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Arbeitsbericht

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ABSTRACT

By optimization of channel settings and a least square fit method it was possible to extend the detection limits to a theoretically determinable range and to measure the activities of ^{3}H, ^{45}Ca, ^{90}Sr, ^{106}Ru, ^{137}Cs *in multilabelled samples simultaneously with a liquid scintillation counter.*

1. Introduction

The calculation of the activities of "n"components in multilabelled ß-active samples using liquid scintillation technique has been regarded in a previous work (1) as a problem of solving a set of "n" simultaneous linear equations.
As "n" becomes large ($n \geqslant 3$) this method exhibits great sensitivity to small errors in experimental data.

It was therefore tried to solve the problem by a curve fitting process. The experimental P_M (i) values which had been defined already (1) are matched by combining P (i) values of the individual nuclides with different weighting factors. The choice of the channel setting is not the same as usually found using liquid scintillation technique. In common it is not possible that the samples are measured by channel settings with optimal conditions for the efficiencies of the nuclides present. As we have shown in (1) the only limiting condition for the application of the derived method consists in the independency of the P (i) values over the considered activity range.

For the solution of the given problem it is necessary that the P (i) values of the nuclides in the sample differ in a certain kind which has to be specified. We therefore tried to solve the problems by taking account to some theoretical considerations based on the system we derived in (2).

As we have shown in (1) we can write for the general case on "n" components and "m" channels

$$\begin{bmatrix} Z_1 \\ \cdot \\ \cdot \\ \cdot \\ Z_m \end{bmatrix} = \begin{bmatrix} P_{11} & \cdots\cdots & P_{1n} \\ \cdot & & \\ \cdot & & \\ \cdot & & \\ P_{m1} & & P_{mn} \end{bmatrix} \begin{bmatrix} x_1 \\ \cdot \\ \cdot \\ \cdot \\ x_n \end{bmatrix}$$

or in the matrix notation: $\underline{Z} = \underline{P} \cdot \underline{x}$ (2).
If $m = n$ the matrix $\underline{P}$ is square and has an inverse $\underline{P}^{-1}$ (unless its characteristic determinant is zero). So if $\underline{P}$ is known and non-singular, its inverse can be found and we obtain

$$\underline{x} = \underline{P}^{-1} \cdot \underline{Z} \qquad (3)$$

which is the solution for the count rates of the components or more general for the activities. If $m < n$ we obtain no solution for the problem. In the case of $m > n$ we have more equations than unknowns and can get a variety of solutions for the $\underline{x}$ matrix. Usually it will not be possible to satisfy equation 2 exactly. But we can obtain matrix $\underline{x}$ which will minimize the function

$$f = \sum_{i}^{m} {}_{e1} (z_i^{Ber} - z_i^{Ex})^2 \qquad (4)$$

As known we can write $f = \underline{(Z^{Ber} - Z^{ex})} \; \underline{(Z^{Ber} - Z^{Ex})}$ (5)
with $\underline{(Z^{Ber} - Z^{ex})}$ being the transpose of $\underline{(Z^{Ber} - Z^{Ex})}$
(interchange of rows and columns).

The least squares criterion is satisfied by solving equation 2 in the following manner:

$$\underline{\underline{P}} \cdot \underline{Z} = \underline{\underline{P}} \cdot \underline{P} \cdot \underline{x} \qquad (6)$$

with $\underline{\underline{P}} \cdot \underline{P}$ being a square matrix. (Dimension: n.n).
Equation 6 is therefore a new set of "n" simultaneous linear equations in the "n" unknown count rates.
Using the same way of solution as in equation 3 we obtain

$$(\underline{\underline{P}} \cdot \underline{P})^{-1} \cdot \underline{\underline{P}} \cdot \underline{Z} = \underline{x}$$

As usual we will define a new matrix $\underline{M} = (\underline{\underline{P}} \cdot \underline{P})^{-1} \cdot \underline{\underline{P}}$
which is a n.m matrix characteristic of the system.

$$\underline{x} = \underline{M} \cdot \underline{Z}$$

the activities or count rates given by:

$$x_i = \sum_{j=1}^{m} M_{ij} \cdot Z_j$$

In (2) we introduced the "zerfallsgruppe" to set up a mathematical scheme for the P (i) values. The "Zerfallsgruppe" we only defined in the sense $\sum_i P_j(i) = 1$. We made no other assumption for it, except that a "Zerfallsgruppe" is defined by the structure of the probability distribution.

Now we will look for mathematical quantities describing the properties of "Zerfallsgruppen".

According to "Information Theory" it seemed possible to define a "Zerfallsgruppe" by its entropy $H = -\sum_i P_j\ (i)\ \ln P_j\ (i)$. The connection of the entropy with the measured quantities is easily seen using equation

$$P_Z\ (Z_1) = \frac{Z!}{Z_1!Z_2!}\ P_1^{Z_1} \cdot P_2^{Z_2} \qquad (1)$$

For $P = P_1^{Z_1} \cdot P_2^{Z_2}$ Shannon (3) showed that P is also $e^{-Z.H}$

and for $\frac{Z!}{Z_1!Z_2!}$ one can write (using Stirlings formula):

$$\frac{Z!}{Z_i!} = \frac{1}{(2\ Z)^{1-I}} \cdot \frac{1}{P(i)}\ e^{Z.H} \cdot e^{-\frac{1}{4Z}\ (1-\ \frac{1}{P(i)})}$$

For the entropy of a mixture one can derive with

$$\frac{Z_A}{Z_A + Z_B} = P\ (A), \frac{Z_B}{Z_A + Z_B} = P\ (B),\ H_j = -\sum_i P_j \ln P_j\ (i)\ \text{and}$$

$$H\ (A,B) = -P\ (A)\ \ln P\ (A) - P\ (B)\ \ln P\ (B)$$

$$H_M = P\ (A)\ H_A + P\ (B)\ H_B + H\ (A,B)$$

The use of the entropy shows some advantages in plotting graphs of the entropy vice activities (Fig.1, 2)

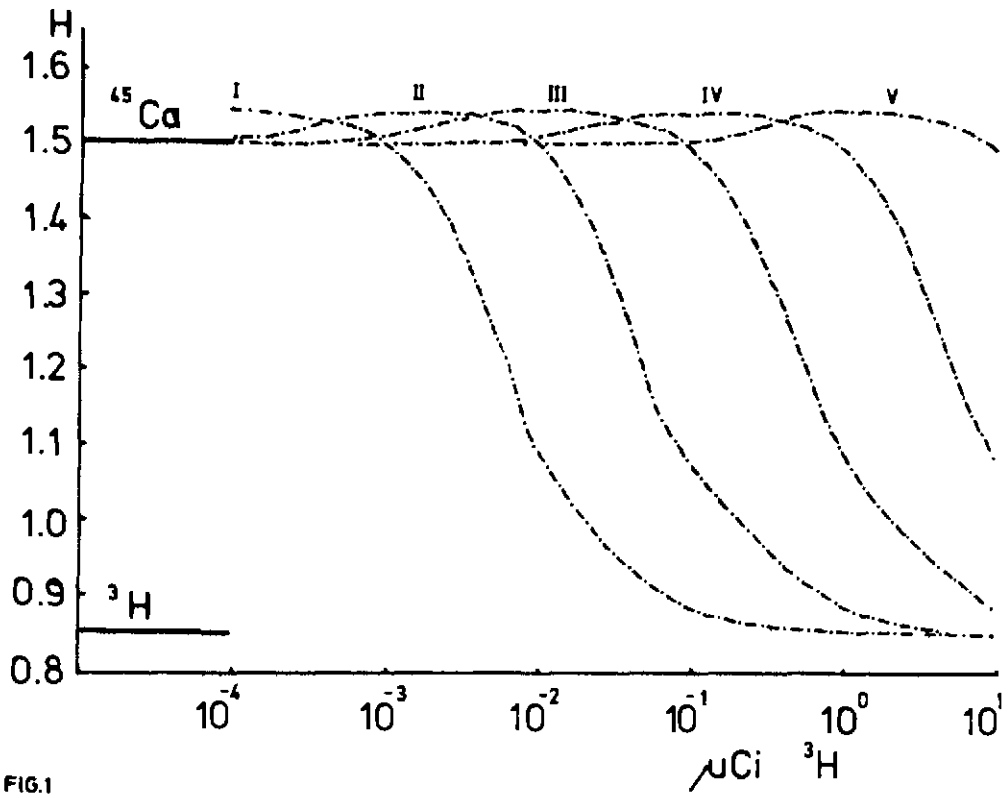

FIG.1

Fig. 1 shows the entropy of different mixtures containing ^{45}Ca, ^{3}H. The determination was done by the use of five channels:

K 1: 50 - 1000, 2% gain	*I: 10^{-4} µCi ^{45}Ca*
K 2: 50 - 1000, 5% gain	*II: 10^{-3} µCi ^{45}Ca*
K 3: 50 - 1000, 10% gain	*III: 10^{-2} µCi ^{45}Ca*
K 4: 50 - 1000, 30% gain	*IV: 10^{-1} µCi ^{45}Ca*
K 5: 50 - 1000, 90% gain	*V: 10^{0} µCi ^{45}Ca*

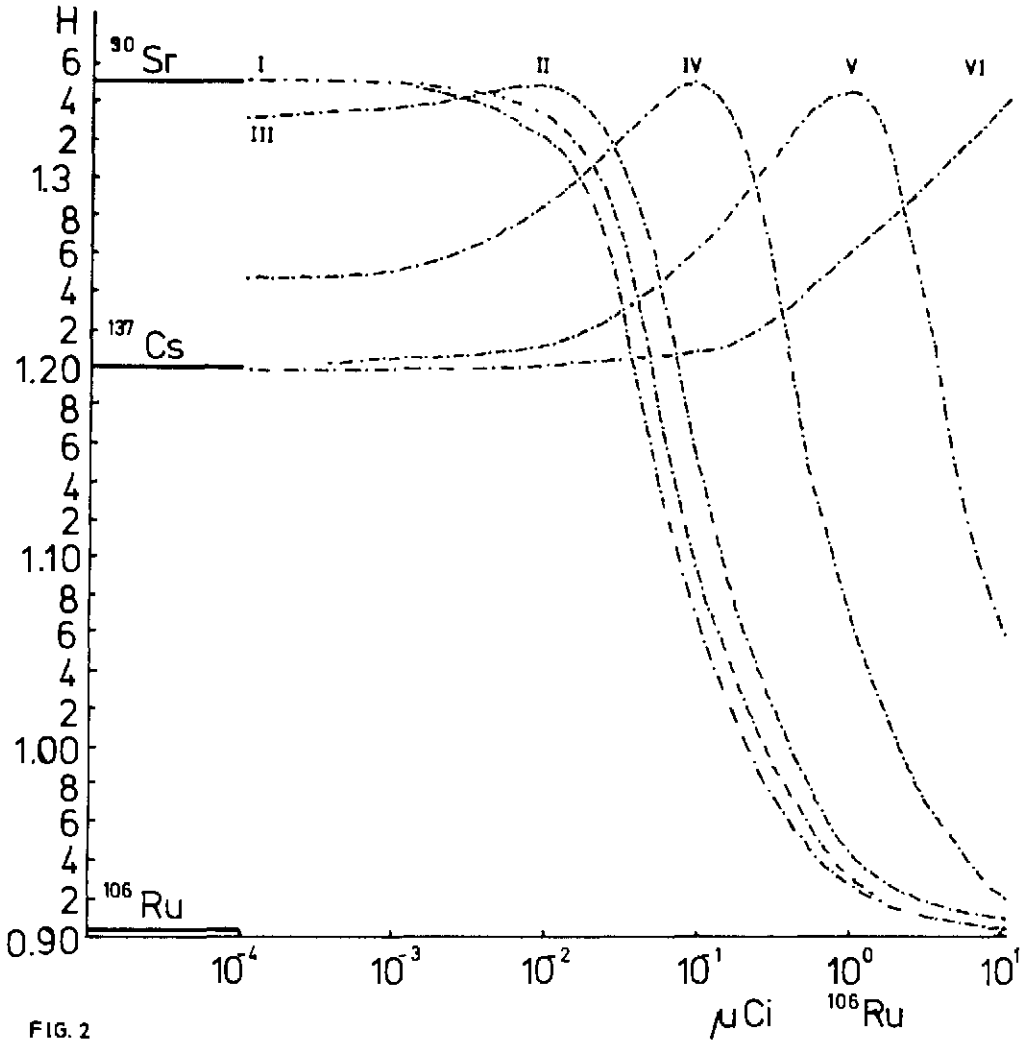

FIG. 2

Fig. 2 shows the entropies of a mixture containing ^{90}Sr, ^{137}Cs, ^{106}Ru, determinated by the use of four channels:

K 1: 200 - 1000, 8% gain
K 2: 300 - 1000, 8% gain
K 3: 500 - 1000, 10% gain
K 4: 500 - 1000, 3% gain

all with 10^{-2} µCi ^{90}Sr and
I: 10^{-4} µCi ^{137}Cs
II: 10^{-3} µCi ^{137}Cs
III: 10^{-2} µCi ^{137}Cs
IV: 10^{-1} µCi ^{137}Cs
V: 10^{0} µCi ^{137}Cs
VI: 10^{1} µCi ^{137}Cs

The activities of ^{106}Ru as to be seen from the figure.

But, for a description of the "Zerfallsgruppe" the entropy is of no great use, because it is not possible to say that for given channel setting if $H_j = H_k$ the nuclides are identical. So, if for the nuclid I the P (i) values are 1/2, 1/4, 1/8, 1/8 and for K say 1/8, 1/4, 1/8, 1/2 the entropies of the two nuclides are equal.

To describe a "Zerfallsgruppe" we therefore have to look for a mathematical expression containing a more directed order. For this reason we will use a kind of vectors.

So, for two nuclides A, B using i channels we get for the defined "Zerfallsgruppen"

$$A = A_1 p_1 + A_2 p_2 + A_3 p_3 + \ldots\ldots$$

$$B = B_1 p_1 + B_2 p_2 + B_3 p_3 + \ldots\ldots$$

with $p_i p_j = 0$ and $p_i p_i = 1$

so $A_i p_i = P_A\ (i)$

and therefore:

$$\begin{bmatrix} P_A(1) \\ . \\ . \\ . \\ P_A(i) \end{bmatrix} = A \qquad \begin{bmatrix} P_B(1) \\ . \\ . \\ . \\ P_B(i) \end{bmatrix} = B$$

Because we can choose the channels arbitrarily and independently these vectors are defined in a i dimensional space.
Now being c_1, c_2 two arbitrary real numbers we can form

$$c_1 A + c_2 A = (c_1 + c_2)\ A$$

With A not altered by variing the activity. By the superposition of two different "Zerfallsgruppen" we get a new one C

$$c_1 A + c_2 B = C$$

Writing this in our P (i) notation we get

$$Z_A P_A\ (1) + Z_B P_B\ (1) = Z\ P_M\ (1)$$

or

$$\frac{Z_A}{Z_A + Z_B}\ P_A\ (1) + \frac{Z_B}{Z_A + Z_B}\ P_B\ (1) = P_M\ (1)$$

now let

$$c_1 = \frac{Z_A}{Z_A + Z_B}\ , \qquad c_2 = \frac{Z_B}{Z_A + Z_B}$$

Than we see that C is only dependent of the ratio c_1/c_2 (Pseudo-zerfallsgruppe).

The vector model therefore seems to be able to describe the channel setting.

3. Optimization criteria

If we consider a measurement made with two or three channels then we get our vectors in a two or three dimensional space.

A, B beeing two nuclides with $A = \binom{1}{0}$ and $B = \binom{0}{1}$ then all P_M (i) values are placed on the line connecting the endpoints of A and B. (Diagonal of the square).

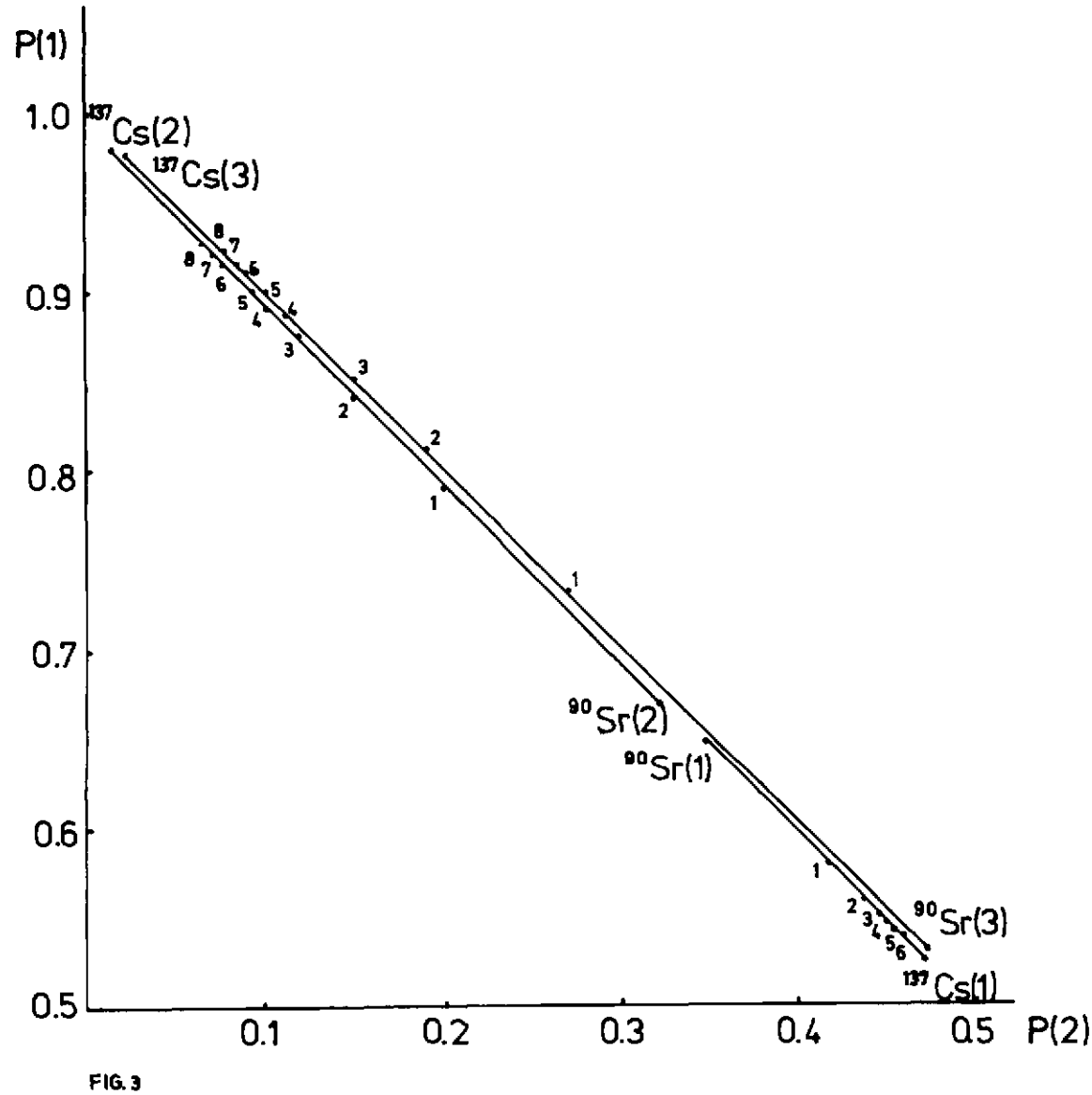

Fig. 3: *P (i) values of a $^{90}Sr/^{137}Cs$ mixture or different channel settings*

Fig. 3 shows mixtures of ^{90}Sr and ^{137}Cs laying on the lines connecting the endpoints of the Cs and Sr vectors at three different channel settings.

Now in the above given example (A-B) = $\sqrt{2}$ and this is the maximum possible difference of two "Zerfallsgruppen". Comparing the difference vector of a given channel setting with this value one will get a picture of the goodness of the choice.

Combining more than two vectors the model has to be expanded. So for three vectors in a three dimensional space the resulting "Pseudo-zerfallsgruppen" are placed on a plane.

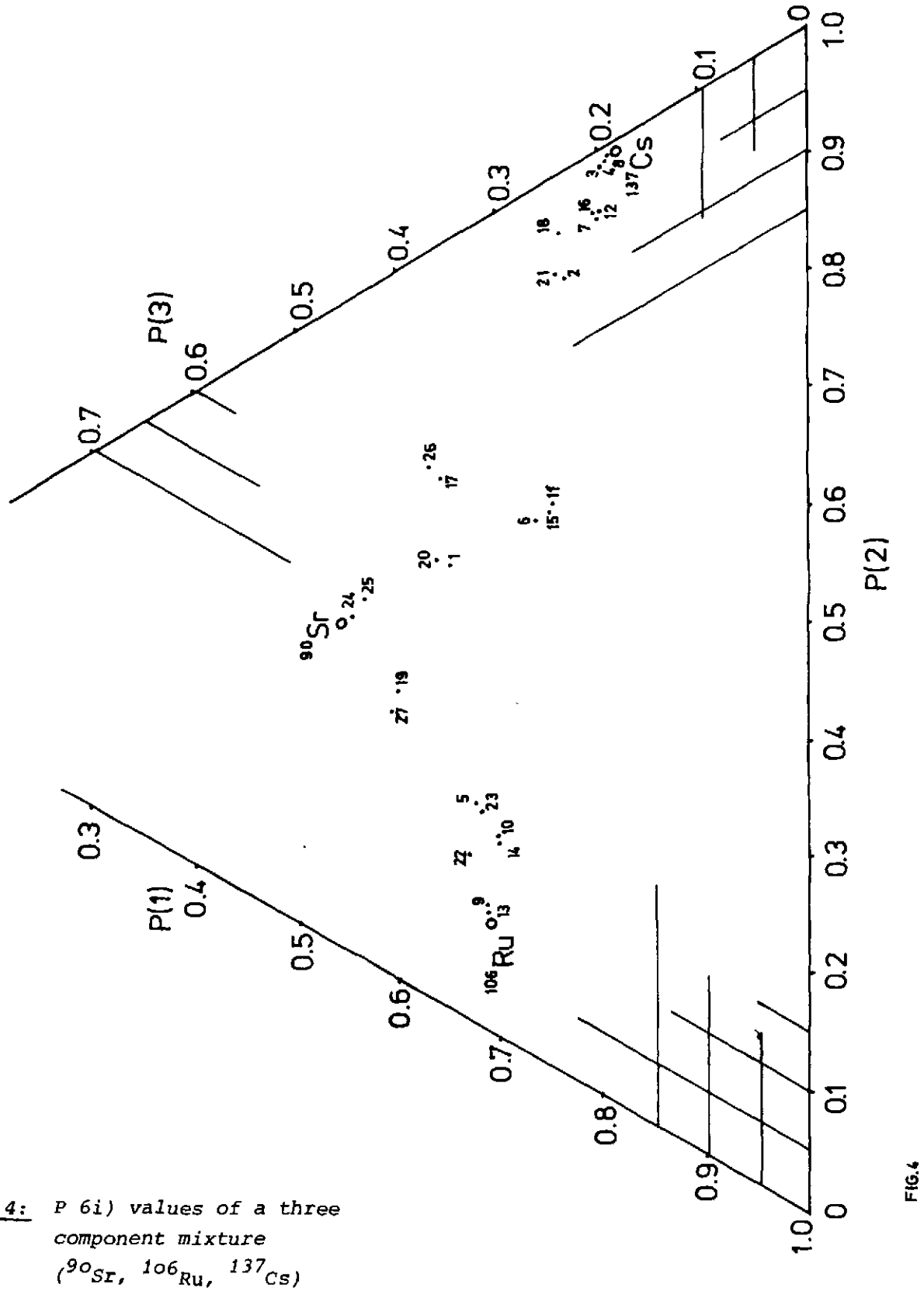

Fig. 4: *P 6i) values of a three component mixture (^{90}Sr, ^{106}Ru, ^{137}Cs)*

Fig. 4 shows the P_M (i) values for different mixtures of ^{9o}Sr, ^{137}Cs and ^{1o6}Ru determined with three channels. As it is easily to be seen that the goodness of the channel choice is represented by the area of this plane. In accordance to crystal theory it is of use to define a vector being a measure for the plane.

$$\bar{h} = A^1 + B^1 + C^1$$

with $A^1 = \frac{A \cdot B}{ABC}$ etc. the dual vectors.

So comparing the $\bar{h}_i$ vectors for different channel settings it is possible to find a optimal setting. Because of the condition $\sum P$ (i) = 1 the difference of the P (i) values will become small in practice if we choose a great number of channels, therefore a large number of channels will not optimize the channel choice. On the other hand one can apply a least square fit method by using a larger number of channels than nuclides for the evaluation of the activities of the component nuclides (4).

So we need a compromise between these facts. On a given case it will depend on the nuclides, their activities and the apparatus if we take more channels than it is necessary for the determination of the nuclides.

Another point of view consists in using determinants which can be formed by combining P (i) values of the vectors representing "Zerfallsgruppen". It is seen vividly by the interpretion of the determinant as the plane fixed by the "Zerfallsgruppen" (or as volume of a parallelepiped in a three dimensional space). The less this area the worse the channel setting. But the worth of the determinant method does not consist only in the optimization of the channel choice, it allows also to estimate the possibilities of computation of the activities in a multi-labelled sample.

Now let us consider the determinant $\begin{vmatrix} P_A\ (1) & P_B\ (1) \\ P_A\ (2) & P_B\ (2) \end{vmatrix}$ as the plane held by the two vectors A and B.
Because no P (i) value can become negative values the determinant with the maximum value is $\begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix} = 1$ corresponding with the difference vector 2. (For three nuclides in three channels we get for the maximum volume of the cube = 1).

The above given determinant is zero if two rows and columns are equal. Now let a nuclid say A being present in such an excess that the P_M (i) values differ by the P_A (i) values only in the limits even measurable with our apparatus. In our case it is about $\pm$ o,ooo2.

so: $$\begin{vmatrix} P_A\ (1) & P_A\ (1) - 2.1o^{-4} \\ P_A\ (2) & P_A\ (2) + 2.1o^{-4} \end{vmatrix} = 2.1o^{-4} = \lambda$$

and for

$$\begin{vmatrix} P_A\ (1) & P_M\ (1) \\ P_A\ (2) & P_M\ (2) \end{vmatrix} = \lambda = \frac{Z_1^A \cdot Z_2^B}{Z_A(Z_A+Z_B)} - \frac{Z_2^A \cdot Z_1^B}{Z_A(Z_A+Z_B)}$$

for the determinant of the P (i) values of the nuclides we obtain

$$\begin{vmatrix} P_A\ (1) & P_B\ (1) \\ P_A\ (2) & P_B\ (2) \end{vmatrix} = \epsilon = \frac{Z_1^A \cdot Z_2^B}{Z_A \cdot Z_B} - \frac{Z_2^A \cdot Z_1^B}{Z_A \cdot Z_B}$$

combining these two equations

$$\frac{\lambda}{\epsilon} = \frac{Z_B}{Z_A + Z_B}$$

for optimal conditions with $\lambda = 2.1o^{-4}$ and $\epsilon = 1$ we obtain

$$\frac{Z_A}{Z_B} \approx o,5 \cdot 1o^4$$

4. Some applications

To compute the optimal channel setting for a given mixture we measured the count rates of various nuclides (using mixtures of 1o ml aqueous phase and 1o ml Instagel^{R}) at different window settings and gains. The so obtained spectres we used on the IBM 113o to form determinants in the above discussed way, comparing the values of the determinants, the bigger one stored and also the next best channel setting.

For $^{11o}Ag/^{137}Cs$ we found for the optimal channel setting window: 5o - 1ooo, 4% gain and 5o - 1ooo, 4o% gain. Using the above derived equations we got for $\frac{Z_{Ag}}{Z_{Cs}} = o,1349 \cdot 1o^{4}$ and for the next best channel setting: 5o - 1ooo, 5% gain, 5o - 1ooo, 4o% gain; $\frac{Z_{Ag}}{Z_{Cs}} = o,1333 \cdot 1o^{4}$.

In the case of $^{11o}Ag/^{1o6}Ru$ we found

optimal	next one
5o - 1ooo, 8% gain	5o - 1ooo, 9% gain
2oo - 3oo, 1% gain	2oo - 3oo, 1% gain
with $\frac{Z_{Ag}}{Z_{Ru}} = o,2536 \cdot 1o^{4}$ and	$\frac{Z_{Ag}}{Z_{Ru}} = 0,2529 \cdot 1o^{4}$.
$^{11o}Ag/^{9o}Sr$	
5o - 1ooo, 3% gain	5o - 1ooo, 3% gain
5o - 1ooo, 2o% gain	5o - 1ooo, 3o% gain
$^{9o}Sr/^{144}Ce:^{137}Cs$	
5o - 1ooo, 2o% gain	5o - 1ooo, 2o% gain
5o - 5oo, 2% gain	5o - 5oo, 2% gain
2oo - 5oo, 2% gain	3oo - 1ooo, 3% gain

$^{90}Sr/^{137}Cs/^{106}Ru$

50 - 1000, 5% gain	50 - 1000, 4% gain
200 - 300, 1% gain	200 - 300. 1% gain
200 - 500, 1% gain	200 - 500, 1% gain

The next best channel setting we used in combination with the optimal channel setting for a least square fit program.

Using the above derived equations for the least square fit difficulties arise. So it is possible to obtain negative activities. This occurs always if one nuclide is in great excess of another.

The reason for this behaviour is given in the few points obtained from measurements with the three channel liquid scintillator. We therefore decided that no solution is written with negative values. If the activity of a component is found to be negative, its value is set equal zero and with this new information another run is done in the computer.

The results of a four component mixture is shown in Table 1.

TABLE 1

Results of a mixture if ^{137}Cs, ^{106}Ru, ^{90}Sr and ^{110}Ag

Channel	$P_M(i)$
1	o,2106
2	o,o372
3	o,o248
4	o,o948
5	o,o279
6	o,1844
7	o,2659
8	o,o823
9	o,o718

Matrix	x)		xx)	
26.613	3o.525	4o.882	35.438	13.663
15.789	11.oo8	13.663	14.459	8.542

x) row and column cancelled at the second run

xx) row and column cancelled at the third run

	computed	real values
^{137}Cs	56,8 pCi/ml	4o pCi/ml
^{106}Ru	1443,2 pCi/ml	15oo pCi/ml
^{90}Sr	o	5 pCi/ml
^{110}Ag	o	5 pCi/ml

DISCUSSION

By the use of the proposed method chemical separation of compounds labelled with different radionuclides can be avoided. By the aid of the derived equations it is possible to estimate the possible ratio of the activities of the radionuclides to be simultaneously determined. The method of optimizing the channel setting is a powerful tool in rising the detection limits of one nuclide in excess of another one. In the case of two nuclides the optimization is done in five minutes. For three nuclides the time required is twelf hours. It is therefore only in the case of serial analysis of practical value to compute an optimization.

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