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ACTIVATION ANALYSIS OF ADMIXTURES IN
CERTAIN SEMICONDUCTIVE MATERIALS

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16. Abstract: The methods for activation detn. of some impurities in Si, As, Tl, and MeSiCl ₃ (I) were worked out on the basis of extn. properties of bis (2-chloroethyl ether (II) and dimethylbenzylalkylammonium chloride (III): In esp. pure As and Si samples, Au, Ga, Sb, and Fe were detd. with a relative error of ± 10 and chem. yields of the elements detd. of 90-7%. Together with standards, 100 mg. As or 400-450 mg. Si is irradiated (1.8×10^{13} neutrons/cm ² sec.) for 8 hours. After the sepn. of As by aqua regia and Si in the form of SiF ₄ , the residue is dissolved in 10N HCl and extd. with II. The γ -spectra of Au, Sb, Ga, and Fe impurities in As and Si are reproduced. The irradiation conditions for the anal. of Tl and I are the same as given above. The greatest part (~90%) of the Tl of the Tl sample is sepd. by extn. with II from 3N HCl; 10N HCl is added to the aq. soln. and Sb, Ga, Fe, and Tl residues are extd. by II. After 3-fold evapn. in a mixt. of HNO ₃ and HF, the aq. phase is dissolved in 6M HF and In, Zn, Cu, and Co are eluted by means of 6M HF on a column contg. Dowex 1 anion exchange resin (F ⁻ cycle).			
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ACTIVATION ANALYSIS OF ADMIXTURES IN
CERTAIN SEMICONDUCTIVE^{or} MATERIALS

P. I. Artyukhin, E. P. Gil'bert and
V. A. Pronin

Silicon, arsenic and thallium are some of the main materials of semi-conductive^{or} technology, therefore great importance is attached to an analysis of the trace contaminants contained in them. No less stiff requirements on the quantity of admixture elements are also made of the initial products for obtaining semiconductor^{or} substances. The activation method is the most sensitive one for analyzing trace contaminants. /169*

A fairly large number of works [1-8] treat activation analysis of admixtures in silicon and the initial products to obtain it. In some of these publications [1-4], a description is given of the analysis of admixtures after breakdown of the sample and the separation of each radioactive element in the radiochemically pure form with the help of ordinary analytical methods. Usually these techniques, although they possess a high sensitivity of analysis, are complicated and labor-consuming. In other works [5-8], the admixture elements were analyzed directly by the γ -spectra without sample breakdown. Admixtures in thallium were analyzed analogously [9].

Direct γ -spectrometric analysis of admixtures even in the most favorable cases (radioactive isotopes of the macrobase--either pure β -emitters, or rapidly break down) is not always possible since, due to the presence of a large number of admixture elements, complex γ -spectra are obtained which are not susceptible to interpretation.

* Numbers in the margin indicate pagination of the original foreign text.

Analysis of admixtures in arsenic by the activation method has been described in only one work [10], which used radiochemical separation of each admixture. Analysis of the trace contaminants in arsenic without breakdown is generally impossible due to the strong activation of the base substance.

Recently, works have begun to appear which combine the γ -spectrometric and radiochemical variants. This approach seems the most expedient to us. The use of extraction and chromatographic operations to separate macrobases, as well as to divide elements into groups convenient for γ -spectrometric analysis significantly simplifies and accelerates the analysis [11]. /170

The studies we conducted on the extraction properties of β, β' -dichlorodiethyl ether (chlorox) [12, 13] and dimethylbenzylalkylammonium chloride (quaternary ammonium compound) [14], as well as the published data on extraction of a number of elements of di-n-butylthiophosphoric acid (DBTFA) [15], and according to chromatographic separation of elements [4, 16], made it possible to develop a number of techniques for activation analysis of certain admixtures in silicon, arsenic, thallium and trichloromethylsilane. Here, especial attention was paid to separation of admixtures in the form of groups suitable for γ -spectrometric analysis.

Extraction by chlorox from hydrochloric acid solutions (≥ 9 N HCl) permits separation of Au, Sb, Ga, Fe and Tl practically from any subjects. Other elements are either not extracted at all or are extracted to an insignificant degree [12, 13]. The nuclear physical characteristics of ^{199}Au , ^{122}Sb , ^{72}Ga and ^{59}Fe make it possible to make a quantitative analysis of the indicated elements by γ -spectra without further separation. ^{204}Tl is a pure β -emitter and in the given case does not provide any obstacles.

We determined the content of Au, Ge, Sb and Fe in extrapure samples of arsenic and silicon.

100 mg of arsenic and 400-450 mg of silicon, together with the standard, were irradiated with a stream of slow neutrons $1.8 \cdot 10^{13}$ neutrons/cm² · sec for 8 hours. After irradiation the samples were etched with hydrochloric acid and

washed with distilled water. Arsenic, together with the carriers, was dissolved *in* aqua regia, the solution was boiled down almost until dry and the residue was dissolved in 3-5 ml of 10 N HCl. Silicon, with the carriers, was dissolved in hydrofluoric acid in the presence of hydrogen peroxide and distilled off in the form of tetrafluoride. The remaining admixtures were dissolved in aqua regia, boiled down almost until dry, and the residue was dissolved in 3-5 ml of 10 N HCl.

From the obtained solutions, an extraction was made with equal volumes of chlorex for 1-2 min. After stratification, the lower phase containing Au, Sb, Ga and Fe was separated and washed twice with 10 N HCl. Arsenic and all the other admixtures remain in the aqueous phase. The chemical output of determinable elements was 90-97%.

Fig. 1 depicts the γ -spectra of the isolated admixtures from arsenic and silicon taken on the AI-100 analyzer with NaJ (Tl) 40 x 40 crystal with resolution of 9% for ^{137}Cs . The mean data from several analyses are given in table 1. The relative error of the method lies within the limits $\pm 10\%$. If it is necessary to analyze a large number of admixtures, the proposed technique of group separation and analyses of Au, Sb, Ga and Fe can serve as a constituent of more complex schemes. /171

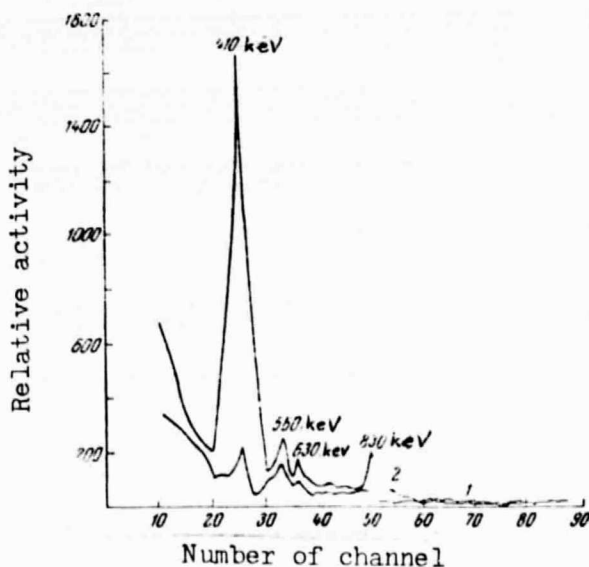


Figure 1. γ -Spectra of Admixtures Au, Sb, Ga, Fe Separated from Silicon (1) and from Arsenic (2)

TABLE 1
ANALYSIS OF ADMIXTURES IN ARSENIC
AND SILICON

Element	Content, %	
	in arsenic	in silicon
Au	$5.5 \cdot 10^{-7}$	$1.6 \cdot 10^{-7}$
Sb	$8.3 \cdot 10^{-8}$	$1.7 \cdot 10^{-8}$
Ga	$3 \cdot 10^{-8}$	$2.5 \cdot 10^{-8}$
Fe	$5 \cdot 10^{-8}$	$< 1 \cdot 10^{-8}$

X-ray irradiation of radioactive isotopes of thallium seriously hinders γ -spectrometric analysis of the admixtures contained in it. Therefore it is desirable to separate the main mass of thallium. In the given case, we used extraction of Tl(III) by chlorex [12, 13] from ≤ 3 N HCl. Under these conditions, only Au(III) passes into the organic phase; the remaining admixtures stay in the aqueous solution.

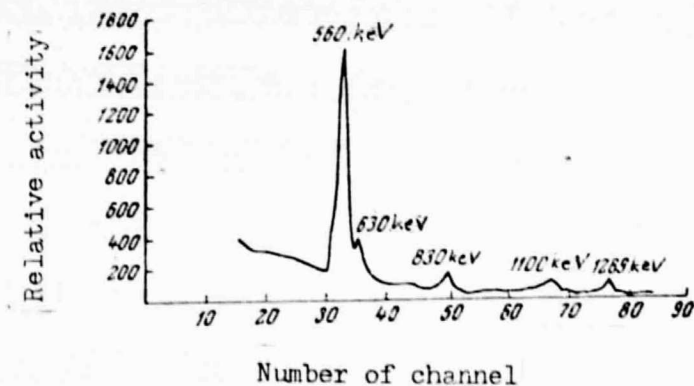


Fig. 2. γ -Spectrum of Sb, Ga and Fe Separated from Thallium

/172

For analysis of the thallium samples, 10-milligram samples were taken. The conditions for irradiation and subsequent treatment were analogous to the conditions for analysis of arsenic. The macrobase was removed by $\sim 90\%$ by extraction with an equal volume of chlorex from 3 N HCl. Then the aqueous solution was boiled down to a small volume, 3-5 ml of 10 N HCl were added, and extraction with chlorex of Sb, Ga, Fe and the remaining amount of thallium was carried out. The organic

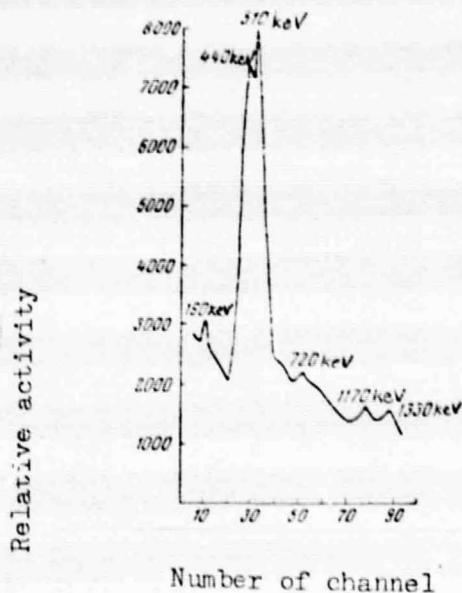


Fig. 3. γ -Spectrum of Zn, In, Cu, Co Separated from Thallium

phase was washed with 10 N HCl, then the γ -spectrum of the separated admixtures was taken. The aqueous phase was boiled down three times in a mixture of HNO_3 and HF almost until dry. The residue was dissolved in a small volume of 6 M HF, and the solution was put into a polyethylene column 2 mm in diameter and 8 mm high filled with anionite Dowex-1 in the F-form. Then In, Zn, Cu and Co were washed with 40 drops of 6 M HF and their γ -spectrum was taken (measurements were made in 20 hours after irradiation when the Mn and Ni isotopes had completely ~~broken down~~ *decayed*). The As, Te and Sn remaining on the column were washed with 60 drops of 17 M HF, transferred into chlorides, and separated on a column filled with Dowex-1 resin in the Cl-form. As was washed with 30 drops of 11 N HCl, Te--20 drops of 0.1 M $\text{H}_2\text{C}_2\text{O}_4$, Sn--30 drops of 0.2 M $\text{H}_2\text{C}_2\text{O}_4 + 2 \text{ M NH}_4\text{NO}_3$. The activity of the separated isotopes was measured on endwindow counter.

The obtained γ -spectra of separated admixtures are presented in fig. 2 and 3. The mean results of analysis with regard for the chemical output are given in table 2.

The subject of analysis for trichloromethylsilane was the product purified by rectification.

Sample + carriers
 Distillation of SiF_4 , dissolving in $\text{HCl} + \text{HNO}_3$ (3:1), boiling down and dissolving of residue in 9-10 N HCl

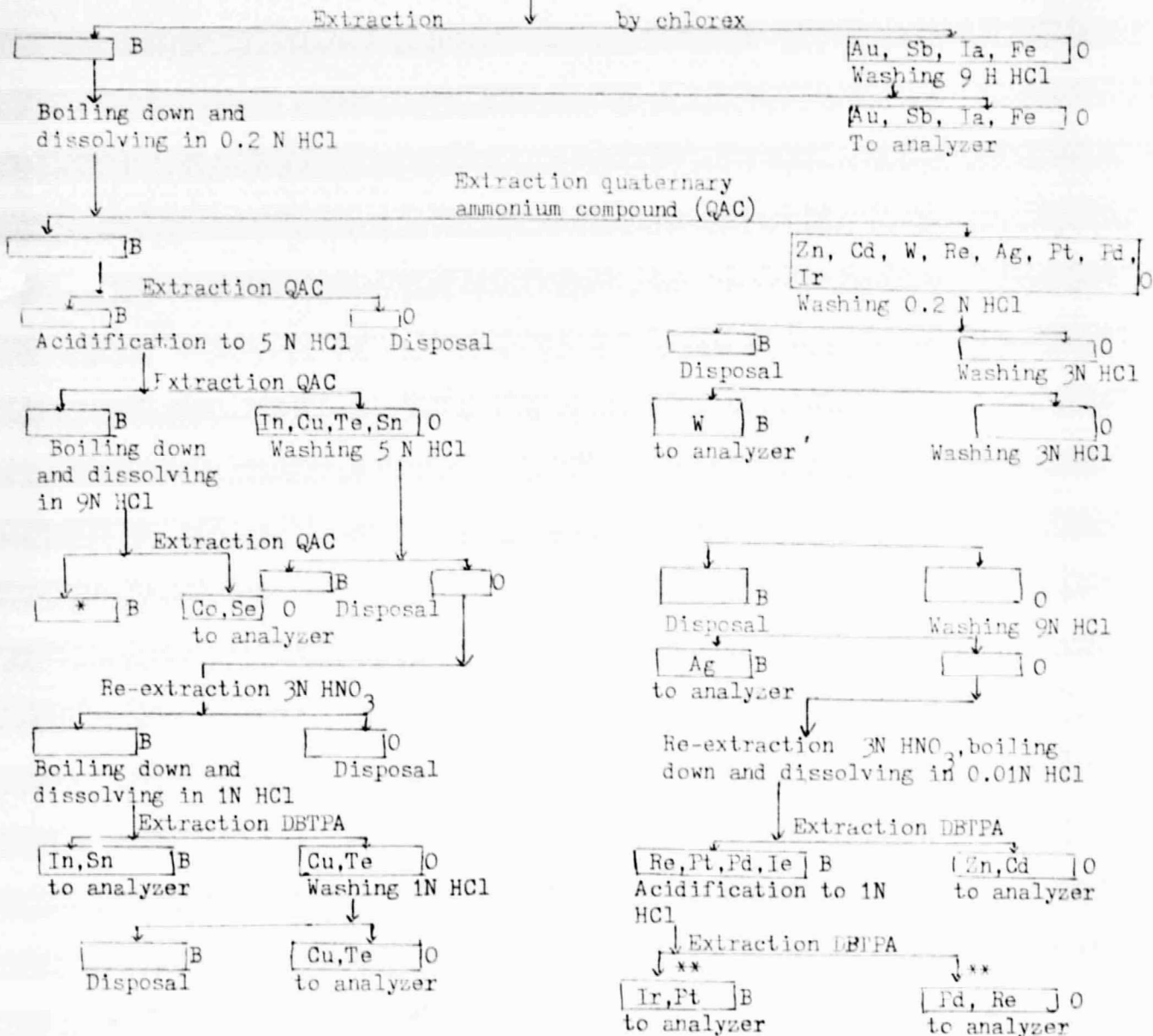


Fig. 4. Schematic Diagram of Extraction Separation of Elements-Admixtures
 B--aqueous phase; O--organic phase; *--analysis in aqueous phase γ -spectrometrically of content of Au, K, Na; **--analysis of content only of Ir and Re; \odot analysis of Pd and Pt requires further separation

Before irradiation, ~300 mg of trichloromethylsilane were subjected to hydrolysis; the residue was dried and irradiated. The irradiation conditions are the same as in the case of silicon analysis.

Fig. 4 depicts the schematic diagram of the extraction separation of admixtures (with carriers) into groups convenient for γ -spectrometric analysis; here certain elements were isolated in the individual state. The following were used as extracting agents: 100% solution of chlorex, 0.08 M solution of quaternary ammonium compound (QAC) (technical product containing 65% base substance) in dichloroethane with addition of 5% isoamyl alcohol and 0.1 M solution of DBTPA in CH_2Cl_2 carbon tetrachloride. The mean results of the analysis of several samples of trichloromethylsilane with regard for the chemical output are given in table 2.

TABLE 2
ANALYSIS OF ADMIXTURES IN THALLIUM AND TRICHLOROMETHYLSILANE

Element	Isotope used for analysis	Energy γ -quanta keV	Content, %	
			in thallium	in silane
Au	^{199}Au	410	—	$<3 \cdot 10^{-9}$
Sb	^{125}Sb	560	$6 \cdot 10^{-4}$	$8 \cdot 10^{-3}$
Ga	^{76}Ga	630, 830	$3.9 \cdot 10^{-4}$	$<4 \cdot 10^{-4}$
Fe	^{59}Fe	1100, 1295	$3 \cdot 10^{-3}$	$<1 \cdot 10^{-4}$
Cu	^{64}Cu	510	$3 \cdot 10^{-3}$	$2.9 \cdot 10^{-1}$
Te	^{125m}Te	140	$1.3 \cdot 10^{-3}$	$<1 \cdot 10^{-4}$
Co	^{60}Co	1170, 1330	$2.3 \cdot 10^{-1}$	$<1 \cdot 10^{-6}$
Se	^{75}Se	140, 270	—	$<3 \cdot 10^{-4}$
In	^{114m}In	190, 550	$5.1 \cdot 10^{-4}$	$1.7 \cdot 10^{-3}$
Sn	^{113}Sn	390	$1.2 \cdot 10^{-4}$	$<2 \cdot 10^{-4}$
Cd	^{115}Cd	520	—	$<3 \cdot 10^{-7}$
Zn	^{69m}Zn	440	$2.8 \cdot 10^{-3}$	$<1 \cdot 10^{-4}$
W	^{187}W	134, 480, 680	—	$<6 \cdot 10^{-6}$
Re	^{186}Re	137	—	$<2 \cdot 10^{-7}$
Ag	^{110}Ag	680, 880	—	$<2 \cdot 10^{-7}$
As	^{76}As	550	$3.6 \cdot 10^{-4}$	$3 \cdot 10^{-3}$
K	^{42}K	1530	—	$7 \cdot 10^{-3}$
Na	^{24}Na	1370, 2750	—	$1.6 \cdot 10^{-3}$

All the proposed techniques were preliminarily verified with the help of tracer atoms. The quantity of each element was determined by a comparison of the activity of the separated admixture and the activity of the corresponding standard.

Conclusions

1. A technique was developed for γ -spectrometric analysis of Au, Sb, Ga and Fe in arsenic and silicon.
2. A technique was developed for analyzing Sb, Ga, Fe, In, Zn, Cu, Co, As, Te and Sn in thallium.
3. A technique was developed for analyzing Au, Sb, Ga, Fe, Cu, Te, Co, Se, In, Sn, Cd, Zn, W, Re, Ag, As, Na and K in trichloromethylsilane. This technique can be used to analyze silicon, silicon carbide and germanium.

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АКАДЕМИЯ НАУК СССР

ТРУДЫ КОМИССИИ ПО АНАЛИТИЧЕСКОЙ ХИМИИ
1968 г. Том XVI

Л. П. АРТЮХИН, Э. М. ГИЛЬБЕРТ,
В. А. ПРОНИН

АКТИВАЦИОННОЕ ОПРЕДЕЛЕНИЕ ПРИМЕСЕЙ
В НЕКОТОРЫХ ПОЛУПРОВОДНИКОВЫХ МАТЕРИАЛАХ

Кремний, мышьяк и галлий являются одними из основных материалов полупроводниковой техники, поэтому определению содержащихся в них микропримесей придается большое значение. Не менее жесткие требования по количеству примесных элементов предъявляются также к исходным продуктам для получения полупроводниковых веществ. Наиболее чувствительным методом определения микропримесей является активационный метод.

Активационному определению примесей в кремнии и исходных продуктах для его получения в литературе посвящено довольно большое количество работ [1—8]. В некоторых из них [1—4] описано определение примесей после разложения образца и выделения каждого радиоэлемента в радиохимически чистом виде с помощью обычных аналитических приемов. Обычно такие методики, хотя и обладают высокой чувствительностью определения, сложны и трудоемки. В других работах [5—8] определение примесных элементов производилось непосредственно по γ -спектрам без разложения образца. Аналогично определялись примеси в галлии [9].

Непосредственное γ -спектрометрическое определение примесей даже в самых благоприятных случаях (радиоизотопы макроосновы — или чистые β -излучатели, или быстро распадаются) не всегда возможно, так как из-за наличия большого числа примесных элементов получают сложные γ -спектры, не поддающиеся расшифровке.

Определение примесей в мышьяке активационным методом описано всего в одной работе [10], использующей радиохимическое выделение каждой примеси. Анализ микропримесей в мышьяке без разложения вообще невозможен из-за сильной активации основного вещества.



В последнее время стали появляться работы, сочетающие γ -спектрометрический и радиохимический варианты. Такой подход нам кажется наиболее целесообразным. Применение экстракционных и хроматографических операций для отделения макроосновы, а также для разделения элементов на группы, удобные для γ -спектрометрического определения, значительно упрощает и ускоряет проведение анализа [11].

Проведенные нами исследования экстракционных свойств β, β' -дихлордипилового эфира (хлорекса) [12, 13] и диметилбензилалкиламмонийхлорида (ЧАО) [14], а также литературные данные по экстракции ряда элементов ди-*n*-бутилтиофосфорной кислотой (ДБТФК) [15] и по хроматографическому разделению элементов [4, 16] дали возможность разработать ряд методик активной и пассивной сорбции для определения некоторых примесей в кремнии, мышьяке, галлии и трихлорметилсилане. При этом обращалось особое внимание на выделение примесей в виде групп, удобных для γ -спектрометрического определения.

Экстракция хлорексом из солянокислых растворов ($\geq 9 N HCl$) позволяет выделить Au, Sb, Ga, Fe и Tl практически из любых объектов. Другие элементы или совсем не экстрагируются, или экстрагируются в незначительной степени [12, 13]. Ядерно-физические характеристики ^{197}Au , ^{125}Sb , ^{72}Ga и ^{204}Tl дают возможность провести количественное определение указанных элементов по γ -спектрам без дальнейшего разделения. ^{204}Tl — чистый β -излучатель и в данном случае никаких помех не вносит.

Нами было проведено определение содержания Au, Ge, Sb и Fe в обособленных образцах мышьяка и кремния.

100 мг мышьяка и 400—450 мг кремния вместе с эталонами облучают потоком медленных нейтронов $1,8 \cdot 10^{13}$ нейтр./см²·сек в течение 8 час. После облучения образцы протравливают соляной кислотой и обмывают дистиллированной водой. Мышьяк вместе с носителями растворяют в царской водке, раствор упаривают почти досуха и остаток растворяют в 3—5 мл 10 N HCl. Кремний с носителями растворяют во фтористоводородной кислоте в присутствии перекиси водорода и отгоняют в виде тетрафторида. Оставшиеся примеси растворяют в царской водке, упаривают досуха и остаток растворяют в 3—5 мл 10 N HCl.

Из полученных растворов производят экстракцию равными объемами хлорекса в течение 1—2 мин. После расслаивания нижнюю фазу, содержащую Au, Sb, Ga и Fe, отделяют и промывают 2 раза 10 N HCl. Мышьяк и все остальные примеси остаются в водной фазе. Химический выход определяемых элементов составляет 90—97%.

На рис. 1 приведены γ -спектры выделенных примесей из мышьяка и кремния, снятые на анализаторе АИ-100 с кристаллом NaI (Tl) 40 × 40 с разрешением 9% по ^{137}Cs . Средние данные из нескольких определений приведены в табл. 1. Относительная ошибка метода лежит в пределах $\pm 10\%$. В случае необходимости определения большого числа примесей предлагаемая методика груп-

Активационное определение примесей в кремниевых материалах 171

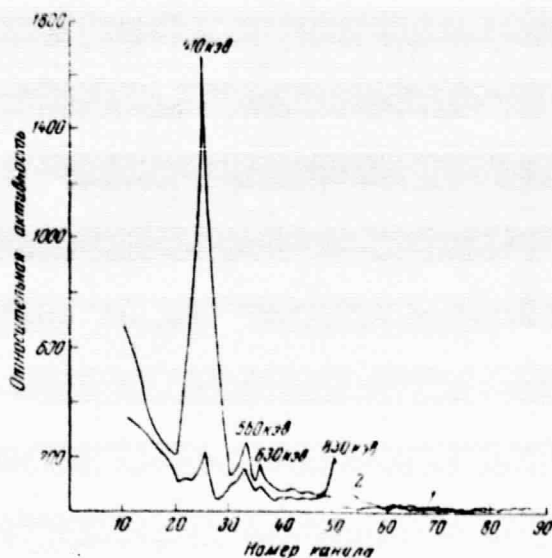


Рис. 1. γ -Спектры примесей Au, Sb, Ga, Fe, выделенных из кремния (1) и из мышьяка (2)

нового выделения и определения Au, Sb, Ga и Fe может служить составной частью более сложных систем.

Рентгеновское излучение радиоизотопов таллия сильно затрудняет γ -спектрометрическое определение содержащихся в нем примесей. Поэтому основную массу таллия желательно отделить. В данном случае мы использовали экстракцию Tl(III) хлорексом [12, 13] из $\leq 3 N HCl$. При этих условиях в органическую фазу переходит только Au(III), остальные примеси остаются в водном растворе.

Таблица 1

Определение примесей в мышьяке и кремнии

Элемент	Содержание, %	
	в мышьяке	в кремнии
Au	$5,5 \cdot 10^{-7}$	$1,6 \cdot 10^{-7}$
Sb	$8,3 \cdot 10^{-8}$	$1,7 \cdot 10^{-6}$
Ga	$3 \cdot 10^{-8}$	$2,5 \cdot 10^{-6}$
Fe	$5 \cdot 10^{-4}$	$< 1 \cdot 10^{-4}$

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и, сочетающие
л. Такой подход
не экстракцион
ия макроосновы,
ные для γ -спект
даст и ускоряет

онных свойств
и диметилбен
температурные дан
фосфорной кис
разделению эле
методик активаци
онии, мышьяке,
ось особое вни
ых для γ -спект

ов ($\geq 9 N HCl$)
ески из любых
агируются, или
]. Ядерно-физи
ют возможность
элементов по γ -
ый β -излучатель

Au, Ge, Sb и Fe

алонами облучают
тенше 8 час. После
мывают дистилли
г в царской водке,
3-5 мл 10 N HCl
ой кислоте в при
рида. Оставшиеся
и остаток раство

авными объемами
ую фазу, содержа
0 N HCl. Мышьяк
еский выход опре

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00 с кристаллом
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сительная ошиб
обходимости оп
методика груп

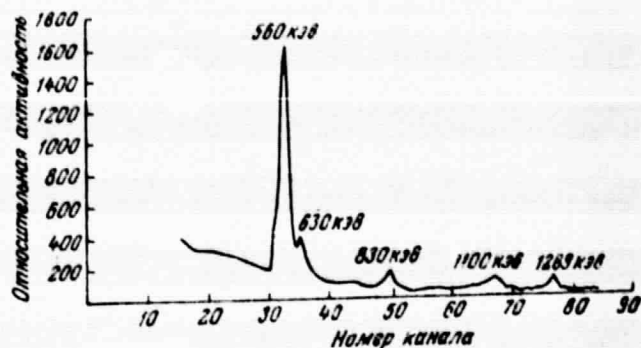


Рис. 2. γ -Спектр Sb, Ga, Fe, выделенных из таллия

Для анализа образцов таллия берут 10-миллиграммовые навески. Условия облучения и последующей обработки аналогичны условиям анализа мышьяка. Макрооснову на $\sim 90\%$ удаляют экстракцией равным объемом хлорекса из 3 N HCl. Затем водный раствор упаривают до малого объема, прибавляют 3–5 мл 10 N HCl и производят экстракцию хлорексом Sb, Ga, Fe и оставшегося количества таллия. Органическую фазу промывают 10 N HCl, затем снимают γ -спектр выделенных примесей. Водную фазу трижды упаривают в смеси HNO₃ и HF почти досуха. Остаток растворяют в

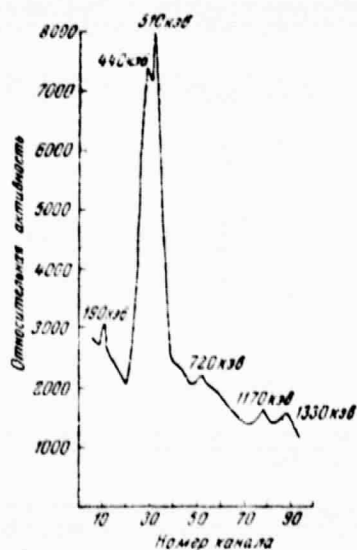


Рис. 3. γ -Спектр Zn, In, Cu, Co, выделенных из таллия

небольшом объеме 6 M HF и раствор вводят в полиэтиленовую колонку диаметром 2 мм и высотой 8 мм, заполненную анниотом Дауэкс-1 в F-форме. Затем 40 каплями 6 M HF вымывают In, Zn, Cu, Co и снимают их γ -спектр (измерения проводят через 20 час. после облучения, когда изотопы Mn и Ni полностью распадались). Оставшиеся на колонке As, Te и Sn вымывают 60-ю каплями 17 M HF, переводят в хлориды и разделяют на колонке, заполненной смолой Дауэкс-1 в Cl-форме. As вымывают 30-ю каплями 11 N HCl, Te — 20-ю каплями 0.1 M H₂C₂O₄, Sn — 30-ю каплями 0.2 M H₂C₂O₄ + 2 M NH₄NO₃. Активность выделенных изотопов измеряют на торцевом счетчике.

Полученные γ -спектры выделенных примесей приведены на рис. 2 и 3. Средние результаты определения с учетом химического выхода приведены в табл. 2.

В качестве объекта при анализе трихлорметилсилана брался продукт, очищенный ректификацией.

Перед облучением ~ 300 мг трихлорметилсилана подвергают гидролизу, остаток высушивают и облучают. Условия облучения такие же, как и в случае анализа кремния.

На рис. 4 приведена схема экстракционного разделения примесей (с носителями) на группы, удобные для γ -спектрометрического определения; при этом некоторые элементы выделялись в индивидуальном состоянии. В качестве экстрагентов применяли 100% - ный раствор хлорекса, 0,08 M раствор ЧАО (технический продукт, содержащий 65% основного вещества) в дихлорэтано с добавкой

Образцы - носители
Оксиды Si, растворение в HCl + HNO₃ (3:1),
уплотнение и растворение остатков
в 8-10% HCl

Растворение в хлорексе

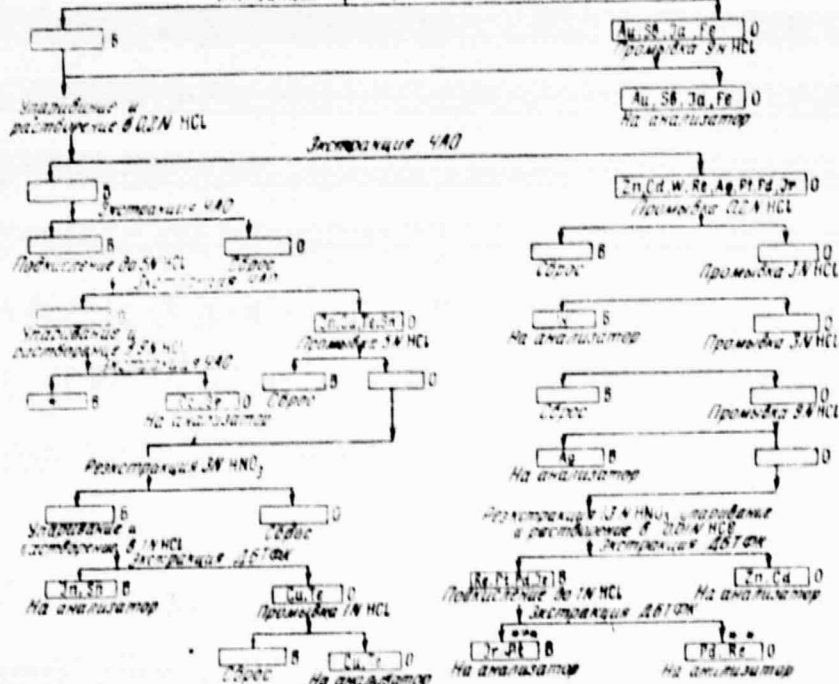


Рис. 4. Схема экстракционного разделения элементов-примесей

B — водная фаза; O — органическая фаза; * — определение в водной фазе γ -спектрометрически содержания Au, K, Na; * * — определение содержания только Ir и Re, для определения Pd и Pt необходимо дальнейшее разделение

№ 1289 к.м
70 80 90

3 таблица

мовые навески. Условиям анализа равным объемом от до малого объема, то хлорексом Sb, Ga, нау промывают 10 N йодную фазу трижды, он растворяют в не- M HF и раствор вво- вую колонку диамет- 8 мм, заполненную -1 в F-форме. Затем F вымывают In, Zn, их γ -спектр (замере- 20 час. после облу- говы Mn и Ni пол- ов). Оставшиеся на Sn вымывают 60-ю переводят в хлориды мюне, заполненной Cl-форме. As вымы- и 1 N HCl, Te — M H₂C₂O₄, Sn — 30-ю), + 2 M NH₄NO₃. Ак- ных изотопов наме- четчики.

γ -спектры выде- й приведены на дние результаты чегом химическо- тены в табл. 2. ъекта при анали- лана брался про- i ректификацией.

Таблица 2

Определение примесей в таллии и трихлорметилсилане

Элемент	Изоп, по кот. форму выделяется	Энергия γ -квантов, КэВ	Содержание, %	
			в таллии	в силане
Au	^{199}Au	410	—	$<3 \cdot 10^{-9}$
Sb	^{125}Sb	550	$6 \cdot 10^{-4}$	$8 \cdot 10^{-3}$
Ga	^{76}Ga	630, 830	$3,9 \cdot 10^{-4}$	$<4 \cdot 10^{-6}$
Fe	^{59}Fe	1100, 1295	$3 \cdot 10^{-3}$	$<1 \cdot 10^{-4}$
Cu	^{64}Cu	510	$3 \cdot 10^{-3}$	$2,9 \cdot 10^{-3}$
Te	^{125}MTe	140	$1,3 \cdot 10^{-3}$	$<1 \cdot 10^{-4}$
Co	^{60}Co	1170, 1330	$2,3 \cdot 10^{-4}$	$<1 \cdot 10^{-6}$
Se	^{75}Se	140, 270	—	$<3 \cdot 10^{-4}$
In	^{114}MIn	190, 550	$5,1 \cdot 10^{-4}$	$1,7 \cdot 10^{-3}$
Sn	^{113}Sn	390	$1,2 \cdot 10^{-4}$	$<2 \cdot 10^{-4}$
Cd	^{115}Cd	520	—	$<3 \cdot 10^{-7}$
Zn	^{69}MZn	440	$2,8 \cdot 10^{-3}$	$<1 \cdot 10^{-6}$
W	^{187}W	134, 480, 680	—	$<6 \cdot 10^{-6}$
Re	^{186}Re	137	—	$<2 \cdot 10^{-7}$
Ag	^{110}Ag	680, 880	—	$<2 \cdot 10^{-7}$
As	^{76}As	550	$3,6 \cdot 10^{-4}$	$3 \cdot 10^{-3}$
K	^{42}K	1530	—	$7 \cdot 10^{-3}$
Na	^{24}Na	1370, 2750	—	$1,6 \cdot 10^{-3}$

5%-ного изоамилового спирта и 0,1 М раствор ДБТФК в четыреххлористом углероде. Средние результаты анализа нескольких навесок трихлорметилсилана с учетом химического выхода приведены в табл. 2.

Все предлагаемые методики предварительно проверены с помощью меченых атомов. Количество каждого элемента определяется сравнением активности выделенной примеси с активностью соответствующего эталона.

Выводы

1. Разработана методика γ -спектрометрического определения Au, Sb, Ga, Fe в мышьяке и кремнии.
2. Разработана методика определения Sb, Ga, Fe, In, Zn, Cu, Co, As, Te, Sn в таллии.
3. Разработана методика определения Au, Sb, Ga, Fe, Cu, Te, Co, Se, In, Sn, Cd, Zn, W, Re, Ag, As, Na, K в трихлорметилсилане. Эта методика может быть применена для анализа кремния, карбида кремния, германия.

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А. Пронин

Таблица 2

хлорметилсилане

Содержание, %

алли	в силане
10 ⁻¹	< 3 · 10 ⁻³
10 ⁻²	8 · 10 ⁻³
10 ⁻³	< 4 · 10 ⁻³
10 ⁻⁴	< 1 · 10 ⁻³
10 ⁻⁵	2,9 · 10 ⁻³
10 ⁻⁶	< 1 · 10 ⁻³
10 ⁻⁷	< 1 · 10 ⁻³
10 ⁻⁸	< 3 · 10 ⁻³
10 ⁻⁹	1,7 · 10 ⁻³
10 ⁻¹⁰	< 2 · 10 ⁻³
10 ⁻¹¹	< 3 · 10 ⁻³
10 ⁻¹²	< 1 · 10 ⁻³
10 ⁻¹³	< 6 · 10 ⁻³
10 ⁻¹⁴	< 2 · 10 ⁻³
10 ⁻¹⁵	< 2 · 10 ⁻³
10 ⁻¹⁶	3 · 10 ⁻³
10 ⁻¹⁷	7 · 10 ⁻³
10 ⁻¹⁸	1,6 · 10 ⁻³

ДБТОК в четырех-
тиза нескольких на-
кого выхода приве-

но проверены с по-
элемента определя-
меси с активностью

ского определения

Ga, Fe, In, Zn, Cu,

Zb, Ga, Fe, Cu, Te,
хлорметилсилане.
за кремния, карби-

Активационное определение примесей в полупроводниковых материалах 175

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indicate that the presence of the O atom in $\text{SbOQ}\cdot 2\text{H}_2\text{O}$ is the main difference between the 2 compds. and the 2 8-hydroxyquinoline mols. in $\text{SbOQ}\cdot 2\text{H}_2\text{O}$ are firmly bound through the N atom. The uv-visible absorption spectra of the Sb(III) complexes are similar to those obtained for other cations contg. no d-electrons; the absorption bands are due to combined org. ligands. The diffuse reflectance spectra indicate that the 2 compds. are structurally different and thus confirm the investigation. JDJN

56694w Qualitative analysis by filtered electron images. Castaing, R.; El Hili, A.; Henry, L. (Fac. Sci., Orsay, France) *Congr. Int. Opt. Rayons X Microanal., 4th Orsay, Fr. 1965* (Pub. 1966), 77-82 (Fr). A method of qual. anal. based on electron images filtered by a magnetic prism and an electrostatic mirror is described. The limits of applying this method depend on the characteristics of the spectra energy losses. Luigi Campanella

56695x Determination of impurities in uranium compounds by atomic absorption. Walker, C. R.; Vita, O. A. (Chem. Anal. Dep., Goodyear At. Corp., Piketon, Ohio). *Anal. Chim. Acta* 1968, 43(1), 27-35 (Eng). A method is described for the detn. of 14 elements (Al, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Zn) in U and U compds. by at. absorption spectroscopy. A sample is dissolved in 6-8N HNO_3 , from which the U is selectively removed by a single extrn. with Bu_3PO_4 . The aq. layer is evapd. to dryness and the residue is redissolved in 0.2N HCl. Any or all of the elements can then be detd. in this 1 soln. by at. absorption spectroscopy. The limits of error in the analyses are $<10\%$. Thus, the method gives about the same precision as colorimetric procedures, and it is much more precise than emission spectroscopy. RCXR

56696y The analysis of silver(II) oxide. Lloyd, C. P. (Univ. Newcastle, Newcastle, Aust.). *Anal. Chim. Acta* 1968, 43(1), 95-107 (Eng). Five methods for the anal. of Ag_2O were crit. examd. and modified procedures are proposed. The effects of varying temp., soln. compn., and amt. of oxide were studied for methods based on: the oxidn. of FeSO_4 in the presence of H_2SO_4 or acetate-buffered media; the oxidn. of iodide ion in neutral satd. soln. or in acetate-buffered soln.; and the oxidn. of H_2O to yield O from strong acid solns. 20 references. RCXR

56697z Potentiometric titrations with ion-exchanging membrane electrodes. III. Experimental results. Ijsseling, F. P.; Van Dalen, E. (Free Univ., Amsterdam, Neth.). *Anal. Chim. Acta* 1968, 43(1), 77-87 (Eng). Potentiometric titrns. with ion-exchanging membrane electrodes for end point detection are described for simple pptn. and acid-base reactions. When only monovalent ions are present, there is a qual. agreement between the titrn. curves obtained and the theoretically calcd. curves. RCXR

56698a Determination of impurities in highly pure substances with the aid of diantipyrylmethane. I. Zhivopistsev, V. P.; Petrov, B. I.; Selezneva, E. A.; Sibiryakov, N. F. *Tr. Kom. Anal. Khim., Akad. Nauk SSSR, Inst. Geokhim. Anal. Khim.* 1968, 16, 80-3 (Russ). Small amts. of Sb, Bi, Cd, Zn, and Sn (impurities) can be extd. with the title compd. (I) in CCl_4 from Cl^- solns. (optimal concn. 2.5-3N HCl) and Se, Hf, Y, U, and rare earth elements from nitrate solns. (optimal concn. 0.2-0.5N HNO_3 for Se, Bi; 6N HNO_3 for Hf). This gives a satisfactory sepn. of the elements of very pure salts, such as salts of Al, Ni, Cr, Be, Mn, alkali, and alk. earths which are not extractable or only slightly extractable. The ext. is evapd., fumed with H_2SO_4 , mixed with Zr standard, and calcd. Samples thus prepd. were analyzed spectrographically (comparison line Zr 2571.4 Å.; slit width 0.004 mm.). Quant. detns. are made with a calibration curve. W. Roubo

56699b Increase in the sensitivity of the spectrographic determination of trace impurities in refractory bases. Moroshkina, T. M. *Tr. Kom. Anal. Khim., Akad. Nauk SSSR, Inst. Geokhim. Anal. Khim.* 1968, 16, 62-6 (Russ). Small amts. (10^{-3} - $10^{-4}\%$) of Fe, Ti, Al, Si, Ca, Ni, Co, Mo, and Ta were detd. in WO_3 , Nb_2O_5 , and Ta_2O_5 . Samples (refractory oxides) were made into disks by sintering equal amts. of the sample and very pure Cu powder for 30-40 sec. in a special elec. furnace. The disks were then arced (a.c.) on supported Cu electrodes (diam. 8 mm.; arc current 8 amp.; voltage 220 v.; exposure time 2 min.). The intensities of lines in the base material or the intensities of the background near the anal. lines of the element being detd. were used as the internal standards. The increase in sensitivity was confirmed for Ca, Ta, and Al in Nb_2O_5 , a somewhat improved sensitivity was found in the detn. of Fe and Nb in Ta_2O_5 ; and a greatly improved sensitivity was found in the detn. of Ti and Ni. 4 references. W. Roubo

56700v Wet-chemical determinations of some common impurities in alumina. Julietti, R. J. (Morganite Res. and Develop. Ltd., UK). *J. Brit. Ceram. Soc.* 1968, 5(1), 47-58 (Eng). Standard methods for the colorimetric detn. of Ti, Fe, Si, V, and Na in high-grade Al_2O_3 are suggested. Ti is detd. by reducing the Fe^{3+} to Fe^{2+} , complexing Al with NaOAc , adding Tiron reagent, adjusting the pH to 3.8 with 8N H_2SO_4

and measuring the absorbance after 20 min. at 380 m μ . To det. $>0.005\%$ Fe_2O_3 , Fe^{3+} is reduced with $\text{NH}_2\text{OH}\cdot\text{HCl}$, the Fe^{2+} 1,10-phenanthroline complex is developed in a $\text{NaOAc}\cdot\text{H}_2\text{O}$ buffer (pH 3.5-4.2), and the absorbance is measured at 510 m μ . To det. 0.002-0.1% Si ($\text{P}_2\text{O}_5 + \text{V}_2\text{O}_5 <0.02\%$), an aliquot of a HNO_3 soln. of the Al_2O_3 is adjusted to ~ 60 ml. with H_2O , and treated with sufficient HNO_3 to adjust a similar aliquot to pH 0.85-0.90, and 5 ml. of 0.06M Na molybdate is added. After 15-25 min. at 20-5°, tartaric acid and H_2SO_4 are added, and the complex is reduced with ascorbic acid. After 10-40 min. the absorbance is measured at 815 m μ . V is detd. by oxidn. to V^{5+} with KMnO_4 , adding *N*-benzoyl-*N*-phenylhydroxylamine in HCl soln., extg. the violet complex with CHCl_3 , and measuring the absorbance at 524 m μ . Cr_2O_3 and TiO_2 must be <0.001 and 0.003%, resp. V is also detd. by catalytic oxidn. with KClO_4 and PhOH as accelerator. The absorbance is measured at 480 m μ . For the detn. of alkali metals, the Al_2O_3 is completely dissolved either by alk. fusion with Li compds. or by decompn. with HCl in a sealed quartz tube. M. Elmslie

56701w Activation determination of impurities in some semiconductor materials. Artyukhin, P. I.; Gilbert, E. N.; Pronin, V. A. *Tr. Kom. Anal. Khim., Akad. Nauk SSSR, Inst. Geokhim. Anal. Khim.* 1968, 16, 169-75 (Russ). The methods for activation detn. of some impurities in Si, As, Tl, and MeSiCl_3 (I) were worked out on the basis of extrn. properties of bis(2-chloroethyl) ether (II) and dimethylbenzylammonium chloride (III). In esp. pure As and Si samples, Au, Ga, Sb, and Fe were detd. with a relative error of ± 10 and chem. yields of the elements detd. of 90-7%. Together with standards, 100 mg. As or 400-450 mg. Si is irradiated (1.8×10^{19} neutrons/cm 2 -sec.) for 8 hrs. After the sepn. of As by aqua regia and Si in the form of SiF_4 , the residue is dissolved in 10N HCl and extd. with II. The γ -spectra of Au, Sb, Ga, and Fe impurities in As and Si are reproduced. The irradi. conditions for the anal. of Tl and I are the same as given above. The greatest part ($\sim 90\%$) of the Tl of the Tl sample is sepd. by extrn. with II from 3N HCl; 10N HCl is added to the aq. soln. and Sb, Ga, Fe, and Tl residues are extd. by II. After 3-fold evapn. in a mixt. of HNO_3 and HF, the aq. phase is dissolved in 6M HF and In, Zn, Cu, and Co are eluted by means of 6M HF on a column contg. Dowex 1 anion exchange resin (F $^-$ cycle). Te, As, and Sn held on the column are eluted with 17M HF, converted to chlorides, and sepd. on a column contg. Dowex 1 in the Cl^- cycle by means of 11N HCl, 0.1M $\text{H}_2\text{C}_2\text{O}_4$, and 0.2M $\text{H}_2\text{C}_2\text{O}_4 + 2M \text{NH}_4\text{NO}_3$ for As, Te, and Sn, resp. The γ -spectra of Sb, Ga, Fe, Zn, In, Cu, and Co, sepd. from Tl, are given. I was hydrolyzed before anal., and the residue was dried and irradiated. A scheme for the extrn. and sepn. of impurities into groups suitable for γ -spectrometric detn. is given. II, 0.08M III in dichloroethane contg. isoamyl alc., and 0.1M dibutylthiophosphoric acid in CCl_4 were used for the extrns. Au, Sb, Ga, Fe, Cu, Te, Co, Se, In, Sn, Cd, Zn, W, Re, Ag, Na, and K can be detd. in I. The same method can be used for the anal. of Si, SiC, and Ge. 16 references. Vaclav Sara

56702x Effect of "third" elements during the spectrographic analysis of alloys. Goryachev, V. N. (USSR). *Sb. Statei Fiz. Vop. Spektrosk.* 1967, 64-70 (Russ). From *Ref. Zh., Khim.* 1968, Abstr. No. 2G25. The effect of various concns. of Zn (5, 15, 25, and 42%) in Cu-Zn alloys on the blackening of Cu lines was studied. Curves in the coordinates $S\text{-log } C_{Zn}$ were obtained previously by V. K. Prokof'ev (1947), which show that, with increasing Zn concn., blackening of Cu lines increases in an arc discharge and decreases in a spark discharge. Without resorting to expt., this phenomenon is assoc. with the change in temp. of the discharge. The Sach equation and a formula, which assoc. line intensity with concn. and degree of ionization of atoms in plasma, and also with temp. of discharge, were used to find values proportional to Cu line blackening. At the same time, it is assumed that $n_{Cu} n_{Zn} = C_{Cu} C_{Zn}$, where n is the element concn. in a discharge and C their concns. in the electrodes. On the basis of Prokof'ev's data, it is assumed that at Zn concns. in an alloy of 5, 15, 25, and 42%, the temp. of an arc discharge is 6000, 6300, 6500, and 6900°, resp., while the temp. in a condensed spark is 9500, 9700, 9800, and 10,000°. The results of computations are presented graphically on the same scale with Prokof'ev's exptl. data. A comparison of exptl. and calcd. graphs shows that the curves are similar for the majority of lines. From this, the conclusion was drawn that the mechanism of the effect of 3rd elements is primarily thermal. MRK

56703y Solid-phase chemical analysis in the field. Voskresenskii, P. I. (Mosk. Geologorazved. Inst. im. Ordzhonikidze, Moscow, USSR). *Izv. Vyssh. Ucheb. Zaved., Geol. Razved.* 1963, 11(3), 61-4 (Russ). Solid phase anal., based on reactions between solid substances, is a promising method for rapid anal. in the field. All qual. chem. reactions that usually occur in solns. also occur in solid substances at normal temp. The solid phase reactions were made both with pure salt and the minerals. Reactions could be made to occur on the surface of minerals or ores, with pure minerals without their decompn., and with

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