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THE USE OF THE MICROTRON FOR THE ACTIVATION ANALYSIS OF PURE METALS AND ALLOYS

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Oxygen and carbon concentrations up to 0.06 ppm and 0.03 ppm respectively were determined in high purity metals such as Fe, Cu, Nb, Mo, In and some others. Analytical procedures and results of the determination of alloying additives in a number of rare metal alloys are given. The relative standard deviation constitutes 0.02 to 0.04. Accuracy of the procedures used is confirmed by a comparison of experimental results with those of the other analytical methods. Experimental data on the sensitivity of determining 35 elements are reported on irradiating them with thermal neutrons and a bremsstahlung emitted by the microtron. For most elements (for radioactive isotopes having a half-life of above 2 min.) sensitivity of the analysis is 10^{-6} to 10^{-8} g, at the microtron current of 30 μA and irradiation time of less than 10 min.

Determination of trace amounts of oxygen and carbon by photon activation

The energy of the accelerated beam of the microtron was 29,2 MeV during the irradiations. Due to some improvements in the construction of the accelerating cavity of the microtron it became possible to obtain an average accelerated current of 35 μA.

The nuclear reactions for the determination of oxygen and carbon were $^{16}O(\gamma, n)$ ^{15}O and $^{12}C(\gamma, n)$ ^{11}C. For rapid isolation of oxygen-15 from irradiated samples the carbon reduction method was employed. The process of extraction was performed in sealed graphite crucibles in the stream of argon at temperature 2000 – 3000 °C. The whole time of extraction did not exceed 2 min.[1]

The results of the determination of oxygen contents in some standard reference materials and samples of pure iron and molybdenum, prepared in Zentralinstitut für Festkörperphysik und Werkstofforschung, Dresden, are given in Table 1.

The sensitivity reached for the most pure iron samples weighing to 1 g is 0.06 ppm of oxygen. The accuracy is about 50% for oxygen contents $\leqslant 0.1$ ppm.

The results on determining oxygen concentration in the samples of pure niobium are presented in Table 2.

Table 1
The results of the determination of oxygen contents in some SRM and samples of pure iron and molibdenum by gamma-activation

NN	Sample	Oxygen content, ppm (quality certificate for SRM)	Determined by gamma-activation ppm
1.	SRM "98" ppm (GDR)	98	90, 130, 93
2.	SRM "Steel-45" (USSR)	32	31, 28.5, 30
3.	SRM N 1094 (NBS, USA)	from 2.5 to 7.5 mean value 4.5	2.9, 2.2, 2.2
4.	SRM N 1090 (NBS, USA)	484 ± 14	479, 481, 488, 442
5.	Iron G 57	–	0.16
	G 58		0.2
	G 59		0.4
	G 60		0.4
	G 22		0.1
	G 23		0.2
	G 102		0.08
	G 103		0.3
	G 116		2.7
	G 117		3.4
	G 118		7.2
	G 1026		0.26
	G 1026a		0.45
6.	Molybdenum		
	Sinter BGW N 1		0.93
	Sinter BGW N 2		0.85
	Sinter BGW N 3		1.60

For the rapid etching of surface layer of irradiated niobium samples melted potassium hydroxide (KOH) was used, the etching time was below 10 sec.

The sensitivity obtained for niobium samples from 0.5 to 1 g by weight is 0.2 ppm.

Table 3 presents the results of gamma-activation determining oxygen in pure indium. The sensitivity for oxygen in case of indium is only 0.2 – 0.3 ppm. This is due to the penetration into the sorber of some amount of atoms ^{113m}In(T = 21 m) and carbon ^{11}C, the half-life of which is also 20 min. Comparing the oxygen content

Table 2
The results of determining oxygen in niobium, prepared in ZFW, Dresden

Nb	Oxygen introduced ppm (calculated)*	Oxygen content		
		Reductive fusion method ppm*	Internal friction ppm*	Gamma-activation, ppm
Z – Nb 160 3/1	60	51	62	50, 58
Z – Nb 160 3/2	100	126	126	150, 110, 120
Z – Nb 161 3/1	200	253	210	150, 140
Z – Nb 161 3/2	25	45	45	65, 77
Z – Nb 170 3/2	–			14, 14, 12
Z – Nb 170 3/1	100 atomic		20	230
G – Zn 122.1	–			0.2, 0.2

*The values were obtained also in ZFW, Dresden.

Table 3
Determination of oxygen in pure indium and alloy

Sample	Oxygen found, ppm	
	Reductive melting in argon	Gamma-activation
In-1	4 ± 1.3	2.3 ± 0.7
In-2		1.0; 0.8
In-3 from peripheral parts of the bar		2.4 ± 0.4
In-3 from central part		0.7 ± 0.09
V-Al alloy		300, 330, 330

in the samples taken from the central parts of the bar with those from its peripheral parts one can see that this quantity is several times smaller in the centre than in the peripheric region, and the quantity of interfering atoms ^{11}C is also different but always proportional to the quantity of oxygen. This may indicate that in indium oxygen and carbon exist in the form of some compound – CO or CO_2 which is extracted from the sample together with dissolved oxygen by the extraction at a high temperature.

In Table 3 the results of the oxygen determination in the V-Al alloy are also presented.

The determination of carbon in high purity iron and molybdenum was made by rapid separation of carbon-11 in the form CO_2. After irradiation and etching of the surface layer of ~ 50 μ the samples were introduced into an alumina crucible containing the oxydizing bath of 87.5% Pb_3O_4 and 12.5% B_2O_3. The crucible with a sample was heated by a high frequency furnace of 2.5 kw.

The extraction procedure was finished within 10 min.[2] The results on the determination of carbon in iron and molybdenum were presented in the previous paper.[3]

The use of the microtron for the activation analysis of alloys

A bremsstrahlung of an energy of up to 29.2 MeV and thermal neutrons emitted by the microtron and characterized with a flux density.[1-3] 10^9 $n \cdot cm^{-2} \cdot sec^{-1}$.were used for irradiation of samples.[4] It was converted to a fast neutron flux with the aid of a lead converter. Water moderator was used to slow down neutrons to thermal level.

Induced activity of the specimens was registered by a semiconductor Ge(Li) spectrometer with a detector volume of 21 cm^3 and a spectrometer resolution of 3 keV along 662 keV gamma line of ^{137}Cs.

The present paper aims at assessing the possibility of using the microtron in combination with a semiconductor gamma-spectrometer in the activation analysis. To this effect, it is necessary to establish the sensitivity of determining elements both by irradiating specimens by neutrons and by gamma-ray quanta from the microtron.

The second aim of the present paper was to set up appropriate procedures for analysing alloys.

The main components and the doping impurities of the alloys are currently determined by chemical or physico-chemical methods.[5,6] There exist extremely few procedures adopted for using the activation method in the analysis of alloys which fact is probably accounted for by its traditionally, preferential use as a high sensitivity method for the analysis of high-purity substances and mineral raw materials. On the other hand using the semiconductor gamma-spectrometry makes it possible not only to perform the high sensitive activation analysis but also to do determinations of rather great concentrations of elements with high sensitivity.[7]

The sensitivity of determination was established experimentally by irradiating quantities of elements which are close to the detection limit (Tables 4 and 5). According to Ref.[8] the detection limit was assumed to be the value of mass proportional to a useful signal which may be measured by a spectrometer with a relative standard deviation of 0.3.

Table 4
The sensitivity of determination of elements at the irradiation by gamma-quanta of the microton. The average current of the microton 10 mkA, time of irradiation 10 min

Element	Sensitivity, g
V, Ce	$n \cdot 10^{-4}$
Al, Sc, Cr, Zn, Ni, Rh, Hf, Pt	$n \cdot 10^{-5}$
Co, Ge, As, Nb, In, Te, Gd, Sm, Re, Ir, Pb, W	$n \cdot 10^{-6}$
Cu, Ga, Zr, Mo, Cd, Sn, Ta, Au	$n \cdot 10^{-7}$

Table 5
The sensitivity of determination of elements at the irradiation by thermal neutrons of the microtron. Thermal neutron flux 10^9 n/cm^2, time of irradiation 10 min

Element	Sensitivity, g
Ge, As, Nb, Pr, Nd, Gd	$n \cdot 10^{-4}$
Nd, Al, Ce, Ti, Se, Rb, Sr, Mo, W, Rh, Pd, Sb, Te, Ba, La, Yb, Hf, Hg	$n \cdot 10^{-5}$
Sc, Cu, Ga, Br, Sm, Ho, Er, Lu, Re, Ir, Th	$n \cdot 10^{-6}$
V, Mn, Co, I, Au, U	$n \cdot 10^{-7}$
In, Eu, Dy	$n \cdot 10^{-8}$

For most elements listed in Table 5 the experimentally found sensitivity coincides with the theoretical one. Discrepancies do not exceed a factor of 1.5 to 2 times, with the exception of ^{60m}Co, ^{94m}Nb, ^{88}Rb, ^{122m}Sb, ^{165m}Dy. The mentioned discrepancies are probably due to our insufficient knowledge on activation cross-sections and emergence of gamma-ray quanta for decay.

Regarding the elements listed in Table 4 we compiled an atlas of gamma-spectra for radioactive isotopes formed by irradiating by bremsstrahlung at an energy of up to 30 MeV. The spectra atlas was used for deciphering the spectra of irradiated specimens, for selecting analitical gamma lines of radioactive isotopes and for estimating levels of reciprocal interference of the elements.

The data concerning thermal and fast neutrons flux density variations in the microtron are reported in Ref.[4]

To prevent eventual errors in the analytical results due to a spatial variation of neutron and gamma fields, the irradiated specimens were placed between the monitors of the elements being determined or the internal reference method was resorted, too.

Several procedures were worked out for the analysis of alloys.

Table 6
The results of the determination of Ge in Nb – Ge alloy

Neutron-activation analytical method (Ge, %)		Chemical analytical method
with a microtron	with a reactor	
20.1 ± 0.7	19.8 ± 0.6	21.4 ± 1.0
22.8 ± 0.7	22.4 ± 0.6	21.2 ± 1.0
27.0 ± 0.9	26.7 ± 0.8	27.4 ± 1.0
30.0 ± 0.9	30.3 ± 0.8	31.6 ± 1.3

The confidence intervals are presented for the confidence probability 0.95.

Determination of germanium in thermal neutron-irradiated Nb–Ge alloy

Specimens weighing some 30 to 50 mg were wrapped in an aluminium foil and irradiated for 20 min in a $1 \cdot 10^9$ n $\cdot$ cm^{-2} $\cdot$ sec^{-1} neutron flux. Germanium standards were being irradiated at the same time. The weight of Ge specimens was 25 to 30 mg. Germanium was determined according to 0.265 MeV gamma line of ^{75}Ge. The results of germanium determination are listed in Table 6.

Determination of germanium and niobium in Nb–Ge alloy on irradiating the specimens with gamma-ray quanta

Germanium was determined using ^{75}Ge formed as a result fo ^{76}Ge(γ, n) ^{75}Ge reaction, while niobium – referring to ^{92}Nb resultant from ^{93}Nb(γ, n) ^{92}Nb reaction.

The gamma-activation analysis revealed the presence in specimen 1 (Table 6) of 20.4 ± 0.6% germanium and 80.0 ± 2.9% niobium, and 30.5 ± 0.9% germanium and 68.9 ± 2.5% niobium in specimen 4.

The procedure of determining the alloy composition on irradiating the specimens by gamma-ray quanta exhibits a lower error due to a greater number of pulses selected in the analytical peack of ^{75}Ge and it makes possible to control accuracy of the analysis of each specimen (in our specific case, the total of niobium and germanium concentrations should be equal to 100%).

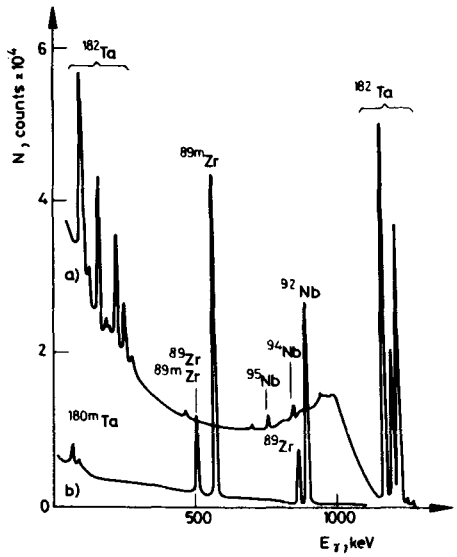

Fig. 1. Apparatus gamma-spectrum of Nb–Zr alloy after the irradiation by thermal neutrons of a pile (curve a) and gamma-quanta of the microtron (curve b)

A study of gamma-spectra of the radioactive isotopes resultant from (γ, n) or (n, γ) reactions showed that ^{92}Nb and ^{75}Ge analytical lines which we selected cannot be superposed uncontrollably by gamma lines of radioactive isotopes of other elements.

Determination of zirconium in Nb–Zr alloy

The determination of zirconium in niobium in neutron fluxes supplied by reactors is virtually impossible due to a low activation cross-section of zirconium and, mainly, due to interferences from tantalum which is normally present in the specimens. Even as low as $(2–3)\cdot 10^{-3}$% tantalum content inhibits any determination of zirconium, if its concentration in a specimen is below 2 to 3%. Zirconium isotopes have an activation resonance, but cadmium-plating of the specimens against tantalum-induced interferences cannot produce any significant sensitivity gain, whereas the analysis becomes much more complicated. On irradiating the specimens by gamma-ray quanta the sensitivity of determining zirconium (using ^{89m}Zr) is 5.10^{-4}% for niobium, and as it was shown by some experiments, tantalum concentrations as high as several per cent could not hinder the determination of such amounts of zirconium. For the illustration of this matter we present Fig. 1. The determination of decimal fractions of a percent and whole percents of zirconium content in an alloy may be performed with a high pre-

cision, since the number of pulses picked-up in the ^{89m}Zr peak is equal to $n \cdot 10^3$ to $n \cdot 10^4$, while the background-to-useful signal ratio is about 30.

In a study of zirconium distribution (Zr about 0.8 to 2%) in the ingots and rolled products manufactured of Nb-Zr alloys, the internal standard method was used, whereas ^{92}Nb was a flux monitor. In this case the specimens were irradiated without standards and the number of samples was increased up to 8 to 10 in one container. When a necessity arose for ascertaining the absolute Zr concentration in the alloy, 2 to 3 specimens out of the whole lot were subjected to irradiation along with the references.

Determination of Mo and Zr in a multi-component alloy

Alloy-made specimens weighing some 40 to 50 mg and containing Mo, Zr and W as alloying admixtures were irradiated by gamma-ray quanta for 15 to 20 min. Some 2 to 3 min after irradiation zirconium was determined as per ^{89m}Zr(E = 589 keV). In neutron-irradiated specimens molybdenum was determined as per ^{101}Tc (E = 304 keV), while in gamma quanta-irradiated ones the determination was done as per ^{99}Mo(E = 140 keV). The results of the determination of these elements are reported in Table 7.

Discussion of the results

The results listed in Tables 4 to 7 demonstrate that the use of the microtron for the neutron- and gamma-activation analysis will be rewarding in determining the main components and alloying additives in the alloys and compounds as well as the impurities contained in pure substances at the concentration levels of 10^{-3} to 10^{-5}%.

For the elements having short-lived radioactive isotopes a relatively high sensitivity may be reached even at irradiating the specimens with a low (as compared to that supplied by a nuclear reactor) neutron flux from the microtron. This fact is accounted for by a possibility of attaining during irradiation activity values in practice which are close to saturation, or at least comparable with saturation activity value. Some 26 out of total number of 35 elements listed in Table 5 fall within this category of elements, at an irradiation time of 1 hr.

On irradiating the specimens with gamma-ray quanta supplied by a microtron, problems which are traditionally considered to be difficult for the instrumental neutron-activation analysis may be solved. For instance, after an irradiation for 6 min. zirconium was determined in hafnium and in niobium at sensitivities of $8 \cdot 10^{-5}$% and $5 \cdot 10^{-4}$% respectively, while niobium was found in tantalum at a sensitivity of $5 \cdot 10^{-4}$% (after an irradiation for 30 min).

On irradiating the specimens by a mixed flux of neutrons and gamma-ray quanta, one has to expect a broadening of the range of the elements being simultaneously determined in various combinations of rare metal-base alloys. As it was shown by a study

Table 7
Mo and Zr determination in alloy by different analytical methods

Molybdenum, %				Zirconium, %	
Analytical method				Analytical method	
Spectral	Chemical	Neutron-activation	Gamma-activation	Spectral	Gamma-activation
2.00 ± 0.06	2.08 ± 0.08	2.01 ± 0.06	2.07 ± 0.06	1.00 ± 0.04	0.98 ± 0.04
2.00 ± 0.06	2.15 ± 0.08	2.00 ± 0.06	–	0.94 ± 0.04	0.97 ± 0.04
2.00 ± 0.06	2.18 ± 0.08	2.07 ± 0.06	2.06 ± 0.06	0.87 ± 0.04	0.86 ± 0.04
2.02 ± 0.06	–	2.08 ± 0.06	2.04 ± 0.06	0.93 ± 0.04	0.95 ± 0.04

The confidence intervals are presented for the confidence probability 0.95.

of the apparatus gamma-spectra of the irradiated elements, a greater complexity of the spectra of the specimens irradiated by a mixed flux does not result in normally a noticeable deterioration of accuracy and speed of an analysis even for the multicomponent alloys consisting of some 3 to 5 rare elements.

All the above-stated facts should convince us that the use of the microtron would be of much expediency for the activation analysis in the commercial analytical laboratories.

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