United States Patent

Goff

[15] **3,665,185**

[45] **May 23, 1972**

[54] ION SCATTERING SPECTROMETER WITH NEUTRALIZATION

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[52] U.S. Cl. .....**250/49.5 P**, 250/41.9 SE, 250/41.9 ME

[51] **Int. Cl.** **H01J 37/00**

[58] **Field of Search** .....250/49.5 P, 49.5 T, 49.5 R, 250/41.9 ME, 41.9 SB

[56] **References Cited**

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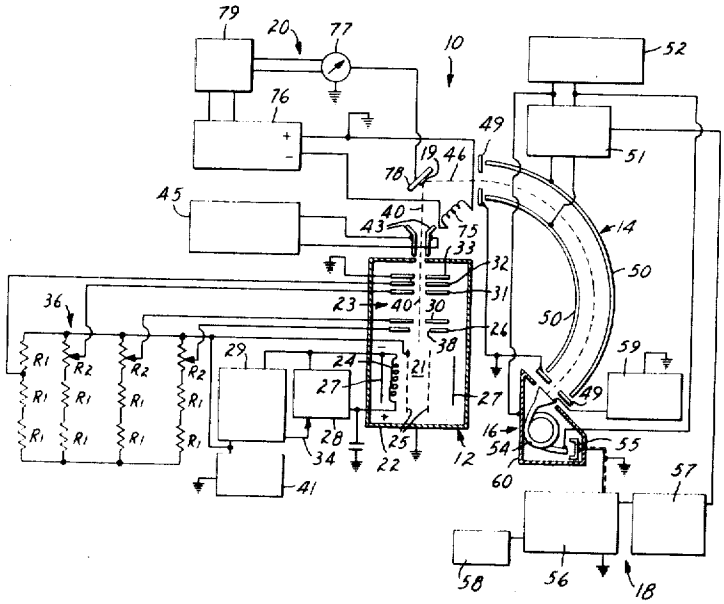
[57] **ABSTRACT**

Ion scattering spectrometer for elemental analysis comprising an ion generator, an energy analyzer, an ion detector, an indicating apparatus and a closed-loop feed-back device for neutralizing an electrically non-conductive target.

5 Claims, 5 Drawing Figures



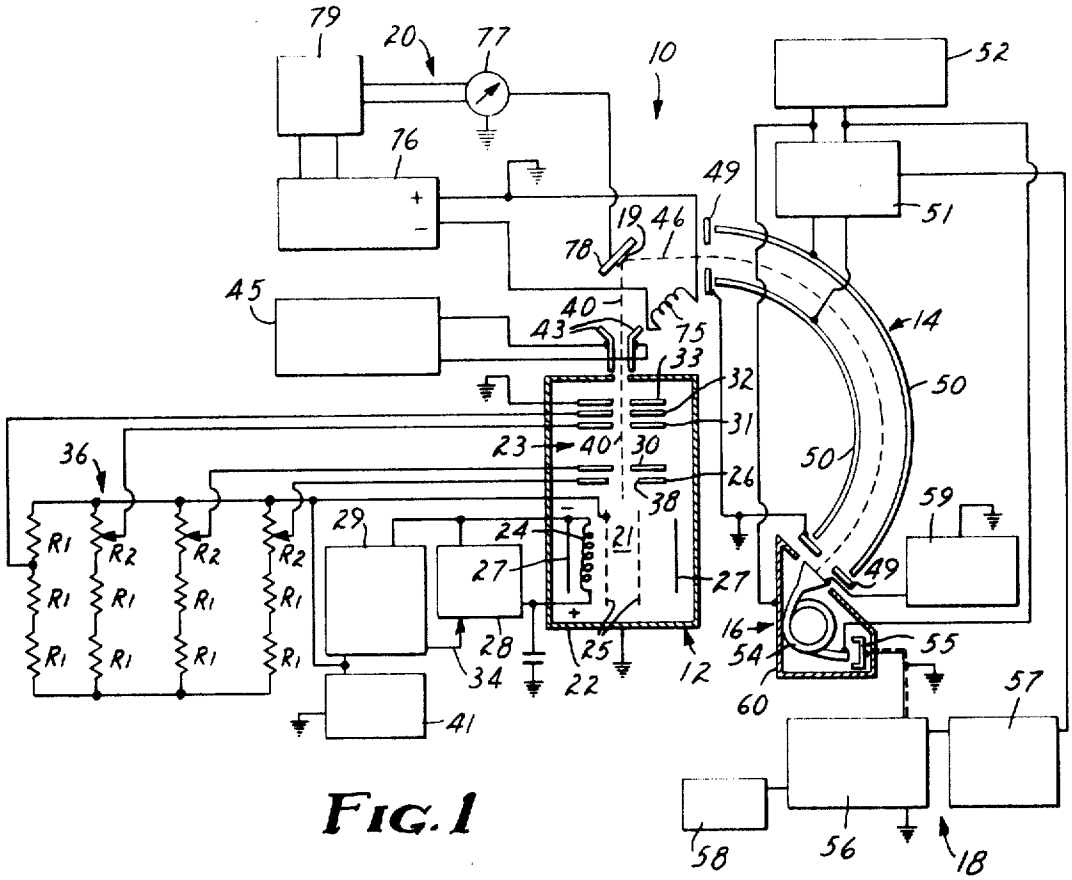


FIG. 1

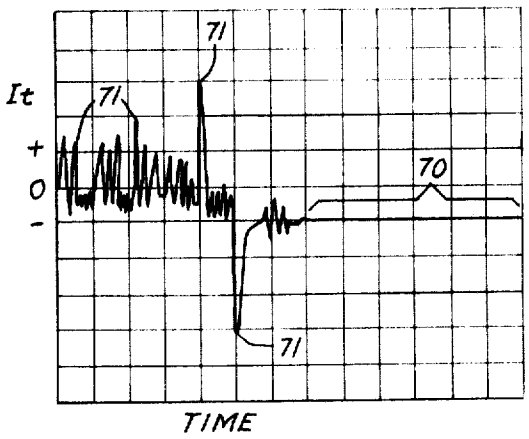


FIG. 2

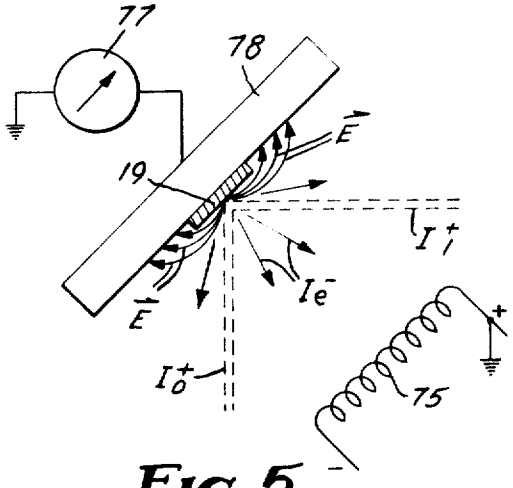


FIG. 5

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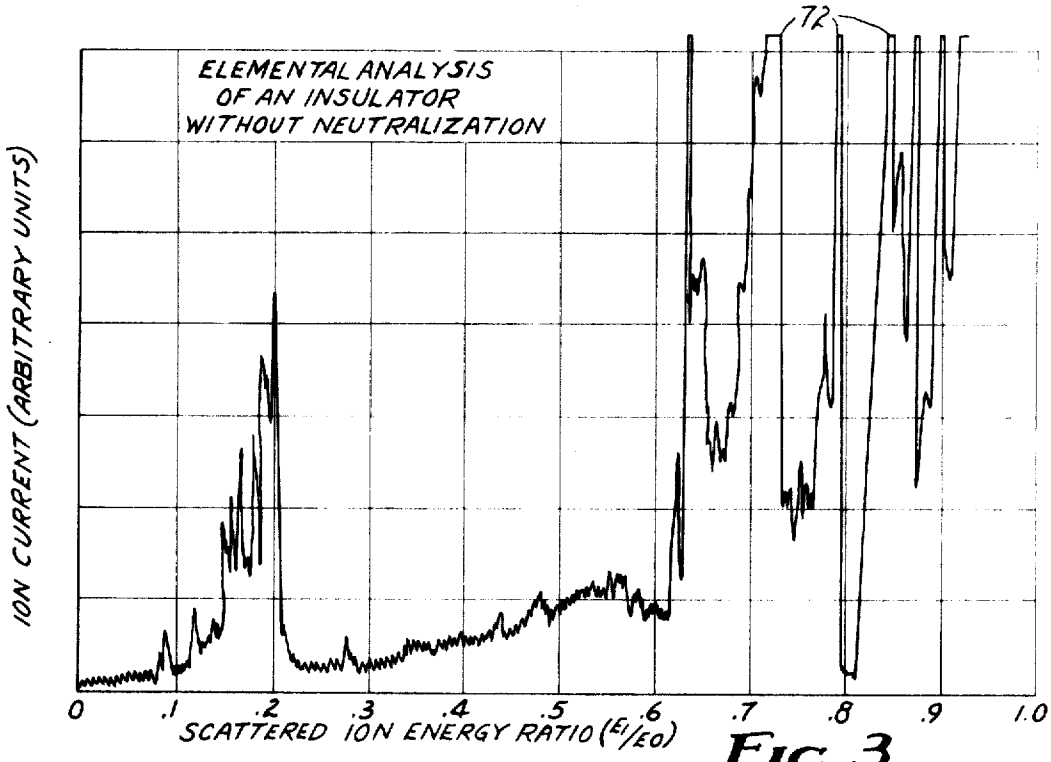

FIG. 3

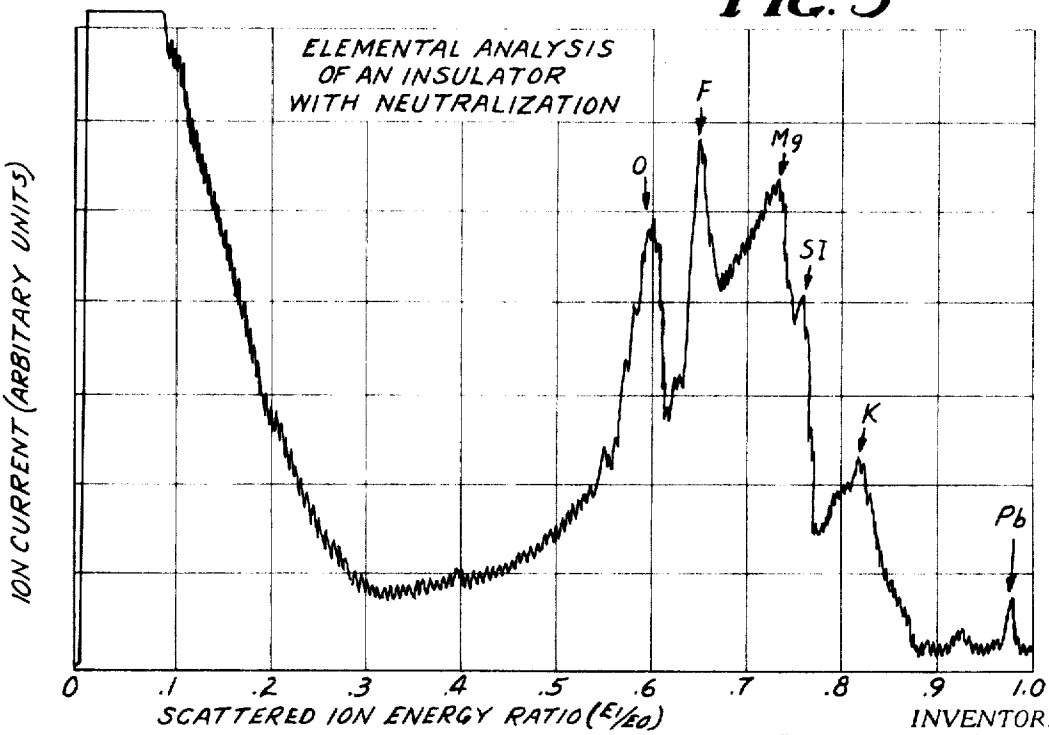

FIG. 4

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ION SCATTERING SPECTROMETER WITH NEUTRALIZATION

BACKGROUND OF THE INVENTION

Elemental surface analysis has many practical and important uses such as surface examination of photographic film emulsions, adhesives or semi-conducting surfaces wherein such surfaces often control the performance of the entire object. One known system, which provides essentially a bulk analysis of a specimen's surface, is the electron microprobe utilizing deeply penetrating electrons to provide, often unwanted, elemental analysis from the surface to a depth on the order of a micron (10,000 Angstroms). Obviously, such an apparatus can not be utilized when it is desired to analyze a single atomic layer of a specimen.

One surface analyzer, which can provide substantially non-destructive elemental analysis of a single atomic layer, is the ion scattering spectrometer of Smith, U.S. Pat. No. 3,480,774. In ion scattering spectrometry, a surface of a target is bombarded with a beam of noble gas ions and a fraction of the bombarding ions experience binary elastic collisions (scattered) with the surface atoms. Energy analysis of the scattered ions enables identification of the surface atoms. Hence, by recording the energy spectra of the scattered ions, surface atoms in the first atomic layer can be detected and identified. The binary elastic collision theory and formulation as taught by the Smith patent is based on the following assumptions. First, it is assumed that the target atoms are essentially unbound from their neighboring atoms. Thus, during collision the target atoms behave as independently as though they were gas atoms. Second, it is assumed that the target atoms are substantially stationary before collision with the primary ions. Third, the energy losses of the primary ions during collision with the target atoms are assumed to be completely kinetic. Based on these three assumptions and the principles of conservation of energy and momentum, a prediction of the post collision energies of the primary ions can be determined in terms of scattering angles, a mass ratio and precollision energies. Most importantly, this is accomplished without recourse to adjustable or empirical factors. The following equation for the kinetic energy ratio of the primary ion after collision to the primary ion prior to collision, and simplified by selection of the scattering angle $\theta = 90°$, becomes:

$$E_1/E_0 = (M_2 - M_1/M_2 + M_1), \text{ provided } M_2 > M_1$$

and when solved for M_2 yields:

$$M_2 = M_1 (1 + E_1/E_0)/(1 - E_1/E_0$$

where

M_1 = mass of primary ion

M_2 = mass of target atoms

E_0 = kinetic energy of primary ion prior to collision

E_1 = kinetic energy of primary ion after collision.

Some of the main components preferred for performing ion scattering surface analysis are: a monoenergetic ion source with good focusing properties at low energies, and energy analyzer capable of defining a precise scattering angle together with good energy resolution, an ion detector, a target holder to precisely position a specimen in a predetermined position for subsequent analysis. To increase the resolution at a given electrical signal level with a low energy scattering instrument it becomes critical to

1. minimize the ion energy spread within the ion beam,
2. to optimize the collimation and focusing of the ion beam prior to bombardment of the sample, and
3. to optimize the energy analyzer resolving power at a known scattering angle.

In obtaining the compromise between the desired high instrument resolution and an adequate electrical signal level it becomes advantageous to locate the ion generating means and the energy analyzer in close proximity to the sample being analyzed.

The Smith apparatus provides excellent elemental analysis of electrically conductive surfaces wherein the bombarding ions will not cause accumulative charging of the target. However, if the target is an insulator, the bombarding ions of the Smith apparatus will cause accumulative charging of the target to disrupt and prevent elemental surface analysis of the insulator.

Prior to the present invention, it has not been possible to elementally analyze the outermost surface of an insulator with an ion scattering spectrometer. Also, prior to the present invention, it has not been possible to perform a depth-profile analysis of an insulator. Many electrically non-conductive specimens are composed of successive sub-layers of differing elemental compositions wherein it could be of fundamental importance to now obtain a depth profile elemental analysis of the thin film layered specimen by analyzing successive atomic layers, layer by layer, of the specimen. In such an analysis, the elemental differences between individual atomic layers may be separately analyzed. For example, an elemental profile analysis of a single egg cell wherein it might be possible to freeze a single ovum with the extraneous membrames and cleave its entire plasma membrame down its center allowing one to evaluate separately the inner surface of the outer leaflet and the outer surface of the inner leaflet might provide important scientific information concerning the atomic arrangement of the cell. Another situation wherein monolayer elemental analysis of insulating surfaces may be of fundamental importance is the study of etiology and metastasis of cancer which in recent years has become a major concern of membrame biologists that have achieved some progress in cataloguing biochemical and physiological differences in the membrames of cancer cells and normal cells. However, these present achievements still suffer from the serious deficiency that no one is quite sure how atoms are arranged architecturally in the membrames of any cell, normal or cancerous. Presently, differences between junctional complexes and normal cancer cells are of prime interest, but discussion of these differences are also of serious deficiency because no published theory of membrame structure is even remotely capable of predicting an electrical event that occurs at junctions between normal cells, and is even less capable of predicting why some cancer cell junctions somehow behave differently. This major gap of knowledge concerning normal cells and especially of the peculiarities of the molecular architecture of cancer cell membrames is a serious detriment to the understanding of the disease.

THE PRESENT INVENTION

The apparatus of the present invention utilizes an ion surface analyzer such as disclosed by the Smith patent and incorporates therewith a device for neutralizing the accumulative charging of the target to permit elemental surface analysis of electrically non-conductive (insulating) specimens such as frozen biological tissue. Thus, the elemental analyzing apparatus of the present invention includes an ion generating means to produce a monoenergetic beam of primary ions and to direct the primary ions along a preselected path toward a target, an energy analyzer to receive primary ions scattered from the surface of the target and selectively transmit scattered primary ions having a preselected kinetic energy value throughout an energy spectrum to an ion detector means for conversion of the transmitted ions into an electrical signal. Neutralization means located adjacent to the target supplies electrons to impinge upon the target and thus neutralize an accumulated charge on the target caused by the bombarding primary ions.

The present invention also includes a method for analyzing the elemental composition of a target by generating a monoenergetic ion beam of noble gas primary ions, directing the ion beam along a preselected path to bombard a monolayer of the target, selectively transmitting scattered primary ions having preselected kinetic energy values, throughout an energy spectrum, and converting the transmitted ions into an electrical signal. The method also includes neutralizing the accumulative charging of the target by provid-

ing a supply of electrons to impinge upon the target and thus neutralize the accumulated charge caused by the primary ions bombarding the target.

This invention will become better understood by reference to the following detailed description when considered in connection with the accompanying drawings wherein like numerals designate like parts throughout the figures and wherein:

FIG. 1 is a block diagram and a partial pictorial schematic diagram illustrating the elemental analyzing apparatus constructed in accordance with the present invention;

FIG. 2 is a graph illustrating sporadic target current versus time when an insulator is being examined without neutralization;

FIG. 3 is a graph illustrating ions scattered from an insulator without neutralization;

FIG. 4 is a graph illustrating elemental analysis of an insulator, with neutralization, showing elemental identification of the insulator as including oxygen, fluorine, magnesium, silicon, potassium, and lead; and

FIG. 5 is a diagrammatical representation of primary ions bombarding a target, subsequent accumulative charging of the target and neutralization of the accumulated charge.

In the accompanying drawings and description of the present invention, and referring in particular to FIG. 1, there is shown an elemental analyzing apparatus **10** including an ion generating means **12**, an energy analyzer **14**, and ion detector **16**, and indicating apparatus **18**, and neutralization means **20**.

The elemental analyzing apparatus **10** is contained within a vacuum chamber (not shown) and a vacuum pump (not shown) evacuates the chamber to a pressure of 10^{-9} Torr. A getter (not shown) is positioned within the chamber to further purify the active elements remaining in the chamber. After the chamber reaches the desired vacuum pressure of 10^{-9} Torr, the evacuation is discontinued by the closing of a vacuum line valve and a noble gas is released into the chamber, by suitable valves, until the static pressure is increased to approximately 5×10^{-5} Torr, as measured on Bayard-Alpert type pressure gauges. All openings to the chamber are then closed and the noble gas atmosphere within the chamber is ionized to produce primary ions which are utilized in the analysis of the elements forming a surface of a specimen or target **19**. Although any noble gas could be used herein, the analyzing apparatus **10** can identify only all elements of mass greater than the mass of primary ions and because of this factor, low atomic mass elements of Helium (He) and Argon (Ar) are commonly used.

The ion generating means **12** comprises a grounded tubular housing **22** adapted to support the operative components of the ion generator **23**. The ion generator **23** includes a heated filament **24** for producing electrons, a highly transparent cylindrical grid **25**, having greater than 80 percent open area, an extractor plate **26** and a tubular repeller **27** encircling the filament and grid.

The filament power supply **28** powers the filament to produce electrons and a grid power supply **29** biases the grid **25** with respect to the filament **24**. The produced electrons from the filament **24** are accelerated, by the relatively transparent grid **25**, to a potential sufficient to ionize the noble gas atoms within the ionization region **21**. The repeller **27** is at filament potential and repels or deflects any approaching electrons to result in a long electron path which increases the probability of the electrons striking an atom of the gas to ionize the gas atom. The ions formed by electron bombardment of the inert gas within the cylindrical grid **25** are extracted axially by first, second, third and fourth anode plates **30, 31, 32, 33**, respectively, and form a primary ion beam (of a current Io^+, see FIG. **5**) of a nominal 1 mm diameter throughout an operating range of 300 – 3,000 eV. In a typical analysis of a specimen, with an electron ionization current of 10 mA at 125 eV, a 1,500 eV He+ ion beam yields a target current of 150 nanoamps at an indicated He pressure of 5×10^{-5} Torr.

The ion beam current Io^+ is directly proportional to the static pressure of the noble gas within the evacuatable chamber and the electron current of the ion generator **23**. Since it is impractical to control the ion beam current Io^+ by controlling the static pressure of the noble gas, the noble gas is maintained at a relatively constant gas pressure and the electron current is regulated to control the ion beam current Io^+. A feed-back stabilization loop **34**, established between the filament power-supply **28** and the grid power-supply **29**, regulates the electron grid current to maintain a predetermined ion beam current throughout static pressure changes within the evacuatable chamber.

An ion gun voltage divider network **36** biases the extractor plate **26** to a potential to extract positive ions from the ionization region **21**. The network **36** includes nine R_1 fixed resistors each having a resistance of 470 kohms, three R_2 10 turn linear potentiometers of 500 kohms arranged in a series and parallel circuit to selectively bias the extractor plate **26** and the anode plates **30, 31**, and **32**, except the fourth anode plate **33** which is grounded.

The extractor plate **26** includes an extractor aperture **38** of about one-quarter inch (0.6 centimeters), located about the beam axis **40**, to initially extract and direct the positive ions into a beam. Each anode plate **30, 31** and, **32** has a controlling potential applied thereto from the network **36**. The first anode plate **30** is primarily used to control, modulate and initially focus the extracted ions into a collimated beam. The second anode plate **31**, which is spaced from the first plate **30** a distance greater than the spacing between the other plates, is the primary beam collimating and focusing anode. The third anode plate **32** is run at a substantially fixed potential from the voltage divider network **36** and the fourth plate **33** is at ground potential or could be connected to one side of a high voltage power supply **41** and biased with respect to ground. The anode plates **30, 31, 32** and, **33** are each formed with a small aperture and of very thin conductive material to control the ion flow and to maintain a monoenergetic beam. The plates are, for example, 0.010 inch thick to minimize the wall surface defining the apertures for minimizing of the interaction of the passed ions with the wall surface and loss of energy in the ions passing therethrough.

The primary ion beam passing out of the tubular housing **22** is now directed through a noble gas atmosphere a distance of less than 10 cm toward the surface of the target **19** to be analyzed. Ion perturbing collisions are estimated to limit the mean free path of ions at this pressure (5×10^{-5} Torr) to about 30 cm. A pair of deflector plates **43**, positioned near the end of the housing **22** and on opposite sides of the beam, serve to deflect the beam to scan the target **19**, such as during a sputtering-cleaning mode. The plates **43** are charged by an ion deflector power supply **45** and may be controlled either manually or programmed. The deflector plates **43** also help in optimizing the scattering angle or aligning the beam on the surface of the target **19** so the axis **46** of the scattered ions is aligned with the entrance diaphragm **48** of the energy analyzer **14** for electrical signal optimization.

When the primary ion beam from the ion generating means **12** bombards the surface of the target **19**, several events are believed to occur. One event is that a fraction of the primary ions are elastically scattered from the atoms that form the surface of the target **19**. These scattered primary ions, having a current I_i^+, are received by the energy analyzer **14** for subsequent analysis. Other events caused by the bombarding primary ions will be discussed hereinafter.

The energy analyzer **14**, which receives the scattered primary ions, comprises a grounded entrance diaphragm **48** spaced about one centimeter from the surface of the target **19** and includes a rectangular entrance slit (long and narrow), a grounded exit diaphragm **49**, having a rectangular exit slit, and two curved electrostatic analyzer plates **50**.

The analyzer plates **50** are charged by the output from an analyzer plate sweeping power supply **51** receiving power from a dual power supply **52**. The analyzer plate sweeping

power supply 51 permits a suitable charge to be applied to the plates to direct ions having a predetermined mass and energy through the slit in the exit diaphragm 49. The analyzer plates 50 have a mean radius of 2 inches. The illustrated energy analyzer 14 is a standard 127° electrostatic analyzer.

The scattered primary ions are thus received from the surface of the target 19 by the energy analyzer 14 and the ions having a predetermined energy value are transmitted therethrough. The number of ions with a preselected energy value being passed by the analyzer 14 are quantitatively detected by the ion detector 16. An electronic signal generated by the ion detector 16 is received by the indicating apparatus 18, and the data is obtained to permit the analysis.

The ion detector 16 converts the transmitted ions into an electron signal, and further amplifies that electron signal with gains typically of 10^6 electron gain. This pulse electron signal is collected by the collector 55 which has a shielded lead into the pulse counting circuit 56. The pulse counting circuit 56 primarily consists of a pulse preamplifier and other various pulse shaping and counting electronics. The output of the pulse counting circuit 56 is fed into the Y axis of the XY recorder 57 (which will produce a graph as exemplified in FIG. 4) whereby the number of counts received at the input to the ion detector 16 are recorded. An oscilliscope 58 can be used to monitor the pulse electron signal entering the pulse counting circuit 56.

The electron multiplier 54 is powered by a stable high voltage power supply 59, and raises the input of the multiplier 54 to relatively high negative voltage (2–3kv) and thereby post accelerates the ions leaving the exit slit 49 of the energy analyzer 14. This post acceleration of the ions results in a much higher and constant ion detection efficiency at the multiplier input. The output of the multiplier 54 is biased negative from ground potential and thereby enables the electrons leaving the multiplier 54 to be accelerated toward the collector 55 which is near ground potential. The multiplier 54 and collector 55 are electrostatically shielded in an enclosure 60 to reduce any extraneous signal from entering the ion detector region. The electrostatic shielding enclosure 60 is biased positively with reference to ground.

Another event that is believed to occur when positive ions bombard an electrically insulating target is for the target to accumulate a positive potential sufficient to prevent subsequent ions from being elastically scattered from the target.

If the charging of the target 19 is not sporadic and if the target 19 does not accumulate a charge potential sufficient to prevent the ions from bombarding the target 19, then elastic scattering of the ions can occur and an energy spectrum with elemental identifying peaks could be produced; however, the shifting of the peaks resulting from the charging of the surface would cause difficulty in interpreting the spectrum. Commonly, an insulating material will exhibit sporadic charging and discharging as illustrated in FIG. 2 wherein target current I_t, is plotted against time. The target began sporadic charging and discharging, as shown by peaks 71, and then with neutralization remained constant as represented by the straight line portion 70 of the detected target current. The insulator used to illustrate sporadic charging and discharging of an insulator (FIG. 2) was Supramica 500 (available from Mycalex Corp. of America) and was also utilized in producing the graphs of FIGS. 3 and 4.

The energy spectrum with FIG. 3 illustrates the unmeaningful results produced by elemental surface analysis of an unneutralized insulating target having sporadic charging and discharging characteristics. The peaks 72 of FIG. 3 do not provide any known correlation between surface constitutents of the insulating target and the energy values of the ions scattered from the surface thereof.

When an insulating target is properly neutralized, as illustrated in FIG. 4, the energy spectrum will begin a zero energy and immediately climb to a high value. As the energy spectrum continues, specific peaks will identify the elements of the surface which for this target included oxygen (O), fluorine (F), magnesium (Mg), Silicon (Si), potassium (K), and lead (Pb).

The neutralization means 20 to FIG. 1 which permits analysis of an insulator, includes a flood filament 75 closely located and in line-of-sight between the target 19 and the filament 75, a charge neutralization power supply 76, a target ammeter 77 electrically connected to the metallic target holder and a neutralization feed-back resistive control circuit 79. Manual adjustment of a potentiometer within the control circuit 79 adjusts the neutralization power supply 76 to regulate the current into the flood filament to control the quantity of electron emitted by the filament which adjusts the current through the target ammeter 77. When a peak resulting from measuring the energy of sputtered ions is developed very close to zero on the energy scale as shown in FIG. 4, the positive charge has been neutralized to a preselected potential which is preferably ground potential. To automatically control the accumulated charge on the surface of an insulating target, the potentiometer is adjusted to obtain on the ammeter 77 a desired current reading (e.g., 150 nanoamps). The ammeter 77 provides a voltage output proportional to the measured ammeter current, which voltage output is sensed by the neutralization feed-back control circuit 79 for subsequent automatic adjustment of the power supply 76 which in turn controls the current flow through the filament 75 thereby ensuring stability in both the measured target current and surface potential. This closed feed-back system of the neutralization means 20 has important utility in the present invention since it is advantageous to precisely neutralize the charge on the surface of the target and not to flood an excessive amount of electrons toward the surface of the target. When precise neutralization is achieved by adjusting the neutralization power supply 76, the low energy peak shown in FIG. 4 will appear at a value of E_1/E_0 between 0 and 0.1. Over neutralization can disrupt and in general reduce the fraction of ions elastically scattered from the surface through neutralization effects on the primary and scattered ions. The neutralization feed-back control circuit 79 enables the correct amount of flood electron current to be precisely preselected and thereby maximize the elastically scattered ion signal used for the elemental analysis. This automatic feed-back system also provides stability in the surface charge state of the target. This stability exemplifies itself in a very stable scattered ion current and subsequent low noise detection of the ion scattering spectrum utilized for elemental analysis. The stable scattered ion current permits semi-quantitative elemental analysis of the surface of the target.

In a typical operation, it has been found desirable to place the flood filament 75 in close proximity to and in line-of-sight condition with the target 19 and target holder 78. Further, this line-of-sight condition permits the utilization of a low electric field between the flood filament and the target holder. This low electric field is established by grounding the positive side of the charge neutralization power supply 76 thereby establishing a slight electric field between the center of the flood filament 75 and the target holder 78 (essentially at ground). This low field (caused by a few volts on the flood filament relative to the target holder 78) causes the flood electrons to drift toward the target holder. The low field imposed on the target holder 78 enables the flood electrons to be preferentially attracted to any region of the target surface which exhibits a charge of only a few volts positive relative to the target holder at ground potential (see $\bar{E}$ of FIG. 5). If high field conditions were erroneously used, the charged regions on the surface of the target would have to compete with the high field established between the filament and target holder and inhibit complete neutralization of the target.

The amount of flood filament current needed for neutralization of an insulating surface will vary depending on the particular surface examined. This variation in the needed flood current, while using constant primary ion beam conditions, is believed to be primarily the result of variations in the emission of electrons from the surface under ion bombardment (gamma electrons, I_e^- of FIG. 5). The loss of these gamma electrons

tends to charge the surface positively and must be compensated for by an increased current flow from the flood filament. The advantage of the neutralization feed-back circuit is that under these changing conditions of electron emission (such as might be encountered in a depth profile analysis of a composite material), the predetermined neutralization will automatically compensate for these changes in the emission of gamma electrons.

While one embodiment has been described in detail, it is appreciated that this was for the purpose of illustration and that additional embodiments could be made without departing from the spirit and the scope of the invention as set forth in the appended claims.

What is claimed as the invention is:

1. An elemental analyzing apparatus adapted to fit within an evacuatable chamber, said apparatus comprising:

a. an ion beam generating means for producing and focusing a monoenergetic beam of noble gas primary ions;

b. an electrically conductive target holder positioned relative to said beam generating means to support a target in the path of a said beam to have the ions of said beam impinge on a surface of said target;

c. energy analyzing means positioned adjacent said target to receive primary ions scattered elastically from an atomic monolayer of a said surface for selectively transmitting the received scattered primary ions having a preselected energy value throughout an energy spectrum;

d. ion detector means for converting the transmitted ions into an electrical signal;

e. a filament means for emitting electrons, said filament means being disposed adjacent said target holder and in line-of-sight with a said target thereon;

f. power supply means for energizing the filament to emit electrons therefrom and to bias said filament negative with respect to said target holder; and

g. circuit means connected to said target holder for sensing a change in current flowing through said target holder as a result of the ion bombardment of an insulating target and the flow of electrons from said filament and for adjusting said power supply means to stabilize the current flowing through said target holder to a predetermined value whereby a said target surface is maintained at substantially the target holder potential.

2. An elemental analyzing apparatus according to claim 1 wherein said power supply means has the positive side connected to said target holder.

3. An elemental analyzing apparatus according to claim 2 wherein said circuit means includes ammeter means for measuring the current flowing through the target holder and for providing a voltage output proportional to the measured ammeter current, said ammeter means being connected to said target holder; and means connected to said ammeter means for adjusting said power supply means to maintain a low electric field between said filament, said target holder and said target surface, wherein electrons emitted from said filament are caused to drift toward positively charged areas on said target surface to maintain said target surface and the target holder at the same stable potential.

4. An elemental analyzing apparatus according to claim 3, wherein means are provided for maintaining said target holder and said positive side of said power supply at ground potential.

5. A method for the precise elemental analysis of a target of an electrically insulating material comprising the steps of:

a. generating a monoenergetic noble gas primary ion beam;

b. positioning a target on an electrically conductive target holder, positioned in the path of a said beam with a surface of said target in the path of said beam to impinge said beam of ions on said surface;

c. analyzing the energy of elastically scattered primary ions throughout an energy spectrum by selectively transmitting the scattered primary ions and producing an electrical signal by ion detector means detecting the transmitted ions;

d. energizing a filament disposed in line-of-sight relationship to said target to produce an electron current flow to said target holder and to place the filament potential at a few volts less than the target holder potential;

e. measuring said current flow through said target holder; and

f. adjusting the current flow through the filament in response to changes in the current flowing through the target holder to neutralize any charges accumulated on the surface caused by ion impingement, and to maintain the target surface and the target holder at the same stable potential.

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