SPECTRAL ANALYSIS OF ISOTOPIC COMPOSITION

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SUCH advances were made in the separation of stable isotopes during the last fifteen years, that it became possible to use materials of fixed isotopic composition not only in laboratory research, but also in industry. The use of heavy water in atomic reactor construction, of enriched uranium, or of fuel elements of atomic power reactors is well known.

An investigation of the isotopic composition of certain elements contained in minerals and meteorites yields evidence of their age and also of processes that have led to differences in the isotopic composition of elements obtained from different natural sources.

To be able to control the separation of isotopes and to determine the isotopic composition of elements, and to be able to monitor the products of the separating apparatus, it is necessary to have sufficiently reliable and exact methods of isotopic analysis, operating at maximum speed. It is desirable that the apparatus used for this purpose be simple and relatively inexpensive. The mass spectrograph, proposed by Aston as early as in 1919, makes it possible in principle to solve in the simplest manner all problems in the determination of the isotopic composition. However, in spite of all the improvements made in this instrument during the past forty years, it does not satisfy the requirements listed above. We can point here to only several of the difficulties connected with the use of mass spectrographs. The operation of all instruments of this class is based on the different motions of ions of different mass in electric and magnetic fields. The principal quantity that determines the behavior of the ion is its charge-to-mass ratio e/M. Depending on this ratio, different ions are focused in different portions of the focal plane of the instrument, and yield spectra whose external appearance recalls that of ordinary atomic spectra. Conversely, moving at different speeds, the ions pass between the electrodes of the instrument in different time intervals, which when measured yield the value of e/M.

The source of ions used in the mass spectrograph is some kind of discharge in which, along with atomic ions, molecular ions can also be produced.

The mass spectrograph can not always differentiate between ions having identical mass numbers and charges, such as Li^{7+} and Li^6H^+ or O^{18+}, H_2O^{16+}, HO^{17+}, DO^{16+}, etc.

Nevertheless, ions with identical mass numbers, do have somewhat different masses, owing to the differences in the binding energies of the nuclei that make up these ions (mass defect). However, to determine these differences from the mass defects we need mass spectrographs with high resolving power, which are still not readily available for analytical use and the operating productivity of which is low. The use of a mass spectrograph with insufficient resolution may lead to errors in the analysis, similar to the errors produced in spectral analysis by a superposition of the line of an extraneous element present in the sample on an analytical line of the determined element. Another source of error arising in the use of a mass spectrograph is the large "memory" of the instrument, which frequently causes the results of the analysis of the sample to depend quite strongly on the composition of the samples that were analyzed in the apparatus beforehand. The cleaning and conditioning of the instrument before each analysis therefore becomes sometimes a serious problem.

These circumstances have necessitated in recent years a search for other ways of determining isotopic composition. Attention was paid here, naturally, to differences in atomic and molecular spectra of different isotopes of the same element. Although these differences are small, they do permit the use of optical spectra as analytical identifying features of a given isotope.

The energy levels of two isotopic atoms or ions are shifted relative to each other. The magnitude of the shift is small and the maximum displacement of spectral lines is observed for isotopes of hydrogen. The isotopic splitting of the alpha lines of hydrogen and tritium amounts to 2.36 A (Fig. 1).

The shift for the $He^3 - He^4$ lines ($\lambda = 6678$ A) amounts to approximately 0.5 A; for lines of the heavier elements the magnitude of the shift is usually less than 0.1 A, and for the spectra of most elements these shifts are so small that they can barely be registered and are quite unsuitable for a reliable resolution of analytical lines.

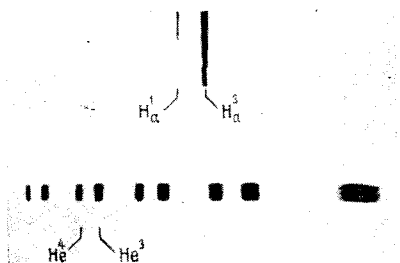Along with the level shift due to the difference

FIG. 1. Isotopic splitting of lines of hydrogen and helium (the helium line was registered with the aid of a Fabry-Perot etalon).[13]

FIG. 2. Isotopic shifts of the $\lambda = 4412$ A band of the CuCl[13] molecule. Above — sample enriched with Cu^{65}. Below — sample of a normal isotopic composition.

in the masses of the two isotopes, one observes also splitting due to differences in the magnetic and mechanical moments of the isotopic nuclei. Such splitting results in a hyperfine structure of spectral lines, the width of which is frequently sufficient to separate the components of the spectral lines of individual isotopes.

Spectral line shifts and splitting due to isotopy cannot yet be calculated theoretically with any degree of reliability.*

Matters are different with shifts of bands of isotopic molecules. The changes in the positions of the vibrational and rotational levels of such a molecule are determined uniquely by the masses of the nuclei of the atoms contained in this composition, and can be calculated with sufficient accuracy from elementary theory. The magnitudes of the isotopic shifts are as a rule greater in molecular spectra than in atomic spectra, but the great widths of the bands and the transposition of the rotational structures raise sometimes specific difficulties in the analysis (Fig. 2).

In spite of the fact that the differences in the atomic and molecular spectra, due to isotopy, have long been used to estimate the isotopic composition, it is only recently that they came to be used to devise quantitative analytical methods, capable of competing in accuracy with mass spectrometry and exceeding it in simplicity and operating convenience.

We shall illustrate here only methods of determining the isotopic composition which are based on the observation of atomic spectra. These methods have been developed in greatest detail and have certain specific features that distinguish them from ordinary spectral-analytic operating procedures.

Quantitative methods of isotopic spectral analysis based on atomic spectra are being developed primarily in four laboratories. In the U.S.S.R. the work is carried out in two laboratories. In one of these, methods of isotopic analysis of hydrogen,[1] mercury,[2] and uranium[3] are being developed. In the second, at-

*An exception are the simplest atoms, hydrogen and helium, for which theory yields sufficiently accurate results.
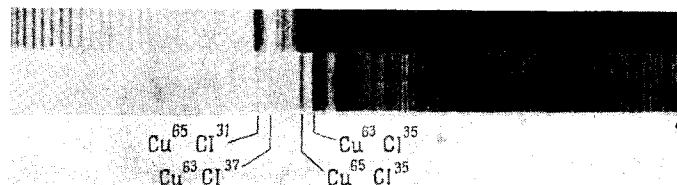
tention is focused on hydrogen,[4,5,6,7] lithium, and lead.[8,9,10] Helium,[11] lithium,[11,12] lead,[11] and uranium[11] are investigated in France. Hydrogen,[13,14] helium,[13] lithium,[15] mercury,[13] lead,[16] and uranium[13,16] are investigated in the U.S.A. The investigations reported here were carried out in 1950—1958. It is clear from this listing that all four laboratories have independently chosen the same elements for investigation. This is partly due to the convenience of applying optical-analysis method to these very elements, but is probably due principally to the need of developing convenient analytic methods for these elements.

1. SPECTRAL APPARATUS

The smallness of the isotopic shifts in the atomic spectra makes it necessary, as a rule, to use instruments of high resolution. Only in individual cases is the resolution of the instruments extensively used in ordinary spectral-analytical practice sufficient.

The resolving power of the ISP 51-A spectrograph or a small diffraction instrument such as DS-1, is sufficient for the analysis of the isotopic composition of hydrogen and uranium. In all other cases of isotopic analysis based on atomic spectra, the real resolving power must be on the order of several hundred thousand, so that the use of large diffraction gratings or of Fabry-Perot interferometers is mandatory.

The use of apparatus with photoelectric recording is the most effective. Scanning of the spectrum by varying the pressure in the Fabry-Perot etalon chamber is apparently the best present method for measuring the intensities of the components of isotopic structure.[17,18]

The optical diagram of apparatus of this type is shown in Fig. 3. The use of dielectric-coated mirrors in the etalon increases the real resolving power of the apparatus to 10^6, and its aperture ratio is sufficient for the registration of the lines of isotopes whose concentration is several tenths of one percent.
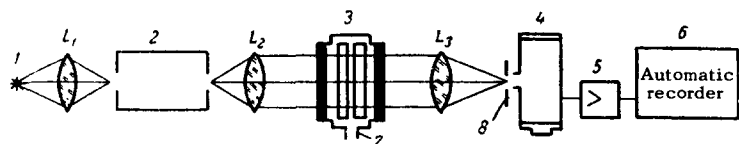
2. LIGHT SOURCES

The light sources used in isotopic spectral analysis must, in addition to satisfying the ordinary requirement of sufficient stability and brightness, also be capable of producing spectral lines with narrow contours. Sparks and arcs produced at atmospheric pressure yield as a rule lines that are much too broad and can be used only in the isotopic analysis of uranium and probably a few other heavy elements.

The use of an arc reduces in all cases the range of concentration accessible for analysis.

The most widely used sources are tubes with cooled hollow cathodes (Fig. 4) and high-frequency electrodeless discharge. The use of the latter is particularly convenient in the analysis of the isotopic composition of gases.

3. MEASUREMENT OF INTENSITIES AND CONCENTRATIONS

In the first approximation it is possible to assume that the ratio of the intensities of the components of the isotopic structure equals the ratio of the concentrations of the corresponding isotopes. If the line has a hyperfine structure, the calculation must be made with allowance for the ratio of the intensities of the components of this structure. However, this connection between intensity and concentration can be used directly for precise determination only in exceptional cases. As a rule, errors are introduced in the intensity ratio by many secondary phenomena that take place in the sources of light and in the recording instrument. The causes of such errors are considered in many papers. We shall mention here but a few of these.

a) Source of light: separation of isotopes, dif-

ferent Doppler broadening, overlapping of the contours of the components of isotopic and hyperfine structure, self absorption, superposition of continuous and molecular spectra.

b) Spectral instrument: finite width of the instrument contour, scattered light.

Combinations of these causes may result in considerable systematic errors in the results of the analysis. As a rule, the importance of these errors increases with decreasing concentration of the determined isotope.

There are therefore two ways of determining the isotopic composition from the measured ratio of the intensities. The most reliable procedure is to plot a calibration curve, using standards of known isotopic composition, similar to the procedure used in ordinary spectral analysis.

A more attractive way is to ascertain the causes of all the errors in the intensity ratio and to introduce the necessary corrections in the measured ratios during the performance of the analysis. This dispenses with the need of using standard specimens and is of particular importance in those cases when standard specimens are not available. Unfortunately, the standardless method of analysis is seldom free of objections. The point is that it is usually impossible to determine all the corrections with a sufficient degree of accuracy, and if these corrections become comparable in order of magnitude with the measured intensity ratio, the resultant error may be unacceptably large.

The principal task of an experimenter developing a method of standardless analysis is therefore to choose the conditions of excitation and registration of the spectrum such that the magnitude of the necessary corrections is small enough to be negli-
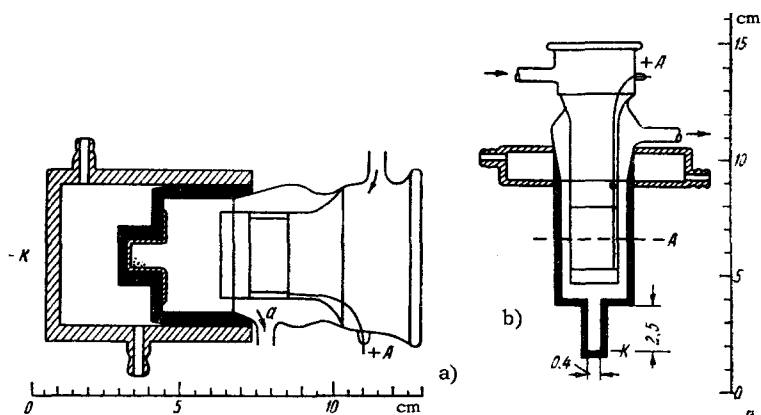

FIG. 4. Hollow-cathode tubes: a — water cooled, b — liquid-nitrogen cooled, A – – – line of immersion in liquid nitrogen, ⨏⨏⨏⨏⨏ — water-cooling jackets, → — direction of gas circulation.

gible, or such that it is at least possible to neglect the errors that creep into the result because of insufficiently accurate determination of the corrections. In other words, the systematic error that is introduced together with the correction should be substantially less than the random error in the measurement of the intensity ratio.

By way of examples of the application of the foregoing principles, let us consider the determination of the isotopic composition of several elements. We have selected investigations that have yielded, in our opinion, the best results.

Hydrogen. Most published papers are devoted to hydrogen, and a paper on its isotopic analysis was delivered at the Tenth All-Union Conference on Spectroscopy. This problem is the simplest, and at medium concentrations it is possible to employ the standardless method, described in detail earlier.[4] By now the sensitivity of this method has been raised[7] to such an extent, that it is possible to determine a concentration of 0.014% of deuterium in natural hydrogen. An analogous method can be used for the analysis of triple mixtures H—D—T (references 1 and 5) and for the analysis of pure tritium.[5]

Helium. The isotopic analysis of helium is considered in references 11 and 14. Artaud et al.[11] recorded the spectrum with a Fabry-Perot interferometer with a plane diffraction grating as a preliminary dispersion monochromator. The source of light was a hollow cathode cooled with liquid nitrogen. The scanning was by changing the air pressure in the etalon. The 6678 A He line was used as the analytical line. A sample record is shown in Fig. 5. The ratio of the widths of the lines (He^3 — 83.4 mK and He^4 — 72.7 mK) is close to $\sqrt{4/3}$, showing the principal role of Doppler broadening and a relatively narrow instrument contour. This makes it possible to measure the concentrations by using the ratio of the heights of the maxima of the curves, with allowance for Doppler broadening, or else directly by

using the ratio of the areas. No data on the sensitivity and accuracy of the method are reported by the authors.

Lithium. The same authors[12] have described the use of an analogous method in the analysis of a Li^6 — Li^7 mixture, with the 4603 A lithium line serving as the analytical line. The ratio of the widths of the lines Li^6 and Li^7 was found to be 1.082, which is the same as $\sqrt{7/6} = 1.081$ within the limits of errors. This makes it possible to perform the measurement without the use of standards, as in the case of helium. The low intensity of the line employed makes the analysis possible only if the Li^6 content ranges from 7 to 97%. This range can be increased by using the more intense 6707-A lithium line and by using standards. The accuracy of the method (for a Li^6 content near 12%) amounts to 0.5% (mean arithmetic error), i.e., approximately 5% of the Li^6 content.

Lead. Natural lead is composed of four isotopes: Pb^{204}, Pb^{206}, Pb^{207}, and Pb^{208}. The lines of the odd isotope Pb^{207} have a hyperfine structure. Therefore the problem of the isotopic analysis of this element is quite complicated. The most detailed investigation was carried out in our own laboratory.[8,9,10] We used apparatus with a hollow-cathode discharge tube as shown in Figs. 3 and 4. The samples of the recorded lines at different isotope ratios are shown in Fig. 6) (PbI line, λ = 4058 A). We investigated various procedures for processing the measurement results, both with and without the use of standard specimens. Better results are obtained when the hollow cathode is cooled with liquid nitrogen. Under these conditions the mass-spectrometric measurements agree with sufficient accuracy with the spectral data obtained by direct measurement of the maxima on the records, with allowance for the overlapping of the contours. Thus, the use of the standardless method is also possible here. However, the accuracy of the results is increased if at least one standard is used as a reference. A comparison of the results of the spectral and mass-spectroscopic measurements is shown in Table I. The relative sensitivity of the method is somewhat less than 1%, so that the isotope Pb^{204}, the content of which is always close to this value in natural lead, can be still determined, but with low accuracy (Table II). The analysis is performed on either metallic lead or lead iodide extracted from mountain rocks. The difficulties of chemical extraction make it necessary to try to reduce the amount of material necessary for the analysis to a minimum. It amounts to approximately 1 mg. Recently G. G. Kund, using electrolytic deposition of lead on the surface of the cathode, was able to reduce this amount to 0.01 mg.
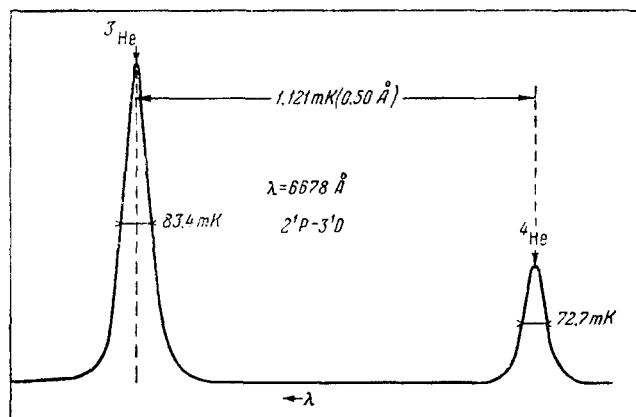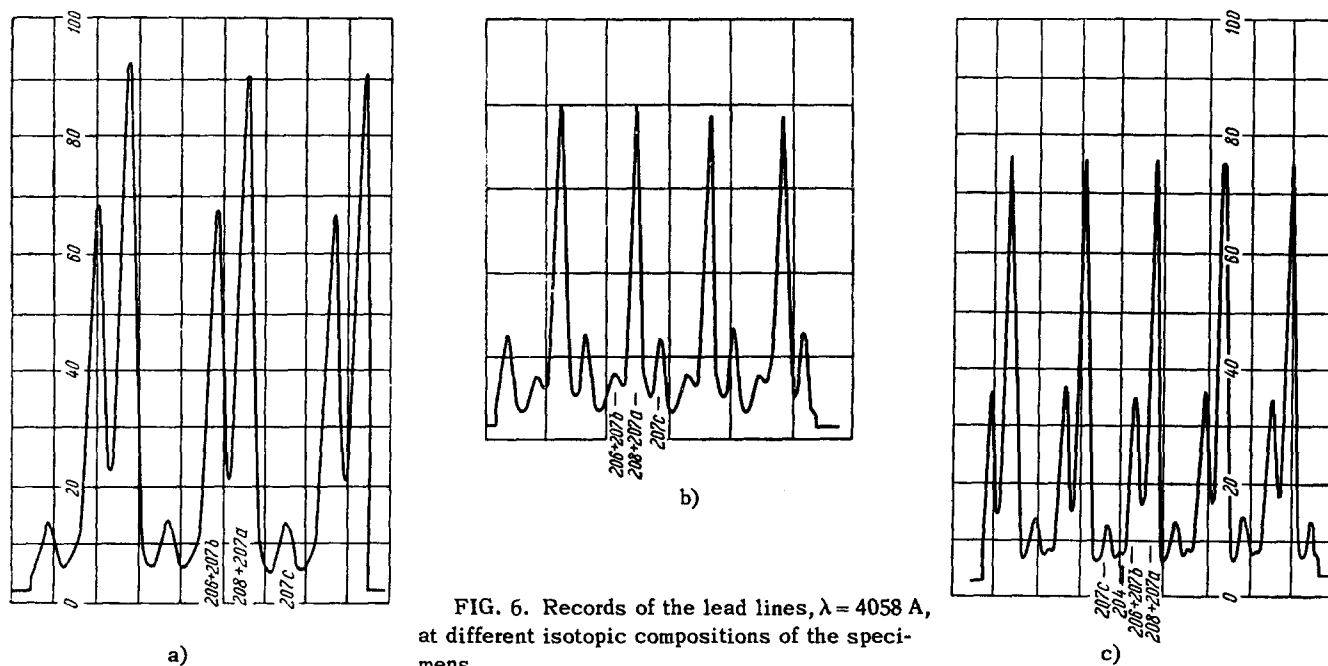

FIG. 5. Record of the helium lines.

a)

b)

FIG. 6. Records of the lead lines, λ = 4058 A, at different isotopic compositions of the specimens.

c)

TABLE I. Results of Analysis of Lead Samples

C_I —Concentration determined by spectral method

C_{II}—Concentration determined with mass spectrograph

$$R = \left| \frac{C_I - C_{II}}{C_{II}} \right| \cdot 100$$

Sample	Method	C_{208} (in %)	R (in %)	C_{207} (in %)	R (in %)	C_{206} (in %)	R (in %)
11	C_I C_{II}	32.0 30.8	3.9	17.6 17.1	2.9	49.5 51.3	3.5
147	C_I C_{II}	35.2 35.3	0.3	56.8 57.5	1.2	8.0 7.2	11
7	C_I C_{II}	52.0 51.7	0.6	21.1 21.9	3.6	25.4 25.0	1.6
68	C_I C_{II}	2.2 0.93	—	10.3 10.3	0.0	87.5 88.8	1.5

Uranium. At relatively large content of U^{235} (> 1%), the analysis can be performed with a dc arc and instruments of low resolution[3] (Fig. 7). Splendid results were obtained by Artaud et al.[11] at smaller concentrations. The analytical line chosen was the 5027.39-A uranium line. The comparison line was the U^{238} line located 0.5 cm^{-1} from the 5027.39-A line, on the long-wave side. This line is 70 times weaker than the 5027.39-A line, and is sufficiently homologous with it.

The records for different concentrations of U^{235} are given in Fig. 8, while a calibration curve, plotted against standards containing U^{235} in concentrations of 0.7% (α), 1.35% (β), and 2.5% (γ) is shown in Fig. 9. As can be seen from the diagram, the sample with a 0.12% concentration of U^{235} fits this

straight line satisfactorily. The error of the method, at U^{235} concentrations of approximately 1%, is 2%

TABLE II. Results of Analysis of Lead Samples for Pb^{204} Content

Sample	Method	C_{204} (in %)	R (in %)
7	C_I C_{II}	1.4 1.37	2
40	C_I C_{II}	1.0 1.10	9
11	C_I C_{II}	0.9 0.73	23
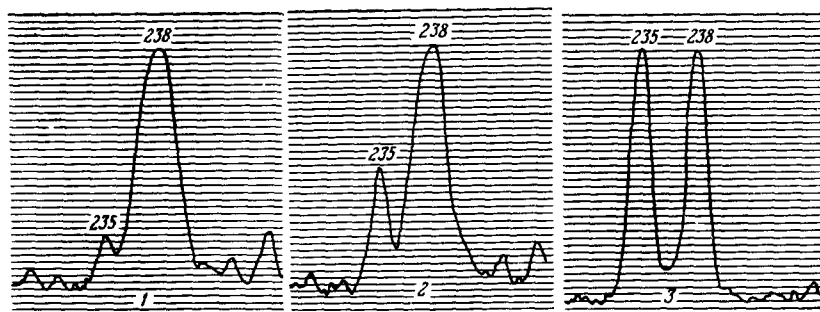
FIG. 7. Microphotogram of the 4424.37-A line of enriched uranium samples. Spectograph ISP 51-A[3]: 1 — 2.82% U^{235}, 2 — 9.52% U^{235}, 3 — 50% U^{235}.
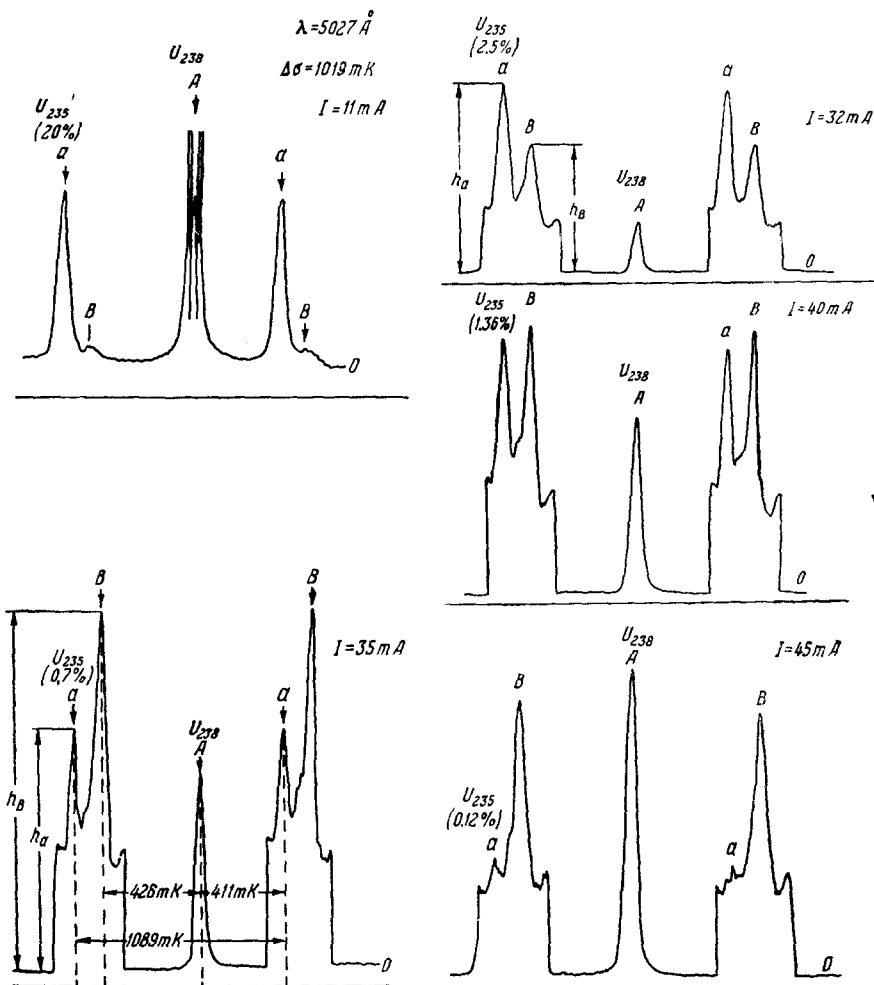

FIG. 8. Records of 5027-A uranium lines at various contents of U^{235}. B — comparison line.[11]

(relative error). It is somewhat greater at lower concentrations of U^{235}.

All the methods described do not differ in essence from the classical methods of spectral analysis.

However, other procedures are also possible, the use of which is of undoubted interest. One such possibility was pointed out by L. A. Tumerman at the preceding congress.[19] He proposed to intensify the effect of isotopic splitting of the lines by observing the radiation from ions accelerated by an electric field. In observations along the direction of motion of the ions, additional line shifts will appear, and the magnitude of these shifts depends on the mass of

the isotope. This effect can cause splitting that exceeds by many times the width of the ordinary isotopic structure. Unfortunately, no experimental verification of the possibilities of this method has yet been made.

Another possibility is indicated in reference 20. It is based on the fact that the coefficient of absorption of the vapor of the element, measured for a certain line of this element, will change with changing isotopic composition of the absorbing vapor (or with changing isotopic composition of the element in the source of light). The possibility of employing this phenomenon for analysis, was experimentally
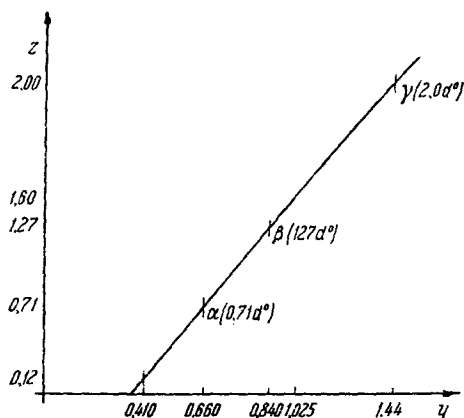
FIG. 9. Calibration curve for the determination of small concentrations of U^{235} (reference 11). $y = h_A/h_B$; ordinates: $z = x/(100 - x)$, where x is the concentration of U^{235} in the sample (%).

FIG. 10. Diagram of apparatus for absorption determination of the isotopic composition of lithium: 1) hollow cathode, 2, 4) optical projection system, 3) modulator, 5) monochromator, 6-9) photoelectric recording apparatus, 10) flame.

verified by E. N. Korennyĭ, Yu. I. Turkin, and the author in the case of lithium, and by G. V. Ostrovskaya in the case of hydrogen.

The apparatus for the analysis of lithium (Fig. 10) consists of a gas burner 10, in the flame of which a solution of the investigated specimen is introduced, a hollow cathode 1, containing lithium of known isotopic composition, and a modulator 3. The light passes through a small monochromator 5, which separates the resonance line of lithium from the spectrum, and strikes photomultiplier 6. The resonant amplifier 8 cuts off the dc component of the photocurrent due to the radiation of the burner itself. The amplified signal, after rectification, is fed to an indicating galvanometer.[9] A calibration curve is plotted against standards. A sample of the curve is shown in Fig. 11. The principal factor determining the accuracy of the method is the constancy of the operating conditions of the burner. To check the
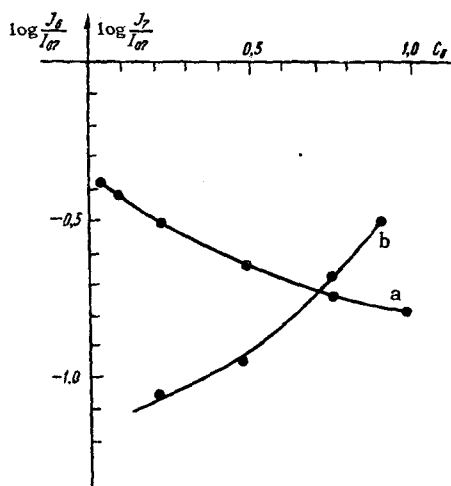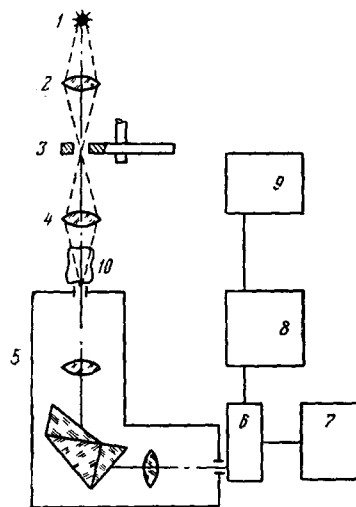

FIG. 11. Calibration curves for absorption determination of the isotopic composition of lithium: a — in source of Li^6, b — in source of Li^7.

reproducibility of the method, the concentration was determined several times in a specimen containing $30 \pm 0.6\%$ of Li^6. The results of the measurements yielded $C_6 = 32 \pm 2\%$ for this sample. An analogous setup was used to analyze the isotopic composition of hydrogen. Since there is no absorption in unexcited hydrogen, the light from the discharge tube containing the analyzed mixture was passed through the positive column of a glow discharge in hydrogen.

The results of the measurements have shown a clear dependence of the coefficient of absorption of the lines of the Balmer series on the isotopic composition of the hydrogen. However, no quantitative results of the investigations can yet be reported.

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27