

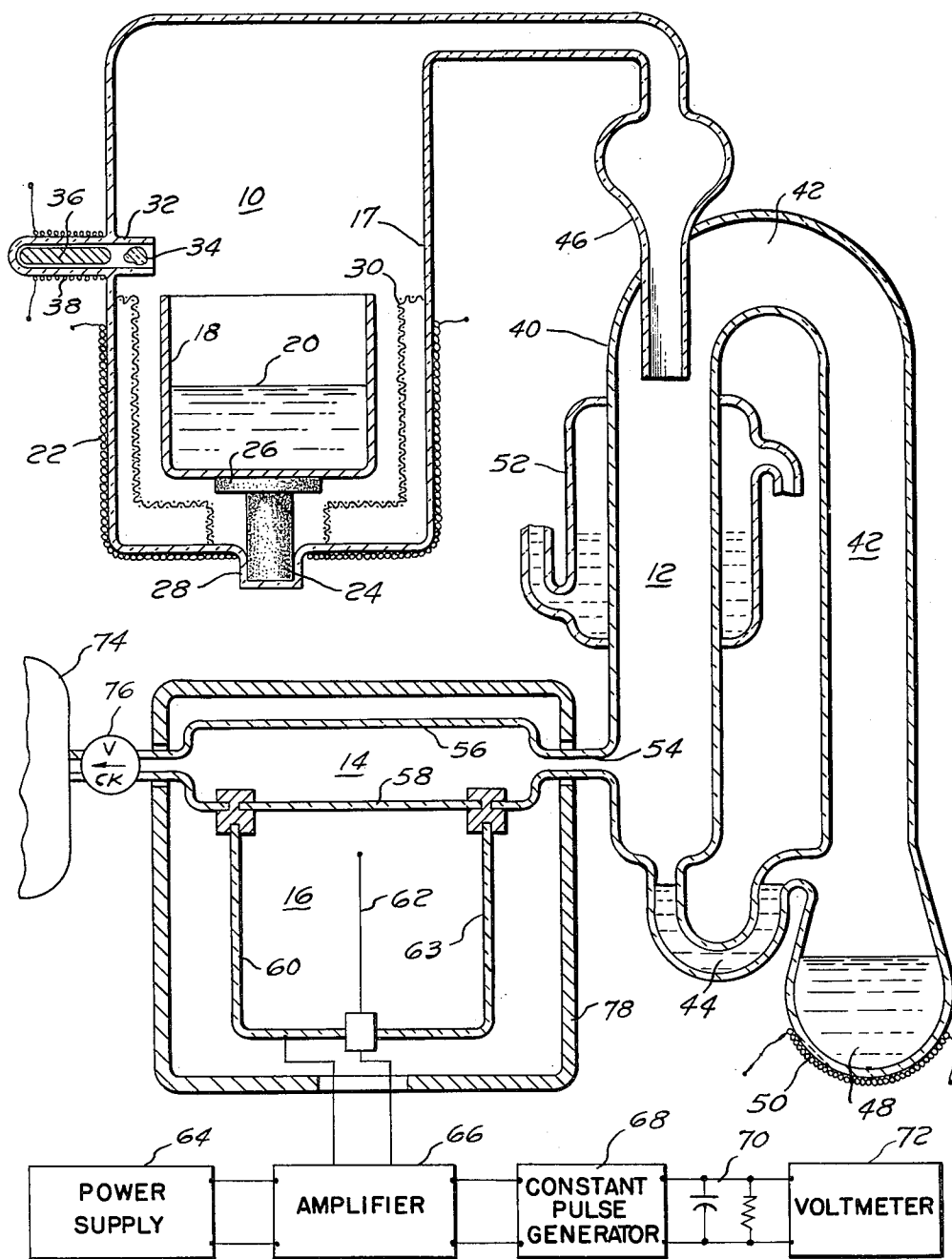
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ANALYTICAL PROCESS AND APPARATUS

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ANALYTICAL PROCESS AND APPARATUS

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The present invention relates to chemical analysis and, more particularly, to processes and devices for analyzing an inorganic sample for oxygen content. Oxygen impurities may tend to adversely affect chemical and physical properties. For example, undesired oxygen affects ductility in chromium and affects transistor characteristics in silicon. It is possible to determine the oxygen content of an inorganic sample by fusing the sample in the presence of carbon for the purpose of converting a proportion of the oxygen content to carbon monoxide and measuring its concentration. However, usually the sample to be analyzed for oxygen content is small and the resulting carbon monoxide is difficult to handle conveniently. For example, one gram of beryllium having an oxygen content of 10 parts per million would provide only .02 cubic centimeter of carbon monoxide at standard temperature and pressure. Prior microanalytic techniques, e.g., selectively freezing or absorbing the carbon monoxide from the gaseous mixture containing it and measuring volumetric change, have been too cumbersome, slow and inaccurate. The present invention contemplates a rapid process and an automatic apparatus that do not involve precision volumetric measurements, that are not subject to operator judgment and that are adaptable to a wide range of sample sizes.

The primary object of the present invention is the microanalysis of a chemical sample for oxygen by novel processes and devices that involve saturating a fused material including a chemical sample with carbon, of which a proportion is radioactive, and measuring the total amount of resulting carbon monoxide by a radiation counter.

Another object of the present invention is to saturate the fused material with a carbon concentration, of which a proportion is radioactive, by contact with a solid component comprising this concentration.

Other objects of the present invention in part will be obvious and in part will appear hereinafter.

The invention accordingly comprises the several steps and the relation and order of such steps with respect to each of the others, and the apparatus possessing the features, properties and relation of elements, which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the present invention, reference should be had to the following detailed description taken in connection with the accompanying drawing wherein an apparatus for effecting a process is illustrated in accordance with the present invention.

In the process of the present invention illustrated specifically herein the oxygen content of an inorganic sample is determined as follows. The sample is dissolved in a liquified inorganic solid bath that is saturated by contact with solid carbon having radioactive carbon (C^{14}) to normal carbon ($C^{12}+C^{13}$) in a predetermined ratio. The oxygen of the sample is reacted with the carbon of the bath to form carbon monoxide including radioactive carbon monoxide (C^*O) and normal carbon monoxide (CO) in a predetermined ratio. Since C^{14} is chemically identical to C^{12} and C^{13} , the initial predetermined ratio $C^{14}/(C^{12}+C^{13})$ is the same as the final predetermined

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ratio C^*O/CO . The surface of the bath is subjected to a vacuum which causes the carbon monoxide to vaporize substantially completely and permits the carbon monoxide to be collected. C^{14} emits β particles with a 0.15 mev. maximum energy and has a 5200 year half life. The activity of the carbon monoxide is measured with a detector that counts the number of β particles emitted per unit time. The original concentration of oxygen in the sample is a function of the activity so determined and the predetermined ratio C^*O/CO . The output of the detector is a direct indication of the concentration of oxygen in the sample.

The liquified solid solvent may be composed of any of a wide variety of low vapor pressure metallic and metalloidal elements and compounds having finite carbon solubility, i.e. .01–4.0% by total weight, and having oxides that are unstable at the pressures and temperatures employed in the system. These materials include, for example: the metallic and metalloidal elements of groups I, II, III, IV and VII of the periodic table of chemical elements, e.g. gallium, germanium, tin and particularly the noble metals, including ruthenium, rhodium, palladium, osmium, iridium, gold and silver; and metallic and intermetallic compounds embodying at least in part the aforementioned elements, e.g. indium antimonide and gallium phosphide. In general the temperature of the solution is that required to ensure the formation of carbon monoxide, e.g. 1000–1700° C. and the ambient pressure range, e.g. 10^{-17} – 10^{-7} mm. Hg is that required to ensure substantially complete vaporization of the carbon monoxide. Although the process of the present invention can be performed by fusing the sample without dissolution in a bath, best results are obtained when the sample is dissolved in the bath in a concentration of at most 10% by total weight.

In the foregoing process, the sample is dissolved in a liquid inorganic solid bath that is saturated by contact with solid carbon having a predetermined $C^{14}/(C^{12}+C^{13})$ ratio. Carbon saturation can be accomplished most advantageously in a crucible, at least the inner lining of which is composed of a carbon material having this predetermined $C^{14}/(C^{12}+C^{13})$ ratio. In one form, the crucible or the liner for the crucible is produced by molding and baking a mixture of amorphous C^{14} and amorphous $C^{12}+C^{13}$ containing a binder in the form of an organic material such as paraffin or an inorganic material such as clay. The binder either volatilizes or remains as the carbon particles sinter to form a homogeneous solid. In other forms, the crucible is composed of a carbon compound, for example a carbide such as silicon carbide of which a proportion of the carbon content is radioactive. For best results the crucible or crucible liner weighs from 1 to 100 grams and ranges in radiocarbon activity from 0.1 to 1000 microcuries per gram of carbon content.

The drawing discloses, in accordance with the present invention, a system comprising a vaporizing region 10, an evacuating region 12, a collection region 14, and a detecting region 16. The components of these regions are confined by and supported within the hermetically sealed communicating components now to be described.

Vaporizing region 10 is defined by jacket 17. Within jacket 17 is a crucible 18 containing a predetermined quantity of an inorganic solid 20 to serve as a liquified solvent. Surrounding jacket 17 is a radio frequency induction coil 22 for heating solid 20 to the liquid state and agitating it to ensure dissolution of the sample rapidly and completely in a manner to be described below. Preferably the radio frequency current in induction coil 22 ranges from 10×10^3 to 10×10^6 cycles per second, lower frequencies being conducive to increased agitation.

Crucible 18 is composed of one of the radioactive carbon materials described above, having a $C^{14}/(C^{12}+C^{13})$ ratio of 10 microcuries per gram of carbon content.

In order to isolate crucible 18 thermally from adjacent remaining components of the system, which are at relatively low temperatures, crucible 18 is supported by a rod 24, the upper end of which is of increased diameter as at 26, to support the crucible and the lower end of which projects into a well 28 depending from the base portion of jacket 17. Rod 24 serves as an insulating support to prevent the conduction of heat from crucible 18 to the base of jacket 17. A radiation shield 30, that blocks radiation directed outwardly from crucible 18 to jacket 17, has a dished conformation that generally surrounds crucible 18. The upper free edges of the conformation are outwardly flanged for the purpose of centering the conformation within jacket 17 and the base of the conformation has a circularly flared opening through which rod 24 may be seated in well 28. Shield 30 is characterized by interrupted metallic portions, for example, has a spiral strip construction, of which the successive substantially isolated convolutions provide only short conducting paths. This shield, although substantially unheated by eddy currents generated by induction coil 22, is capable of reflecting the bulk of thermal radiation emanating from liquified solvent 20.

Projecting through tubular jacket 17 is a tube 32 composed of the same material as is the jacket. The outer end of tube 32 normally is sealed. The inner end of the tube, which is open, projects substantially to a point in superposition above the edge of crucible 18. At the open inner end of tube 32 may be placed a specimen 34, the oxygen content of which is to be determined. In the remainder of tube 32 is a magnetic slug 36, which when actuated by a solenoid 38, propels specimen 34 from the open end of tube 32 into liquified solid 20 for dissolution. Slug 36 is encased in glass for the purpose of preventing any chemical reactivity between the slug and the remainder of the system. When specimen 34 dissolves in bath 20, its oxygen combines with the carbon of bath 20 to form carbon monoxide. This gas is exhausted from vaporizing region 10 through evacuating region 12 into collecting region 14. Since the mean free path within vaporizing region 10 is thousands of times the size of the vaporizing region it is virtually certain that once a carbon monoxide molecule has left the bath it will not see another molecule in the vaporizing region. Therefore, any gettering action of other vaporized portions of the sample will not take place until collecting region 14 has been reached. Any gettering action which might take place there is of no importance since collecting region 14 nevertheless would contain all the carbon atoms that combined with the oxygen atoms initially in the bath.

Evacuating region 12 is provided by a mercury diffusion pump 40. Pump 40 provides a mercury vaporizing region 42, which communicates with evacuating region 12 freely at 42 their upper extremities and through a mercury trap at 44 their lower extremities. A conduit 46 from vaporizing region 10 protrudes into the upper extremity of evacuating region 12. A mercury reservoir 48 is heated by a coil 50 at the lower extremity of mercury vaporizing region 12. In operation, mercury vapor is directed up through mercury vaporizing region 42, past conduit 46 and down through vaporizing region 10. The mercury vapor entrains carbon monoxide and other molecules from conduit 46 and is liquified by a water cooling jacket 52. The carbon monoxide molecules are exhausted into collecting region 14 through a conduit 54.

Region 14 is defined by a tube 56, one wall 58 of which may constitute the window of a β counter tube 60 of the Geiger-Müller type. This window is either mica or aluminum and has a low enough mass per unit area to prevent undue absorption of β rays emitted by carbon monoxide molecules in collecting region 14. Any such absorption

is accounted for in the measuring components to be described below.

Counter tube 60, itself, is filled with a gas mixture, such as argon-ethanol, which enables counting of the β rays with optimum efficiency. In conventional fashion, counter tube 60 includes an anode 62 and a cathode 63 in the form of a metal housing, which are operatively connected to a suitable electrical measuring system including a power supply 64, an amplifier 66, a constant pulse generator 68, a filter 70 and a voltmeter 72. The counting rate, corrected for background radiation β ray absorption by window 58, counter tube geometry, and the $C^{14}/(C^{12}+C^{13})$ ratio of crucible 18, directly indicates the total number of carbon monoxide molecules evolved from sample 34 during fusion. Alternatively, a scintillation counter utilizing a suitable phosphor or other fluorescent material may be employed. The presence of other gases does not affect the carbon monoxide activity appreciably. The system initially is evacuated and outgased by connection to a mechanical pump 74 through a stop-cock 76, which then is closed to permit the apparatus to operate under hermetic conditions during analysis. A shield 78 tends to isolate the collecting region and counter from stray radiation.

Example

The lower limit of oxygen content that reasonably can be measured in the disclosed system is indicated by considering a sample 34 composed of beryllium weighing one gram of which 10 parts per million (0.0018% by total weight) is oxygen on an atomic basis. This sample is fused in a bath 20 composed of 50 grams of platinum at 1400° C. under a pressure of 10^{-6} mm. Hg. Bath 20 is contained in a crucible 18 having a $C^{14}/(C^{12}+C^{13})$ ratio of 10^{-6} . A total of 6.6×10^{-17} carbon monoxide molecules are produced of a total of 6.6×10^{-11} C^*O molecules present. The 5200 year half life of C^{14} results in an activity of about 160 counts per minute for this amount of C^*O . Even if the counting efficiency is as low as 10%, 16 counts per minute are obtained. This counting rate is measurable with care since background counting rates are below this level. The conditions presented above represent the conservative lower limit of the oxygen level which can be determined in a one gram sample. Higher oxygen contents or larger samples would make measurement depend partly on the total number of counts recorded and partly on the experimental technique, viz. the degree to which outgasing of the system removes residual oxygen and water vapor from the walls, etc. With bath 20 consisting of 50 grams of metal, several samples of beryllium can be added to the bath before it becomes too contaminated for further use.

Since certain changes may be made in the above processes and devices without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted in an illustrative and not in a limiting sense.

What is claimed is:

1. A system for analyzing a chemical sample for oxygen, said system comprising a vaporizing assembly, an evacuating assembly, a collecting assembly and a detecting assembly, said vaporizing assembly including a jacket, a crucible within said jacket, a predetermined quantity of a liquified inorganic material within said crucible, a radio frequency induction coil surrounding said jacket for maintaining said inorganic material liquified, said crucible presenting a surface in contact with said liquified inorganic material, said surface being composed of a material containing carbon having a radioactivity of from 0.1 to 1000 microcuries per gram of carbon, a heat insulating support between said jacket and said crucible, a radiation shield surrounding said crucible within said jacket, means within said jacket for propelling a specimen into said liquified inorganic material, said evacuating assembly including a mercury diffusion pump for exhaust-

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ing gaseous products from said vaporizing system, said collecting system providing a conduit through which said gaseous products advance from said mercury diffusion pump and an auxiliary pump for continuously evacuating said conduit, said detecting system including a radioactivity counting unit contiguous with said conduit.

2. The system of claim 1 wherein said liquefied inorganic material is a metallic or metalloidal material having finite carbon solubility.

3. The system of claim 1 wherein said liquefied inorganic material ranges from 1000–1700° C. in temperature.

4. A system for analyzing a chemical sample for oxygen, said system comprising a vaporizing assembly, an evacuating assembly, a collecting assembly and a detecting assembly, said vaporizing assembly including a jacket, a crucible within said jacket, a predetermined quantity of a liquified inorganic material within said crucible, a radio frequency induction coil surrounding said jacket for maintaining said inorganic material liquified, said crucible presenting a surface in contact with said liquified inorganic material, said surface being composed of a material containing carbon having a radio-activity of from 0.1 to 1000 microcuries per gram of carbon, a heat insulating support between said jacket and said crucible, a radiation shield surrounding said crucible within said jacket, means within said jacket for propelling a specimen into said liquified inorganic material, said evacuating assembly including a pump for exhausting gaseous products from said vaporizing system, said collecting system providing a conduit through which said gaseous products advance from said pump for continuously evacuating said conduit, said detecting system including a radioactivity counting unit contiguous with said conduit, said liquified inorganic material being selected from the metallic and metalloidal materials having finite carbon solubility, said liquified inorganic material ranging from 1000 to 1700° C. in temperature.

5. A device for analyzing a high melting point compound for oxygen, said device comprising crucible means, a predetermined quantity of an inorganic material within said crucible means, said inorganic material being selected from the class consisting of the metallic materials and metalloidal materials characterized by finite carbon solubility, heating means for maintaining said inorganic material in the liquid state, solid carbon means in contact with said liquefiable means, at least a part of which contains a predetermined ratio of radioactive carbon to normal carbon, pump means for withdrawing carbon monoxide formed in said crucible means when a sample containing oxygen is dissolved in said inorganic material and radiation detection means for determining the activity of said carbon monoxide.

6. The device of claim 5 wherein said part possesses an activity of from 0.1 to 1000 microcuries per gram.

7. The device of claim 5 wherein said inorganic material possesses a carbon solubility of from .01 to 4.0%.

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8. The device of claim 5 wherein said inorganic material, when operative, ranges in temperature from 1000 to 1700° C.

9. A process for analyzing a chemical sample for oxygen, said process comprising liquefying at a predetermined temperature a predetermined quantity of an inorganic material selected from the class consisting of the metallic and metalloidal materials having a finite carbon solubility, contacting said inorganic material with a solid component having a predetermined ratio of radioactive carbon to normal carbon, dissolving an oxygen containing sample in said inorganic material, said elevated temperature being such that said carbon and said oxygen are reacted to form carbon monoxide, removing said carbon monoxide from said inorganic material and determining the activity of said carbon monoxide.

10. A system for analyzing a chemical sample, said system comprising housing means and in association therewith a vaporizing assembly, an evacuating assembly, a collecting assembly and a detecting assembly, said vaporizing assembly including a heating means, a crucible in association with said heating means, a predetermined quantity of inorganic material within said crucible, said crucible presenting a surface in contact with said liquefied inorganic material, said surface being composed of a material containing carbon having a radioactivity of from 0.1 to 1000 microcuries per gram of carbon, a heat insulating support between said housing means and said crucible, and means for propelling a specimen into said liquified inorganic material.

11. The system of claim 10 wherein said liquefied inorganic material is selected from the class consisting of metallic and metalloidal materials having a finite carbon solubility.

12. The system of claim 10 wherein said liquefied inorganic material ranges from 1000 to 1700° C. in temperature.

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