

INVESTIGATIONS OF SOME MOTOR OIL ADDITIVES BY NEUTRON ACTIVATION

By

L. GY. NAGY* and L. SZOKOLYI**

Department of Physical Chemistry, Polytechnical University, Budapest

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Presented by Prof. Dr. G. SCHAY

The problem of motor oil additives is a topic under constant research all over the world as well as in this country. As a result of these researches the proportion of the additive treated motor oils to the straight motor oils keeps increasing in Hungary, too.

The important types of motor oil additives are the antioxidants and the detergent-dispersators. These additives are organic compounds containing elements such as *sulphur*, *phosphorus*, *zinc*, *barium*, etc.; the required effect is attained at 0.5—5% content of active ingredient. The content of active ingredient in the additives and additive treated oils can be checked by determining the mentioned elements. Studies have been made as to whether the method of neutron activation could be applied instead of the chemical analysis of each element.

These attempts were thought to be promising as petroleum is an excellent matrix material for neutron activation, its major components: carbon and hydrogen possess most favourable nuclear properties, for they are not actually activated under reactor neutron activation conditions. The method of neutron activation can be considered as advantageous in this field, too, because to solve a given task under the conditions of the usual test of additives (laboratory, bench and road tests) there is no need of large quantities of motor oil, marked by radioactive isotopes, but the test can be done with inactive materials; at appropriate intervals samples are taken and evaluation of the phenomena to be investigated (additive deterioration, motor wear etc.) can be made by the *subsequent activation* and analysis of samples in small quantities (0.1—1 g).

* Department of Physical Chemistry, Polytechnical University, Budapest, Prof. Dr. G. SCHAY.

** Hungarian Oil and Gas Research Institute, Budapest—Veszprém, Prof. Dr. M. FREUND

Relations [1]

It can be shown, that the formed activity of a radionuclide after an arbitrary irradiation time is:

$$W(t) = \frac{\Phi \cdot m \cdot N^0 \cdot f \cdot \sigma_{ac} (1 - \exp(-\lambda t))}{A} \quad (1)$$

For sufficiently long irradiation times, $\exp(-\lambda t)$ approaches zero and we have saturation activity:

$$W(\infty) = \frac{\Phi \cdot m \cdot N^0 \cdot f \cdot \sigma_{ac}}{A} \quad (2)$$

Where:

- Φ = the neutron flux ($n/cm^2 \cdot s$),
- m = the mass of the element to be determined in the sample (gramm),
- N^0 = Avogadro's number (atom/g-atom),
- f = the fractional isotopic abundance of the target nuclide,
- σ_{ac} = the activation cross-section ($cm^2/atom$)
- A = the atomic weight of the element to be determined (g/g.atom)
- $\frac{m \cdot N^0}{A}$ = number of the target nuclides.

The activity $W(t)$ decreases according to the characteristic disintegration constant of the radionuclide, therefore after an elapsed time t' where the irradiation has been completed $W(t)$ will be

$$\begin{aligned} W(t') &= W(t) \cdot (\exp(-\lambda t')) = \\ &= W(\infty) \cdot (1 - \exp(-\lambda t)) \cdot \exp(-\lambda t'). \end{aligned} \quad (3)$$

The relation (3) can be used to calculate the activity present at the end of irradiation from the activity detected at time t' .

This is important then, when the performance of detection which is generally impossible after immediately, completing the irradiation (mainly in the case of reactor activation).

The assumption of applying (1) is that the neutron flux and the average neutron energy should be constant in the course of irradiation. The activation cross-section (σ_{ac}) being the function of the neutron energy, its value will only at constant energies be unchanged. There is a further assumption, that the number of the target nuclei should not decrease considerably during the irradiation. *The relations because of the above mentioned reasons can only be applied to approximate estimations for activity levels and detection sensitivities.*

**Interfering and competing reactions
in the irradiation of S, P, Zn and Ba [2]**

In order to accomplish a given task the element composition of the sample to be investigated as well as the distribution of the neutron flux energy, must be taken into consideration, as these factors will limit whether a material of given composition can be analysed by the method of neutron activation in a given neutron source.

Attention must be paid to the fact, that the neutron flux given by the reactor has no homogeneous energy. The neutron energy spectrum as well as the percentage of the thermal neutrons vary from reactor to reactor and even with the location within a single reactor.

Consequently the presence of fast neutrons must also be taken into account, which means the increasing probability of (n, p) , (n, α) and possibly $(n, 2n)$ nuclear reactions. For example, the cross section of $^{32}\text{S}(n, p)^{32}\text{P}$ reaction grows with the increase of the neutron energy, on the contrary this reaction comes into prominence.

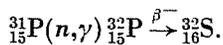
The interfering phenomena that will be encountered in different cases, can be divided into two large groups: interfering and competing nuclear reactions.

Interfering primary nuclear reactions are those which are induced by the principal irradiating particles, in the present case by thermal neutrons, as an original sample, constituents other than the element of interest.

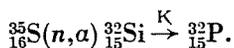
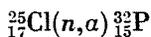
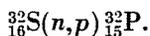
For thermal neutron activation, the principal sources of interference with (n, γ) reaction in an element of atomic number Z are fast neutron induced (n, p) and (n, α) reactions in elements having atomic number $Z + 1$ and $Z + 2$, respectively.

In these cases the same product nuclides as in the principal reaction (n, γ) can be produced, which consequently yields a greater activity than would be expected due to the element of interest. These interfering reactions may either directly occur or through an activation reaction followed by beta decay of the primary activation product.

The principal reaction e. g. in the case of phosphorus is:

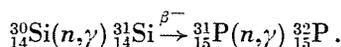


Interfering primary reactions occurring directly are:



In order to calculate the results of the activation, analysis must be considered as a possibility of accomplishing the above mentioned reactions, which depends on the elementary composition of the material to be assayed, on the cross section of nuclear reactions, on the relative intensity and energy distribution of the fast neutrons.

Two types of interfering second-order reactions occur: those which enhance the production of an activation product, and those decreasing its concentration. Reactions of the first type usually occur when a major constituent of the sample and the (trace) element (of interest) have adjacent atomic numbers. The activation products of this major constituent may decay into a stable isotope of the trace element so adding to its concentration. Again according to the example of phosphorus:



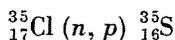
This interference depends on the concentration of the two elements, their activation cross section and the half-life of the intermediate product.

In order to eliminate the interference the duration or intensity of the irradiation must be decreased. Both result in a reduced detection sensitivity.

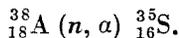
The *second-order reaction* has a diminishing effect, if the capture cross section of the product nucleus, relative to the irradiating particles, is not negligible. The extent to which this effect interferes is to be determined by the ratio of the half-life and cross section of the product nuclei.

Competing reaction can be spoken about, when the trace element has several stable isotopes of which more than one is activated, i. e. several radioactive nuclides are formed simultaneously from an element. At the same time these can also be regarded as primary or second-order interfering reactions. The interference of the competing nuclides varies, depending on the type of radiation and on the radioactivity measuring equipment.

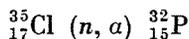
In case of S, P, Zn, Ba the following interferences should be considered: In case of sulphur impurities, such as chlorine and argon, there can interfere according to the nuclear reactions as follows:



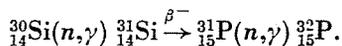
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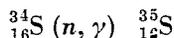
On determining phosphorus, chlorine and silicon can interfere:



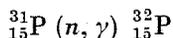
and



In the simultaneous presence of *sulphur* and *phosphorus*, besides the principal reactions



and

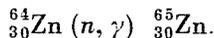


the primary interfering reaction

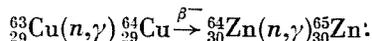


as an example already mentioned which proceeds with appreciable probability. Its effect can be estimated, if nuclear data are known. According to data of the literature [3,4] but also from our own experiences, in a short reactor irradiation time the content of sulphur in the sample can be determined by this reaction.

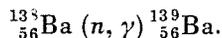
The determination of Zn (irradiated in a reactor) is based on the reaction:



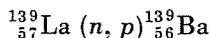
In this case copper as an impurity may cause interfere on the base of the following reactions:



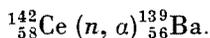
Barium in principle can be detected on the base of the reaction:



Here lanthanum and cerium can interfere through the following reactions



and



Experimental part

The investigated materials were the following:

a) Base oil: Premium grade motor oil of Tujmaz: TMM-60

Content of sulphur: 0.76%

b) Motor oil antioxidant

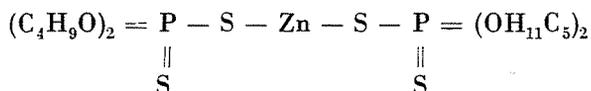
Symbol mark: M-200

The additive is put on the market diluted with white oil to 50% active ingredient content. Usual mixing ratio: 1.0 weight %.

Active ingredient: Zn-salt of diisoamyl-diisobutyl-dithiophosphoric-acid

Brutto formula: $C_{18}H_{40}O_4P_2S_4Zn$

Structural formula:



Molecular weight calculated:

$$C_{18} : 18 \cdot 12.011 = 216.198$$

$$H_{40} : 40 \cdot 1.008 = 40.320$$

$$O_4 : 4 \cdot 16.000 = 64.000$$

$$P_2 : 2 \cdot 30.975 = 61.950$$

$$S_4 : 4 \cdot 32.066 = 128.264$$

$$Zn : 1 \cdot 65.380 = 65.380$$

$$\hline 576.112$$

Distribution of the elements according to weight %:

C	37.5
H	7.0
O	11.1
P	10.8
S	22.3
Zn	11.3
	<hr/> 100.0

The analytical data of the investigated industrial product having 50% white oil:

	weight%
Ash	15.7
Zinc	5.5
Sulphur	10.8
Phosphorus	5.2
Water	0.13

Its reaction is shown with bromine phenol blue as basic.

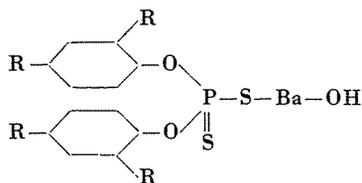
c) Motor oil additive (a type of combined antioxidant inhibitor and detergent-dispersator).

Symbol mark: M-167

The issued concentrate has 46% active ingredient. The usual mixing ratio of the concentrate is: 10.0 weight %.

The active ingredient is the basic salt of 0.0'-di(dialkylphenol)-dithiophosphoric acid.

Structural formula:



Molecular weight of dialkylphenol: 800—1000.

The analytical data of M-167 concentrate having 46% active ingredient:

	weight%
Ash	3.94
Sulphur	1.67
Phosphorus	0.83
Barium	3.68

Estimation of expected activities

For the estimation of the expected activities the quantity of the element in the sample which is of interest, the fractional isotopic abundance of the target nuclide participant in (n, γ) nuclear reaction, the neutron flux and the irradiation time must be taken into account.

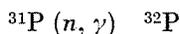
The stages of the calculation are:

1. Giving the quantity of the elements in the sample in μg .
2. Calculation of the saturation activity in regard to 1 g sample.
3. Calculation of the saturation factor taking the neutron flux $\Phi = 10^{13} \text{ n/cm}^2\text{s}$ into account, when the irradiation time is 20 and 24 hours.
4. Calculation of activity in respect to the saturation factor.
5. Giving the integral activity per sample.

On the basis of data from Table I the activation of S, P and Zn has to be counted with. In Table II the quantities of these elements are shown based on 1 g samples, according to the analytical data stated above, for materials given in the table.

From the data in Table II the saturation activity value $W(\infty)$ was calculated for each element taking into account the $10^{13} \text{ n/cm}^2 \cdot \text{s}$ neutron-flux values (Tables III, IV) on basis of relation (2).

In Table VI the expected activities in the single materials are grouped according to the product nuclides. The ^{32}P activities formed in



and

$^{32}\text{S} (n, p) \ ^{32}\text{P}$ nuclear reactions are summarized.

Table I
Nuclear data

Element		Isotope			Activation product			Principal reaction (n, γ)	Interfering nuclear reactions
Sign atomic number	atomic weight	Sign	Abundance f %	σ_{ac}	Half life	Radiations(MeV)			
						β (%)	γ (%)		
${}_1\text{H}$	1.008	${}^1\text{H}$ ${}^2\text{H}$	100 0.015	— $0.57 \pm 0.01\text{mb}$	stable 12.26a	0.018(100)	\emptyset	${}^2\text{H}(n, \gamma){}^3\text{H}$	${}^6\text{Li}(n, \alpha){}^3\text{H}$; ${}^3\text{He}(n, p){}^3\text{H}$
${}_6\text{C}$	1.2011	${}^{12}\text{C}$ ${}^{13}\text{C}$	98.89 1.11	— $0.9 \pm 0.3\text{mb}$	stable 5568a	— 0.155(100)	— \emptyset	${}^{13}\text{C}(n, \gamma){}^{14}\text{C}$	${}^{17}\text{O}(n, \alpha){}^{14}\text{C}$; ${}^{14}\text{N}(n, p){}^{14}\text{C}$
${}_8\text{O}$	16.000	${}^{16}\text{O}$ ${}^{17}\text{O}$ ${}^{18}\text{O}$	99.59 0.037 0.204	— — $0.21 \pm 0.04\text{mb}$	stable — 29.4s	— — —	— — —		
${}_{15}\text{P}$	30.975	${}^{31}\text{P}$	100	$0.19 \pm 0.01\text{b}$	14.22d	1.707(100)	\emptyset	${}^{31}\text{P}(n, \gamma){}^{32}\text{P}$	${}^{32}\text{S}(n, p){}^{32}\text{P}^*$; ${}^{35}\text{Cl}(n, \alpha){}^{32}\text{P}$ ${}^{30}\text{Si}(n, \gamma){}^{31}\text{Si} \beta \rightarrow$ $\rightarrow {}^{31}\text{P}(n, \gamma){}^{32}\text{P}$
${}_{16}\text{S}$	32.066	${}^{32}\text{S}$ ${}^{33}\text{S}$ ${}^{34}\text{S}$ ${}^{36}\text{S}$	95.018 0.750 4.215 0.017	— — $0.26 \pm 0.05\text{b}$ $0.14 \pm 0.04\text{b}$	87d — — 5.04m	— — 0.167(100) 1.6(90) 4.3(10)	\emptyset — \emptyset 3.09(90)	${}^{31}\text{S}(n, \gamma){}^{36}\text{S}$ — ${}^{36}\text{S}(n, \gamma){}^{37}\text{S}$	${}^{35}\text{Cl}(n, p){}^{36}\text{S}$; ${}^{38}\text{A}(n, \alpha){}^{36}\text{S}$; ${}^{37}\text{Cl}(n, p){}^{37}\text{S}$; ${}^{40}\text{A}(n, \alpha){}^{37}\text{S}$

³⁰ Zn	65.38	⁶⁴ Zn	48.89	0.44 ± 0.05b	245d	K(98.5)	1.119	⁶⁴ Zn(n, γ) ⁶⁵ Zn	⁶³ Cu(n, γ) ⁶⁴ Cu → → ⁶¹ Zn(n, γ) ⁶⁵ Zn
		⁶⁶ Zn	27.81	—	—	—	—	—	
		⁶⁷ Zn	4.11	—	—	—	—	—	
		⁶⁸ Zn	18.56	97 ± 10mb	13.8h	∅	IT(100)	⁶⁸ Zn(n, γ) ⁶⁹ ^m Zn	⁶⁹ Ga(n, p) ⁶⁹ ^m Zn; ⁷² Ge(n, α) ⁶⁹ ^m Zn
		⁷⁰ Zn	0.62	1.2 ± 0.2b	52m	0.897/100	∅	—	
⁵⁶ Ba	137.36	¹³⁰ Ba	0.101						
		¹³² Ba	0.097	7 ± 2b	38.8h 7.2a	∅ K(100)	IT(100) multiple		
		¹³⁴ Ba	2.42						
		¹³⁵ Ba	6.59						
		¹³⁶ Ba	7.81						
		¹³⁷ Ba	11.32						
		¹³⁸ Ba	71.66	0.5 ± 0.1b	84m	multiple	0.163(26)	¹³⁸ Ba(n, γ) ¹³⁹ Ba	¹³⁹ La(n, p) ¹³⁹ Ba; ¹⁴² Ce(n, α) ¹³⁹ Ba

* Activation cross section of ³²S(n, p)³²P interfering with nuclear reaction at reactor activation: $\sigma_{ac} = 5.7 \cdot 10^{-2}$ barn⁽⁵⁾.

K = electron capture
IT = isomeric transition
a = year
d = day
h = hour
m = minute

Table II

	Quantity g	Sulphur		Phosphorus		Zinc	
		%	μg	%	μg	%	μg
base oil	1.0000	0.76	7600	—	—	—	—
M-200	1.0000	10.8	108000	5.2	52000	5.5	55000
M-167	1.0000	1.67	16700	0.83	8300		
99 parts by weight of base oil	0.9900		7524				
1 part by weight of M-200	0.0100		1080		520		550
base oil + M-200	1.0000	0.86	8604	0.052	520	0.055	550
90 parts by weight of base oil	0.9000		6840	—	—	—	—
10 parts by weight of M-167	0.1000		1670		830	—	—
base oil + M-167	1.0000	0.851	8510	0.083	830	—	—

Table III

Analysis for	Nuclear reaction	Atomic weight of element (g)	f (%)	σ_{ac} (barn)	$\frac{N^0 \cdot f \cdot \sigma_{ac}}{A}$
S	$^{34}\text{S}(n, \gamma)^{35}\text{S}$	32.066	4.215	0.26	$2.05 \cdot 10^{-4}$
	$^{32}\text{S}(n, p)^{32}\text{P}$		95.018	0.057	$1.01 \cdot 10^{-3}$
P	$^{31}\text{P}(n, \gamma)^{32}\text{P}$	30.975	100	0.19	$3.69 \cdot 10^{-3}$
Zn	$^{64}\text{Zn}(n, \gamma)^{65}\text{Zn}$	65.38	48.89	0.44	$1.98 \cdot 10^{-3}$

To make the data of Table VI. clearer the percentage distribution of the activities of the base oil and the two additive treated motor oils are compared in Table VII.

Sensitivity estimation

Taking the $W(t) = 10^3$ dpm as a minimum detectable disintegration rate, into the relation

$$m = \frac{10^3 \cdot A \cdot W(t)}{\Phi \cdot N \cdot f \cdot \sigma_{ac} \cdot S} \mu\text{g}$$

the values of the minimum detectable quantity of the element viz. sensitivity are shown in Table VIII.

Table IV

Element	Sample	Nuclear reaction	m (g)	$W(\infty)$ (dpm) $\Phi = 10^{12}$ $n/cm^2 \cdot s$
S	base oil	$^{34}S(n, \gamma)^{35}S$	$7.60 \cdot 10^{-3}$	$9.35 \cdot 10^8$
		$^{32}S(n, p)^{32}P$		$4.60 \cdot 10^9$
	base oil + M-200	$^{34}S(n, \gamma)^{35}S$	$8.60 \cdot 10^{-3}$	$1.06 \cdot 10^9$
		$^{32}S(n, p)^{32}P$		$5.21 \cdot 10^9$
	base oil + M-167	$^{34}S(n, \gamma)^{35}S$	$8.51 \cdot 10^{-3}$	$1.05 \cdot 10^9$
		$^{32}S(n, p)^{32}P$		$5.16 \cdot 10^9$
P	base oil + M-200	$^{31}P(n, \gamma)^{32}P$	$0.52 \cdot 10^{-3}$	$1.15 \cdot 10^9$
	base oil + M-167		$0.83 \cdot 10^{-3}$	$1.84 \cdot 10^9$
Zn	base oil + M-200	$^{64}Zn(n, \gamma)^{65}Zn$	$0.55 \cdot 10^{-3}$	$6.52 \cdot 10^8$

Calculation of the saturation factor (S)

$$S = 1 - x$$

$$x = \exp(-0.693 t/t_{1/2})$$

Isotope	half-life $t_{1/2}$ (hour)
^{35}S	2088
^{32}P	341
^{65}Zn	5880

Table V

	Irradiation time (hour)					
	Sulphur		Phosphorus		Zinc	
	20	24	20	24	20	24
$10^3 \cdot t/t_{1/2}$	9.58	11.5	58.6	70.4	3.40	4.08
x	0.993	0.992	0.960	0.931	0.99	0.996
$10^3 \cdot S$	7	8	40	69	1.3	4

Table VI

Product nuclide	Nuclear reaction	Sample	$W(t)$ (dpm)	
			26 ^h	24 ^h
³⁵ S	n, γ	base oil	$6.55 \cdot 10^6$	$7.48 \cdot 10^6$
		base oil + M-200	$7.42 \cdot 10^6$	$8.48 \cdot 10^6$
		base oil + M-167	$7.35 \cdot 10^6$	$8.40 \cdot 10^6$
³² P	n, γ	base oil	—	—
	n, p		$1.84 \cdot 10^8$	$3.17 \cdot 10^8$
	n, γ	base oil + M-200	$4.60 \cdot 10^7$	$7.93 \cdot 10^7$
	n, p		$2.08 \cdot 10^8$	$3.59 \cdot 10^8$
	Σ		$2.54 \cdot 10^8$	$4.38 \cdot 10^8$
	n, γ	base oil + M-167	$7.36 \cdot 10^7$	$1.27 \cdot 10^8$
	n, p		$2.06 \cdot 10^8$	$3.56 \cdot 10^8$
	Σ		$2.80 \cdot 10^8$	$4.83 \cdot 10^8$
⁶⁵ Zn	n, γ	base oil + M-200	$8.48 \cdot 10^5$	$2.61 \cdot 10^6$

Irradiation

The above-mentioned three materials were activated in the reactor. The samples were filled into clean, dry quartz vials with syringe to about one third of their volume. The weighed amounts are:

Sample	
Sign	Weight (g)
TMM-60 (base oil)	0.3259
TMM-60 + M-200	0.4717
TMM-60 + M-167	0.4045

Before sealing, the vials were heated for a short time so to 150° that in a closed state after cooling the pressure in them should be less than outside, lest the formation of gas — possible by irradiation — should make them explode.

Table VII

Sample (1g)	Radio-nuclide	Activity 10^{-6} dpm	Percentage distribution of activities
Base oil	^{35}S	6.55	3.4
	^{32}P	184.00	96.6
		190.55	100.0
Base oil + M-200	^{35}S	7.42	2.9
	^{32}P	254.00	96.8
	^{65}Zn	0.85	0.3
		262.27	100.0
Base oil + M-167	^{35}S	7.35	2.5
	^{32}P	280.00	97.5
		287.35	100.0

Table VIII

Element	t (hour)	m (μg)	
	$W(t)$ dpm	20	24
S		69.5	60.9
P		0.677	0.392
Zn		38.8	12.6

The irradiation time t was 20 hours and the samples from the reactor were got on the 13th day after termination the irradiation.

The materials of the samples kept their original colour, but solidified and enclosed relatively large gas bubbles. The samples heated to 70° — 80° in closed vials did not melt. On opening overpressure was observed. All three materials were elastic, but were easy to crumble. Without chemical destruction none of them melted.

Ligroine, benzene, acetone, chloroform and carbon tetrachloride were tried out to dissolve small quantities of the materials, but without any success. In the last two solvents, placed in the cold, the distention of the materials could be seen. Therefore, for counting and measuring gamma energy the total quantity of the material was suspended in a tenfold volume of carbon tetrachloride and the suspensions were put into small aluminium dishes previously measured. The picture of the preparation from sample TMM-60 is shown in Fig. 1.

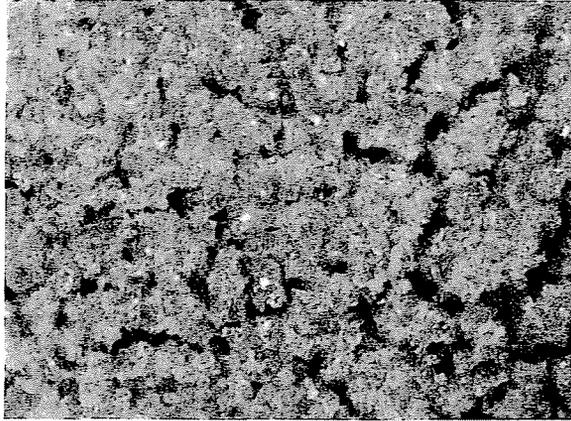


Fig. 1. Picture of the activated TMM-60 sample

From each samples some layers having different weight i. e. of different thickness on a given dish surface were applied, so that the self-absorption of the material of the sample series could be taken into account.

Detection

To detect the radiation of the nuclides formed on the irradiation — for counting and gamma energy measuring — the laboratory scaler EKCO N 530 F with integral discriminator and scintillation counter EKCO N 664 A were used. To measure the energy of gamma-radiation 1 in. \times 1 in. NaJ (Tl) crystal, to count the beta particles plastic phosphorus with 6 cm² sensitive surface (light-closing Al thickness 1–1.2 mg/cm²) were used.

The calibration of the detecting apparatus was made according to the expected irradiated elements with ³⁵S, ³²P and ⁶⁵Zn isotope preparations, as well as with ¹³¹I and ¹³⁷Cs.

Gamma spectroscopy

Our apparatus was equipped with an integral discriminator monotonously registrating the diminishing count rates for a given radiating material, increasing the discriminator voltage per 5, 2 or 1 volts. Plotting the values gained versus the discriminator voltage an integral height distribution curve could be obtained. The differential pulse height distribution curve characterizing the energy relations of gamma emitters could be obtained by graphic differentiation from the former. But in practice an approximation of the differential curve is enough, so that the counting rates one after the other for the single discriminator positions are subtracted from each other and the differences of the counting rates are plotted versus the functions of the discriminator voltage. Thus



Fig. 2. Spectrum of Cs-137

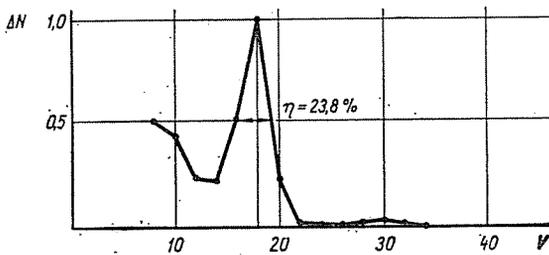


Fig. 3. Spectrum of J-131

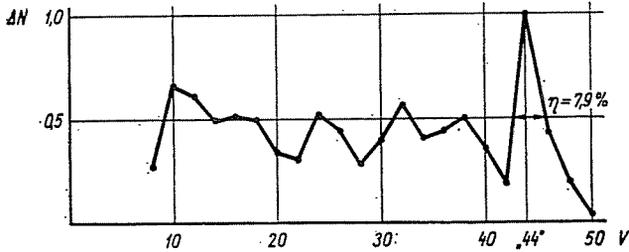


Fig. 4. Spectrum of Zn-65

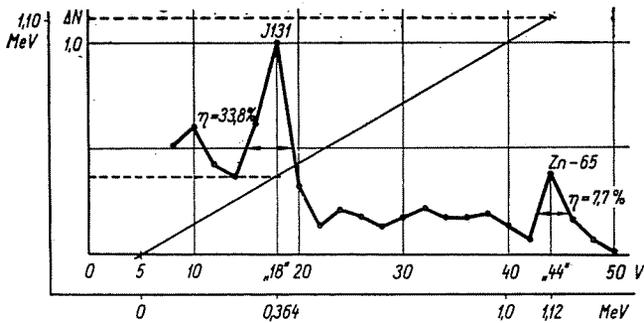


Fig. 5. Common spectra of J-131 and Zn-65

we have the value of the pulse height of the photopeak characterizing the energy of the radiation. For this work the latter method was applied.

If we have a radiochemically pure preparation, by the place of the photopeak the scale of the discriminator bias of our instrument can be calibrated to energy. Taking the energy spectrum of the gamma emitter isotope, of known intensity and of a sample containing the same emitter in an unknown concentration, the unknown concentration can be obtained from the ratio of the areas under photopeak.

The governing factor is the ability of the instrument to differentiate between photopeaks of gamma rays having similar energies. This can be experi-

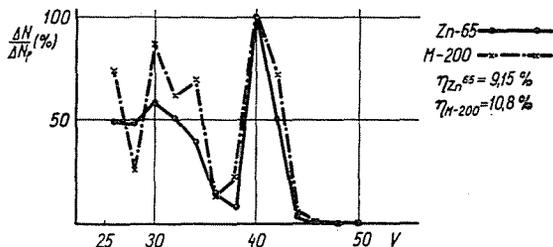


Fig. 6. Spectra of Zn-65 and sample M-200

mentally given by the value of the relative half width of the photopeak. The spectrum of ^{137}Cs ($E = 0.662$ MeV) obtained from our apparatus is shown on Fig. 2. Figures 3, 4, 5 show the spectra of ^{131}I , ^{65}Zn and their two joint ones, too. Fig. 5 also shows the energy calibration.

From our investigated materials the gamma spectrum of the motor oil treated with Zn containing M-200 was taken, applying 1.3 cm thick lead collimator and 3 mm thick Al absorber, which removed the beta radiation of 1.71 MeV maximum energy of ^{32}P which accompanied the Zn. The obtained energy spectrum is shown together with that of the ^{65}Zn preparation used as a standard for quality in Fig. 6. For an easier comprehension of the spectra the counting rates were put on the ordinate in percents of the photo peak.

Beta absorption measurements

The energy spectra of the beta radiation of S, P and Zn in all likelihood to be activated were obtained with the aluminium absorber. The individual intensities were given in the layer thickness percentage of the zero absorber, to make the difference in the absorption of each beta emitters more perspicuous. The results are shown in Fig. 7. The range and the maximum energy E_{max} values obtained from the absorption curves are shown in Table IX compared with the data in literature [6].

From Fig. 7 it is to be seen that the slopes of the absorption curves of the examined radioisotopes are rather different and the samples contain gamma

emitter components, too. So there is a possibility to lay down qualitative and quantitative estimations of the material without chemical separation, on simultaneous investigation.

According to the estimation of the expected activities the bulk of the sample originates from ^{32}P . Thus according to the foregoing, if the absorption curve of the sample assumedly containing phosphorus is taken, no breaking

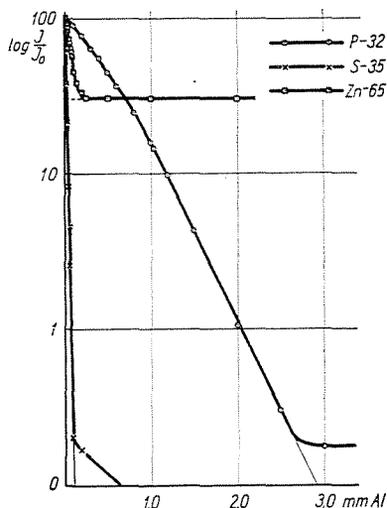


Fig. 7. Aluminium absorber curves of P-32, S-35 and Zn-65

Table IX

Nuclide	R measured g/cm ²	E _{max} (MeV)	
		calculated	literary
^{32}P	0.794	1.71	1.701
^{35}S	0.0324	0.16	0.18
^{65}Zn	0.0647	0.26	0.324

point — showing the presence of beta emitters of different energy can be seen. This assumption was verified by our experimental results shown in Figures 8, 9 and 10. The intensity (cpm_x) due to each absorber thickness is given in the percentage of the initial intensity (cpm₀).

The absorption curves of the examined materials differ from those of ^{32}P only to that degree which is due to experimental error, i. e. our materials unanimously showed only phosphorus activity.

On ground of previous calculations it was probable, that the determination of sulphur on ground of $^{34}\text{S}(n, \gamma) ^{35}\text{S}$ nuclear reaction would fail. This assumption was also verified by experimental results.

The cause of this is not to be found in detection difficulties, but in the fact that only some percents — not exactly known, but maximally 10% — of the neutron flux in the reactor is of thermal energy.

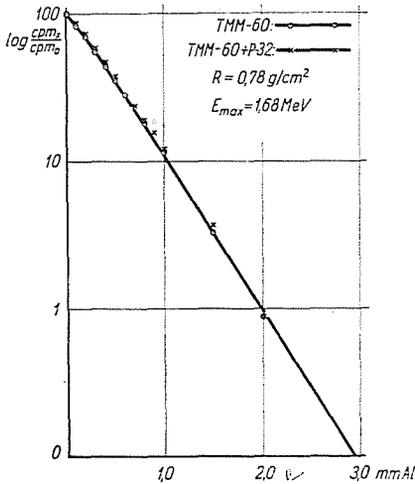


Fig. 8. Beta absorption curves of the samples TMM-60 and TMM-60 + P-32

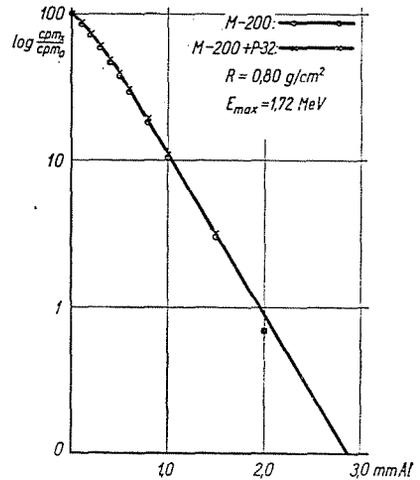


Fig. 9. Beta absorption curves of the samples M-200 and M-200 + P-32

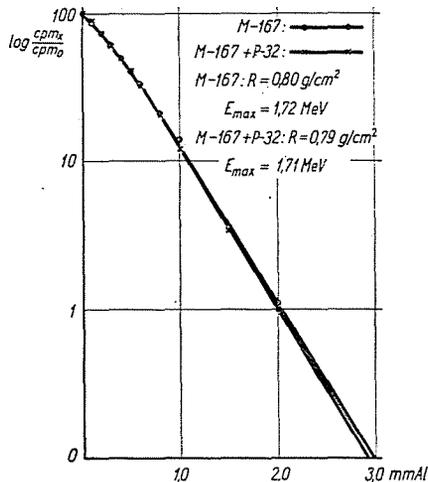


Fig. 10. Beta absorption curves of the samples M-167 and M-167 + P-32

Gamma Ray Absorption

On investigating beta absorption a certain gamma background was found by all three materials which is only justifiable in case of M-200 — therefore, gamma ray absorption was also measured with aluminium and lead absorbers.

The plot of $\lg I$ versus thickness of absorber produces a straight line if gamma rays are monoenergetic; if several different energy gamma rays are emitted, each energy is represented by a straight line having a different slope. Our results are shown in Fig. 11. From the slope of each straight line the mass absorption coefficient and the $d_{1/2}$ half thickness could be determined. In the

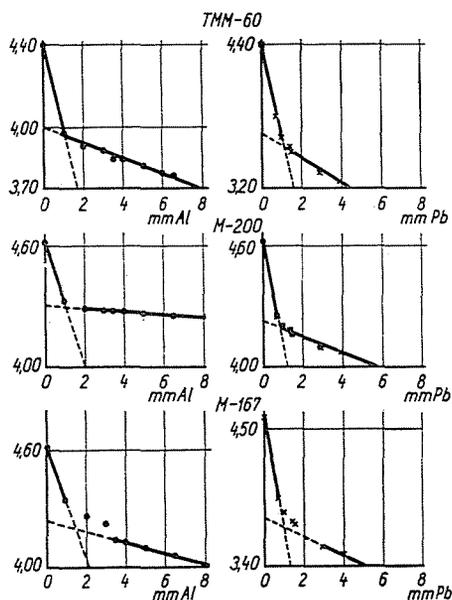


Fig. 11. Gamma absorption curves of the samples TMM-60, M-200 and M-167

Table X

Sample	Absorber	μ' (cm ⁻¹)	μ (cm ² /g)	$d_{1/2}$ (g/cm ²)	E MeV
TMM-60	Al	10.2	3.78	0.183	0.02
		0.67	0.25	2.78	0.06
	Pb	17.8	1.57	0.44	0.16
		2.38	0.21	3.30	0.41
M-200	Al	6.45	2.39	0.29	0.02
		0.14	0.053	13.1	1.40
	Pb	1.21	0.11	6.50	0.67
		0.84	0.074	9.32	0.96
M-167	Al	6.68	2.48	0.280	0.02
		0.64	0.24	2.92	0.07
	Pb	2.07	1.83	0.38	0.16
		1.54	0.14	5.13	0.60

possession of these data the energy of the gamma ray was determined from empirical curves (6). These calculated data are shown in Table X.

From the table it can clearly be seen that the situation is far from being as simple, as the picture obtained from the previous calculations. The most energetic gamma rays are found undoubtedly in the oil sample with additive M-200 containing Zn, but the two other samples are not free from impurities emitting gamma rays, either.

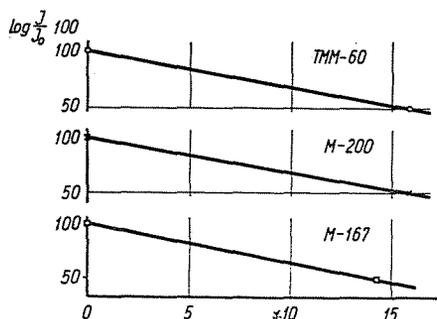


Fig. 12. Decay curves of the samples TMM-60, M-200 and M-167.

Half life determination

As was mentioned in the foregoing, on preparing the samples for counting they were made of different layer thicknesses, so that the effect of self-absorption could at the decay curve be taken into account. The decay curves in Fig. 12 were obtained with counting rates of self-absorption. On ground of Fig. 12 the half life of the different samples are:

	$t_{1/2}$ (day)
TMM-60	16.0 ± 0.2
M-200	15.9 ± 1.45
M-167	14.3 ± 0.8

In the examined samples ^{32}P beta radiation could be detected. It is interesting to compare the expected activity values calculated from the quantities with the detected ones. In order to compare them, the counting rates measured on the 24th day after irradiation were related to $t' = 0$, knowing the half life.

Comparing the values of the expected activity (dpm) and the measured counting rates (cpm) calculated to $t' = 0$, the apparent efficiency of the counting can be approximately obtained. The results are shown in Table XI.

From the known sulphur content of TMM-60 and from the values of the measured counting rates it can be computed, what proportion of the total counting rates corresponds to the phosphorus content of the M-200 and M-167

Table XI

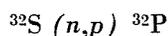
Sample	Weight (g)	$10^{-6} \cdot \text{cpm}$		10^{-6} dpm $t' = 0 \text{ day}$	Efficiency (%) $\frac{\text{cpm}}{\text{dpm}} \cdot 100$
		$t' = 24 \text{ days}$	$t' = 0 \text{ day}$		
TMM-60	0.3259	1.49 ± 0.04	4.80	62.1	7.7
M-200	0.4717	3.26 ± 0.03	10.5	123.7	8.5
M-167	0.4045	2.99 ± 0.04	9.65	116.2	8.4

samples, if the counting rates belonging to $1 \mu\text{g}$ phosphorus are given. Taking the quantities of sulphur and phosphorus in 1 g of each examined sample from Table XII the following results can be obtained:

Table XII

Sample	Counting rate		
	$10^{-6} \cdot \text{cpm/g}$ sample	$10^{-3} \cdot \text{cpm}/\mu\text{g}$ sulphur	$10^{-2} \text{cpm}/\mu\text{g}$ phosphorus
TMM-60	14.72	1.935	0
M-200	22.25	1.935	11.7
M-167	23.85	1.935	9.00

From the values $\text{cpm}/\mu\text{g}$ it can be seen on the one hand, that there is a difference in order (of magnitude) between the values obtained for phosphorus and sulphur to the advantage of phosphorus, on the other hand, though the two values relating to the phosphorus, are rather different, it seems proper to take into consideration the



nuclear reaction.

Summarizing it could be ascertained, that the phosphorus, sulphur and zinc contents of the motor oil additives were to be detected by the neutron activation method — with the aid of suitable comparing samples. The investigations contain the determination of the half-life, the measuring of the absorption of the beta radiations and gamma rays as well as the gamma ray spectrometry.

On ground of the results of our investigations it could be established, that for “post-activation isotope indication” for similar oils such isotopes must be chosen, the activation products of which are gamma emitting, their cross sections are relatively large and their half-life are of hour order — so they could be activated with a laboratory neutron source. In this case the P, S and Zn contents do not cause any trouble, because they can hardly be activated.

Summary

The possibilities of the detection of the contents of phosphorus, sulphur and zinc in motor oils containing several additives were examined with different measuring methods by neutron activation.

Our work can be look upon as a preinvestigation for the application of the post-activation isotope "indication". The contents of phosphorus, sulphur and zinc in the motor oils containing additives can be detected in a reactor after irradiation — with suitably chosen comparing samples — by gamma ray spectrometry, as well as by measuring the β , γ absorption and the half-life.

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Dr. Lajos György NAGY, }
László SZOKOLYI, } Budapest XI., Budafoki u 8. Hungary