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X-RAY SPECTROMETER HAVING AN X-RAY SOURCE WITH
A CONTINUOUSLY CLEANED X-RAY TARGET
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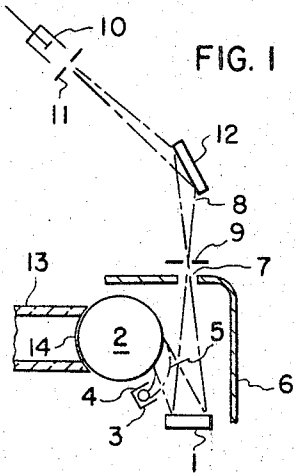


FIG. 1

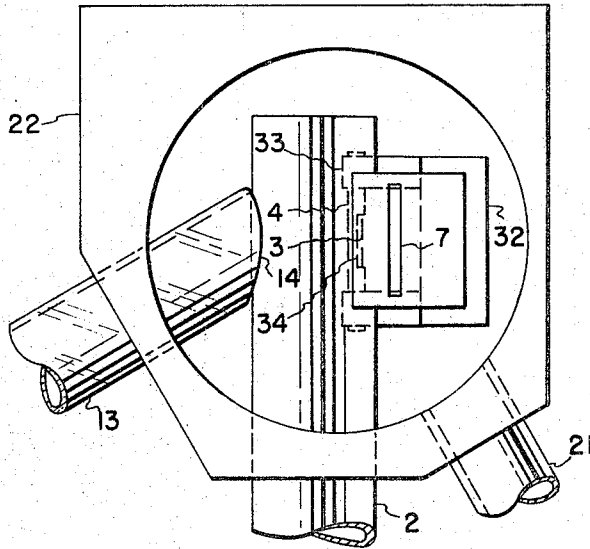


FIG. 4

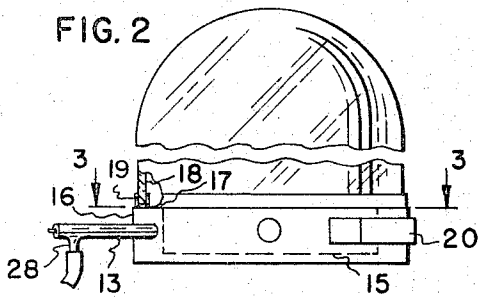


FIG. 2

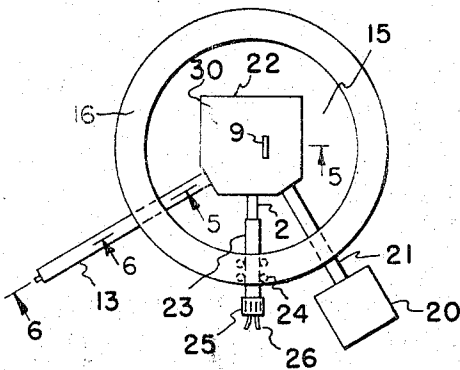


FIG. 3

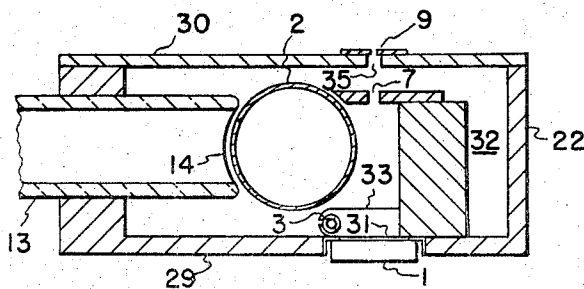


FIG. 5

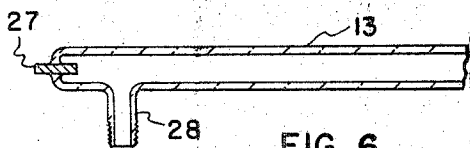


FIG. 6

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X-RAY SPECTROMETER HAVING AN X-RAY SOURCE WITH A CONTINUOUSLY CLEANED X-RAY TARGET

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ABSTRACT OF THE DISCLOSURE

An ion source, an electron emitter, a moveable X-ray target and a surface of a sample undergoing X-ray emission analysis are in an evacuated chamber which has an exit slit for characteristic X-rays emitted by the sample. Ions from the source clean the target so that periodically or continuously, a clean surface is presented where X-rays are produced on the target by the electron beam from the emitter. Characteristic X-rays emerging from the slit are analyzed with a crystal and detector which are in an evacuated enclosure surrounding the chamber.

The present invention is concerned with improving the ability of an X-ray spectrometer to measure the concentration of low atomic number elements in a sample undergoing emission analysis.

The invention relates to spectrometers of the type that have an X-ray source which emits primary rays that excite the chemical elements in a sample to fluoresce and to emit radiation of wavelengths that are characteristic of the elements. The characteristic X-ray spectrum so produced is dispersed by a diffracting crystal and the intensities of the spectra are detected to give an indication of the kind and concentration of the elements present in the sample.

Efficient excitation of characteristic X-ray requires that the energy of the primary or exciting radiation be a little greater than the energy that corresponds with the absorption edge of the element being excited. Characteristic radiations from low atomic number elements have low energy and hence the exciting radiation should also be of relatively low energy. This results in high absorption of the radiation in the path from the X-ray tube to the sample and from the sample to the diffracting crystal and detector. To minimize absorption and to facilitate detecting as many as possible of the characteristic ray photons that are emitted by the sample, the paths are made as short as possible and a vacuum or lightweight gas ambient is used.

Optimizing the transmissibility and geometry of the X-ray path is not the only problem, however. A more difficult problem has been to reduce background radiation at wavelengths that are near or coincide with the wavelengths or particular photon energies being measured. Stated in another way, the problem is to obtain a high ratio of peak intensity to background intensity so that the photon intensity one desires to detect is not obscured by the unwanted background radiation.

One of the causes of low peak-to-background radiation is the presence of contaminants on the sample surface, in the environment and on the X-ray target. For example, if there is a molecular coating of carbon or its compounds on the X-ray target, the electron beam that produces the primary X-rays will also excite carbon to emit its characteristic radiation. Some of this radiation will get into the detector which is ordinarily unable to discriminate these photons from those being emitted by a sample in which the concentration of carbon is being determined. Another more significant effect of the X-ray target being contaminated is that both the intensity and

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the spectral distribution of the primary exciting radiation may change with the character and degree of contamination. This causes both variations in the quantity of characteristic photons from the sample and inconsistent analytical results.

Accordingly, an object of this invention is to overcome the above-noted problems and to provide a more sensitive, accurate, and precise instrument for measuring small concentrations of low atomic number elements in a sample.

A more specific object is to provide for continuous and thorough cleaning of a moveable X-ray generating target, particularly by means of impinging gas ions on the target and thereby sputtering off surface impurities in one region while X-rays are being generated on another region of the target.

Another object is to use ions for cleaning the sample when spectroscopic analysis is in progress.

Achievement of the foregoing and other objects will appear from time to time throughout the instant specification.

The invention will be illustrated in connection with a spectrometer that comprises a housing for the X-ray optical system, the source, and the sample to be analyzed. The housing may be filled with low pressure X-ray permeable gas or it may be evacuated. Within the housing there is a chamber that may be at a different pressure or state of evacuation and in which a rotating cylindrical X-ray target extends. An electron emitting cathode and the sample are in proximity with one side of the target. A tubular ion generating and accelerating tube extends through the wall of the housing into the chamber. The inside end of the ion tube is open and curved to bring it into close proximity and conformity with the surface of the cylindrical target. A gas inlet in the tube outside the housing permits entry of gas for ionization. The ions strike the target, which is at an appropriate electric potential to attract them at high velocity, and the contaminant molecules and some of the parent metal atoms are sputtered off of the target. The sputtered material collects on the interior of the tube for periodic removal. Thus, as the target rotates, it continuously presents a clean surface to the electron beam that produces the primary exciting radiation. The new cleaning method may be used with X-ray targets that are adapted for translational movement as well as rotational.

A more detailed description of a preferred embodiment of the invention will now be given in reference to the drawing in which:

FIGURE 1 is a diagram of an X-ray spectrometer embodying the invention;

FIGURE 2 is an elevational view of an X-ray spectrometer embodying the invention with some parts being omitted and others being broken away;

FIGURE 3 is a top view taken on a line corresponding with 3—3 in FIGURE 2;

FIGURE 4 is an enlarged top view of the chamber 22 shown in FIGURE 3 with its top removed;

FIGURE 5 is a vertical sectional view taken on a line corresponding approximately with 5—5 in FIGURE 3; and,

FIGURE 6 is a fragmentary vertical sectional view of the ion tube 13 taken on a line corresponding with 6—6 in FIGURE 3.

The essential features of a spectrometer embodying the invention are schematized in FIGURE 1 to which attention is now invited. The sample 1 to be analyzed for its unknown elements is located in a plane beneath a cylindrical rotating X-ray target or anode 2. A heated electron emitting filament 3 is located to the side of sample 1 so the latter can be brought as near as possible to anode 2 without interference. The cathode is surround-

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ed in part by a tubular metal shield 4 which has an open side from which electrons emanate in the curve trajectory represented by broken lines 5 whereupon they are attracted to the periphery of target 2 under the influence of a high positive potential which is applied to it relative to the cathode. X-rays that are generated on the target surface radiate back to the top surface of the sample whereupon they excite elements of the sample to emit their characteristic radiation.

The electron exit opening in the shield 4 is oriented so that the hot cathode is not in the line of sight of the anode 2 or the sample 1. This prevents deposition of tungsten vapor from the filament 3 on the anode or on the sample. Background may be reduced further by maintaining the filament 3 and sample 1 at the same potential in which case the latter will not attract electrons. The anode 2 is maintained at ground potential, the cathode 3 is held zero to sixteen kilovolts below ground, while the sample may be at either potential. For characteristic ray excitation with X-rays, the sample 1 is held at the same potential as the cathode 3. For direct electron excitation, the sample may be grounded. Thus, the sample may be excited by X-rays or electrons.

Rotating anode 2 may be of any metal that has an appropriate X-ray spectrum for exciting the elements in the sample being analyzed. The K radiation from aluminum and the L radiation from copper, titanium, and iron anodes has been successively used for samples with low atomic number elements. Another series of anodes consists of a copper cylinder plated with gold, silver, and chromium which produce L radiation that yields the desired results with some of the lower atomic number elements.

To further minimize background radiation and to establish a proper electrostatic field configuration for the electron beam from cathode 3, there is provided an electron scatter shield 6 of any suitable metal. Stray electrons that strike the scatter shield are deflected onto anode 2 where they generate primary radiation. The electrons may be focussed with a magnetic field as well as with an electrostatic field, if desired.

Shield 6 has a slot 7 in its top from which the characteristic radiation emanating from the sample 1 may emerge for spectral analysis by an X-ray optical system. The path of the secondary characteristic radiation is designated by broken lines 8 and is seen to pass through a slit 9 whereupon it falls on a diffracting crystal 12 which deflects a particular wavelength band toward a detector 10 in front of which there is another slit 11. Detector 10 is preferably a flow proportional counter with a thin window that is permeable to the soft X-radiation being detected. In one practical embodiment, the flow counter had a thin polypropylene window, not shown, which transmitted 77% of carbon K radiation. The X-ray optical system including the detector 10, slits 9, 11 and diffracting crystal 12 and the mechanism for relating these elements to each other in the proper Bragg relationship forms no part of the instant invention. An X-ray optical system that is used in a practical embodiment of this invention is shown in U.S. Patent 2,898,469 which issued on Aug. 4, 1959 to L. R. Rose and is assigned to the assignee of the present invention.

In FIGURE 1 the new means for keeping anode 2 clean and the X-ray spectrum pure is also shown. The cleaning means comprises an insulating tube 13, preferably glass, which is shown in this view partly broken away. The tube is curved at its end 14 and contoured to conform to the circular periphery of anode 2 essentially contiguously but with a small clearance gap. As will be explained later, ions are created and accelerated in tube 13 along its axis whereupon they impinge on the periphery of X-ray target 2. The ions have sufficient velocity to detach contaminants from the target 2 surface and to sputter away the contaminants and a small amount of the target surface. The sputtered material collects on

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the interior of tube 13 for easy removal when occasion arises after extended operation. The rate of cleaning and the amount of sputtering depends on the ion current and this is controlled by regulating the voltage on the ion tube.

Attention is now invited to FIGURE 2 which shows an outline of the new spectrometer in elevation with parts removed. The spectrometer comprises a housing base 15 which is essentially a hollowed-out metal cylinder which has up-standing walls 16 and a smooth upper surface 17. An inverted glass bell jar 18 encloses housing 15 so that a vacuum can be created in it. The bell jar 18 is provided at its lower edge with a gasket 19 of pliable material for producing a vacuum tight seal. Although the X-ray optical system that is schematized in FIGURE 1 is not shown in FIGURE 2, it will be appreciated that this system extends upwardly into the bell jar 18. Bell jar 18 and housing 15 may be evacuated through openings in the base of the latter which are not shown.

After the bell jar 18 is pumped down to a fairly high vacuum with an external vacuum pumping system, not shown, the vacuum may be further improved by an ion pump 20 which, as may be seen in FIGURE 3, has a tube 21 that extends through the wall of housing 15 into an internal chamber 22. With this arrangement, the interior of chamber 22 may be even more highly evacuated than bell jar 18. This is because there are restricted gas flow paths between chamber 22 and bell jar 18 as will be explained shortly hereinafter.

In FIGURE 3 it will be seen that anode 2 is carried on a shaft 23 which passes through the wall of housing 15 and through a pair of O-rings 24 which effect a vacuum tight seal. This vacuum seal is not shown in greater detail because it forms no part of the instant invention. At the outer end of shaft 23 is shown a gear 25 which may be coupled with a motor drive, not shown, which rotates anode 2 at a selected speed. Suitable tubes 26 are provided for admitting cooling water to the interior of shaft 23 and anode 2.

The ion accelerating tube 13 that is used for cleaning target 2 is also shown in FIGURE 3 as extending through the wall of housing 15 and into internal chamber 22. The details of the ion accelerating tube 13 may be seen in FIGURE 6. At one end of tube 13 there is sealed-in an electrode 27 which may be connected to the positive side of a D-C power supply, not shown. The voltage on electrode 27 should be no higher than necessary to produce enough ion current to affect cleaning of the particular target being used. A low pressure gas which is identified below may be admitted to the interior of tube 13 through a hose connection 28. When in operation, an electric field is produced between positive electrode 27 in the ion gun and target 2 which is at ground potential. This field causes some of the gas to become positively ionized. The positive ions are attracted to anode 2 on which they impinge to produce the cleaning and sputtering action which was discussed above.

Various gases such as argon, neon, hydrogen, and oxygen may be used in ion tube 13 but best results have been obtained with helium at a pressure of 100 microns or lower. The lowest possible pressure that will yield the necessary ion current for cleaning the target is preferred because any excess of gas will just place a greater burden on the vacuum pumping system. With the proper control of pressure, any excess gas that escapes through the end 14 of tube 13 will not be sufficient to attenuate X-rays within chamber 22 significantly. In some cases the bombarding gas may be reacted with the target contaminant; for example, oxygen may be reacted with carbon to form carbon monoxide or carbon dioxide which can be pumped away. In practice, a variable resistor is used in series with the D-C lines to the ion gun to control the ion current.

The arrangement of the parts within chamber 22 may be seen more clearly in FIGURES 4 and 5. In FIGURE 5 the chamber is seen to be enclosed by a bottom 29 and a

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cover plate 30. Ion cleaning tube 13 passes through a wall of the chamber 22. Tube 13 should make a substantially vacuum tight fit with the chamber 22 which may be achieved by using O-rings, not shown. At the bottom of the chamber there is provided a recess in which there is an opening 31 through which the top surface of sample 1 is presented to the interior of the chamber for irradiation with X-rays. For supporting the cathode 3 within chamber 22 there is provided a frame 32 that has a pair of lower extensions 33 which are spaced from each other and bridged by the cathode assembly. In FIGURE 4 one may see that the cathode assembly comprises a metal tubular shield 4 having a filament 3 extending through it with clearance around it. The filament is exposed in the region of a slot 34 so that electrons may emanate radially outwardly from the filament when it is heated.

Cathode 3 is so located as to be shielded from any field which would attract ions to the cathode and destroy it. This results from anode target 2 intervening between the end 14 of the ion tube 13 and the cathode and being in a plane above the cathode. Thus, there is no field for attracting any ions over the top of anode 2 and if any follow a path along its bottom they will strike the back of cathode shield 4 instead of impinging directly on the cathode.

Another advantage of having the cathode 3 positioned where it is very near the anode 2 is that the cathode is in an intense electric field which attracts the electrons to the anode. This eliminates space charge in the vicinity of the hot cathode and allows it to be operated primarily in an emission limited rather than a space charge limited mode.

In FIGURE 5 one may see that for reasons which were explained earlier, the emerging electrons may be attracted in a curved trajectory to the periphery of target 2 to produce primary X-rays. These X-rays are generated in a region slightly below a horizontal plane passing through the center of target 2 so that they may be projected downwardly onto sample 1 between extensions 33. Characteristic X-rays that are produced on the surface of target 2 radiate upwardly through a slit 7 which is in a deflector plate that is fastened to frame 32. X-rays pass out of chamber 22 through an elongated opening 35 in cover plate 30. The deflector and other metal parts serve to shape the electric field so that essentially all of the electrons emitted by the filament arrive on the target.

In a practical embodiment means are provided for holding and permitting the lateral adjustment and alignment of another slit 9 which may be chosen to give the best resolution and intensity in accordance with known principles.

Sample 1 may be held on a device that permits its alignment with opening 31 at the bottom of chamber 22 and that enables it to be pressed in a fairly good vacuum tight relationship with the margins of opening 31. A thin vacuum tight window may cover opening 31, if desired. The mechanism for positioning sample 1 is not shown because it forms no part of the instant invention.

From the foregoing description it is seen that chamber 22 is fairly vacuum tight but for minor leakage around ion tube 13, the sample 1 and through slit 9. As a result, it is possible to maintain the interior of chamber 22 at a lower pressure, or higher vacuum with ion pump 20 than the remainder of the space. Condensable gases are also removed with a cryogenic cold surface, not shown. These gases can then be pumped away by the ion pump when the cold surface is allowed to reach ambient temperature.

The invention also features electronic pumping of the gases that may reside in the interior of chamber 22 and cleaning of the sample 1 with ions. Some of the excess gas which is not ionized in ion tube 13 emerges from its end 14 into chamber 22. Other gases may also be present. A part of these gases are ionized by some of the electrons which emanate from cathode 3 on their way to target 2. The positive gas ions so produced are attracted to the sample 1 surface through window opening 31 in FIGURE 5 in which case they sputter off a small amount of sample

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including any surface contamination. Of course, this requires maintaining the sample relatively negative in order that positive ions be attracted. An effect of this process is to remove gas that might attenuate X-rays from the chamber 22. When the ions strike the sample 1 or other parts such as shield assembly 32 they are neutralized and subject to occlusion by material that is sputtered. To use this process that is, to make the sample 1 negative so it will work, it is desirable to have the gas pressure at least as low as 5×10^{-4} torr so the ion yield will not be too great.

To operate the spectrograph the bell jar 18 is brought down on housing 15 to form an enclosure. The enclosure is pumped down by a suitable vacuum pumping system to a pressure 5×10^{-6} torr. Filament 3 is then allowed to heat and the high voltage is applied to X-ray target 2. Prior to this time, ion pump 20 may be energized to reduce the pressure in chamber 22 further. Voltage is then applied to electrode 27 in ion tube 13 and low pressure gas is admitted through tubulation 28. Anode target 2 is then caused to rotate at a continuous speed whereby it may be cleaned by the ions which impinge on it. As soon as an area of the target that has been cleaned under the end of ion tube 13 has rotated sufficiently far around to present a clean surface to the electrons coming from cathode 3, measurement may proceed. Thereafter, a clean target surface will be presented to the electron beam during the course of the analysis. Any contaminants sputtered off of the target surface will collect on the interior of ion tube 13 from which they are easily cleaned after withdrawing the tube. In a practical case, good results were obtained with a target having a diameter of about one inch that is rotated at one revolution per minute. On some occasions the operator may choose to rotate the target periodically instead of continuously if cooling is adequate. The ion gun may also be turned off in some cases after the target is cleaned and the gun may be re-energized periodically as necessary.

Although a preferred embodiment of the invention has been described, such description is to be considered illustrative rather than limiting, for the invention may be variously embodied and, particularly, different forms of ion cleaning guns may be used and different ways of moving the X-ray target may be used without departing from the basic inventive concepts which are covered in the appended claims.

It is claimed:

1. An X-ray spectrometer comprising:

- (a) an evacuable enclosure means,
- (b) a moveable X-ray target within the enclosure means,
- (c) a source of electrons,
- (d) said target having a first surface region on which impinging electrons are attracted from the source to produce primary X-rays,
- (e) an ion gun means having a discharge opening for ions that impinge on a second surface region of the target to clean the same remotely from the first region,
- (f) whereupon movement of the target presents the second region as a clean first region target surface to the impinging electrons,
- (g) means for locating a sample near the target for exciting the same with primary X-rays to produce X-rays that are characteristic of the elements in the sample,
- (h) an X-ray detector, and
- (i) a diffracting crystal located to intercept characteristic X-rays from a sample and diffract particular wavelengths thereof into the detector.

2. An X-ray spectrometer comprising:

- (a) an evacuable enclosure means,
- (b) a cylindrical X-ray target that is adapted for continuous rotation about its axis and is disposed within the enclosure means,
- (c) an electron emitter that is located adjacent the

- periphery of the target for producing a beam of electrons that impinge on a first surface region of the target to produce primary X-rays,
- (d) an ion gun means having an ion discharge opening in proximity with a second target surface region for ions to impinge thereon and thereby sputter contaminants from the target surface, 5
- (e) whereby rotation of the target means effects continuous presentation of a clean target surface in the path of the electrons, 10
- (f) means for locating a sample near the target for exciting the same with primary X-rays to produce X-rays that are characteristic of the elements in the sample,
- (g) an X-ray detector, and 15
- (h) a diffracting crystal located to intercept characteristic X-rays from a sample and diffract particular wavelengths thereof into the detector.
3. The invention set forth in claim 2 including:
- (a) a chamber means within the enclosure, said chamber means being adapted to maintain a different degree of evacuation than in said enclosure, 20
- (b) an active part of said X-ray target and the ion gun projecting inside of said chamber,
- (c) The said electron emitter also being inside the chamber, and 25
- (d) the said chamber having an X-ray exit slit that offers restricted gas pressure communication between the chamber and the enclosure, whereby to reduce the likelihood of contaminants entering the chamber. 30
4. The invention set forth in claim 3 wherein:
- (a) said chamber has an opening for presenting a surface of the sample to be analyzed to the primary X-rays from said target, and
- (b) said electron emitter is located beside the X-ray path from the target to the sample. 35
5. In an X-ray spectrometer:
- (a) an evacuable chamber means,
- (b) a rotatable X-ray target in the chamber means, 40
- (c) an electron emitter from which electrons may emanate to impinge on a first region of the target to produce primary X-rays,
- (d) means for presenting a sample to be analyzed to the interior of the chamber in a position that is more remote from the target than is the electron emitter whereby primary X-rays may radiate to the sample to excite characteristic X-rays therefrom. 45
- (e) an ion source in the chamber means from which source ions may be attracted to the target to clean surface contaminants from another region thereof,
- (f) the said target being located at least in part in the space between the ion source and the electron emitter 50

- to thereby shield the electron emitter from any electric field that might attract ions onto the electron emitter,
- (g) the said chamber having an opening from which the characteristic X-rays may exit for spectral analysis.
6. In an X-ray spectrometer:
- (a) an evacuable chamber means,
- (b) a rotatable cylindrical X-ray target projecting axially into the chamber means,
- (c) a cathode from which electrons may emanate to impinge on a first region of the surface of the cylindrical target to produce primary X-rays,
- (d) the said cathode being located in plane that is parallel with and between planes through the axis of the target and its surface, respectively, and being located radially outwardly from the target surface,
- (e) an ion source means projecting into said chamber means and having an ion discharge opening that is contiguous with the target,
- (f) the said discharge opening being located so as to have a portion of the target intervening between it and the cathode, whereby the target acts as a shield that prevents ions from reaching the cathode and whereby discharged ions may impinge on a second region of the target to clean contaminants therefrom for providing a clean region to the electron beam when the target is rotated, and
- (g) means for presenting a sample to be analyzed in a position that is more remote radially from the target than is the cathode, the said chamber having an opening for emergence of a spectral analysis of characteristic X-rays from the sample when it is excited by primary X-rays.

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