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Activation Analysis

OVERALL INSTRUMENTAL THERMAL NEUTRON ACTIVATION ANALYSIS OF
HIGH PURITY MATERIALS

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Summary

A more or less routine method for the determination of up to 55 trace elements down to the p.p.b. range is described. To obtain this, irradiation in a high thermal neutron flux followed by Ge(Li)- γ - spectrometry with large detectors and off-line computerized evaluation of the spectra is necessary. To cover the range of half-lives of the nuclides formed, spectrum measurements are carried out about one hour, one day, one week and one month after irradiation. Only in the case of highly active and rather long living matrices is chemical separation of the matrix from all impurities necessary. The computer program is written in ALGOL-60.

Introduction

For the overall analysis of high purity materials the samples are irradiated in a thermal neutron flux of several times 10^{14} n.cm⁻².sec⁻¹ for about 24 hours. As we use the single comparator method for the calculation of the impurity contents, 0.5% Co-Al-wires are irradiated simultaneously. For each sample up to four Ge(Li)- γ -ray spectrum measurements are carried out, e.g. one hour, one day, one week and one month after irradiation, in order to cover the range of half-lives. The analysis can be done purely instrumentally in weakly active or short-living matrices such as Si, SiC, SiO₂, water, etc., but

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for highly active matrices (Ge, GaAs, Se, etc.) chemical separation of the matrix from all impurities is necessary. The spectra are processed by means of a large off-line computer (Philips Electrologica X8, language: ALGOL-60). In the two computer programs much attention is paid to reliability, accuracy and convenience for the user, which may be seen from the following features:

1. versatile library of nuclear and efficiency data, easy to up-date
2. reliable location of the peaks, separation of doublets
3. corrections for dead-time losses in the detector-to-amplifier system
4. first identification of the nuclides from the energies and their abundances
5. final decision of the presence of elements by means of the half-lives (not possible in the case of one measurement)
6. sufficient number of efficiency-calibrated measuring positions (2 Ge(Li)-detectors, 2 vial sizes, point sources, various sample-to-crystal distances and sample volumes)
7. corrections for decay during counting
8. corrections for summing effects of cascades
9. corrections for epithermal/thermal flux ratio in the comparator method
10. calculation of the limit of detection for the elements not observed.

Up to now we have been able to determine 30 to 40 elements in Si, SiO₂ and SiC and could give the limits of detection for the rest of the 55 elements.

Description of the method

Our method of evaluating the Ge(Li) gamma spectra consists of two main steps:

1. location and area determination of the peaks
 - 2a. identification of the nuclides followed by
 - 2b. quantitative evaluation of the impurity contents.

It will be evident that after having found the significant peaks with their energies (in keV), areas (in counts per second) and standard deviations of the areas (in per cent) in each

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spectrum, the next step is the identification of the nuclides. Only when this is done, the decay correction with the proper half-lives and verifying the half-lives can be carried out, followed by the quantitative evaluation.

These are the reasons that the computer processing must be performed in two stages: for the second stage the results of all the spectra of a certain sample must be brought together, and of course this can only be done if all measurements of a sample are finished. The first stage is carried out by means of the "photopeak analysis program" PAF, which has been described earlier¹. The output of this program contains for each spectrum: the name etc. of the sample, codes for the measuring position, the decay time and the measuring time and further, as mentioned before, for each peak the energy, area and standard deviation of the area.

The peak data are already corrected for dead time losses according to Wyttenbach² and the limit of detection in counts per second is printed along the energy axis.

The aim of the program NAA ("neutron activation analysis", see fig. 1) which carries out the second stage, is as follows:

a. in each spectrum:

1. Determine from which nuclides the peaks can be, by comparing the energies. The criterion for this is a maximum difference³:

$$\Delta E = \Delta E_1 + \Delta E_2 E / 10^3 \quad (1)$$

where ΔE_1 = constant difference in keV (usually 0.7)

ΔE_2 = additional difference (usually 0.5)

E = energy of the peak in keV.

2. Decide whether a nuclide is probably present, depending on the presence of the most abundant peaks.

b. for each sample:

1. Collect the nuclides found according to (a) in all the spectra of the sample
2. Correct for decay (also during counting⁴) and check the half-lives. The standard deviations of the areas are used for the weight factors in the calculations for the definitive decision of whether a nuclide is present.

As a measure for the fit of the decay curve (checking the half-life) we use:

$$z/s_z < \text{crit} \quad (2)$$

where

$$z = s_{\text{extern}}/s_{\text{intern}} \quad (3)$$

$$s_z = \{2(n-1)\}^{-1/2} \quad (4)$$

$$s_{\text{extern}} = \frac{100}{\bar{c}} \sqrt{\frac{\sum_{i=1}^n f_i \Delta_i^2}{(n-1) \sum_{i=1}^n f_i}} \quad (5)$$

$$s_{\text{intern}} = \left(\sum_{i=1}^n f_i \right)^{-1/2} \quad (6)$$

crit = criterion for the half life check

f_i = weight factor = s_i^{-2} (s_i in %)

Δ_i = $c_i - \bar{c}$

c_i = count rate at end of irradiation

\bar{c} = average count rate at end of irradiation

n = number of measurements.

It will be evident, that s_{intern} depends entirely on the standard deviations (c.q. counting statistics) of the separate observations, whereas s_{extern} depends also upon the differences between the observations⁵. For samples taken from an infinite normal population, z equals unity with standard deviation s_z (eq. 4). If z differs from unity by an amount much greater than is to be expected on the basis of statistical fluctuations, it may be concluded

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that systematic errors are likely to be present. In our case this means that we used the wrong half-life, and therefore the peaks belong to another nuclide. Up to now we have used $\text{crit} = 10$.

If a sample is measured only once, then the above mentioned half life check is not possible. The only thing that can be done in this case is to reject those nuclides for which the decay correction factor exceeds a certain value.

3. Calculate the average count rates with standard deviations at the end of irradiation for the main peaks of each nuclide which is found.
4. Correct these count rates for the efficiencies of the detector to obtain the disintegration rates (including corrections for summing effects from cascades⁶) with the proper efficiency equations for the relevant measuring position, sample volume etc.
5. Calculate the impurity contents by means of the single comparator method. This method is applied in such a way, that the neutron flux is monitored by means of a Co-Al-wire and that we suppose the Cd-ratio for cobalt to be constant during longer times. In the well-known activation formula we use for the effective cross section σ_{eff}

$$\sigma_{\text{eff}} = \sigma_0 \left\{ 1 + \frac{I/\sigma_0}{(R_{\text{Co}} - 1)(I/\sigma_0)_{\text{Co}}} \right\} \quad (7)$$

where

- σ_0 = thermal neutron cross section (barns)
- I = resonance integral (barns)
- R_{Co} = cadmium ratio for cobalt.

The library of data which is used in this program contains the parameters for the detector efficiencies as a function of the energy for 18 measuring positions and the nuclear data for about 130 activation reactions.

These data are: the half-life, atomic weight, isotopic abundance, cross section, resonance integral/cross section ratio, up to 10 energies (if there are) with their abundances, indications of

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which peaks are cascades, indications of the two "main peaks" that are used for the quantitative calculations and the coefficient of internal conversion for the first (= most abundant) main peak.

For the convenience of the user we made the output rather extensive. An example of a part of the final output is given in fig. 2.

Drawbacks of the program

A difficulty that we have not overcome up to now is the overlap of main peaks of two nuclides, e.g. the only peak of ^{51}Cr (320 keV), ^{64}Cu (511 keV), ^{103}Ru (497 keV), ^{198}Au (412 keV) and Hg^{203} (279 keV) interferes with a peak of ^{147}Nd , annihilation, ^{131}Ba , ^{152}Eu and ^{75}Se , respectively.

As can be seen from fig. 2, the 1121 keV peak of ^{46}Sc and ^{182}Ta overlap, which leads to too large contents calculated from this peak. Another example in fig. 2 is the incorrectly calculated Cu-content from the 511 keV-peak, which is in fact an annihilation peak due to ^{24}Na .

Though correction of these interferences will lead to a rather large extension of the program, it must be possible to overcome these difficulties to a considerable extent.

The full text of the computer programs is available from the authors.

References

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4. B.W. Hoffmann and S.B. van Camerik, Anal. Chem. 39 (1967) 1198.
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Fig. 1. Simplified flow sheet of the program.

Fig. 2. Part of the output from the computer for one sample.

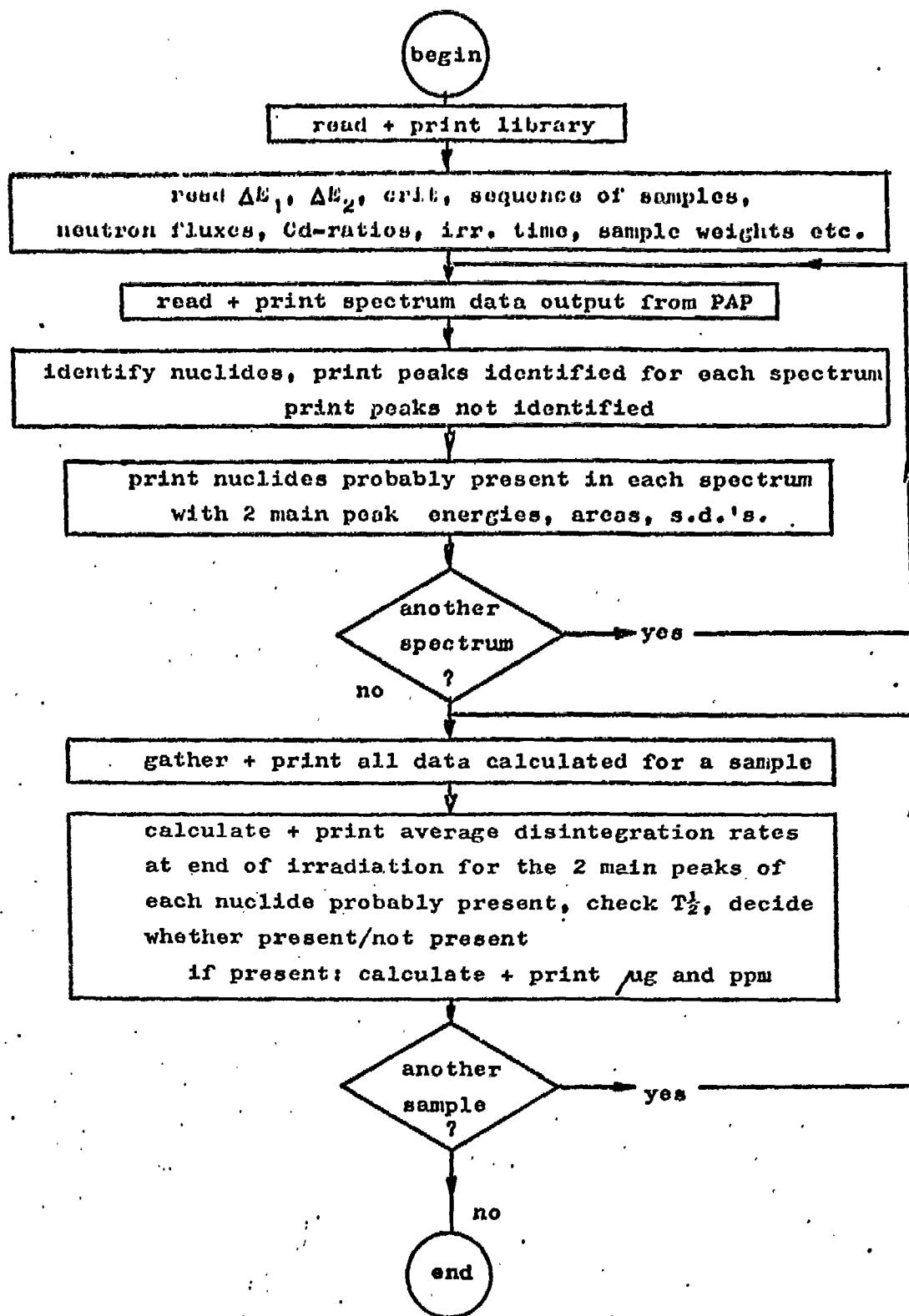


Fig. 1. Simplified flow sheet of the program NAA

NEUTRON FLUX=1.42E+15 N/CM2.SEC CD-RATIO FOR COBALT 19.69 IRRADIATION TIME 24.000 HRS SAMPLE WEIGHTS .00500 G
 SAMPLE NR 1 TAPE NR: CPS 1 5.PCT CORFAC DPS,CORID CORFAC 3PS,CORID CORFAC 4 5.PCT DPS AVERAGE
 NUCLIDE NAME,HRS CPS 2 5.PCT CORFAC DPS,CORID CORFAC 3PS,CORID CORFAC 4 5.PCT DPS SEX,PCT SIN,PCT UGRAN PPM
 ENERGIES,KV DPS,CORID CORFAC DPS,CORID CORFAC 3PS,CORID CORFAC DPS,CORID CORFAC 4 5.PCT DPS Z/S < 10

NEUTRON FLUX 1.42e15 N/CM2.SEC		C/R RATIO FOR COALTS 19.69		IRRADIATION TIME 24,000 HRS		SAMPLE WEIGHTS .00580 G	
SAMPLE NRS 1 TAPE NRS 1	CPS 1	S/PCT CPS 2	S/PCT CPS 3	S/PCT CPS 4	S/PCT OPS	SEX.PCT SIN.PCT	USGRAN PPM
NUCLIDE NRS 1 TAPE NRS 1	CPS 1	S/PCT CPS 2	S/PCT CPS 3	S/PCT CPS 4	OPS	SEX.PCT SIN.PCT	USGRAN PPM
ENERGIES.KEY	OPS,COINVS CORPAC	OPS,COINVS CORPAC	OPS,COINVS CORPAC	OPS,COINVS CORPAC	OPS,COINVS CORPAC	Z/B C 10	
NA 24	0.150e+02	11.011e+02	0.300e+00		0.842e+07	0.350e+08	0.927e+01
	1368.65	842.07	300.04		0.00e+00		
	2784.10						
SC 46	0.201e+04	11.0192e+00	0.757e+01	0.166e+00	0.372e+01	0.153e+00	0.267e+01
	899.21	0.277e+02	0.136e+01	0.249e+02	0.155e+01	0.238e+02	0.258e+02
		21.0251e+05	0.577e+01	0.261e+00	0.194e+01	0.260e+00	0.137e+01
	1120.32	0.451e+02	0.505e+02	0.515e+02	0.157e+01	0.235e+00	0.760e+00
CR 31	0.657e+03	11.0469e+00	0.693e+01		0.202e+03	0.693e+01	0.717e+02
	320.08	0.202e+03	0.120e+01				
FE 39	0.105e+04	11.0133e+00	0.124e+02	0.126e+00	0.621e+01	0.117e+00	0.442e+01
	1099.22	0.404e+02	0.112e+01	0.440e+02	0.129e+01	0.459e+02	0.144e+01
		21.0993e+01	0.125e+02	0.106e+00	0.682e+01	0.977e+02	0.468e+01
	1291.56	0.463e+02	0.589e+02	0.589e+02	0.589e+02	0.579e+02	0.244e+01
CO 50	0.461e+05	11.0191e+00	0.131e+02	0.214e+00	0.319e+01	0.211e+00	0.231e+01
	1173.25	0.353e+02	0.130e+01	0.385e+02	0.101e+01	0.320e+02	0.101e+01
		21.0372e+00	0.732e+01	0.177e+00	0.273e+01	0.125e+00	0.185e+00
	1332.48	0.353e+02	0.309e+02	0.309e+02	0.378e+02	0.378e+02	0.378e+02
CU 54	0.129e+02	11.0845e+00	0.393e+01		0.187e+01	0.359e+01	0.595e+00
	511.01	0.187e+07	0.136e+03				
ZN 55	0.585e+04	11.0285e+00	0.732e+01	0.284e+00	0.211e+01	0.295e+00	0.189e+01
	1113.32	0.913e+02	0.102e+01	0.939e+02	0.105e+01	0.979e+02	0.107e+01
				0.950e+02	0.111e+01	0.950e+02	0.111e+01
AS 76	0.263e+02	11.0137e+00	0.310e+00		0.236e+06	0.231e+00	0.790e+01
	559.10	0.231e+06	0.103e+03		0.277e+06	0.277e+06	0.277e+06
	637.04						
SE 91	0.938e+00	11.0252e+01	0.174e+01		0.100e+00	0.972e+01	0.107e+02
	103.00						
BR 92	0.359e+02	11.0251e+00	0.719e+01		0.972e+03	0.318e+02	0.972e+03
	776.05						
	534.24						
TA 132	0.278e+04	11.0251e+00	0.977e+01	0.281e+00	0.194e+01	0.250e+00	0.137e+01
	1321.27	0.117e+03	0.139e+01	0.180e+03	0.110e+01	0.223e+03	0.155e+01
	222.11	0.403e+00	0.800e+01	0.301e+00	0.812e+01	0.380e+00	0.812e+01
		0.783e+02	0.970e+02	0.584e+02	0.584e+02	0.584e+02	0.584e+02

