THE ACTIVATION ANALYSIS OF ELECTRONIC SCRAP SAMPLES ELEMENTAL COMPOSITION

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A series of aspects related to the problems of electronic scrap materials (lamp and semiconductor electronics, UHF-technique, etc.) utilization have been considered, namely: evaluation of the element composition of samples in the "black box" mode (lack of apriori information on the objects under study); estimation of profitability and expediency of extraction of different-type metals (first, Au and Ag, also W, Mo, Ni ets.); choice and ranking of methods of analysis and extraction during utilization. The analysis of the problems was carried out on the basis of the activation analysis experimental data at the M-30 microtron (Institute of Electron Physics, Ukr. Nati. Acad. Sci.).

To estimate the possibilities of "electronic scrap" samples analysis the corresponding experiment has been performed at the M-30 microtron.

The analysis of the nuclear constants has allowed the most suitable experimental plan to be chosen aimed to solve the above problem. This was the so-called randomized experiment, the principal feature of which is the lack of any priority (e.g. certain optimizing criteria). The experiment randomization enables one, in particular, to carry out the simultaneous irradiation of a great number of sample and any subsequent series of measurements. The randomized experiment forms a basis of any multi-element AA of samples of unknown composition.

Sample preparation

This preparation included certain procedures, in particular: a) presorting of samples by their types; b) weighing; c) sample preparation for irradiation and packing.

If should be noted that items a) and b) are not mandatory, i.e, the "black box" AA regime is possible that constitutes one of the essential advantages of this method over other ones.

Irradiation

The energy of the accelerated electrons was 18.5 MeV. The γ-beam was made free of low-energy (soft) electrons. Seven irradiation cycles were carried out (irradiation duration was $T_i = 1$—4 h).

Induced γ-activity measurements

The induced γ-activity was measured by means of a γ-spectrometric complex (GeLi-semiconductor detector DGDK-100B mounted inside the combined (Pb-Cu-Al-Cd-Fe) protection. 90 measurements were carried out, the duration of measurements being 5—25 min.

The irradiation regimes and geometry allow, in principle, the initialization of neutron: (n, γ), (n, n'), $(n, 2n)$, (n, p), (n, α) and photo-nuclear: (γ, n), (γ, p), (γ,γ'), (γ, α)-reactions for samples differing in shape and mass. They also allow the γ-spectrometry of samples within the 0—4 MeV γ-quanta energy range for γ-active nuclides (GAN) with half-decay period $(T_{1/2})$ varying from 1 min. to more than 100 days with a sufficient statistical provision.

Problem studying

In accordance with the goal of the present studies series of problems to be solved were formulated. They are as follows.

Qualitative analysis stage: selection of the most specific (informative) samples by their spectral composition and errors characterizing the randomized experiment dispersion (irradiation procedures, activity measurement procedures); photopeak (total absorption peak (TAP)) identification by energy and physical character, determination of GAN energy lines and possible chemical elements (CE); calculation of quantitative characteristics of energy lines and GAN time parameter function; formation of identified GAN list.

Quantitative analysis stage:— expansion of analytical scheme and line list for the determination of Au content by obtained quantitative characteristics; estimation of possible optional time regimes; estimation of economical profitability of noble metal extraction on the basis of element composition data.

Qualitative analysis of experimental data (analytical scheme selection)

Gold. Among the possible GAN production schemes, which represent the gold in the samples, one may consider the following analytical schemes for basic nuclear reactions (γ, n), $(n, 2n)$, (n, γ):

$_{79}Au^{197}$ (γ, n), $(n, 2n)_{79}Au^{196m2}$: E_γ keV $(n_\gamma, \%)$ = 333.0 (24); 355.72 (93.6); 426.0 (7.0); 1091.24 (0.17); $(T_{1/2} = 9.7$ hours).

$_{79}Au^{197}$ (γ, n), $(n, 2n)_{79}Au^{196}$: 326.2 (0.051); 333 (23.7); 355.7 (90.0); 426.1 (6.86); 521.4 (0.04); 759.1 (0.046); 1091.34 (0.17); $(T_{1/2} = 6.18$ days).

$_{79}Au^{197}$ $(n, \gamma)_{79}Au^{198m}$: 97.21 (68.9); 180.3 (64.7); 204.1 (50.3); 214.9 (77.1); 333.8 (15.4); $(T_{1/2} = 2.3$ days).

$_{79}Au^{197}$ $(n, \gamma)_{79}Au^{198}$: 411.8 (95.5); 675.9(1.06); 1088 (0.229); $(T_{1/2} = 2.7$ days).

Silver. Among the possible GAN production schemes, which represent the silver in the sample, the basic analytical schemes are as follows:

$_{47}Ag^{107}$ (γ, n), $(n, 2n)_{47}Ag^{106}$: 511 (11.9); 511.6 (16.9); 616.6 (0.265); 622.8 (0.26); 873.4 (0.173); 1050 (0.163); 1128 (0.103); $(T_{1/2} = 23.96$ min.).

$_{47}Ag^{107}$ (γ, n), $(n, 2n)_{47}Ag^{106m}$: 406.2 (13.5); 429.6 (13.2); 451.0 (28.4); 511.8 (88.2); 616.2 (21.7); 717.3 (29.1); 748.4 (20.7); 804.3 (12.4); 824.7 (15.4); 847.8 (4.1); 1046 (29.7); 1128 (11.8); 1199 (11.3); 1528 (16.4); $(T_{1/2} = 8.41$ days).

$_{47}Ag^{109}$ (γ, n), $(n, 2n)$ $_{47}Ag^{108m}$; $_{47}Ag^{107}$ $(n, \gamma)_{47}Ag^{108m}$: 72.9 (6.78); 433.9 (90.3); 614.4 (90.8); 722.9 (90.9); $(T_{1/2} = 127$ years).

$_{47}Ag109$ (γ, n), $(n, 2n)_{47}Ag^{108}$; $_{47}Ag^{107}$ $(n, \gamma)_{47}Ag^{108}$: 511(0.463); 433.9 (0.501); 618.9 (0.262); 633 (1.75); $(T_{1/2} = 2,37$ min.).

$_{47}Ag^{109}$ $(n, \gamma)_{47}Ag^{110m}$: 657.7 (94.7); 677.6 (10.7); 706.7 (16.7); 763.9 (22.4); 884.7 (72.9); 937.5 (34.3); 1384 (24.3); 1505 (13.1); $(T_{1/2} = 249.9$ days).

$_{47}Ag^{109}$ $(n, \gamma)_{47}Ag^{110}$: 657.7 (4.5); 815.3 (0.382); 1126 (0.0153); $(T_{1/2} = 24.6$ s).

The identification was performed both for the samples under study and for the standards:

— formation of identified GAN list. At this stage the GAN and CE list was formed for the samples studies as an example of the most identified and interesting samples: GAN — Ag^{110m}, Ag^{110}, Ag^{108}, Ag^{106m}, Au^{196m}, Au^{196}, Au^{198}, Au^{198m}, Au^{197m}, Pd^{111m}, Pt^{187m}, Ni^{65}, Br^{82}, Co^{57}, Pd^{101}, Co^{58}, Mn^{56}, Co^{61}, Fe^{59}, Co^{60}, Co^{60m}, Cu^{64}, Na^{24}, Ni^{57}, Pd^{111}, K^{40}; possible CE — Au, Ag, Ni, Br, Fe, Co, Mn, Cu, K, Na, Pd, Pt.

— calculation of TAP quantitative characteristics. For each TAP selected in all the scrap samples their basic quantitative characteristics have been calculated.

The TAP area ΔS is a characteristic of the analytical line E_γ and is the experimental value determined from the apparatus γ-spectrum:

$$\Delta S = \sum_{i=1}^{i=r} N_i - \Phi \ ;$$

$$\Phi = \frac{1}{2}(N_l + N_r) \cdot (r - l),$$

where l, r are the left and the right edges of a TAP, respectively; N_i is a number of readings in the i-th channel; Φ is a background.

Quantitative analysis. Estimation of the use of possible analytical schemes for Au and Ag determination

The analysis of the possible analytical schemes shown above indicates the complexity of the GAN decay process, therefore, to estimate the possibilities of their use in the quantitative determination of Au and Ag content the following analytical lines have been chosen for further study: Au[196]: 333.0 (24); 355.72 (93.6) (I); Au[196m]: 333.0 (23.7); 355.72 (90.0) (II).

Then: taking into account such parameters as the activation cross section, half-decay time, quantum yield, etc., the variant (I) was selected for further calculations.

The Au[198m] line (333.8 (17.5) — III) has also attracted much attention as the competing line to the analytical line Au[196]: 333.0 (24) when performing the calibration. Therefore this line has been selected for the calculations and was calculated in parallel with the line Au[196]: 333.0 (24).

It should be noted that the most interesting for the quantitative determination of Au content is the analytical line Au[198]: 411.8 (95.5) (IV).

The Ag[110m] has been selected for quantitative Ag determination, and all the lines (except E_γ (n_γ) = 1505 (13.1)) were calculated as the analytical ones.

The necessity to expand the possible, though complicated, analytical schemes and, respectively, the analytical lines, is due to the complexity of the element composition of the samples under study and respectively, their apparatus spectra. To perform that stage such quantitative characteristics as the time parameter function TP were calculated:

$$TP = \frac{1}{\lambda}\left(1 - e^{-\lambda T_i}\right)e^{-\lambda T_D}\left(1 - e^{-\lambda T_c}\right),$$

where $\lambda = \ln2/T_{1/2}$ is a decay constant, T_i is the irradiation exposure, T_D is the cooling time (i.e. the time between the end of irradiation and the start of the induced activity measurement), T_c is the induced activity measurement duration.

TP values were calculated both for the standards and the samples. Having the ΔS and TP values, one may calculate the absolute amount (mass) of CE in the sample for the relative AA variant by the following simple relation:

$$m = \frac{m_e T P_e}{\Delta S_e} \cdot \frac{\Delta S}{T P},$$

where e denotes the standard parameters.

To estimate the determination limit, the expression was used based on the known statistical "three-root background" criterion:

$$m_{min} = \frac{m \cdot 3\sqrt{\Phi}}{\Delta S},$$

where Φ is the background in that region of the apparatus spectrum, where the TAP of the ΔS area should lie.

In the case if the TAP is not revealed, one took $\Delta S = 1$. Thus, the above formulae attained the form:

$$m^* = \frac{m_e T P_e}{\Delta S_e} \cdot \frac{1}{T P}.$$

Element concentration in the sample was calculated by the following formula:

$$C = m/K,$$

where K is a mass of the sample.

To determine the multi-measurement error the following expression was used:

$$\overline{C} = \left(\sum_i C_i\right) \cdot \frac{1}{i}; \quad |\overline{C} - C_i| = \Delta C_i;$$

$$\overline{\Delta C_i} = \left(\sum_i \Delta C_i\right) \cdot \frac{1}{i};$$

$$\varepsilon_1 = \frac{\overline{\Delta C_i}}{C_i} \cdot 100 \ \%,$$

where i is a number of measurements; ε_1 being the relative error. In the case of single measurement, relative error ε_2 was derived

from $\varepsilon_2 = \dfrac{\sqrt{\Delta S + 2\Phi}}{\Delta S} = \dfrac{1}{\alpha}$.

All these relations hold in the case of the relative AA variant, when: the analytical schemes of standard and sample are totally the same; the irradiation is simultaneous in the same geometry at the irradiation unit; the geometry of measurements is the same.

Estimation of possible optimal time regimes

The estimation of possible optimal durations of irradiation (T_i) and measurements (T_c) was performed earlier and is, respectively, $T_i = (1—4\text{ h})$ and $T_c = (100—1000\text{ s})$. The choice of these values is governed by the economical and technological conditions of exploitation of such complicated nuclear physical setup as the M-30 microtron. The analysis of the data obtained at that stage indicates that the optimal cooling time is 24 h.
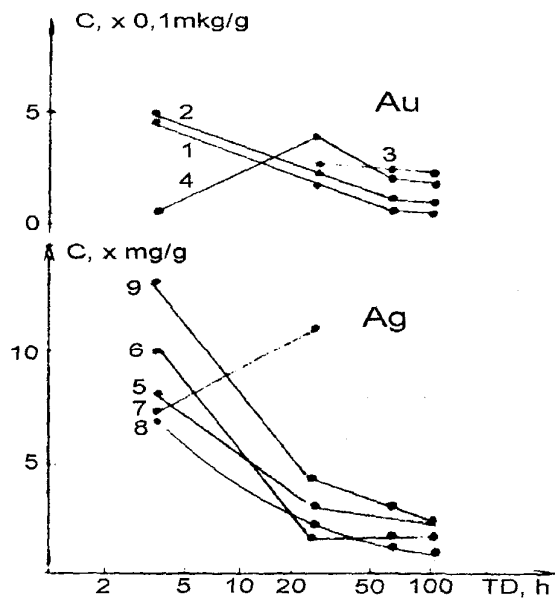

Fig.1. Concentration C as function of time of delay TD (hours) for Au (1 – 333,0 keV Au^{196}; 2 – 333,8 keV Au^{198m}; 3 – 355,7 keV Au^{196}; 4 – 411,8 keV Au ^{198}) and for Ag (5 – 657,7 keV Ag ^{110m}; 6 – 706,7 keV Ag ^{110m}; 7 – 763,9 keV Ag ^{110m}; 8 – 884,7 keV Ag ^{110m}; 9 – 937,5 keV Ag ^{110m}).

Estimation of profitability of metal extraction from electronic scrap samples

To estimate the profitability of noble metal extraction from electronic scrap consider a simple calculation scheme. Let the sample of mass m consist of two metals A and B with corresponding costs of W_A (UAH/g) and W_B(UAH/g), respectively at the metal concentrations C_A and C_B, respectively. The total sample cost is W(UAH/g).

In order to extract metals A and B (or only A) the chemical reagents of W_x(UAH/g) cost are used (their quantity is $m_x = k \cdot m$ (1)), where k is the excess coefficient. Then the following relations are valid:

$$m = m_A + m_B; \quad C_A + C_B = 1;$$

$$W_A \cdot m_A + W_B \cdot m_B = W,$$

where m_A and m_B are the total masses of A and B, respectively.

Consider some cases.

1. Let the technology be able to extract both metals. Then, the following relations must hold:

$$W_A \cdot m_A + W_B \cdot m_B > W_x\, m_x = W_x \cdot k \cdot m,$$

or

$$W_A \cdot C_A + W_B \cdot C_B > k \cdot W_x$$

2. If the technology fails to extract B, then the following relationships must hold:

$$W_A \cdot m_A > W_x\, m_x + W_B \cdot m_B,$$

or

$$W_A \cdot C_A > W_x \cdot k + W_B \cdot C_B,$$

or

$$W_A \cdot C_A > 1/2\,(k \cdot W_x + W)$$

3. If one neglects the cost of metal B $(W_B \neq 0)$: then $W = W_A \cdot m_A$, or $W_A \cdot C_A > k \cdot W_x$

Let us calculate the values: $W_A = 57$ UAH/g (Au), $W_B = 5 \cdot 10^{-2}$ UAH/g (approximate costs of W, Mo, Ni), $W_x = 1 \cdot 10^{-3}$ UAH/g (approximate cost of HCl, HNO$_3$), $W = 2.5 \cdot 10^{-3}$ UAH/g (approximate average costs of non-ferrous scrap), $K = 30$ (experimental value of all expences).

For the case 1 $(C_A = 5 \cdot 10^{-6}\text{ g/g} = C_{au})$ we have found the C_B value at which the profitability condition holds: $C_B > 0.6$ g/g = 600 g/t. For the case 2 we have found the C_A

value at which the profitability condition holds: $C_A > 2.85 \cdot 10^{-4}$ g/g = 285 g/t. For the case 3 we have found the C_A value at which the profitability condition holds: $C_A > 5.26 \cdot 10^{-4}$ g/g = 526 g/t.

A brief analysis of the C_B; C_A; C_A values allows one to conclude the necessity of development of the methods for C_A values increasing (case 2, 3) prior to the chemical extraction procedures and the reality of B metal extraction (W, Mo, Ni). Since fail to say a priori which et the cases 1–3 can be used, evidently the necessity to estimate the element composition of the samples under study by instrumental methods, i.e. the additional number of analyses does exist.

Conclusions

1. The fact of element composition in homogeneity of different-type electronic scrap samples has been confirmed justifying their artefact. Samples differ both in the Au, Ag and Mo, K, W, Ta, Ni, Fe, As, Mn, etc. content.

2. Based on the AA data the partitioning of electronic scrap into four types has been suggested: a) Cu-based scrap samples (wave guides and others); b) samples with large organic-material content (chips); c) various-capacity transistors; d) electron lamp elements. In this relation, at further application of the activation methods one has to solve a problem of development of corresponding multi-element standards.

3. In order to reduce the uncertainties in inhomogeneous sample analysis it is necessary to develop more sophisticated irradiation and measurement techniques, in particular, with the use of one- or two-axes sample rotation at irradiation and γ-activity measurement.

4. With the aim to increase the profitability of "electron scrap" recycling, it has been suggested to soft the samples after the first AA stage into the following groups: with higher and lower noble metal content; with low noble metal content, but with large content of other metals being of certain value, and so on.

5. The expediency of extraction of Mo, W, Ta, Cu and Ni for the second AA stage or storage (at the lack of other technologies) of such samples with large content of the above CE has been found.

АКТИВАЦІЙНИЙ АНАЛІЗ ЕЛЕМЕНТНОГО СКЛАДУ ЗРАЗКІВ ЕЛЕКТРОННОГО БРУХТУ

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Виконано розгляд низки питань, пов'язаних із проблемами утилізації електронного брухту (лампова та напівпровідникова електроніка, НВЧ-техніка і т.д.), зокрема оцінки елементного складу зразків у режимі "чорного ящика" (відсутність апріорної інформації про склад досліджуваних об'єктів); оцінки рентабельності та доцільності вилучення різних металів, у першу чергу золота та срібла; вибору та місця методів аналізу та вилучення цих металів у послідовності етапів утилізації. Розгляд проблематики виконано на основі експериментальних даних активаційного аналізу зразків електронного брухту на мікротроні М-30 ІЕФ НАНУ.