APPROXIMATE CALCULATION OF SECONDARY MAXIMA OF THE FUNCTION FOR THE RADIO-FREQUENCY MASS-SPECTROSCOPIC ANALYSER

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In this paper is shown the correction of the secondary maxima position. This applies to analysers, in which the number of the cycles between the individual stages does not differ very much, or for these types of analysers, in which the value $(\lambda_1 - \lambda_2)/(\lambda_1 + \lambda_2)$ is sufficiently small (it follows from the relation (5)).

The case of the correction of the secondary maxima position brings big mathematical difficulties (solution of the transcendental equation with the parameter), if λ_1 and λ_2 are arbitrary. For this problem no satisfactory solution has been obtained yet.

INTRODUCTION

According to the relations derived in [1] we can assume that the function $\Delta W(\alpha)$, expressing an energy gain of ions in the analyser of the radio-frequency mass spectrometer is a very quickly oscillating function. This function has, apart from the main maximum, also secondary maxima. The course of this function was obtained for a 7—5 and a 9—7 cycle analyser by means of an analogue computer [2].

Dekleva and Ribarič [3] have derived the relation for the approximate calculation of values of the secondary maxima, but they did not discuss its precision and the boundary of the application. In this paper the same relation (5) is obtained in another way. Paper [2] enabled to compare the values of the secondary maxima of the $\Delta W(\alpha)$ function generated by an analogue computer with the values obtained by approximate calculation (5). According to the executed calculation it was shown that the calculation according to the relation (5) is a good approximation for the practice, mainly for those types of analysers in which the number of cycles between the single stages does not differ very much (7—5, 9—7).

For illustration only the values for a 7—5 cycle analyser [2] are introduced. The accuracy of the computer according to the advance of the coordinate x is $\pm$ 0.3 %, and for the amplitude it is better than $\pm$ 1 %. This accuracy is

sufficient for practical aims. Next we shall assume that the values obtained from the graph [2] are accurate and we shall compare with these all other values.

Further, there are derived the first and the second approximation for the correction of the secondary maxima position when $\lambda_1 \doteq \lambda_2$.

DERIVATION OF THE APPROXIMATE RELATION FOR THE CORRESPONDING SECONDARY MAXIMUM VALUE

Let a three-stage analyser of the radio-frequency mass-spectrometer (Fig. 1) be considered. A more detailed description is given in [1] and [5].

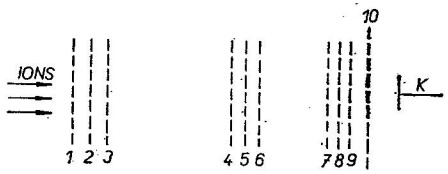

Fig. 1.

For the energy gain of the resonant ion in [1] the following relation is derived

$$\Delta W(\alpha) = 2eU_0 \frac{1 - \cos\alpha}{\alpha}\left\{3 + 2\left[\cos k_1 \frac{\alpha}{\alpha_0} + \right.\right.$$

$$\left.\left. + \cos k_2 \frac{\alpha}{\alpha_0} + \cos(k_1 + k_2)\frac{\alpha}{\alpha_0}\right]\right\}^{\frac{1}{2}} \qquad (1)$$

where $\alpha = \omega s/v$, ω is the angular frequency of the radio-frequency accelerating field, v the ion velocity, s the distance between grids in the stage of the analyser. α_0 is the first root of the transcendental equation $\operatorname{tg}\alpha_0/2 = \alpha_0$. ($\alpha_0 = 2.331$), $k_i = 2\pi\lambda_i$, λ_i is the number of cycles executed by the radio-frequency field when the ion passes between the individual stages of the analyser.

From the relation (1) we obtain that the energy gain is maximum if $\alpha = \alpha_0$. Its value is

$$\Delta W(\alpha_0)_{max} = 6eU_0 \frac{1 - \cos\alpha_0}{\alpha_0}. \qquad (2)$$

The function of the grid No 10 follows from the principle of the analyser activity. The retarding potential of this grid effects the required ion selection. For the minimum value of this potential we have from [1] the relation

$$\frac{\Delta W(\alpha_n)}{\Delta W(\alpha_0)_{max}} = \frac{U_{BR}}{\Delta U_m(\alpha_0)} = \frac{U_{BR}}{6.15\, U_f} \qquad (3)$$

where $\Delta W(\alpha_n)$ is the highest value of the secondary maxima, U_f the effective value of the radio-frequency potential. As it follows from the relation (3), it is necessary to know also the values of the highest secondary maxima of the function (1). A relatively good approximation for the calculation of the secondary maxima was obtained if we chose

$$\frac{\alpha_n}{\alpha_0} = x_n = \frac{2\pi n}{k_1 + k_2} \qquad (4)$$

because their number in the expression

$$\{3 + 2[\cos k_1 x_n + \cos k_2 x_n + \cos(k_1 + k_2)x_n]\}^{\frac{1}{2}}$$

was determined by the term $\cos(k_1 + k_2)x_n$. By the approximately determined position of the secondary maxima according to (4) for the sedondary maxima values we obtain the expression

$$\Delta W(\alpha_n) = 2eU_0 \frac{1 - \cos\alpha_n}{\alpha_n}\left[5 + 4(-1)^n \cos\left(n\pi \frac{\lambda_1 - \lambda_2}{\lambda_1 + \lambda_2}\right)\right]^{\frac{1}{2}}. \qquad (5)$$

The thus determined value of the n-th secondary maximum is an approximate one and differs from the real value the less the smaller the difference is between a real position of the secondary maximum x_n^* and an approximate value x_n given by the relation (4).

CALCULATION OF $x_n^* - x_n$

The condition for the existence of an extreme of the function (1) is that the function

$$y(x) = \cos k_1 x + \cos k_2 x + \cos(k_1 + k_2)x \qquad (6)$$

has an extreme. Consequently it must be

$$k_1 \sin k_1 x_n^* + k_2 \sin k_2 x_n^* + (k_1 + k_2)\sin(k_1 + k_2)x_n^* = 0 \qquad (7)$$

where x_n^* is the position of the n-th maximum. From (4) it follows that $k_1 x_n = 2\pi n - k_2 x_n$, from which we get

$$\cos k_1 x_n = \cos k_2 x_n \qquad (8)$$

$$\sin k_1 x_n = -\sin k_2 x_n.$$

For the case $\lambda_1 \doteq \lambda_2$ it is possible to replace single terms in (7) by the Taylor development in the vicinity of the point

$$x_n = \frac{n}{\lambda_1 + \lambda_2} = \frac{2\pi n}{k_1 + k_2},$$

then

$$\sin k_1 x_n^* = \sin k_1 x_n + k_1 \cos k_1 x_n (x_n^* - x_n)$$

we get

$$k_1 \sin k_1 x_n + k_2 \sin k_2 x_n = (x_n - x_n^*)\,[k_1^2 \cos k_1 x_n + \\ + k_2^2 \cos k_2 x_n + (k_1 + k_2)^2]\,. \tag{9}$$

If we use the relation (8), then for x_n^* we get the expression

$$x_n^* = x_n - \frac{(k_2 - k_1) \sin k_2 x_n}{(k_1^2 + k_2^2) \cos k_1 x_n + (k_1 + k_2)^2}\,. \tag{10}$$

The relation (10) gives a connection between the parameters which charcterize a given analyser (λ_1, λ_2) and the secondary maxima position of the function (1). The correction

$$Cx_1 = \frac{(\lambda_1 - \lambda_2) \sin [\lambda_2\, 2\pi n/(\lambda_1 + \lambda_2)]}{4\pi\{(\lambda_1^2 + \lambda_2^2) \cos^2 [n\pi\lambda_1/(\lambda_1 + \lambda_2)] + \lambda_1\lambda_2\}} \tag{11}$$

is very small. The values Cx_1 are given in Table 1.

If we consider the second term in the Taylor development, we obtain the second approximation of the correction

$$Cx_2 = \\ = \frac{2(k_1 - k_2) \sin k_2 x_n}{a \cos k_1 x_n + b + [2ab(1 + \cos k_1 x_n) + a(k_1^2 - k_2^2) \sin^2 k_1 x_n + 4k_1^2 k_2^2 \cos^2 k_1 x_n]^{\frac{1}{2}}}\,,$$

where $a = k_1^2 + k_2^2$ and $b = (k_1 + k_2)^2$. This expression gives for $\lambda_1 \doteq \lambda_2$ the values nearly equal to the expression (11). E. g. for a 7—5 cycle analyser with $n = 14$ we get for Cx_2 the value -0.0014, while $Cx_1 = -0.0016$.

COMPARISON OF THE SECONDARY MAXIMA VALUES DETERMINED ACCORDING TO (5) WITH THE VALUES DETERMINED FROM THE FUNCTION COURSE (1) GENERATED BY AN ANALOGUE COMPUTER

The function (1) is a very quickly oscillating function, therefore it is very laborious to obtain its course from a numerical calculation. In paper [2] its course was obtained by an analogue computer. The course $A = \Delta W(\alpha)/\Delta W(\alpha_0)_{max}$ as the function of x_n for the 7—5 cycle analyser is in Fig. 2. Although it was shown that the values Cx_1 are very small with respect to the slope of function (1) in the vicinity of the maxima, the difference $A_n - K_n$ can attain values which

cannot be neglected. A_n are the values calculated from the function course A in Fig. 2. K_n are the values obtained from the approximate relation (5). In order to appreciate this error the concrete numerical calculation for the 7—5 cycle analyser was executed. The results are shown in Table 1. In Table 1 the first four values of the secondary maxima are not shown. They are very small and for practical purposes unimportant. It must be noted that the values A_n in Table 1 are not quite precise. They are loaded with an error, partly derived from the measurement of single maxima coordinates from the graphic course and partly from error of the computer. As it is obvious from Table 1 the numerical calculations confirm the right to use the approximate relation (5) for the analysers with $\lambda_1 \doteq \lambda_2$.

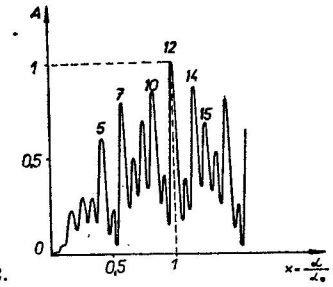

Fig. 2.

The values Kn_1 are computed from the relation (5) with respect to Cx_1.

If λ_1 is very different from λ_2 (e. g. for a 2—10 cycle analyser), then for the highest secondary maximum instead of the value 0.90 [1] the approximate calculation gives the value 0.96. From this it follows that an approximate calculation for such a case is impossible.

Decisive for the application of the radio-frequency mass-spectrometer are its current efficiency and the resolving power. Both these quantities are functions of $1 - K$. Similarly, the width of the region, in which the retarding potential U_{BR} can vary, is dependent on $1 - K_n$, or $1 - A_n$, respectively, where K_n corresponds to the highest secondary maximum. Therefore the error brought about by an approximate calculation must be related to this difference and not to the secondary maximum height. For further consideration of an accuracy of the approximate method a quantity $\varkappa$ is introduced (its values see in Table 1), the importance of which is shown in Fig. 3.

$$\varkappa[\%] = \frac{\Delta y_n - \Delta y_n^*}{\Delta y_n^*} \cdot 100 = \frac{A_n - K_n}{1 - A_n} \cdot 100\,.$$

The dependences $\varkappa(n)$ and $\varkappa_C(n)$ are represented in Fig. 4. The values $\varkappa_C$ are obtained by application of the values Kn_1. One can see that $\varkappa$ reaches relatively

high values for some maxima (even λ_1 and λ_2 do not differ very much) and thus it can be said that the approximate method has a limited range of application.

Table 1

n	x_n	Cx_1	K_n	A_n	Kn_1	$\varkappa$ [%]	$\varkappa_c$ [%]
5	0.416	0.0008	0.599	0.605	0.600	1.5	1.2
6	0.500	0.0000	0.236	0.237	0.236	0.1	0.1
7	0.583	—0.0008	0.778	0.789	0.780	5.2	4.2
8	0.667	—0.0014	0.501	0.505	0.504	0.8	0.2
9	0.750	—0.0020	0.690	0.695	0.691	1.7	1.3
10	0.833	0.0016	0.854	0.858	0.855	2.8	1.2
11	0.916	0.0020	0.408	0.410	0.407	0.4	0.5
12	1.000	0.0000	1.000	1.000	1.000	0.0	0.0
13	1.083	0.0020	0.410	0.400	0.409	—1.7	—1.5
14	1.166	—0.0016	0.853	0.860	0.856	5.0	2.8
15	1.250	0.0020	0.697	0.686	0.694	—3.5	—2.5

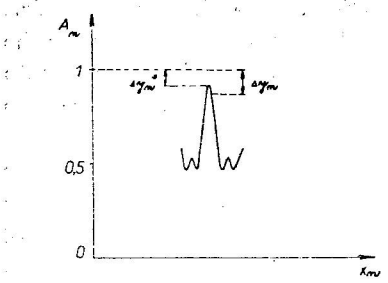

Fig. 3.

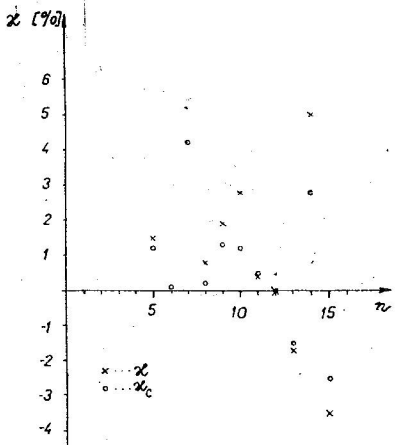

Fig. 4.

CONCLUSIONS

This paper compares the accurate secondary maxima values of the $\Delta W(\alpha)$ function with the values obtained from approximate calculation according to the relation (5). It was shown that the correction (11) of the secondary maxima position is very small. In case of $\lambda_1 \doteq \lambda_2$, the calculation of the approximation Cx_2 confirms the application of the more simple expression (11).

From comparison of the values A_n and K_n or A_n and Kn_1, respectively, it follows that for practical purposes (e. g. for the choice of U_{BR}) it is not necessary to know the whole course of the $\Delta W(\alpha)$ function. It is sufficient to calculate the highest maxima values from the relation (5). Although the numerical values A_n and K_n are slightly different, the above introduced quantity $\varkappa$ is relatively large, especially for the highest secondary maxima.

In the case of $\lambda_1 = \lambda_2$ the approximate method gives completely accurate results, but the greater the difference is between λ_1 and λ_2, the greater the possible error. In this case, if an accurate secondary maxima value is required, this method cannot be used directly, but we must do a direct calculation according to (1) *

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