SOVIET PHYSICS USPEKHI VOLUME 2(68), NUMBER 3 MAY-JUNE, 1959

*SPECTRAL ANALYSIS OF PURE MATERIALS**

L. V. LIPIS

Usp. Fiz. Nauk **68**, 71-80 (May, 1959)

ONE of the foundations of modern technical progress, particularly in the field of the new technologies — atomic, rocket, and semiconductor — is the manufacture of pure and extra-pure metals, compounds, and alloys. Permitting ourselves a far-fetched analogy, we can call pure materials the vitamins of modern industry.

It must be pointed out beforehand that the concept "pure material" has changed radically during the last ten or fifteen years. The requirement that a specimen contain not more than 10^{-3} or 10^{-4}% impurities by weight is no longer considered unusual or impossible. The number of impurities "harmful" to a given material has grown immensely. The concept "purity" has come to include requirements concerning the isotopic composition of the material. Isotopically-pure materials are no longer a rarity in modern technology.

In addition to extraneous impurity elements, in many cases it becomes important to preserve in a solid, such as a semiconductor, certain stoichiometric relations, violation of which changes the structure and consequently important properties. The presence of several impurity atoms is enough to make a semiconducting material unsuitable. For example, one impurity atom (say, boron) per 10^8 or 10^9 atoms of germanium changes greatly the conductivity of the germanium crystal. This means that the presence of 10^{-13} of impurity in one gram of germanium is already significant.

It is also known that a concentration of several times 10^{-5}% of boron in uranium or in some other fissionable material is most harmful to the nuclear properties of the latter, and a relatively small sum of impurities may make the chain reaction impossible.[1]

The increased demands on the properties of materials have been accompanied by improved production methods. Sensitive purification techniques and the development of materials with prescribed properties are no longer confined to the laboratory but have become large-scale manufacturing processes.

Naturally, methods for the control of pure materials cannot lag the manufacturing technology but must anticipate these requirements, to provide tests of the effectiveness of the procedures developed for purification and manufacture.

It is now well known from many published reports, for example, that nuclear materials must not contain impurities (for the most part light elements and certain rare earths) in concentrations exceeding 10^{-5} or 10^{-4}%. Many of the impurities can affect the mechanical and corrosion resistance of nuclear materials subjected to strong radiation.[2]

Even stricter requirements are imposed on semiconducting materials. Here impurities in concentrations of 10^{-6} or 10^{-7}% may prove to be so harmful as to render the materials unsuitable in some cases. Equally stringent requirements must be satisfied by materials used in rocket technology.

It is worth while citing still another branch of science, in which the determination of micro-impurities is a very substantial problem, although the objects of research cannot indeed be called "pure" materials. We have in mind modern biology and biophysics, in which knowledge of the distribution of metallic and other impurities important for normal functioning of the organism is quite essential for clarification of the causes of pathological changes resulting, say, from radioactive or other damage.

We can cite many such examples. We must therefore evaluate the capabilities of modern methods of analysis and the paths that lead to increased sensitivity and reliability of methods for the control of pure materials.

To evaluate the situation in spectral analysis of pure materials, allow me to compare the youngest and most rapidly growing method — radioactivation method — with the method of spectral analysis, which is much older and therefore slower to develop.

An examination of the most recent data, as reported at the Second Geneva Conference on Peaceful Use of Atomic Energy in September 1958, shows that radioactivation analysis has made considerable progress. Its undisputed advantage is the freedom from worry over extreme purity of the reagents

*Paper delivered at the Twelfth All-Union Conference on Spectroscopy, November, 1958.

TABLE I. Results of determination of impurities in polycrystalline silicon

Impurity contents in percent							
Mn	Ni	Cu	Zn	Ga	Rare Earths (based on Eu)	As	Sb
$2 \cdot 10^{-6}$	$1.3 \cdot 10^{-5}$	$1.8 \cdot 10^{-5}$	$3.1 \cdot 10^{-5}$	$4.5 \cdot 10^{-7}$	9.10^{-7}	$1.2 \cdot 10^{-5}$	$8 \cdot 10^{-5}$

and standards, a very troublesome difficulty in chemical and spectral methods. As can be seen from Table I,[3] the impurity content in silicon can be determined with a very high sensitivity, with a relative error of 30 to 40 percent. Quite interesting is the work by Kent, Cali and Thompson on neutron-activation analysis of silicon, in which 12 elements were determined, with a sensitivity of $10^{-5} - 10^{-9}\%$, by chemical separation of the radioactive impurities,[4] In the somewhat obsolescent paper of Meinke,[5] a comparison was made of the sensitivities of various analytical methods. If one disregards the specific conditions of the analysis, as was done by Meinke, it must be admitted that the radioactivation method is now the most sensitive. By means of a good radioactivation method it is possible to obtain, even in materials that are difficult to analyze, an absolute sensitivity of impurity determination of 10^{-17} g, and in unusual cases 10^{-20} g, i.e., on the order of several tens of atoms.

It must be recognized, naturally, that the possibilities of using activation analysis are not so broad as to permit the use of this method for regular manufacturing control. In this respect, it can replace spectral analysis only in individual cases. Nevertheless, its principal potentialities, as shown in the cited examples, are very great.

The question arises of whether spectral analysis can compete successfully with these other most recent methods. In many practical problems the spectral method is fully capable of coping with the demands, and requires no replacement in view of its simplicity, reliability, and availability of technical means. In those cases, however, when its sensitivity is no longer sufficient, there are possibilities of increasing it considerably. In this respect, the potential of spectral analysis is far from exhausted.

It is known that the absolute sensitivity of determination of many elements by the spectral method amounts to $10^{-8} - 10^{-9}$ g, in exceptional cases 10^{-14} g, with a total sample weight of 10^{-11} g. For example, the limit of detection of sodium amounts to 10^{-10} g and less.

It is interesting to follow the development of the methods of spectral analysis during the past ten or fifteen years, using as an example an element of great importance in atomic and semiconductor technology, boron. In 1946 it was believed that the limiting sensitivity for boron amounts to approximately 10^{-2} or $10^{-1}\%$. Boron was classified in the same series as zirconium, arsenic, tungsten, tantalum, and uranium.[6] It was noted furthermore that to attain this sensitivity some of the technical means have to be pushed hard and the spectroscopist must have a high degree of skill.

We know now that already in 1947 the sensitivity of determination of boron, even in objects rather difficult to analyze, could be increased to 10^{-5} or $5 \times 10^{-6}\%$.[7]

In a recent paper by Morrison and Rupp[8] on the determination of boron in semiconductor silicon, a sensitivity of $10^{-7}\%$ was obtained for samples weighing 1 g, with an acceptable relative accuracy of $20 - 25\%$. The authors state that a more thorough purification of the reagents (essentially NaOH) used in the chemical enrichment, will make possible a sensitivity of $10^{-8}\%$, i.e., detection of 10^{-10} g of boron, a quantity close to the limit of spectroscopical determination. Thus, after 10 or 12 years the sensitivity in the determination of boron has increased by 5 or 6 orders of magnitude, a remarkable accomplishment in spectral analysis.

One can, naturally, cite many such examples of known growth in the sensitivity of methods of spectral analysis, but what is more important at the present time is an evaluation of the possibilities of further increase in sensitivity. Obviously, to answer this question it is necessary to examine, albeit in the most general outline, the present status of sensitivity in spectral analysis, i.e., to evaluate the methods necessary to reach the present-day level. Three important factors must be noted here:

1) The known progress in the design and construction of spectral instruments with large angular dispersion and a noticeably increased practical aperture ratio. This pertains primarily to diffraction instruments. We know, however, that by improving the instruments and selecting them ju-

diciously we can increase the sensitivity by a factor of several times, but not by one order of magnitude and more. This must always be borne in mind.

2) The noticeable improvement in the quality of photographic materials, principally progress in the use of photoelectric methods of spectrum registration. This method affords an increase in sensitivity in many cases, but the ratio of signal to background can obviously not be increased beyond a certain limit.

3) The fact that the major progress was made in methods of spectral analysis, i.e., sample-preparation procedures and light sources, whereas the light sources themselves have undergone no noticeable change or improvement during the past years. An analysis of the facts that pertain indeed to this aspect of the matter, will permit us a better estimate of the possibilities of raising the sensitivity of spectral analysis.

One feature of the last few years has been the rapid development of methods of enriching samples prior to ordinary spectral procedure. Much less was done to improve the light sources themselves so as to allow direct methods of spectral analysis to yield the same results as methods employing the enrichment procedures.

Particularly great progress was made in the development of chemical methods of impurity concentration. This is due primarily to the rapid development of extraction and chromatographic methods of separation. The possibility of monitoring of the enrichment process with radioactive tracers has rapidly accelerated the development of chemical and physical separation methods.

A good example is the already-mentioned work by Morrison and Rupp on the determination of boron in silicon. To concentrate the boron, the silicon sample was dissolved in an excess of sodium hydroxide. The excess sodium was then removed by dialysis and the dissolved sodium borate was washed out of the silicic acid. The suspended residue of silicic acid, containing the sodium borate together with the internal standard — indium — was burned in a dc arc (21 amp) in an argon atmosphere. The spectrum was photographed with a medium Bausch and Lomb spectrograph. The procedure was well thought out and the correction for idling was quite small. Using this method and an approximately hundred-fold concentration, a sensitivity gain of 2 or 2.5 orders of magnitude was obtained over the direct method, determination of boron in silicon, with a relative error of 20 or 25%.

Another successful concentration of a large group of impurities was attained by Koch,[9] who used multiple extraction with three extracting agents at different values of the pH of the sample solution. The extracted impurities were then concentrated in a small batch of BeO, which together with a KNO_3 buffer was placed in a carbon electrode and burned in a source of light (Feissner spark or arc) under ordinary conditions. In this manner Koch determined simultaneously 24 to 26 elements in one-gram samples of zirconium, aluminum, selenium, and titanium, at a sensitivity of $\sim 10^{-5}$% and a relative error of ± 5 to 15%.

A characteristic feature of this method of increasing the sensitivity is a certain refinement in the chemical methods of enrichment and the relative simplicity and routine nature of the spectral-analysis procedures. Essentially, the enriched concentrate, mixed with a standard and with carbon powder or another buffer, is introduced into the crater of the electrode of a dc arc. The air atmosphere is sometimes replaced by argon or some other inert gas. In some investigations the concentrate obtained after enrichment is deposited as a thin layer on the end face of a carbon or copper electrode and is burned in an arc or a spark. Included among such investigations are the papers of Fred, Nachtrieb, and Tomkins on the analysis of plutonium.[10] The original method of securing a sample in the form of a thin surface layer on a carbon electrode was developed by Zil'bershtein.[11] The same method of burning a thin layer of concentrate was used by A. N. Zaĭdel and his associates in the determination of rare earths in uranium and thorium.[12]

We must also emphasize here that the number of successful investigations, employing separation of the base by precipitation from the solution or by other methods, has increased in recent years. These methods have previously raised some objections, but with cautious and correct use, controlled with the aid of radioactive tracers, it becomes possible to concentrate simultaneously a large number of impurities from the base, provided a precipitant carefully chosen for this base is used. Much was done in our country by A. G. Karabash and Sh. I. Peĭzulaev towards the development of such methods.[13]

Another enrichment method, based on the phenomenon of fractional distillation, yielded a considerable number of good analysis methods and was developed in the past 10 or 12 years by many investigators. Noteworthy here is the important role of Soviet scientists, primarily A. K. Rusanov and the late S. A. Borovik, who were among the first to use fractional distillation in a dc arc to

improve the conditions of the analysis of ores and mineral raw material. Rusanov's systematic investigations of the evaporation of samples from the crater of a carbon arc were in many respects the basis for subsequent work on the improvement of analysis methods.[14]

The phenomenon of fractional distillation, intensified in a suitable manner, was the principal factor in the development of a method of analysis of nuclear materials, titanium, tungsten, molybdenum, and other metals, which play an important role in the production of refractory alloys.

To intensify the fractionization, Scribner and Mullin[15] used the method of introducing a "carrier" in an analysis of uranium by fractional distillation in a dc arc. However, in subsequent investigations, in which the method of fractional evaporation of the impurities was used, it was possible to avoid the use of a carrier without loss in sensitivity and accuracy of the determinations, and even to demonstrate that the carrier did not play a substantial role in these modified methods.[16]

Nevertheless, an investigation of the role of the carrier can, in our opinion, be the starting point for further improvement in methods of analysis of pure materials.

A considerable step forward was the development, by Soviet investigators, of a method in which the extraction of the impurities was separated from the excitation of the spectrum, making it possible to concentrate the impurities and to produce the spectrum under controllable and optimum conditions. This method served as the base for many investigations developed during the past 10 years, which have insured manufacture and control of nuclear materials and many other pure metals and their compounds. The principal role in the development of this progressive method of evaporation was played by the investigations of S. L. Mandel'shtam and A. N. Zaĭdel and their associates.[7,17] These investigations are very well known, and there is no sense in mentioning them in detail.

To illustrate the results obtained with the aid of the evaporation method let us cite one published table. As can be seen from Table II, there is a certain advantage in the evaporation method over the Scribner method. It should be pointed out that this advantage is much greater than appears at first glance, since different criteria were used to estimate the sensitivity in the two methods, namely: we consider the limiting sensitivity to be that at which reproducibility of the analysis is insured within a 20 – 25% interval of mean-squared error of a single determination. Obviously, that in the semi-quantitative estimate, characteristic of the Scribner method, the "sensitivity" can be increased by a factor of 5 or 10.

TABLE II. Comparison of absolute sensitivities of the methods of evaporation and fractional distillation with a "carrier"

Element	Absolute sensitivity of the evaporation method in mγ (10^{-9} g) (50 mg sample)	Absolute sensitivity of the Scribner and Mullin method in mγ (100 mg sample)
Au	15	30
As	500	500
Ag	5	5
Al	250	500
B	5	8
Be	5	10
Cd	10	7
Co	25	100
Cr	100	300
Cu	10	30
Fe	50	100
Ge	15	20
In	15	50
K	100	200
Li	1	10
Mg	50	50
Mn	5	100
Na	50	50
Ni	50	200
Bi	2	50
Pb	20	100
P	500	5000
Sb	100	1000
Si	50	1000
Sn	10	100
Zn	100	200

A characteristic feature of this table is that for a considerable group of elements, determined simultaneously, the absolute sensitivity lies in the interval of several times 10^{-9} g. Recognizing that the table is based on the results of a group determination of impurities in such difficult materials as uranium, thorium, zirconium, and others, the capabilities of the method of physical enrichment become immediately clear. A tenfold increase in the absolute sensitivity, for individual elements, is apparently not an exceedingly difficult problem. The use of various additives, stimulating the formation of volatile compounds, also contributes to an increase in sensitivity.

As in the case of chemical methods of impurity concentration, it is possible and sometimes useful to employ separation of the principal component by evaporation and concentration of the impurities on an extraneous collector or else on the residue of the base. This procedure was successfully used

by L. M. Ivantsov and E. B. Gerken[18] in the analysis of molybdenum, and also by D. M. Shvarts et al.[19] to determine the impurities in semiconductor materials, zinc, tin, and thallium. The relative sensitivities obtained were $5 \times 10^{-6} - 8 \times 10^{-5}\%$ for lead, copper, tin, bismuth, antimony, and cadmium.

Keck et al.[20] used, in the analysis of silicon, the method of melting and sublimation of a portion of a silicon crystal in high vacuum and burning the SiO_2 residue. In this case the enrichment coefficient ranges from 50 to 200 and the sensitivity of determination is suitably increased to $10^{-6}\%$ for aluminum, calcium, and magnesium and to $10^{-5}\%$ for titanium and zinc.

The foregoing examples illustrate quite clearly the present status of the sensitivity of spectral analysis. Thus, using enrichment methods, it is possible to obtain for a considerable group of elements a relative sensitivity of $\sim 5 \times 10^{-6}$ to $10^{-5}\%$. In individual cases it is possible to attain a relative sensitivity of 10^{-7} or $10^{-6}\%$. The absolute sensitivity of determination ranges from 10^{-11} to 10^{-8} g.

It follows therefore that spectral analysis is faced with the problem of increasing the sensitivity by approximately 100 times. Undoubtedly a solution to the problem lies in a correct utilization of the sources of light. We have already mentioned that in the method of fractional distillation the principal role was played by the carrier. Investigation of the role of the carrier[16] and many other interesting investigations (Ya. D. Raĭkhbaum,[21] N. A. Makulov,[22] and others) have shown the decisive importance of the removal of substance from the discharge zone. Let us examine in greater detail the results obtained in the clarification of the role of the carrier in the method of fractional distillation and in the method of evaporation. We lean here principally on the research by A. N. Zaĭdel with his associates[16] and Yu. I. Belyaev and É. E. Vaĭnshteĭn.[23]

The principal conclusion that can be reached by investigating the effect of the carrier on the sensitivity with which the impurities can be determined is the following: The carrier changes the time variation of the diffusion and convection of a substance from the discharge plasma, but does not change the rate of evaporation, although it does influence the steady-state temperature of the plasma and of the electrodes with the sample. This conclusion is also confirmed by the already-mentioned investigation of Belyaev and Vaĭnshteĭn, which is quite interesting, both in the procedure and in the results. They succeeded in showing that the presence of a carrier (in other words, of a macro-component) leads to a change in the spatial distribution of the impurities in the discharge zone and changes correspondingly the rate at which they are carried away from this zone. Carriers of the Ga_2O_3 type are characterized by a symmetrical dome-like distribution in the discharge zone with a sharp maximum in the center. Furthermore, a concentration of impurities is observed in this central discharge zone, even though each impurity by itself is characterized, in the absence of a carrier, by its own distribution law. This circumstance prevents rapid removal of the substance from the discharge zone and results in a non-selective increase in sensitivity. I do not speak here of other favorable effects of the carrier (stabilization of the arc discharge or of the electrode temperature during the time of evaporation of the carrier, etc.).

Gamma-ray photographs of zinc, sodium, gallium, and cobalt (Fig. 1) illustrate clearly the

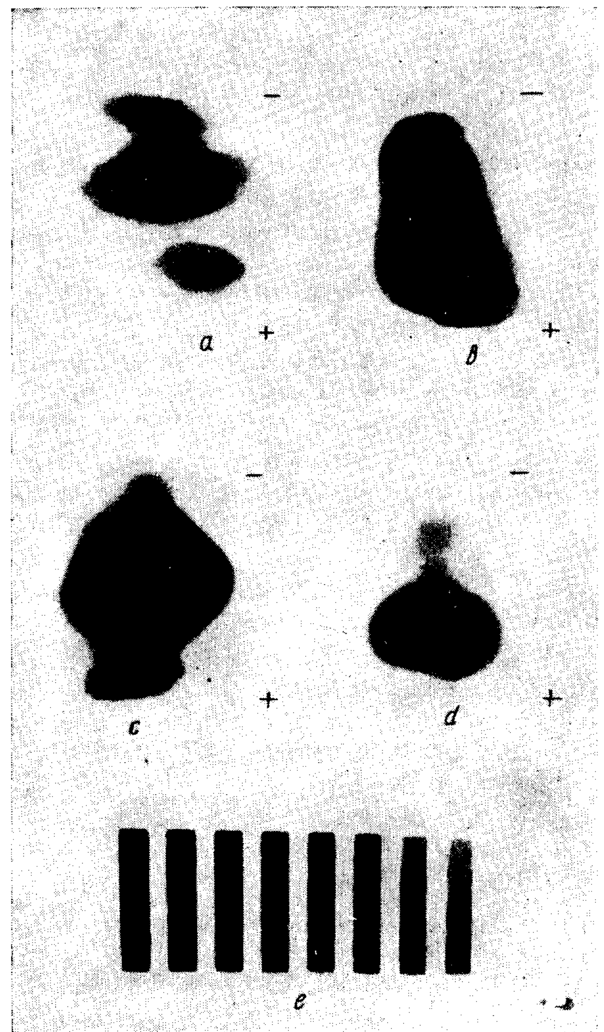

FIG. 1. Gamma-ray photograph of the radioactive isotopes Zn^{65}, Na^{24}, Ga^{72}, and Co^{60}, characterizing the distribution of these elements, evaporated from oxides of uranium, in the plasma of a dc arc (8 amperes). a – sodium, b – cobalt, c – gallium, d – zinc, e – density markers (after Yu. I. Belyaev and É. E. Vaĭnshteĭn[23]).

character of the distribution of these elements in a dc arc. Similar conclusions were drawn by Ya. D. Raĭkhbaum[24] in a study of the processes in the arc and in an investigation of the influence of "third" elements on the intensity of lines of individual impurities. He believes that when a large amount of metal vapor enters into the discharge zone, the speed of diffusion and convection of the impurities from the discharge plasma is reduced. In addition to these new investigations, attention was called also in many of the older investigations to the useless removal of substance from the discharge zone. A simple calculation shows that in the best case only 0.1 to 1% of the amount of impurity entering into the discharge participates at least once in the emission of light and in the formation of the spectrum of the determined element. The remainder is irretrievably lost. Were it possible to cause the atoms and ions of the determined element to remain in the discharge zone for a longer time and to participate more than once in the formation of the spectrum, a tremendous gain would be achieved.

In our opinion, in addition to the so called guiding "carriers" in open sources of light, it is necessary to resort more to closed carriers, which operate at reduced pressures, such as hollow cathodes or high-frequency discharge. The complications in the operating techniques are fully justified by the increased sensitivity. By way of an example we can cite a paper delivered to the Second Geneva Conference on Peaceful Uses of Atomic Energy, in September of this year, describing a direct analysis of ZrO_2 in a hollow cathode.[25] As can be seen from Table III, these results are not inferior to the better methods that involve enrichment. In addition, this paper contains a solution to the problem of simultaneous determination of calcium, aluminum, titanium, and vanadium, which cannot be determined by the evaporation method. It is possible simultaneously to determine the halogens, say fluorine, with a sensitivity of 10^{-4} to 10^{-5}%. If the procedure is modified somewhat, namely, if the cathode is cooled instead of used hot, then, by placing concentrates of samples without carrier, the sensitivity can be increased by one more order of magnitude. No less promising for the analysis of small samples or concentrates is, in many cases, high-frequency electrodeless discharge. Samples weighing several micrograms can be used for a long time in this case.[26] An analytical application of this method may become quite promising.

One of the important advantages of enclosed sources is the exceedingly small consumption of base material during the excitation process. In fact, is it really worth while to expend so much effort in concentrating an impurity, and then burn fractions of a milligram of the hard-earned concentrate together with several tens of milligrams of carbon or graphite (by placing the concentrate in the crater of an arc) and contaminate the enriched sample with random impurities? It is clearly necessary to exert every effort to reduce the danger of uncontrolled contamination in the source of light, and this can be done when the material of the electrode does not participate or hardly participates in maintainance of the discharge. This can be attained best of all in discharge tubes with hollow cathodes or in the electrodeless high frequency discharge.

Thus, combining the modern enrichment methods with the use of enclosed sources of light is an urgent problem of spectral analysis, the solution of which will undoubtedly lead to a further increase in the sensitivity of determinations by one or two orders of magnitude above the existing level.

TABLE III

Element	Element lines, A	Lines of internal standard, A	Sensitivity, %	Sensitivity by the evaporation method[7,17] %
Al	I 3082.1	I 3044.0	$1\cdot10^{-4}$	—
Be	I 2348.6	II 2363.8	$1\cdot10^{-5}$	$1\cdot10^{-5}$
B	I 2497.7	2500.7	$1\cdot10^{-5}$	$1\cdot10^{-5}$
V	I 3184.0	I 3044.0	$1\cdot10^{-3}$	—
Bi	I 3067.7	I 2719.6	$3\cdot10^{-5}$	$5\cdot10^{-6}$
Fe	II 2395.6	II 2363.8	$3\cdot10^{-4}$	$2\cdot10^{-3}$
Cd	I 2288.0		$1\cdot10^{-5}$	$1\cdot10^{-5}$
K	I 7664.9		$1\cdot10^{-4}$	$1\cdot10^{-3}$
Co	I 3405.1		$1\cdot10^{-4}$	$5\cdot10^{-5}$
Si	I 2881.6	I 3044.0	$1\cdot10^{-4}$	—
Li	I 6707.8		$3\cdot10^{-6}$	$2\cdot10^{-6}$
Mg	II 2790.8	II 2580.3	$1\cdot10^{-5}$	—
Mn	II 2576.1	2500.7	$3\cdot10^{-5}$	$1\cdot10^{-5}$
Cu	I 3247.5		$3\cdot10^{-5}$	$5\cdot10^{-5}$
As	I 2350.0		$1\cdot10^{-4}$	—
Na	I 3302.3		$3\cdot10^{-4}$	
	I 5889.9		$3\cdot10^{-4}$	$1\cdot10^{-3}$
Ni	I 3050.8	I 3044.0	$3\cdot10^{-4}$	$1\cdot10^{-4}$
Sn	I 2840.0	I 2719.6	$1\cdot10^{-4}$	$5\cdot10^{-5}$
Pb	I 2833.1	I 2719.6	$1\cdot10^{-4}$	$5\cdot10^{-5}$
Ag	I 3280.7		$1\cdot10^{-5}$	—
Sb	I 2528.5	2500.7	$1\cdot10^{-4}$	$1\cdot10^{-4}$
Ti	II 3349.0	I 3044.0	$1\cdot10^{-3}$	—
Cr	II 2835.6	II 2580.3	$1\cdot10^{-4}$	$2\cdot10^{-4}$
Zn	I 3345.0		$1\cdot10^{-4}$	$1\cdot10^{-3}$

Note. The sensitivity to Na, Cu, Zn, and Mg is limited by contamination of the base of the standard.

It is also possible that under conditions of enclosed sources of light, operating at reduced pressure, it will be possible to use external control fields, making use of the experience accumulated in the investigation of hot plasma. In any case, there is no doubt that a friendly competition between the various physical methods of analysis, leading to mutual beneficial exchange of ideas in technical means, will not find spectral analysis lagging.

[1] H. D. Smyth, Atomic Energy for Military Purposes, Princeton Univ. Press, 1945.

[2] A. S. Zaĭmovskiĭ et al., Атомная энергия (Atomic Energy) **5**, 412 (1958).

[3] Yu. V. Yakovlev, A. I. Kulak, et al. Paper delivered at the Second Geneva Conference on Peaceful Uses of Atomic Energy, No. 2023, Geneva, 1958.

[4] Kant, Cali, and Thompson, Anal. Chem. **28**, 1867 (1956).

[5] W. W. Meinke, Science **121**, 177 (1955).

[6] S. L. Mandel'shtam, Введение в спектральный анализ (Introduction to Spectral Analysis) M., 1946.

[7] Mandel'shtam, Semenov, and Turovtseva, J. Analyt. Chem. (U.S.S.R.) **11**, 9 (1956).

[8] G. H. Morrison and R. L. Rupp, Anal. Chem. **29**, 892 (1957).

[9] O. G. Koch, Microchimica Acta **1**, 3, 92, 151, 347, 402 (1957).

[10] Fred, Nachtrieb, and Tomkins, J. Opt. Soc. Am. **37**, 279 (1947).

[11] E. I. Zil'bershteĭn J. Tech. Phys. (U.S.S.R.) **25**, 1491 (1955).

[12] A. N. Zaĭdel', N. I. Kaliteevskiĭ, et al. Spectral Determination of Rare Earths in Beryllium, Thallium, and Uranium. Редкоземельные элементы (Rare-Earth Elements), U.S.S.R. Acad. Sci. Press, M., 1958.

[13] Sh. I. Peĭzulaev A. G. Karabash, et al. Заводская лаборатория, (Plant Laboratory), No. 6, 723 (1958). Труды Всесоюзн. конференции по применению изотопов в науке и народном хозяйстве, (Trans. All-Union Conf. on Application of Isotopes in Science and National Economy), U.S.S.R. Acad. Sci. Press, M., 1958.

[14] A. K. Rusanov, Спектральный анализ руд и минералов (Spectral Analysis of Ores and Minerals), Gosgeolizdat, M., 1948.

[15] B. F. Scribner and H. R. Mullin, J. Bur. Stand. **37**, 379 (1946).

[16] A. N. Zaidel' et al., Оптика и спектроскопия (Optics and Spectroscopy) **2**, 28 (1957).

[17] A. N. Zaidel' et al., J. Analyt. Chem. (U.S.S.R.) **11**, 21 (1956); **12**, 17 (1957); Оптика и спектроскопия (Optics and Spectroscopy) **3**, 16 (1957).

[18] L. M. Ivantsov and E. B. Gerken, Материалы 2-го Совещания спектроскопистов цветной металлургии, (Proc. Second Conf. of Nonferrous-Metallurgy Spectroscopists), M., 1957. Труды X-го Совещания спектроскопии (Trans. Tenth Conf. on Spectroscopy), vol. II, L'vov, 1958.

[19] D. M. Shvarts et al., Доклады на 3-м Совещании спектроскопистов цветной металлургии (Papers at Third Conf. of Nonferrous-Metallurgy Spectroscopists), M., December 1957.

[20] Keck, MacDonald, and Millichamp, Anal. Chem. **28**, 955 (1956).

[21] Ya. D. Raĭkhbaum Доклад на 3-м Совещании спектроскопистов цветной металлургии (Paper at Third Conf. of Nonferrous-Metallurgy Spectroscopists), M., December 1957.

[22] N. A. Makulov, ibid.

[23] É. E. Vaĭnshteĭn and Yu. I. Belyaev, J. Analyt. Chem. (U.S.S.R.) **13**, 388 (1958).

[24] Ya. D. Raĭkhbaum. Доклад на XII Совещании по спектроскопии (Paper at Twelfth Conference on Spectroscopy), M., November 1958.

[25] Yu. D. Korovin and L. V. Lipis, Оптика и спектроскопия (Optics and Spectroscopy) **5**, 334 (1958); Paper at Second Intl. Conf., Geneva, Sept. 1958.

[26] W. F. Meggers, F. O. Westfall, et al., J. Bur. Stand. **44**, 447 (1950); **58**, 41 (1957); **61**, 95 (1958); Anal. Chem. **28**, 616 (1957).

Translated by J. G. Adashko