and other elements. Moreover it has been shown experimentally in uranium atomic absorption work (A. Goleb, Anal. Chem Acta (1966) 135 – 165) that the Uranium-234, -236 and -238 components of the 4155A line do not interfere with the Uranium-235 component.

In the event that the precise laser tuning to the U-235 wavelength 4153A, or 5027A prove difficult, it may be advantageous to use an absorption cell with U-234, -236, and -238 to absorb out these components before the light beam performs the separation process.

For uranium atoms impinging on the tungsten surface, the degree of ionization (f_A) for $V_{TH} = 0.2$ev, $\delta = 4.54$ev is from equation (2) $f_A = 2 \times 10^{-4}$. For uranium excited by $\lambda = 4153$A, the excited level $W_e = 2.98$ev and with $W_i = 6.22$ev there is obtained for equation (3) $W_i - W_e - \delta = 6.22 - 2.98 - 4.54$ or $f_X = 1$ and therefore, 100 percent ionization should occur.

Consequently, of the ionized species coming off the tungsten surface, almost all of the U-235 is ionized and only 2×10^{-4} of the other isotopes is ionized.

Detection of Minor Constituents, Pollutants & Isotopes

The present method depends on the existence of differential optical spectra of the minor constituent pollutants which is the only species excited to a resonance level and subsequently preferentially ionized at the surface. Whereas in the purification or isotopic separation application a continuous light source is desired to obtain a large throughput, in the detection application, a pulse or modulated light signal is preferred in order to utilize the well-known advantages in signal-to-noise ratios of a narrow band signal for detection purposes.

Such detection devices are available and include locked amplifiers, etc., and are well known in the art.

The technique disclosed herein thus represents photon-assisted surface ionization techniques in which the minor constituent or pollutant ion current can be uniquely marked with an alternating or modulated current or, if desired, a direct current. In the present technique, the photon is used to place the atom in the excited state for subsequent surface ionization in contract to other techniques which detect by photon absorption or scattering with an associated photo-detector.

Formation of Specific Ion Beams and Plasmas

The foregoing techniques may also be employed to create unique ion sources and beams and plasmas for various purposes. The photo-assisted surface ionization techniques in effect create a new type of ion source since the effective work potential of the ionizing surface becomes:

$$\delta_E = \delta + h \quad (8)$$

Where δ_E = effective work functions, δ = work function of the surface, and $h\,\nu$ = photon energy.

For example, if a surface has a δ (work function) of 8 electron volts, for species absorbing 2ev photons and having an ionization potential of 10ev, abundant ionization can be created when the ground state would have little ionization. Consequently new types of ion beams, or if a plasma mode of extraction is preferred, new types of plasmas may be created. This new type of ion source and beams have applicability in ion implantation systems such as tailoring the surface properties of semi-conductor devices, mass spectroscopy, etc. The new type plasma source may be used for scientific purposes such as the construction of new types of Q machines or industrially in electronics for such applications as forming thin films, chemical reactions, etc.

Having thus described the invention, what I claim and desire to obtain by Letters Patents of the United States is:

1. The method of separating certain particles which absorb radiation of one frequency from other particles that absorb radiation of different frequencies, comprising the steps of directing all types of said particles against an ionizing surface and irradiating in close proximity to the ionizing surface all of said particles with electromagnetic energy of said one frequency whereby said certain particles are selectively excited to a level less than the work function of said surface to be surface ionized upon contact with said surface, and then separating the surface ionized particles from all other particles.

2. The method of claim 1 wherein said energy is light.

3. The method of claim 2 wherein said light is a laser beam.

4. The method of claim 1 wherein said particles are in the form of a beam.

5. The method of claim 1 wherein said particles are in the form of a gas.

6. The method of claim 1 wherein said particles and said surface are in a vacuum.

7. The method of claim 1 including the step of collecting the surface ionized particles.

8. The method of claim 7 wherein said surface ionized particles are formed into a plasma beam and focussed into a receptacle.

9. The method of claim 1 wherein said energy is pulsed.

10. The method of claim 1 wherein said energy is continuous.

11. The method of claim 1 including the step of measuring electrical current flow at said surface.

12. Apparatus for separating certain particles which absorb electromagnetic radiation of one frequency from other particles that absorb radiation of different frequencies, comprising

a. a housing,

b. a member of selected material in said housing and providing an ionizing surface,

c. means for directing particles against said surface,

d. means for heating said surface,

e. radiation means for irradiating said particles in close proximity to said surface with radiation of said one frequency whereby said certain particles will be selectively excited to a level less than the work function of said surface to be surface ionized upon contact with said surface, and,

f. means for separating the surface ionized particles from all other particles.

13. Apparatus according to claim 12 wherein said radiation means is tuneable to different discrete frequencies.

14. Apparatus according to claim 12 wherein said radiation means is a laser.

15. Apparatus according to claim 14 including a plurality of spaced ionizing surfaces in said housing and optical means operatively associated with said laser for dividing said laser beam into a plurality of separate beams and forming each said separate beam into proximity to each of said spaced surface.

16. Apparatus according to claim 15 wherein said optical means includes optical fibers.

17. Apparatus according to claim 15 wherein said optical means include mirrors.

18. Apparatus according to claim 12 including evacuating means connected to said housing for evacuation thereof.

19. Apparatus according to claim 12 wherein said directing means includes an oven adapted to generate a beam of said particles.

20. Apparatus according to claim 12 including collection means in said housing for collecting the selectively ionized particles.

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