Information

Permanent working collection of high purity substances

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The work of the collection of high purity substances in the research on the composition of impurities in high purity substances is evaluated. On the basis of the materials available, the present state and future perspectives of the study of high purity substances are discussed.

1. Introduction

The All-Union permanent collection of high purity substances was founded in 1974 at the Institute of Chemistry of the Academy of Sciences of the USSR by the Presidium of the Academy of Sciences of the USSR.[1] The reason for its establishment was the necessity of having the most exhaustive and reliable data possible on the level of purity of high purity substances being obtained in the country. The exhibition continues its work nowadays at the Institute of Chemistry of High Purity Substances of the RAS (Nizhnii Novgorod), which was founded in 1987 on the basis of the Department of Volatile Compounds of Metals and High Purity Substances of the Institute of Chemistry of the Academy of Sciences of the USSR. The purpose of the collection is to monitor the level of purity of compounds and to reveal and analyze problems of the chemistry of high purity substances. A special research program is being realized to fulfill this aim. This program includes:[1–3]

- collection of samples of the purest substances that are synthesized in research organizations or produced by industrial enterprises;
- analysis of these samples in order to obtain the most exhaustive and reliable information possible concerning their composition and any impurities present; certification of samples;
- creation of a data base of high purity substances; this data base includes results of analysis of samples from the collection, as well as data from various normative documents (standards, technological norms) and from catalogues of Western companies that sell high purity substances;
- development and use of methods of analysis of data on impurities present; these methods should make it possible to study the general tendencies of the composition of impurities in high purity substances and to predict the content of impurities in samples.

2. Sampling

The collection established and maintains contacts practically with all organizations of Russia and other countries of the FSU that are involved either in research or into production of high purity substances and materials. The list amounts to about 100 organizations total, including academic and applied research institutes; research divisions of universities and other institutes of higher education; and industrial enterprises.

Nowadays the collection consists of about 500 samples of substances and materials. They represent mostly two classes of substances: elements and volatile compounds of elements — volatile inorganic hydrides, halides, and organometallic compounds. Table 1 shows the distribu-

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tion of the samples among the various classes of substances. Many organizations that have maintained constant contact with the exhibition throughout all 20 years of its existence donate samples repeatedly. This makes it possible to have an idea not only of the purity of similar samples, but also of the dynamics of the increase in purity.

3. Control analyses and certification of samples

In order to obtain the most exhaustive and reliable information possible concerning the fine composition of samples submitted to the collection, along with the data obtained from the producer of the sample in question, control analyses are carried out. Practically all of the leading analytical laboratories of Russia participate in this additional testing of samples. The list of these organizations includes: laboratories of Institutes of the Academy of Sciences (Institute of Chemistry of High Purity Substances of the RAS, Institute of Geochemistry and Analytical Chemistry of the RAS, Institute of Problems of Technology of Microelectronics and High Purity Materials of the RAS, Institute of General and Inorganic Chemistry of the RAS, Institute of Inorganic Chemistry of the Siberian Branch of the RAS) and those of the applied Institutes (State Research and Design Institute of Rare Metals Industry, GIDROZVETMET, Research Institute of Chemical Reagents and High Purity Substances, Research Institute of Materials Technology).

When these control analyses are performed, the collection does its best to obtain information on the maximum number of impurities. The impurities that are usually present in relatively larger quantities and for this reason determine the total amount of impurities present are analyzed in every case when possible. These impurities were listed when the collection was established and the list is still in use with some minor additions.[2]

For samples of solid elements this list includes: gas forming elements (H, C, N, O); widely spread elements (Na, K, Mg, Ca, etc.); the most abundant element of each subgroup of the Periodic System; neighbouring basic substances along the period; analogous impurities and impurities that are difficult to remove during purification. Semi-conducting materials, mainly silicon and germanium, are analyzed to determine the difference concentration of the charge carriers, and the content of small electroactive impurities, and deep centers.

For samples of volatile substances the following components are determined: contamination by widely distributed elements (non-volatile forms); water; oxygen; traces of organic substances; impurities that are difficult to remove; and generic impurities (molecular forms). Also analyzed are impurities in the form of dispersed particles of sub-micron size.[3]

For metals the relative residual electrical resistance at the temperature of liquid helium is used as a measure of purity. This quantity is closely related to the amount of impurities present. However, special investigations have determined that residual electrical resistance can not be used as an integral measure of purity level (and especially of total purity). The value of residual electrical resistance depends upon the chemical and phase form of an impurity, the homogeneity of distribution of it throughout the sample, and crystal-lattice imperfections.[4]

Table 1. Samples presented from the collection

Class of substance	Number of substances	Number of samples
Elements, as:	75	336
solids	68	310
gaseous	7	14
SS*	7	12
Volatile substances, as:	68	147
halides	27	78
hydrides	7	17
OMC**	30	46
organic	3	6

*SS — standard samples of high purity substances.
**OMC — organometallic compounds.

In Table 2 are presented some characteristics of analytical methods used for analysis of samples of the collection. These characteristics were obtained by statistical treatment of results of control analyses. Starting from this point all analytical results are presented as atomic per cents. For analysis of solids, mass spectrometry and gas chromatography (for volatiles) were mostly used. These are the most universal methods in the sense of number of impurities determined simultaneously. During control analyses it is possible to determine some of the impurities quantitatively. Let us designate this part as the measured content (C_m). The content of the other impurities is below the detection limits of the analytical methods in use. In this situation the results of the control analysis can be expressed as the respective detection limit (C_l). The corresponding mean values, which are given in Table 2, represent detection limits that can be achieved in real practice. These values are 1—1.5 orders of magnitude lower (in the case of impurities of gas-forming elements this value equals 1—2 orders of magnitude) than the corresponding values reported in the literature; the latter are characteristics of the fundamental possibilities of each method. Table 2 indicates that the mean detection limits are close to the mean impurity contents (see also Fig. 2). This causes the fraction of determined impurity content in the total number of analyses (d_m) to be much lower than unity. The highest ratio of determined impurity content to the total number of analyses is found in gas chromatogra-

Table 2. Some characteristics of analytical methods

Analytical method	N_a	n	δ_m	M_l	M_l-M_m
MC	319	31	0.33	5.0	0.8
AC	157	14	0.36	5.4	0.6
AA	63	17	0.29	6.9	0.7
ГЭ	144	2	0.62	2.5	0.3
ГХ	214	4	0.47	4.8	1.3
ХС	117	13	0.28	6.0	0.4

Note. Abbreviations used for designating methods of analysis of solid elements: MS — mass spectral methods of analysis, AS — atomic spectral methods of analysis, AA — activation methods of analysis, GE — methods of determination of impurities of gas-forming elements. Designations for methods of analysis of volatile substances: GC — gas chromatographic methods, CS — chemical spectral methods of analysis. N_a — number of analyses performed by a particular method. n — average number of impurities determined simultaneously. d_m — fraction of determined impurities of the total number of impurities monitored. $M_l = <-\log C_l>$ — mean value of the detection limit on a logarithmic scale, $M_m = <-\log C_m>$ — mean value of measured content of impurities.

phy. Activation and spectrochemical analyses have the lowest detection limits. The latter often uses concentration of impurities. The number of elements analyzed by these methods is relatively small and the methods are rather laborious; as a result fewer analyses are performed by these methods. At present the analytical methods for determining traces of gas-forming elements have the most serious problems. For illustration, it is enough to indicate high level of background noise at all stages of analytical procedure. In some cases the amount of gas-forming elements is not monitored at all (e.g., mercury, phosphorus, arsenic). For this reason determination of these elements was not performed for every sample collected; the detection limits of these elements are lower than those of all of the other elements.

The number of control analyses of a sample depends upon the completeness of the data supplied by the producer of the sample. Also of importance is the level of correlation of the supplied data with the results of the first control analyses. When the discrepancy is not negligible additional control analyses are performed. Thus, as a result of control analyses, generated is a set of pairs representing the results of the determination of the same

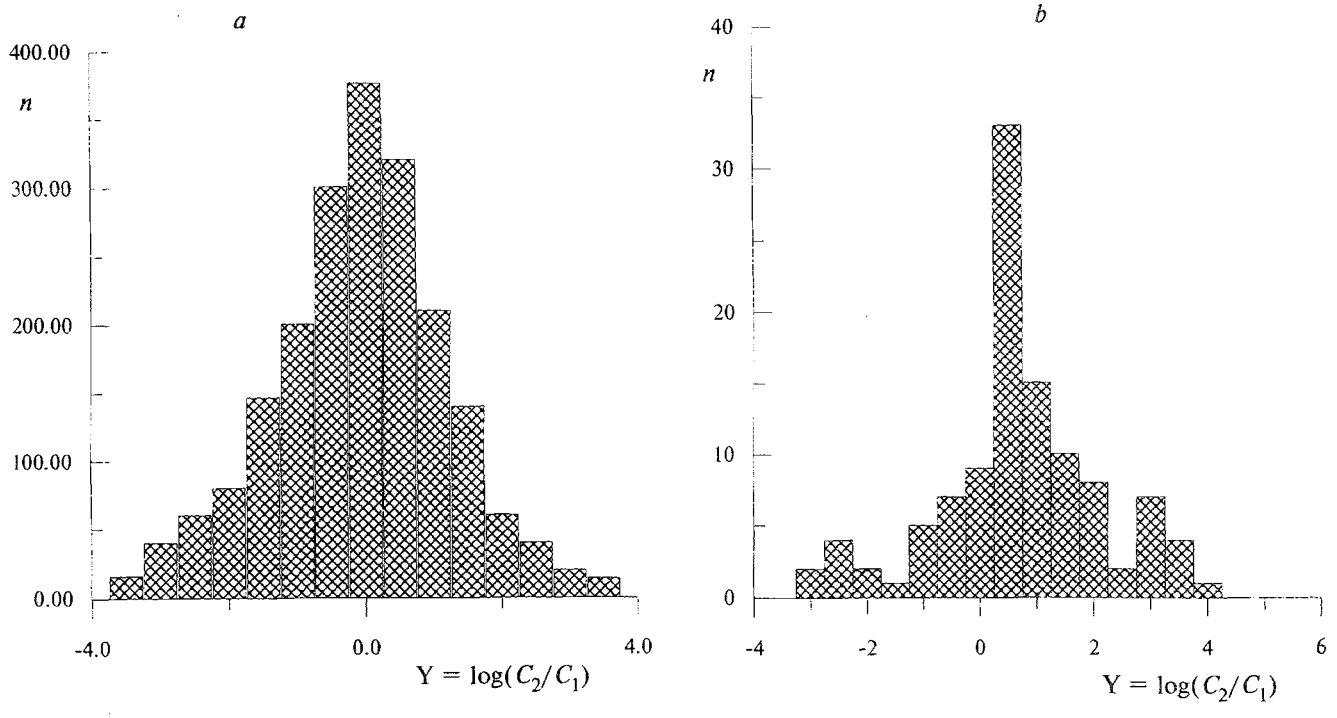

Fig.1. Distribution of deviation values of control analyses of samples of the collection: *a* — solid elements, *b* — volatile impurities in samples of volatile substances. $Y = \log(C_2/C_1)$, C_1 and C_2 are results of two independent determinations of impurity content; in all cases C_2 is the result of the more recent analysis. n is number of results within the given interval of Y values.

impurity by different analytical procedures is generated. This set of pairs makes it possible to study inter-laboratory differences, which are characteristic of high purity substances. In Fig. 1 given are distributions of the discrepancy values for analysis of solid elements and for determination of volatile impurities in volatile substances. In both cases the magnitude of the discrepancy is about the same as the value of the impurity content. Analysis of literature[5,6] indicates that this situation is typical for all analytical methods and all analytical laboratories.

Work on creating of standard samples was initiated[7] to increase the reliability of the results of analyses (see Table 1 for the number of developed samples). These samples represent one of the most important components of the metrological garantee of trace analysis in high purity substances; at the same time these samples were practically absent until recently. Every standard sample of copper, silicon, tin, and cadmium developed recently[7,8] has certified contents of 20—30 impurities in the range 10^{-3}—10^{-7} % and the upper limits of the contents of another 30—40 impurities is in the range 10^{-5}—10^{-12} %. In addition to analysis of inter-laboratory discrepancies, the development of standard samples for the collection, has made it possible to detect the main sources of errors in the analysis of samples of high purity substances. For solid elements these sources include[5,7] non-homogeneity of samples and their residual contamination, inaccuracy of calibrations, influence of the matrix on the analytical response of an impurity, overlap of analytical lines, losses during concentration, memory of analytical instruments, errors of control analysis. Expert evaluation of the results supplied by the producer of a sample and the results of control analyses form the basis for certification of a collected sample. The collection certificate gives a better idea of the purity of a sample being certified than the preliminary results of the

Table 3. Content of impurities in one of the purest samples of germanium

Impurity	Content (atomic %)	Impurity	Content (atomic %)
Ag	$<2.0\cdot10^{-8}$	Fe	$<1.0\cdot10^{-7}$
Al	$<8.0\cdot10^{-9}$	Ga	$<1.0\cdot10^{-10}$
Al*	$1.0\cdot10^{-10}$	Ga*	$<1.0\cdot10^{-12}$
As*	$<1.0\cdot10^{-12}$	In	$<3.0\cdot10^{-7}$
Au	$<1.0\cdot10^{-7}$	K	$<6.0\cdot10^{-7}$
B	$<7.0\cdot10^{-8}$	Li	$<1.0\cdot10^{-10}$
B*	$7.0\cdot10^{-12}$	Mg	$<2.0\cdot10^{-7}$
Be	$<2.0\cdot10^{-7}$	Mn	$<7.0\cdot10^{-8}$
Bi	$<1.0\cdot10^{-7}$	Na	$3.0\cdot10^{-7}$
C	$<6.0\cdot10^{-6}$	Ni	$<9.0\cdot10^{-7}$
Ca	$<2.0\cdot10^{-6}$	O	$<5.0\cdot10^{-5}$
Cd	$<2.0\cdot10^{-7}$	P*	$5.0\cdot10^{-11}$
Co	$<1.0\cdot10^{-7}$	Pb	$<3.5\cdot10^{-8}$
Cr	$<7.0\cdot10^{-7}$	Si	$<3.0\cdot10^{-5}$
Cu	$<6.0\cdot10^{-8}$	Ti	$<1.0\cdot10^{-6}$

* Content of impurities in electroactive form.

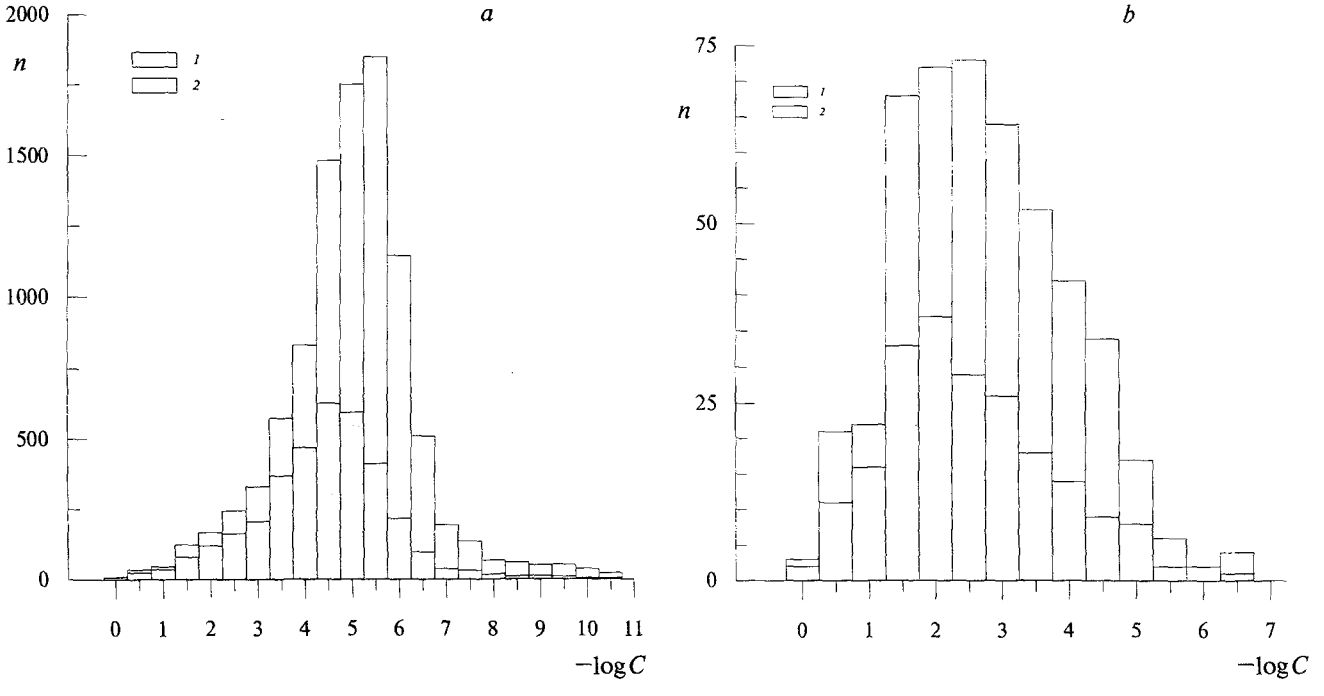

Fig.2. Distribution of impurities in samples of solid elements of the collection: *a*, all impurities; *b*, impurities of gas-forming elements; (*1*) determined percentages, (*2*) detection limits.

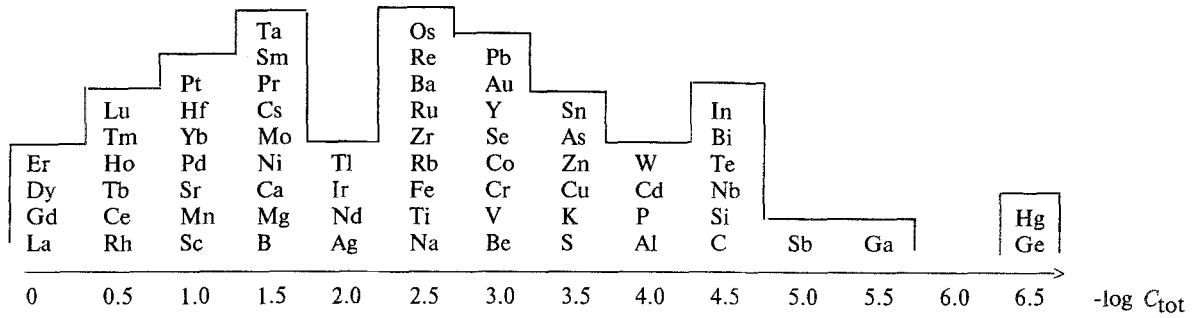

Fig.3. Distribution of total content of impurities for the purest samples of elements of the collection. The distribution was plotted using the determined percentages; the position of the element symbol on the X axis corresponds to the total amount of impurities in the sample of the element.

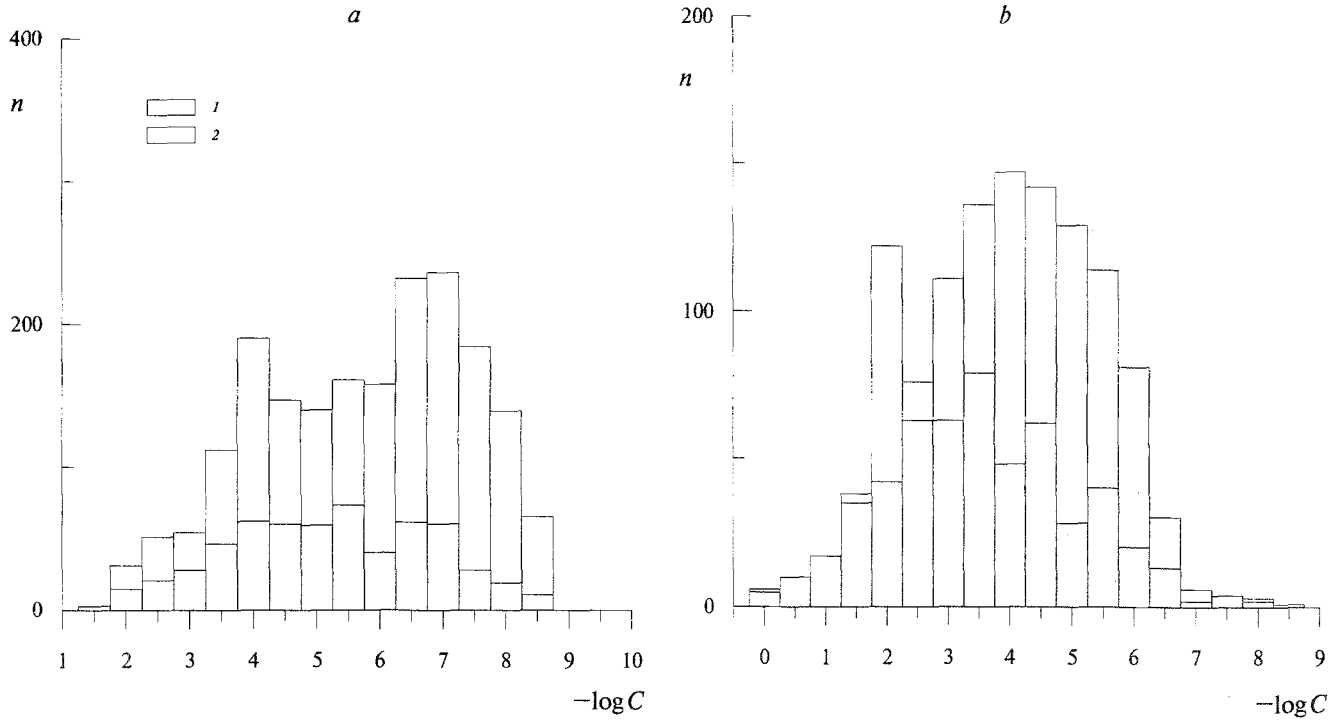

Fig.4. Distribution of impurities in samples of volatile substances of the collection: *a*, elemental impurities; *b*, molecular impurities, (*1*) determined percentages, (*2*) detection limits.

control analyses. For the latter, as was mentioned above, considerable discrepancies are possible. The certificate is forwarded to the producer of the sample and it is used for study of the general tendencies of the composition of impurities in high purity substances by comparison with data on other samples of the substance, and data known from normative documents and catalogues. The certificate of a collected germanium sample is given in Table 3 as an example. Certificates for the purest (at the date of publication) samples of major collected substances are reported in Refs. 2, 3, 9—14.

4. General charachterization of the purity level of high purity substances

The results obtained during the study of the composition of impurities in the collected samples form a data base (DB) of high purity substances. The data base also includes information on the composition of impurities in high purity substances retrieved from normative documents (standards, technological norms) and catalogues of western companies. At present the DB includes about 38,000 determinations of impurity content.

Figure 2 gives the distributions of percent impurity in the samples of solid elements that are included in the collection. In the most general way these distributions characterize the impurity content in samples based on the collection certificates. The distribution of the determined percentage characterizes typical values of impurity content; comparing it with the detection limits shows that the low number of determined impurities with percentage lower than 10^{-5} % is due to insufficiently low detection limits. The left wing of the distribution is correlated mostly with impurities of gas-forming elements (H, C, N, O) (Fig. 2, *b*). It is these elements that contribute most to the number of impurities determined in the high percentage range. Figure 3 gives the distribution of the total amount of impurities for the purest collected samples; the values of C_{tot} were found from the determined percentages. Most of the samples have a total impurity content greater than 10^{-4} %. Among the samples with a total impurity content less than 10^{-5} % are pure samples of silicon, germanium, indium, and gallium.

In the analysis of volatile substances some analytical methods give the percentages of elements only, while others also give the amounts of the specific molecular forms. In addition, the amount of suspended particles is determined in volatile substances. The elemental form is usually non-volatile metals' impurities. The molecular forms of impurities are first water, organic compounds, constant gases, and compounds analogous to the main substance. About 130 compounds total have been identified in samples of the collection.

Figure 4 gives the distributions of the determined percentages of the elemental and molecular forms of impurities in collected samples of volatile substances. The content of the molecular form is much higher (on average almost two orders of magnitude higher) than that of the elemental form. At high percentages ($>10^{-2}$ %) there are mainly impurities of volatile substances. The detection limits for the elemental form of impurities are 1.5 orders of magnitude lower than those for molecular forms of impurities. As in the case of elements, the decrease of distribution of the determined impurity contents is preceded by a maximum in the distribution of the detection limits.

The materials of the collection make it possible to evaluate the tendencies in the changes in detection limits and purity levels over the 20 years during which the collection has been operating. It is important to emphasize that these results were obtained on the actual samples of the exhibition. They are neither the detection limits reported during the development of an analytical procedure, nor the lowest detected impurity contents found during the development of a purification procedure.

Figure 5 shows the variation of the detection limits of various methods of analysis of high purity substances. The results of control analyses of collected samples, which were accompanied by the sign "less", were used to determine the mean values of the detection limits. It can be seen that over the years no changes have occurred in the limits of detection by mass spectrometry and by methods used for determination of impurities of gas-forming elements. During these years no new mass spectrometers have appeared in our country with lower detection limits; and methods with chemical pre-concentration of impurities have not found wide application. In other cases the detection limits have improved: in analysis of solid elements by one order of magnitude, in analysis of volatile substances they have decreased by 1—2 orders of magnitude. In spectral methods this progress is attributed to the development of methods of concentrating impurities, and in gas chromatographic methods to usage of new detectors and capillary chromatography.

Analysis of the purity level of samples of solid elements from some sub-groups of the Periodic System (Fig. 6) demonstrated that the purer a substances is (from sub-groups IIb, IIa—VIa), the more its purity level varies; the value of the mean total content varies more than the value of the mean impurity content. This fact can be attributed to more intense work on purification of elements from these sub-groups. Figure 7 shows the variation in the of purity level of samples of some volatile substances submitted to the collection by the Institute of Chemistry of High Purity Substances of the RAS over a period of several years. The content of elemental form of impurities has decreased by one order of magnitude and that of the molecular form has decreased by 1—2 orders of magnitude. The increase of the purity level of chlorides during these years has been caused first of all by the needs of the fiber optics industry, while that of hydrides and organometallic compounds is due to the needs of the microelectronics industry.

Analysis of the data presented in the collection and in catalogues of foreign companies that sell high purity substances shows that although the distributions of the determined impurities are qualitatively similar, the high purity substances produced by foreign companies have a relatively higher proportion of impurities in the range of high concentrations of about 10^{-2} % (Fig. 8).

The development of the chemistry of high purity substances as a branch of science is characterized by three major parameters: the number of substances obtained in high purity form N; the average level of monitored impurities $<C>$; the average number of monitored impurities n. Let us consider an index of the development of the chemistry of high purity substances that is a combination of these three parameters, i. e., $Ind = N n/<C>$.[15] Figure 9 shows the change in this index throughout the last century. Values of the index were calculated[15] using data from handbooks, catalogues, and the collection. In Refs. 16, 17 quantitative data on purity level are not given; an estimate of the index was calculated assuming that $n = 3$—6, $<C> = 10^{-1}$—10^{-2}, and $n = 5$, $<C> = 10^{-1}$—10^{-2} respectively.

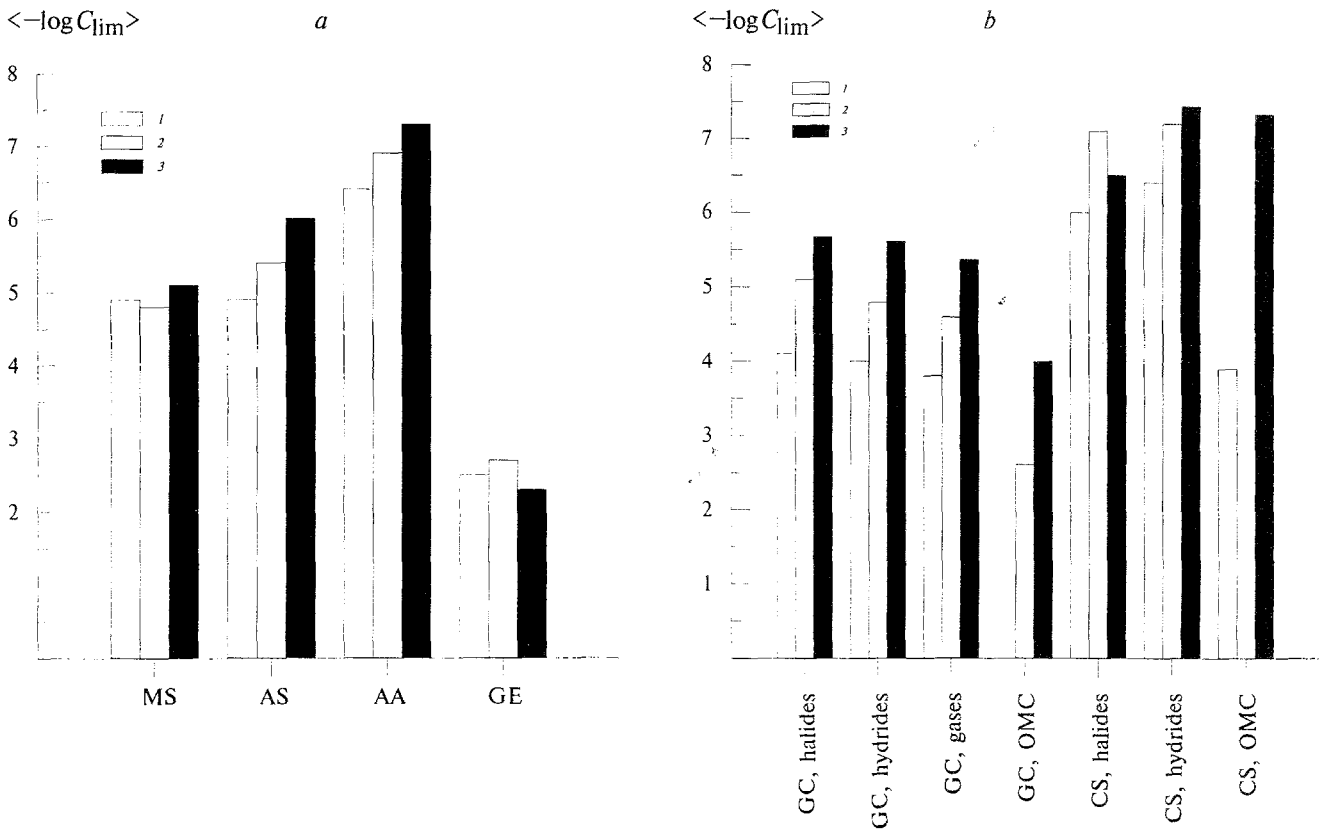

Fig.5. Average values of detection limits by various methods of analysis of samples of the collection as a function of control analyses dates : *a*, solid elements; *b*, various classes of volatile substances, (*1*), 1974—1980, (*2*), 1981—1985, (*3*), 1980—1993.

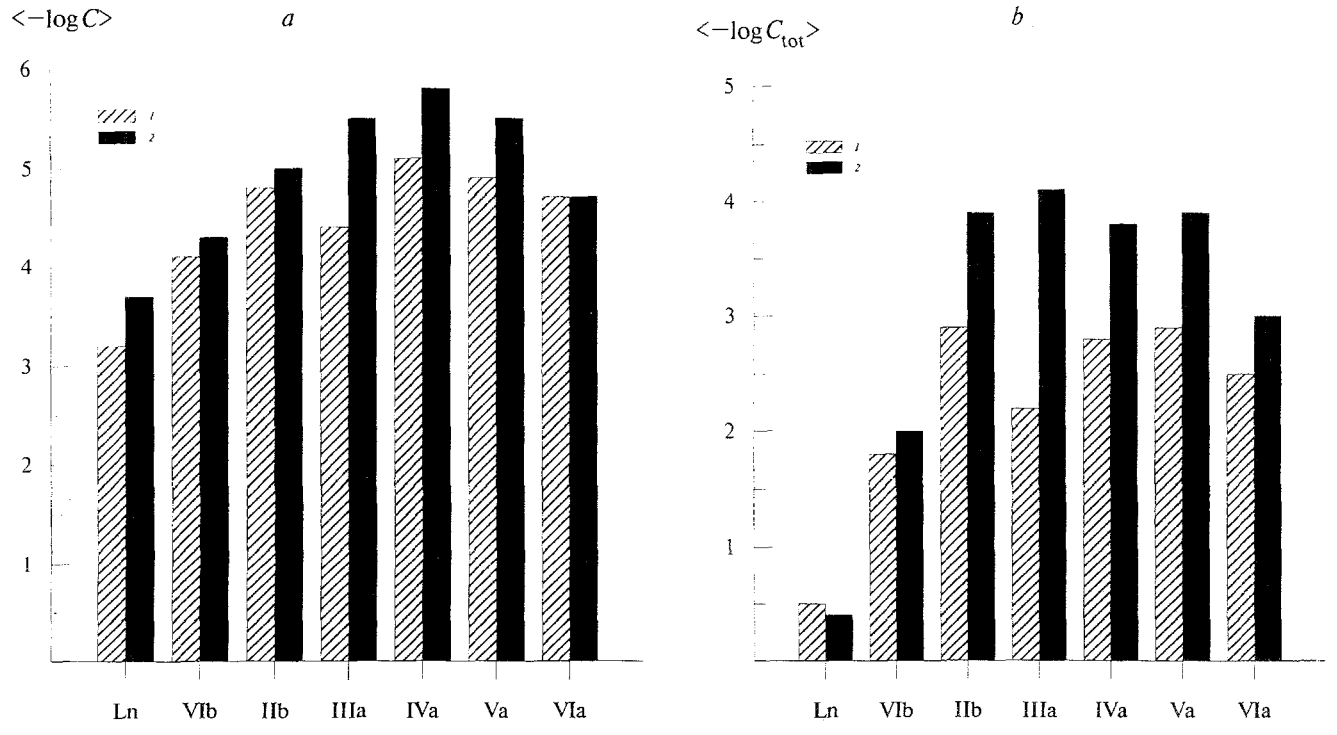

Fig.6. Impurities in samples of solid elements from some of the subgroups of the periodic table: (*1*), samples submitted in 1970s, (*2*), samples submitted in 1980s; (*a*), mean content of impurities, (*b*), mean total content of impurities.

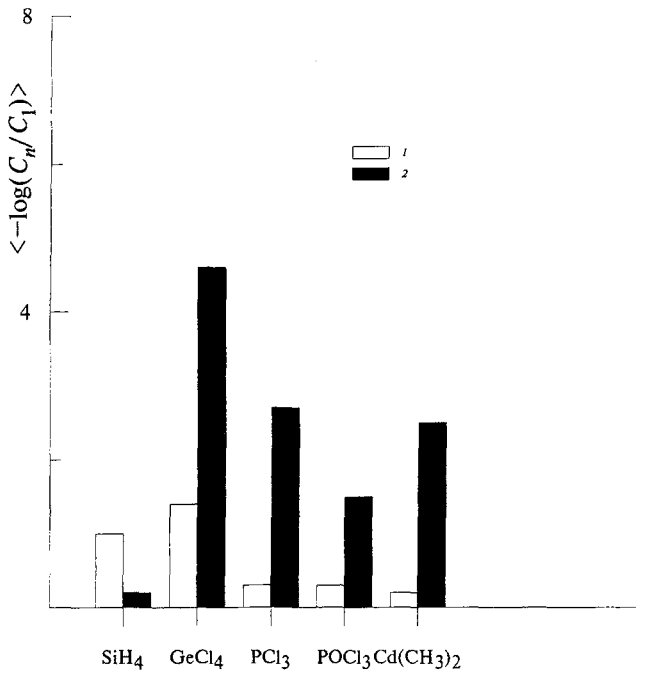

Fig.7. Variance of purity level of samples of some volatile substances submitted to the collection by the Institute of Chemistry of High Purity Substances of the RAS. Compared are the level of purity of the first (C_1) and the last (C_2) sample of the particular substance. *1*, elemental form; *2*, molecular form.

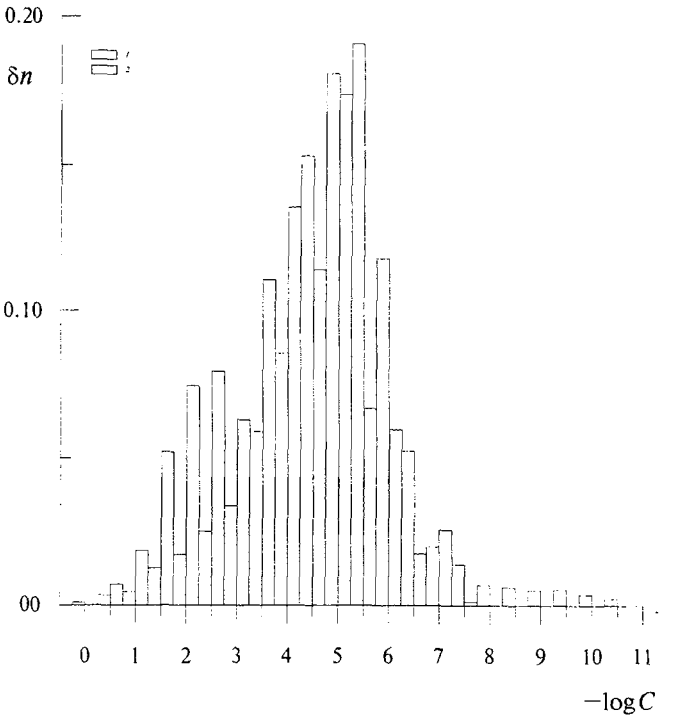

Fig.8. Normalized distributions of the determined impurities in samples of solid elements, based on data from the collection (*1*) and in catalogues from foreign companies (*2*). d*n*, ratio of number of impurities in a given interval of -log*C* values to total number of impurities in the whole range of concentrations.

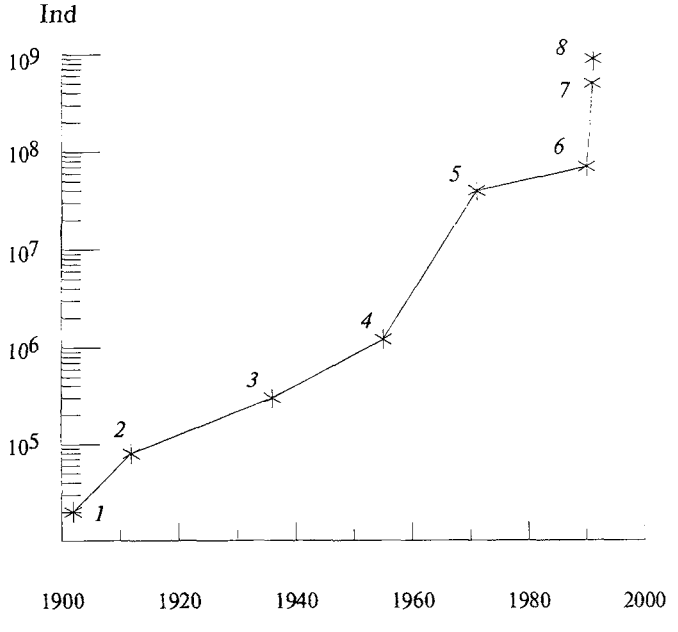

Fig.9. Index of the development of the chemistry of high purity substances. *1* — Korenblit[16]; *2,8* — Merck[17,20]; *3,4* —Karyakin[18,19]; *5,6* — IREA; *7* — the collection[21].

In other publications[18–20] the index was estimated using either the presented tables of impurity composition or tables for high purity substances.[21] When several tables with impurities contents existed for one particular substance (different grades of the substance), then the table with the lowest concentrations of impurities was chosen. The two last points on the plot, which have the highest value of the index, differ from the others either by the wide variety of high purity substances (Merck) or by the high number of monitored impurities as well as the low average content of impurities (the of collection).

Figure 7 clearly shows the linear (in semi-logarithmic coordinates) increase in the index of the development of the chemistry of high purity substances. This situation is typical for intensely developing branches of science. Three periods of time can be distinguished on this plot. The first one covers the years for which quantitative data on the level of purity of reagents were not reported.[16,17] The second one corresponds to the period when reference data started to include quantitative parameters on purity level,[18,19] mostly as a result of the influence of the nuclear industry. The last period started in the 1960s, when a variety of chemical reagents started to evolve high purity substances for various applications; this situation was created at first by the

rapidly developing semiconductor industry and later by the fiber optics industry.

5. Conclusions

Studies of the composition of impurities in high purity substances, which were conducted within the framework of the collection, have made it possible to obtain a much more complete and reliable picture of the research and development of the chemistry of high purity substances in the territory of the former Soviet Union, than was possible before. It is important that after completion of the study it became possible to get rid of a series of rather stable illusions on the level of purity achieved, and on the real confidence of the results of the analysis of high purity substances. The accumulation of the unique body of information of impurity composition made it possible to formulate the general tendencies of the impurity composition of high purity substances, to characterize them quantitatively, and to use them to predict complete impurity composition.

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References

1. G. G. Devyatykh, *Vestnik AN SSSR*, 1982, N7, 25 (in Russian).
2. G. G. Devyatykh, Yu. A. Karpov, I. D. Kovalev, S. G. Krasnova, G. A. Maximov, L. I. Osipova, S. V. Yan'kov, *Vysokochistye veshchestva*, 1990, No 1, 7 (in Russian).
3. G. G. Devyatykh, V. A. Krylov, I. D. Kovalev, L. I. Osipova, S. V. Yan'kov, E. N. Volkova, *Vysokochistye veshchestva*, 1990, No 4, 7 (in Russian).
4. V. M. Il'in, Ph. D. Thesis, Institute of Chemistry of the AS USSR, Gor'kiy, 1982 (in Russian).
5. I. D. Kovalev, S. G. Krasnova, Yu. B. Makarov, S. V. Yan'kov, *Vysokochistye veshchestva*, 1987, No 2, 147 (in Russian).
6. H. M. Ortner, *Fresenius J. Anal. Chem.*, 1992, **343**, 695.
7. G. G. Devyatykh, I. D. Kovalev, G. A. Maximov, *Rossiyskiyi Khimicheskii Zhurnal. Zhurn. Ros. khim. obshch im. D. I. Mendeleeva*, 1994, **27**, 69 [*Mendeleev Chem. J.*, 1994 (Engl. Transl.)].
8. G. G. Devyatykh, T. A. Burmistrova, I. D. Kovalev, A. M. Potapov, S. V. Kovalevsky, V. N. Lubimov, I. R. Shelpakova, *Vysokochistye veshchestva*, 1994 (in Russian).
9. G. G. Devyatykh, Yu. A. Karpov, I. D. Kovalev, L. I. Osipova, S. V. Yan'kov, *Vysokochistye veshchestva*, 1991, No 2, 22 (in Russian).
10. G. G. Devyatykh, V. A. Krylov, I. D. Kovalev, L. I. Osipova, S. V. Yan'kov, E. N. Volkova, *Vysokochistye veshchestva*, 1991, No 4, 7 (in Russian).
11. G. G. Devyatykh, Yu. A. Karpov, I. D. Kovalev, G. A. Maximov, L. I. Osipova, S. V. Yan'kov, *Vysokochistye veshchestva*, 1992, No 5—6, 12 (in Russian).
12. G. G. Devyatykh, Yu. A. Karpov, I. D. Kovalev, G. A. Maximov, L. I. Osipova, S. V. Yan'kov, *Vysokochistye veshchestva*, 1992, No 5—6, 25 (in Russian).
13. G. G. Devyatykh, V. A. Krylov, I. D. Kovalev, L. I. Osipova, S. V. Yan'kov, *Vysokochistye veshchestva*, 1993, N1, 27.
14. G. G. Devyatykh, V. A. Krylov, I. D. Kovalev, L. I. Osipova, S. V. Yan'kov, *Vysokochistye veshchestva*, 1993, No 4, 7 (in Russian).
15. G. G. Devyatykh, S. V. Yan'kov, *Vysokochistye veshchestva*, 1993, No1, 19 (in Russian).
16. A. I. Korenblit. *Khimicheskie reactivy, ikh poluchenie, svoistva, ispytaniya i upotreblenie* [Chemical Reagents, Their Purification, Properties, Testing, and Use], 2nd ed., Moscow, 1902 (in Russian).
17. E. Merck. *Prüfung der Chemischen Reagenzien auf Reinheit.* Darmstad, 2 Aufgabe, 1912.
18. Yu. V. Karyakin, *Chistye khimicheskie reaktivy. Rukovodstvo k laboratornomu prigotovleniyu neorganicheskikh preparatov.* (Pure Chemical Reagents. Handbook for Laboratory Preparation of Inorganic Substances), ONTI, Leningrad, 1936 (in Russian).
19. Yu. V. Karyakin, I. I. Angelov, *Chistye khimicheskie reaktivy* (Pure Chemical Reagents), Goskhimizdat, Moskva, 1955 (in Russian).
20. E. Merck. *Reagents, Diagnostics, Chemicals*, 1992/93.
21. O. A. Gol'dina, Yu. S. Kuznetsova, T. G. Ivanova et al. *Khimicheskie reaktivy i vysokochistye khimicheskiye veshchestva. Katalog* (Chemical Reagents and High Purity Substances. Catalog), Khimiya, Moskva, 1990 (in Russian).

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