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THERMALLY EXCITED X-RAY SPECTROMETER

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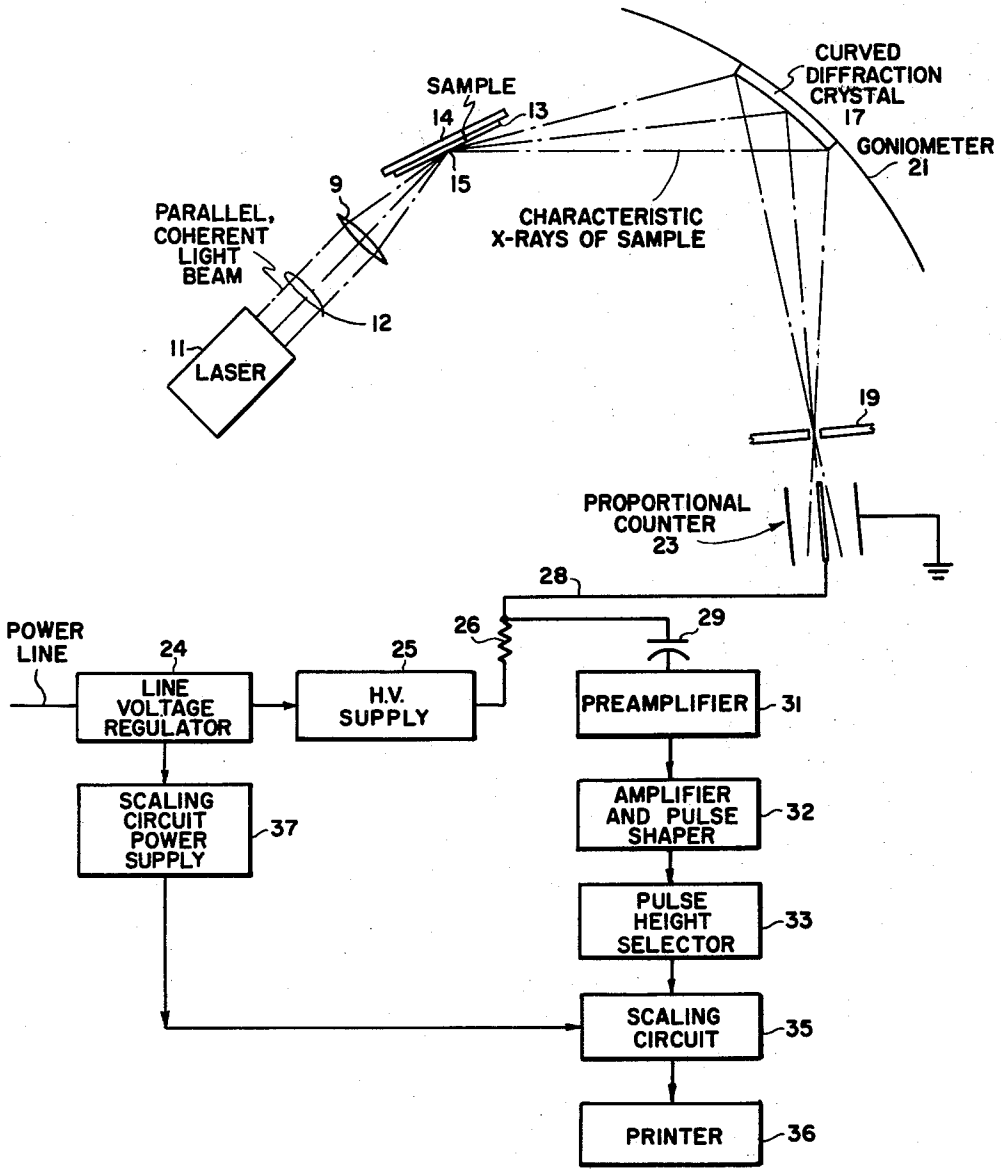

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THERMALLY EXCITED X-RAY SPECTROMETER

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This invention relates to the spectrometric analysis of materials through the utilization of characteristic X-ray emission radiation from the materials under analysis, and more particularly to the use of thermal excitation to generate the characteristic X-radiation.

In the quantitative and qualitative analysis of materials, there are several spectrometric procedures which utilize well known principles of operation and apparatus. Each has advantages over some or all of the others and certain disadvantages. In spectrometric analysis by X-ray diffraction, wherein the generation of characteristic X-rays of the material being analyzed is obtained by exciting the test sample material itself by X-rays, the exciting source of X-rays is ordinarily generated in an X-ray tube and then directed to the sample. The generation of characteristic X-rays in this manner is obtained by the photoelectric absorption process wherein electrons are dislodged from their inner orbits to thereby excite the atoms. In such an arrangement, there is negligible continuous X-ray spectrum generated in the sample, and as a consequence, there is low background radiation, i.e., there is little radiation due to other elements and X-radiation scattered by the sample. However, in such an arrangement, it is extremely difficult to have a small portion of a sample examined, since as a general consideration the excitation per unit area by X-rays of the sample is relatively low and therefore the intensities for small spots are low.

The problem of examining a minute area of a sample is solved to a substantial extent by the use of electrons, rather than X-rays, directly impinging upon the sample so that the trajectory electrons can dislodge inner orbit electrons of the atoms of the sample to thereby excite the atoms. Since an electron beam can be focused to a much greater extent than X-rays, extremely fine spots on the test sample may be excited and examined. The X-radiation that is generated as a consequence of this excitation is treated in the same way as if X-rays themselves excited the test material. Not only is the spot excited quite small, but it receives a high level of excitation. However, in this electron probe technique, the path from the electron source to the test sample must be under a high vacuum to preclude impeding the electron trajectory and most especially, suffers from the disadvantage of generating considerable amounts of continuous radiation due to the deceleration of the electrons in the sample (the Bremsstrahlung effect). Furthermore, it is ordinarily necessary that the test sample used in the electron spectrometer situation be of conductive material, or else it may happen that a surface charge develops on the test material whereby the electron beam approaching the test sample may be deflected slightly from the desired point of impact to the wrong part of the sample.

Accordingly, it is highly desirable, and it is an object of this invention, to provide a spectrometric system wherein the spot size is smaller than has heretofore been possible; the system need not be operated under vacuum, no restrictions are placed upon the conductivity of the test material, and there is a low level of background radiation.

These objects are accomplished in accordance with the principles of the invention by exciting the test sample, not with X-rays, nor with electrons, but by a source of thermal excitation. In particular, the invention comprehends an X-ray spectrometric system wherein the test material is excited by a high intensity coherent beam of

light from a laser source. It is to be understood that in this system, the laser excites the material for subsequent examination, not in an optical spectrometric system, but in an X-ray spectrometer. Thus, the thermal excitation of the test sample is not used to heat the test material to an incandescent state for the purpose of optical spectrometric examination, but rather is used to apply thermal energy to the test sample sufficient to excite the atoms to a high enough energy state to generate characteristic X-ray emission radiation for that material. It has been determined, in accordance with the principles of this invention, that the thermal excitation that may be provided by a laser beam can result in the application of a quantum energy greater than the photon energy which it is desired to produce, and as a consequence constitutes a means of analyzing the material which absorbs the quantum and emits the photon.

It is an important feature of this invention that thermal excitation may be used to produce the characteristic X-rays even though the temperature of the beam corresponds to an average molecular energy less than that required to provide the excitation necessary for the atom to generate the specific photon energy of interest. In accordance with the principles of the invention, advantage is taken of the basic physical principle that the distribution of molecular energy varies as a Maxwellian distribution, providing energy levels as much as a hundred times as high, at one end of the curve, as the average of the distribution. These highly energetic molecules are the ones responsible for the generation of the characteristic X-radiation subsequently examined and analyzed in the X-ray spectrometer.

An important advantage flowing from the invention resides in the fact that the temperature of the coherent light spot applied to the test sample may be controlled by controlling the intensity of the laser beam. This means that a level of excitation may be applied to the test sample which is appropriate for the elements of interest within the test sample. Appropriateness as used in this sense means that the energy used to excite the atoms is just slightly in excess of that required for exciting the characteristic radiation from the element in the sample whose quantitative or qualitative analysis is being sought. This is important, since if the excitation level is too high, other elements in the sample having higher atomic numbers may also be excited and produce their own radiation, which would have to be discriminated against in order to get the proper intensity measurement of the element of interest. Such high energy, shotgun type excitation provides an additional problem due to what is known in the art as interference effects. Thus, if the higher atomic number elements in the sample are excited and produce their characteristic radiation, this additional radiation may itself additionally excite the element of interest in the sample, such that it emits a greater amount of its characteristic radiation than it ordinarily would (i.e., a greater amount of characteristic radiation than due solely to the laser beam exciting it). This interference effect causes "enhancement" which is the undersirable production of intensities of characteristic X-radiation for the element of interest that is not linearly related to the quantity of the element in the test sample.

The term "laser" is the acronym for "light amplification by the stimulated emission of radiation," and is sometimes referred to as optical "maser," which itself is the acronym for "mircowave amplification by the stimulated emission of radiation." The expression laser will hereinafter be used for the light amplifier providing the thermal energy used for increasing the kinetic energy of the atoms to thereby radiate X-radiation which is characteristic of the test sample.

The novel features believed to be characteristic of this invention are set forth with particularity in the appended claims. The invention itself, however, both as to its organization and method of operation together with further objects and advantages thereof may best be understood by reference to the following description taken in connection with the accompanying single sheet of drawing. The drawing shows as an illustrative embodiment in accordance with the principles of the invention and given by way of example a thermally excited X-ray spectrometer using a laser excitation source with an X-ray diffraction analysis system.

Referring to the figure in greater detail there is shown a thermally excited X-ray spectrometer in accordance with the principles of the invention. A pulsed ruby laser **11** provides an extremely narrow beam of coherent light **12** which is focused by lens **9** to a fine point on a sample **13** supported in a sample holder **14**. Laser **11** includes, although not shown in detail, a high voltage power supply, electrical control means, exciting flash lamp and optics to concentrate light on the ruby, reflecting ends on the ruby and optical elements and control means to permit "overpumping" to get short pulses. Due to the high power of the beam, and the small spot **15** on sample **13**, there is a high and concentrated enough power input at spot **15** on the sample to thermally excite characteristic X-radiation from sample **13**. The sample material is actually vaporized at spot **15**. The nature and relationships of the sample material and the power output of the laser will be discussed in greater detail hereinafter. For the moment, however, it is to be understood that the net result is that sample **13** has generated therefrom characteristic X-radiation, as if from a point source; the point source being, of course, spot **15** at which coherent light beam **12** intercepts sample **13**.

The X-radiation from spot **15**, therefore, goes outward omnidirectionally, and a portion thereof enters the X-ray diffraction spectrometer and impinges on curved diffraction crystal **17**. A curved diffraction crystal is used in this instance so that the X-radiation may be concentrated towards the slit or aperture **19** to the maximum extent possible. If a flat diffraction crystal were utilized with the effective point source **15**, a greater amount of the characteristic X-radiation would be precluded from entering the detection portion of the X-ray spectrometer. Diffraction crystal **17** is mounted upon goniometer **21** in manner well known in the art. Although many goniometer arrangements may be utilized, a particularly effective arrangement is disclosed in United States patent application serial No. 789,910, filed January 29, 1959, now Patent No. 3,073,952, by Lloyd R. Rose, entitled, "X-Ray Diffraction Apparatus." The uniformity in operation of the spectrometer is maintained to an unusually great extent in the goniometer arrangement of the Rose patent application.

An X-ray detector **23** in the form of a proportional counter, for example, is arranged in the spectrometer to receive the characteristic X-radiation from slit **19**. Proportional counter **23** is powered from a power line through a line voltage regulator **24**, and thence through a high voltage power supply **25** coupled to counter **23** through resistor **26**. Output conductor **28** of detector **23** is coupled through capacitor **29** to preamplifier **31**, and thence to amplifier **32**. Preamplifier **31** is utilized since the low voltage output pulses from the proportional counter are too weak to be transmitted over any substantial distance without problems of intereference; typically, preamplifier **31** may be contained within the same housing as counter **23**. The pulses originally generated in the counter are properly amplified in amplifier **32** and are then passed to pulse height selector **33**.

Pulse height selector **33** has a window and base line appropriate to select pulse amplitudes representative of the element of interest, that is, representative of the element in the test sample whose quantity or appearance is

of interest in the spectrometric analysis. A pulse height selector particularly useful and appropriate in this system is disclosed in United States patent application Serial No. 131,650, filed August 15, 1961, by Stanley Bernstein, and entitled, "Pulse Height Selector." These pulses are thence passed from pulse height selector **33** to scaling circuit **35**. Scaling circuit **35** is a typical counting circuit which is scaled such that its output is much smaller and in a constant ratio to the number of input pulses thereto. Scaling circuit **35** is supplied from scaling circuit power supply **37**, taking its input in turn from line voltage regulator **24**. The output of scaling circuit **35** is applied to printer **36**, which records the count for that particular goniometer setting.

X-ray spectrometric systems are well known in the art, and are explained extensively, for example, in standard exts such as "X-ray Diffraction Procedures," by Klug and Alexander, 1954, and "X-ray Absorption and Emission in Analytic Chemistry," by Liebhafsky et al., 1960, both published by John Wiley and Sons, New York. All of the circuits of the X-ray spectrometer discussed are well known in the art, and their structure and operation are disclosed in such texts as these, as well as certain preferred forms of them being disclosed in the patent applications cited herein.

The operation of the X-ray spectrometer is well known in the art, and in addition to the description presented thus far, it is to be understood that diffraction crystal **17** is disposed successively at different angular orientations by virtue of the action of the goniometer **21**, so that angularly related counts registered on printer **36** for the different angular orientations of the diffraction crystal provide an indication of the presence or absence of the element of interest.

The function of laser **11** is to generate a light beam so that sample **13** is sufficiently excited by the absorption of light energy to cause the atoms to vibrate violently enough to strip off electrons therefrom down to the orbits corresponding to energy levels available in the thermally excited mass. The vibrating charged ions, and particularly the vibrating electrons, radiate a continuous spectrum of electromagnetic radiation according to black body radiation laws, so that to some extent there is excitation of atoms that are not fully ionized by absorption of radiation from more excited atoms. This description is believed to be representative of the physical action provided by the thermal excitation caused by the laser beam. However, it is not suggested that this is a definitive theory, but rather the presently most plausible explanation of the phenomenon. The intense thermal concentration at spot **15** results in destruction of the test sample at that spot. However, this is an extremely small spot, and in many applications, such destructive analysis in such a restricted area is of no consequence.

To obtain the appropriate intensity and concentration of light energy, in the present state of the art, a pulsed rather than continuous wave laser must be used. There are many types of pulsed lasers currently available, most of which are of the ruby crystal type with various amounts and types of doping materials used, which can provide the thermal excitation necessary for the generation of characteristic X-rays from various types of elements. Thus, for example, a laser producing a coherent light beam of 15 megawatts with a one-half micron spot produces a calculated temperature of five million degrees Kelvin, based on radiation equilibrium. With a 55 micron spot, a 490,000 degree Kelvin temperature is obtainable. With the lower temperature, mean particle energy would correspond to 44 electron volts. The energy distribution for black body radiation demonstrates that output per increment of wavelength spectrum is as high as one-tenth peak value for particle energies ten times the mean thermal energy. Consequently, it would be possible to excite elements up to nitrogen in the atomic scale with the fifty-five micron spot, and up to calcium with the

half-micron spot. As higher power, or more concentratedly focused beam lasers, or both, become available, characteristic X-rays may be generated from elements of higher and higher atomic numbers. Although there are many present forms of pulsed lasers appropriate for utilization in the system of the invention as represented by the embodiment of the drawing, the pulsed ruby laser which is controlled and modulated ultrasonically as disclosed, for example, in "Electronics" of October 5, 1962, page 40, FIGURE A, is capable of providing a giant output pulse from a ruby laser within a rather short pulse period.

While the principles of the invention have now been made clear in illustrative embodiments, there will be immediately obvious to those skilled in the art many modifications in structure, arrangement, proportions, the elements, materials, and components, used in the practice of the invention, and otherwise, which are particularly adapted for specific environments and operating requirements, without departing from those principles. The appended claims are therefore intended to cover and embrace any such modifications, within the limits only of the true spirit and scope of the invention.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. X-ray spectrometric apparatus for ascertaining the qualitative or quantitative content, or both, of a test sample, comprising: a source of high power concentrated thermal energy of a character such as to induce X-ray emission radiation when focused upon said test sample; and X-ray photon energy selective means disposed to receive X-radiation from said sample for sensing and analyzing characteristic radiation from said test sample.

2. X-ray spectrometric apparatus for ascertaining the qualitative or quantitative existence, or both, of an element of interest in a test sample, comprising: thermal energy generating means focused upon said test sample for generating thermal energy sufficiently concentrated and of high enough power to produce characteristic X-ray emission radiation of said element of interest from said test sample; and X-ray photon energy selective means responsive to said X-radiation from said sample for sensing and indicating said characteristic X-ray emission.

3. X-ray apparatus comprising: means for supporting a test sample; a laser focused upon the test sample region contiguous to said support means said laser operative to provide thermal energy to induce characteristic X-ray emission radiation therefrom; and an X-ray spectrometer oriented to receive X-rays emanating from said region.

4. X-ray apparatus as recited in claim 3 wherein said X-ray spectrometer comprises X-ray diffraction apparatus including a curved diffraction crystal.

5. X-ray apparatus as recited in claim 3 wherein said laser is a pulsed beam overpumping laser.

6. X-ray apparatus for analyzing a test sample for an element having an atomic number up to that of calcium, comprising: a laser focused upon said test sample having the capacity to produce a five million degree Kelvin temperature at said test sample; and X-ray diffraction apparatus positioned to receive X-rays from said test sample.

References Cited by the Examiner

"Analysis by Laser," Steel, January 22, 1962, page 66.

"Ruby Optical Maser as a Raman Source," by S. P. S. Porto et al., Journal of the Optical Society of America, volume 52, No. 3, March 1962, pages 251–252.

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