

# A Method for the Study of Correlated Events in Time-of-Flight Mass-Spectrometry and its Application to Fission-Fragment Induced Desorption

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For experiments on fission-fragment induced desorption the detection of significant correlations between desorbed ions has been reported [1]. In this paper the method for the detection and quantitative description of these correlations will be described. The statistics of the desorption-process leads to equations for mass-line intensities of ion spectra. Using a time-to-amplitude-converter for flight-time measurements these intensities depend on interdependences of different ions desorbed by the same fission-fragment. The equations allow the computation of correlation-coefficients whose interdependence with desorption probabilities of the respective ions can be shown in Venn-diagrams. Results are given and an interpretation is suggested for fission-fragment desorbed thiamine molecular and fragment ions.

## 1. Introduction

The time-of-flight technique (TOF) in mass spectrometry (MS) allows the simultaneous registration of a large range of ion masses. In the case of low ion currents single-ion-counting with a time-to-amplitude-converter (TAC) is a customary method. The “clock” (capacitor) of the TAC gets a start signal corresponding to the start of the ion on its flight-path and is stopped after the ion has reached some kind of stop-detector at the end of the path. The TAC produces pulses with amplitudes proportional to the flight times  $t = t_{\text{stop}} - t_{\text{start}}$  of the different ions.  $t$  is proportional to the square-root of the ion mass. Summarizing a great number of pulses in a multi-channel-analyzer (MCA) gives a spectrum of flight times corresponding to the different ion masses.

As a TAC once started will be stopped by the first ion arriving, the mass spectra show too low count rates for mass lines of longer flight times in all cases where more than just one ion is produced by a single desorption event [2]. This usually disturbing effect can be used for detecting interdependences (correlations) between different ions during the ion-creating process initiated by a single fission fragment.

## 2. Experimental Setup

The experimental setup is described in detail elsewhere [1, 3]. Only details necessary for an understanding of the statistical analysis will therefore be given here (Figure 1). Fission-fragments (f.f.) from a  $^{252}\text{Cf}$ -fission source desorb ions of atoms and molecules adsorbed at the front surface of a  $5\ \mu\text{m}$  thick Al-foil. After penetration of the foil the f.f. produce a signal in the start detector (start rate: about  $20\ \text{s}^{-1}$ ).

Assuming a Poisson-distribution

$$P(N) = \lambda^N / N! e^{-\lambda}$$

for the probability of  $N$  desorbed ions by a single f.f. the mean is about  $\lambda = 2$  in our spectra [1]. The ions are accelerated in an electric field and can produce a signal in the stop detector at the end of

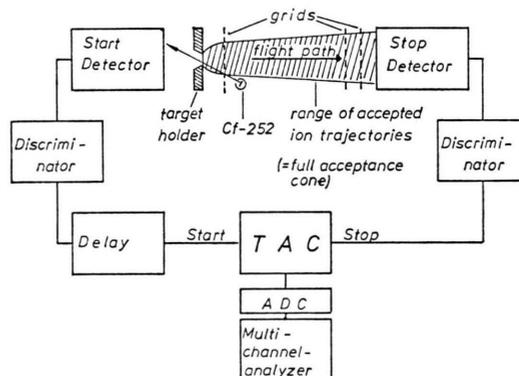


Fig. 1. Experimental setup. Ion drift path between first and second grid. Block diagram of electronic circuitry.

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a flight path of 13.6 cm. The TAC accepts the signal of the fastest ion and produces a pulse amplitude proportional to the flight time  $t$  which is stored in the corresponding channel of the MCA. For the given distributions of initial energy and angle [1] all the desorbed ions will be accepted by the spectrometer. Therefore the overall detection probability is determined only by three grids in the flight path of the ions ( $p_T \approx 0.65 \pm 0.1$ ) and the detection efficiency of the stop detector ( $p_D \approx 0.7 \pm 0.2$ ) [1]. This gives an overall detection efficiency  $\varepsilon = p_T \cdot p_D \approx 0.5 \pm 0.2$ .

The start signal can be delayed electronically for suppressing any part of the mass spectrum corresponding to flight times shorter than a chosen time  $t_{\min}$ . In this way any mass line can be chosen as the first line of the spectrum.

### 3. Theory

The method for the detection and quantitative description of interdependences between desorbed ions of different kind will be explained in two steps. First we will treat the case of independently desorbed ions with accidental coincidences only. In the second step possible correlations between different ions are taken into consideration. In both steps the mathematical formalism is first derived for the simplest possible case: a spectrum of two mass lines only and then generalized for the n-peak-spectrum. The mathematical treatment will be based on classical probability theory. First a list of events of certain probabilities  $p(i)$  will be introduced.

We assume two kinds of ions to be desorbed by the bombardment of fission fragments, named  $i = 1$  and  $i = 2$  giving an idealized MC TOF spectrum with zero background intensity as shown in Figure 2. There are four possible desorption events per f.f.:

- desorption of no ion: event  $d_0$ ,
- desorption of ion 1: event  $d_1$ ,
- desorption of ion 2: event  $d_2$ ,
- desorption of ions 1 and 2: event  $d_{12} = d_1 \wedge d_2$ .

The probabilities of these events are named:

$$d(d_0), \quad d(d_1), \quad d(d_2), \quad d(d_1 \wedge d_2).$$

The overall detection efficiency  $\varepsilon < 1$  makes it necessary to define a new set of events happening on the stop side of the spectrometer:

- no ion is detected by the stop detector: event  $w_0$ ,
- ion 1 is detected by the stop detector: event  $w_1$ ,
- ion 2 is detected by the stop detector: event  $w_2$ ,
- ions 1 and 2 are detected by the stop detector:  $w_{12} = w_1 \wedge w_2$ .

The probabilities of these events are named:

$$p^w(w_0), \quad p^w(w_1), \quad p^w(w_2), \quad p^w(w_1 \wedge w_2).$$

The events  $w_1, w_2, w_{12}$  produce signals in the stop detector which can stop the TAC. However not all of them do so as in the case of event  $w_{12}$  the TAC will be stopped by the fastest ion ( $i = 1$ ) only. That is why for the description of the measured intensities in a spectrum a further set of events has to be introduced:

- no flight time measurement: event  $m_0$ ,
- flight time measurement of ion 1: event  $m_1$ ,
- flight time measurement of ion 2: event  $m_2$ .

These events happen with probabilities:

$$p^m(m_0), \quad p^m(m_1), \quad p^m(m_2).$$

The sets  $\{m_i\}$  are subsets of  $\{w_i\}$ ,  $i = 0, 1, 2$  and consist of exclusive events. So  $\{m_0, m_1, m_2\}$  is a set of elementary events. In the following the superscripts  $w$  or  $m$  will denote quantities related to events  $w_i$  or  $m_i$  respectively. If  $T$  start signals have produced a total number of  $N^m$  stop events which are stored in the MCA as intensities of line 1 ( $N^m(1)$ ) and line 2 ( $N^m(2)$ ) with

$$N^m = N^m(1) + N^m(2)$$

it is clear that  $N^m \leq T$ . The probabilities for measuring ion 1 or 2 are thus given by  $p^m(1) = N^m(1)/T$  and  $p^m(2) = N^m(2)/T$  respectively. The probability

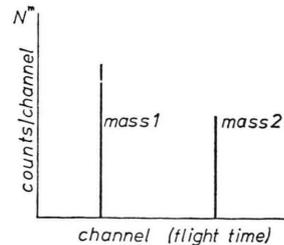


Fig. 2. Model TOF spectrum with two mass lines 1 and 2.

for measuring no stop event per f.f. is  $p^m(0) = N^m(0)/T$ . Corresponding to the set of elementary events we can write

$$p^m(0 \vee 1 \vee 2) = \sum_{i=0}^2 p^m(i) = 1. \quad (1)$$

In our example the TAC has lowered the true probability  $p^w(2) = N^w(2)/T$  of ion 2 to a measured one  $p^m(2)$ .

### 3.1. Mass Spectra of Independent Events

If ions 1 and 2 are desorbed independently from each other  $p^w(1)$  and  $p^w(2)$  can be computed from the measured probabilities  $p^m(i)$  as follows:

Ion 2 is registered by the TAC only if 2 produces a stop signal and 1 does not. The set  $\{w_2\}$  is lowered by  $\{w_1\} \cap \{w_2\}$  to give  $\{m_2\}$ . The corresponding probabilities can be written as

$$\begin{aligned} p^m(2) &= p^w(2)(1 - p^w(1)) \\ &= p^w(2) - p^w(1)p^w(2). \end{aligned} \quad (2)$$

By definition  $p^m(1) = p^w(1)$  if we assume that no more than one ion of the same kind is desorbed by the same f.f. This latter assumption appears reasonable for the small desorption cross section of about  $10 \text{ \AA}^2$  [1] in the experiments discussed here.

Equation (2) will now be generalized for a spectrum with  $n$  mass lines. As background signals are statistically independent as was assumed for the ion signals, this theory can directly be used for a background correction as well. For independent events we can write

$$p^m(n) = p^w(n) \prod_{i=1}^{n-1} (1 - p^w(i)) \quad (3)$$

as measured probability for an event in the  $n$ th channel or

$$p^w(n) = p^m(n) / \prod_{i=1}^{n-1} (1 - p^w(i)) \quad (3a)$$

as the true probability.

Given

$$p^w(2) = p^m(2)/(1 - p^m(1)) \quad (4)$$

as start of the induction the following statement can be proved inductively [4]:

$$p^w(n) = p^m(n) / \left(1 - \sum_{i=1}^{n-1} p^m(i)\right). \quad (5)$$

Assuming independently desorbed ions Eq. (5) can be used for correcting mass spectra from measured intensities to true ones.

### 3.2. Mass Spectra of Correlated Events

Experiments show [1], that ions desorbed by the same f.f. are generally not produced independently of each other (which means that the probability for a certain number of desorbed ions per f.f. can not be described by a Poisson-distribution). This can be taken into account by introducing the ‘‘conditional probability’’ [6, 7]. Generally for two events A and B the conditional probability is defined by [7]  $p(A|B) = p(A \wedge B)/p(B)$  so that  $p(B|A) = p(A \wedge B)/p(A)$  from which follows:

$$p(A \wedge B) = p(B)p(A|B) = p(A)p(B|A).$$

The events are called independent if  $p(A|B) = p(A)$  in which case  $p(A \wedge B) = p(A) \cdot p(B)$ .

If events  $w_1$  and  $w_2$  depend on each other Eq. (2) must be written as

$$p^m(2) = p^w(2) - p^w(1 \wedge 2) \quad (6)$$

$$= p^w(2) - p^w(1|2)p^w(2) \quad (7)$$

where  $p^w(1 \wedge 2)$  is the true probability for 1 and 2 being desorbed by the same f.f. and  $p^w(1|2)$  is the probability for registration of 1 by the stop detector (event  $w_1$ ) under the condition that ion 2 produces a stop signal as well ( $w_2$ ).

Now the overall detection efficiency has to be taken into consideration. The probability of desorption of ion  $i$   $d(i)$  is given by the equation

$$p^w(i) = \varepsilon d(i). \quad (8)$$

As  $p^w(1|2)$  and  $p^w(2)$  are independent (7) and (8) give

$$p^m(2) = \varepsilon d(2) - \varepsilon^2 d(1|2)d(2). \quad (9)$$

The degree of correlation between 1 and 2 can be described by a factor

$$\alpha(1, 2) = d(1|2)/d(1) = d(2|1)/d(2) \quad (10)$$

with  $\alpha = 1$  for independent events.

As this ‘‘correlation-factor’’ is independent of  $\varepsilon$ , we can replace the desorption probability  $d$  by  $p^w$ . This leads to

$$p^m(2) = p^w(2) - \alpha(1, 2)p^w(1)p^w(2). \quad (11)$$

The value of  $\alpha$  varies between

$$\alpha_{\min} = 0 \leq \alpha(1, 2) \leq 1/d(j) = \alpha_{\max} \quad (12)$$

with  $j$  denoting the more intense of the two lines. The maximum value of  $\alpha$  is thus determined by the desorption probability of the more intense mass line. This can be demonstrated by a Venn-diagram

[5] (Figure 3). For determination of the correlation-factor (11) is written as

$$\alpha(1, 2) = (p^w(2) - p^m(2))/(p^w(1) p^w(2)). \quad (11a)$$

Two measurements are needed for determining  $p^w(1)$ ,  $p^w(2)$ , and  $p^m(2)$ . In the first one the whole spectrum, as shown in Fig. 2 is taken, whereas for the second one the delay time is increased to suppress line 1 rendering line 2 the first one in the spectrum.

For extension of the formalism to a  $n$ -peak spectrum one takes Eq. (3) and multiplies each product of probabilities with a correlation-factor. In this way one gets correlation-factors up to the  $(n-1)$ -st order with  $\alpha(i, j)$  the one of first order. We now assume that correlations of higher than first order are neglectible. The physical reason is as follows: Correlation between two ions obviously means that both originate from a doubly charged molecular complex. Because the probability of multiple charges induced by a single activation process in a molecular complex clearly decreases with increasing number of charges correlations of higher order decrease accordingly. It will be shown later that this hypothesis is supported by our results. Through this assumption we can set all correlation-factors of higher than first order equal

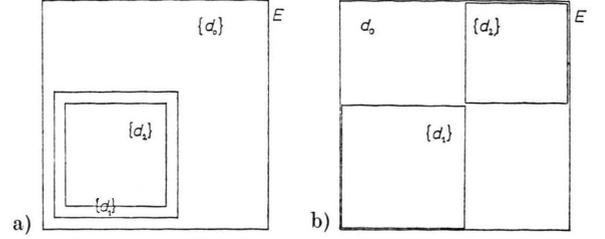


Fig. 3. Venn diagrams for desorption probabilities  $d(i)$  with a) 100% correlation ( $\alpha = \alpha_{\max}$ ) and b) 100% anti-correlation ( $\alpha = \alpha_{\min} = 0$ ).

to 1 implying that we have only accidental coincidences for the desorption (registration) of more than two ions per f.f. The resulting  $\binom{n}{2}$  correlation-factors  $\alpha(n-r, k)$  with  $1 \leq r \leq n-1$  and  $n-r+1 \leq k \leq n$  can be determined through registration of a sequence of  $n$  spectra with the delay time increased in steps of successive mass lines from spectrum to spectrum. The intensities of the mass lines in these spectra are  $p_{n-r}^m(k)$  with the subscript denoting the number of the spectrum in the sequence. Spectrum  $(n-r)$  gives the true intensity for peak no.  $(n-r)$ :  $p_{n-r}^m(n-r) = p^w(n-r)$ . As indicated above all  $p_{n-r}^m(k)$  with  $n-r \neq k$  can be expressed in terms of  $p^w(k)$  and  $\alpha(i, k)$ ,  $(n-r) \leq i \leq (k-1)$ . E.g. the measured probability of mass line  $n$  in spectrum  $(n-r) = 1$  is

$$p_1^m(n) = p^w(n) \left( 1 - \alpha(i, n) \sum_{i=1}^{n-1} p^w(i) + \sum_{\substack{i,j=1 \\ i < j}}^{n-1} p^w(i, j) - \sum_{\substack{i,j,k=1 \\ i < j < k}}^{n-1} p^w(i, j, k) + \dots + (-1)^{n-1} \prod_{i=1}^{n-1} p^w(i) \right) \quad (13)$$

where products of probabilities are written as  $p^w(i, j)$  instead of  $p^w(i) p^w(j)$  etc. As the number of  $p_{n-r}^m(k)$ -values with  $k \neq n-r$  is equal to the number of  $\alpha(n-r, k)$ -values we get the correlation factors as single valued solutions of an inhomogeneous linear system of equations (the coefficientmatrix being of rank  $\binom{n}{2}$ ).

A general solution for all combinations of  $n$  and  $r$  can be derived [4]. For this sake we write (13) as

$$\begin{aligned} \alpha(n-r, k) p^w(n-r, k) &= \Delta_{n-r}(k) \\ &- p^w(k) \sum_{i=n-r+1}^{k-1} \alpha(i, k) p^w(i) + p^w(k) \sum_{\substack{i,j=n-r \\ i < j}}^{k-1} p^w(i, j) - \dots + (-1)^{k-n+j} p^w(k) \prod_{i=n-r}^{k-1} p^w(i) \end{aligned} \quad (14)$$

with  $\Delta_{n-r}(k) = p^w(k) - p_{n-r}^m(k)$ .

Writting (14) as matrix with rows  $k = n-r+1, \dots, n$  we can prove inductively that following system is valid for all combinations of  $n$  and  $r$ :

$$\begin{pmatrix} \alpha(n-r, n-r+1) & 0 & 0 & \dots & 0 \\ 0 & \alpha(n-r, n-r+2) & 0 & \dots & 0 \\ 0 & 0 & \alpha(n-r, n-r+3) & \dots & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & \dots & \alpha(n-r, n) & \end{pmatrix} \begin{pmatrix} p^w(n-r+1) \\ p^w(n-r+2) \\ p^w(n-r+3) \\ \cdot \\ \cdot \\ \cdot \\ p^w(n) \end{pmatrix} = \begin{pmatrix} \Delta_{n-r}^{(n-r+1)} & / (p^w(n-r) p^w(n-r+1)) \\ (\Delta_{n-r}^{(n-r+2)} - \Delta_{n-r+1}^{(n-r+2)}) & / (p^w(n-r) p^w(n-r+2)) \\ (\Delta_{n-r}^{(n-r+3)} - \Delta_{n-r+1}^{(n-r+3)}) & / (p^w(n-r) p^w(n-r+3)) \\ \cdot & \cdot \\ \cdot & \cdot \\ \cdot & \cdot \\ (\Delta_{n-r}^{(n)} - \Delta_{n-r+1}^{(n)}) & / (p^w(n-r) p^w(n)) \end{pmatrix}$$

$$+ \begin{pmatrix} 0 \\ p^w(n-r+1) \\ \sum_{i=n-r+2}^{n-r+1} p^w(i) \\ \vdots \\ \sum_{i=n-r+1}^{n-1} p^w(i) \end{pmatrix} - \begin{pmatrix} 0 \\ 0 \\ p^w(n-r+1, n-r+2) \\ \vdots \\ \sum_{\substack{i,j=n-r+1 \\ i < j}}^{n-1} p^w(i, j) \end{pmatrix} + \dots + (-1)^r \begin{pmatrix} 0 \\ 0 \\ 0 \\ \vdots \\ \prod_{i=n-r+1}^{n-1} p^w(i) \end{pmatrix} \begin{pmatrix} p^w(n-r+1) \\ p^w(n-r+2) \\ p^w(n-r+3) \\ \vdots \\ p^w(n) \end{pmatrix}. \quad (15)$$

Although useful in deriving the mathematical formalism, the correlation factor  $\alpha$  is not well suited for comparing the results of spectra from different samples of the same substance. This is caused by the fact that desorption-probabilities  $d(i)$  differ significantly from sample to sample ( $\alpha_{\max} = 1/d(i)$ , see above). Linear correlation between two accidental events is commonly described [6] by a correlation coefficient ranging between  $-1$  (= 100% anticorrelation) and  $+1$  (= 100% correlation). From  $\alpha$  we get such a coefficient  $q$  by following transformation:

- 1) correlation ( $d(j) \leq d(j|i) \leq 1$ )  
 $0 \leq q \leq +1$  by  

$$q = \frac{\alpha - 1}{\alpha_{\max} - 1} = \frac{d(j|i) - d(j)}{1 - d(j)} \quad (16)$$
- 2) anticorrelation ( $0 \leq d(j|i) \leq d(j)$ )  
 $-1 \leq q \leq 0$  by  

$$q = \alpha - 1 = \frac{d(j|i) - d(j)}{d(j) - 0}.$$

#### 4. Experimental Results

For getting correlation factors significantly outside the statistical error a good ion transmission and overall-detection efficiency is necessary. We got full ion acceptance by using a short drift path which on the other hand resulted in a low mass resolution of  $M/\Delta M \approx 40$ . As substance for testing our method we took Thiamine (Vitamin B<sub>1</sub>). The spectrum shows dominant mass lines at mass numbers 122, 144 and 265 (Figure 4). Measurements were made with two different samples prepared by the electrospray-method [3, 8, 9]. The results of one series of measurements are shown in Table 1. The errors are those of the counting statistics. The desorption probabilities for different samples vary by a factor of about 2.5 (e.g. 14–36% for  $p^m(1)$ ). The target load is typically 100 ng/cm<sup>2</sup>.

Table 1. Measured probabilities ( $p^m(i) = N^m(i)/T$  in %) for sample 2.

measurement no.	$p^m(1)$	$p^m(2)$	$p^m(3)$
1	$36.24 \pm 0.19$	$4.08 \pm 0.07$	$4.81 \pm 0.07$
2	—	$4.65 \pm 0.06$	$5.30 \pm 0.05$
3	—	—	$9.70 \pm 0.07$
mass	122	144	265

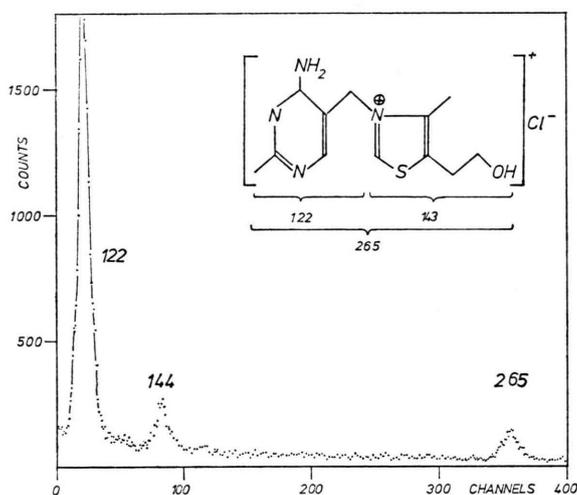


Fig. 4. Low resolution mass spectrum ( $M/\Delta M \approx 40$ ) of thiamine showing the range from  $M = 122$  to  $M = 265$ . Inset: structure-formula of the molecule with corresponding fragments.

From (15) we easily get the equations necessary for computing the correlation factors of this 3-peak-spectrum:

$$r = 1: \quad \alpha(2, 3) = (\Delta_2(3) - \Delta_3(3))/(p^w(2) p^w(3)),$$

$$r = 2: \quad \alpha(1, 3) = (\Delta_1(3) - \Delta_2(3))/(p^w(1) p^w(3))$$

$$+ p^w(2), \quad (17)$$

$$\alpha(1, 2) = (\Delta_1(2) - \Delta_2(2))/(p^w(1) p^w(2)).$$

Besides the statistical error a systematical one by the uncorrelated background events has to be

sample	$\alpha(122, 144)$	$\alpha(122, 265)$	$\alpha(144, 265)$	$\alpha_{\max}(144, 265)$
1	$0.6 \pm 0.4$	$0.1 \pm 0.3$	$25.1 \pm 1.8$	$\varepsilon \cdot (32.1 \pm 0.8)$
2	$0.3 \pm 0.1$	$0.2 \pm 0.1$	$8.7 \pm 0.3$	$\varepsilon \cdot (10.3 \pm 0.1)$

Table 2. Correlation factors for sample 1 and 2 as computed by Eq. (13 a) after correction of background effects.

taken into account. It lowers the intensities  $p^m$  of all but the mass line appearing at the beginning of the spectrum to an intensity  ${}^u p^m$  and thus would make correlation factors too great. Because of the independence of background and mass signals this error can be corrected for. As an example the correction of peak 3 in spectrum 1 is given:

$${}^u p_1^m(3) = [p^w(3) - \alpha(1, 3) p^w(1, 3) - \alpha(2, 3) p^w(2, 3)] \prod_{l=1}^f (1 - u^w(l)) \quad (18)$$

$u^w(l)$  is the true background intensity in the  $l$ -th channel (normalized to  $T$ ) and  $f$  the last channel before peak 3. Thus  $p_{n-r}^m(k)$  is given by

$$p_{n-r}^m(k) = {}^u p_{n-r}^m(k) / \prod_{l=1}^f (1 - u^w(l)). \quad (19)$$

As a rough approximation the whole measured background intensity  $U_k$  before peak  $k$  is summarized and with  $U_k/f = \bar{u}_k$  a mean intensity per channel computed.  $\prod_{l=1}^f (1 - u^w(l))$  reduces to  $(1 - \bar{u})^f$  which can be expanded into series. In the measurements reported here  $\bar{u}$  was always of the order of  $10^{-4}$  and only the linear term of the series retained. Thus we get

$$\begin{aligned} p_{n-r}^m(k) &= {}^u p_{n-r}^m(k) / (1 - f \bar{u}_k) \\ &= {}^u p_{n-r}^m(k) / (1 - U_k). \end{aligned} \quad (20)$$

The greatest correction is in  ${}^u p_1^m(3)$  with about 10% of the measured value. After correcting the measured  ${}^u p^m$ -values the correlation factors can be computed. They are shown in Table 3 and in the case of  $\alpha > 1$  compared with  $\alpha_{\max}$ . The errors are computed based on counting statistics.

As mentioned above the correlation coefficients  $q$  should be compared for different measurements with different samples rather than the  $\alpha$ 's. For the transition of the  $\alpha$ 's to the  $q$ 's  $\alpha_{\max}$  must be known for  $\alpha > 1$  which implies knowledge of the magnitude of  $\varepsilon$ . As by definition  $\alpha$  cannot be greater than  $\alpha_{\max}$  the above results give a lower limit for  $\varepsilon$ :  $\varepsilon = 0.8 \pm 0.1$ . This contrasts to the value of  $\varepsilon = 0.5 \pm 0.2$

Table 3. Correlation coefficients as computed by Eq. (17) with  $\alpha$ -values of Table 3 and  $\varepsilon = 0.8$  in the case  $q > 0$ .

sample	$q(122, 144)$	$q(122, 265)$	$q(144, 265)$
1	$-0.4 \pm 0.4$	$-0.9 \pm 0.3$	$+1.0 \pm 0.1$
2	$-0.7 \pm 0.1$	$-0.8 \pm 0.1$	$+1.1 \pm 0.1$

as estimated from the grid geometry and the detection efficiency. This discrepancy will be discussed in Chapter 5. Table 3 gives the resulting correlation coefficients  $q$  for  $\varepsilon = 0.8$ .

The results of sample 2 are illustrated in a Venn diagram (Fig. 5a) whereas Fig. 5b shows the corresponding hypothetical case with no correlation (all  $\alpha(i, j) = 1$ ). In an attempt to relate the diagrams to the structure-formula of thiamine the results may be formulated as follows: Desorption of the 122<sup>+</sup>-fragment ion happens with the greatest probability, hindering the desorption of the complementary 144<sup>+</sup>-fragment as well as that of the 265<sup>+</sup> mother ion. However if the 144<sup>+</sup>-ion is desorbed the mother ion is desorbed too with 100% probability. This indicates the involvement of at least two thiamine-molecules in this desorption process. So 144<sup>+</sup> seems to always originate from a

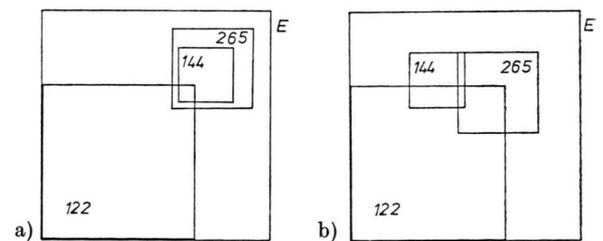


Fig. 5. Venn diagrams with desorption probabilities  $d(i)$  showing the degree of correlation as overlap of areas. The values of desorption probabilities  $d(i)$  for the various ions are given by the area of the corresponding square divided by the area of the circumscribing square,  $E$  representing the sum  $T$  of all start events. a) results of sample 2, assumed an overall detection efficiency of  $\varepsilon = 0.8$ . b) hypothetical case of no correlation, given the desorption probabilities of sample 2. The overlap of all three areas should be equal for a) and b) corresponding to  $\beta(1, 2, 3) = 1$  (see Chapter 3.2).

twofold positively charged dimer. As the intensity of the 265<sup>+</sup>-peak is greater than that of the 144<sup>+</sup> there are mother ions of different origin. The assumption of a dimer for explaining our results is in agreement with observations of Macfarlane [10] who showed intermolecular proton-transfer-reactions within dimers to be the origin of equal intensities of the ( $M+1$ )<sup>+</sup> and ( $M-1$ )<sup>-</sup> quasi-molecular peaks in many spectra. The above results indicate that there are two different reaction paths, one involving a single charge (122<sup>+</sup> or 265<sup>+</sup>) the other involving two charges (144<sup>+</sup> and 265<sup>+</sup>). In order to give a rough estimate of the probabilities for these two paths, as a first approximation 100% anticorrelation is assumed for the pairs (122<sup>+</sup>, 144<sup>+</sup>) and (122<sup>+</sup>, 265<sup>+</sup>) to appear (= zero overlap of the corresponding areas in Figure 5a). After normalizing the single desorption probabilities of the resulting three possible events (122<sup>+</sup>, 265<sup>+</sup>, 144<sup>+</sup> and 265<sup>+</sup>) to the overall probability of any of these events taking place the probabilities for the two reaction paths turn out to

- desorption of 144<sup>+</sup> and 265<sup>+</sup>:  
 $d(144^+ \wedge 265^+) \approx 0.1$ ,
- desorption of 122<sup>+</sup> or 265<sup>+</sup>:  
 $d(122^+ \vee 265^+) \approx 0.9$ .

## 5. Discussion

The described method and results leave a few minor uncertainties unresolved. Minor systematical errors (smaller than the statistical ones) for the computed  $\alpha$ -values, arising from the rough correction of the uncorrelated background events cannot be excluded. A remaining problem is the discrepancy in the overall detection efficiency  $\varepsilon$ . Calculated from the optical transparency of the grids and the estimated detection efficiency of the stop-detector a value of  $0.5 \pm 0.2$  (see Chapter 2) is arrived at whereas our results for  $\alpha(144, 265)$  and  $\alpha_{\max}(144, 265)$  indicate a lower limit of  $0.8 \pm 0.1$  (see Table 2). This second value could change with improved background correction. A method which could be of help is described by Lowe et al. [2]. Although within the given accuracy there seems to be no indication for higher than first order correlation this cannot be excluded with absolute certainty. The same holds for possible correlations between ions of the same kind. A careful analysis of single mass

lines could possibly reveal such an effect. Whereas higher order correlations would have no influence on our  $\varepsilon$ -value of 0.8 the other effects could possibly add and account for the discrepancy mentioned above. It appears however that the estimate of the detection efficiency  $p_D$  is the main source of uncertainty [1]. Also the product of the optical transparencies of the single grids as used for the computation of  $p_T = 0.5$  will presumably give only a lower limit for  $p_T$ . This because the transparencies of the grids possibly are not independent of each other for an ion traversing through its acceleration- and drift-paths.

## 6. Conclusion

The significant and reproducible correlation and anticorrelation in the case of fission-fragment induced desorption of thiamine ions show the applicability of this simple method thereby avoiding coincidence techniques. For its application in TOF mass-spectrometry two more points are of essence besides single ion counting.

- Mass line intensities must be normalizable for getting desorption probabilities.
- The overall-detection-efficiency must not be too small for getting correlation factors significantly outside the statistical errors.

If there exist correlations of higher than first order these cannot be quantitatively determined by use of a TAC for time measurement. In this case e.g. a time-to-digital converter with multiple stop facility would be helpful, as described by Hall et al. [11].

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