

## LITERATURE CITATIONS, PART I

1913

## 1. COOLIDGE, W. D.

A Powerful Röntgen-Ray Tube with a Pure Electron Discharge.

*Physic. Rev.*, (2) 2, 409-430 (1913).

*C. A.*, 8, 1388.

A description is given of a new and powerful Röntgen-ray tube which differs in principle from the ordinary type in that the discharge current is purely thermionic in character. Both the tube and electrodes are as thoroughly freed from gas as possible, and all the characteristics seem to indicate that positive ions play no appreciable role. The tube allows current to pass in one direction only, and can therefore be operated from either dc or ac. The intensity and penetrating power of the Röntgen-rays produced are both under the complete control of the operator, and each can be instantly increased or decreased independently of the other. When in operation the tube shows no fluorescence of the glass, and no local heating of the anterior hemisphere. It can be continuously operated for hours without showing an appreciable change in either the intensity or the penetrating power of the resulting radiation, and it permits of the realization of intense homogeneous primary Röntgen-rays of any desired penetrating power. The starting and running voltages are the same.

## 2. MOSELEY, H. G. J.

The High-Frequency Spectra of the Elements. *Phil. Mag.*, 26, 1024-1034; cf. *C. A.*, 7, 3710 (1913).

*C. A.*, 8, 463.

Taking advantage of the interference phenomena exhibited by X-rays when scattered by a crystal, a method has been devised to photograph the spectra emitted by metallic targets excited by a stream of sufficiently fast cathode rays. Twelve elements have so far been examined, and 10 of these forming a continuous series with only one gap (Ca to Zn, Sc omitted) show distinct regularities, the spectrum of each element consisting of 2 lines, a stronger called  $\alpha$  and a weaker called  $\beta$ . These results have been obtained by short exposures; prolonged exposures may reveal more complex spectra. The method at once shows lines due to impurities, and suggests a powerful method of chemical analysis. Values of  $Q = (\nu/\frac{3}{2}\nu_0)$  have been calculated for

the wavelengths found for the principal spectrum line  $\alpha$ ,  $\nu$  being the frequency of the radiation  $\alpha_1$  and  $\nu_0$  the fundamental frequency of ordinary line spectra.  $Q$  increases by a constant amount for successive elements, using the chemical order of the elements in the periodic table. This indicates that there is a fundamental quantity in the atom, which increases by regular steps as we pass from one element to the next, and that this quantity is the charge on the central positive nucleus, so that the results lend strong support to the views of Rutherford (*C. A.*, 5, 3538) and of Bohr (abstract above) regarding the structure of atoms. The very close similarity between the X-ray spectra of the different elements shows that these radiations originate inside the atom, and have no direct connection with the complicated light spectra and chemical properties which are governed by the structure of its surface.

## 3. MOSELEY, H. G. J.

The High-Frequency Spectra of the Elements.

II.

*Phil. Mag.*, 27, 703-714 (1913).

*C. A.*, 8, 2307.

The method of photographing the X-ray spectra of the elements as described in a previous research (*C. A.*, 8, 463) in which 12 elements had been examined has been used for obtaining the spectra of some 30 other elements. The same crystal of  $K_4Fe(CN)_6$  was employed as an analyzer. Since the long wavelengths can penetrate but a short distance through air, the photographs were taken inside an exhausted spectrometer. It has been found that every element from Al to Au is characterized by an integer,  $N$ , which determines its X-ray spectrum, and hence every detail in the spectrum of an element can be predicted from the spectra of its neighbors. The value of  $N$ , the atomic number of the element, is identified with the number of positive units of electricity contained in the atom nucleus. The atomic numbers of the elements from Al to Au have been tabulated on the assumption that  $N$  for Al is 13. The order of the atomic numbers is the same as that of the atomic weights except when the latter disagrees with the order of the chemical properties. Known elements correspond to all the numbers between 13 and 79 except 3. There are then at least 3 possible elements undiscovered. The

frequency of any line in the X-ray spectrum is approximately proportional to  $A(N-b)^2$  where  $A$  and  $b$  are constants characteristic of each line.

## 1914

4. SIEGBAHN, MANNE  
Röntgen-Ray Spectra.  
*Arkiv Mat., Astron., Fysik*, **10**, No. 17, 6 pp.  
Monograph (1914).  
*C. A.*, **9**, 750.

The ray was reflected by a crystal of NaCl placed on a small accurate turntable, and recorded and noted on a fluorescent screen (cf. *C. A.*, **7**, 2009, 3710; **8**, 459, 1235). The high frequency spectra of Ag as calculated from Moseley's formula to be  $0.550 \times 10^{-8}$  and by later determination measured to be  $0.560 \times 10^{-8}$  was found by Siegbahn to be of  $0.561 \times 10^{-8}$  cm wavelength, and the 2nd line of  $0.497 \times 10^{-8}$  cm wavelength. Siegbahn explains the occurrence of only 2 spectral bands (as usually reported by authors) as due to the inability of the AgBr photographic plate to record the others. Comparing the absorption constant of the rays in Al and the wavelength of the ray of the strongest spectral line for the elements (Ca, Fe, Co, Ni, Cu, Zn, Mo, Ag) Siegbahn finds that the absorption is proportional to the 3rd power of the wavelength. This is in harmony with the conclusion of Kauffmann (*C. A.*, **7**, 2902).

## 1915

5. COOLIDGE, W. D.  
Summary of Physical Investigation Work in Progress on X-Ray Tubes and Accessories.  
*Am. J. Röntgenology*, **2**, 881-892 (1915);  
*J. Franklin Inst.*, **181**, 425 (1916).  
*C. A.*, **10**, 1965.

This article is an illustrated discussion of the objects, progress and outlook of some of the X-ray researches being prosecuted in the research laboratory of the General Electric Co. The following points are considered in detail: Target design for sharp definition requiring uniform energy distribution and cooling of the focal spot; materials, water-cooling, constant current excitation, rotation, focussing of cathode rays; hooded target to cut out secondary radiations; reduction in size of bulb to 4 in. at least; ti; less bulb; high potential tube with hooded and water-cooled target; current supply and voltage regulation; transformer requirements; exact control of filament temperature; measurement of tube voltage.

## 1916

6. DE BROGLIE, M.  
X-Ray Absorption Phenomena.  
*J. Physique*, **5**, 161-168 (1916); *Sci. Abstracts*, **21A**, 110.  
*C. A.*, **12**, 2066.

The X-ray spectrum is obtained in a manner previously described (*C. A.*, **8**, 2649). Thin screens of different substances are placed in the path of the reflected beam, and the spectra obtained show existence of absorption bands characteristic of the substances interposed. The edges of the bands are very sharp for the longer wavelengths, but fall off in distinctness for shorter wavelengths. For different elements the sharp edges of the  $K$ -absorption bands appear at different angles, from which, by means of the relation  $\lambda = 5.63 \times 10^{-8} \times \sin \alpha$  (when the rays are reflected from the (100) face of a rock salt crystal), the corresponding wavelengths may be calculated. The observed values for the angle  $\alpha$  are given for 26 elements. In the  $L$ -radiation, for certain elements, as many as 3 bands are observed.

7. HULL, A. W.  
Röntgen-Ray Spectra.  
*Am. J. Röntgenology*, **2**, 893-899 (1915);  
*J. Franklin Inst.* **181**, 423-424 (1916).  
*C. A.*, **10**, 1964.

A first report is given of work upon the accurate measurement of the quality and intensity of X-rays from a standard Coolidge tube. The spectrometer used was of the usual form with a crystal of rock-salt substituted for the prism, and an ionization chamber in place of a photometer. Wavelength and intensity values for the X-ray spectra from a  $W$  target at 5 different voltages from 20,000 to 40,000 show a very rapid decrease in wavelength with rise in voltage, and at the same time an increase in intensity for all wavelengths. Hence, a penetrating ray free from soft radiations can be obtained only by using a filter exhibiting selective absorption for the latter. Measurements of the spectrum at 70,000 v with and without a filter of 3 mm of Al indicate that the intensity of the soft rays has been reduced much more than that of the penetrating, but there is still a good deal of the former left. Use of still heavier filters to reduce further the intensity of soft rays would also cut down the intensity of the penetrating rays to a small fraction, but with a very powerful tube such as is in process of development, there may be left sufficient for practical work. The principles upon which the work is based, the operation of the spectrometer, and the method of obtaining constant voltage are explained in detail with diagrams, curves and oscillograms.

8. SIEGBAHN, M. AND FRIMAN, EINAR  
High-Frequency Spectra of the Elements Arsenic to Rhodium.  
*Ann. Physik*, **49**, 611-615 (1916); *J. Chem. Soc.*, **110**, II, 362.  
*C. A.*, **10**, 2664.

Wavelength measurements of the lines  $\alpha_1$ ,  $\alpha_2$ ,  $\beta_1$ ,  $\beta_2$  ( $K$  series) in the spectra of As, Se, Br, Rb, Sr, Cb and Rh are recorded. For each series of lines the square root of the frequency is a linear function of the atomic number as re-

quired by Mosley's formula. The wavelengths of the Cs lines have also been measured.

9. SIEGBAHN, MANNE AND FRIMAN, EINAR  
High-Frequency Spectra (*L* Series) of the Elements Tantalum to Bismuth.  
*Ann. Physik*, **49**, 616-624 (1916); *J. Chem. Soc.*, **110**, II, 362.  
*C. A.*, **10**, 2664.

Previous measurements of the wavelength of lines in the spectra of these elements have been extended, with the result that the existence of at least 11 groups of lines has been established. The wavelengths of these are recorded and it is shown that the Mosley relation between the frequency and the atomic number of the element holds for each group of lines.

10. SIEGBAHN, M. AND FRIMAN, E.  
Vacuum Spectrograph for High-Frequency Spectra Investigations. Applications to the Study of the Rare Earths.  
*Physik. Z.*, **17**, 176-178 (1916); *Sci. Abstracts (A)*, **19**, 281.  
*C. A.*, **10**, 2833.

An interesting description is given of a "self-contained" instrument which is readily adapted to the study of X-ray spectra. The slit, revolving crystal table, and photographic plate are suitably mounted in a highly evacuated chamber, with a neat arrangement for revolving the crystal at the required rate. A reproduction of the spectrum of aldebaranium obtained with this instrument shows a number of extremely sharp and well defined lines. The following table gives the result of a series of wavelength measurements for the rare earths:

 $\lambda \times 10^6$ , cm

Atomic Number	Element	$\alpha_1$	$\alpha_2$	$(1/\lambda \times 10^{-4})_i$ $\alpha_1$	Difference
73	Ta	1.518	1.528	0.812	
72	W II				13
71	Cp	1.619	1.629	0.786	13
70	Ad	1.670	1.681	0.774	12
69	W I				13
68	Er	1.783	1.794	0.749	12
67	Ho	1.843	1.854	0.737	12
66	Dy	1.907	1.916	0.724	13
65	Tb	1.973	1.983	0.712	12
64	Gd	2.043	2.054	0.700	12
63	Eu	2.121	2.131	0.687	13
62	Sa	2.200	2.210	0.674	13
61					12
60	Nd	2.369	2.379	0.650	12
59	Pr	2.462	2.472	0.637	13

11. SIEGBAHN, MANNE AND FRIMAN, EINAR  
High-Frequency Spectra (*L*-Series) of the Elements Tantalum-Uranium.  
*Phil. Mag.*, **32**, 39-49 (1916); cf. *C. A.*, **10**, 2664.  
*C. A.*, **10**, 3028.

Eleven different line groups were found in the *L* series spectra of most of these elements. For

Po only the  $\alpha_1$  and the  $\beta_1$  lines were found and for Ra only a weak  $\alpha$  line, owing to the small quantities employed. These were sufficient to establish the ordinals of Po and of Ra as 84 and 88, respectively. The groups  $\alpha_1$ ,  $\alpha_2$  and  $\beta_2$  when plotted against the atomic numbers form right lines and follow the Mosley relation,  $\alpha_1$  and  $\alpha_2$  being nearly parallel. The remaining lines are curved concavely toward the frequency axis. Pb forms the intersection point of two of the strongest groups,  $\beta_1$  and  $\beta_2$ . Comparison of the Pb spectrum with Rutherford and Andrade's  $\gamma$ -ray spectrum of RaB (*C. A.*, **8**, 2307) shows excellent agreement and confirms the identity of the atomic numbers of these 2 elements.

12. SIEGBAHN, M. AND FRIMAN, E.  
High-Frequency Spectra (*L* series) of the Elements Polonium, Radium, Thorium and Uranium.  
*Physik. Z.*, **17**, 61-62 (1916); see *C. A.*, **10**, 3028.  
*C. A.*, **10**, 3029.

## 1917

13. WAGNER, E.  
X-ray Spectroscopy.  
*Physik. Z.*, **18**, 405-419, 432-443, 461-466, 488-494 (1917); *Sci. Abstracts*, **21A**, 64-65.  
*C. A.*, **12**, 2065.

A comprehensive compilation of the exptl. work of various investigators in the field of crystal structure. Complete tables of the principal series of lines in the X-ray spectra of the elements given. Comparative photographs of the "rotating" and "stationary" crystal methods are given in the case of the *L*-series of Pt. X-ray absorption and emission spectra are discussed, and it is demonstrated that Stokes' law is verified even for the extremely short wavelengths of the gamma rays from RaB and RaC. The consequences of Einstein's relation  $V_k e = h\nu_a$ , are shown for particular cases. In conclusion the spectral theory of Bohr and Moseley's law of frequencies and atomic numbers are reviewed at length.

14. WEBSTER, DAVID L. AND CLARK, HARRY  
Intensities of X-rays of the *L*-Series.  
*Proc. Nat. Acad. Sci.*, **3**, 181-185 (1917).  
*C. A.*, **11**, 1594.  
*C. A.*, **10**, 2070.

Following the results of Siegbahn and Friman (*C. A.*, **10**, 3028) the lines  $\alpha_2$ ,  $\alpha_1$ ,  $\beta_2$  and  $\beta_3$  of the *L* series form a separate line group, here called to *L*<sub>1</sub> series which is very similar in appearance to the *K* series. As in the case of the latter, the intensity graphs of the  $\alpha_1$  and  $\beta_2$  of the *L*<sub>1</sub> series of Pt leave the potential axis at the potential required to give an electron an energy quantum of the proper frequency but follow the line for general radiation only until they reach a critical potential where there is a

sudden increase in intensity, indicating the first appearance of the spectrum line. This, in the case of both  $L_1$  lines, was at 11.45 kv, which is the quantum potential of the  $\beta_3$  line, the shortest of the series. This series is thus wholly analogous to the  $K$  series. The three lines  $\beta_3$ ,  $B_1$  and  $\gamma_1$  of the  $L_2$  series also show a similar critical potential at 13.2 kv. This, however, corresponds to a wavelength of  $0.937 \text{ \AA}$ , which is not only longer than that of the shortest line of the series, the  $\gamma_4$  line, but is longer than the  $\gamma_3$  and  $\gamma_2$  lines as well. These three lines are all faint and their nature may be questioned. From the critical voltages of the five lines and Siegbahn and Friman's wavelength measurements the value for Planck's  $h$  calculated by Duane and Hunt's formula (*C. A.*, **10**, 1004) has a mean value of  $6.53 \times 10^{-27}$  erg sec. In the  $L_1$  and  $L_2$  series of Pt and the  $K$  series of Rh all lines increase in intensity approximately in proportion to the  $3/2$  power of the difference between the p. d. applied and the critical potential of the series.

## 1919

## 15. SIEGBAHN, MANNE

Precision Measurements in X-ray Spectra.

*Phil. Mag.*, (6) **38**, 601-613 (1919).

*C. A.*, **13**, 2634.

Feeling that the theoretical side of the investigation of atomic structure by means of X-ray spectra has advanced faster than the experimental and that more precise data are necessary for testing some of the theoretical formulas, Siegbahn has developed more refined apparatus for the determination of X-ray wavelengths. The estimated increase in precision is about 100-fold for the longer waves, those greater than  $1 \text{ \AA}$ . Siegbahn's principle consists in the determination of the angle of the reflected ray as the angle through which the same photographic plate has to be turned in order to receive the impression of the  $n$ th-order reflection on both sides of the direct ray, the angles being read off on an accurate circle scale. A very elegant form of spectrograph is described, for the details of which the original should be consulted. The construction of the X-ray tube has also been modified as regards accurate adjustment of the slit, crystal and plate, special apparatus being constructed for the purpose of orientation. Some of the experimental results are as follows: wavelength of the  $K\alpha$  line for Cu  $1537.358 \pm 0.033 \times 10^{-11}$  cm. The lattice constant for calcite was carried out with three characteristic radiations the  $K\alpha$  lines for Cu and Fe and  $L\alpha$  for Sn giving as the most probably value  $\log 2d = 0.7823347$  (where the value for rock salt is taken as  $\log 2d = 0.7503541$ ) or  $d = 3029.04 \times 10^{-8}$  cm. For the lattice constant of  $K_4\text{Fe}(\text{CN})_6$ ,  $d = 8.409 \times 10^{-8}$  cm. The wavelength for the  $K$  lines of elements Cu through Cl also were determined. The fine structure of the lines in the  $K$  group was also studied

as well as the formulas of the  $K\alpha$  series by Sommerfeld, Debye and Kroo. The exptl. results prove that the formula of Kroo is the most accurate, the values of Sommerfeld being high especially for elements with atomic numbers 20-30.

## 16. SIEGBAHN, MANNE

Precision Measurements in the X-ray Species.

II.—The X-ray Spectra of Tungsten.

*Phil. Mag.* **38**, 639-646 (1919). *C. A.*, **13**, 2634.

*C. A.*, **14**, 689.

The X-ray spectrum of W is of especial interest on account of the general use of W as target in X-ray tubes. The very hard lines belonging to the  $K$  series are produced only with very high voltages such as are employed in Coolidge tubes, whereas the  $L$  lines which are produced in all tubes are so nonpenetrating as to be largely absorbed by the walls of the tube and are hence of no technical importance. The  $M$  lines which are also produced from W will be reported in the Thesis (Lund) of Wilhelm Stenström. A special spectrograph for very hard rays was used in these measurements. The results give the following values in terms of  $\text{cm} \times 10^{-11}$  designated as  $X$  unit:  $K\alpha_2$  213.52;  $K\alpha_1$  208.85;  $K\beta_1$  184.36;  $K\beta_2$  179.40. In the  $L$  series both calcite and rock salt were employed with good agreements as gratings. The mean results in the  $L$  series are:  $L\beta_2$  1484.52;  $L\alpha_1$  1473.48;  $L\beta_1$  1279.17;  $L\beta_3$  1241.91;  $L\gamma_1$  1095.53; for other lines see the original. The frequency differences which Sommerfeld has indicated to be constant appear to diminish slightly with decreasing wavelength. III. An X-ray spectrograph for medium wavelengths. Manne Siegbahn and A. B. Leide. *Ibid.*, 647-651. An X-ray spectrograph is described for the measurements of medium wavelengths. They can be reached with the instruments for the long and for the short lengths, but not quite with the desired degree of accuracy, so that a third instrument has been constructed for the intermediate region, with a suitable range of 2 to  $0.5 \text{ \AA}$  unit. For the details of construction consult the original.

## 17. SIEGBAHN, MANNE AND LEIDE A. B.

Precision Measurements in the X-ray Species.

III.—An X-ray Spectrograph for Medium Wavelengths.

*Phil. Mag.* **38**, 647-651 (1919).

## 18. WOOTEN, BENJ. ALLEN

Energy of the Characteristic X-ray Emission from Molybdenum and Palladium as a Function of the Applied Voltage.

*Physic Rev.*, **13**, 71-86 (1919).

*C. A.*, **13**, 812.

The relations between the energy of the lines of the  $K$  series characteristic X-ray radiation of Mo and Pd and the voltage between them have been studied. It was found that in each metal the  $\alpha$  and  $\beta$  radiation appeared at a certain volt-

age, 19.2 kv for Mo and 24 kv for Pd. For Mo this measured critical voltage is almost exactly that required by the Planck hypothesis to produce the  $\beta$  line, while for Pd it is that required by the same hypothesis to produce a wavelength slightly shorter than the  $\beta$  line. Curves of the voltage squared versus the intensities of the  $\alpha$  and  $\beta$  radiations for both metals show that these intensities vary directly as the square of the voltage for potentials not too near the critical voltage. The ratio of the intensity of the  $\alpha$  line to that of the  $\beta$  line becomes constant as the voltage is increased. The straight line parts of the curves, if produced, backcut the voltage-squared axis in the same point, and this point was found to bear the same relation to the atomic number of the metal of the anti-cathode that the point at which the curves themselves cut the axis bears, that is, the square root of the coordinate represents a voltage proportional to the square of the atomic number of the radiator. Absorption coefficients for wavelengths of the  $\alpha$  and  $\beta$  lines of Mo and Pd in glass and in Mo and Pd, respectively, were found to vary approximately as the cube of the wavelength of the radiation. The observed intensities of the  $\alpha$  and  $\beta$  lines of each metal were corrected for absorption in the glass of the X-ray tube. By application of the theory of Bergen Davis it was possible to calculate the ratio of the intensity of the  $\alpha$  radiation to that of the  $\beta$  radiation as given by a single atom. The curves obtained by plotting the theoretical equation were found to agree excellently with the experimental curves.

## 1920

19. SIEGBAHN, M. AND WINGARDH, K. A.  
A Method for the Measurement of the Intensity of Röntgen-Rays and Some Preliminary Determinations of Absorption.  
*Physik. Z.*, **21**, 83-88 (1920).  
*C. A.*, **14**, 2127.

The method described is a null method in which 2 monochromatic rays from the same X-ray tube enter 2 separate ionization chambers, charged to the same potential differences, but in the opposite direction, and with the 2 insulated electrodes connected together to the electrometer. The stronger ray is cut down to equality with the weaker by means of adjustable rotating sectors. The relative intensity is thus measured. For the resolution of the X-rays 2 half-spectrometers are mounted on the same base, each provided with separate slits and crystal. The 2 half-spectrometers can be rotated about a common vertical axis so that they can both be directed to the same point of the anti-cathode. Absolute rest of the electrometer needle cannot thus be obtained, but at the point of balance small vibrations take place about the zero position. The method was tried out by measuring the absorption by Cu and Al. In order to obtain sufficiently intense rays it was necessary to work with fairly wide slits, so that the rays could not

be strictly called monochromatic; but this point will be improved. The results obtained agree well with those previously obtained by others. No trace of a J-radiation from either metal was found.

## 1921

20. COSTER, D.  
Recent Results in Röntgen Spectroscopy.  
*Physics*, **1**, 332-343 (1921).  
*C. A.*, **16**, 381.  
A review.
21. SIEGBAHN, MANNE  
New Precision Instruments in the X-ray Spectrum.  
*Compt. rend.*, **173**, 1350-1352 (1921).  
*C. A.*, **16**, 2073.  
With an improved form of apparatus Siegbahn finds for the  $K$  radiation of Cu the value  $1537.302 \times 10^{-11}$  cm. Deviations from Bragg's law as observed by Stenström for gypsum were found for calcite also.
22. SIEGBAHN, MANNE, LINDH, AXEL E. AND STENSSON, NILS  
A Method of Spectrum Analysis by Means of X-rays.  
*Z. Physik*, **4**, 61-67 (1921).  
*C. A.*, **15**, 1654.

The substance to be examined is made the anticathode in an X-ray tube and the elements present are identified by their characteristic  $K$  or  $L$  radiation. The tube, which is of metal, has a helical filament giving a long focal spot, which sends the radiation through a narrow slit to a stationary crystal. The reflected beam can be photographed over a range of 40 deg on a circular film. The whole apparatus is evacuated and the tube water-cooled to carry 30 ma. All elements from Na to U can be identified in 2 exposures of 2 hr each, one with calcite (1 to 4.6 Å) and one with gypsum (2.6 to 11.6 Å).

## 1922

23. SIEGBAHN, MANNE  
Increase of Accuracy of Measurement in Röntgen Spectra.  
*Z. Physik*, **9**, 68-80 (1922).  
*C. A.*, **16**, 2072.

The method and apparatus for accurate measurement of X-ray wavelengths, by means of a crystal spectrograph, are described in detail under the following headings: adjustment, slit-and-line width, X-ray tube, and test results in which the  $K\alpha$  radiation of Cu is derived as  $1.53702 \text{ \AA}$  with a probable error of about 0.002 per cent.

24. SIEGBAHN, MANNE  
Report on the Latest Developments of

Röntgen Spectroscopy. (Experimental Technic and Observational Data.)  
*Jahrb. Radioakt. Elektronik*, **18**, 240-292 (1922).

*C. A.*, **16**, 2073 and 2074.

Continuing an earlier report (*C. A.*, **13**, 296) the more important data of X-ray spectroscopy are reported. The list of all papers on the subject is extended to the middle of 1921. The wavelengths of all X-ray lines are tabulated. Full but concise instructions for the excitation and observations of X-ray spectra are given, and this section of the paper should be of great use to students of the subject.

**25. TERRILL, H. M.**

A Precision X-ray Spectrometer.

*J. Optical Soc. Am., Rev. Sci. Instr.*, **6**, 287-290 (1922).

*C. A.*, **16**, 2641.

**1923**

**26. COSTER, D.**

X-ray Spectroscopy As a Means of Qualitative and Quantitative Chemical Analysis.

*Chem. News*, **127**, 65-70 (1923).

*C. A.*, **17**, 3833.

The X-ray emission from the anticathode of and X-ray tube consists of two essentially different parts: (1) the heterogeneous radiation depending only on the voltage and (2) the characteristic radiation or line spectrum which characterizes the elements present on the anticathode. The range of wavelengths which can be measured in the present state of X-ray spectroscopy lies between 13.5 and 0.1 Å. X-ray spectroscopy has some advantage over optical spectroscopy: (1) The X-ray spectra are simpler; (2) it is of no importance in what mixtures or compounds the element in question occurs; (3) one per cent of a certain element, of which only 1 mg is available, is enough to be detected. It has been used successfully by Coster and others in the examination of Hf in Zr minerals and some details are given of the procedure and sources of error. A main feature of the method is the addition to the substance to be examined of a known quantity of an element with an atomic number in the neighborhood of that element and the determination of the X-ray spectrum of the mixture. By comparison (Moll microphotometer) of the intensity of the lines of the added element to that of the corresponding lines of the element under investigation an estimation of the concentration of the latter element can be obtained.

**27. COSTER, D. AND HEVESY, G., VON**

Missing Element of Atomic Number 72.

*Nature*, **111**, 79 (1923).

*C. A.*, **17**, 923.

Dauvillier's (*C. A.*, **16**, 2638) discovery of lines belonging to the X-ray spectrum of this element (which Urbain (*C. A.*, **16**, 3804) has

identified with the supposed rare earth celtium) is questioned on the following grounds: (1) The two lines discovered by Dauvillier are extremely faint and differ by about  $4 \times 10^{-11}$  cm in wavelength from the values calculated by interpolation in the measurements of Hjalmar and Coster; (2) according to the Bohr theory 72 should not be a rare earth but a homolog of Zr; (3) general views based on the periodic system lead one to expect a Zr homolog rather than a rare earth in this space. Coster and Dauvillier have studied the X-ray spectrum of Zr preparations, and find 6 lines which must be ascribed to element 72 (Siegbahn's  $L \alpha_1, \alpha_2, \beta_1, \beta_2, \beta_3$  and  $\gamma$ ). The values of  $\chi$  are 1565.5, 1576, 1371.4, 1323.7, 1350.2, 1177 X unit, which agree with the interpolated values. In a Norwegian Zr mineral the new element is estimated to be present to the extent of 1 per cent. The name hafnium (for Copenhagen) is proposed for element 72.

**28. COSTER, D. AND HEVESY, G., VON**

The New Element Hafnium.

*Nature*, **111**, 182 (1923).

*C. A.*, **17**, 923.

*C. A.*, **17**, 1356.

By the addition of a known quantity of Ta to the samples and comparing intensities of the Ta and Hf lines, it is found that all Zr minerals investigated, from whatever source, contained 5 to 10% Hf. (Surprising in view of the negative spectroscopic and chemical results of Hauser and Wirth, *C. A.*, **4**, 872, 2421, and 3056.—Abstr.). One sample of compound  $ZrO_2$  showed 5% of Hf. From this were prepared several g of material showing 50% Hf. Conversely Zr has been prepared which shows no Hf lines.

**29. COSTER, D. AND HEVESY, G., VON**

Celtium and Hafnium.

*Nature*, **111**, 462-463 (1923).

*C. A.*, **17**, 1922.

Polemical. Urbain's "discovery" of Ct in 1911 is discredited on the ground stated in the preceding abstract. It is concluded that the "Ct" X-ray lines reported by Dauvillier in 1922 (*C. A.*, **16**, 2638) were not due to contamination of his preparation (presumably an impure specimen of  $Lu(NO_3)_3$  by a trace of the element 72, but had some other source (Zr?). Urbain had attempted carefully to purify the specimen from all elements not rare earths, and, indeed its optical spectrum showed lines neither of Zr nor of element 72. Now Hf can easily be separated from rare earths, as can Zr, and it is unlikely that some Hf and no Zr would have survived Urbain's purification. Further the 2 faint "Ct" lines were the only that deviate in wavelength from Coster's measurements, (but cf. Dauvillier, *C. A.*, **17**, 1752). The lines of the elements 70 and 71 agreed closely. Coster and Hevesy therefore reiterate their claim to priority and to the name hafnium.

## 30. EDER, J. M.

The Spectrum Analysis of the Rare Earths.

*Ann. Physik*, **71**, 12-18 (1923).

*C. A.*, **17**, 3833.

Eder has been engaged for many years in the study of rare earths La, Pr, Nd, Sa, Eu, Gd, Tb, Y, Dy, Ho(Nh), Er, Tu, Cp and Ce. The spectra of Ce, La, Pr and Nd are well known but the others need further study. The characteristics of the spectra of these rare earths are briefly reviewed.

## 31. GÜNTHER, PAUL AND STRANSKI, IWAN

An X-ray Spectrograph for Analytical Chemical Purposes.

*Z. physik. Chemie*, **106**, 433-444 (1923).

*C. A.*, **18**, 602.

A modified Siegbahn X-ray vacuum spectrograph is used to analyze rare earth residues. The instrument is described in detail.

## 32. HODDING, A.

Mineralienanalyse nach Röntgen Spektroskopischer Methode.

*Z. anorg. Chemie*, **122**, 195 (1923).

## 33. KETTMANN, G.

The Intensity of X-ray Spectral Lines at Higher Voltages.

*Z. Physik.*, **18**, 359-371 (1923).

*C. A.*, **18**, 623.

A method for the photographic measurement of the intensities of spectral lines is specified, and intensity-voltage curves for the *K*-series of Cr, Cu, Ag and for the *L*-series of La and Pb are given. The results are in harmony with former measurements by Webster and Wooten on other materials and in a shorter range. At high voltages, the intensity reaches a maximum, which is given by the absorption of the X-rays in the anticathode. Whether the intensity of the *L*-lines rises as the transgression of the *K*-resonance potential exceeds a certain limit is renewed, remains unknown. The theory of Davis (*C. A.*, **12**, 2162) is discussed and found to be in agreement with the facts. Assuming the validity of the Davis theory a simple method is given of calculating the retarding power for cathode rays from a measured curve. For small absorption of X-rays in the anticathode, a linear increase of the intensity with  $V^2$  is given.

## 1924

## 34. COSTER, D.

Quantitative and Qualitative Analysis by Means of Röntgen-rays.

*Chem. Weekblad*, **21**, 59-62 (1924).

*C. A.*, **18**, 1622.

Coster reviews his previous work (cf. *C. A.*, **17**, 3833, 3846).

## 35. GÜNTHER, P.

The Analytical Chemical Use of Röntgen Spectroscopy.

*Z. angew. Chemie*, **37**, 355-357 (1924).

*C. A.*, **19**, 2610.

The method depends upon counting the Ag grains on the photographic plate in the spectrum lines. Analyses accurate to within 2% are claimed. (For Zr and Hf, cf. Coster and Nishina, *C. A.*, **19**, 2000).

## 36. GÜNTHER, PAUL AND WILCKE, GERTRUD

An X-ray Spectroscopic Method for Quantitative Chemical Analysis.

*Ann.*, **440**, 203-212 (1924); cf. *C. A.*, **19**, 2610.

*C. A.*, **19**, 3217.

A mixture of Fe and Co oxides is deposited on a Ag cathode of an X-ray tube. The small current necessary is supplied from either a small transformer or an induction coil. The  $K\alpha$  lines of Fe and Co are resolved by the reflection method by a  $\text{CaF}_2$  crystal. The relative intensities of the 2 lines on a photographic plate are determined by counting and evaluating the average degree of distribution of Ag particles under 800 magnification. Correction is made for the blackening of the film due to diffuse radiation by determining the average number of particles in the film at points on the border of the  $K\alpha$  lines. The X-ray method gave results agreeing within 2% with gravimetric determination. The method is to be applied to the rare earths.

## 1925

## 37. CORK, J. M.

A Short-wave X-ray Spectrograph and Some *K*-Series Emission Wavelengths.

*Physic. Rev.*, **25**, 197-200 (1925).

*C. A.*, **19**, 1225.

A transmission type spectrograph for short rays similar to that used by Rutherford and Andrade is described. Accurate determinations of the *K*-lines for elements of atomic numbers above 50 were made. The lines are included in a table.

## 38. COSTER, D. AND GOUDSMIT, S.

The Intensity of Röntgen Spectral Lines.

*Naturwissenschaften*, **13**, 11-12 (1925).

*C. A.*, **19**, 1226.

A discussion of recent publications by Stoner (cf. *C. A.*, **19**, 209) and by Burger and Dorgelo (*C. A.*, **18**, 2467).

## 39. COSTER, D. AND NISHINA, Y.

Quantitative Chemical Analysis by Means of X-ray Spectra.

*Chem. News*, **130**, 149-152 (1925).

*C. A.*, **19**, 2000.

The separation of Hf from Zr is extremely difficult but by means of X-ray spectra it is possible to establish the Zr content of a sample of  $\text{HfO}_2$  down to 0.1% with an accuracy of 1 part in 10. If precautions are taken to keep the

experimental conditions unchanged, the relative intensity of spectral lines is constant for a definite chemical compound of the preparation used although it does not give directly the relative chemical concentration of the elements in it. Those interested in spectral analysis should read this paper.

**40. GLOCKER, R. AND FROHNMEYER, W.**

The Röntgen-Spectroscopic Determination of the Quantity of an Element in Mixtures and Compounds.

*Ann. Physik*, **76**, 369-395 (1925).

*C. A.*, **19**, 1547.

After a theoretical discussion of the applicability of X-ray analysis to quantitative analysis some practical examples are shown. Thus the Ba content of a sample of glass was found to be 5.45% whereas by the usual method 5.8% Ba was found; in a silicate 3.35% Sb was indicated by X-ray spectra and the probable content was 3.6% Sb; in a sample of alvite, 3.5% of Hf was indicated which was probably approximately correct; in a mixture of  $\text{NH}_4$  molybdate, tartar emetic,  $\text{BaCl}_2$  and  $\text{LaCl}_3$  the ratio 1 Sb: 2.25 Ba:1.17 La was indicated by X-ray spectra whereas in reality it was 1:2.5:1.5. The possibilities of such quantitative estimations by X-ray analysis, therefore, are greater than was to have been expected from the known fact that the intensity of the spectral lines is not strictly proportional to the contents of individual elements.

**1926**

**41. COOLIDGE, W. D.**

The Production of High-Voltage Cathode Rays Outside of the Generating Tube.

*J. Franklin Inst.*, **202**, 693-721 (1926); cf. *C. A.*, **20**, 2615.

*C. A.*, **21**, 1056.

A detailed description of the mechanical features of the type of cathode-ray tube which can be sealed off from the pump and is capable of operation at several ma and 350,000 v is given. The suitability of various high-voltage sources for operating the tube, the operation of the tube, the distribution of cathode rays in front of the window, the emission of X-rays by air and other substances in front of the window and the possibility of using still higher voltage is discussed.

**42. GOLDSCHMIDT, V. M.**

Remarks on P. Günther and G. Wilcke's Article: Contributions to Röntgen Spectroscopy.—11.

*Z. physik. Chemie*, **122**, 250-253 (1926).

*C. A.*, **20**, 3385.

A criticism of the analysis of a gadolinite sample offered by Günther and Wilcke as illustrative of their method of Röntgen spectroanalysis (*C. A.*, **20**, 2281).—Reply. 11. Paul Günther and Gertrud Wilcke. *Ibid.*, 254-256 (1926).—The criticisms of Goldschmidt are ac-

cepted and the conclusion is drawn that for the analysis of complex chemical systems 2 Röntgen spectrograms, of different exposure times, are desirable for deriving the data from the strong and weak lines, respectively.

**43. GÜNTHER, P. AND WILCKE, G.**

X-ray Spectral Analysis.—11. The Application of the Method of Silver Grain Counting to the Photometry of X-ray Spectral Lines.

*Z. physik. Chemie*, **119**, 219-246 (1926); cf.

*C. A.*, **19**, 2610.

*C. A.*, **20**, 2281.

It is possible to estimate the intensity of an X-ray spectral line by counting the number of Ag grains per sq cm in its impression on a photographic plate. The technic of this method is fully described, and it is claimed that estimates reliable to a few tenths of a per cent may be made in the d. range 0.08 to 0.27. By this means the absorption curve of an X-ray film is measured in the range 0.9 to 1.7 Å unit. This method is applied to the analysis of chemical mixtures and used to follow the fractionation of rare earth residues which cannot easily be detected by ordinary means.

**1913**

**44. DELAUNEY E.**

The Atomic Character of Certain Properties of X-rays.

*Compt. rend.*, **185**, 193-195 (1927).

*C. A.*, **21**, 3551.

The fluorescent X-radiation of one element from a mixture of adjacent elements is not proportional to the concentration of that element in the mixture. Mixtures of  $\text{SrCl}_2$  and  $\text{BaCl}_2$  were irradiated and the fluorescent radiation was measured by an ionization method. The intensity increased less rapidly than the concentration of  $\text{BaCl}_2$ . The intensities of the fluorescent radiation from two elements in such a mixture are given by the relations:

$$I_1 = I_0 p_1 [n_1 / (a_1 n_1 + a_2 n_2)] [1 - e - (a_1 n_1 + a_2 n_2) E]$$

and

$$I_2 = I_0 p_2 [n_2 / (b_1 n_1 + b_2 n_2)] [1 - e - (b_1 n_1 + b_2 n_2) E]$$

where  $I_0$  is the intensity of the monochromatic primary beam;  $p_1$  and  $p_2$  are the emissive powers of the two elements;  $n_1$  and  $n_2$  their concentrations; and  $a_1$ ,  $a_2$ ,  $b_1$  and  $b_2$  are given by:  $a_1 = v_1 - v_1'$ ;  $a_2 = v_2 - v_2'$ ;  $b_1 = v_1 - v_1''$ ;  $b_2 = v_2 - v_2''$  where  $v_1$  and  $v_2$  are the absorption coefficients of the two elements for the primary radiation, and  $v_1'v_2'$  and  $v_1''v_2''$  are the coefficients for the fluorescent radiation.

**45. HEVESY, G., VON AND BÖHM, J.**

Determination of Ta by Means of X-ray Spectra.

*Z. Anorg. Chemie*, **164**, 69 (1927).

## 46. LARSSON, AXEL

Experimental Research on Refraction and Dispersion of X-rays in Crystal Reflection from Calcite.

*Z. Physik*, **41**, 507-515 (1927).

*Phil. Mag.*, (7) **3**, 1136 (1927).

*C. A.*, **21**, 2100.

The angles of reflection of the Mo and FeK $\alpha_1$  lines from calcite, in the first 3 orders for the Mo line and the first 2 orders for the Fe line, have been measured by Siegbahn's method with a Siegbahn vacuum spectrograph. Values of  $\delta$  are calculated from these angles and compared with the theoretical value, calculated from the optical dispersion formula,  $\delta = (Ne^2)(2\pi mv^2)$ , where  $N$  is the number of electrons per unit volume,  $e$  is the charge on the electron,  $m$  is the mass of the electron,  $v$  is the frequency of the rays.  $\delta/\lambda^2$  should be constant. The theoretical value is  $3.69 \times 10^{-6}$ . The experimental values are 3.83, 3.62 and  $3.92 \times 10^{-6}$ . Hence it is concluded that the optical dispersion formula is value for X-rays refracted in calcite. The Bragg law corrected for refraction becomes

$$n\lambda = 2d[1 - (4d^2\delta/n^2\lambda^2)] \sin\theta_n$$

whence:  $d_n = d[1 - (4d^2\delta/n^2\lambda^2)]$  where  $d$  is the actual lattice constant. Siegbahn's value of  $d_1 = 3.02904 \text{ \AA}$  unit is used to calculate  $d$  instead of using Compton's value of  $d = 3.02904 \pm 0.001 \text{ \AA}$  unit since more accurate determinations of refractions will then only cause small changes in  $d$ , and not introduce variations in the wavelengths already calculated on the Siegbahn basis. Furthermore,  $d$  calculated by Siegbahn's method falls within the limits of error of Compton's value. The corrected wavelengths are: Mo K $\alpha_1 = 0.707830$ ; Fe K $\alpha_1 = 1.932050 \text{ \AA}$  unit.

## 47. GLOCKER, R. AND SCHREIBER, H.

Quantitative Röntgen Spectrum Analysis by Means of Cold Excitation of the Spectrum.

*Ann. Physik*, **85**, 1089-1102 (1928).

*C. A.*, **22**, 2280.

A method of quantitative X-ray analysis is described in which the sample to be analyzed is excited to emission of characteristic X-rays by exposure to a stream of primary X-rays from the anticathode of the tube. The advantages of this method are that the sample remains cold and undergoes no change in its composition, as might be the case if it were excited by cathode particles, with consequent increase in temperature. The disadvantage lies in the prolonged exposure time required to get spectrograms of suitable dimension for measurement. The method has been applied successfully to the analysis of steels containing V, Ti and W, the proportions of each being determined from the relative intensities of their K $\alpha$  lines. In experiments with a mixture of oxides of Sb and Sn in CaSO $_4$ , containing the same number of Sb and Sn atoms, the ratio of intensities of the L $\alpha$  lines

was Sb:Sn=1:1, while with exposure made with the sample on the anticathode and excited by cathode rays the ratio was Sb:Sn=1:6. The effect on the line intensities of the tube voltage and the presence of foreign substances was also investigated and was found to have no detrimental influence on the method of analysis.

## 48. LORENZ, EGON

The Intensities of Röntgen Spectrum Lines, Especially of the K-Series of Aluminum as Dependent on the Voltage of the Tube.

*Z. Physik*, **51**, 71-94 (1928).

*C. A.*, **23**, 31.

The effect of very high exciting voltages on the intensities of X-rays was measured, first qualitatively for W, and then quantitatively for Al. The stray rays emitted by a W anticathode are attributed to excitation by secondary electrons coming from the focus of the primary electron stream. The difference between the voltage corresponding to the stray rays of shortest wavelength and that of the shortest ray directly excited by the primary electrons determines the X-ray levels from which the secondary electrons are ejected. When the voltage applied to the tube becomes 40 times that required to excite an electron in a particular level the liberation of secondary by primary electrons becomes nil; i.e., the intensity of the corresponding series lines becomes a zero. Quantitative results of the same character, derived from experiments on Al in which thick Al and very thin foil were used for anodes, show that the intensities of the K-series increase as the square of the tube voltage until a voltage twice that of the excitation potential is reached. Thence the increase is more gradual, reaching a maximum at a voltage 11 times the excitation potential. At higher voltages there is a decline in intensity, until at 40 times the excitation potential (for the foil) the intensities are zero.

## 49. SCHWARZSCHILD, M. M.

Theory of the Double X-ray Spectrometer.

*Physic. Rev.*, **32**, 162-171 (1928).

*C. A.*, **23**, 30.

The geometric factors in the construction and use of the double X-ray spectrometer are examined in detail. The resolution of the instrument is not affected by the width of the slits but the height of the slits must be limited to preserve resolution. A formula is given for the limiting value of the ratio of the average height of effective slits to the distance between effective slits for any particular width of observed line, in order that the width observed be the result principally of the physical factors. The physical factors, namely, crystal imperfection, line width, diffuseness of absorption limits, are also discussed and formulas are derived by means of which the experimental curves found with the instrument may be interpreted physically.

50. WEBSTER, D. L., CLARK, H., YEATMAN, R. M., AND HANSEN, W. W.  
Intensities of *K*-Series X-rays from Thin Targets.

*Proc. Nat. Acad. Sci.*, **14**, 679-686 (1928).  
*C. A.*, **23**, 31.

The intensities of the AgK-lines were measured as a function of the voltage, the Ag targets being films deposited on Be and so thin (280 A units thick and less) that there was no appreciable retardation of the cathode rays. The results, which give the relative probability of direct *K*-electron ionization as a function of the energy of the cathode rays, are only in quality agreement with the theories of Davis, of Rosse-land, and of Thomas. An empirical equation is given which satisfies the observed data.

## 1929

51. COOLIDGE, WM. D.  
Röntgen-ray Tubes.  
*Brit. Patent* 364, 706, Oct. 18, 1929.  
*C. A.*, **27**, 2347.  
Structural features.

52. EDDY, C. E., LABY, T. H., AND TURNER, A. H.  
Analysis by X-ray Spectroscopy.  
*Proc. Roy. Soc. (London)*, **A124**, 249-268 (1929).  
*C. A.*, **23**, 4905.

In spectral analyses with X-rays an element is usually identified by its 4 *K*-series lines or by at least 6 of its *L*-series lines. With very small quantities of an element in a mixture some of these lines may be undiscernible. As compared with other methods of spectral analysis, X-ray spectra have the following advantages: (1) the number of lines is small; (2) Mosley's law simplifies the identification of a line; (3) a minimum potential is required to excite a group of lines, so the 2nd or higher order lines can be excluded. In this paper the technic of constructing the X-ray tube and spectrometer and the identification of the lines are described. Results show that the method is capable of detecting as little as 0.0003 of an impurity in a metal. Seven samples of Zn were examined, one of which was spectroscopically pure and the others were of composition known by analysis or synthesis.

53. SCHREIBER, H.  
Quantitative Chemical Analysis by Means of Röntgen Emission Spectrum.  
*Z. Physik.*, **58**, 619-650 (1929).  
*C. A.*, **24**, 1312.

The comparison of corresponding lines of neighboring elements and the empirical mixing method of von Hevesy and Coster were studied with respect to the sources of errors which could not be completely avoided even in the latter case. At the high temperatures used, decompositions are likely to result, which cause changes

in the original concentration relations. To avoid the high heating, a new general method was developed in which the excitement of the individual radiation results from primary X-rays. The new "fluorescence method" was tested with various mixtures and it was found that the effect of impurities was now inappreciable. The sources of error of the new method are discussed and it is shown that the total possible error in determining the concentration of an element is not over 7 per cent.

54. SLACK, C. M.  
Lenord X-ray Tube with Glass Windows.  
*J. Optical Soc. Am.*, **18**, 123 (1929).

## 1930

55. CALVERT, J. T.  
The Determination of Potassium in Soil Samples by the Application of an X-ray Method.  
*Trans. Faraday Soc.*, **26**, 509-514 (1930).  
*C. A.*, **24**, 5912.

The method of quantitative analysis by the X-ray method are briefly discussed. Experiments are described on the determination of *K* in soil samples and in certain minerals. In the former case the method consists of mixing a known quantity of MnO<sub>2</sub> with the soil sample and comparing the intensities of the potassium *Kα*<sub>1</sub> and the manganese *Kβ*<sub>1</sub> lines excited by X-rays of shorter wavelength. Cd was used as a reference substance in the other determinations. A brief description and drawing of the tube are included. The secondary-ray method in which the sample is outside the high vacuum of the X-ray tube has been used.

56. EDDY, C. E. AND LABY, T. H.  
Quantitative Analysis by X-ray Spectroscopy.  
*Proc. Roy. Soc. (London)*, **A127**, 20-42 (1930).  
Cf. *C. A.*, **23**, 4905.  
*C. A.*, **24**, 3193.

Quantitative analysis of alloys of elements of nearly equal atomic number by means of X-rays is described. The intensities of analogous spectral lines on photographic films were measured photometrically and the percentage compositions of the alloys calculated with an accuracy of about 1 in 200. Cu-Zn, Sn-Cd, Pb-Bi and Sn-Zn alloys were investigated and good results obtained except for the Sn-Zn alloys where the atomic numbers differ greatly. Heterogeneity of the alloy when used as the X-ray tube target has very little effect upon the results.

57. HEVESY, G., VON  
Quantitative Analysis by X-rays.  
*Nature*, **125**, 776-777 (1930).  
Cf. *C. A.*, **24**, 1312.  
*C. A.*, **24**, 3964.

The sensitiveness of X-ray detection of an element depends on the composition of the alloy

and its state of aggregation. Although in some cases (cf. Laby and Eddy, *C. A.*, **24**, 3456) very accurate tests can be made directly on an alloy, most substances will require the addition of a reference substance.

58. HEVESY, G., VON, BÖHM, J., AND FAESSLER, A.  
Quantitative Spectroscopic Analysis with Secondary X-rays.  
*Z. Physik*, **63**, 74-105 (1930).  
*C. A.*, **24**, 5609.

X-rays, coming from the suitably excited substance, whose composition has to be determined, are analyzed spectroscopically. From the intensities of the emission lines (e.g.,  $K\alpha$ ) compared with those from a suitable element added to the sample in known quantity, the concentration of the former may be obtained. It has been found that it is necessary to use secondary X-rays to excite the compound to be analyzed, because the ordinary electron impact alters the composition by selective evaporation. The X-ray tube consists of a glowing cathode surrounded by a cylinder with a little carrier which contains the compound to be analyzed and is placed at a short distance from the anticathode supplying the primary X-rays. The intensity of current through the X-ray tube may be considerable (20 ma) as the ray coming from the cathode must not be centered. A maximum intensity is obtained, when the primary K-radiation of the anticathode is about 200 X units harder than the K absorption edge of the secondary radiator, the continuous spectrum contributing but little to the total radiation. The yield of secondary radiation increases considerably for a given input when the tension is raised; therefore it is advisable to run the X-ray tube with low intensity of current. The intensity of lines, whose potential of excitation does not differ more than 250 X units, is independent of the tension applied to the tube. The time of exposure was generally 2-3 hr, the precision of estimation 0.01, if the element was present in a concentration of 1%. The various sources of error are discussed and a list of elements of reference is given.

59. LABY, T. H., AND EDDY, C. E.  
Quantitative Analysis by X-rays.  
*Nature*, **125**, 524-525 (1930).  
*C. A.*, **24**, 3456.

The method is based on the fact that in an alloy of 2 elements of nearly equal atomic number, the ratio of the number of atoms present is equal to the ratio of the intensities of the corresponding lines in the spectrum of the alloy provided that the lines are excited under the same conditions. A third element in the powdered mixture does not interfere in the accuracy of the determination for alloys.

60. HEVESY, G., VON  
X-ray Spectroscopic Microanalysis.

*Mikrochemie Emich Festschr.*, 163-165 (1930).  
*Cf. C. A.*, **25**, 25.  
*C. A.*, **25**, 3264.

The advantages of X-ray spectroscopic methods for the detection and determination of quantities of material as small as 0.001 mg, or even less, are described. The lines of the L series should preferably be sought, on account of the relatively low tube voltage necessary for their production.

61. LABY, T. H.  
Quantitative Analysis by X-rays.  
*Nature*, **125**, 818 (1930).  
*Cf. C. A.*, **24**, 5606.  
*C. A.*, **25**, 3262.

In a reply to Hevesy (*C. A.*, **24**, 3964), it is reaffirmed that the K X-ray spectrum of an element present to less than 0.0001% in a metal can be photographed.

62. LABY, T. H.  
Atomic Analysis by X-ray Spectroscopy.  
*Trans. Faraday Soc.*, **26**, 497-509 (1930).  
*C. A.*, **24**, 5606.

The X-ray method of determining the atomic constituents of a substance is compared with other methods, viz.: (1) chemical, (2) optical spectroscopic and (3) positive-ray methods. Spectroscopic methods are in general to be preferred to chemical ones when only very small quantities of the sample are available, or when the unknown substance is present only in very minute traces. The X-ray method has the following advantages over the optical: simplicity and relatively short range of the X-ray spectrum due to a given atom; certainty of identification of lines of elements according to Moseley's law; the fact that, for elements of nearly the same atomic number, the intensities of corresponding emission lines, excited with equivalent excitation potentials, are in the same ratio as that of the respective numbers of atoms of the elements in the mixture. The last consideration makes possible the use of the X-ray method for other than very small concentrations, a condition necessary for the quantitative interpretation of results obtained by the optical method. The X-ray method is probably more sensitive than the optical, although sensitiveness depends to a great extent upon the elements investigated and experimental technique. Elements have been detected in concentrations as small as 1 part in  $10^6$ . The experimental methods of X-ray analysis are briefly discussed, and a short description and an illustration of the apparatus are included. The importance of a satisfactory experimental technique is stressed.

63. RICHTMYER, F. K., BARNES, S. W., AND RAMBERG, E.  
Direct-reading Two-crystal Spectrometer for X-rays.  
*Phys. Rev.*, **35**, 1428 (1930).  
*C. A.*, **25**, 5085.

The two-crystal X-ray spectrometer has been improved until it is now capable of absolute wavelength measurement of very high precision.

## 1931

64. ALLISON, SAMUEL K.  
The Resolving Power Attainable in X-ray Spectroscopy by Photographic Methods.  
*Phys. Rev.*, **38**, 203-11 (1931).  
*C. A.*, **25**, 5084.

65. COMPTON, ARTHUR H.  
A Precision X-ray Spectrometer and the Wavelength of Mo K.  
*Rev. Sci. Instr.*, **2**, 365-376 (1931).  
*C. A.*, **25**, 4467.

The instrument has 2 crystals in series. The first is mounted on an arm projecting from the frame. The second is placed on the central table whose position is read from a precision circle. For the  $K\alpha_1$  line of Mo the reflection maxima from calcite (cor. to 18 deg) occur at  $\Theta_1 = 6^\circ 42' 35.5''$  and  $\Theta_2 = 27^\circ 51' 33.0'' \pm 0.25''$  in each case. If the apparent grating space for the first order is  $3.02904 \text{ \AA}$  units then  $\lambda = 707.830 \pm 0.002 \text{ \AA}$  units. Comparison of  $\Theta_1$  with  $\Theta_2$  gives  $n$  for calcite,  $1 - \mu = (2.10 \pm 0.15) \times 10^{-6}$ .

66. EDDY, C. E. AND LABY, T. H.  
Qualitative Analysis of Alloys by Means of X-ray Spectroscopy.  
*J. Phys. Chem.*, **35**, 3635-3638 (1931).  
*C. A.*, **26**, 1213.

A commentary on an article by Terrey (*C. A.*, **25**, 2914). It is found that reproducible results of X-ray analysis of alloys are obtained. Factors such as inefficient cooling of the target, poor control of voltage and current, the use of a spark gap instead of an electrostatic kilovoltmeter, the use of the wedge method for measuring intensities and failure to rock the spectrometer crystal uniformly may cause the unreliable data obtained. Data for alloys of elements of nearly equal atomic numbers are included.

67. FONDA, GORTON R. AND COLLINS, GEORGE B.  
The Cathode-Ray Tube in X-ray Spectroscopy and Quantitative Analysis.  
*J. Am. Chem. Soc.*, **53**, 113-125 (1931).  
*C. A.*, **25**, 870.

A method is described by which the X-ray spectrum of a sample is excited by directing upon it a stream of electrons transmitted by the Al window of a cathode-ray tube. The usual photographic method of recording is replaced by a system consisting of an ionization chamber together with amplifying apparatus in which the new 4-element vacuum tube, FP-54, is employed. The law governing intensity variation,  $I = C(V - V_0)^2$  is discussed for the case of the  $K\alpha$  radiation of Fe and Mo. The exponent is found

to be correct up to a voltage four-fold that of  $V_0$ , the exciting voltage for Mo, and eleven-fold for Fe. Quantitative results are presented of the analysis of certain metallic alloys.

68. FONDA, GORTON R.  
The Cathode-Ray Tube in the X-ray Spectroscopic Analysis of Columbium and Tantalum.  
*J. Am. Chem. Soc.*, **54**, 115-122 (1931).  
*C. A.*, **26**, 1210.

The Coolidge tube has been used for exciting X-radiation in the spectrum analysis of Cb and Ta. A technic suitable for measurement of these elements has been perfected. Tantalites and mixtures of oxides and carbides were examined. The results are in agreement with chemical analysis. An absolute error of about 2% exists independent of quantity.

69. HOHT, ARCHER AND DU MOND, JESSE  
Breadth of the Compton Modified Line with the Double Crystal Spectrometer.  
*Physic Rev.*, **37**, 1443-1451 (1931).  
*C. A.*, **25**, 5085.

70. JOHANN, H. H.  
More Intense X-ray Spectra Obtained with Concave Crystals.  
*Z. Physik*, **69**, 185-206 (1931).  
*C. A.*, **26**, 1510.

The possibilities of X-ray reflection spectra from concave crystals is discussed from theoretical and experimental standpoints.

71. WILLIAMS, JOHN H.  
An Experimental Study of the Natural Widths of the X-ray Lines in the L-series Spectrum of Uranium.  
*Physic Rev.*, **37**, 1431-1442 (1931).  
*C. A.*, **25**, 5084.

The half widths at half maximum of the rocking curves in parallel positions of the double X-ray spectrometer with calcite crystals reflecting in the 1st order have been investigated as a function of wavelength. This function is shown to be linear. The rocking curves of  $U L\alpha$  in 3 different anti-parallel positions of the instrument give a natural width practically independent of the dispersion. The natural widths of  $U L\alpha$  and  $U L\beta$  show no dependence on voltage. The half widths at half maximum of 12 lines in the U L-series spectrum are given. The results are discussed from classical and quantum theory points of view.

## 1932

72. EDDY, C. E.  
A Self-Rectifying Demountable X-ray Tube of High Power.  
*J. Sci. Instr.*, **9**, 354-358 (1932).  
*C. A.*, **27**, 209.

73. EDDY, C. E. AND LABY, T. H.  
The Sensitivity of Atomic Analysis by X-rays.  
*Proc. Roy. Soc. (London)* **A135**, 637-656 (1932).  
*C. C. A.*, **23**, 4905.  
*C. A.*, **26**, 3745.  
The sensitivity of X-ray spectroscopy in detecting the presence of elements of atomic numbers greater than 21 in Pb, Fe, Sn and Zn has been further studied. Under proper operating conditions the presence of 1 or even 0.1 ppm of a metallic element in an alloy can be detected. However, improper screening of the photographic film from radiation scattered by the crystal and slit or failure to maintain sufficiently high vacuum in the X-ray tube may lower the sensitivity to 0.0% or even 0.1 per cent.
74. MARTIN, L. H. AND LANG, K. C.  
X-Ray Absorption Coefficients in the Range 0.3 to 2.0 Å units.  
*Proc. Roy. Soc. (London)*, **A137**, 199-216 (1932).  
*C. A.*, **26**, 5835.  
Two balance methods, an ionization and a photographic, for measuring X-ray absorption are described. With the first, absorption coefficients ( $\mu/\delta$ ) were determined for Fe, Ni, Cu, Mo, Pd and Ag over a wavelength range of 0.3 to 0.6 Å units; with the second, for Fe, Ni, Cu, Zn, Ag and Sn over a range up to 2.0 Å units. In the first method the X-ray beam is diffracted from a calcite crystal into 2 ionization chambers in series, between which a foil of the sample and a rotating sector of variable aperture are placed. The currents are adjusted to balance with and without the foil in the beam path. In the second system the beam is split by 2 slit system into 2 beams, one above the other. The photographic intensities are compared when one beam is partially absorbed by an Al standard foil, the other by the material in question, and when no foils are present in either path. The 2 methods yield concordant results in the overlapping range. The values of  $\mu/\rho$  are given and compared with earlier results. The values of the  $K$  jump are shown  $E_K/E_{II}$  for Fe, Ni, Cu, Zn, Pd and Ag; and an equation for the  $K$  absorption of these elements in terms of the atomic number and the wavelength is given.
75. PARRATT, LYMAN G.  
Design of a Double-Crystal X-ray Vacuum Spectrometer.  
*Physic Rev.*, **41**, 553-560 (1932).  
*C. A.*, **26**, 5836.
76. PARRATT, LYMAN G.  
X-ray Diffraction from Calcite for Wavelengths 1.5 to 5 Å unit.  
*Physic Rev.*, **41**, 561-576 (1932).  
*C. A.*, **26**, 5836.  
Theoretical expressions for the coefficient of reflection, percentage reflection and width of the line to be expected from the second crystal of a double spectrometer in the (1, -1) position, based on Darwin's theory of reflection from a perfect crystal, as modified by Prins, are evaluated for calcite for 6 lines in the region 1.54 to 5 Å unit. This region includes, at 3.06 Å unit, the critical absorption limit of Ca. These properties of the rocking curve from the second crystal for 10 wavelengths  $CuK\alpha$  radiation and 9 spectrum lines selected from the  $UM$ -series are measured experimentally with a special double-crystal spectrometer. The results are compared with the calculated values. The agreement of the rocking curve widths is excellent throughout the entire region and gives no evidence of mosaic structure in the crystals. The calculated values of percentage reflection are consistently above those observed by some 16%. Good agreement is obtained for the values of the coefficient of reflection for wavelengths shorter than 4 Å unit including those close to, and on either side of, the Ca absorption limit.
77. FONDA, GORTON R.  
Effect of Particle Size on Intensity in X-ray Spectroscopic Analysis.  
*J. Am. Chem. Soc.*, **55**, 123-127 (1933).  
*C. A.*, **27**, 1571.  
The decrease in intensity of diffracted X-ray beams, due to surface irregularities of the target, is studied for grids of various sizes, and powers of various particle-diams.
78. GLOCKER, R.  
Principles of Quantitative X-ray Analysis of the Concentration of Metal Phases in an Alloy or Mixture.  
*Metallwirtschaft*, **12**, 599-602 (1933).  
*C. A.*, **28**, 1003<sup>b</sup>.  
No general rules can be set down for X-ray analysis of metal phases, such as the rules for X-ray spectrum analysis. For each individual case equations must be deduced and several correction factors determined. The most difficult to determine are the temperature and the extinction factors. 28 references.
79. VON HEVESY, G. AND ALEXANDER, E.  
Praktikum der Chemischen Analyse mit Röntgenstrahlen.  
*Akademische Verlagsgesellschaft*, M.B.H., Leipzig (1933).
80. PARRATT, LYMAN G.  
Double-Crystal X-ray Spectrometry.  
*Trans., Illinois State Acad. Sci.*, **25**, 175-177 (1933).  
*C. A.*, **28**, 3657<sup>b</sup>.  
The analysis of X-ray beams by the single-crystal and double-crystal methods is presented from a mathematical viewpoint.
81. SANDSTROM, A. AND CARLSSON, E.  
Preliminary Photographs of Emission and Absorption Spectra with Bent Crystals as Transmission Gratings.

- Z. Physik*, **80**, 597-603 (1933).  
*C. A.*, **27**, 4478.  
 Emission spectra MoK and AgK were obtained in four orders, and absorption spectra of K-edges of Br and Mo were obtained with bent gypsum crystals.
- 82. SIEGBAHN, MANNE AND MAGNUSSON, T.**  
 The Spectroscopy of Ultra-soft Röntgen Radiation. II.  
*Z. Physik*, **87**, 291-309 (1933).  
*Cf. C. A.*, **24**, 5212.  
*C. A.*, **28**, 2994<sup>5</sup>.
- 83. CAUCHOIS, Y.**  
 Extension of the X-ray Spectrograph. Spectrograph Focused by a Curved Crystal. X-ray Emission Spectra of Gases.  
*Ann. Physik* (11), **1**, 215-266 (1934).  
*Cf. C. A.*, **27**, 4165.  
*C. A.*, **28**, 2994<sup>2</sup>.
- 84. HONL, H.**  
 Atomic Scattering Factors for Röntgen Rays as a Problem of the Dispersion Theory (for the K-Levels).  
*Ann. Physik*, **18**, 625-655 (1934).  
*Cf. C. A.*, **26**, 5003.  
*C. A.*, **28**, 2612<sup>6</sup>.  
 Math. The dispersion formula of Waller (*C. A.*, **22**, 912) is divided into two parts, the first corresponding to the geometric interference theory of atomic scattering factors and the second to anomalous scattering by electron shells. This second part is developed on the basis of an additional theorem for spherical functions according to the idea of multipoles. A parameter  $\chi$  is introduced equal to  $2\pi a/\lambda$  where  $a$  is the mean shell radius of the layer concerned. Calculation of the relation of frequency is given for the dipole and quadripole of the K shell. The calculated atomic scattering factor curves are in general in good agreement with recent measurements.
- 85. PARRATT, LYMAN G.**  
 X-ray Reflectivity and Resolving Power of the (10.0) Planes of Etched Quartz Crystals.  
*Rev. Sci. Instr.*, **6**, 113-115 (1935).  
*Cf. Ibid.*, **5**, 395 (1934).  
*C. A.*, **29**, 4259<sup>9</sup>.  
 Measurements of the width of the (1, -1) rocking curve, percentage reflection and coefficient of reflection are reported for the range  $0.56 < \lambda < 7.11 \text{ \AA}$ . The rocking curves are sym. The percentage reflection decreases with increasing wave length for  $1.93 < \lambda < 5.40 \text{ \AA}$ , but suddenly increases at the SiK absorption limit,  $6.7 \text{ \AA}$ . The resolving power is greater than that of calcite when  $\lambda > 3 \text{ \AA}$ .
- 86. SIEGBAHN, MANNE AND MAGNUSSON TORSTEN**  
 X-ray Spectra of the L-Series of Silicon and Silica.  
*Nature*, **133**, 257 (1934).  
*C. A.*, **28**, 2994<sup>2</sup>.  
 Differences in the lines of Si and SiO<sub>2</sub> at about  $135 \text{ \AA}$  are described and compared with the analogous case of Al and Al<sub>2</sub>O<sub>3</sub>.
- 1935**
- 87. BEARDEN, J. A. AND SHAW, S. H.**  
 Shapes and Wave Lengths of K Series Lines of Elements Ti22 to Ge32.  
*Physic Rev.*, **48**, 18 (1935).
- 1936**
- 88. BACKHURST, IVOR**  
 X-ray K-Fluorescence Yield.  
*Phil. Mag.*, **22**, 737-752 (1936).  
*C. A.*, **31**, 606.  
 The K-fluorescence yield coefficient  $w_k$  was determined for Mo, Rh, Pd, Ag, Cd, Sn, Sb, Te and Ba. The value of  $w_k$ , which is independent of the wavelength of the incident radiation, is represented by  $w_k = 1 - [1/(1 + bZ^4)]$ , in which  $Z$  is the atomic number and  $b = 1.035 \times 10^{-6}$ . Previous determinations of  $w_k$  are discussed. On the average, the values for  $Z < 42$  are in agreement with the above equation.
- 1937**
- 89. HÄMOS, L., VON**  
 A New X-ray Method for Chemical Analysis of Plane-Polished Surfaces.  
*Tek. Tidskr.*, **67**, *Uppl. A-C. Bergsvetenskap*, 1-4 (1937).  
*C. A.*, **31**, 3818<sup>6</sup>.  
 A new spectrograph is described having a curved crystal for collecting X-rays. Instead of the usual X-ray lines a series of monochromatic X-ray images are obtained showing the distribution of chemical elements on the surface. Diagrams based on calculations by von Hämos show the positions on the film occupied by spectral images belonging to different elements. Typical spectrograms of metals and ores are included.
- 1938**
- 90. HÄMOS, L., VON**  
 X-ray Image Method of Chemical Analysis.  
*Am. Mineralogist*, **23**, 215-226 (1938).  
*Cf. C. A.*, **28**, 3300<sup>6</sup>, 6367<sup>8</sup>; **32**, 4014<sup>7</sup>.  
*C. A.*, **32**, 5727<sup>7</sup>.  
 By use of a curved crystal reflecting surface, true X-ray images can be produced. Their distances from the specimen, and thus their positions on the photographic plate, depend on the  $\lambda$  of the secondary radiation, which in turn depends upon the chemical elements present. Quantitative data can be had by comparison

with series of known compositions. The method is particularly suitable for small samples and for the investigation of chemical heterogeneities.

**91. HÁMOS, L., VON**

Röntgen Spectrographic Surface Analysis for Metallographic Purposes.

*Jernkontorets Ann.*, **122**, 170-174 (1938).

*C. A.*, **32**, 7379<sup>o</sup>.

Primary rays are directed on the surface to be examined and the secondary radiations are focussed, by the concave surface of a crystal cylinder, on a photographic plate. The secondary radiations are characteristic of the chemical composition. Extraneous radiations are screened from the plate. A specially constructed scale enables the operator to measure the focal distance and thereby identify the element. The quantity is indicated by the amount of darkening on the plate. A high degree of resolution was obtained by arranging the optical system so that the focussed rays strike the plate at right angles. With the cylindrical radius of curvature equal to 17 mm a magnification of 30 is obtained. The method has been used to study the distribution of Cr in Al alloys, and in chrome steels and is especially valuable for small particles which produce photographic markings even when as small as 0.000001 mg.

**1939**

**92. HÁMOS, LÁZLÓ, VON**

Apparatus for Quantitative Analysis by X-rays.

*Brit. Patent* 506, 022, May 22, 1939.

*C. A.*, **33**, 8454<sup>r</sup>.

The apparatus comprises an X-ray source, at least 1 crystal having a concave surface formed by a bent cleavage plane for focusing the X-rays and 2 ionization chambers which receive 2 spectral images from the sample(s). The sample to be analyzed and the sample of known composition are both subjected to X-rays that produce secondary X-rays of wavelength and intensity dependent on the chemical composition of the samples.

**1940**

**93. RIVOIR, L. AND ÁRA, A.**

Chemical Analysis by X-rays. II. Analysis of Alloys.

*Anales soc. españ. fis. quim.*, **36**, 20-25 (1940).

*Cf. C. A.*, **31**, 6575<sup>o</sup>.

*C. A.*, **34**, 7203.<sup>3</sup>

Quantitative analyses were made of various alloys of Zn, Cu and Ni by the X-ray method. Corrections for atomic weight, tube windows and air absorption of the camera required multiplying the Zn line intensity by 1.13 for the Siegbahn, and by 1.09 for the Siemens camera. With Cu-Ni, the Cu intensities must be multiplied by 1.08. Analyses must be carried out rapidly.

Usually 10-20 min exposure is sufficient to obtain photometric intensities. Differences between results obtained by this and by chemical methods are about 3 per cent.

**1941**

**94. RIVOIR, L. AND BARREDO, J. M. G.**

Chemical Analysis with X-rays. III. Finding the Appropriate Voltage for the Realization of Quantitative Analysis by the Method of Direct Comparison.

*Anales soc. españ. fis. quim.*, **37**, 48-57 (1941).

*C. A.*, **35**, 7826<sup>o</sup>.

**1942-43**

**95. AMINOFF, G.**

The Use of New Crystals in Chemical X-ray Spectrography.

*Arkiv Kemi Mineral. Geol. (Ser. A16)*, No.

**10**, 5 pp. (1942). *Chem. Zentr.*, **I**, 2423 (1943).

*C. A.*, **38**, 4510<sup>r</sup>.

The author suggests the following as spectrometer crystals for chemical X-ray spectrography: 2131 of calcite, 110 of zinc blende, 111 of diamond, 100 of rock salt, 1011 of calcite, 210 of barytes or 010 of gypsum. (On new crystals to be used in chemical X-ray spectrography-I and II *Arkiv Kemi*, **16B-10**, 1 (1942); **18B-14**, 1 (1944).)

**1944**

**96. AMINOFF, G.**

Large Dispersion in X-ray Spectrography Obtained by Using Ground Faces.

*Nature*, **157**, 517 (1946).

*Cf. K. Vetenskapsakad. Ark. Kemi, etc.*, **18B**, No. **14**, (1944).

*C. A.*, **40**, 5333<sup>o</sup>.

With Iceland calcite, the spacings for the natural faces 211 and 310 are 3.029 and 1.532 Å, respectively; for the ground faces 655,744, and 10.3.3. they are 1.032, 0.716, and 0.533 Å, respectively. Values of  $d\theta/d\gamma$  are tabulated for these planes for the  $K\alpha_1$  lines of Mo, Cu, and Sc, and a formula is given for calculating the displacement of a line.

**1945**

**97. CAUCHOIS, YVETTE**

Universal X-ray Spectrograph for Use up to 20 Å.

*J. phys. radium*, **6**, 89-96 (1945).

*C. A.*, **40**, 1090<sup>o</sup>.

Alternative focusing by reflection or transmission by means of a simple shift in the position of the tube relative to a curved crystal analyzer permits use from 0.3 to 18 Å. The

instrument comprises an evacuated box with cathode and insulator fixed to the top and anti-cathode fixed to the bottom. The tube occupies either of 2 positions. In each case regulation is obtained by rotation of the spectrograph about a vertical axis passing through the generatrix common to the crystal and the focusing cylinder. The photographic plate is tangential to this cylinder.

1946

98. ROGERS, T. H.  
A High-Intensity Source of Long-wave X-rays.  
*Ind. Radiography*, **4**, 35-39 (1946).  
*C. A.*, **40**, 2070<sup>r</sup>.

The new X-ray tube operates at 50,000 v and 50 ma to produce a beam with a measured intensity of 5.5 million Röntgens per min. Essential features are a Be-foil dome on one end of the tube and an annular filament around the target. Filament and dome are at ground potential so that the electrons describe a curved trajectory to the focal spot on the target. The tube is especially adapted for researches in photochemistry and bacteriology.

1947

99. CRAGGS, J. D. AND JAFFE, A. A.  
Discharge Spread in Geiger Counters. I. With Self-quenching Gases.  
*Physic Rev.*, **72**, 784-792 (1947).  
Cf. preceding abstr.; also Korff, and Present,  
*C. A.*, **38**, 3545<sup>s</sup>.  
*C. A.*, **42**, 1496(a).

Despite the work of Korff, Stever, and others, many aspects of Geiger counter behavior are as yet unexplained. In particular, the extent to which the photons produced in the counter discharge are of importance and the manner in which they are absorbed in the counter gas seem to have been insufficiently studied. The experiments described here were made with single wire, divided-cathode counters of various types. The results show that photon absorption seems to be less complete than is often thought, but that when such absorption is fairly small, it may be almost entirely manifest as a cathode, not a gas effect, as shown by experiments with a new type of divided-cathode counter, in which the cathode effect is virtually eliminated.

100. CURRAN, S. C. AND RAE, E. R.  
Some Properties of Counters with Beaded Wires.  
*J. Sci. Instr.*, **24**, 233-238 (1947).  
*C. A.*, **42**, 1495(f).

A comparison is reported of some properties of two identical standard Geiger counters, the wire of one of which was studded with glass beads. Fundamental values such as length of working plateau, starting voltage, efficiency, de-

gree of localization, and dead time were examined. The addition of closely spaced beads to the wire is shown to have no serious effects on the length or flatness of the plateau. The presence of glass beads requires higher voltages to raise the field to the counting value. Owing to production of insensitive regions, beads result in reduction of over-all efficiency. Degree of localization was found to be sensitive to such features as condition of cathode, nature and pressure of the gas or mixture of gases, and voltage on the tube. The effective value of the dead time for a tube containing a wire with many beads is small enough to permit counting rates of several thousands per sec.

101. LIEBSON, S. H.  
The Discharge Mechanism of Self-quenching Geiger-Muller Counters.  
*Physic. Rev.*, **72**, 602-608 (1947).  
Cf. Stever, *C. A.*, **36**, 1842<sup>r</sup>.  
*C. A.*, **42**, 1495(h).

A split counter arrangement was used to investigate the absorption coefficient of the radiation which causes the discharge to spread along the wire of a counter after the triggering of a pulse. The counters used were filled with methylene bromide and A at various pressures, and with EtOH and A. The results indicate that the vapor dissipates electron energies; this reduces the number of photons produced during the discharge. It was also observed that the absorption coefficient is a function of the A alone, from which it was concluded that photoionization of the A is responsible for spreading the discharge along the wire. This behavior was also observed with He and Ne in combination with alcohol or methylene bromide.

102. BURKHART, L. E., PEED, W. F., AND SAUNDERS, B. G.  
X-ray Spectrum of Element 43.  
*Physic Rev.*, **73**, 347-349 (1948). (U. S. Atomic Energy Comm.) MDCC-1124 (1947).  
*C. A.*, **42**, 2413(b).

The X-ray spectrum of element 43 was obtained from 1.5 mg of material which contained 0.7 mg of element 43. The observed wavelengths (in X unit) and their assignments are:  $K\alpha_1$ , 673.5;  $K\alpha_2$ , 677.8;  $K\beta_1$ , 601.4;  $K\beta_2$ , 589.9. These wavelengths agree closely with values calculated by interpolation between elements 41, 42, 44, and 45. Tables are given of the second-order interference lines, and of the experimental conditions for the exposures.

103. KRACHTER, HANS AND JAGER, WILLI  
Determination of Alloying Elements in Steel by the X-ray Fluorescence Spectrum Analysis.  
*Arch. Eisenhüttenw.*, **28**, 633-639 (1947).  
*C. A.*, **52**, No. 3, Feb. 10, 1958, 1854(i).

Instead of the chemical analysis the spectrochemical X-ray fluorescence method can success-

fully be applied where elements with higher order numbers have to be determined for which the light optical method requires apparatus with especially high resolving power because of the many lines. The disadvantage that with this method elements below the atomic No. 22 cannot be determined becomes an advantage in investigations of alloys containing little Ni, Cr, or Cu besides Al, Mg, or Si, i.e. elements of atomic No. 22 (Ti) plates now counters of the intensity are used preferably as they permit instantaneous indication of intensity and evaluation. The X-ray tube with a *W* anode throws its radiation into the sample which sends it after reflection on the analyzer crystal into the counter. Preparation of samples, evaluation, and actual determinations are described in detail. The accuracy of the method for determining alloy contents is about 2 per cent.

## 1948

## 104. ABBOTT, J. L.

X-ray Fluorescence Analysis.

*Iron Age*, **162**, No. **18**, 58-62, No. **19**, 121-124 (1948); Pt. I., Oct. 28; Pt. II, Nov. 4.

*C. A.*, **43**, 961(*d*).

The principles and equipment are described. Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn can be analyzed without complications. Elements with atomic numbers up to and including Mo have been analyzed satisfactorily. Elements, up to and including Sn, can be analyzed by this procedure. The method is particularly suited to the analysis of alloy steels and heat-resistant and high-temperature alloys. Its application to specific analytical problems is discussed.

## 105. LIEBSON, S. H. AND FRIEDMAN, H.

Self-quenching Halogen-Filled Counters.

*Rev. Sci. Instr.*, **19**, 303-306 (1948);

*Cf. C. A.*, **42**, 1495(*h*).

*C. A.*, **42**, 6643(*g*).

Geiger counters filled with inert gases containing additions of halogens are compared with A-alcohol filled tubes. Threshold voltages are shown for A-Br, Ne-Cl, and A-Cl mixtures. The counting rates are very nearly the same as for A-alcohol fillings. No harm results from over-voltages exceeding the plateau limit, and the lifetime of these tubes is apparently unlimited.

## 106. CORDOVI, MARCEL A.

Rapid Quantitative Analysis by X-ray Fluorescence.

*Steel*, **123**, No. **25**, 88-94 (1948).

*C. A.*, **43**, 959(*h*).

A progress report indicating that a few modifications in present equipment will bring the accuracy within limits required in routine determinations of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr, Rb, Sr, Y, Zr, Cb, Mo, Ma, Ru, Rh, Pd, Ag, Cd, In, and Sn.

## 107. FRIEDMAN, H. AND BIRKS, L. S.

A Geiger-Counter Spectrometer for X-ray Fluorescence Analysis.

*Rev. Sci. Instr.*, **19**, 323-330 (1948).

*C. A.*, **42**, 6649(*b*).

The *K*-series lines are used for elements of atomic numbers 22-50; for higher numbers, the *L* series spectra are used. In the middle range, the sensitivity was 1 part in 10,000 for short counting periods. Applications to routine analysis of alloys are cited.

## 108. PRÉVOT, ANNETTE

Detection and Determination of Rhenium by Means of X-ray Emission Spectrum.

*J. chim. phys.*, **45**, 251-257 (1948).

*C. A.*, **43**, 8304(*e*).

The sample is mounted by evaporation of a solution on a Cu anticathode and is excited by 50 kv. The radiation is analyzed photographically with a Cauchois spectrograph and a curve mica crystal. With pure  $KReO_4$  it is possible to detect 0.02  $\gamma$  Re by the  $L\alpha_1$  line. In the presence of Mo the  $L\beta_1$  line is preferred and can detect 0.5  $\gamma$  Re with 10 mg  $MoO_3$  present.

## 109. ALEXANDER, LEROY, KUMMER, ELIZABETH, AND KLUG, HAROLD P.

Dead Time and Nonlinearity Characteristics of the Geiger-Counter X-ray Spectrometer.

*J. Applied Phys.*, **20**, 735-740 (1949).

*C. A.*, **43**, 8852(*g*).

The satisfactory use of Geiger-counter methods for the measurement of diffracted X-ray intensities demands that the observed counting rates be corrected for the nonlinear response of the counter. Both the multiple-foil method of calibrating the nonlinearity of response and the two-source method of Beers for measuring counter dead time have been found to be unsatisfactory; but electronically controlled oscillographic techniques for the direct measurement of dead time are much more satisfactory. With a knowledge of the dead time,  $\tau$ , the true counting rate,  $\bar{N}$ , can be calculated from the observed counting rate,  $N_0$ , by employing the formula  $\bar{N} = N_0 / (1 - N_0\tau)$ . For a pulsating X-ray source the effective counting rate is faster than the observed by a factor which is characteristic of the type of rectification employed, the target material, and the voltage applied to the X-ray tube. This factor can be obtained by oscillographic observation of the pulse pattern and in some cases by mathematical analysis.

## 110. HANNA, G. C., KIRKWOOD, D. H. W., AND PONTECORVO, B.

High-Multiplication Proportional Counters for Energy Measurements.

*Phys. Rev.*, **75**, 985-986 (1949).

*Cf. C. A.*, **42**, 8071(*h*) and preceding abstracts and 2nd following abstract.

*C. A.*, **43**, 6076(*b*).

The characteristics and performance of counters suitable for electron energies of 200-50,000 ev are described.

- 111. MARMIER, P., BLASER, J. P., PREISWERK, P., AND SCHERRER, P.**

Spectroscopic Measurements of X-rays from Radio-Elements.

*Helv. Phys. Acta*, **22**, 155-163 (1949).

*Cf. C. A.*, **42**, 8268(*h*).

*C. A.*, **43**, 6908(*i*).

A curved-crystal X-ray spectrometer of the Cauchois type was designed and constructed. Special consideration was given to intensity problems where strong perturbing radiation also occurs. Either film or a Geiger counter can be used as the detector. For 50-min Tc, the following X-ray wavelengths were obtained, in good agreement with other investigators (Burkhart et al, *C. A.*, **42**, 2513(*b*));  $K\alpha_2$ , 677.9;  $K\alpha_1$ , 673.4;  $K\beta_1$ , 600 X units.

- 112. MORTON, G. A. AND MITCHELL, J. A.**

Motion of 931-A Type Multiplier As a Scintillation Counter.

*Nucleonics*, **4**, No. 1, 16-23 (1949).

*Cf. C. A.*, **43**, 4111(*f*).

(*RCA Rev.* 10, 164 Dec. 1949).

*C. A.*, **43**, 6076(*f*).

The 931-A type of multiplier is by its construction not very well suited for use in a scintillation detector but with proper care a good one can be designed to use it. Curves are given for dark-current pulse distribution and the effect of temperature, shield potentials, and cathode dynode voltage.

- 113. MORTON, G. A. AND ROBINSON, K. W.**

A Coincidence Scintillation Counter.

*Nucleonics*, **4**, No. 2, 25-29 (1949).

*C. A.*, **43**, 4111(*f*).

A differential coincidence circuit utilizing 1 N34 crystals is used in conjunction with a pair of electron photomultiplier tubes. Anthracene and thallium-activated alkali iodides are used as phosphors. KI yielded an efficiency of 10%. A low background counting rate is reported.

- 114. BIRKS, L. S., BROOKS, E. J., FRIEDMAN, HERBERT, AND ROE, R. M.**

X-ray Fluorescence Analysis of Ethyl Fluid in Aviation Gasoline.

*Anal. Chem.*, **22**, 1258-1261 (1950).

*C. A.*, **45**, 3585(*d*).

The X-ray fluorescence apparatus of Friedman and Birks (cf. *C. A.*, **42**, 6649(*c*)) was used for the simultaneous determination of Pb and Br in aviation gasoline, with the advantage that cell depth has no influence on the results providing a minimum depth is exceeded. By monitoring the primary X-ray beam wide fluctuations in its intensity are made allowable without affecting the accuracy of the results. The X-ray lines which are utilized are the  $L\alpha$  of Pb at 1.17 Å and the  $K\alpha$  of Br at 1.04 Å. The determination of both Pb and Br becomes possible if both lines are measured and their relative intensities are referred to a series of calibration curves based on different ratios of the two elements.

The instrument can be modified to accommodate several samples simultaneously. The presence of S does not interfere with the fluorescence analysis in the spectral region chosen. This method may be adapted to semiautomatic plant-control problems.

- 115. BLOKHIN, M. A.**

X-ray Spectral Analysis by Means of the Secondary Spectrum. I.—An X-ray, Short Wavelength, Fluorescence Spectrograph.

*Zavodskaya Lab.*, **16**, 681-687 (1950).

*C. A.*, **49**, 12177(*d*).

A spectrograph is described which uses the secondary spectrum (X-ray fluorescence) for determining the presence of many elements in ores, minerals, alloys, etc. The determination can be done very rapidly and small quantities can be determined quite accurately (for presence of 0.1% Cu, error is approximately 3% and time required for determination is only 10-15 min). II. Long wavelength X-ray fluorescence spectrograph. *Ibid.*, 941-948. A spectrograph is described for the quantitative determination of the elements S ( $Z=16$ ) through Ni ( $Z=28$ ) by the  $K$  series and from Mo ( $Z=42$ ) to Lu ( $Z=71$ ) by the  $L$  series by the X-ray fluorescence method. The spectrum is not photographed but registered by means of a counter for the radiation.

## 1951

- 116. BIRKS, L. S.**

Apparatus for Vacuum X-ray Fluorescence Analysis of Light Elements.

*Rev. Sci. Instr.*, **22**, 891-1004 (1951).

*C. A.*, **46**, 6029(*i*).

An apparatus is described adaptable to X-ray fluorescence analysis of the elements from Mg to Ti. Because of adsorption by air of the longer X-rays (3.5-10 Å), an evacuated system or an atmosphere of  $H_2$  or He was used. The evolved radiation was analyzed in a standard, single-crystal, Geiger-counter spectrometer. However, the usual mica window, opaque to radiation of wavelengths greater than 5.36 Å, was replaced by a pressurized double nitrocellulose film. A typical quantitative analysis of S in light oil is discussed and a calibration curve given.

- 117. BIRKS, L. S. AND BROOKS, E. J.**

Analysis of Uranium Solutions by X-ray Fluorescence.

*Anal. Chem.*, **23**, 707-709 (1951).

*C. A.*, **45**, 7915(*f*).

U nitrate solutions (aq) were analyzed for U content by first evaporating 1 ml of the solution in a shallow Al dish heated electrically to about 100° F. The X-ray fluorescence of the dried salt was measured by using the  $L\alpha$  line. Standards were prepared and measured in the same way. The presence of other elements had no

interference except Pb when it exceeded 10% of the U concentration. As little as 0.05 g per liter of U could be detected with an accuracy of 5% of the amount present at 1 g per liter concentration.

**118. DEM'YANINOV, I. G.**

Application of an Aluminum Wedge to Quantitative X-ray Analysis with a Spectrograph Having a Bent Crystal.

*Izvest. Akad. Nauk SSSR (Ser. Fiz.)*, **15**, 239-242 (1951).

*C. A.*, **45**, 8875(e).

An Al wedge can be used for quantitative analysis with X-rays. Mixtures of Zr and Y oxides were analyzed; the measurements indicate the ratios of the elements and are independent of the absolute content. To effect the analysis for a certain element a spectrogram is taken to detect the presence of other elements. One element is selected for comparison and 3 different mixtures are photographed to plot the dependence of  $\log P_2/P_1$  on  $l = (l_2 - l_1)$  ( $l$  = line length,  $P$  = intensity). Such analysis does not require photometry of the plates.

**119. EHRENBERG, W. AND SPEAR, W. E.**

An Electrostatic Focusing System and Its Application to a Fine-Focus X-ray Tube.

*Proc. Phys. Soc.*, **64B**, 67-75 (1951).

*C. A.*, **46**, 7872(a).

Description of an electrostatic focusing system by which electrons emitted from the tip of a hairpin filament are reunited at a distance of 2 to 3 cm. No intermediate potentials are required. The electron spot has a diameter of about 40  $\mu$ . A fine-focus X-ray tube is designed, with a peak specific target loading of about 11 kw per sq mm.

**120. WEST, H. I., JR., MEYERHOF, W. E., AND HOFSTADTER, R.**

Detection of X-rays by Means of NaI(Tl) Scintillation Counters.

*Physic Rev.*, **81**, 141-142 (1951).

Cf. Hofstadter and McIntyre, *Nucleonics*, **7**, No. 3, 32 (1950).

*C. A.*, **45**, 2306(b).

With NaI(Tl) crystals with uncooled RCA 5819 photomultiplier tubes, individual X-ray quanta were detected in the range of 5-80 ekv with an efficiency of near 100%. X-rays of 2 ekv, were detected with an efficiency of 50-80%. Results were given for X-rays of 2-411 ekv.

**1952**

**121. BREWSTER, GORDON F.**

Calculated X-ray Mass Absorption Coefficients of Glass Components.

*J. Am. Ceram. Soc.*, **35**, 194-197 (1952).

*C. A.*, **46**, 9272(f).

Victoreen (*C. A.*, **37**, 1927<sup>3</sup>; **44**, 1795(b)) published a method of calculating empirically the mass absorption coefficients of all ele-

ments (atomic numbers 1-96) from short wavelengths to their characteristic  $K$  absorption edges. Sun and Sun (*C. A.*, **43**, 2091(d)) showed that the mass absorption coefficients of a compound is a summation of weight fractions of all component elements times their corresponding mass absorption coefficients. But since glass components are usually expressed in terms of oxides, it would be more convenient to calculate mass absorption coefficients, and consequently X-ray absorption, from mass absorption coefficients of the component oxides. Therefore the mass absorption coefficients of oxides used in glassmaking were calculated for wavelengths from 0.010  $\text{\AA}$  to those of the  $K$  absorption edges, and are given in convenient tables. The oxides included are:  $\text{Li}_2\text{O}$ ,  $\text{BeO}$ ,  $\text{B}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{GeO}_2$ ,  $\text{As}_2\text{O}_3$ ,  $\text{SrO}$ ,  $\text{ZrO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{MoO}_3$ ,  $\text{CdO}$ ,  $\text{Sb}_2\text{I}_3$ ,  $\text{BaO}$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{WO}_3$ ,  $\text{PbO}$ ,  $\text{Bi}_2\text{O}_3$ , and  $\text{ThO}_2$ .

**122. BRISSEY, RUBEN M.**

Attainment of High Resolution in X-ray Fluorescent Analysis. Simplification of X-ray Fluorescent Analysis Procedures.

*Anal. Chem.*, **24**, 1034-1035 (1952).

*C. A.*, **46**, 9011(e).

Measurements can be made at the angle of maximum intensity for the La lines of Ta and W without interference from second-order  $K\alpha$  radiation of Nb when a bent mica diffracting crystal is used with a GE XRD-3 Fluorescent Analyzer. Excellent resolution is obtained in analyzing mixtures of Mo, Nb, Ta, and W.

**123. DESPUJOLS, JACQUES**

Application de la Spectrométrie des Rayons X au Dosage de Faibles Teneurs de Métaux dans les Minerais.

Measurement of Small Metal Content in Ores with an X-ray Spectrometer.

*J. phys. radium*, **13**, (Suppl. to No. 2), 31A-41A (1952).

*C. A.*, **46**, 6548(e).

A curved crystal spectrometer is used to determine the metals present in ore samples. Of the 3 methods tried, emission spectrometry with fluorescence excitation gave the best results for determining Zn with a precision of 5-10% for about 1% present in the ore. The presence of Pb can be determined if 1.2% is present. The methods of cathodic emission and differential absorption were also tried. In the later method a comparison is made between the Geiger-counter intensities recorded by 2 samples of different thickness. Zn is detected when more than 2% is present. The method of fluorescence analysis is shown to require the simplest apparatus setup and is the quickest and easiest to perform.

**124. GILLAM, E. AND HEAL, H. T.**

Some Problems in the Analysis of Steels by X-ray Fluorescence.

*Brit. J. Appl. Phys.*, **3**, 353-358 (1952).

*C. A.*, **47**, 2085(b).

By placing a specimen in a strong X-ray beam chosen so that each element in the specimen is excited and emits its own characteristic spectrum, the proportion of elements of atomic number higher than 20 in steels may be measured. The method was studied with a Geiger-counter spectrometer, primarily with the object of determining the suitability of the fluorescence technique as a rapid means of analysis during the steel-making process, especially for high alloy steels. Apparatus similar to that of Friedman and Birks (cf. *C. A.*, **42**, 6649(c)) with addition of a monitoring system to compensate for fluctuations in X-ray tube output is described. A Co target operated at 50 kv and 10 ma was used. From measurements on Fe-Cr-Ni steels, it appears that unless a very powerful X-ray tube is used, the method gives quick results of high accuracy only when more than 10% of the alloying element is present. It is also shown that in some cases standard diagrams would have to be drawn to allow for "mutual fluorescence." An appendix gives the theory of X-ray fluorescence analysis.

**125. HERGLOTZ, H.**

A Röntgen Tube with Transparent Anode for Secondary Excitation of Röntgen Spectra. *Osterr. Ing.-Arch.*, **6**, 135-140 (1952). *C. A.*, **46**, 8512(h).

Because the excitation of Röntgen spectra usually requires placing the substances in the high vacuum of the Röntgen tube, the investigation of substances with high vapor pressure is automatically excluded. The characteristic spectra of such substances can be excited in air outside the tube by using the Al window of the tube as an anode and bringing this as close as possible to the sample. Details for constructing and operating such a Röntgen tube are given, and its application to the excitation of fluorescence is demonstrated with various substances.

**126. KOH, P. K. AND CAUGHERTY, BETTY**

Metallurgical Applications of X-ray Fluorescent Analysis. *J. Applied Phys.*, **23**, 427-433 (1952). *C. A.*, **46**, 6568(f).

Techniques are described for fluorescent analysis by means of an X-ray Geiger counter goniometer. The effects of potential variations, specimen preparation and thickness of the diffracting crystal are considered. Intensities of fluorescent spectra were measured on constituents of Fe-Ni, Fe-Cr, and Fe-Ni-Cr alloys. Calibration curves correlating line intensity with weight percentage are included for binary Fe-Ni and Fe-Cr alloys. The thickness beyond which the fluorescent intensity becomes constant was determined for pure Fe, Ni, and Cr. Up to this thickness an empirical plot of fluorescent intensity against thickness of layer was established; these can be applied to measure the thickness of very thin coatings. The fluorescent analytical technique is applied to the study of

oxidation and diffusion processes in metallic systems. An Al holder is used for analyzing small quantities of powder derived from chemical or electrolytic extn. of certain phases from alloys. Fluorescent analysis on the extracted phase supplements the diffraction data when a wide solid-solidity exists.

**127. KOH, P. K., CAUGHERTY, B., AND BURKET, R. E.**

Intensity Calculation for Determining Weight Percentage in a Binary Alloy by X-ray Fluorescent Analysis.

*J. Applied Phys.*, **23**, 698 (1952).

Cf. *C. A.*, **46**, 6568(f).

*C. A.*, **46**, 7871(i).

When a binary alloy consisting of 2 neighboring elements in the periodic table is to be analyzed by X-ray fluorescence, the effect of mutual excitation, absorption edge, and difference in absorption becomes insignificant so that a simple calculation gives weight percentages of the alloying elements.

**128. MORTIMORE, D. M. AND ROMANS, P. A.**

X-ray Spectroscopy as a Control Method in the Production of Zirconium and Hafnium. *J. Optical Soc. Am.*, **42**, 673-677 (1952).

*C. A.*, **46**, 11025(g).

An X-ray spectrographic method was developed for routine analysis of mixtures of Zr and Hf oxides in the range of concentrations from 0.5 to 99.5% Hf in Zr. The method makes use of the newly perfected X-ray fluorescence analysis equipment incorporating a Geiger tube together with associated scaling and recording circuits for measurement of intensities. A single analysis requires 5-10 min to complete, including preparation of sample and final calculations. The average per cent deviation at concentrations of 1% Hf is 3.3% and at 40% Hf about 0.5%.

**129. PATRICK, ROBERT F.**

Some Applications of the Fluorescent X-ray Spectrometer in Ceramics.

*J. Am. Ceram. Soc.*, **35**, 189-193 (1952).

*C. A.*, **46**, 9274(b).

A General Electric SPG fluorescent X-ray spectrometer was used in conjunction with the XRD-3 X-ray diffraction unit. Essential parts of the apparatus were a W X-ray tube, a sample holder with focusing beam tunnel, a mica crystal-bending mechanism, a Geiger tube with preamplifier mounted on a spectrogoniometer, and the necessary auxiliary equipment. Application is limited to detecting and measuring elements above Ti in atomic numbers. While it is useful chiefly in metallurgy, it has value in ceramic work, particularly in enamels. Among its applications are the determination of Ni plated out in Ni pickling, the determination of Co and Ni deposited on the base metal during the firing of enamel ground coats, and determining the Pb content of glaze frits. In any raw ma-

terial the amount of any element above Ti in atomic numbers can be determined; for example, Fe in pyrophyllite, or Nb in  $\text{TiO}_2$ . While it cannot replace optical spectroscopy, or X-ray diffraction analysis, it affords helpful supplementary data.

**130. SANDSTROM, ARNE ELD**

Large Bent-Crystal Vacuum Spectrograph. *Arkiv Fysik*, **4**, 517-534 (1952) (in English). *C. A.*, **46**, 8512(f).

A new, large, bent-crystal X-ray vacuum spectrograph is described and illustrated in detail. The instrument, based on experience gained on older types, is capable of (1) high resolution, (2) adaptation to recording of small intensities, (3) operation in high vacuum, making it especially useful for long wavelengths, and (4) covering most of the wavelength region from 3500 X-unit (calcite) to 19,600 X-unit (mica).

**131. SHAW, C. H.**

Chemical Analysis by X-rays. *Ohio J. Sci.*, **52**, 134-145 (1952). *C. A.*, **46**, 8512(i).

The analysis of a sample in terms of the elements present is described by using both emission and absorption. Analysis for compounds, by measurement of lattice parameters is also described. Various available instruments for these analyses are suggested.

**132. TOURNAY, MADELEINE**

Determination of the Relation Between the Atomic Concentrations of Thorium and Uranium in Minerals by X-ray Spectrography.

*Compt. rend.*, **234**, 2527-2529 (1952). *C. R. Acad. Sci.*, **234.26**, 2527 (1952). *C. A.*, **46**, 9014(c).

The two lines  $UL\beta_2$  ( $\lambda = 75314$  X unit) and  $Th L\beta_1$  ( $\lambda = 76363$  X unit) were used as analysis lines without the addition of any internal standard. The samples of 2-3 mg of  $\text{ThO}_2$  and  $\text{UO}_2$  were placed on the anticathodes and exposed to the electron beam for 5-20 min. A plot of  $\log(D_{Th}/D_U)$ , where  $D_{Th}$  and  $D_U$  are microphotometer readings for the 2 rays, against  $\log(n_{Th}/n_U)$ , ratio of atomic concentration of  $Th$  and  $U$ , was a straight line. A Cauchois type of spectrograph was used with mica lined-up on the (100) plane. The limit of detection was at  $n_{Th}/n_U = 0.01$ . The maximum relative error was 5%; in small concentration ranges the error was 1-2%. This method of analysis is applicable to thorianites, uraninites, broggerites, and cleveites.

**133. VAINSHTEIN, E. E., SHEVALEEVSKII, I. D., AND KAKHANA, M. M.**

Methodology of Quantitative X-ray Analysis. *J. Anal. Chem. (USSR)*, **7**, 403-416 (1952) (English translation) See *C. A.*, **47**, 5839(a).

*C. A.*, **48**, 4355(e).

**1953**

**134. ADELL, OVED, BROGREN, GOSTA, AND AND HAEGGBLOM, LARS ERIK**  
The X-ray Diffraction from Quartz. *Arkiv. Fysik*, **7**, 197-211 (1953). *C. A.*, **48**, 3749(h).

The Darwin (*C. A.*, **8**, 1702, 2306)-Ewald-Prins (*C. A.*, **24**, 5607) dynamic theory for the X-ray diffraction in a perfect absorbing crystal was applied to the 10 $\bar{1}0$ , 20 $\bar{2}3$ , 22 $\bar{4}3$ , and 11 $\bar{2}0$  planes in quartz. The width of the rocking curve in a two-crystal spectrometer, the percentage reflection and the double crystal coefficient of reflection were calculated and experimentally determined in the region 560-2500 X. The results show that quartz can be considered a perfect crystal, at least for certain specimens. All crystals were etched with 40% HF until spectroscopic measurements were no longer affected by etching. Some quartz planes give more intense reflections than do the most intense calcite planes with the same spacings, e.g. 10 $\bar{1}1$ , 20 $\bar{2}3$ , 30 $\bar{3}1$ , and 50 $\bar{5}2$ . Some planes have the advantage that higher-order structure factors are small compared with the 1st-order. The characteristic temperature of quartz seems to be so high that the effect of thermal vibration can be neglected. The hardness and inertness of quartz make it very durable and constant in its diffraction properties.

**135. ADLER, ISIDORE AND AXELROD, JOSEPH M**

A Multiwavelength Fluorescence Spectrometer.

*J. Opt. Soc. Amer.*, **43**, 769-772 (1953). *C. A.*, **48**, 39(d).

A basic multiwavelength X-ray fluorescence spectrometer has been designed and a two-goniometer prototype built. The instrument is of the dispersive type, with separate crystals, Geiger-Müller detectors, and counting circuits. The system, by providing for the simultaneous determination of more than one element, results in economy of testing time and in improved precision. Finally, an application to one type of ore analysis is described.

**136. BIRKS, J. B.**

Scintillation Counters, McGraw-Hill Book Co., Inc., New York, N. Y., 156 pages (1953).

*C. A.*, **48**, 9207(f).

**137. BIRKS, L. S., BROOKS, E. J., AND FRIEDMAN, H.**

Fluorescent X-ray Spectroscopy. *Anal. Chem.*, **25**, 692-697 (1953). *C. A.*, **47**, 11964(g).

Instrumentation is reviewed, and typical quantity applications are cited for determination of compositions of alloys, for Fe in blood, for S in oil, for Pb and Br in gasoline, and for platings on metals.

## 138. BRISSEY, R. M. AND CHASE, G. A.

X-ray Fluoroscopy Analyzer Alloys.  
*Amer. Machinist*, 132, April 27 (1953).

Very elementary paper, no interest designed for working group of machinists.

## 139. BROGREN, GOSTA

The Possibility of Using Ground Calcite Crystals as X-ray Gratings.

*Arkiv Fysik*, 6, 479-490 (1953) (*in English*); cf. Aminoff, *C. A.*, 40, 4333<sup>b</sup>.

*C. A.*, 47, 9762(*e*).

The possibility of grinding calcite to get faces parallel to suitable at planes and obtain a crystal grating is pointed out. Methods for calculating crystal structure factor,  $F$ , and integrated reflection,  $R$ , are described, and calculated values are given of the spacing and of  $F$  of a number of planes in calcite arbitrarily chosen, which seem usable in X-ray spectroscopy. These planes are not found in natural surfaces but can be obtained by first grinding surfaces parallel to the desired plane, sawing out the plate, and carefully polishing the surface. A series of such crystal plates were prepared with surfaces parallel to the planes (211), (310), (655), (741), and (1033), and their quality was tested. To obtain accurate values of the axis lengths, the spacing of planes (655) and (1033) was determined with an instrument and by a method described earlier (Larson, *C. A.*, 21, 2606). Results are given in tables. The lengths of the axes of the primitive hexagonal cell were obtained from these spacings and the spacing of plane (211) as  $a = 4980.02 \pm 0.03$  X unit and  $c = 17025.12 \pm 0.10$  X unit. By assuming that calcite is a perfect crystal, the per cent reflection,  $P$ , the double-crystal coefficient of reflection,  $R$ , and the width of the rocking curve,  $w$ , can be calculated. The crystal plates were etched with 0.7N HCl until constant values of  $P$ ,  $R$ , and  $w$  were obtained. An etching time of 5 sec proved sufficient in all cases. Calculated and observed values of  $P$ ,  $R$ , and  $w$  are compared. Agreement between values of  $R$  is very good. Experimental values of  $w$  at half maximum intensities are always greater than those calculated but the experimental values of  $P$  are less. The quantities  $R$ ,  $P$ , and  $w$  were determined previously (Parratt, *C. A.*, 30, 2103<sup>b</sup>). A comparison with his results shows very good agreement, indicating that the sawing and polishing influence only a very thin surface layer. When this is removed by etching with HCl a crystal grating is obtained, the qualities of which are in good agreement with what is predicted by the theory of perfect crystals. The crystal can be used in X-ray spectroscopy to determine wavelengths by the method of Kossel (*C. A.*, 30, 7028<sup>b</sup>).

## 140. BROGREN, GOSTA AND ADELL, OVED

The Transmission and Absorption of X-rays in Calcite Near the Bragg Angle.

*Arkiv. Fysik*, 7, 1-5 (1953) (*in English*).  
*C. A.*, 47, 9762(*a*).

When X-rays are transmitted through a perfect crystal in the direction of the incident beam at a position where Laue diffraction occurs, anomalous intensities are obtained. This effect is investigated in calcite in the region 700-1800 X unit with a 2-crystal spectrometer (*C. A.*, 46, 2903(*h*)) provided with 2 Geiger-Müller counters so that both the transmitted and the Laue-diffracted intensities could be registered simultaneously. Experimental results are given as 10 curves, counts per min as a function of  $\phi$ , the angle between the incident X-radiation and the reflecting atomic plane, in the region of about one degree around the Bragg angle  $\phi_B$ . Curves are plotted for both  $R_T$ , the intensity of the transmitted radiation, and  $R_L$ , that of the Laue diffracted radiation, for wavelengths corresponding to the characteristic X-ray lines, Mo  $K\alpha_1$ , Au  $L\beta_1$ , Au  $L\alpha_1$ , Cu  $K\alpha_1$ , and Co  $K\alpha_1$ . From the curves the observations are made: (1) Anomalous absorption appears only within a very small region about  $\phi_B$ . (2) the transmission curve is asymmetric in all cases. The region of anomalous transmission is wider below than above  $\phi_B$ . (3) If  $R_T$  and  $R_L$  are added there remains a region where  $R_T + R_L$  is less than the normally transmitted intensity in all cases where there is a minimum in  $R_T$ . (4) The angular distance between  $R_T$  and  $R_L$  decreases with increased wavelength. (5) All rocking curves in the transmission (Laue) case are asymmetrical. As the reflection plane (121) cuts the surface at an angle of 75 deg, the paths of the 2 X-ray beams are not the same and  $R_T$  and  $R_L$  are not directly comparable. Therefore no absorption coefficients and no values of the integrated reflection are calculated. Shapes of the curves are, in general, in good agreement with theoretical calculations (*C. A.*, Hirsch, 46, 7872(*e*), 6929(*i*)).

## 141. BROGREN, GOSTA AND HAEGGBLOM, LARS ERIK

Some Atomic Planes in Quartz Suitable as Lattices in X-ray Spectroscopy.

*Arkiv Fysik*, 6, 171-176 (1953) (*in English*).  
*C. A.*, 47, 6247(*b*).

Earlier work by Brogren (*C. A.*, 43, 7816(*f*)) on the use of quartz as a crystal grating in a Sieghahn-type X-ray spectrometer (*C. A.*, 21, 2606<sup>b</sup>) is extended. Measurements of the angle of diffraction of Zn  $K\alpha_1$ , Cu  $K\alpha_1$ , and Mo  $K\alpha_1$  characteristic X-rays by the quartz lattice planes (1122), (2023), (3031), and (2243) are reported with a maximum error of 1 sec (corresponding to 0.02 X unit). The crystal plates were cut parallel to the diffracting planes and bent to effect a great increase in intensity under focusing conditions.

## 142. BROOKER, T.

X-ray Spectrograph for Rapid Elemental Analysis.

*Canadian Chemical Processing*, 105, Oct. 1953.

A general introduction to the laymen, no theory or technique described.

**143. HÄMOS, L., VON**

X-ray Microanalyzer Camera.  
*Trans. Roy. Inst. Technol.*, (Stockholm),  
**68**, 3-67 (1953) (*in English*).  
*C. A.*, **48**, 1140(*h, i*).

X-ray image spectroscopy is based on the property of cylindrically bent crystals of producing monochromatic images from layers emitting X-rays. The theory and instrumentation of the method are described. Thicknesses of surface layers between 0.2  $\mu$  and 3  $\mu$  thick can be determined. Microanalysis of very small volumes of alloys can be carried out. Point-by-point analysis of surfaces can also be performed. 37 ref.

**144. KOKOTAILO, G. T. AND DAMON, G. F.**

Determination of Bromine in Liquids by X-ray fluorescent Spectroscopy.  
*Anal. Chem.*, **25**, 1185-1187 (1953).  
*C. A.*, **47**, 12118(*i*).

Br in liquid hydrocarbons was determined in 15 min with an accuracy of  $\pm 0.01\%$  in the 0 to 0.4% range. Sc (Et selenide in benzene and decane) was used as an internal standard to correct for errors due to impurities such as Fe and S. For a given weight per cent of Br, the intensity of the characteristic radiation increases slightly with increasing density of the base stock. Correction for varying densities was made by preparing a family of calibration curves ( $I_{B-K\alpha}/I_{ScK\alpha}$  versus weight % Br) for densities varying from 0.70 to 0.92.

**145. MORLET, J.**

X-ray Spectrograph for the Range 2 to 20  $\text{\AA}$ ;  
 L-emission spectra in the range 9 to 14  $\text{\AA}$ .  
*Bull. classe sci., Acad. roy. Belg.*, **39**, 205-216 (1953) (*in French*).  
*C. A.*, **47**, 9763(*g*).

A vacuum spectrograph with velocity selection of the exciting electron beam makes it possible to study X-ray emission spectra with wavelengths up to 20  $\text{\AA}$ . L-series spectra for Zn and Cu are presented. The effects of alloying on the spectra are discussed.

**146. ROWLAND, ROBERT E.**

Analysis of Fluorescent X-radiation by Means of Proportional Counters.  
*J. Appl. Phys.*, **24**, 811-812 (1953).  
*C. A.*, **47**, 11964(*h*).

A Be-window proportional counter is used to detect fluorescent radiation, which must be collimated without allowing the detector to see extraneous fluorescent material. The counter evaluates the energy and hence the source of spurious X-rays.

**147. VAJNSHTEIN, E. E. AND TURANSKAYA, N. V.**

Methodology of Quantitative X-ray Analysis. II.

*Zhur. Anal. Khim.*, **8**, 346-352 (1953); cf.  
*C. A.*, **47**, 5839(*a*); **48**, 1799(*g*).  
*C. A.*, **48**, 5712(*d*).

Previously outlined X-ray methods are applied to rare earths. The sum of rare earths or the absolute content of one of them in a sample is obtained by any of known methods, and the content of others in the sample is calculated from  $A_i = n_i A_0$  where  $A_i$  is the content of the sought element,  $n_i$  is a coefficient characterizing the relative composition of the sample, and  $A_0$  is the content of the element used for comparison. If the sum of rare earths in the sample ( $S$ ) is known, individual calculation can be made from  $A_i = n_i S/i = 13$ .

$\Sigma n_i$ . Two cases for experimental determination of  $n_i$  are discussed:  $i=0$  when the analyzed sample contains all the elements of the rare earths group and possibly elements of the subgroups in appreciable quantities and when the analyzed sample contains only some of the rare earths. In the first case, the width of spectral line method is used and  $n_i$  is obtained from the intensities ratio of 2 lines. In the 2nd case, it is preferable to use the previously discussed transformation of the darkening function. Details of calculations are given.

**1954****148. ADLER, ISIDORE AND AXELROD, J. M.**

Aluminum Powder as a Binder in Sample Preparation for X-ray Spectrometry.  
*Anal. Chem.*, **26**, 931-932 (1954).  
*C. A.*, **48**, 10476(*i*).

The sample is ground with an equal amount of Al powder and briquetted at 30,000 psi. Nb in  $Fe_2O_3$  matrix shows intensity loss no greater than 10%. Homogeneity tests show no differences greater than 1.3% for two sides of one briquet. The technique provides ease of mixing, storing, and incorporation of internal standard, as well as adequate reproducibility and nonhydroscopicity of the preparation.

**149. BEATTIE, H. J. AND BRISSEY, R. M.**

Calibration Method for X-ray Fluorescence Spectrometry.  
*Anal. Chem.*, **26**, 980-983 (1954).  
*C. A.*, **48**, 11915(*d*).

If it were not for absorption effects, the fluorescent X-ray intensity due to an element in an alloy would be proportional to the atomic density of that element. A 1st-order linear correction for the absorption effects of the elements in an alloy on fluorescent X-ray intensities is developed empirically. The best solutions are obtained by distinguishing the most abundant element in the alloy and dividing throughout by the unknown representing the relative weight of the abundant element so as to reduce the effective number of unknowns by one. For a quaternary alloy, the result is 4 equations in 3 unknowns, each equation containing a constant term. In the simultaneous equations,

the unknowns represent composition, the diagonal coefficients are determined by intensity measurements on the unknown alloy, and pure elements and the nondiagonal coefficients are calculated from intensity measurements on analyzed binary alloys. The calculating procedure is described and values agree to  $\pm 5\%$  of those obtained by chemical analysis.

150. BRENTANO, J. C. M. AND LADANY, I.  
Scintillation Counting of Low-energy Photons and Its Use in X-ray Diffraction.  
*Rev. Sci. Instr.*, **25**, 1028-1029 (1954).  
*C. A.*, **49**, 12119(*h*).

The basic conditions under which scintillation counting of X-ray photons may be carried out are discussed. Among the factors that interfere are radioactive contamination and thermal electron emission from the photomultiplier cathode. Methods for minimizing these difficulties are presented.

151. BRISSEY, R. M., LIEBHAFSKY, H. A., AND PFEIFFER, H. G.  
Examination of Metallic Materials by X-ray Emission Spectrography.  
Symposium on Fluorescent X-ray Spectrographic Analysis, 43-56 (1954).  
(Issued as separate technical publication *ASTM STP. No. 157.*)  
*C. A.*, **48**, 9258(*a*).  
A review with 19 references.

152. BROGREN, GOSTA  
Relation Between the Width of an X-ray Line and the Resolving Power of the Double-Crystal Spectrometer.  
*Phys. Rev.*, **96**, 589 (1954).  
*C. A.*, **49**, 2861(*h*).

The widths of some  $K\alpha_1$  lines were measured in a double-crystal spectrometer in the (1, +1) position. It was found that the difference between the experimental width of the line and the width of the rocking curve had a constant value when perfect crystal gratings were used.

153. BROGREN, GOSTA  
Bromine-Quenched and Iodine-Quenched Geiger-Muller Counters.  
*Arkiv. Fysik*, **9**, 101-105 (1954) (*in English*);  
cf. Present, *C. A.*, **41**, 7243 (*c*); Liebson,  
*C. A.*, **42**, 6643(*g*).  
*C. A.*, **49**, 8707(*i*).

Br and I vapors were investigated as quenching agents in Geiger-Muller counters filled with Ne, A, Kr, and Xe. In a Br-Kr counter the best results were obtained with about 0.2 mm Br. Results are compared with those for normal Kr-alcohol counters. Threshold voltages of Kr counters mixed with various quenchers follow: 10 mm methylal, 1350 v; 0.2 mm Br, 1140 v; and 0.2 mm I, 640 v. Argon-iodine counters had a threshold voltage of 550 v; Ne-I, 390 v; Xe-I, 1150 v. Overvoltages with I-quenched counters caused multiple pulses to appear, but

did not destroy the counters; continuous counting for longer periods did not influence the counters greatly. When tested with a potential reversing flip-flop circuit (schematically illustrated), I-quenched A and Kr counters worked with the circuit, as did Br- and org. vapor-quenched counters, but multiple pulses appeared about 30 v over the threshold voltage. It is concluded that Br is to be preferred as quenching gas in connection with rare gases since it gives fewer multiple pulses than I-quenched counters. The multiple pulses may be kept as low as possible by working at voltages rather near the threshold of the counter mixture.

154. CAMPBELL, WM. J. AND CARL, HOWARD F.  
Quantitative Analysis of Niobium and Tantalum in Ores by Fluorescent X-ray Spectroscopy.  
*Anal. Chem.*, **26**, 800-805 (1954).

Author's abstract.—The application of fluorescent X-ray spectroscopy to the analysis of niobium (columbium) and of tantalum in their ores was undertaken to provide a rapid yet accurate method for the determination of both of these elements. Three techniques are described: the first is the determination of the niobium-tantalum ratios in oxides chemically separated from ores. The second method consists of several applications of internal standard techniques and the third method is essentially an additive technique. The accuracy of the final results of these methods is believed to be superior to existing chemical methods. Between ten and fifty samples per day can be analyzed, depending on the type of material.

155. CARL, HOWARD F. AND CAMPBELL, WM. J.  
Fluorescent X-ray Spectrographic Analysis of Minerals.  
Symposium on Fluorescent X-ray Spectrographic Analysis, 63-68 (1954).  
Issued as separate technical publication *ASTM STP No. 157.*  
*C. A.*, **48**, 9258(*b*).

Minerals are grouped according to their complexity. Analyses for each group are illustrated by examples chosen for difficulty of analysis by conventional methods.

156. CLARK, G. L. AND TERFORD, H. C.  
X-ray Analysis of Foundry Dusts for Quartz and Iron in Relation to Silicosis and Siderosis. II. Fluorescent Spectral Analysis for Iron.  
*Anal. Chem.*, **26**, 1416 (1954).  
*C. A.*, **49**, 2952(*i*).

The fluorescent spectral analysis for Fe in the dusts described is proved to be far more reliable and convenient than chemical analyses. Powdered Ni is used as an internal standard and the ratio of intensities of Fe  $K\alpha$  to Ni  $K\alpha$  gives a linear calibration curve against percentage Fe. This amount varies from 19.36 to 1.20%.

- 157. DAVIS, ELWIN N. AND VAN NORDSTRAND, ROBERT A.**  
Determination of Barium, Calcium, and Zinc in Lubricating Oils—Use of Fluorescent X-ray Spectroscopy.  
*Anal. Chem.*, **26**, 973–977 (1954).  
*C. A.*, **48**, 13525(e).  
X-ray spectroscopy of liquid samples by using a He path provides a rapid analysis for Ba and Ca above 0.05% and for Zn above 0.005% with 2% accuracy. Interferences due to absorption by other elements in the sample are described.
- 158. DYROFF, G. V. AND SKIBA, PAUL**  
Determination of Trace Amounts of Iron, Nickel, and Vanadium on Catalysts by Fluorescent X-ray Spectrography.  
*Anal. Chem.*, **26**, 1774–1778 (1954).  
*C. A.*, **49**, 2938(f).  
A rapid, highly precise method for determining traces of Fe, Ni, and V makes use of analyzing the fluorescent X-ray spectra of the solid sample.
- 159. FINE, S. AND HENDEE, C. F.**  
Instability in Methylal-Quenched X-ray Detectors.  
*Rev. Sci. Instr.*, **25**, 830 (1954).  
*C. A.*, **49**, 52(d).  
Methylal-quenched counting tubes exhibit high current sensitivity, low intensity-voltage slope, and linearity over a wide intensity range. Intermittent violent current fluctuations and photosensitivity are eliminated by sparking the tube shell in Br vapor and by adding trace amounts of  $\text{CH}_2\text{Br}_2$  to the gas filling, respectively.
- 160. FRIEDMAN, H., BIRKS, L. S., AND BROOKS, E. J.**  
Basic Theory and Fundamentals of Fluorescent X-ray Spectrographic Analysis. Symposium on Fluorescent X-ray Spectrographic Analysis, 3–26 (1954).  
(Issued as separate technical publication *ASTM STP No. 157*.)  
*C. A.*, **48**, 9257(h).  
A review with 11 references.
- 161. HASLER, M. F. AND KEMP, J. W.**  
Use of Multichannel Recording in X-ray Fluorescent Analysis. Symposium on Fluorescent X-ray Spectrographic Analysis, 34–42 (1954).  
(Issued as separate technical publication *ASTM STP No. 157*.)  
*C. A.*, **48**, 9257(i).  
The application of multichannel recording to nondispersive X-ray instruments is described and shown to lead to improved speed and accuracy.
- 162. HENDEE, C. H. AND FINE, S.**  
Moseley's Law Applied to Proportional-Counter Resolution of Adjacent Elements.  
*Phys. Rev.*, **95**, 281–282 (1954).  
*C. A.*, **48**, 9808(a).  
The proportional counter can be used in some applications as an X-ray spectrometer in a non-dispersive system. The energy resolution and its variation with energy are examined. It was found that (a) the half-width of the pulse-height distribution produced by the characteristic radiation of an element is approximately proportional to the atomic number of the element. The percentage half-width, therefore, is a means of identifying elements, provided the half-width for a known energy has been determined. (b) The ability of a proportional counter to resolve characteristic X-radiations of adjacent elements is approximately constant over the elements. The use of the proportional counter for the identification of elements is also contingent on the absorption properties of the gas-filling, the window, and the source X-ray intensity.
- 163. HERGLOTZ, H.**  
X-ray Analysis of the Elements Titanium to Zinc.  
*Radex Rundschau*, **1954**, 194–202 (1954).  
*C. A.*, **49**, 5961(f).  
An X-ray tube with thin target was used on conjunction with a simple but nonrevolving back-reflection camera built on the principle of Regler's ring film camera (cf. *Z. tech. Phys.*, **24**, 291 (1943)).
- 164. LIEBHAFSKY, HERMAN A.**  
X-ray Absorption and Emission.  
*Anal. Chem.*, **26**, 26–31 (1954).  
*C. A.*, **48**, 3186(c).  
Annual Review.
- 165. MARIEE, M.**  
Analysis of Steel by Fluorescence of X-rays.  
*C. A.*, **50**, No. **22**, 11–25–56; *Compt. rend., 27e congr. intern. chim. ind.* (Brussels 1954), **2**; *Industrie chim. belge.*, **20**, *Spec. No.*, 423–426 (1955).  
16556(h).  
Secondary X-rays, which are emitted when the chemical elements are bombarded with radiating X-rays, were used to prepare standardization curves for Ni and Cr. The X-ray tube emitted X-rays under the load of 50 kv and 50 ma and the time ranged from 6.67 min to 13.3 min. These secondary X-rays are characteristic of the chemical elements and proportional to concentration.
- 166. MORTIMORE, D. M., ROMANS, P. A., AND TEWS, J. L.**  
X-ray Spectroscopic Determination of Niobium and Tantalum in Rare-earth Ores.  
*Appl. Spectroscopy*, **8**, No. **1**, 24–28 (1954).  
*C. A.*, **48**, 6907(d).  
A method is presented for the determination of Nb and Ta in monazite or similar ores. This method involves the use of X-ray spectroscopic

techniques employing the latest instrumentation. The intensity of the Nb and Ta spectra is calculated and related to corresponding Zr and Hf spectra as internal standards. These intensity ratios are then converted to concentration by the use of typical working curves. The lower concentration limit is 0.05% for Nb and 0.2% for Ta, and the standard deviation is approximately 5% at concentrations of 2% of either element. Single determinations can be made in 40 min.

**167. NOAKES, GORDON E.**

An Absolute Method of X-ray Fluorescence Analysis Applied to Stainless Steels.

Symposium on Fluorescent X-ray Spectrographic Analysis, 57-62 (1954).

(Issued as separate technical report *ASTM STP No. 157.*)

*C. A.*, **48**, 9258(a).

A method by which absolute analyses can be carried out by X-ray fluorescence is developed. A successful experimental check with alloys of Fe, Ni, and Cr is described.

**168. SHERMAN, J.**

Correlation Between Fluorescent X-ray Intensity and Chemical Composition.

Symposium on Fluorescent X-ray Spectrographic Analysis, 27-33 (1954).

(Issued as separate technical publication *ASTM STP No. 157.*)

*C. A.*, **48**, 9257(i).

Methods for the calibration of a Geiger counter and the correlation of fluorescent X-ray intensity with concentrations have been derived and confirmed by experiment.

**169. STEVENSON, JOHN S.**

Determination of Niobium in Ores by X-ray Fluorescence.

*Am. Mineralogist*, **39**, 436-443 (1954).

*C. A.*, **49**, 13825(g).

Spectrometer determinations with orthoclase feldspar as matrix and Mo as internal standard gave good results on pyrochlor ores in the range 0.1-2.5% Nb<sub>2</sub>O<sub>5</sub>.

**170. TOURNAY, M.**

Determination of Tungsten by X-ray Spectrography and by Colorimetry in Weakly Mineralized Metamorphosed Limestones. *C. A.*, **51**, No. **10**, 7236(g); Protectoret République Française au Maroc, Direction des productions industrielles et mines, Division mines et géologie, Service géologique. *Notes et mémoires*, No. **121**, 97-104 (1954).

The X-ray spectrographic method was used with a Ta filament and Pb as an internal standard. Precision was 10-15% in the range 0.1-1% WO<sub>3</sub>, and 20% in the range 0.05-0.1% WO<sub>3</sub>. The thiocyanate colorimetric method was used; the 2 methods gave good agreement.

**1955**

**171. P. K. BHATTACHARYYA**

Analysis of Some Indian Ores and Minerals by Bent Mica Crystal Spectrograph.

*Indian J. Phys.*, **29**, 292-295 (1955); *Sci. Abstr.*, **59A**, 358 (1956).

*Mineral. Chem., C. A.*, **51**, No. **11**, June 10, 1957, 7953(b).

A transmission-type bent mica crystal X-ray spectrograph has been constructed in which each wavelength chooses its own Bragg angle, and an X-ray spectrum from Fe to U could be taken in one setup. With the help of this instrument the presence of trace elements in some Indian ores and minerals has been studied and some new results have been obtained.

**172. BIRKS, L. S. AND BROOKS, E. J.**

Applications of Curved-Crystal X-ray Spectrometers. Microanalysis and Simultaneous Analysis.

*Anal. Chem.*, **27**, 437-440 (1955).

*C. A.*, **49**, 8636(d).

The use of a curved, reflection-type, focusing crystal for fluorescent X-ray spectroscopy for single and simultaneous analyses is described. By using a 1-mg specimen, the standard deviation for ppm of Nb, Hf, Ta, Th, and U averaged 13%. An arrangement for the simultaneous determination of Cr, Ni, and Mo in steel with 3 crystals and 3 detectors is described.

**173. BIRKS, L. S. AND BROOKS, E. J.**

Miniature Fluorescent X-ray Spectrograph.

*Anal. Chem.*, **27**, 1147-1149 (1955).

*C. A.*, **49**, 14392(e).

A simple, inexpensive spectrograph, capable of simultaneous analysis of 2 specimens, is described. Primarily qualitatively, the instrument covers the same range of elements as other X-ray spectrographs with 0.02 Å resolution.

**174. BOROVSKII, I. B.**

X-ray Spectral, Chemical Microanalysis at Separate Points in a Polished Section.

*Problemy Met. Moscow: Izdatel. Akad. Nauk. SSSR* 135-139 (1953). *Referat. Zhur., Fiz.*, No. **5803** (1955).

*C. A.*, **50**, 3145(b).

An analysis is made of the principal systems in existing X-ray spectrographs with a curved crystal. The variants which are possible in using curved crystals for increasing the intensity of the diffracted monochromatic emission are obtained by geometric construction. Attention is given to the possibility of making effective use of an "inverse" method, by which the source point of the X-rays is placed on the focal surface of the curved crystal (Rowland's circle), and the diffracted pencil of monochromatic rays passes through the crystal and is registered, for example, by an electronic multiplying machine. A metallographic polished section, at the points

where X-ray chemical analysis can be made is used as the anode of the source point of X-rays. The focal point must not measure more than 50  $\mu$ , and 5  $\mu$  is better.

- 175. CAMPBELL, WM. J. AND PARKER, JOHN G.**  
Relationship of Density to Composition in the Columbite-Tantalite Series.  
U. S. Bureau of Mines.  
*Rept. Invest. 5150*, 25 pp. (1955).  
*C. A.*, **49**, 13840(*f*).

To evaluate Cb-Ta minerals as possible ores it is necessary to determine the ratio of Cb to Ta, as well as the total amount of the 2 elements present. The series was studied by various instrumental techniques to establish the relationship of density to composition. Each sample was analyzed by fluorescent X-ray spectroscopy for Fe, Mn, Cb, and Ta. It was concluded that the series is completely isomorphous up to the concentrations of Ta studied, about 65 mole % Ta<sub>2</sub>O<sub>5</sub>. The total weight % FeO+MnO in the mineral will vary with the Cb<sub>2</sub>O<sub>3</sub>-Ta<sub>2</sub>O<sub>5</sub> ratio because of the difference in the atomic weight of Cb and Ta. The relationship of density to the mole % Ta<sub>2</sub>O<sub>5</sub> offered a method of analysis having an accuracy comparable to the time-consuming chemical methods now employed. Minor impurities (<5%) did not appreciably affect the results.

- 176. CAMPBELL, W. J. AND PARKER, J. G.**  
Conversion Tables for Fluorescent X-ray Spectroscopy.  
U. S. Bur. Mines I. C. 7725, (1955) 79 pp.  
*C. A.*, **50**, 2281(*h*).

The *K* spectral lines of elements having atomic numbers from 19-63 determined with a NaCl analyzer, the *K* spectral lines of elements having atomic numbers from 21-63 determined with a LiF analyzer, the *K* spectral lines of elements having atomic numbers from 22-63 determined with a quartz analyzer, and the *L* series for elements above atomic numbers 50 are listed in 7 tables.

- 177. FINE, S. AND HENDEE, C. F.**  
X-ray Critical Absorption and Emission Energies in ekv.  
*Nucleonics*, **12**, No. 3, 36-37 (1955).  
*C. A.*, **49**, 9380(*g*).

Energy values of *K* and *L* absorption and emission series are tabulated in ekv for all elements.

A table of X-ray *K* and *L* emission and critical absorption energies for all elements—*Technical Report No. 86* (1954), Philips Laboratories, Irvington on Hudson, N. Y.

- 178. GULBRANSEN, L. B.**  
Barite Analysis with the X-ray Spectrograph.  
*Anal. Chem.*, **27**, 1181-1182 (1955).  
*C. A.*, **49**, 14571(*h*).

Quantitative analysis of powdered barite ores is accomplished with X-ray spectrograph and Ba *L*<sub>β</sub> radiation. Agreement to within 0.5% of

wet chemical methods by using an established working curve is normal, involving a total analysis time of about 3 min.

- 179. HASLER, M. F., DAVIDSON, E., ORR, H., AND BARRY, WM. H.**  
New Universal Emission Quantometer and Its Application.  
*Mikrochim. Acta*, 596-609 (1955).  
*C. A.*, **49**, 11422(*e*).

New 1.5-m and 20-m spectrometers are described and pictured. The difference between the old type model and the new is that the position of the phototubes is much more flexible and the maximum numbers of tubes is increased to 50 in the smaller instrument and 68 in the larger. The console has been improved although the principle of the electrical features remains the same but the control system is different. Instead of stepping switches, the new instrument has polarized relays and the maximum number of channels is increased to 240. Recent results obtained in the analysis of P and steel are described briefly.

- 180. HERGLOTZ, H.**  
New Methods and Results of Röntgen Spectroscopy.  
*Mikrochim. Acta*, 684-695 (1955).  
*C. A.*, **49**, 12134(*i*).

A Röntgen tube is described with a radiating anode for the convenient excitation of X-ray spectra. With it, it was possible to explain the secondary activation of the  $\alpha_3$  satellites of Cr. The tube is suitable for use with the elements Ti(22) up to Zn(30) and with high accuracy.

- 181. HORTON, WM. S.**  
Some Statistical Aspects of X-ray Fluorescence Spectrometry.  
*Appl. Spectroscopy*, **9**, No. 4, 173-177 (1955).  
*C. A.*, **50**, 3144(*f*).

The use of characteristic X-ray spectra of elements for identification and determination has evolved as X-ray fluorescence spectrometry. The detector most commonly used for X-rays is a Geiger tube with an auxiliary scaling circuit to count the pulses initiated by the X-ray photons. A simple derivation of the probability distribution function for the time to accumulate a preset number of counts is outlined. The result is applied to X-ray fluorescence spectrometry in order to establish the expected precision of the various measures of quantity of an element. Examples are given to show how the results can be used as a practical guide in this field of analytical chemistry.

- 182. LANG, GERHARD**  
X-ray Spectral Analysis with Counter Goniometers.  
*Z. Metallkunde*, **46**, 616-620 (1955).  
*C. A.*, **50**, 102(*f*).

A review of German and U.S. practices of X-ray goniometry in analysis. 19 references.

183. LIEBHAFSKY, H. A., PFEIFFER, H. G., AND ZEMANY, P. D.

Precision in X-ray Emission Spectrography. *Anal. Chem.*, **27**, 1257-1258, correction **1399** (1955).  
*C. A.*, **49**, 15467(f).

X-ray emission spectrography may be regarded as a random process, but only when operating conditions are ideal. Under such conditions, the standard deviation, background assumed negligible, should be predictable and equal to the square root of the mean number of counts, as in radioactivity. This was verified experimentally. When the actual standard deviation significantly exceeds the predicted, operating conditions are not ideal.

184. NELSON, J. T. AND ELLICKSON, R. T.

Scintillation Counter for Detection of X-rays. *J. of the Amer. Ceramic Soc.*, July 1957, 167(g); *J. Opt. Soc. Am.*, **45**, (11) 984-986 (1955).

A scintillation counter using a sodium iodide crystal activated with thallium in conjunction with a sensitive photomultiplier tube is described. The sensitivity is such that the yield of photoelectrons is about 3.5/1000 ev. X-ray energy, and the response is linear over an intensity range of  $5 \times 10^8$ . The counter is superior to a Geiger counter for wavelengths of 1 Å or less. 7 Figs., 20 references.

185. REGLER, F.

Fluorescence Spectroscopy with Röntgen Rays.

*Mikrochim. Acta*, 671-683 (1955).  
*C. A.*, **49**, 12134(g).

The simplicity of X-ray spectra, as well as their insensibility toward chemical binding, makes it likely that X-ray spectroscopy is often best suited for spectral analysis. The method is rarely used for several reasons. The sample is often placed on the anode of the Röntgen tube and bombarded with electrons, and this has disadvantages. It is only recently that technical equipment was available for fluorescence activation outside the X-ray tube. Regler has constructed a tube for this purpose. Fundamentally when the excitation is carried out externally in air, only elements with atomic numbers larger than 21 can be detected. For elements with higher numbers, the *L* series can be used successfully, but the anode material of the Röntgen tube must be chosen so that the wave length of the tube is 150-200 at most and 600 times shorter than the absorption edge of the series which is to be studied. If a sample containing inclusions is irradiated with a suitable X-ray beam, the inclusions can be shown by a camera picture and localized.

186. TAYLOR, JEANNE AND PARRISH, WM.

Absorption and Counting-Efficiency Data for X-ray Detectors.

*Rev. Sci. Instr.*, **26**, 367-373 (1955).  
*C. A.*, **49**, 12145(g).

Mass absorption coefficient data for 0.1 to 50 Å are plotted for Al, Be, and mica (used for X-ray windows) and for Xe, Kr, A, and Ne (used in X-ray detectors). A graph of percentage transmission of windows is presented. Quantum-counting efficiencies from 0.1 to 15 Å are shown for an end-window A-filled Geiger counter, side-window Xe, Kr, A, and Ne proportional counters, and a NaI(Tl) scintillation counter.

187. VAINSHTEIN, E. E., AND SHEVALEEVSKII, I. D.

Use of  $W_1W_2$ -diagram of X-ray Spectrum Analysis.

*Zhur. Anal. Khim.*, **10**, 184-188.

*J. Anal. Chem. USSR*, **10**, 173-176 (1955) (Engl. translation).

*C. A.*, **49**, 15604(c).

Designating the photod. of spectrum lines by  $W = \log(1-T)/T$  where  $T$  is the coefficient of transmission and equals the ratio of transmitted to incident light,  $W_1W_2$  diagrams were constructed. The values were obtained by changing the exposure and thereby the intensity of a series of lines. The diagrams were then plotted by laying-off the values  $W$  of one line on the abscissa and of another line on the ordinate. In the visible range of the spectrum the lines of equal intensity ratio of spectrum lines in the  $W_1W_2$  field represent a pencil of straight lines emanating from one point. The relation between  $W$  and exposure ( $E$ ) is given with sufficient accuracy by  $W = W_0 + aE^b$  where  $W_0$ ,  $a$ , and  $b$  are constants (cf. Noar, *C. A.*, **45**, 7899(a)). This property of the  $W_1W_2$  diagram was tested in the X-ray region of the spectrum with the  $K\alpha_{1,2}$  lines of Cu and  $L\alpha_{1,2}$  lines of W. For  $W$  values of -1 to +1.8 the lines of equal intensity ratio of a  $W_1W_2$  diagram within the X-ray region were straight lines. A further analysis of these results showed that the  $W_1W_2$  diagram method is applicable also to spectrum analysis in the X-ray region.

188. WARD, A. L. AND KRUMBEIN, A. D.

Some Characteristics of Chlorine Quenched Geiger-Muller Counters.

*Rev. Sci. Instr.*, **26**, 341-351 (1955).

*C. A.*, **49**, 12145(a).

The Lauterjung equation holds for the starting potentials of Cl quenched counters. The consideration of secondary Townsend processes gives a new interpretation of Lauterjung constants. A nomograph is derived for Ne-Cl counters that correlates counter dimensions, total gas pressure, and percentage Cl. The plateau length is an increasing linear function of Cl concentration. Plateau slopes decrease initially with increasing Cl concentration and then remain constant.

- 189. WEYMOUTH, J. W. AND BAUER, N.**  
Bent Mica Focusing X-ray Spectrograph for a Course in Atomic Physics.  
*Amer. J. Phys.*, **23**, 510 (1955).  
*Phys. A.*, **59**, No. 391 (1956).

Describes a simple bent mica X-ray spectrograph that was built for use in a senior course. The theory and construction of the spectrograph are discussed and its application to the study of the properties of X-rays by means of the recording of direct and fluorescent radiations is described.

## 1956

- 190. CAMPBELL, WM. J.**  
Determination of Germanium by Fluorescent X-ray Spectrography.  
*Univ. Microfilms* (Ann Arbor, Mich.), Publ. No. **16632**, 156 pp. (microfilm, \$1.95; paper enlargement, \$15.60); *Dissertation Abstr.*, **16**, 1059-1060 (1956).  
*C. A.*, **50**, 12738(i).

- 191. CAMPBELL, WM. J. AND CARL, HOWARD F.**  
Fluorescent X-ray Spectrographic Determination of Tantalum in Commercial Niobium Oxides.  
*Anal. Chem.*, **28**, 960-962 (1956).  
*C. A.*, **50**, 12743(f).

Ta  $L_{\alpha}$  line intensities up to 750 counts per min are obtained in good resolution from samples of 5% Ta<sub>2</sub>O<sub>5</sub> in Nb<sub>2</sub>O<sub>5</sub> by using a Mo anode in the X-ray tube, a quartz analyzing crystal, and a 4-in. Soller slit collimator with 0.005 in. spacing. Hand-mixed standards are prepared by adding minus 325 mesh Ta<sub>2</sub>O<sub>5</sub> to minus 325 mesh Nb<sub>2</sub>O<sub>5</sub>; these standards were compared to chemically prepared standards and found to be equally reliable. Except for TiO<sub>2</sub>, the impurities in com. Nb<sub>2</sub>O<sub>5</sub> contribute negligible errors. By preparing samples of Ta<sub>2</sub>O<sub>5</sub> in ZrO<sub>2</sub> it was found that Nb<sub>2</sub>O<sub>5</sub> contained 0.03% Ta<sub>2</sub>O<sub>5</sub>. The method is accurate to  $\pm 5\%$  in the concentration range 0.5-10% Ta<sub>2</sub>O<sub>5</sub>. An analysis takes about 10 min after the standards are prepared.

- 192. DESPUJOLS, J. AND LUMBROSO, D.**  
Determination of Small Quantities of Hafnium in Zirconium by X-ray Spectroscopy.  
*J. Chim. Phys.*, **53**, 108-110 (1956).  
**AA3**, 2690.

By measuring the intensity of the  $L\beta_2$  radiation from Hf with a spectrometer of the curved-crystal type and a Geiger counter, it has been found possible to determine several hundredths of 1 per cent of Hf with an absolute error of the order of  $1.5 \times 10^{-4}$ .

- 193. DRAHOKOUPIL, JIRI**  
Rapid Determination of Tungsten in Steels by Secondary X-ray Analysis.  
*Hutnicke Listy*, **11**, 233-237 (1956).  
*C. A.*, **50**, 12744(i).

The suitability of this method is shown by analyzing samples of 3 types of steel containing about 4, 9, and 18% W, respectively. An X-ray quantometer is shown for the simultaneous determination of several elements. The analysis requires 0.5-1.5 min.

- 194. DRAHOKOUPIL, J.**  
The Influence of Total Reflection from a Soller Slit on the Resolving Power of an X-ray Spectrograph.  
*Physics Abstracts*, **59**, No. **708**, Dec. 1956; *Czech. J. Phys.*, **6**, No. **1**, 35-38 (1956). (In Russian, with summary (200 words) in English.)  
9044.

Experiment showed that X-rays (FeK $\alpha$ ) totally reflected from the aluminium foils of a Soller slit could be suppressed by roughening the foils of emery. In the particular apparatus a 20% increase in resolving power was obtained.

- 195. LEWIS, GEO. J. AND GOLDBERG, EDWARD D.**  
X-ray Fluorescence Determination of Barium, Titanium, and Zinc in Sediments.  
*C. A.*, **50**, 11-10-56, 15342d; *Anal. Chem.*, **28**, 1282-1285 (1956).

Ba, Ti, and Zn were determined in various marine sediments. The internal standard for Zn was As while La served for Ba and Ti. For Zn concentrations of 0.004-0.6%, the As<sub>2</sub>O<sub>3</sub> addition was 0.6% of the total weight; for Ti and Ba concentrations of 0.01-2.0%, La<sub>2</sub>O<sub>3</sub> was added in the amount of 2.5% of the sample weight. The  $L_{\alpha 1}$  line for Ba was used and the K $\alpha$  lines for Zn and Ti were satisfactory. The Ba  $L_{\alpha 1}$  and Ti K $\alpha$  peaks overlapped and empirical corrections had to be made. The lower limits of detectability were 0.01% of Ti and Ba and 0.004% for Zn.

- 196. REITH, A. M. AND WEISERT, E. D.**  
Rapid Chemical Analysis with the X-ray Spectrograph.  
*Metal Progr.*, **70**, No. 1, 83-87 (1956).  
*C. A.*, **50**, 12727(e).

Data are given for the determination of W, Mn, Ni, Cr, Co, Fe, Mo, and V in Co-Ni-Fe alloys.

- 197. PANAKHI, SH. A.**  
Plasticity of Rock Salt.  
*C. A.*, **51**, Aug. 25, 1957, 11804-b-c; *Trudy Azerbaidzhan. Ind. Inst. im. M. Azizbekova*, **1956**, No. **12**, 61-67.

The plastic deformation of NaCl at various temperatures begins at the following pressures: 15 C, 1850 kg per sq cm; 60 C, 1220; 100 C, 880; 150 C, 648; 200 C, 510.

## 1957

- 198. ACHEY, FREDERICK AUGUSTUS**  
X-ray Fluorescence from Thin Films.

*C. A.*, **51**, No. **14**, 7-25-57, 10229(*j*); *Univ. Microfilms* (Ann Arbor, Mich.), Publ. No. **20308**, 97 pp. (microfilm, \$2.00; paper enlargement, \$9.70); *Dissertation Abstr.*, **17**, 509 (1957).

**199.** BARIEAU, ROBERT E.

X-ray Absorption Edge Spectrometry as an Analytical Tool. Determination of Molybdenum and Zinc.

*C. A.*, **51**, No. **12**, 6-25-57, 8579(*h*); *Anal. Chem.*, **29**, 348-352 (1957).

By using the continuous X-ray radiation from a copper X-ray diffraction tube, in combination with a modern X-ray spectrophotometer, it was possible to make X-ray absorption measurements on materials as a function of monochromatic wavelength. By making measurements near and on each side of an absorption edge, a specific elemental scheme of analysis is possible for the element characterized by the edge. The method is independent of the other atoms present, specific, and nondestructive. The method is preferred to X-ray fluorescence because of the absence of a matrix effect at higher concentrations. Calibration equations and methods of measurements are presented for the determination of Mo and Zn. The technique was applied to the determination of Mo and Zn in liquid hydrocarbons, Pb and Br in engine combustion chamber deposits, and Mo, Ni, and Pi in solids.

**200.** BEDO, DONALD E.

K-emission Spectrum of Metallic Lithium.

*C. A.*, **51**, 8-10-57, 11055(*c*); *Univ. Microfilms* (Ann Arbor, Mich.).

Publ. No. **21074**, 93 pp. (microfilm, \$2.00; paper enlargement, \$9.30); *Dissertation Abstr.*, **17**, 1097-1098 (1957).

**201.** BIRKS, L. S. AND BROOKS, E. J.

Electron Probe X-Ray Microanalyzer.

*Rev. Sci. Instr.*, **28**, No. **9**, Sept. 1957, p. 709.

A 1-3  $\mu$  electron probe of simplified design has been constructed for X-ray spectrochemical analysis of metallic and nonmetallic specimens. At operating conditions of 20-30 kv and less than 0.1  $\mu$  amp beam current, counting rates of about 3000 counts per sec are obtained from pure elements such as iron; thus compositions as low as a few tenths per cent are detectable. At increased voltage and current and with a beam size of 10-20  $\mu$ , counting rates may be increased to 50,000 counts per sec. Applications include analysis of inclusions in metals and minerals, mass transfer material from liquid-metal cooling systems, phase composition, and intermediate diffusion studies.

**201a.** BROOKS, E. J. AND BIRKS, L. S.

Compton Scattering Interference in Fluorescent X-ray Spectroscopy.

*C. A.*, **52**, No. **3**, Feb. 10, 1958, 1837(*i*); *Anal. Chem.*, **29**, 1556 (1957).

In fluorescent X-ray spectroscopy, whenever the sample matrix contains mostly light elements, common plastics, hydrocarbon liquids, etc., Compton scattering may be strong enough to interfere with the analysis. Interference may occur not only at the primary X-ray wavelengths but also at wavelengths corresponding to the Compton scattering associated with the primary wavelengths. An example of Compton scattering from a lucite sample is given.

**202.** CASTAING, R., PHILIBERT, J., AND CRUSSARD, C.

Electron Probe Microanalyzer and Its Application of Ferrous Metallurgy.

*C. A.*, **51**, No. **12**, 6-25-57, 8606(*c*); *J. Metals*, **9**, *AIME Trans.* **209**, 389-394 (1957).

The apparatus described uses the properties of X-radiation, emitted by substances under electron bombardment, as a means of rapid chemical point analysis. The method is based upon the principles of emission X-ray spectrography pioneered by Moseley in 1913 (cf. *C. A.*, **8**, 2307). A very finely focussed beam of electrons (the electron probe) is projected on the surface of a sample, which has a very large area compared with the beam diameter, at the point where it is desired to know the chemical composition. The minute volume of the sample which is thus irradiated emits a complex X-ray spectrum consisting principally of the characteristic radiations of the elements present in the volume. Measurement of the wavelength and intensity of each component of this spectrum thus affords a simple method of determining the chemical identity and concentration of these elements. It is possible to carry out local analyses of non-conductors (such as ores) as well as metals or alloys of one or more phases and further, to measure all the variations of components within one phase such as a segregate. The very light elements cannot be determined. The relative error is about 1% for percentages which are not too low. The detection threshold of an element seems to be at concentrations of about 0.2 to 0.3%.

**203.** HAUDEK, HELMUT

X-ray Reflection by Spherically Deformed NaCl Crystal Plates.

*C. A.*, **51**, Aug. 25, 1957, 11804(*g*); *Z. angew. Phys.*, **9**, 73-82 (1957).

Cleavage plates (100) of NaCl single crystals were spherically bent by hydroplastic and thermoplastic methods. Laue diffractions showed that the lattice planes in the deformed plates are essentially parallel. The mean deviation of the lattice constant of the spherical plates, as compared with the nondeformed crystal, was 0.15%. The plates can be used as spherical mirrors for producing X-ray images. Enlarged X-ray photographs of the focus of an X-ray tube and a wire-mesh screen are shown. For Cu  $K\alpha$  radiation a spherical reflector of 17 mm

curvature radius has a resolving power of 0.1 mm.

**204. HOWER, JOHN AND FANCHER, THOMAS W.**  
Analysis of Standard Granite and Standard Diabase for Trace Elements.

*C. A.*, **51**, 8-10-57, 11173 (*f, g*); *Science*, **125**, 498 (1957); cf. Fairbairn, et al, *C. A.*, **46**, 11007i.

A standard granite and a standard diabase sample were analyzed for Mn, Ni, Cu, Zn, Rb, Sr, and Zr by an X-ray fluorescence method. The accuracy for elements with concentrations greater than 25 ppm is estimated at 10%; for those below 25 ppm, about 15 per cent.

**205. ROOS, CHARLES E.**

K-fluorescence Yield of Several Metals.

*C. A.*, **51**, 8-10-57, 11055 (*e*); *Phys. Rev.*, **105**, 931-935 (1957).

The K-fluorescence yield has been measured by a solid angle method; variation of the solid angle subtended by a sample foil at a NaI(Tl) crystal permits separation of collimated primary and isotropically fluorescent X-rays. The yields for Fe, Ni, Cu, Zn, Zr, Nb, Mo, Rh, Pd, Ag, Cd, and Sn are, respectively  $0.308 \pm 0.015$ ,  $0.366 \pm 0.011$ ,  $0.410 \pm 0.012$ ,  $0.446 \pm 0.012$ ,  $0.70 \pm 0.02$ ,  $0.73 \pm 0.02$ ,  $0.73 \pm 0.02$ ,  $0.786 \pm 0.015$ ,  $0.790 \pm 0.014$ ,  $0.821 \pm 0.015$ ,  $0.827 \pm 0.014$ , and  $0.846 \pm 0.012$ . In NaI(Tl),  $8 \pm 2$  but not 0.2 msec decay was observed.

**206. SAURIER, CLAUDE**

Quantitative and Qualitative Analysis of Alloy Surfaces by X-ray Fluorescence.

*C. A.*, **51**, No. 10, 7234 (*f*); *Rev. met.*, **54**, 1-8 (1957).

The surfaces of Xn-Pb, Pb-Bi, Bi-Sn, Sn-Zn, Zn-Dc, and Sn-Bi-Pb alloys are investigated. The absolute error of the determination lies between 0.2 and 3.7%.

**207. SILVERMAN, LOUIS, HOUK, WM. W., and MOUDY LAVADA A.**

Determination of Uranium Dioxide in Stainless Steels by the X-ray Fluorescence Method.

*C. A.*, **51**, No. 14, 7-25-57, 10307 (*g*); U. S. Atomic Energy Comm. *NAA-SR-1848*, 11 pp. (1957); cf. *C. A.*, **45**, 7915 (*f*).

UO<sub>2</sub> in UO<sub>2</sub>-stainless steel mixtures is determined in HClO<sub>4</sub> solution by using X-ray fluorescence and a LiF analyzing crystal HCl, HF, and HNO<sub>3</sub> are used to acid solution, but are expelled subsequently. No separation is necessary. Measured is the  $L\alpha$  line of U. The accuracy reported is 5%. SrNO<sub>3</sub> can be used as an internal standard. The accuracy is improved to 2%. The  $K\alpha$  line of Sr is measured.

**208. WEBBER, G. R.**

Applications of X-ray Emission Spectrometry to Rock and Ore Analysis.

*C. A.*, **51**, No. 14, 7-25-57, 10296 (*d*); *Trans. Can. Inst. Mining Met.*, **60** (in *Can. Mining Met. Bull.*, **540**, 222-226 (1957)).

Elements which can be detected range from atomic number 12 (Mg) to 92 (U). The lightest elements have low sensitivities, and specialized equipment is necessary for their detection. Standards were prepared by adding various amounts of Nb<sub>2</sub>O<sub>5</sub> to a feldspar base. Five g of each standard was mixed with 0.05 g MoO<sub>3</sub> by hand in a mullite mortar for 5 min. Similarly, 5 g of each unknown was mixed with 0.05 g MoO<sub>3</sub>. A General Electric XRD-3 X-ray spectrometer containing an AEG-50T W-target X-ray tube, a thick mica analyzing crystal, a No. 1 argon Geiger counter tube, and a 0.3 deg detector slit was set to measure the counting rate of the Nb<sub>K $\alpha$</sub>  and the Mo<sub>K $\alpha$</sub>  lines. Background was also measured, subtracted from peak intensities, and the Nb<sub>K $\alpha$</sub>  - Mo<sub>K $\alpha$</sub>  intensities were computed. Lines of U, Yt, Zr, and Th can cause interference if the concentrations are high enough. A general method of analysis by diluting with NaCl gave results differing from chemically analyzed standards by an average of about 5% of the amount present for K, Ca, and Fe, and by about 8% of the amount present for Ti.

**209. WILSON, HARRY M. AND WHEELER, G. V.**  
Determination of Uranium in Solution by X-ray Spectrometry.

*C. A.*, **51**, No. 12, 6-25-57, 8581 (*b*); U. S. Atomic Energy Comm., *IDO-1 4393*, 17 pp. (1957).

A rapid precise method for the determination of U in HNO<sub>3</sub> solution is presented. The U in solution is excited by a primary X-ray beam from a Mo tube. The intensity of fluorescent U  $L\alpha_1$  line is measured by means of a crystal spectrometer employing a scintillation counter and pulse height analyzer. This intensity is converted to concentration relating to standard solutions which are prepared by dissolving pure U oxide (U<sub>3</sub>O<sub>8</sub>) in nitric acid and diluting to the desired concentration.

**210. GARBER, R. I., OBRIMOV, I. V., AND POLYAKOV, L. M.**

The Production of Ultramicroscopic Nonuniformities During the Plastic Deformation of Rock Salt.

*C. A.*, **51**, Aug. 25, 1957, 11804 (*b*); *Soviet Phys. "Doklady,"* **1**, 314-315 (1956) (*English translation*).

See *C. A.*, **51**, 3223 (*e*).

**211. BURNHAM, H. D., HOWER, JOHN, AND JONES, L. C.**

Generalized X-ray Emission Spectrographic Calibration Applicable to Varying Compositions and Sample Forms.

*C. A.*, **52**, No. 6, 3-25-58, 4385 (*i*); *Anal. Chem.*, **29**, 1827-1834 (1957).

A general scheme of analysis based on Sherman's equations is given. For a 3-component system the working equations take the form of 3 simultaneous equations, linear with respect to concentrations and reciprocal intensities, and 3rd order with respect to a geometrical factor. Graphical solution of these equations have been employed. The X-ray emission spectrographic method developed can handle quantitatively samples of nonidentical geometry, e.g., plate, wire, chips, turnings, and filings.

**212. IVOILOV, A. S. AND LOSEV, N. F.**

Determination of Titanium from Secondary X-ray Spectra.

*C. A.*, **52**, No. 6, 3-25-58, 4392(*h*); *Izvest. Akad. Nauk SSSR (Ser. Fiz.)*, **21**, 1465-1468 (1957).

The ore preparations were pasted on an Al plate with adhesive, compressed with a pressure of 100-150 kg per sq cm, and fired to remove the adhesive. The  $K\alpha_1$  line was used for reference. The presence of Fe increased the intensity of the line, and the presence of Ca decreased the intensity. The density of the filler also changed the intensity. Thus a direct method was not possible, and the preparation had to be diluted with a buffer ore (containing 70%  $\text{SiO}_2$ ). In this case and for  $\text{TiO}_2$  concentrations of 1050% and accuracy of 10% was obtained with a sensitivity of 0.7-0.8% and a speed of 8-10 analyses per day.

**213. LYTLE, FARRELL W., BOTSFORD, JAMES I., AND HELLER, HENRY A.**

X-ray Emission Spectrographic Analysis of Bastnaesite Rare Earths.

*C. A.*, **52**, No. 6, 3-25-58, 4396(*f*); U.S.

Bur. Mines, *Repl. of Invest.*, No. 5378, 16 pp. (1957).

The method includes determination of Yt, Th, La, and the rare-earth elements in various complex mixtures. The analysis technique is based upon comparing the samples with synthetic standards approximating the composition of the samples. Working curves are plotted on an absolute intensity basis, with no correction for background. An oxide sample can be prepared and completely analyzed in 35 min. The average error of analysis was about 3% of the amount present in the range from 5 to 100% and about 7% of the quantity present from 0.2 to 5%. Rare-earth oxalates were used as sample material instead of oxides when rapid hydration and carbonation occurred.

**214. SILVERMAN, LOUIS, HOUK, WILLIAM W. AND MOUDY, LAVADA**

Determination of Uranium in Stainless Steel. X-ray Fluorescent Spectrographic Solution Technique.

*C. A.*, **52**, No. 6, 3-25-58, 4407(*g*); *Anal. Chem.*, **29**, 1762-1764, (1957).

A 10-g sample of stainless steel is dissolved in 20 ml aqua regia. Several drops of HF and 15 ml of  $\text{HClO}_4$  are added and the solution evaporated to fumes. The solution is cooled, diluted, and 2 ml of standard  $\text{Sr}(\text{NO}_3)_2$  solution added. The solution is then made up to a volume of 100 ml with water. Approximately 10 ml of this solution is used to fill the solution cell. The time required, 40-70 sec, to record 204, 800 counts is measured for the  $K\alpha$  line of Sr and the  $L\alpha$  line of U. The ratio of counting time of Sr to the U is calculated and the concentration of U is obtained from a working curve.