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APPARATUS FOR ANALYZING MATERIAL BY EXCITED X-RAYS

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3 Sheets-Sheet 1

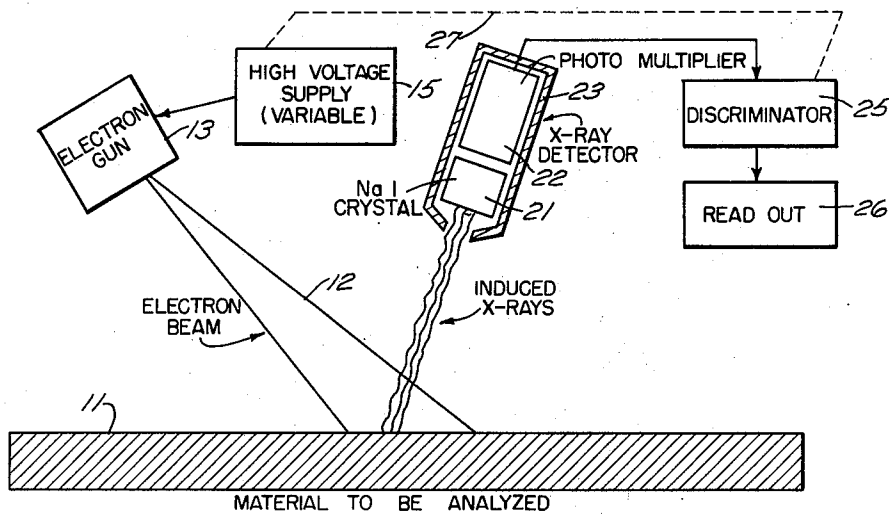


FIG. 1

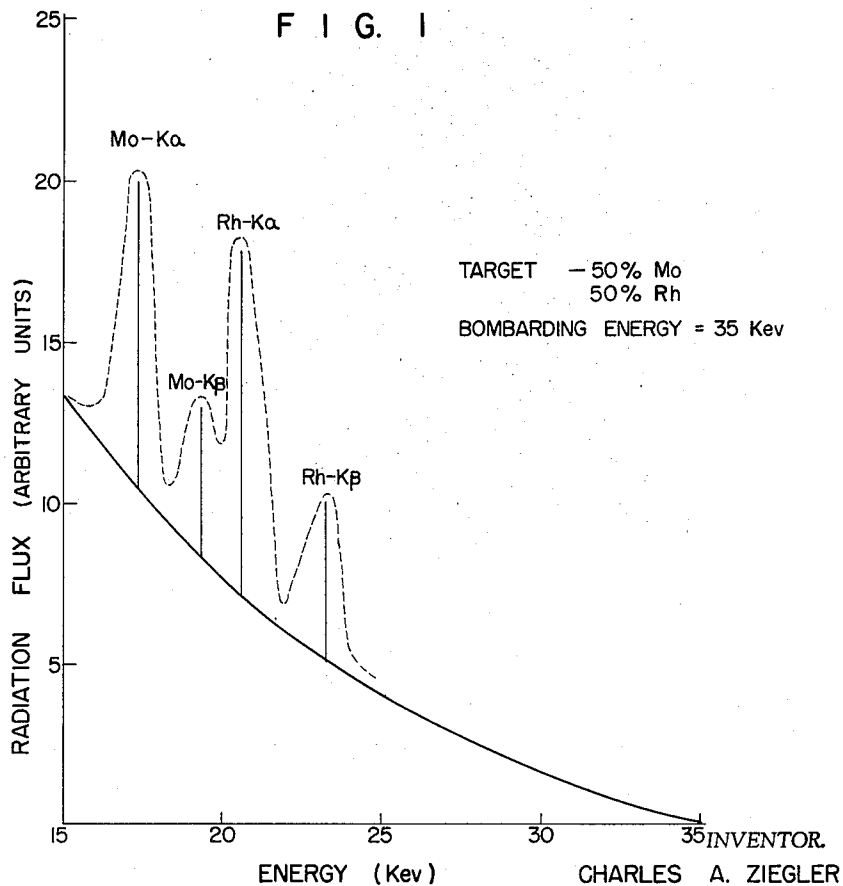


FIG. 2

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3 Sheets-Sheet 2

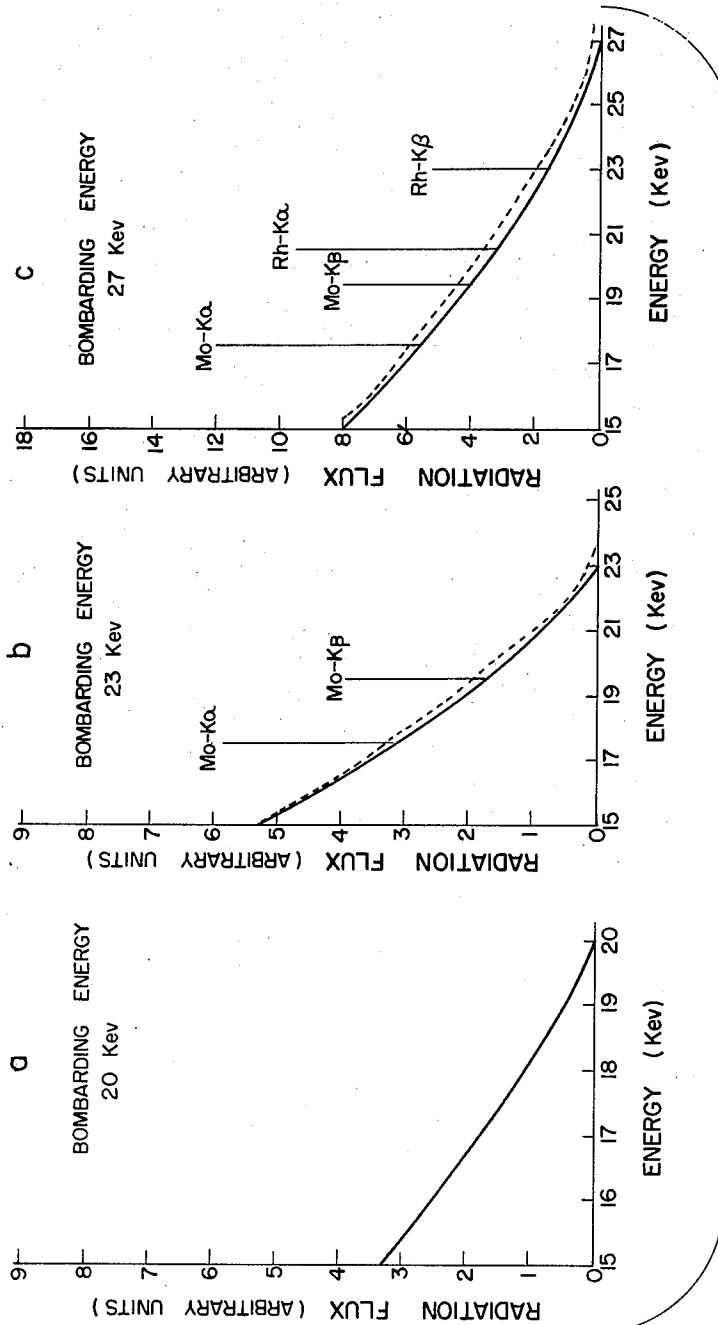


FIG. 3

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3 Sheets-Sheet 3

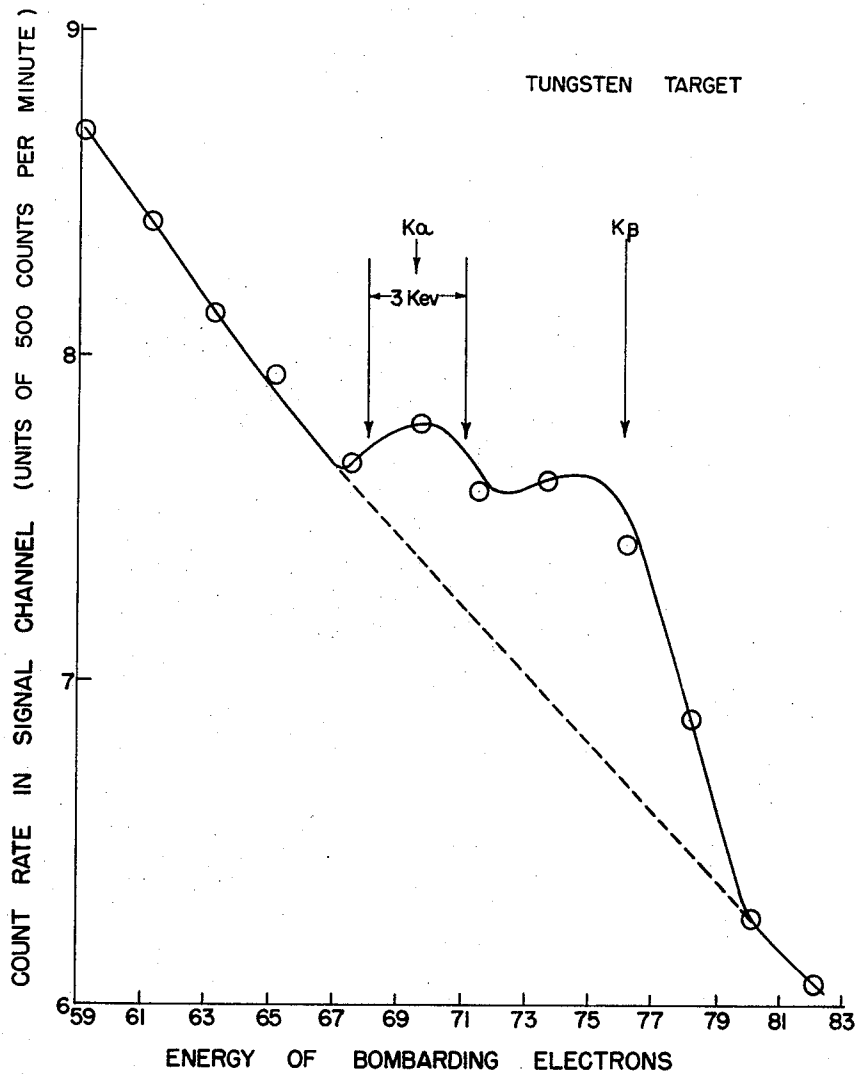


FIG. 4

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APPARATUS FOR ANALYZING MATERIAL BY EXCITED X-RAYS

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This invention relates in general to X-ray spectroscopy and, more particularly, to an X-ray spectrometer for composition analysis of materials.

Analysis of the composition of the surface of material, both qualitatively and quantitatively, by means of electron probe analysis is a well known technique. In this technique, an electron beam is directed at the surface to be analyzed and the characteristic X-ray line spectrum caused by the bombarding of electrons is examined. The energy of the emitted X-rays is related to the atomic number of the material being bombarded and, hence, is indicative of the material. This relationship between atomic number and X-ray energy arises from the nature of the emission process for characteristic, or fluorescent, X-rays. Thus, if an atom of material is supplied with sufficient energy, a K electron may be expelled from the K shell of the atom. This vacancy in the K shell is filled immediately by an electron from the L, M or N shell whose place in turn is taken by an electron from one of the higher energy shells. In this way, the atom, to which the energy has been supplied, returns in steps to its original ground state, each such step being accompanied by the emission of an X-ray of corresponding energy. The series of energies (or wave lengths) for electron transition terminating in the K shell is referred to as the K series, and its main spectral lines are designated K_α and K_β to indicate whether the electron has come from the L or M shell respectively. In similar fashion an L and M series are defined. The energies of the K_α lines for elements from Mg to U range from 1.25 to 98.43 kev. The energies are determined only by the energy shells of the atoms and are independent of the chemical or physical state of the atoms. An almost linear relation exists between the reciprocal of the wave lengths of the lines of a characteristic series and the square of that number which is one less than the atomic number of the atom emitting the X-rays. Thus, an analysis of the energies of the emitted X-rays from a material may be used to determine the chemical composition of the material. The energy for exciting the material to emit the characteristic X-rays may be supplied either by bombardment by electrons or by irradiation with high energy X-rays.

The analysis of the energies of the emitted X-rays is accomplished by means of an X-ray spectrometer. The merit of an X-ray spectrometer may be measured by its ability to distinguish between two adjacent energy lines. One technique which has been employed as the basis of a spectrometer is the dispersive technique. In this method, the spectrum of characteristic X-ray photons is allowed to fall upon a diffraction grating, usually a crystal, which then disperses the photons in various directions according to their energy. Thus, if an X-ray detector is placed at a specific angle with respect to the crystal, it provides a measurement of virtually a single wave length of X-rays.

In this method, the radiation detector itself need have no energy resolving power.

Another technique which has been employed utilizes a detector such as a proportional counter or a sodium iodide crystal whose output is directly indicative of X-ray energy. The dispersive technique provides excellent resolution over a wide range of energy. However, it requires elaborate mechanical equipment and is subject to instability caused by mechanical vibrations and tem-

perature variations. Furthermore, it is highly inefficient. The second technique does not provide adequate resolution over the energy ranges generally demanded by analytical work. Typically, a proportional counter will provide a resolution of 6 to 8% for photon energies up to about 10 kev., while sodium iodide detectors provide about an 8% resolution at 700 kev., but the resolution deteriorates to 25% at 70 kev. and becomes even worse at lower energies. Thus, in the important energy region between 10 and 70 kev., the characteristics of these detectors provide a severe limitation on their use for even qualitative X-ray fluorescent composition analysis.

It is, therefore, a primary object of the present invention to provide an X-ray spectrometer capable of providing high resolution over a wide range of energies.

It is another object of the present invention to provide an X-ray spectrometer of the non-dispersive type capable of distinguishing between two adjacent energy lines in the region between 10 and 70 kev.

It is still another object of the present invention to provide an efficient, economic, rugged, high resolution X-ray spectrometer for analysis of the composition of materials.

It is still another object of the present invention to provide a method of X-ray fluorescence composition analysis which operates over a wide range of energies and which does not require a dispersive type of X-ray spectrometer.

Broadly speaking, the spectrometer of the present invention employs an electron beam to bombard the surface of the material to be analyzed in order to produce X-rays. The produced X-rays are detected by means of a sodium iodide crystal or proportional counter. The output pulses from the sodium iodide crystal or proportional counter are applied to an electronic pulse height discriminator which will only pass pulses of a predetermined amplitude. The pulses passed by the discriminator are then applied to a readout device, such as a scaler or rate-meter. The accelerating voltage of the electron beam which controls the energy of the incident electrons is synchronized with the lower gate of the electronic pulse height discriminator. The overall effect, as will be described in more detail below, is that the total system provides excellent energy resolution despite the fact that the inherent energy resolution of the X-ray detector itself is insufficient to provide adequate spectroscopy. In order to provide a clear understanding of the principle of operation of this apparatus, the generation of characteristic radiation in the material will first be discussed in a quantitative fashion.

In the case of an electron beam incident upon a target material, the emission of characteristic X-rays is affected by the accelerating voltage of the electrons in the following manner:

(1) If the electron accelerating voltage, V , is less than V_0 , then the characteristic line emission is nil, where V_0 is that voltage at which

$$V_0 \times e = h \times a$$

where e is the electronic charge, h is Planck's constant and a is the frequency of the absorption edge of the target atoms.

(2) If the electron accelerating voltage, V , is greater than V_0 , α and β lines of the K characteristic radiation are emitted. The intensity of these lines increases with increasing V according to the relation

$$I = C(V - V_0)^n$$

where C is a constant and n is a constant nearly equal to 2 over a wide range of target elements and voltages.

(3) The spread in energy between the critical absorption energy and the energy of the emitted K_α and K_β radiation becomes larger as the Z of the target increases.

The above factors control the emission of characteristic X-rays from the bombarded material. However, the bombarded material also emits X-rays not characteristic of the particular atom but due only to the rapid deceleration of the bombarding electrons. This latter type of radiation is proportional to the accelerating voltage and has an intensity which may be expressed as

$$I = K \left(\frac{E_m}{E} - 1 \right)^2$$

where E_m is the energy of the bombarding electrons and K is a constant depending on the target Z and the number of impinging electrons.

Thus the spectrum of energies emitted from the target material which is to be analyzed by the spectrometer consists of a superposition of the characteristic X-ray lines on top of the X-ray spectrum generated as a result of the deceleration of the incident electrons. If, then, the electron accelerating voltage is slowly varied from a low value to increasingly high values over the range necessary to excite the various characteristic lines that may be present in the material to be analyzed, then at any given value of V , no lines will be excited whose corresponding V_0 is greater than V . While all characteristic lines corresponding to a V_0 less than V will be excited, the pulse height discriminator is set to vary in synchronism with V such that its lower threshold is always only a small increment lower than V and, hence, only those characteristic lines giving rise to pulses lying near or within this incremental difference will be recorded.

Other objects and advantages will become apparent from the following detailed description when taken in conjunction with the accompanying drawing in which:

FIG. 1 is an illustration in diagrammatic form of the spectrometer apparatus of this invention;

FIG. 2 is a graphical representation of the intensity of X-rays emitted from a target material composed of equal amounts of Mo and Rh as a function of energy of the emitted radiation;

FIG. 3 is a graphical representation of the intensity of emitted X-rays for a target material of Mo and Rh as a function of emission energy for three different values of electron accelerating voltage; and

FIG. 4 is a graphical representation of the output signal of a spectrometer in accordance with the principles of this invention as a function of the energy of bombarding electrons for a tungsten target material.

With reference now specifically to FIG. 1, a composition analysis spectrometer in accordance with the principles of this invention is illustrated. The material to be analyzed **11** is bombarded with a beam of electrons **12** from an electron gun **13**. The accelerating voltage for the electron gun is supplied from high voltage supply **15**. A collimated X-ray detector **20**, which typically would consist of a sodium iodide crystal **21** and photomultiplier **22** enclosed within a collimating shielding member **23** is positioned to measure the X-rays induced from the surface of the material **11** by the action of the incident electron beam **12**. The output of the photomultiplier tube is applied to a pulse height discriminator **25**, which typically would be a single channel pulse amplitude discriminator, and the output of this discriminator is applied to a readout unit **26**. The position of the acceptance channel in the pulse height discriminator is varied in accordance with variations applied to the high voltage supply **15** for the electron gun as is indicated by the dotted line **27**.

Having described the general configuration of the apparatus, the components will be discussed in somewhat more detail before describing the operation of the equipment as a composition analysis X-ray spectrometer. The electron gun **13** may be any source of electrons with accelerating electrodes such that the high voltage may be varied in a predetermined fashion to vary the energy of the electron beam in the same fashion. While the X-ray detector **20** is illustrated as a sodium iodide crystal photo-

multiplier combination, it may be any suitable X-ray detector which provides output pulses related to the energy of the incident X-rays, for example a proportional counter. The pulse height discriminator unit **25**, again, may be any conventional pulse height discriminator of the type having at least a lower threshold which is variable over a relatively wide range. The primary function of the pulse height discriminator is to provide upon its output only pulses having an amplitude lying above the lower threshold. As will be more fully understood from the discussion below an operation of this system, the discriminator in this instance need not have an upper threshold limitation, although in some instances, it may provide increased accuracy. The readout unit **26** may be any conventional type of readout, such as a scaler or count rate meter providing an indication of the number of pulses appearing on the output of the discriminator unit **25** as a function of time. The readout unit **26** may also include a pen recorder to provide a visual record of output pulses for varying discriminator settings. As indicated by the dotted line **27**, the discriminator and high voltage supply **15** are ganged together such that when the high voltage supply is varied the discriminator is varied in synchronism with it.

In order to facilitate an understanding of the operation of this system, the nature of the X-ray spectrum induced on the target in response to a bombarding electron beam will first be considered.

With reference now specifically to FIG. 2, there is shown the radiation flux as a function of the emission energies of X-rays from the surface of a target composed of a 50% Mo and 50% Rh which is being bombarded with an electron beam having an energy of 35 kev. The solid line indicates the true spectrum being emitted and this spectrum consists of the K_α and the K_β lines from Mo and Rh added to the more diffuse spectrum resulting from the X-rays emitted from the deceleration of the electrons. Since the absorption edge for X-ray emission from Mo is 20.2 kev. and that for Rh is 23.2 kev, then the lines of both of these elements are excited. The dotted line, on this curve, represents the spectrum that would be obtained using a device having excellent resolution such as a spectrometer utilizing the dispersive method.

Turning now to FIG. 3, there are three curves, A, B, and C shown in which the radiation flux is plotted against the emission energy in kev. The target material for the curves in FIG. 3 is again 50% Mo and 50% Rh and each of the curves A, B, and C represents a different bombarding energy of the incident electron beam. Since the bombarding energy in curve A is 20 kev., which is below the absorption edge of both Mo and Rh, no spectral lines are excited and the spectrum shown is that purely from the X-rays generated by the deceleration of the electrons. The bombarding energy represented in curve B is 23 kev. which is above the 20.2 kev. absorption edge of Mo, but below the 23.2 absorption edge of Rh. Hence, the spectral lines of Mo are excited and, therefore, represented in the true spectrum superimposed once again on the broad spectrum from electron deceleration. In this instance, the spectrum for electron deceleration is increased in value in accordance with the relationship presented earlier as to flux vs bombarding energy. The dotted line in curve B represents the response of a relatively poor resolution X-ray detector, such as a sodium iodide crystal, and it is seen that the K_α and K_β lines are not distinguishable with such a detector.

FIG. 3C shows the spectrum when the bombarding energy is 27 kev. above the absorption edge of both Rh and Mo. In curve C the spectral lines of both Mo and Rh are present in addition to the broad X-ray spectrum and, here again, the dotted line representing a poor resolution detector is indicative of the fact such a detector does not resolve these lines. Thus, the spectrum obtained with a relatively poor resolution X-ray detector does not yield information which will distinguish the composition of materials of the target, since the spectral lines, themselves, are not distinguishable.

With reference now to an apparatus of the type illustrated in FIG. 1, if the energy of the electron beam is swept from a low value to successively higher values at regular intervals and if the pulse discriminator lower threshold is maintained at an energy a predetermined amount below the energy of the electron beam at all times with the upper threshold of the pulse height discriminator established at a point intermediate the lower threshold energy and the electron beam energy, then, what is being measured at the output of the apparatus, is radiation flux over a small energy interval which lies just below the bombarding energy of the electron beam. In this instance, with a properly selected channel width and energy lag, the spectral lines will be distinguishable.

With reference now specifically to FIG. 4, the response of a sodium iodide detector as a function of the energy of the bombarding electrons is plotted in the case of a tungsten target. In this instance, the channel width of the signal channel corresponds to a 5 kev. spread in energy and the lower threshold is lagged 7 kev. behind the electron bombarding energy. As is illustrated by the upper approximately straight line section of this curve, together with the dotted line extension, the X-ray spectrum resulting from decelerating electrons yields a signal channel count rate which decreases with the energy of bombarding electrons. While, as previously discussed, the intensity of the generated X-ray spectrum from deceleration of electrons tends to increase with increasing bombarding energy, the response in the signal channel tends to decrease with an increasing setting on the lower threshold, and the overall response is one of a decreasing output count rate as a function of increasing energy. Tungsten has a K_{α} line at 59.5 kev. and a K_{β} line at 67.0 kev. with the absorption edge located at 69.3 kev. As is indicated in FIG. 4, for the above conditions of discriminator channel lag and width, both the K_{α} and the K_{β} peaks are clearly resolvable with a half width resolution of about 3 kev. for the K_{α} peak. Since the energy resolution of the detector alone is in the order of 20 kev., this represents an almost sevenfold increase in energy resolving power by the use of the apparatus of this invention. Since the K_{α} and K_{β} lines of tungsten are separated by less than 20 kev., the detector alone would be incapable of resolving the two peaks.

While in the apparatus described a sodium iodide crystal in conjunction with a photomultiplier has been used as a detector, as previously mentioned any detector exhibiting output pulses which are related to the energy of the incident rays can be used in this invention. In view of the fact that numerous modifications and improvements may now be made by those skilled in the art, the invention herein is to be construed as limited only by the spirit and scope of the appended claims.

What is claimed is:

1. Apparatus for analyzing the composition of a material comprising means for directing electrons upon said material; means for varying the energy of said electrons incident upon said material; an X-ray detector disposed to receive X-rays emitted from said material, said detector being adapted to provide output pulses in response to incident X-rays, said output pulses having an amplitude related to the energy of said incident X-rays; means adapted to pass only output pulses falling within predetermined amplitude limits, means for maintaining one of said amplitude limits at a value corresponding to an X-ray energy a small increment less than the energy of said incident electrons, and means to provide a readout indication of the number of pulses passed between said predetermined amplitude limits.

2. Apparatus for analyzing the composition of a material comprising, a source of electrons adapted to emit a beam of electrons incident upon said material; means for systematically varying the energy of said electrons incident upon said material; an X-ray detector disposed to receive X-rays emitted from said material, said detector being adapted to provide output pulses in response to incident

X-rays, said output pulses having an amplitude related to the energy of said incident X-rays; pulse discrimination means adapted to pass only output pulses falling within predetermined amplitude upper and lower limits, means for maintaining said lower amplitude limit at a value corresponding to an X-ray energy a small increment less than the energy of said incident electrons; means coupled to the output of said pulse discrimination means adapted to provide a readout indication of the number of pulses passed by said pulse discrimination means.

3. Apparatus for analyzing the composition of a material comprising, an electron source; means for accelerating said electrons from said electron source onto said material, said accelerating means being adapted to be varied over a relatively large range such that the energy of said electrons striking said material may be varied over a relatively large range; an X-ray detector disposed with a respect to said material in such a manner as to receive X-rays emitted from said material, said detector being adapted to provide output pulses having an amplitude related to the energy of said received X-rays; gating means coupled to said detector means adapted to pass only pulses falling within predetermined amplitude limits, the lower one of said amplitude limits being maintained at a value corresponding to an X-ray energy less than said incident electron energy by a predetermined amount; means for varying said accelerating potential and said lower amplitude limit from a substantially low electron energy to increasingly higher electron energies; readout means adapted to provide an output indication of the number of pulses passed by said gate as a function of the value of said lower amplitude limit.

4. Apparatus in accordance with claim 3 wherein said X-ray detector is a sodium iodide crystal-photomultiplier combination.

5. Apparatus for analyzing the composition of a material comprising a source of electrons; accelerating means adapted to accelerate said electrons to strike said material; means for controllably varying said accelerating means to controllably vary the energy of said electrons striking said material; an X-ray detector positioned to receive X-rays emitted from said material in the region of said electrons striking said material, said X-ray detector being adapted to provide in response to incident X-rays output pulses having an amplitude related to the energy of said incident X-rays; pulse discrimination means coupled to the output of said X-ray detector and adapted to pass only pulses exceeding a predetermined lower amplitude limit, said lower amplitude limit being maintained at a value corresponding to the amplitude of pulses resulting from incident X-ray having an energy a predetermined amount less than the energy of said striking electrons; means for varying said accelerating means such that said striking electron energy is varied from a low energy value through a series of intermediate energy values to a substantially higher energy value; readout means coupled to the output of said discriminator means and providing an output indication of the number of pulses passed by said discriminator means as said electron energy is increased.

6. A method for material analysis comprising the steps of: impinging a beam of electrons upon said material while varying the energy of said electrons from a relatively low value through intermediate values to a relatively high value; detecting X-rays emitted from said material as the result of said impinging electrons, determining the quantity of said emitted X-rays having energy less than the energy of the respective impinging electrons by a relatively small increment.

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