X-RAY SPECTRAL ANALYSIS

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X-RAYS were discovered 64 years ago in 1895 by W. K. Röntgen. In 1912 it was established that natural crystals serve as analyzers of the spectral composition of x-rays. From that time onwards began an intensive development of the study of atomic structure of solids and the investigation of the fundamental regularities of the structure of x-ray spectra.

In 1914, owing to the brilliant work of Moseley, the fundamental law of x-ray spectroscopy was discovered, which established the relation between the wavelength of the characteristic x-ray spectrum and the atomic number of the element.[1] In analytic form it can be written as

$$\frac{\nu}{R} = (Z - \sigma)^2 \left(\frac{1}{n^2} - \frac{1}{m^2} \right), \tag{A}$$

where $\nu = \frac{1}{\lambda}$ is the wave number, R is the Rydberg constant, while n, m, and σ are constants.

The characteristic x-radiation arises in the following manner. An atom, ionized through interaction with electrons or photons, may give up its excess energy in the form of characteristic x-radiation. On returning to the normal state corresponding to the minimum potential energy by means of successive cascade transitions of electrons from higher lying atomic levels into vacant levels. Such x-radiation produces a line spectrum of exceedingly simple structure. The set of lines due to the transitions of electrons from a discrete set of levels to one common level is called a series. The structure of similarly named series of the characteristic spectra of the atoms of the periodic system is practically the same (this served as a direct confirmation of the similarity of the structure of electronic shells of atoms of the periodic system). The origin of x-ray spectra and their form are schematically shown in Figs. 1 and 2.

If an electron from the deepest lying electronic level is removed from an atom the result is the so-called K series of the characteristic x-ray spectrum; this series has the shortest wavelengths for a given element. All subsequent series of the characteristic spectrum, having greater wavelengths for a given atom, are respectively labelled the L, M, N etc. series. The characteristic x-ray spectra of all the series (with the exception of the K series) are complex. Thus the L series consists of 3 subseries; the M series consists of 5 subseries, etc. The set of lines whose final transition level is the L_{III} level can be excited independently of those lines for which the final levels of the transition are L_{II} and L_I. Similarly, one can separately excite the set of lines for which the final level of the transition is L_{II} or L_{III}. However, when the L_I subseries is excited, all the lines of the complex L series of the characteristic x-ray spectrum appear.

The following are two features that distinguish the characteristic x-ray spectra from the optical spectra: a) An exceedingly weak dependence of the wavelengths of the lines and of their relative intensities on the composition of the chemical compound into which the atoms of the element under investigation may enter. b) The lines of any one series of the characteristic x-ray spectrum lie within a spectral region that is narrower than the separation between two neighboring series by a factor of 4 to 6.
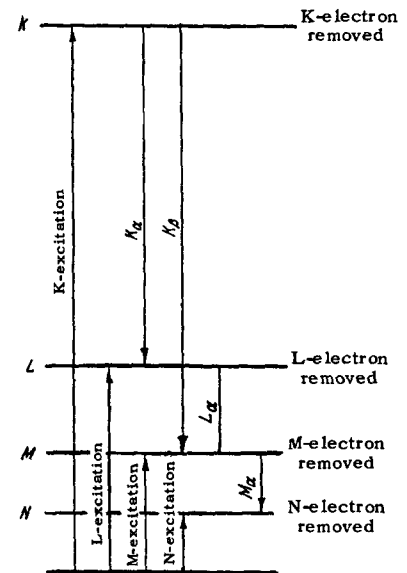

FIG. 1. Schematic diagram of the origin of characteristic x-ray absorption and emission spectra.

The frequencies of the predominant majority of the lines of the characteristic x-ray spectra can be expressed as differences between two quantities called terms. The quantities ν/R are adopted as terms in x-ray spectroscopy. In these terms ν stands for frequencies corresponding to frequencies of the characteristic absorption spectra of the dif-
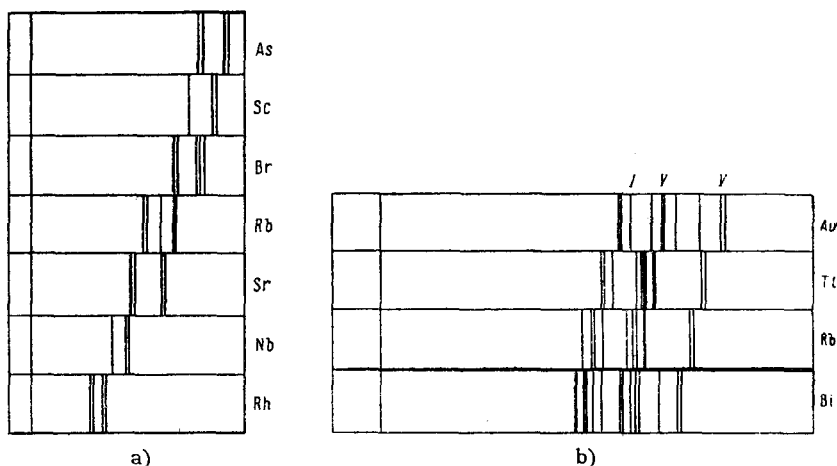
FIG. 2. Characteristic x-ray spectra of the K and L series.

ferent spectral series. The frequency of the characteristic x-ray absorption spectrum is determined from the position of a sharp change in the value of the absorption coefficient. This change in the magnitude of absorption is associated with the work done in removing one of the inner electrons of the atom to the first unoccupied level (internal photoeffect).

Lines arising in the transition of electrons between various levels are denoted by Greek letters. The main lines of the K, L, and M series are shown in Fig. 3.

The lines of the different series of the x-ray spectra fall into groups of pairs of lines forming the so-called screening doublets and spin-relativistic doublets. These pairs of lines are characterized by definite dependence of the wavelength difference (or frequency difference) between them on the atomic number of the element. Thus, for example, in the case of spin-relativistic doublets $\Delta\lambda$ is of order 4 XU for all elements from calcium to uranium independently of the atomic number of the element.

To analyze x-rays one can use either a natural crystal, which serves as a three-dimensional diffraction grating for x-rays, or the ordinary ruled diffraction grating used in optical spectroscopy. However, in the case of x-rays it is not the lines themselves that are operative, but the areas between them. The angle of incidence of x-rays on these areas varies from several tens of seconds to several degrees.

Photographic and ionization methods are used to register the intensities of x-ray spectra. In the case of the photographic method, a rule used in x-ray spectroscopy is that one absorbed quantum corresponds to one developed grain. The effectiveness of the ionizing action of x-rays, just as the physical action of any electromagnetic radiation, is proportional to the fraction of the absorbed radiation.
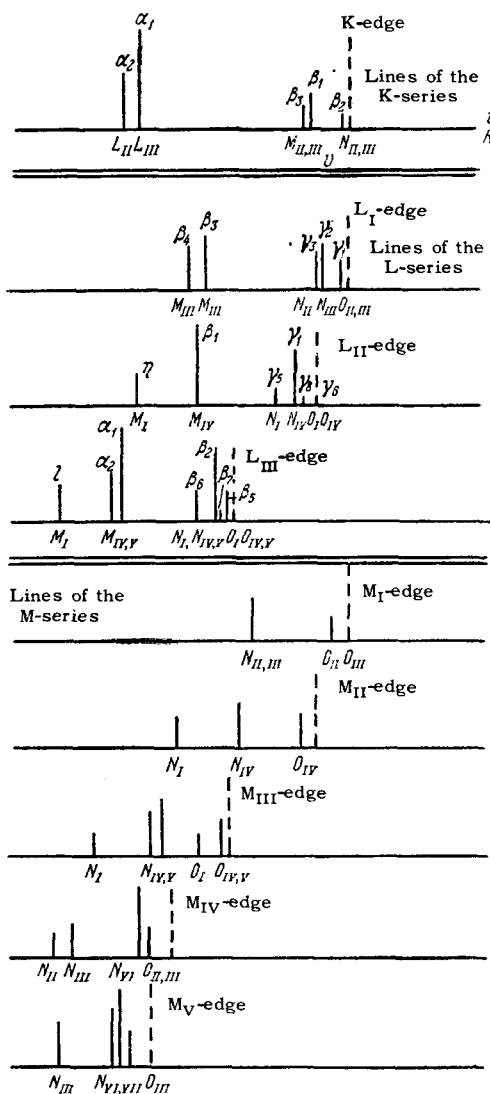

FIG. 3. Principal lines of the K, L and M series.

A schematic diagram of an x-ray spectrograph is given in Fig. 4. X-ray spectrographs of highest aperture are those that utilize bent crystals. (A single crystal plate bent into a cylindrical surface
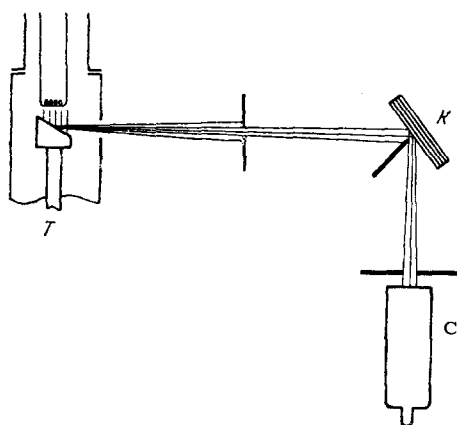
FIG. 4. Schematic diagram of an x-ray spectrograph: T – demountable x-ray tube, K – crystal, C – Geiger-Müller counter.

increases the intensity of the reflected x-rays by 2 or 3 orders of magnitude, compared to a plane crystal.)

One of the principal practical consequences of Moseley's law is the possibility of determining the atomic number of an element from the wavelengths of the lines of the characteristic spectrum. In spite of the obvious nature of this consequence of the application of x-ray spectra to the analysis of chemical composition, work in this direction was begun only about 25 years ago: in 1922 in Sweden by Hadding and Hevesy. As early as in 1923 the work of Hevesy and Coster culminated in the discovery of the 72nd element of the periodic table, hafnium, in zirconium minerals.[2] Almost simultaneously with Hevesy x-rays began to be used for analytic purposes by Goldschmidt and his students in Norway and by Noddack in Germany. As a result of the work of the last named authors, the 75th element of the periodic system, rhenium, was discovered in 1925 by means of its x-ray spectrum.[3] It may be noted that to obtain any appreciable concentration of hafnium in zirconium minerals Hevesy and Coster had to carry out approximately one hundred recrystallizations of fluorine compounds of hafnium-zirconium. Noddack discovered rhenium in products of commercial processing of Mannsfeld shales, in which rhenium was concentrated by a factor of one thousand.

The work of V. M. Goldschmidt[4] was devoted to a systematic study of the quantitative distribution of the elements of the rare earth group in ores and minerals of different origin throughout the world. This work played an important role in the study of the geochemistry of these elements and indicated methods of searching for them.

Since the wavelengths of the characteristic x-ray spectrum are determined in the first place by the

nuclear charge, it is equally easy to determine by means of x-ray spectra the simultaneous presence of any element, including elements which are very close in their chemical properties. It is just because of this that during more than 20 years (out of 26) x-ray spectrochemical analysis was used for the analysis of elements of the rare earth group and of such pairs of elements as hafnium-zirconium, niobium-tantalum, vanadium-titanium etc. It is only during the last five or six years that x-ray spectral analysis has begun to be widely used for the analysis of almost all the elements of the periodic system under industrial and factory laboratory conditions.

Quantitative x-ray spectrochemical analysis is based on the assumption that the intensity of lines of the characteristic spectrum is directly proportional to the number of atoms of the element in the excited volume. In principle it is possible to determine directly the quantity of the element in the sample by determining the true line intensity. However, this seemingly simplest method of quantitative analysis is not used because it is not possible to take the influence of experimental conditions into account by means of calculations. Therefore all the methods of quantitative x-ray spectral analysis are based on measurements of the relative intensity of the line of the element under investigation and of a "standard" comparison line. Moreover, it is also possible to choose for the standard the intensity of the total background or of the background directly adjacent to the line under investigation.

The intensity of a line of the characteristic spectrum is not always exactly proportional to the number of atoms in the excited volume. If the analyzed sample contains atoms of elements whose characteristic radiation may either selectively excite the spectrum of the element being analyzed, or selectively absorb radiation of wavelengths corresponding to the element being analyzed, then a deviation from such direct proportionality may be observed. The simplest method of eliminating effects of selective excitation or absorption, for example in the case of fluorescent radiation belonging to a particular element, is to utilize very thin layers (of the order of several microns) of the analyzed substance. When this cannot be done, a correction may be introduced by means of a special calculation, or by preparing a standard which in its quantitative composition is close to the composition of the analyzed sample.

The state of development of the application of x-ray spectra in analytical chemistry has its explanation first of all in the relatively low sensitivity

of the x-ray spectral method, and secondly in the relatively high degree of complexity of the apparatus required for its application.

However, in evaluating any method of analysis, one should pay attention not only to its sensitivity, but also to the reliability of results, and to the specific advantages for the analysis of particular groups of elements. Moreover, one should have in mind that the sensitivity of the method may be significantly increased by a combination of spectral and chemical methods. Thus, for example, one may refer to the method of the carrier element, which is an exceedingly simple chemical operation, and enables one to separate reliably a whole group of elements (for example, calcium may be used as the carrier element to separate all the 14 elements of the rare earth group).

It was possible to simplify x-ray spectrochemical analysis quite considerably by utilizing the secondary (fluorescent) method of exciting spectra, and by increasing the sensitivity of recording the intensity of the radiation. In the case of fluorescent x-ray analysis the radiation of atoms in the analyzed sample results from irradiation by means of a special x-ray tube. Difficulties of fundamental nature arise in x-ray spectrochemical analysis only when it comes to the determination of elements of low atomic numbers. This is due to the fact that the relative yield of characteristic x-radiation decreases sharply with decreasing atomic number of the element (approximately as Z^4). Certain difficulties of analysis also arise in the region of long wavelengths, where the absorption of the radiation on the way from the radiator to the recording apparatus is quite appreciable. Secondary x-radiation is characterized by isotropic distribution in space. This fact greatly simplifies the possibility of simultaneous recording of different x-ray spectrum wavelengths belonging to different atoms included in the analyzed sample. To achieve simultaneous recording of several elements it is evidently necessary to place, within the confines several x-ray spectrographs, each "tuned" to a definite wavelength, within the confines of a hemisphere above the source of secondary x-rays.

The sensitivity of modern methods of fluorescent analysis amounts to $10^{-2}\%$. It is a function of the atomic number of the element, reaching a maximum value of $10^{-3}\%$, and falling by almost three orders of magnitude in the most unfavorable cases.[5]

The most accurate results of quantitative analysis may be obtained by utilizing the so-called monitor method.[5] At present it is used in all the multi-channel systems that are employed for the simultaneous determination of a large number of elements.

In principle the monitor arrangement contains at least two channels, one tuned to the spectral line of the investigated element, and the other to the line of the comparison element or to the background. For the average statistical error to be the same and independent of the content of the element, the measurement of the intensity of spectral lines is carried on for a period of time during which the monitor counts a predetermined number of pulses. The latter is chosen to be of the order of several thousand. In using such a method of quantitative analysis the accuracy may attain 2-5% of the quantity being measured.
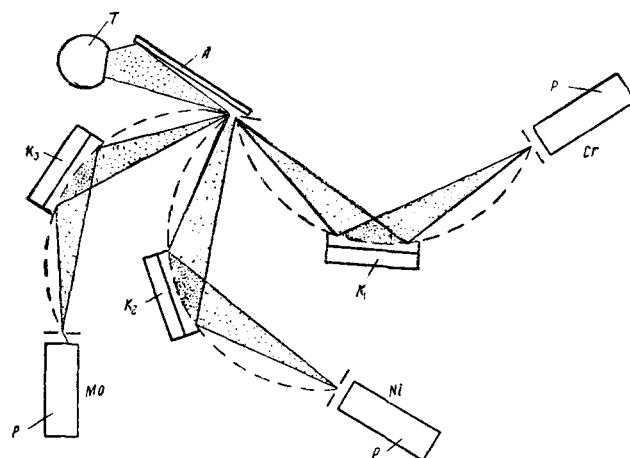

FIG. 5. Schematic diagram of a three-channel x-ray spectrograph: T — x-ray tube, A — analyzed emitting sample, K_1, K_2, K_3 — plates of single crystal polished over a cylindrical surface of radius R and bent into a cylindrical surface of radius R/2. Each crystal is set up at the Wulff-Bragg angle corresponding to the reflection of K_α lines of the following elements: chromium, nickel and molybdenum, P — recording devices (counters, photo-electric multipliers).

ured. Figure 5 is a schematic diagram of a three-channel fluorescent x-ray spectrograph. Each channel consists of an x-ray spectrograph with a bent crystal, in which the detector of the radiation is a Geiger-Müller counter. Figure 6 is a schematic diagram of a multi-channel x-ray spectrograph with a single monitor for all the channels.

It has recently been widely advocated in the American literature that the intensity of the background of the continuous spectrum or the total intensity of the continuous radiation be used for comparison standards. The principles of this method were developed here in the U.S.S.R. fifteen years ago and were first used in the photographic method of recording the spectrum.[7] It is precisely by using the principles of this method that it was possible to design the modern multi-channel x-ray spectrographs.

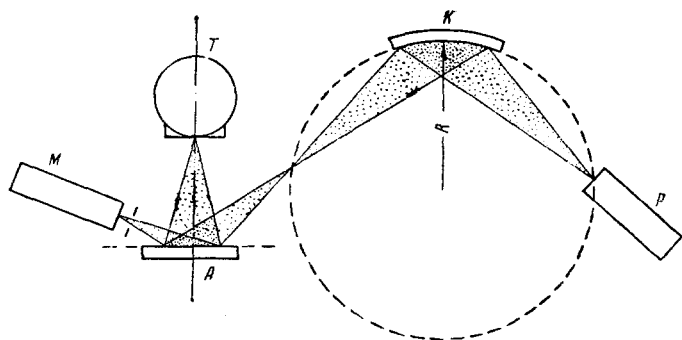In many cases it is sufficient to determine not the absolute quantities of the elements but their

FIG. 6. Schematic diagram of a multi-channel x-ray spectrograph: T — x-ray tube, A — analyzed emitting sample, M — monitor, K — crystal, P — recording device. 12 or 24 similar spectrographs are placed within the limits of a hemisphere above the sample A.

relative concentrations. This occurs, for example, in factory control analyses of standard types of steel, in analyses of the elements of the rare earth group, in the determination of the age of minerals by their uranium-thorium-lead ratio, etc. In such cases the method of the so-called width of the standard line may be successfully used. The latter consists of using the width of one line at the maximum of the other as the measure of the relative intensity of the two lines. The accuracy of this method increases as the difference in the relative content of the two elements becomes larger. A necessary condition for the practical applicability of this method is a knowledge of the frequency distribution of intensity within the limits of the emission line.[8]

The speed of carrying out a quantitative analysis by the fluorescent method varies from several minutes to one or two hours.

The method of x-ray absorption analysis has been used rather extensively, particularly in the petroleum and chemical industries. This method has turned out to be most effective for determining the content of some heavy element in a standard medium consisting of light elements, for example, sulphur in oil, lead in gasoline, or certain metals in plastics.[9] It is based on determining the relative attenuation of x-radiation after passing through the sample under analysis. From the point of view of construction, such an apparatus is essentially an x-ray photometer. A fairly effective method is absorption analysis based on the comparison of the intensities of two emission lines, one of which lies on the short-wave side of the characteristic absorption discontinuity of the analyzed element, while the other one lies on the long-wave side. The change in the relative intensities of these lines depends on the concentration of the investigated element.[10] A disadvantage of this method is that it can be utilized only in very limited cases.

Quantitative x-ray analysis can thus be deemed advantageous for determining elements at concentrations from 0.1% to several times ten percent. It is just in this range that x-ray spectral analysis has no equals with respect to speed and accuracy.[11] In utilizing x-ray spectral analysis for the determination of small amounts of an element, it is necessary, as has been already pointed out earlier, to combine it with chemical analysis. The object of the latter is to concentrate the contents of a certain group of elements in the sample.

At present x-ray spectral analysis again appears very promising because of a recently proposed and developed method of x-ray spectral investigation of chemical composition of micro-volumes of substances.[12]

The new method is characterized by the following parameters: it can be used to study and to determine quantitatively the chemical composition of thin sections of alloys, minerals, slags, organic and inorganic compounds of elements from lithium up to uranium with a localizability of 0.1 to 2μ, and to investigate the distribution of any one of the elements found "at a particular point" in any predetermined direction along the section. By localizability in this case we mean that on an area 0.1 to 2μ in diameter it is possible to determine with a local sensitivity of 10^{-13}—10^{-14} g, and with an accuracy of 2–10%, the amount of any one of a number of specified elements, and to trace, at intervals of 0.1 to 2μ, the possible variation in the quantitative content of any one of the elements found there.

The essential points of the method are shown in Fig. 7. A system of electromagnetic lenses is used to produce a narrow beam of electrons, which is focused onto a probe 1 to 3μ in. diameter. The electrons of this narrow beam, accelerated by a voltage of several tens of kilovolts, excite over the area of the anode section characteristic x-rays
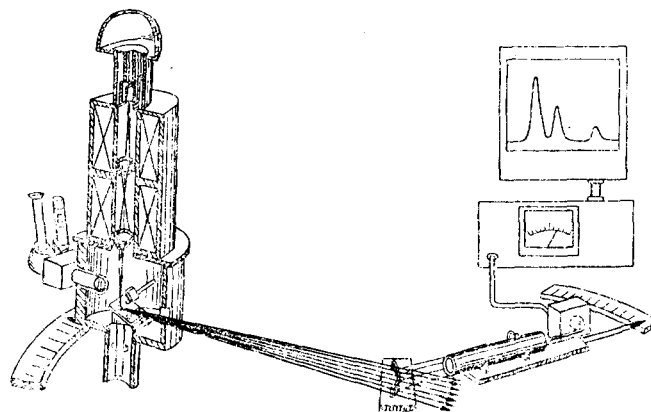

FIG. 7. Schematic diagram of the x-ray spectral method of investigating chemical composition in micro-samples of substances.
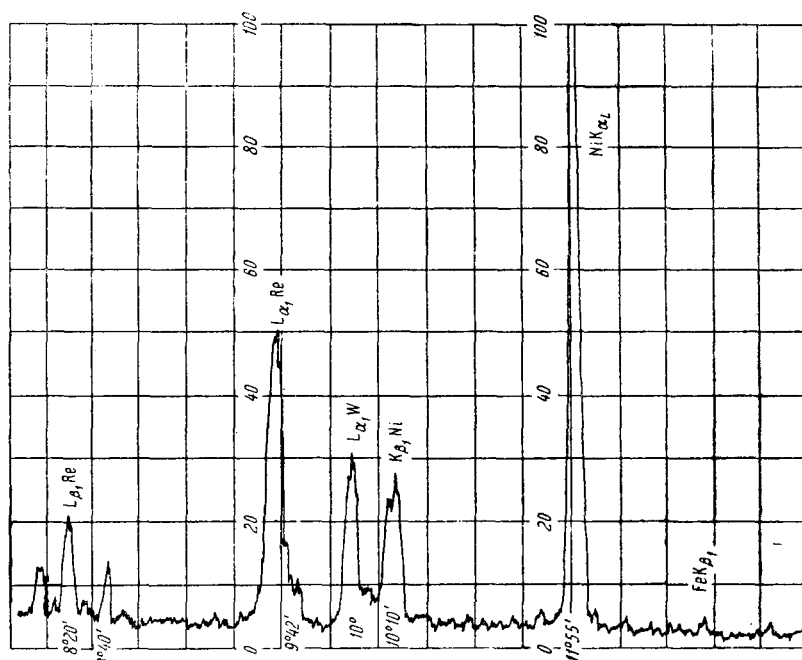
FIG. 8. Record of the results of qualitative analysis of chemical composition at a "point."

of the atoms present there. These rays are analyzed by a bent crystal, into a spectrum and are recorded by a quantum counter. By means of a special microscope it is possible to select on the section under investigation any desired region for investigating the composition, and also any desired direction in which to investigate the distribution of elements found at any point.

The RSASh-2 apparatus for x-ray spectral investigation of the chemical composition of microsamples is the first to employ the inverted passage method (the so-called Du-Mond method) for purposes of x-ray spectral research. Because of the large aperture ratio of the apparatus, the number of counts in recording a pure element by means of the most intense line of its spectrum amounts to 10^3 to 10^5 pulses per second, with an operating current of $10^{-6} - 10^{-8}$ amp, and with a focus $1 - 3\mu$ in diameter. An instrument having these parameters can determine an element at a sensitivity of $0.01 - 0.5\%$ and can record automatically the concentration curves for an element content of $0.2 - 0.5\%$. By varying the speeds of the section carriage $(10 - 100\mu/\text{min})$ and of the chart of the automatic recording potentiometer, it is possible to plot concentration curves with an effective magnification of 400 to 1600.

The high local sensitivity of the new method, the possibility of choosing and recording the analyzed micro-sample, and the possibility of automatic recording of concentration curves, have helped solve a remarkably wide range of problems in very diverse fields of science and technology.

The most widely used and the simplest is the

analysis of composition at a particular point of the section. Figure 8 shows the record of the results of such an analysis on the chart of a automatic recording potentiometer. By using such curves it is possible not only to determine the qualitative composition "at the point," but also to carry out a semi-quantitative analysis for the content of a specified element. Exact quantitative analysis is carried out by the method of comparing the intensities of the lines of the elements "at the point" with lines from a standard sample with a known content of the investigated element. The most important results were obtained in the investigation of the continuous distribution of elements in a chosen direction on the section.

Recently the new x-ray spectral method of determining the chemical composition in micro-samples has been widely applied to the study of the process of diffusion and to the determination of the diffusion constants, to the study of the influence of ordering processes on the magnitude of mutual diffusion, to the study of the effect of impurities on diffusion, to the study of the characteristic features of the processes of diffusion occurring in the formation of substructures in single crystals, to the investigation of solution exchange between a liquid and a solid medium, and to many similar problems.

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