July 12, 1966 **P. DUNCUMB** **3,260,845**

METHOD FOR THE ANALYSIS OF X-RAYS FROM AN ELECTRON PROBE DEVICE

Filed July 10, 1962 2 Sheets-Sheet 1

FIG.1.

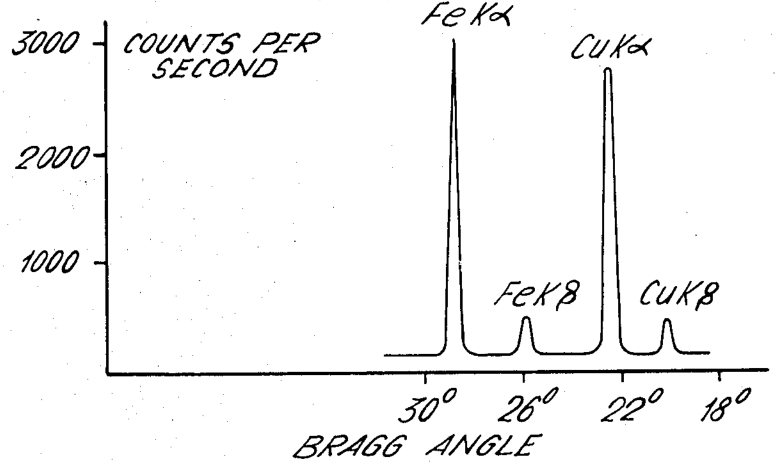
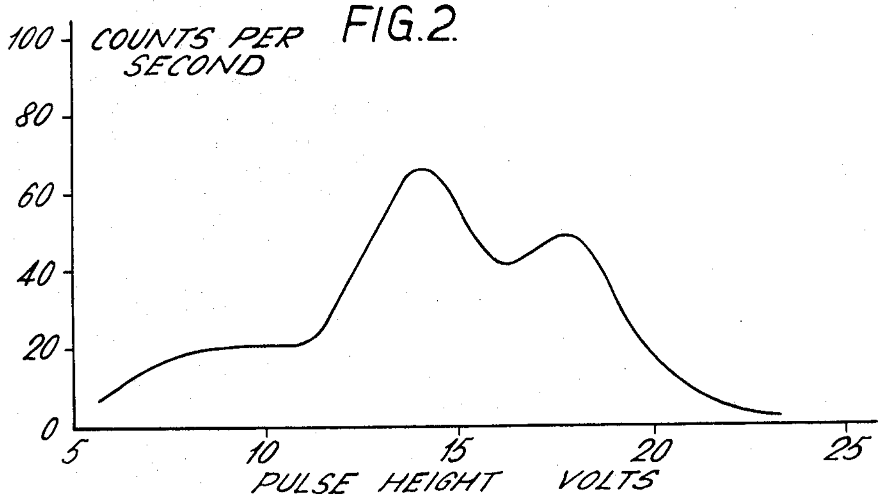


FIG.2.



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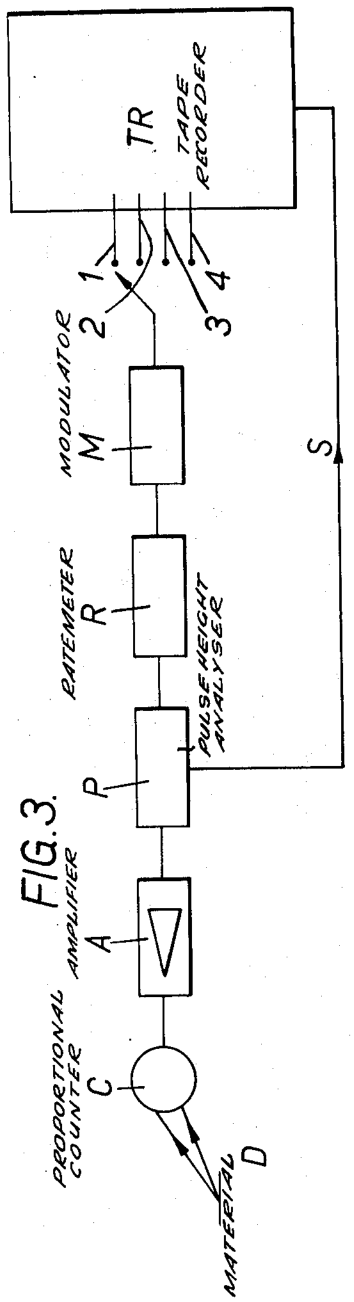

FIG. 3.

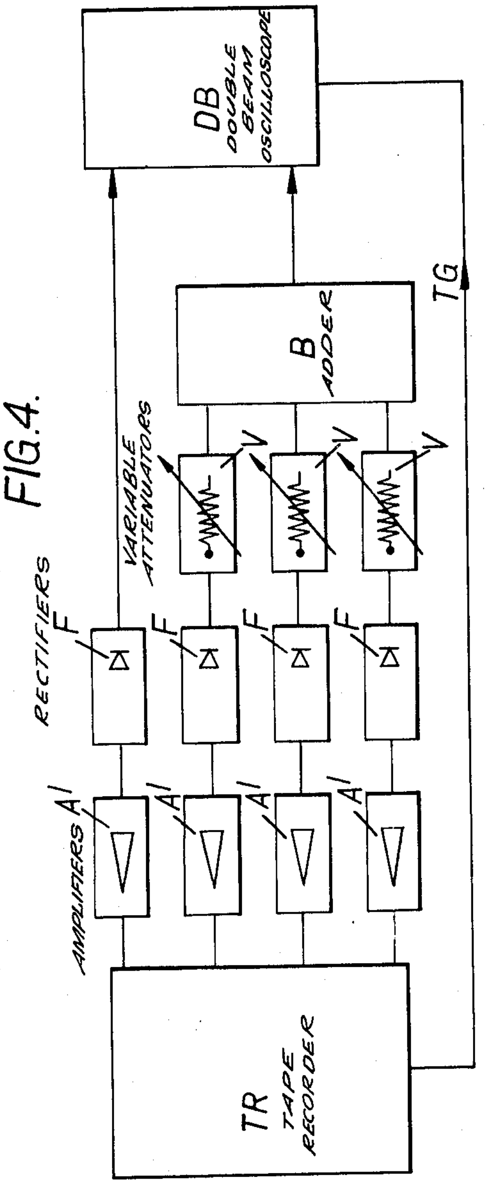

FIG. 4.

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3 Claims. (Cl. 250—49.5)

This invention relates to the analysis of materials by spectrometry, in particular X-ray spectrometry, although the same principles may be applied to spectrometry by means of other radiations, such as infra-red or gamma rays.

The conventional techniques of crystal spectrometry for the analysis of X-rays become difficult to apply to wavelengths greater than ten Angstrom units, mainly because of the lack of suitable crystals having a large enough lattice spacing. Diffraction gratings have been used for wavelengths up to several hundred Angstrom units but these require a high emitted intensity, and often the recording time that is needed is a matter of hours. Both of these requirements are difficult to meet in X-ray emission micro-analysis where the power of the electron beam may be several orders of magnitude lower than in a conventional X-ray tube, and considerations of stability and of contamination of the specimen often prevent analysis times of more than about ten to thirty minutes.

It has therefore been proposed to use a proportional counter for the non-dispersive study of the emitted spectrum by pulse height analysis. As well as avoiding reflection losses, the counter can be placed close to the source of X-rays, to subtend a very much greater solid angle than diffraction grating and thus to give a corresponding increase in collection efficiency. The main drawback of the proportional counter is its poor energy resolution which results from the statistical fluctuation in the ion pairs generated by quanta of a given energy and which gives a corresponding spread in the heights of the pulse produced at the anode of the counter. The resultant blurring of the recorded spectrum is such that neighbouring emission lines appear to overlap and in practice it is not possible to separate directly the K characteristic radiation from elements of which the atomic numbers are separated by less than three. As this statistical spread is a fundamental limitation, depending on the ionisation potential of the gas in the counter, which varies little from gas to gas, it is unlikely that much improvement can be expected in this direction in the normal proportional counter.

It is an aim of the invention to provide a method and apparatus for analysing X-ray and other radiation spectra on the basis of pulse height analysis by means of a proportional counter, overcoming the drawback mentioned above. According to the invention in the analysis of materials by spectrometry, using X-ray or other radiation spectra, the pulse height distribution of the emitted radiation is analysed by a pulse height analyser fed from a counter and the resulting distribution curve is compared with or balanced against an empirically produced curve synthesised by combining previously obtained curves characteristic of the known elements present, and the relative proportions of these curves necessary in the synthesis to give a curve that matches the observed curve reveals the proportions of those elements in the material under examination.

The previously prepared curves from which the synthesis is made are conveniently stored in a magnetic store, preferably on a magnetic tape, and are initially fed onto the tape by applying the counter and the pulse height analyser to each of the known elements in turn and feeding the output to the tape, conveniently in a form amplitude-modulating or frequency-modulating an alternating current signal.

The invention will now be further described by way of example with reference to the accompanying drawings, in which:

FIGURE 1 shows the spectral response curve of a given material analysed by crystal spectrometry;

FIGURE 2 shows, for comparison, the response curve of the same material analysed by the use of a proportional counter;

FIGURE 3 is a block circuit diagram of the arrangement used for recording onto tape the spectral response curve of a material, using a proportional counter; and

FIGURE 4 is a block circuit diagram of the arrangement used for interpreting the response curve obtained from the circuit of FIGURE 3.

Referring first to FIGURE 1 this shows the spectrum of a given copper-iron alloy obtained by crystal spectrometry, using a lithium fluoride crystal. The angle is plotted along the X-axis and the counts per second along the Y-axis. Iron and copper only differ in atomic number by three, but the very sharp resolution of the crystal clearly separates the responses from the alpha and beta K shells of the iron from one another and from those of the copper. Comparison of the heights of the responses enables one to determine the relative proportions of these two constituents.

As indicated earlier, crystal spectrometry cannot easily be used with X-rays of wavelengths greater than about ten Angstrom units, and proportional counters have been proposed instead, in conjunction with pulse height analysis. The heights of the pulses are characteristic of the energy of the radiation, and by plotting the pulse height against the number of pulses per second of a given height, one can build up a spectral response curve which is characteristic of the material under test. However, there is considerable statistical spread which causes the curves from the different elements to overlap to a substantial extent. This is illustrated by FIGURE 2 which shows the pulse height analysis curve of the same copper-iron alloy as used for the curve of FIGURE 1. Along the X-axis is shown the heights of the pulses and along the Y-axis the number of pulses per second falling within the successive half-volt spans of pulse height.

If the statistical spread of pulse heights that leads to the overlap is assumed to be approximately Gaussian, it is not impossible to analyse the curve of FIGURE 2 mathematically to work out the relative proportions of copper and iron that must be present to produce this curve. However, this assumes that only copper and iron are present and the presence of an unsuspected third component is not easily revealed. Furthermore, the analysis is no longer easy when three, four or more elements are known to be present, especially where they differ little in atomic number. In any case the analysis required is troublesome and time-consuming.

The method now proposed for analysing a curve like that of FIGURE 2 employs the equipment shown in FIGURES 3 and 4. The X-rays emitted from a material D under test when subjected to bombardment with electrons are allowed to fall on a proportional counter C. The resultant successive electrical pulses generated in the counter are amplified in an amplifier A and fed to a pulse height analyser P which analyses them in accordance with height, that is to say, it gives an indication of the number of pulses having an energy between 0 and half a volt, the number having an energy between half a volt and one volt, and so on. It does this by sweeping a gate or window successively through the different voltage levels, and the output is fed to a ratemeter R, the signal from which is passed to a modulator M that uses the signal to modulate, by frequency or amplitude-modulation, a carrier signal which is in the present example of a frequency of three hundred cycles per second. This is fed to one track of a multi-track tape recorder TR, the start of the movement of the tape being controlled by a synchronising signal S from the pulse height analyser, indicating the start of the traverse of its window through the spectrum of pulse heights. To enable reasonable statistical accuracy the traverse should extend over about two to four minutes.

We then have on one track of the tape a signal of which the modulating envelope has a shape similar to that of FIGURE 2, the X-axis being represented by the length of the tape. The analysing process is then repeated with known pure elements in place of the unknown material, these elements being the ones present or suspected of being present in the material. We thus obtain on the remaining tracks of the tape signals characteristic of these elements. In the example illustrated it is assumed for simplicity that there are only three elements present, and so a four-track tape is sufficient, but it will be understood that more tracks could be used.

The recorded signals are then played back with the tape recorder connected in the circuit shown in FIGURE 4. Each of the signals is amplified in an amplifier A′ and demodulated in a rectifier F, and then the signal from the first track is fed directly to the Y-deflection plates of one beam of a double-beam oscilloscope DB, while the remaining signals are fed through variable attenuators or amplifiers V to be combined in an adder B the output of which controls the other beam of the oscilloscope. For this playback the tape is formed into a closed loop which runs repeatedly through the recorder, and it is speeded up about thirty times to give a playback time of only a few seconds. A trigger signal on one of the tracks at the start of the traverse is fed through a path TG to trigger the time base of the oscilloscope.

The oscilloscope screen has sufficient persistence to keep the whole of the two traces visible and the three variable devices V are adjusted manually until the trace from the adder B matches that from the first track. From the mechanical settings of knobs controlling the devices V one can then read off the relative proportions of the three elements in the material under test.

In an alternative arrangement, instead of using a double beam oscilloscope one could feed the signal from the first track and that from the adder B in opposition to the Y-plates of a single-beam tube, and the controls of the devices V are adjusted to make the trace a straight line along the X-axis.

With a playback cycle time of only a few seconds the oscilloscope can use an ordinary long persistence tube, but if for any reason the cycle time has to be longer than this it may be of advantage to make use of a storage oscilloscope having a variable persistence that can maintain the traces indefinitely.

I claim:

1. A method of testing materials to determine their constituents by spectrometry comprising bombarding the material with an electron beam to produce pulses of characteristic X-rays from the material, detecting said X-ray pulses to produce electrical pulses, analyzing the electrical pulses by producing a display of the pulse height distribution characteristic of the material, producing a second display synthesized by combining signals characteristic of electrical pulses produced by spectrometry from known materials, adjusting mechanically the relative proportions of these last mentioned signals until the two displays match each other, and establishing from the degree of mechanical adjustment of the last mentioned signals an indication of the proportions of the constituents of the material under test.

2. A method according to claim **1** in which the two displays are produced by separate overlapping beams.

3. A method according to claim **1** in which the two displays are produced by a single beam, the respective signals of the displays being opposed to each other in said single beam, the matching being achieved by adjusting the relative proportions of the said last-mentioned signals until the resultant display is a straight line.

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