April 14, 1953 M. A. CORDOVI 2,635,192

FLUORESCENT SPECTRAL ANALYSIS

Filed Oct. 24, 1949 5 Sheets-Sheet 1

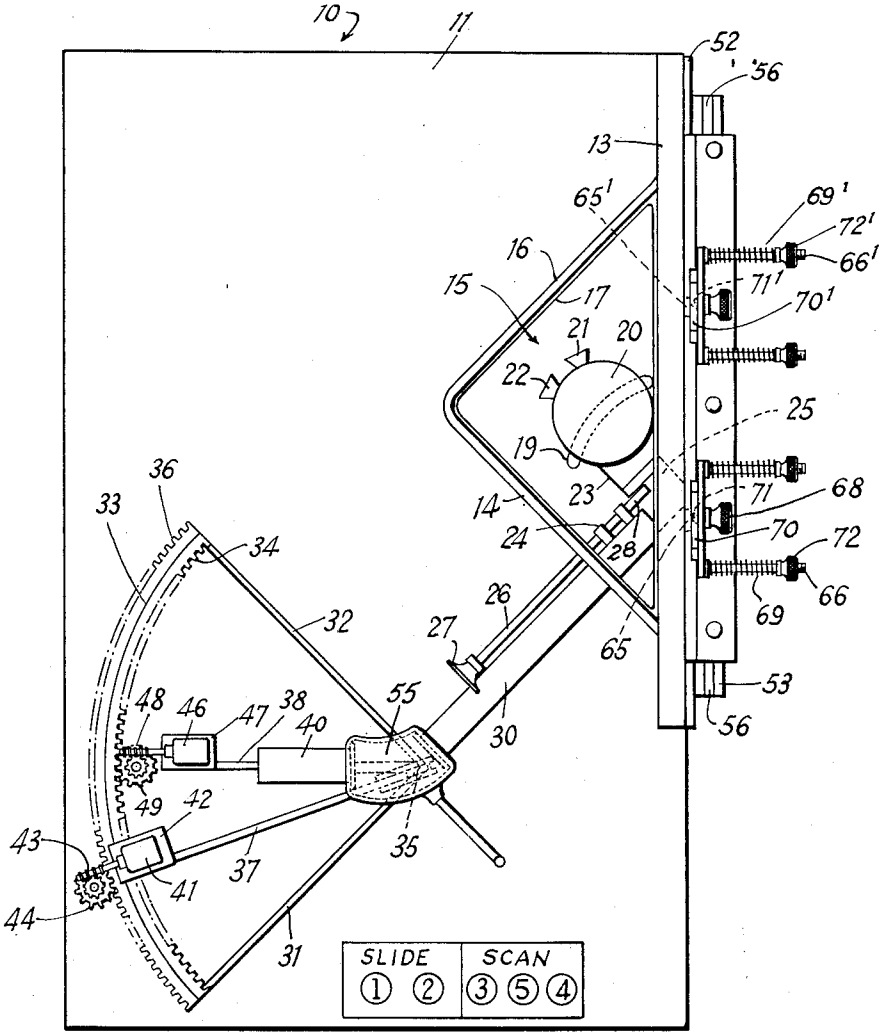


FIG. 1

INVENTOR
Marcel A. Cordovi
BY
J. P. Moran
ATTORNEY

April 14, 1953 M. A. CORDOVI 2,635,192

FLUORESCENT SPECTRAL ANALYSIS

Filed Oct. 24, 1949 5 Sheets-Sheet 2

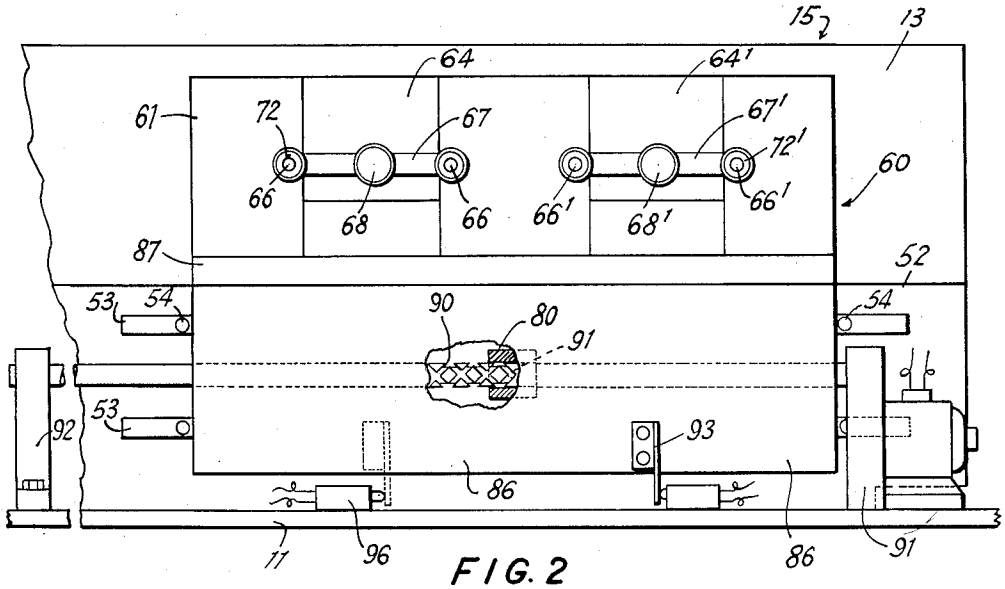


FIG. 2

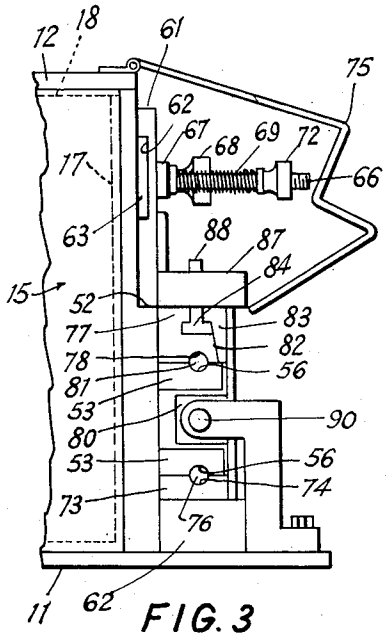


FIG. 3

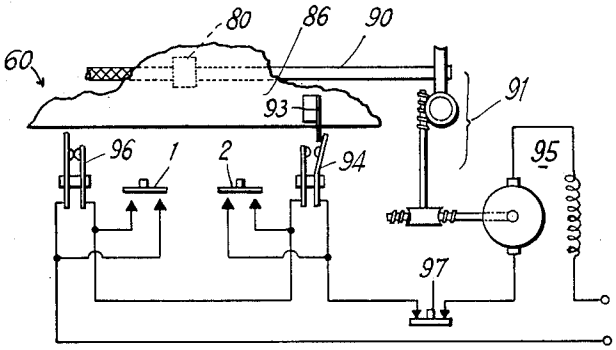


FIG. 4

INVENTOR
Marcel A. Cordovi
BY
J. P. Moran
ATTORNEY

April 14, 1953 M. A. CORDOVI 2,635,192

FLUORESCENT SPECTRAL ANALYSIS

Filed Oct. 24, 1949 5 Sheets-Sheet 3

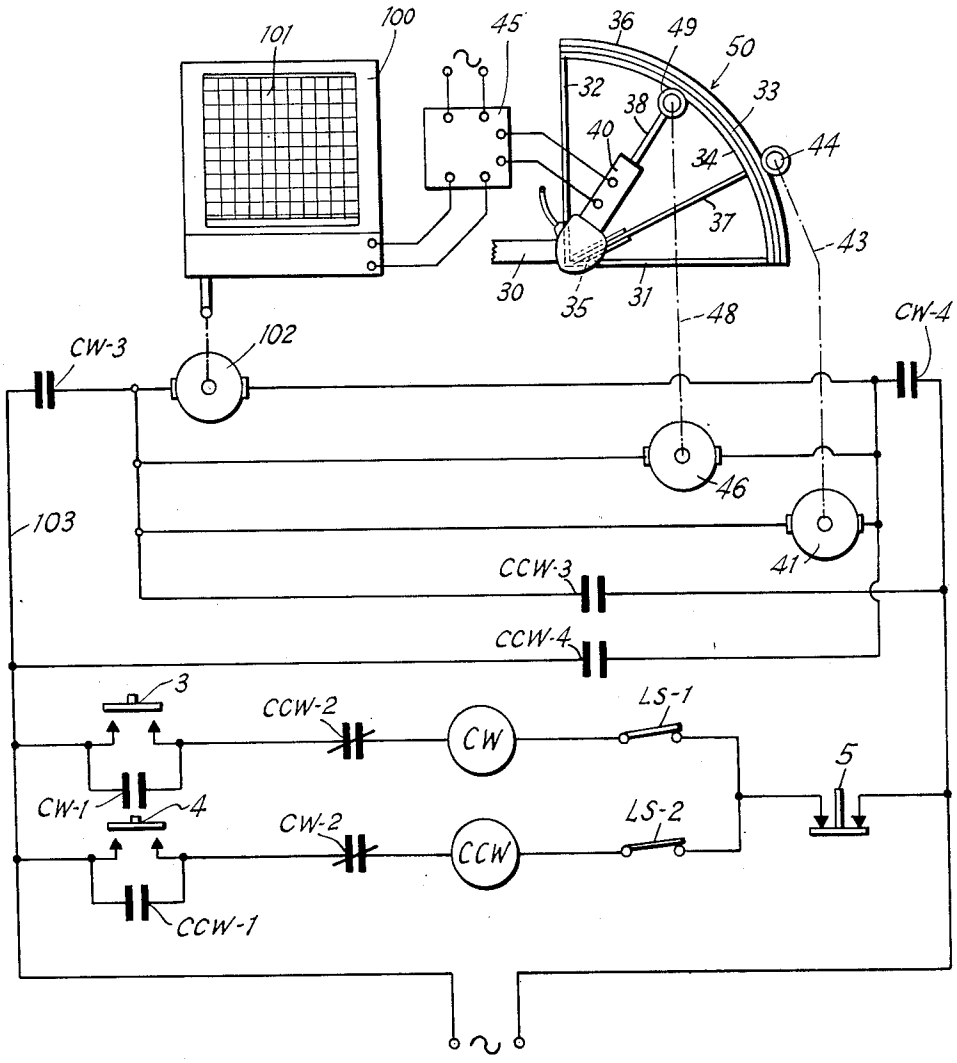


FIG. 5

INVENTOR
Marcel A. Cordovi
BY
J. P. Moran
ATTORNEY

April 14, 1953 M. A. CORDOVI 2,635,192

FLUORESCENT SPECTRAL ANALYSIS

Filed Oct. 24, 1949 5 Sheets-Sheet 4

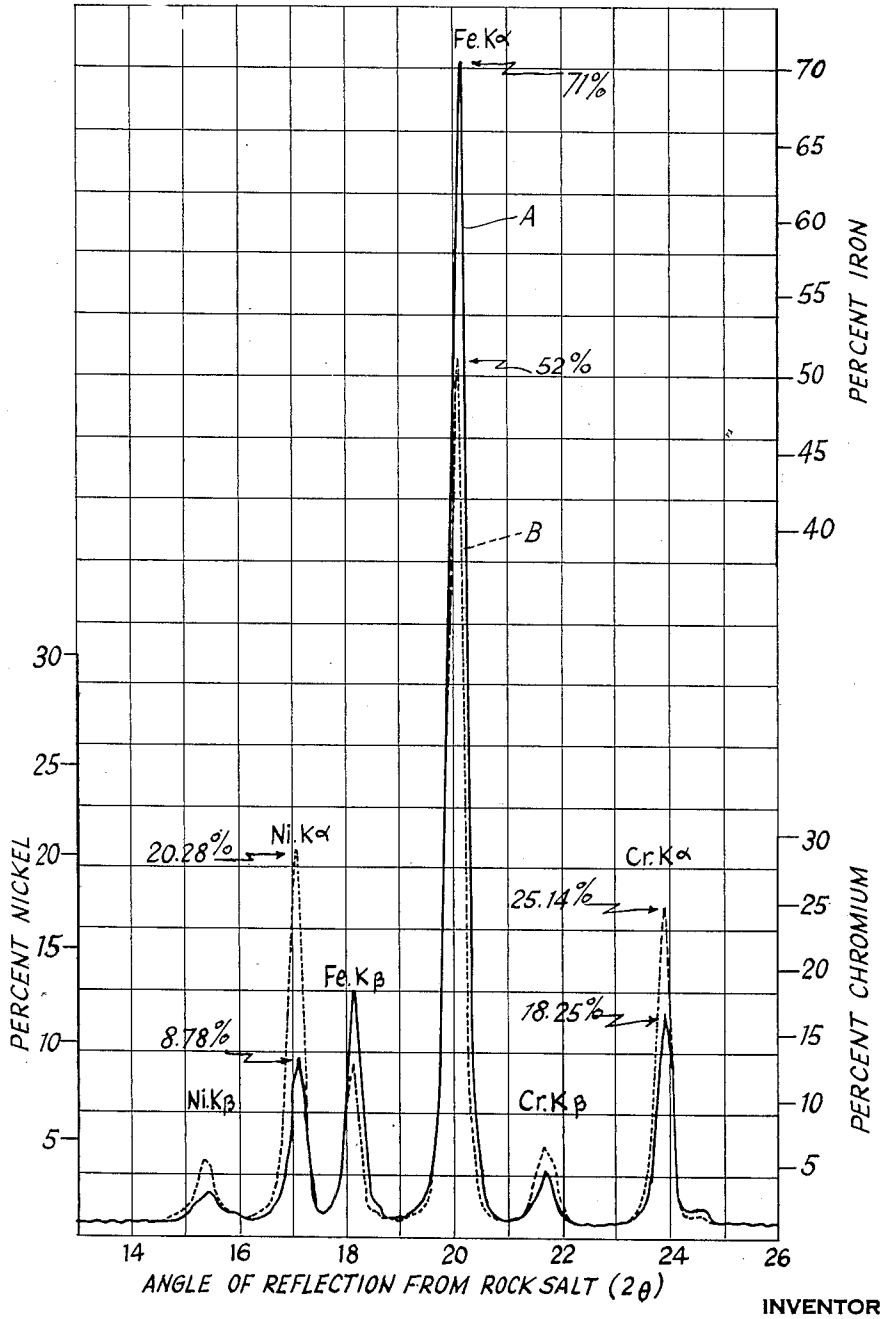


FIG. 6

INVENTOR
Marcel A. Cordovi
BY
ATTORNEY

April 14, 1953 M. A. CORDOVI 2,635,192

FLUORESCENT SPECTRAL ANALYSIS

Filed Oct. 24, 1949 5 Sheets-Sheet 5

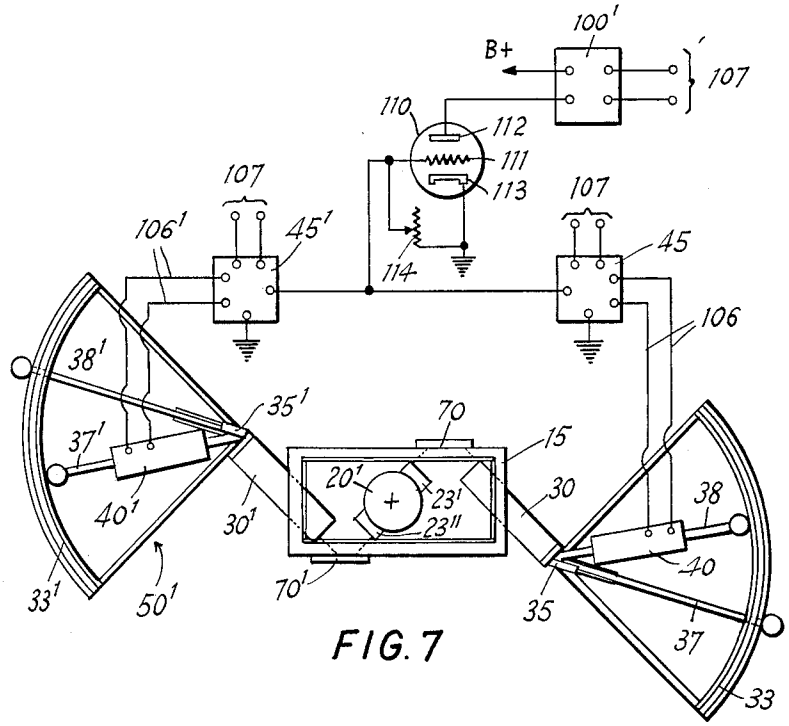


FIG. 7

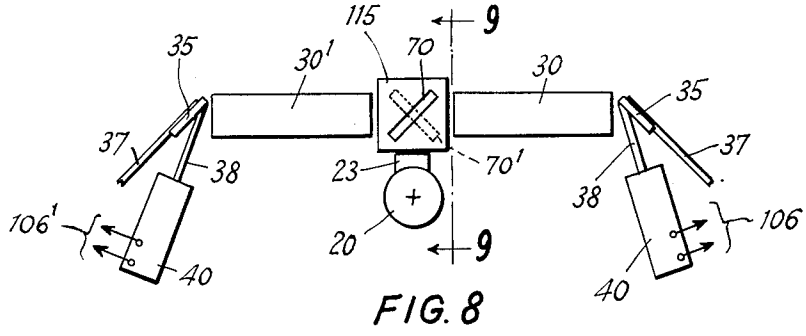


FIG. 8

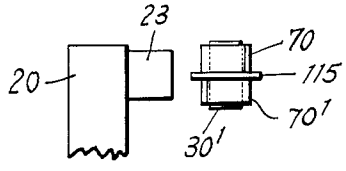


FIG. 9

INVENTOR
Marcel A. Cordovi
BY
J. P. Moran
ATTORNEY

Patented Apr. 14, 1953

2,635,192

UNITED STATES PATENT OFFICE

2,635,192

FLUORESCENT SPECTRAL ANALYSIS

Marcel A. Cordovi, Forest Hills, N. Y., assignor, by mesne assignments, to The Babcock & Wilcox Company, Jersey City, N. J., a corporation of New Jersey

Application October 24, 1949, Serial No. 123,165

15 Claims. (Cl. 250—53)

1

This invention relates to the quantitative and qualitative analysis of chemical elements and compounds, such as metals, alloys, minerals, ores, liquids, etc., with respect to their elemental constituents and, more particularly, to an improved crystal spectrometer for analyzing the fluorescence spectra of such elements or compounds when bombarded, for example, by X-rays.

The theory of fluorescence analysis is based upon elementary concepts associated with radiation spectra. When a material is bombarded by cathode rays, the resulting X-ray emission consists of a general or continuous ("white") spectrum and a superposed characteristic ray spectrum extending over a range of wavelengths from about 10^{-6} to 10^{-9} centimeters. The continuous spectrum is independent of the target material and its general features preclude the possibility of directly associating it with its emission source. The monochromatic rays of the characteristic X-radiation, however, are grouped in simple series, with wavelengths depending upon the atomic number of the emitting element.

Emission of characteristic X-rays is due to the inner electrons of the atom. According to Bohr's theory, these electrons are supposed to occupy shells, designated as K, L, M, etc., around a central nucleus and to whirl around it in the same way that the planets revolve about the sun. Thus, when an impinging electron collides with an atom of the target and ejects one of its electrons, say from the innermost (K) orbit, the vacancy is filled instantly by an electron from the outer shells (L, M, etc.). As a result, a line of the K series will be emitted, its energy value depending on the source of the replacement electron.

Wave lengths of the spectral lines comprising the K, L, M etc. series are inversely proportional to the square of the atomic number. In other words, the higher the atomic number of the target material, the shorter the wavelength of radiation and the greater its penetrative power. The K emission lines represent the shortest wave length group and are the most important of the various series in view of their comparative simplicity and high intensity. The K series of all elements, except the lightest, consists of four principal lines, of which the $\alpha_1\alpha_2$ doublet is the most intense and closely spaced. By comparison, the L series spectrum is more complex in view of the numerous lines (about thirty have been identified) of much lesser intensity than the K series.

2

Chemical analysis by X-rays is made possible by the specific and distinguishing features of characteristic rays for each element in the target and by the direct, though not necessarily linear, relationship existing between the percentage of these elements and the intensities of their emission lines. These conditions will be satisfied also if a sample is irradiated outside the X-ray tube, provided the primary radiation is of sufficiently short wave length and the X-ray quanta have energies nearly approaching those of the electrons in the cathode beam. The fluorescence spectra, i. e. the line radiation resulting from the excitation of an atom by the absorption of X-rays, can be then conveniently identified with a crystal spectrometer. Secondary fluorescence spectra are of much lower intensity as compared to direct excitation. This is so because, when a sample is irradiated outside the X-ray tube, the intensity of exciting radiation per unit area falls off with the inverse square of the distance from the focal spot. This drawback, however, is largely overshadowed by several important advantages pertaining to the secondary fluorescence spectrum which make it the most practical source of radiation for chemical identification purposes.

There is now available to the art a fluorescence analyzer for use in quantitative analysis of elemental constituents in metals, minerals, and ores. Some of the outstanding features claimed for this analyzer are that (1) determinations may be made either on an absolute basis or a comparative basis on percentages up to 100%, with a reproducibility to better than 5%; (2) the unit does not require exceptional stabilization of line potential; (3) determinations are independent of phase or structure; and (4) the analyses are speedy and the unit does not require specialized technical training for operation.

Experimental work undertaken to evaluate this analyzer, from an industrial viewpoint for routine chemical analyses of metallic materials, indicates that the above claims are not substantiated. For example, in 90 out of 100 tests, reproducibility of results was only between 6% and 20%, or from 1% to 15% outside the claimed accuracy range for comparative analyses, and would be even further outside the claimed range if analyses were attempted on an absolute basis. In the latter case, furthermore, exceptional technical skill and tedious procedures become mandatory for evaluation of many correction factors such as crystal reflectivity, counter or detector sensitivity, mutual excitation and

absorption of component elements of the specimen, air absorption, and proportionality factors.

I have found further that the present commercial analyzer cannot be usefully employed for routine analyses of metals and alloys without exceptional stability of the line potential. In such routine analyses, the principal technological requirement stipulates an accuracy and reproducibility of results to better than ±1%, and this is possible only with special equipment assuring the highest degree of voltage stabilization.

I have also found that, contrary to the above claims, determinations are dependent on the structure and predominant phase of the specimen, and comparative analyses cannot be made between samples which are chemically similar in more than one major constituent but differ in structure or predominant phase. For example, a cast specimen cannot be analytically compared with a wrought specimen, though chemically similar thereo in more than one major constituent. Nor can a ferritic steel be analytically compared with a solid solution austenitic alloy even though both specimens have one or more constituents in the same amounts. Thus, a ferritic specimen containing 18% chromium can not be analytically compared with an austenitic specimen containing 18% chromium and also 8% nickel but can be compared with a ferritic specimen containing 9% chromium and 1% molybdenum.

Considering these factors, the prior art analyzer is not adapted for routine chemical analyses in the production or processing of metallic materials and components. Accordingly, the present invention is directed to an improved and practical fluorescent analyzer, in which the foregoing and other deficiencies of the prior art are eliminated, the invention analyzer being especially adapted for routine production analyses of iron, steel and other metallic materials.

In order to afford a better understanding of the underlying principles of the invention, a brief description of the operational procedure with the mentioned prior art analyzer will be of assistance. This analyzer operates in the following manner. An unknown sample is subjected to intense, short-wave-length primary radiation from a tungsten X-ray tube. The secondary fluorescence spectra of the sample are passed through a collimator and allowed to strike a crystal analyzer. The latter acting as a diffraction grating, separates the component radiations and, by proper positioning, reflects them at a characteristic Bragg angle. Individual quanta of radiation are detected by a Geiger counter, which transmits the impulses received to an electronic scaling and counting unit. Counts are totalized over a definite period of time and the percentage of the element under investigation is obtained by proportioning with similar data obtained from a sample of known elemental content.

A high voltage generator is used to energize the X-ray tube, which has a tungsten target sealed off by a beryllium window. The specimen is irradiated outside the X-ray tube (50 kvp.; 20 ma.) and is positioned at 45 degrees to the axis of the cone of incident X-rays. The sample is similarly positioned with respect to the collimator, which consists of a honeycomb of thin-walled nickel tubing ($\frac{1}{16}$ diameter; 0.002-inch wall; 4-inch, 8-inch or 16-inch long) packed into an aluminum frame of rectangular cross-section. The collimator serves to transmit a nearly parallel beam of fluorescence radiation to the crystal analyzer, which is usually rock salt or calcium fluorite.

The NaCl crystal is satisfactory for the K series of the elements ranging from about titanium ($K\alpha_1$=2.74681 A. U.) to zirconium ($K\alpha_1$=0.78851 A. U.). The spectra of elements above atomic number 30 decrease in intensity in proportion to the sine of the Bragg angle. To compensate for the diminishing dispersion in the spectra of such elements, it is necessary to use crystal planes with smaller grating constant. This requirement is partially met by fluorite, whose atomic plane spacing, (220) plane, is 1.93 A. U. as compared to 2.814 A. U. for rock salt, (100) plane.

With this fluorescence analysis unit, it is possible to analyze that group of elements whose atomic number falls between about 22 and 50. The limited peak voltage (50 kilovolts) in the primary X-ray spectrum is insufficient to excite efficiently the K spectra of elements with higher atomic number. On the other hand, the wave lengths of the lighter elements suffer from serious air absorption with attendant great reduction of their K series intensities.

The elements above atomic number 50 may be analyzed by their L series lines, using extended counting intervals to compensate for the comparatively low intensities of these spectra ($L\alpha_1$:$K\alpha$=1:10).

The X-ray tube is mounted within a sheet metal housing into which the collimator extends, these elements being so arranged that the axis of the incident cone of X-rays and the axis of the collimator extend at 45° to the specimen. The latter is mounted in a rotatable indexing type holder arranged to hold four specimens, one or more of which may have a known analysis for comparison with the other specimens. The specimen acts as a secondary radiator of fluorescent radiation when exposed to an incident beam of X-rays.

The total amount of fluorescence is a direct function of the area of the secondary radiator (specimen) which is exposed to the incident cone of X-rays. The intensity of radiation is also influenced by the geometrical arrangement of the sample and the X-ray tube. On the basis of these considerations, the specimen holder of the analyzer is not only impractical but also is conducive to analytical errors. Its impracticability stems from the tedious, hence costly, machining of specimens to the specified dimensions in order to avoid variations in the amount of area exposed. Furthermore, the lead shield, which serves as a stop for the specimen, may be easily deformed by the pressure exerted upon it while inserting thick specimens in the holder. Resulting variation in the set position of the samples with respect to the X-ray tube, will produce changes in intensity which become critical—especially in the case of elements which are present in residual amounts.

Another difficulty encountered in the practical operation of the unit results during changing of the specimens in the holder. During these operations, the housing must be opened to allow access to the specimen holder. Consequently, to prevent hazardous exposure of operating personnel to X-rays, it is necessary to deenergize the X-ray tube while the housing is open. Even though such deenergization may be of a very small duration, such as a few seconds for example, the restarting of the X-ray tube takes up to ten or more times the duration of the interruption to reach a stabilized condition. This seriously delays the analytical procedure.

To overcome the foregoing defects in the specimen holder and to eliminate such delays in the analytical procedure, one feature of the present invention is the provision of an improved specimen holder. This improved specimen holder comprises a flat slide reciprocable longitudinally of the external surface of an apertured wall of the X-ray tube housing. The wall aperture is arranged substantially at the intersection of the X-ray cone axis with the central plane of the collimator and has chamfered walls so as not to block any radiation. On its inner surface, the slide has a lining of lead, and means are provided to hold the slide firmly against such wall with the lead lining in smooth surface-to-surface juxtaposition therewith.

The front or outer face of the slide has two or more longitudinally spaced recesses in which specimens may be held by suitable clamping means. At substantially the center of each recess, a hole is formed through the slide, these holes being selectively alignable with and forming a continuation of the X-ray housing aperture by longitudinal movement of the slide. The slide may be manually operated, but preferably is motor driven under the control of indexing push buttons. Thereby, to align a selected specimen with the housing aperture, the operator presses the proper push button and the motor automatically indexes the slide to the correct position for such specimen. A relatively large lead shield is hingedly mounted on the housing cover and, when the apparatus is in operation, is suspended therefrom in covering relation to the portion of the slide adjacent the housing aperture.

The invention specimen holder permits a rapid succession of analyses to be made without deactivating the X-ray tube. During movement of the holder from one indexed position to another, the housing aperture is sealed by the lead lining on the inner surface of the slide, preventing exit of X-radiation from such aperture. The specimens are quickly and easily positoned in the recesses from the front of the slide, when the recesses are out of alignment with the aperture and either side of the external movable lead shield or cover. For any extended break in analysis, an externally controlled lead curtain or shield, movably mounted within the housing, may be moved to a position blocking the window of the X-ray tube to cooperate with the external shield in blocking exit of radiation.

As stated above, the unknown and the standard specimens being compared must be closely representative of each other with respect to metallurgical phases, major constituents, structural conditions, and surface preparation. In most industrial analyses, this does not present any difficulty, as the approximate analysis of the sample being analyzed is known, and it is merely necessary to use a similar standard. However, with a sample whose approximate analysis is unknown, it is necessary first to establish its identity qualitatively and, after the elemental constituents have been identified, to then run a quantitative comparison analysis with a similar standard specimen.

A feature of the invention is the provision for making a simultaneously recorded quantitative and qualitative analysis rapidly and automatically. For this purpose, a synchronous motor is used to drive the crystal mounting arm over the goniometer scale through the area to be analyzed. A synchronous motor driven recording instrument, such as a recording potentiometer, is connected to the frequency meter circuit of the analyzer. With the recorder and the goniometer initially synchronized, the recorded quantitative and qualitative analysis can be carried out without manual attention.

The analysis is depicted by a graph line on the recorder chart. Provided a properly calibrated chart is utilized, the quantitative analysis can be made on an absolute basis, i. e. without the use of a standard specimen for comparison analyses. This requires a differently calibrated chart for the different types of alloys or compositions being analyzed. For example, the calibration of the percentage scale for chromium in straight chromium (ferritic) steels would differ from the calibration of the percentage scale for chromium in chromium-nickel (austenitic) steels. The calibrated charts may take any one of several forms. If quantitative analyses are being made solely for chromium, charts may be used which have a plurality of chromium percentage scales each calibrated for the chromium percentages in different types of chromium bearing alloys. On the other hand, if quantitative and qualitative analyses are being made for all the elemental constituents of selected specimens, the charts used will have calibrated percentage scales for all elements, such as iron, nickel, chromium, etc., of a particular type of alloy, charts having differently calibrated percentage scales being used for each different type of alloy. To determine the particular type of alloy to which an unknown specimen is germane, a rapid, qualitative and relatively quantitative analysis can be made before the final quantitative analysis.

The elemental analysis to classify an unknown specimen may be greatly facilitated by the use of standard charts for comparison with the recorded chart produced by the elemental analysis. For example, with standard charts prepared for 18–8, 25–20, and other alloys, a comparison of the standard charts with the recorded chart will provide an indication of the relative chart peaks and their relative locations. Thus, the magnitudes of the similarly located peaks may be compared to obtain an approximation of the relative intensities of radiation, thereby classifying the specimen as to type.

To facilitate these analyses, a push button control of the scanning operation is provided. Additionally, the specimen holder may be motor operated between its analyzing positions under the control of push buttons and limit switches.

Experimental analyses have further shown that an analyzer arrangement involving angles of 45° between the sample and the axis of the incident cone of X-rays and between the collimator and the sample, thus providing an included angle of 90° between the X-ray cone axis and the collimator, is not always the best angular arrangement for optimum results. For instance, incident angles, other than 45°, in the range from 30° to 60° produce better results with certain elements. Accordingly, the invention analyzer is capable of adjustment of the angular relationships.

For accurate reproducibility of results, it is essential to constantly maintain a uniform atmosphere for the passage of the radiation from the specimen through the collimator and past the analyzer to the radiation detector. The aforementioned air absorption may be reduced by using an inert gas, such as helium, for the uniform atmosphere, or the system may be evacuated. For this purpose, the invention analyzer includes a gas-tight housing for the X-ray tube, into which

the collimator extends in sealed relation, and a flexible gas-tight hood interconnecting the radiation detector and the outer end of the collimator and enclosing the crystal analyzer. The enclosed system may be connected to a suitable source of an inert gas or may be connected to a vacuum pump, as may be necessary or desirable during a particular analysis.

In an analyzer adapted for routine production analyses of metallic materials, the protection and mounting of the crystal analyzer are important in securing uniform results and in facilitating the analyses. To prevent any change in the reflectivity properties of the crystal analyzer, such as due to hygroscopic action, the crystal analyzer is coated with an extremely thin coating of a protective material, such as "liquid envelope," for example, which "weatherproofs" the surface of the crystal analyzer without affecting the characteristics of the crystal analyzer. Also, in setting up the apparatus, the crystal analyzer must be carefully adjusted both angularly and otherwise, to obtain the optimum reflecting relation to the radiation detector. This initial adjustment must be carefully made and requires a considerable amount of time. If the crystal analyzer is replaced, the time consuming initial adjustment must be performed again. To eliminate this undesirable re-adjustment, the crystal holder of the invention analyzer is provided with micrometer adjustments, whereby a record of the optimum settings for different crystals may be made and such settings rapidly reproduced.

With the foregoing in mind, it is an object of the invention to provide an improved X-ray type crystal spectrometer or analyzer for analysis of compositions utilizing fluorescent radiation therefrom and which is particularly efficient in the accurate analyses of metals and alloys.

Another object is to provide such an analyzer having an improved specimen holder capable of providing more accurate and speedier analytical results.

A further object is to provide such an analyzer in which a suitable gas or evacuation is employed as a means of providing a uniform atmosphere, other than air, thereby eliminating absorption of radiation.

Yet another object is to provide such an analyzer including automatic specimen holder positioning means and automatic scanning means.

Still a further object is to provide such an analyzer including means for making direct quantitative analyses of the elemental constituents of unknown compositions of known types.

An additional object is to provide such an analyzer in which it is not necessary to interrupt the X-ray tube energization between analyses.

Another and additional object is to provide a fluorescence spectra analyzer with which a quantitative analysis of an unknown specimen may be made by simultaneously analyzing the unknown specimen and a comparison or standard specimen of the same type as the unknown and charting the differential intensities of radiation at common characteristic Bragg angles.

These and other objects, advantages and novel features of the invention will be apparent from the following description and the accompanying drawings. In the drawings:

Fig. 1 is a plan view of a fluorescence analyzer in accordance with the present invention, the drive for the specimen holder being omitted to simplify the illustration;

Fig. 2 is an elevation view of the analyzer, showing improved specimen holder and its drive;

Fig. 3 is an end elevation view of the specimen holder and a portion of the X-ray tube housing;

Fig. 4 is a schematic wiring diagram of the automatic positioning control for the specimen holder;

Fig. 5 is a schematic wiring diagram of the automatic scanning control;

Fig. 6 is a reproduction of a calibrated chart illustrating an actual quantitative and qualitative analysis performed by the invention analyzer;

Fig. 7 is a schematic plan view of the invention analyzer as arranged to simultaneously quantitatively analyze a known and an unknown specimen, and record the differential intensities of radiations at common characteristic Bragg angles;

Fig. 8 is a partial schematic plan view, corresponding to Fig. 7, but using a single X-ray tube; and

Fig. 9 is a partial schematic elevation view of the X-ray tube and specimen of Fig. 8.

Referring more particularly to Figs. 1, 2 and 3 of the drawings, the analyzer 10 includes a base plate 11, of aluminum, steel, or any desired material, on which is mounted a housing 15, of suitable metal, having a removable cover 12. In plan, housing 15 and its cover 12 may, for example, be triangles, with the vertex angle being opposite the longer forward wall 13 which extends beyond the other walls 14, 16 of the housing at either end. The interior of housing 15 is lead lined, as indicated at 17, and cover 12 has a lead lining 18 on its under surface.

Within housing 15, adjacent wall 13 and substantially midway of the latter, is mounted an X-ray tube 20 having water cooling connections as indicated at 21, 22. The axis of the X-ray cone, in the angular relations shown in Fig. 1, is directed at 45° to wall 13 and intersects the collimator cone axis substantially at the outer surface of wall 13 and at the center of aperture 25. Collimator 30 comprises a honeycomb of thin walled nickel tubing packed into an elongated, rectangular aluminum frame. Alternatively, the frame may be transversely subdivided by closely spaced, parallel longitudinal partitions to form a plurality of elongated slits extending through the frame. Within housing 15, collimater 30 carries a pair of brackets 24, 24 which slidably support a rod 26 extending through wall 14 and having an operating handle 27 on its outer end. On its inner end, rod 26 supports a lead shield or curtain 28 for longitudinal movement into and out of a position intercepting X-rays directed from tube 20 toward aperture 25 and essentially blocking the X-ray tube window.

It has been found that maximum excitation of the characteristic spectra of certain elements is obtained when the element is bombarded by a primary X-ray beam at angles smaller or larger than 45° but usually lying between 30° and 60°. For this reason, tube 20 is mounted for adjustment along an arcuate track 19 having its center at the intersection of the X-ray cone axis and the collimator axis.

The X-rays from tube 20 directed through aperture 25 impinge, at the selected angle, upon a specimen mounted, in a manner to be described, in flush relation with the outer surface of wall 13. The resultant secondary fluorescent spectra from the irradiated specimen are directed through the collimator 30 and allowed to strike a crystal analyzer 35. The latter acts, as previously stated,

as a diffraction grating to separate the component spectra and, by proper positioning, to reflect them at a characteristic Bragg angle. The individual quanta of radiation are detected by a Geiger counter 40 which transmits the received impulses to an electronic scaling and counting unit 45 (Fig. 6).

For this purpose, and in accordance with the present invention, crystal analyzer 35 and Geiger counter 40 are mounted on a 0°–90° goniometer 50 having one fixed radial arm 31 aligned with collimator 30 and another fixed radial arm 32 perpendicular thereto, the outer ends of the fixed arms being interconnected by a quadrant 33 having arcuate racks 34 and 36 along its radially inner and outer edges, respectively, and being graduated from 0° to 90°. Crystal analyzer 35 is mounted on the inner end of a movable radial arm 37 pivoted at the axis of goniometer 50, and Geiger counter 40 is mounted on another movable radial arm 38 likewise pivoted at the goniometer axis.

In the operation of the apparatus so far described, arms 37 and 38 are angularly adjusted along quadrant 33 to change the angle of crystal analyzer 35 relative to collimator 30 and the angle of Geiger counter 40 relative to analyzer 35. During such adjustment, the angle between arm 37 and arm 31 is substantially one-half (½) the angle between arm 38 and arm 31, with a tolerance of several degrees of the secondary arm 37. In other words the angle between the axes of Geiger counter 40 and collimator 30 is always substantially twice the angle between the plane of crystal analyzer 35 and the collimator axis. The characteristic Bragg angle for any particular element is the angle between arms 37 and 38 when the spectra due to such elements are at a maximum intensity as indicated by Geiger counter 40 and counting and scaling unit 45. The foregoing angular relations of the collimator, crystal analyzer, and Geiger counter are known to the art.

In known fluorescent analyzers, arms 37, 38 are manually adjusted over quadrant 33, a vernier adjustment being provided on one or both arms. In the present invention, and as somewhat schematically indicated in Fig. 1, a small reversible motor 41 is mounted on a bracket 42 on arms 37 and includes a worm drive 43 arranged to drive a pinion 44 meshing with the outer rack 36 of quadrant 33. Similarly, a small reversible motor 46 on a bracket 47 on arm 38 has a worm reduction unit 48 driving a pinion 49 meshing with inner rack 34 of quadrant 33. To provide the described angular relation of arms 37 and 38, motor 41, and its drive 43, 44, is arranged to operate arm 37 at substantially one-half the rate of operation of arm 38 by motor 46 and its drive 48, 49. The described driving arrangements form part of an automatic scanning system which will be described more fully in connection with the schematic wiring diagram of Fig. 5.

In order to assure accurate reproducibility of results, it is absolutely essential that a uniform atmosphere be constantly maintained between the irradiated specimen and the radiation detector. If an inert gas, such as helium, is introduced into the system, the air absorption of radiations may be reduced. Furthermore, evacuation of the system will eliminate radiation absorption by air. In either case, the system must be sealed between the specimen and the entrance to the Geiger counter.

The housing 15 can be made substantially air tight due to the compressibility of the lead linings 17, 18, or a sealing gasket can be used between the housing and its cover, and collimator 30 and rod 26 can be mounted in air tight relation through the wall 14, aperture 25 being sealed by the specimen holder and specimens, as will be described. A flexible, gas-tight sleeve 55, of rubber or similar material, interconnects the outer end of collimator 30 to the inner end of Geiger counter 40, being sealed to both of these elements and enclosing crystal analyzer 35. A connection 51 is provided on sleeve 55 and may be connected to a suitable source of an inert gas, or to a vacuum pump, dependent upon the desired conditions. Such connection may, of course, be located elsewhere in the system, as at the housing 15.

It should be noted, at this point, that aperture 25 is suitably chamfered or bevelled so that there is substantially no obstruction to the X-rays entering the aperture and, more importantly, to the fluorescent spectra passing from the specimen to the collimator 30. Also, the illustrated arrangement of X-ray tube 20 and collimator 30 substantially decreases the distance between the tube and the specimen, as compared to prior arrangements in which the specimens were mounted in an indexing holder within the housing 15. For example, the X-ray tube is ⅛'' closer the specimen than hitherto possible. As the intensity of secondary radiation is inversely proportional to the square of the distance between the X-ray tube and the sample, any decrease in such distance is very markedly effective in increasing the intensities of the fluorescent spectra.

Another improvement is in the collimator. In known prior art analyzers, the collimator is packed with $\frac{1}{16}$'' diameter nickel tubing. By packing the collimator with $\frac{1}{32}$'' nickel tubing, or by providing it with closely spaced, slit-forming separators of suitable thickness, the resolution of the spectra is greatly improved but at a small sacrifice in intensity. However, such reduction in intensity is more than compensated by the above-mentioned decrease in the distance between the X-ray tube 20 and the specimen.

To weatherproof crystal analyzer 35, when the latter is hygroscopic, for example, the crystal analyzer is provided with a very thin film of a coating, such as the one known to the art as "liquid envelope." This coating when properly applied, does not interfere with the diffraction grating action of the crystal analyzer.

The construction and mounting of the novel specimen holder 60 will be best understood by reference to Figs. 1, 2, and 3. The upper section of wall 13 of housing 15 is reduced in thickness, by machining or the like, providing a shoulder 52. On the thicker wall portion below this shoulder are mounted a pair of rails 53, 53 extending longitudinally of wall 13 and in vertically spaced relation to each other. Rails 53 are secured by bolts 54 to wall 13, and each rail has a longitudinally extending, semi-cylindrical groove 56 in one horizontal surface, the grooves opening in opposed vertical directions as seen in Fig. 3.

Specimen holder 60 includes a vertical panel 61 substantially aligned with shoulder 52. The rear surface of panel 61 has a longitudinal channel 62 therein containing a lead lining 63, channel 62 and its lining being aligned with aperture 25 and extending a substantial amount above and below the same. The forward face of panel 61 is formed with a pair of longitudinally spaced, vertically extending grooves 64, 64', the base of each having a chamfered hole 65, 65' each somewhat

larger than aperture 25. When the corresponding groove is longitudinally centered with aperture 25 its hole 65 or 65' is aligned with the aperture. Holes 65, 65' extend through lead lining 63.

Grooves 64, 64' receive the specimens 70, 70', respectively, one of which may be an unknown and the other a standard, or vice versa. To hold the specimens against the bases of the grooves, bolts or studs 66, 66' extend outwardly on each side of each groove. Each pair of bolts supports a bar 67, 67' having a stud 68, 68' centrally mounted therethrough and formed with a hardened point 71, 71' to engage a specimen. Nuts 72, 72' mounted on studs 66, 66' compress springs 69, 69' engaging bars 67, 67'. When in position, specimens 70, 70' rest on blocks 73, 73', respectively, set in the lower ends of grooves 64, 64', and are held flush against the bases of the recesses by the pointed studs 68, 68'.

Specimen holder 60 is supported for longitudinal sliding movement on tracks 53, 53 in the following manner. An elongated bar 73 has, in its upper surface, a semi-cylindrical groove 74 complementing groove 56 of lower track 53, and groove 74 has secured therein plugs 76 retaining ball bearings engaged in groove 56. A block 77 has, in its lower surface, a semi-cylindrical groove 78 complementary to groove 56 of upper track 53 and having secured therein plugs 81 retaining ball bearings in upper groove 56. Bar 73 and block 77 have vertical inner surfaces engaged with wall 13. The outermost surface 82 of block 17 is tapered for cooperation with the tapered surface of a horizontally elongated wedge 83. Block 77 and wedge 83 cooperatively form a T-slot receiving an inverted T-bar 84. A vertical cover plate 85 is secured to the outer surfaces of bar 73 and wedge 83.

The vertical panel 61 is secured to a rectangular bar 87 which is adjustably secured to the stem of T-bar 84 by studs 88. As these studs are tightened, T-bar 84 is drawn toward bar 87, but its upward movement is limited by the portion of the T-slot formed in block 77. A force is exerted downwardly on wedge 83 by bar 87, in turn forcing T-bar 84 and bar 87 inwardly toward wall 13. This acts to force panel 61, and particularly lead lining 63, tightly against the surface of wall 13. To protect against the X-rays passing through specimens 70, 70', a lead shield 75, of substantial extent, is hingedly mounted on cover 12 in alignment with aperture 25 so that it covers whichever specimen is aligned with the aperture.

Specimen holder 60 may be manually operated to selectively position specimens 70, 70' in front of aperture 25 for irradiation by X-ray tube 20. Preferably, however, the specimen holder is automatically selectively positioned under control of push buttons 1 and 2 (Fig. 1) which may be conveniently mounted on plate 11. For this purpose, a nut 80 is secured to the inner surface of plate 86 and has a cylindrical bore receiving a reversely threaded screw 90 engaged by a pin 91 in the bore of nut 80. As shaft 90 is continuously rotated in one direction, pin 91 travels alternately along each of the reversely directed threads to reciprocate holder 60. Shaft 90 is rotated by a motor 95 through the medium of reduction gearing 91 serving to mount one end of the shaft. The opposite shaft end is rotatably supported in a bearing bracket 92 on plate 11.

The operation of the automatic holder positioning system will be clear from Figs. 3 and 4. A limit switch operator 93 is secured to plate 86 and is arranged to open either of a pair of normally closed limit switches 94, 96, one at each limit of travel of holder 60 and both connected in series with motor 95. Switches 94, 96 are so located as to open the circuit of motor 95 whenever one or the other of the specimens 70, 70' is aligned with aperture 25.

For example, assuming that holder 60 is so positioned that specimen 70 is aligned with aperture 25. In such position, operator 93 will have opened switch 94, breaking the motor circuit. To position specimen 70' for analysis, push button 2 is depressed to shunt switch 94. As holder 60 moves toward the left, operator 93 disengages switch 94, which closes so that the motor continues to operate even though push button 2 is released. When specimen 70' reaches the analysis position, operator 93 engages and opens switch 96 to stop movement of holder 60. Positioning of specimen 70 in the analysis position is effected by pressing push button 1 shunting switch 96. Holder 60 may be stopped in any intermediate position by operating push button 97 which, while shown as a push button, may be an "on-off" snap switch.

The automatic positioning control arrangement of Fig. 4 is used in making analyses wherein an unknown specimen 70' is compared with a known specimen 70 having an analysis and production history comparable to that of the unknown specimen. Holder 60 is positioned at an intermediate location with lead lining 63 effectively sealing aperture 25 so that the X-ray tube may be activated to "warm-up" while the known and unknown specimens are being clamped in holder 60. Rod 26 is preferably moved inward to position shield 28 in front of the X-ray tube window to block X-rays from aperture 25. The specimens are preferably prepared with a flat ground surface finished with emery paper. After the specimens have been positioned, shield 28 is withdrawn, lead shield 75 is lowered over the holder, switch 97 is closed, and push button 1 operated to position specimen 70 in front of aperture 25.

Specimen 70 is then analyzed by shifting arms 37, 38 over the quadrant 33, the counts from Geiger counter 40 being totaled over a predetermined time interval at each characteristic Bragg angle position. This operation may be effected manually or specimen 70 may be automatically scanned, as will be described in connection with Fig. 5. When analysis of specimen 70 is completed, push button 2 is operated to position unknown specimen 70' in front of aperture 25, and specimen 70' is analyzed in the same manner. Comparison of the two analyses will provide a quantitative analysis of specimen 70' within the accepted limits of accuracy and reproducibility of results. To insure such accuracy, a sensitive voltage stabilizer is included in the energizing circuit X-ray tube 20, as there is a direct relation between intensity of fluorescence and the voltage across the X-ray tube. With the usual line potential fluctuations common in industrial plants, such X-ray tube voltage stabilization is of the utmost importance for accurate analyses.

Fig. 5 schematically illustrates an automatic scanning arrangement utilizing the motors 41 and 46 driving arms 37 and 38, respectively, through the associated reduction gearings 43 and 48. As stated, arm 38 is moved at substantially twice the speed of arm 37 so that the angle between arms 31 and 38 is substantially twice that between arms 31 and 37. The counting and scal-

ing unit 45, having its input connected to Geiger counter 40, has its output applied to a recording potentiometer 100. The chart 101 of the potentiometer is driven by a motor 102, preferably synchronous, in such manner that, with the chart calibrated in Bragg angle degrees, its calibrations will be synchronized with the characteristic Bragg angles as read from goniometer 50. As arms 37, 38 move over quadrant 33, chart 101 is correspondingly moved so that the movable needle or pen (not shown) of recorder 100 is always at a point on the chart corresponding to the Bragg angle determined from goniometer 50. The pen is moved in accordance with the intensity of fluorescent radiation, as registered by Geiger counter 40 and translated by unit 45 for application to recorder 100. Consequently, a graphic qualitative analysis of a specimen is quickly produced on chart 101 by the automatic scanning arangement.

If chart 101 is suitably calibrated to indicate percentages of elemental constituents, a rapid quantitative analysis may also be produced by the automatic scanning arrangement. Such quantitative analyses require individual charts for each type of composition, such as for a low straight chromium alloy, a chrome-nickel austenitic alloy, etc. Additionally, the charts have independent percentage scales for each elemental constituent, such as a chromium scale, copper scale, iron scale, etc., dependent upon the type of alloy undergoing analysis. For analyzing quantitatively for a single element in an unknown specimen, charts may be used having differently calibrated percentage scales for such element, each scale corresponding to a particular type of alloy, or the like. These charts are prepared empirically by fluorescent analysis of specimens of known percentage compositions, and their use obviates the necessity for comparative analyses utilizing standard specimens of known composition.

Referring to Fig. 5, a supply circuit is indicated as including conductors 103, 104. Operation of arms 37, 38 in a clockwise direction is effected by a relay CW which is energized by operation of push button 3. Closure of contacts CW–1 completes a holding circuit for the relay through closed contacts CCW–2 of counterclockwise relay CCW, clockwise limit switch LS–1, and "stop" push button 5. Contacts CW–3 and CW–4 close to energize all three motors 41, 46, and 102 for operation of the system in the clockwise scanning direction. The scanning may be continued until limit switch LS–1 opens, or may be limited to a particular area of interest by operating "stop" push button 5.

Counterclockwise scanning is effected in a similar manner by energizing counterclockwise relay CCW through momentary depression of push button 4. It will be noted that contacts CW–2 and CCW–2 interlock the relay circuits so that only one circuit can be closed at a time. While three motors are shown for the system, if greater assurance of synchronism of the chart movement with the goniometer movement is desired, chart 101 can be driven by motor 41 or motor 46. Thereby, the chart operation is mechanically locked to the goniometer operation.

The automatic scanning system provides for rapid qualitative and/or quantitative analyses without the time consuming mathematical computations necessary with manual scanning, thus greatly expediting the analytical procedure.

An outstanding feature of the apparatus is that the size of the specimens is not limited by the size of grooves 64, 64'. Should it be desired to analyze a specimen which is too large to fit in one of these grooves, holder 60 can be readily removed by loosening studs 88 and detaching bar 87 from T-bar 84. With bar 87 and panel 61 removed, the outsize specimen can be clamped to wall 13 directly in front of aperture 25. Should either specimen be smaller than an opening 65, 65', a sleeve or a shim of appropriate size may be inserted in the opening.

Fig. 6 is a reproduction of actual graphic analyses of two structurally similar alloys of the same predominant phase, both analyses being recorded on the same chart. The solid line A is the recorded analysis of an alloy of 18.25% chrome, 8.78% nickel, balance substantially iron, while the broken line B is the recorded analysis of an alloy of 25.14% chrome, 20.28% nickel, balance substantially iron. The respective curves were recorded on a quadrilaterally ruled chart having calibrated percentage scales for chromium, nickel and iron, the abscissae corresponding to characteristic Bragg angles.

By reference to the chart, it will be noted that the Ni $K\alpha$ point of the broken line B, representing 20.28% Ni is a little over twice the magnitude of the corresponding point of the solid line A representing 8.78% Ni. Similarly, the Cr $K\alpha$ peak of the broken line B, representing 25.14% Cr is about ⅓ higher than the corresponding peak of solid line A, representing 18.25% Cr. The two Fe $K\alpha$ peaks are likewise proportional to the respective Fe percentages.

The depicted chart has calibrated percentage scales for nickel, iron and chromium in austenitic alloys of the chromium-nickel type. For other types of alloys, differently calibrated percentage scales are used. Alternatively, the chart may have only chromium scales, for example, each calibrated for the chromium percentage in a different type of alloy. The latter type of calibrated chart is particularly useful in analyzing for a single constituent such as chromium, nickel, etc. Additionally, the charts are calibrated in accordance with the particular crystal analyzer used, such as rock salt, fluorite, etc.

Figs. 7, 8 and 9 schematically illustrate the invention analyzer as arranged for making comparative analyses by simultaneously irradiating both the standard and unknown specimens from a single source of primary radiation and recording the differentials of the percentages of the constituents to quantitatively analyze the unknown specimen. In these figures, the apparatus elements have been given the same reference numerals, primed or double-primed when duplicated, as used in Figs. 1 through 5.

In the arrangement of Fig. 7, the known specimen 70 and the unknown specimen 70', both mounted in specimen holders 60 (not shown) on outer wall surfaces of housing 15 are simultaneously irradiated by a single source of primary radiation, such as an X-ray tube 20' having two windows 23' and 23''. The resulting characteristic secondary radiation from specimen 70 is rectified by collimator 30, diffracted by crystal analyzer 35, and the component spectra at selected Bragg angles detected by a Geiger counter 40. The latter, and analyzer 35, are mounted on arms 38, 37, respectively, movable over quadrant 33 by synchronized motors, as previously described. The characteristic secondary radiation of specimen 70' is rectified by collimator 30', diffracted and detected in the same manner, the corre-

sponding elements bearing the same reference characters primed.

The output of detector 40 is applied, through leads 106 to a scaling and counting unit 45 energized from source 107. Similarly, the output of detector 40' is applied through leads 106' to scaling and counting unit 45' likewise energized from source 107. The outputs of units 45, 45' are applied, through leads 108, 108', respectively, and in opposition, to the grid 111 of an electronic valve 110. The latter has an anode 112 connected to B+ through a recording potentiometer 100' energized from source 107 and having its chart movement coordinated with the movements of the goniometer arms, as described in connection with Fig. 5. Cathode 113 of valve 110 is schematically indicated as grounded, with the grid bias being derived by an adjustable resistance 114.

In operation, the goniometers 50, 50' are adjusted to known corresponding points where the outputs of units 45, 45' are balanced, and resistance 114 adjusted until the recorder movable element is on the zero percentage difference line of the recorder chart. The two specimens 70, 70' are then simultaneously irradiated, and scanned in the manner described for Fig. 5. The differences between the outputs of units 45, 45' is recorded, on a properly calibrated recorder chart, as percentage differentials at characteristic Bragg angles with the quantitative analysis of specimen 70 being known, that of specimen 70' is readily computed from the graphic representation on the chart.

Figs. 8 and 9 illustrate an alternative arrangement for simultaneously irradiating both specimens from a single source, such as X-ray tube 20 having a single window 23. The specimens 70, 70' are arranged one above the other, in front of but at substantially different angles to window 23, a 90° relation being shown by way of example. A horizontal lead shield 115 keeps the characteristic secondary radiation beams separated for rectification by appropriately directed collimators 30 and 30'. The remainder of the arrangement, and its operation, are identical to those of Fig. 7.

While an X-ray tube has been referred to as the source of primary radiation, this has been by way of example only. To obtain the primary radiation incident upon the specimen, radiation sources other than an X-ray tube may be used, such as, for example, radium or a suitable isotope of a radio-active material.

While specific embodiments of the invention have been shown and described in detail to illustrate the application of the invention principles, it will be understood that the invention may be embodied otherwise without departing from such principles.

I claim:

1. In a fluorescent spectra analyzer of the type comprising a radiation source for directing primary radiation onto a specimen to irradiate the same, a collimator for resolving the resulting characteristic secondary radiation emanating from the irradiated specimen, a diffraction grating arranged adjacent the exit end of the collimator in the path of the characteristic secondary radiation and operative to separate the same into its component spectra, a radiation detector arranged to receive characteristic secondary radiation from the grating, means mounting the grating detector for angular adjustment relative to each other and to the incident secondary radiation for detecting the component spectra at selected Bragg angles; a lead lined housing enclosing the radiation source and the entrance end of the collimator and having a side wall, said wall having an aperture therethrough and the radiation source and collimator being so arranged that the axes of the primary and secondary radiation beams intersect substantially adjacent the outer surface of said wall and at the center of the aperture; a panel movably mounted on the outer surface of said wall, in surface-to-surface engagement therewith, and having a lead lining on its wall engaging surface of an area greater than that of the aperture; said panel having an opening therethrough alignable with the wall aperture; and means operable to position a specimen on the outer side of said panel and overlying the opening therein; said panel being movable on said wall between a position in which its lead lining covers the wall aperture and a position in which the opening is aligned with the aperture.

2. In a fluorescent spectra analyzer of the type comprising a radiation source for directing primary radiation onto a specimen to irradiate the same, a collimator for resolving the resulting characteristic secondary radiation emanating from the irradiated specimen, a diffraction grating arranged adjacent the exit end of the collimator in the path of the characteristic secondary radiation and operative to separate the same into its component spectra, a radiation detector arranged to receive characteristic secondary radiation from the grating, means mounting the grating and detector for angular adjustment relative to each other and to the incident secondary radiation for detecting the component spectra at selected Bragg angles; a lead lined housing enclosing the generator and the entrance end of the collimator and having a side wall, said housing being substantially airtight and said collimator extending in sealed relation through a wall thereof; a flexible air-tight enclosure connecting the outer end of the collimator to the detector and enclosing the diffraction grating; and means operable to constantly maintain a uniform atmosphere other than air in said housing, collimator, and enclosure to minimize or eliminate absorption of fluorescent spectra between the specimen and the detector.

3. In a fluorescent spectra analyzer of the type comprising a radiation source for directing primary radiation onto a specimen to irradiate the same, a collimator for resolving the resulting characteristic secondary radiation emanating from the irradiated specimen, a diffraction grating arranged adjacent the exit end of the collimator in the path of the characteristic secondary radiation and operative to separate the same into its component spectra, a radiation detector arranged to receive characteristic secondary radiation from the grating, means mounting the grating and detector for angular adjustment relative to each other and to the incident secondary radiation for detecting the component spectra at selected Bragg angles; a lead lined housing enclosing the radiation source and the entrance end of the collimator and having a side wall, said wall having an aperture therethrough and the radiation source and collimator being so arranged that the axes of the primary and secondary radiation beams intersect substantially adjacent the outer surface of said wall and at the center of the aperture; an elongated panel mounted in surface-to-surface engagement with the outer surface of said wall and reciprocable longitudi-

nally thereof, and having a lead lining on its wall engaging surface of an area greater than that of the aperture; said panel having longitudinally spaced openings therein selectively alignable with the wall aperture; and means operable to position specimens on the outer side of said panel and each overlying an opening therein; said panel being movable on said wall between positions in which its lead lining covers the wall aperture and positions in which the openings are selectively aligned with the aperture.

4. In a fluorescent spectra analyzer of the type comprising a radiation source for directing primary radiation onto a specimen to irradiate the same, a collimator for resolving the resulting characteristic secondary radiation emanating from the irradiated specimen, a diffraction grating arranged adjacent the exit end of the collimator in the path of the characteristic secondary radiation and operative to separate the same into its component spectra, a radiation detector arranged to receive characteristic secondary radiation from the grating, means mounting the grating and detector for angular adjustment relative to each other and to the incident secondary radiation for detecting the component spectra at selected Bragg angles; a lead lined housing enclosing the radiation source and the entrance end of the collimator and having a side wall, said wall having an aperture therethrough and the radiation source and collimator being so arranged that the axes of the primary and secondary radiation beams intersect substantially adjacent the outer surface of said wall and at the center of the aperture; an elongated panel mounted in surface-to-surface engagement with the outer surface of said wall and reciprocable longitudinally thereof, and having a lead lining on its wall engaging surface of an area greater than that of the aperture; said panel having longitudinally spaced openings therein selectively alignable with the wall aperture; means operable to position specimens on the outer side of said panel and each overlying an opening therein; mechanism, including an electric motor, operable to reciprocate said panel along said wall; control means operable to energize said motor; and means automatically operable to deenergize said motor whenever an opening is aligned with the aperture; the lead lining of said panel sealing the aperture in intermediate positions of said panel.

5. In a fluorescent spectra analyzer of the type comprising a radiation source for directing primary radiation onto a specimen to irradiate the same, a collimator for resolving the resulting characteristic secondary radiation emanating from the irradiated specimen, a diffraction grating arranged adjacent the exit end of the collimator in the path of the characteristic secondary radiation and operative to separate the same into its component spectra, a radiation detector arranged to receive characteristic secondary radiation from the grating, means mounting the grating and detector for angular adjustment relative to each other and to the incident secondary radiation for detecting the component spectra at selected Bragg angles; a lead lined housing enclosing the radiation source and the entrance end of the collimator and having a side wall, said wall having an aperture therethrough and the radiation source and collimator being so arranged that the axes of the primary and secondary radiation beams intersect substantially adjacent the outer surface of said wall and at the center of the aperture; a slide mounted for longitudinal reciprocation on the outer surface of said wall; an elongated panel disengageably supported on said slide in surface-to-surface engagement with the outer surface of said wall, and having a lead lining on its wall engaging surface of an area greater than that of the aperture; said panel having longitudinally spaced openings therein selectively alignable with the wall aperture; and means operable to position specimens on the outer side of said panel and each overlying an opening therein; said slide being movable between positions in which the lead lining of said panel covers the aperture and positions in which a panel opening is selectively aligned with the aperture.

6. In a fluorescent spectra analyzer of the type comprising a radiation source for directing primary radiation onto a specimen to irradiate the same, a collimator for resolving the resulting characteristic secondary radiation emanating from the irradiated specimen, a diffraction grating arranged adjacent the exit end of the collimator in the path of the characteristic secondary radiation and operative to separate the same into its component spectra, a radiation detector arranged to receive characteristic secondary radiation from the grating, means mounting the grating and detector for angular adjustment relative to each other and to the incident secondary radiation for detecting the component spectra at selected Bragg angles; a lead lined housing enclosing the radiation source and the entrance end of the collimator and having a side wall, said wall having an aperture therethrough and the radiation source and collimator being so arranged that the axes of the primary and secondary radiation beams intersect substantially adjacent the outer surface of said wall and at the center of the aperture; a slide mounted for longitudinal reciprocation on the outer surface of said wall; an elongated panel disengageably supported on said slide in surface-to-surface engagement with the outer surface of said wall, and having a lead lining on its wall engaging surface of an area greater than that of the aperture; said panel having longitudinally spaced openings therein selectively alignable with the wall aperture; means operable to position specimens on the outer side of said panel and each overlying an opening therein; and wedge means cooperable with said slide to force said panel into tight surface engagement with the outer surface of said wall; said slide being movable between positions in which the lead lining of said panel covers the aperture and positions in which a panel opening is selectively aligned with the aperture.

7. In a fluorescent spectra analyzer of the type comprising a radiation source for directing primary radiation onto a specimen to irradiate the same, a collimator for resolving the resulting characteristic secondary radiation emanating from the irradiated specimen, a diffraction grating arranged adjacent the exit end of the collimator in the path of the characteristic secondary radiation and operative to separate the same into its component spectra, a radiation detector arranged to receive characteristic secondary radiation from the grating, means mounting the grating and detector for angular adjustment relative to each other and to the incident secondary radiation for detecting the component spectra at selected Bragg angles; a lead lined

housing enclosing the radiation source and the entrance end of the collimator and having a side wall, said wall having an aperture therethrough and the radiation source and collimator being so arranged that the axes of the primary and secondary radiation beams intersect substantially adjacent the outer surface of said wall and at the center of the aperture; a slide mounted for longitudinal reciprocation on the outer surface of said wall; an elongated panel disengageably supported on said slide in surface-to-surface engagement with the outer surface of said wall, and having a lead lining on its wall engaging surface of an area greater than that of the aperture; said panel having longitudinally spaced openings therein selectively alignable with the wall aperture; longitudinally spaced recesses formed in the forward face of the panel, each surrounding one of the openings therein and arranged to have a specimen mounted therein and overlying the opening, and gripping means associated with each recess to engage a specimen and retain it in the recess; said slide being movable between positions in which the lead lining of said panel covers the aperture and positions in which a panel opening is selectively aligned with the aperture; said panel being disengageable from said slide to provide for an outsize specimen to be clamped directly to the outer surface of said wall overlying the aperture.

8. In a fluorescent spectra analyzer of the type comprising a radiation source for directing primary radiation onto a specimen to irradiate the same, a collimator for resolving the resulting characteristic secondary radiation emanating from the irradiated specimen, a diffraction grating arranged adjacent the exit end of the collimator in the path of the characteristic secondary radiation and operative to separate the same into its component spectra, a radiation detector arranged to receive characteristic secondary radiation from the grating, means mounting the grating and detector for angular adjustment relative to each other and to the incident secondary radiation for detecting the component spectra at selected Bragg angles; a lead lined housing enclosing the radiation source and the entrance end of the collimator and having a side wall, said wall having an aperture therethrough and the radiation source and collimator being so arranged that the axes of the primary and secondary radiation beams intersect substantially adjacent the outer surface of said wall and at the center of the aperture; a panel movably mounted on the outer surface of said wall and in surface-to-surface engagement therewith and having a lead lining on its wall engaging of an area greater than that of the aperture; said panel having an opening therethrough alignable with the wall aperture; means operable to position a specimen on the outer side of said panel and overlying the opening therein; said panel being movable on said wall between a position in which its lead lining covers the wall aperture and a position in which the opening is aligned with the aperture; a lead shield mounted within said housing for movement between a retracted position and a position blocking x-rays directed from the tube toward the aperture; and operating means for said lead panel disposed outside said housing.

9. In a fluorescent spectra analyzer of the type comprising a radiation source for directing primary radiation onto a specimen to irradiate the same, a collimator for resolving the resulting characteristic secondary radiation emanating from the irradiated specimen, a diffraction grating arranged adjacent the exit end of the collimator in the path of the characteristic secondary radiation and operative to separate the same into its component spectra, a radiation detector arranged to receive characteristic secondary radiation from the grating, means mounting the grating and detector for angular adjustment relative to each other and to the incident secondary radiation for detecting the component spectra at selected Bragg angles; a lead lined housing enclosing the radiation source and the entrance end of the collimator and having a side wall, said wall having an aperture therethrough and the radiation source and collimator being so arranged that the axes of the primary and secondary radiation beams intersect substantially adjacent the outer surface of said wall and at the center of the aperture; a panel movably mounted on the outer surface of said wall and in surface-to-surface engagement therewith and having a lead lining on its wall engaging surface of an area greater than that of the aperture; said panel having an opening therethrough alignable with the wall aperture; means operable to position a specimen on the outer side of said panel and overlying the opening therein; said panel being movable on said wall between a position in which its lead lining covers the wall aperture and a position in which the opening is aligned with the aperture; and a lead shield movably mounted on said housing for positioning over the portion of said panel adjacent the aperture.

10. In a fluorescent spectra analyzer of the type comprising a radiation source for directing primary radiation onto a specimen to irradiate the same, a collimator for resolving the resulting characteristic secondary radiation emanating from the irradiated specimen, a diffraction grating arranged adjacent the exit end of the collimator in the path of the characteristic secondary radiation and operative to separate the same into its component spectra, a radiation detector arranged to receive characteristic secondary radiation from the grating, means mounting the grating and detector for angular adjustment relative to each other and to the incident secondary radiation for detecting the component spectra at selected Bragg angles; a lead lined housing enclosing the radiation source and the entrance end of the collimator and having a side wall, said wall having an aperture therethrough and the radiation source and collimator being so arranged that the axes of the primary and secondary radiation beams intersect substantially adjacent the outer surface of said wall and at the center of the aperture; a panel movably mounted on the outer surface of said wall, in surface-to-surface engagement therewith, and having a lead lining on its wall engaging surface of an area greater than that of the aperture; said panel having an opening therethrough alignable with the wall aperture; means operable to position a specimen on the outer side of said panel and overlying the opening therein; said panel being movable on said wall between a position in which its lead lining covers the wall aperture and a position in which the opening is aligned with the aperture; and means mounting the radiation source for angular adjustment relative to the aperture about an arc having a radius centered at the intersection of the primary and secondary radiation beams.

11. In a fluorescent spectra analyzer of the type comprising a radiation source for directing primary radiation onto a specimen to irradiate the same, a collimator for resolving the resulting characteristic secondary radiation emanating from the irradiated specimen, a diffraction grating arranged adjacent the exit end of the collimator in the path of the characteristic secondary radiation and operative to separate the same into its component spectra, a radiation detector arranged to receive characteristic secondary radiation from the grating, and means mounting the grating and detector for angular adjustment relative to each other and to the incident secondary radiation for detecting the component spectra at selected Bragg angles, the mounting means comprising a pair of radial arms relatively adjustable about a center adjacent the exit end of the collimator, one of said arms supporting said grating for angular adjustment relative to the axis of said collimator and the other arm supporting said detector for angular adjustment relative to said grating and the axis of said collimator; an automatic specimen scanning system including a movable chart recorder having its chart calibrated in Bragg angles; means operative to apply the output of said detector to the indicating mechanism of said recorder; and driving means associated with each of said arms and with said chart and operable to drive said arms and said chart in coordinated relation with each other to produce a record of the relative intensities of secondary radiation at characteristic Bragg angles.

12. In a fluorescent spectra analyzer of the type comprising a radiation source for directing primary radiation onto a specimen to irradiate the same, a collimator for resolving the resulting characteristic secondary radiation emanating from the irradiated specimen, a diffraction grating arranged adjacent the exit end of the collimator in the path of the characteristic secondary radiation and operative to separate the same into its component spectra, a radiation detector arranged to receive characteristic secondary radiation from the grating, and means mounting the grating and detector for angular adjustment relative to each other and to the incident secondary radiation for detecting the component spectra at selected Bragg angles, the mounting means comprising a pair of radial arms relatively adjustable about a center adjacent the exit end of the collimator, one of said arms supporting said grating for angular adjustment relative to the axis of said collimator and the other arm supporting said detector for angular adjustment relative to said grating and the axis of said collimator; an automatic specimen scanning system including a movable chart recorder having its chart calibrated in Bragg angles; means operative to apply the output of said detector to the indicating mechanism of said recorder; driving means associated with each of said arms and with said chart and operable to drive said arms and said chart in coordinated relation with each other to produce a record of the relative intensities of secondary radiation at characteristic Bragg angles; and a conjoint control system for said motors including manually operable circuit closure means, automatic circuit breaker means operative at the limits of movement of the arms, and manually operable circuit breaker means.

13. In a fluorescent spectra analyzer of the type comprising a radiation source for directing primary radiation onto a specimen to irradiate the same, a collimator for resolving the resulting characteristic secondary radiation emanating from the irradiated specimen, a diffraction grating arranged adjacent the exit end of the collimator in the path of the characteristic secondary radiation and operative to separate the same into its component spectra, a radiation detector arranged to receive characteristic secondary radiation from the grating, means mounting the grating and detector for angular adjustment relative to each other and to the incident secondary radiation for detecting the component spectra at selected Bragg angles; a lead lined housing enclosing the generator and the entrance end of the collimator and having a side wall, said housing being substantially air-tight and said collimator extending in sealed relation through a wall thereof; a flexible air-tight enclosure connecting the outer end of the collimator to the detector and enclosing the diffraction grating; and means operable to constantly maintain a vacuum in said housing, collimator, and enclosure to minimize or eliminate absorption of fluorescent spectra between the specimen and the detector.

14. In a fluorescent spectra analyzer of the type comprising a radiation source for directing primary radiation onto a specimen to irradiate the same, a collimator for resolving the resulting characteristic secondary radiation emanating from the irradiated specimen, a diffraction grating arranged adjacent the exit end of the collimator in the path of the characteristic secondary radiation and operative to separate the same into its component spectra, a radiation detector arranged to receive characteristic secondary radiation from the grating, means mounting the grating and detector for angular adjustment reltative to each other and to the incident secondary radiation for detecting the component spectra at selected Bragg angles; a recorder chart calibrated in characteristic Bragg angles and having percentage scales for elemental constituents calibrated in accordance with known relations of spectral intensities to element percentages; and means constructed and arranged to indicate on said chart at each characteristic Bragg angle the spectral intensity; whereby an unknown specimen may be simultaneously quantitatively and qualitatively analyzed.

15. For use in a fluorescent spectra analyzer of the type comprising a radiation source for directing primary radiation onto a specimen to irradiate the same, a collimator for resolving the resulting characteristic secondary radiation emanating from the irradiated specimen, a diffraction grating arranged adjacent the exit end of the collimator in the path of the characteristic secondary radiation and operative to separate the same into its component spectra, a radiation detector arranged to receive characteristic secondary radiation from the grating, means mounting the grating and detector for angular adjustment relative to each other and to the incident secondary radiation for detecting the component spectra at selected Bragg angles, the mounting means comprising a pair of radial arms relatively adjustable about a center adjacent the exit end of the collimator, one of said arms supporting said grating for angular adjustment relative to the axis of said collimator and the other arm supporting said detector for angular adjustment relative to said grating and the axis of said collimator, an automatic specimen scanning system including a movable chart

recorder, means operative to apply the output of said detector to the indicating mechanism of said recorder, driving means associated with each of said arms and with said recorder and operable to drive said arms and said recorder in coordinated relation with each other to produce a record of the relative intensities of secondary radiation at characteristic Bragg angles; a chart for said recorder calibrated in characteristic Bragg angles and having percentage scales for element constituents calibrated in accordance with known relations of spectral intensities to element percentages, to quantitatively determine the composition of the test specimen.

MARCEL A. CORDOVI.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,347,638	McLachlan, Jr.	Apr. 25, 1944

Number	Name	Date
2,442,752	Armstrong	June 8, 1948
2,445,132	Berman	July 13, 1948
2,449,066	Friedman	Sept. 14, 1948
2,452,045	Friedman	Oct. 26, 1948
2,521,772	Beeghly	Sept. 12, 1950
2,540,821	Harker	Feb. 6, 1951

FOREIGN PATENTS

Number	Country	Date
382,518	Great Britain	Oct. 27, 1932

OTHER REFERENCES

A new Precision X-Ray Spectrometer by Walter Soller, Physical Review, vol. 24, 1924, pp. 158–167.

A High-Temperature X-Ray Camera for Precision Measurements, Jay, Physical Society of London Proceedings, vol. 44, 1933, pages 635–642.