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EVALUATION OF INTERFACIAL SURFACE AREAS IN ULTRA-LOW-LOADED GAS CHROMATOGRAPHIC COLUMNS

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SUMMARY

A special type of gas chromatographic column, called "ultra-low-loaded", was studied. The packings contain very small amounts of stationary phase, able ultimately to form a complete monolayer on the solid support. These packings are considered as poly-phase systems, each comprising, in general, three interfacial surface areas: a gas–monolayer, a monolayer–solid and a gas–solid interface. As no experimental technique allows the measurement of these interfacial areas separately, a calculation procedure is proposed that appears to be the only way of evaluating them. The procedure is demonstrated with two series of packings that meet the requirements for ultra-low-loaded columns. The accuracy of the calculation is discussed.

INTRODUCTION

The term "low-loaded" columns has been introduced in gas–liquid chromatography (GLC) to indicate column packings containing small amounts of stationary phase (1–2%) deposited on a solid support[1]. In this study, however, a special type of column was considered, the packings of which contain either "inert" or "active" supports, loaded with very small amounts of stationary phase able to form a mostly complete monolayer on the solid surface. Such columns are called here "ultra-low-loaded". In accordance with the given definition, we can consider the efforts of Eggertsen and co-workers[2,3] to reduce tailing in gas–solid chromatography (GSC) (by adding small amounts of high-boiling liquids to the adsorbents) as the first attempt to employ ultra-low-loaded columns. Further, the so-called modified adsorbents (obtained by partial coverage of the surface of active solids with polar or non-polar stationary phases) have been successfully applied to the solution of particular analytical tasks[4–11]. Some theoretical aspects of both the low-loaded and the ultra-low-loaded columns have also been considered to account for the complexity of the packings and of solute retention[12–21].

It has been demonstrated elsewhere[22,23] that small amounts of stationary phase, deposited on a wide-pore support, can form an incomplete monolayer on the solid surface, provided that the latter is well wetted by the stationary phase. Hence, the column packing may be considered as a poly-phase system that comprises three interfacial surface areas: (i) a gas–monolayer interface or the surface area of the

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incomplete stationary phase monomolecular layer (A); (ii) a monolayer–solid interface or the support surface area covered by the stationary phase monolayer (A_C); and (iii) a gas–solid interface or the bare (uncovered) surface area of the support (A_B).

Although, in principle, the specific surface area of a sorbent is easily obtainable, it is disappointing that no experimental technique permits the separate measurement of the above-defined packing interfaces in ultra-low-loaded columns. Taking this into account, in this paper a calculation procedure for evaluating the interfacial surface areas is proposed, based on our previous theoretical treatments[22,23] and on area measurements carried out by a modification of the conventional BET technique[24].

THEORETICAL

In the following, we shall adhere to the convention that all of the above-defined interfacial areas, and also all quantities additionally introduced to represent other types of surfaces, are considered as specific surface areas, *i.e.*, relative to 1 g of solid support. Thus, as found earlier[22], the formation of a stationary phase monolayer on the solid surface can be represented by the simple equation

$$A = c_0 V \qquad (0 \leqslant V \leqslant V_0) \tag{1}$$

where V is the stationary phase volume deposited on the surface of 1 g of solid support, to produce an incomplete monolayer of surface area A and V_0 represents that value of V at which a complete monolayer is formed. Correspondingly, c_0 is a constant given by

$$c_0 = \nu A_S / V_0 \tag{2}$$

where A_S is the specific surface area of the solid support and ν is a parameter accounting for the so-called geometric non-homogeneity of the surface, being typical of most porous solid materials[23]. As this is the reason why a complete or incomplete stationary phase monolayer has a smaller surface area than that covered by it, ν is defined by

$$\nu = A_0/A_S \equiv A/A_C \tag{3}$$

where A_0 is the specific surface area of the complete monolayer. Therefore, when V varies within the range $[0, V_0]$, the inequalities $A_0 < A_S$ and $A < A_C$ hold and permit ν to be considered as a characteristic constant for each stationary phase–solid support system, thus being usually close to, but always less than, unity.

Because it is impossible to measure A separately, a suitable approach has been developed[23] for verifying eqn. 1 after its reasonable rearrangement into the equation

$$A_S - A_P = g[P/(100 - P)] \qquad (0 \leqslant P \leqslant P_0) \tag{4}$$

Here P and $100 - P$ are the percentage contents of the stationary phase and the solid support, respectively, the latter being considered as ingredients of the packing for an ultra-low-loaded column; P_0 is that value of P at which a complete monolayer is deposited on the support surface, and A_P is the sum of the interfacial areas A and A_B, and is called the specific surface area of the column packing. As eqn. 4 is derived from eqn. 1 and, in contrast to the latter, involves three measurable quantities (P, A_S and A_P), it has been used for an indirect verification of eqn. 1. The plot of $A_S - A_P$ *vs.* $P/(100 - P)$ is a straight line passing through the origin and having a slope equal to the constant g[23].

The above equations can be successfully employed to derive expressions for the interfacial surface areas of the packing in an ultra-low-loaded column. For instance, taking into account that

$$V = P/(100 - P)\rho \tag{5}$$

where ρ is the stationary phase density, eqn. 1 can be rearranged into

$$A = vc_{p0}[P/(100 - P)] \qquad (0 \leqslant P \leqslant P_0) \tag{6}$$

the constant c_{p0} being defined as

$$c_{p0} = A_S[(100 - P_0)/P_0] \tag{7}$$

Further, referring to eqn. 3, we can equate the expression $A = vA_C$ with eqn. 6, thus obtaining

$$A_C = c_{p0}[P/(100 - P)] \qquad (0 \leqslant P \leqslant P_0) \tag{8}$$

As, by definition,

$$A_B + A_C = A_S \tag{9}$$

by combining eqns. 8 and 9 we obtain

$$A_B = A_S - c_{p0}[P/(100 - P)] \qquad (0 \leqslant P \leqslant P_0) \tag{10}$$

Eqns. 6, 8 and 10 permits, in principle, the evaluation of the corresponding interfacial areas, provided that the constants v and c_{p0} are known or can be determined. As will be shown later, v can be calculated but, in spite of this, a possibility of evaluating A will be demonstrated that does not require a knowledge of v. Thus, bearing in mind that

$$A_P = A + A_B \tag{11}$$

combination of eqns. 10 and 11 gives the expression

$$A = A_P - A_S + c_{p0}[P/(100 - P)] \qquad (0 \leqslant P \leqslant P_0) \tag{12}$$

which, analogously to eqns. 8 and 10, contains the measurable quantities P, A_S and A_P. On the other hand, eqns. 8, 10 and 12 involve the constant c_{p0}, which can be calculated from eqn. 7, if P_0 is known.

Hence, it becomes evident that P_0 plays an important role in the evaluation of the interfacial surface areas of the packings. Although P_0 cannot be determined experimentally, we shall demonstrate how it can be obtained on the basis of a reasonable calculation procedure. Correspondingly, we can employ the equation

$$A = c_1 V \ln V - c_2 V + c_3 \qquad (V \geqslant V_0) \tag{13}$$

which was derived[22] to represent the dependence of the stationary-phase surface area (A) on the phase volume (V) when the amount of the stationary phase is sufficiently large to form a complete polymolecular layer on the support surface, *i.e.*, $V \geqslant V_0$. For the sake of convenience, we shall use eqn. 5 to transform eqn. 13 into the form

$$A = c_{p1}[P/(100 - P)]\ln[P/(100 - P)] - c_{p2}[P/(100 - P)] + c_{p3} \tag{14}$$

which holds at $P \geqslant P_0$; here c_{p1}, c_{p2} and c_{p3} are constants, the values of which can be determined by means of a suitable calculation procedure[22]. When $P = P_0$ eqn. 14 is also valid, bearing in mind that A is then equal to A_0. Analogously, referring to eqn. 4, when $P = P_0$ we have $A_p = A_0$ and, as this equation holds, it can be combined with eqn. 14 to give

$$P_0 = \frac{100(A_S - c_{p3})}{c_{p1}\ln[P_0/(100 - P_0)] - c_{p2} - c_{p3} + A_S + g} \tag{15}$$

thus eliminating A_0. However, eqn. 15 is seen to have a typical transcendental form and hence it can be properly solved with respect to P_0 by using the Newton iterative procedure[25].

Further, let us equate eqn. 4 (with $P = P_0$ and $A_P = A_0$) with the expression $A_0 = vA_S$, derived from eqn. 3. It follows that

$$v = 1 - gP_0/A_S(100 - P_0) \tag{16}$$

Obviously, eqn. 16 permits the evaluation of v if P_0 is previously calculated and the value of g is known. As indicated above, the calculation of g is possible, so that eqn. 16 can be employed in practice. Then, having the values of P_0 and v at our disposal, we shall be able to evaluate the interfacial surface areas A, A_C and A_B, and also the specific surface area (A_0) of the complete stationary-phase monolayer, by referring again to eqn. 3.

From a purely theoretical point of view, the equations derived above may be considered as sequential steps of a common algorithm, intended to solve the general problem of evaluating the interfacial areas in ultra-low-loaded columns. However, some specific problems must be discussed before employing this algorithm in practice. The problems arise from the necessity to perform a series of experimental procedures. Thus, a limited number (n) of column packings must be prepared from the same solid support and stationary phase. A wide variation of the phase amount (P_i) in the particular packings ($i = 1,2,\ldots, n$) should be used, starting at values of P_i less than P_0. For instance, to ensure a reasonable correctness of the calculation procedure, the set of column packings must consist optimally of 3–5 packings with different P_i less than P_0, together with 5–7 packings with $P_i > P_0$.

This fact immediately poses the problem of knowing (or determining) P_0 for the series of column packings. Experience shows that for solid supports of specific surface area $A_S < 5\,m^2g^{-1}$ it is usual that $P_0 \leqslant 0.5\%$, whereas for those of $A_S = 5$–10 m^2g^{-1} P_0 varies within the range 0.5–1.0%. Hence this means that in some instances the choice of P_i values in preparing the packings might be made empirically without a previous knowledge of the correct value of P_0. However, when conventional GLC supports are used for ultra-low-loaded columns, it must be borne in mind that serious difficulties can occur in the preparation of packings and in the experimental determination of both the stationary phase percentage (P) and the specific surface area (A_P) of these packings. Such solid supports usually have A_S values between 1 and 2 m^2g^{-1} and require amounts of stationary phase that are too small to obtain P_i values less than P_0, thus giving rise to inaccuracy in determining P. On the other hand, packings of low P_i values will exhibit low and close specific surface areas (A_{Pi}), the differences between them being comparable to the possible error of measurement.

It can be concluded from the above discussion that satisfactory results with the application of the algorithm described might be expected mainly with column packings prepared from supports of $A_S > 5$ m^2g^{-1}. Moreover, for the precise determination of the stationary phase percentage the so-called evaporation technique[26] can be recommended, whereas for reliable surface area measurements it will be preferable to employ the modified BET technique, described by Bliznakov *et al.*[24]. In order to reduce the number of A_{Pi} measurements for packings of $P_i > P_0$, another algorithm[27] for the calculation of A_{Pi} in a series of column packings could be applied, the requirement for this being that one must have at least three packings available with values of P_i and A_{Pi} that have been previously determined.

EXPERIMENTAL

Two GLC solid supports, *viz.*, Rysorb (0.3–0.5 mm) (Chemapol, Prague, Czechoslovakia) and Sterchamol (0.2–0.3 mm) (Schuchardt, Munich, F.R.G.) and the stationary phase Carbowax 20M (Carlo Erba, Milan, Italy) were selected for preparing two series of column packings, denoted I and II. The supports, having specific surface areas of 7.62 and 9.62 m^2g^{-1}, respectively, were covered with stationary phase according to as procedure described earlier[23,27] to give packings of different P_i values for each series. Special care was taken to meet the above-defined requirements concerning the optimal distribution of stationary phase percentages in the packings within a series. All weighings were carried out with an accuracy of $\pm 2 \cdot 10^{-6}$ g, thus creating a prerequisite for obtaining reliable results by determining both the stationary phase percentage[26] and the specific surface area[24] of the packings. The maximal absolute error achieved in estimating P_i, *i.e.*, ΔP_i, did not exceed $4.0 \cdot 10^{-4}\%$, and that of the specific surface area measurements (A_S or A_{Pi}) was the same as indicated previously[24], *i.e.*, $\Delta A_S = \Delta A_{Pi} = 5.0 \cdot 10^{-2}$ m^2g^{-1}.

All calculations concerning the verification of the algorithm described were performed on a Model 9845 computer (Hewlett-Packard, Palo Alto, CA, U.S.A.) using the author's BASIC programs.

RESULTS AND DISCUSSION

Table I summarizes all the experimentally determined values of both the sta-

TABLE I

EXPERIMENTAL DATA FOR THE COLUMN PACKINGS IN SERIES I AND II

Packing No. (i)	*Series I: Carbowax 20M–Rysorb (0.3–0.5 mm) ($A_S = 7.62\ m^2g^{-1}$)*		*Series II: Carbowax 20M–Sterchamol (0.2–0.3 mm) ($A_S = 9.62\ m^2g^{-1}$)*	
	P_i (%)*	*A_{Pi}** (m^2g^{-1})*	*P_i* (%)*	*A_{pi}** (m^2g^{-1})*
	$P_i < P_0$	$A_{Pi} > A_0$	$P_i < P_0$	$A_{Pi} > A_0$
1	0.1488	7.17	0.1508	9.36
2	0.2145	7.06	0.2474	9.22
3	0.3011	6.86	0.3100	9.05
4	0.4192	6.42	0.4619	8.89
5	0.5003	6.16	0.5020	8.77
	$P_i > P_0$	$A_{Pi} < A_0$	$P_i > P_0$	$A_{Pi} < A_0$
6	1.008	5.96	1.385	8.09
7	2.995	4.92	3.002	7.23
8	5.002	4.38	4.999	6.46
9	9.982	3.37	10.003	4.88
10	15.001	2.93	14.994	3.87
11	20.008	2.79	25.002	2.72
12	24.993	2.92		

* The maximal absolute error in determining P_i is $\Delta P_i \leqslant 4.0 \cdot 10^{-4}\%$.

** The maximal absolute error in determining A_S and A_{Pi} is $\Delta A_S = \Delta A_{Pi} \leqslant 5.0 \cdot 10^{-2}\ m^2g^{-1}$.

tionary phase percentage and the specific surface area for the packings of series I and II. Data are also given for the solid supports used. The data for each series are separated into two sets: the packings for which, according to experience, one expected to have both $P_i < P_0$ and $A_{Pi} > A_0$ fall into the first set, and those having $P_i > P_0$ and $A_{Pi} < A_0$ are included in the second.

Data from the first set were employed to calculate g in eqn. 4 for each series

TABLE II

VALUES OF THE CALCULATED CONSTANTS AND PARAMETERS AND THEIR MAXIMAL ABSOLUTE ERRORS

Symbol	*Dimension*	*Series I*		*Series II*	
		Value	*MAE**	*Value*	*MAE**
g	m^2g^{-1}	$2.864 \cdot 10^2$	$6.8 \cdot 10^1$	$1.639 \cdot 10^2$	$6.7 \cdot 10^1$
c_{p1}	m^2g^{-1}	$1.58871 \cdot 10^1$	$3.9 \cdot 10^{-4}$	$1.68087 \cdot 10^1$	$5.9 \cdot 10^{-4}$
c_{p2}	m^2g^{-1}	-6.8290	$1.2 \cdot 10^{-4}$	$6.027 \cdot 10^{-1}$	$5.5 \cdot 10^{-4}$
c_{p3}	m^2g^{-1}	6.52	$5.0 \cdot 10^{-2}$	9.08	$5.0 \cdot 10^{-2}$
P_0	%	$5.2 \cdot 10^{-1}$	$4.4 \cdot 10^{-2}$	$6.7 \cdot 10^{-1}$	$1.0 \cdot 10^{-1}$
v	–	$8.0 \cdot 10^{-1}$	$1.8 \cdot 10^{-2}$	$8.8 \cdot 10^{-1}$	$1.8 \cdot 10^{-2}$
c_{p0}	m^2g^{-1}	$1.456 \cdot 10^3$	$1.3 \cdot 10^2$	$1.423 \cdot 10^3$	$2.2 \cdot 10^2$
A_0	m^2g^{-1}	6.1	$1.8 \cdot 10^{-1}$	8.5	$2.2 \cdot 10^{-1}$

* MAE = Maximal absolute error of the corresponding quantity.

of packings. For this purpose, a previously described procedure[23] was applied, based on linear regression analysis. Using another calculation procedure[22], c_{p1}, c_{p2} and c_{p3} (eqn. 14) were evaluated from the data for the second set. This permitted the calculation of P_0 from eqn. 15, v from eqn. 16, c_{p0} from eqn. 7 and A_0 from eqn. 3.

All values obtained together with their calculated maximal absolute (MA) errors (see Appendix) are listed in Table II. As can be seen, the accuracy of calculating c_{p1} and c_{p2} is very high in comparison with that of c_{p3}. This discrepancy is obviously responsible for the relatively low accuracy of P_0 and also of the constants v and c_{p0}. From a purely theoretical point of view, the accuracy achieved in evaluating the last-mentioned quantities is certainly poor. However, in the absence of any technique for direct determination, the calculation procedure considered seems at present to be the only approach. This statement also holds for the specific surface area of the complete stationary phase monolayer (A_0). A simple additional calculation shows that for both series of packings the maximal relative (MR) error of calculating A_0 does not exceed 3%, thus ensuring adequate reliability of the values obtained.

The data in Table II were further employed with eqns. 6, 8 and 10 to calculate the interfacial specific surface areas, A_i, A_{Ci} and A_{Bi}, of the packings in both series. In Table III, the corresponding values obtained are listed, together with the MA errors, as functionally dependent on the stationary phase percentage. It can be seen that the MA errors, ΔA_{Ci} and ΔA_i, are equal for each i value within a particular series. They increase in parallel with the increase in the corresponding interfacial areas, A_C and A, thus ensuring comparatively permanent MR errors of calculating these quantities. In series I, for instance, the MR errors of calculating A_C and A do not exceed 10 and 12%, respectively, and in series II they are less than 16 and 18%, respectively. Certainly the values just reported are large compared with the MR errors obtainable with conventional surface area measurements (5–10%). Nevertheless, we may consider them to be acceptable, because it is impossible to determine experimentally the corresponding interfacial areas. Ultimately, the MR errors of calculating A_C and A remain of the same order as those observed on applying the BET technique.

Considering the calculated A_{Bi} values, representing the uncovered (bare) parts of the support surface at different stationary phase loadings ($P_i < P_0$), it is evident from Table III that the MA errors, ΔA_{Bi}, increase with decreasing A_{Bi}. This is as expected, bearing in mind that the A_{Bi} values are a result of subtracting the very close values of the quantities A_S and A_{Ci} (see eqns. 9 and 10). Then, rigorously following the logic of theoretical error analysis, the A_{Bi} values should be considered to be fairly unreliable, especially those for the last three packings in each series. However, it should be also taken into account that the actually admitted absolute errors in calculating all interfacial areas (including A_{Bi}) are a consequence of an algebraic summing of numbers of different signs. In contrast, the MA errors of these quantities are calculated as a sum of absolute (positive) values of the same numbers. Hence, owing to an internal compensation in the algebraic sum itself, the actual errors are usually considerably less than the corresponding theoretically defined MA errors.

The data in the last three columns in Table III illustrate satisfactorily the above consideration. The first of these columns gives the values of the calculated specific surface areas, A_{Pi}^{calc}, of the packings with their MA errors. According to eqn. 11, A_{Pi}^{calc} values involve the unreliably computed A_{Bi} values, thus becoming unreliable themselves. Accordingly, the MA error increases with decreasing A_P, giving rise to

TABLE III

CALCULATED VALUES OF A_C, A, A_B AND A_P AND THEIR MAXIMAL ABSOLUTE ERRORS FOR THE COLUMN PACKINGS IN SERIES I AND II

Series	*Packing No.* *(i)*	P_i *(%)*	$A_{Ci} \pm \Delta A_{Ci}$ (m^2g^{-1})	$A_i \pm \Delta A_i$ (m^2g^{-1})	$A_{Bi} \pm \Delta A_{Bi}$ (m^2g^{-1})	$A_{Pi}^{calc} = A_i + A_{Bi}$ (m^2g^{-1})	A_{Pi}^{exp} (m^2g^{-1})	$A_{Pi}^{exp} - A_{Pi}^{calc}$ (m^2g^{-1})
I	1	0.1488	2.17 ± 0.20	1.74 ± 0.20	5.45 ± 0.25	7.19 ± 0.45	7.17	−0.02
	2	0.2145	3.13 ± 0.29	2.50 ± 0.29	4.49 ± 0.34	6.99 ± 0.63	7.06	0.07
	3	0.3011	4.40 ± 0.41	3.52 ± 0.41	3.22 ± 0.46	6.74 ± 0.87	6.86	0.12
	4	0.4192	6.13 ± 0.57	4.90 ± 0.57	1.49 ± 0.62	6.39 ± 1.19	6.42	0.03
	5	0.5003	7.32 ± 0.67	5.86 ± 0.67	0.30 ± 0.72	6.16 ± 1.39	6.16	0.00
II	1	0.1508	2.15 ± 0.34	1.89 ± 0.34	7.47 ± 0.39	9.36 ± 0.73	9.36	0.00
	2	0.2474	3.53 ± 0.55	3.11 ± 0.55	6.09 ± 0.60	9.20 ± 1.15	9.22	0.02
	3	0.3100	4.43 ± 0.69	3.90 ± 0.69	5.19 ± 0.74	9.09 ± 1.43	9.05	−0.04
	4	0.4619	6.60 ± 1.00	5.81 ± 1.00	3.02 ± 1.05	8.83 ± 2.05	8.89	0.06
	5	0.5020	7.18 ± 1.10	6.32 ± 1.10	2.44 ± 1.15	8.76 ± 2.25	8.77	0.01

an increase in the corresponding MR error from 6 to 23% in series I and from 8 to 26% in series II. Notwithstanding this, the A_{Pi}^{calc} values agree well with the respective experimentally determined A_{Pi}^{exp} values listed in the next column of Table III. The observed agreement is quantitatively confirmed with the values of the absolute deviations ($A_{Pi}^{exp} - A_{Pi}^{calc}$), presented in the last column of Table III. As can be seen, the actual absolute deviations for some packings appear to be 10 or 100 times less than the corresponding calculated MA errors.

In conclusion, it should be mentioned that the above-demonstrated comparison of absolute deviations with MA errors cannot be considered to be a rigorous proof of the accuracy of the computational procedure described. Undoubtedly, however, it shows that although the MA and MR errors in calculating A_{Bi} values are large, the latter must be considered to be acceptable. Despite their greater uncertainty when calculated, the A_{Bi} values, similarly to the other computable interfaces (A_{Ci} and A_i), can be very useful in studying packings for ultra-low-loaded columns. This is enough to justify the application of the present procedure to the evaluation of the interfacial surface areas in such GC columns.

APPENDIX

Following the fundamental concepts of the error theory[25], the absolute error, $|\Delta Q|$, of a quantity Q [being a function of n parameters r_i, *i.e.*, $Q = f(r_1, r_2, \ldots r_n)$] is defined by the approximate expression

$$|\Delta Q| \approx |\mathrm{d}f(r_1, r_2, \ldots, r_n)| = \left|\sum_{i=1}^{n} \frac{\partial f}{\partial r_i} \Delta r_i\right| \tag{A1}$$

where $\mathrm{d}f$ is the total differential of the function and Δr_i are the absolute errors of the parameters.

It is evident from eqn. A1 that all the partial derivatives $\partial f/\partial r_i$, and also the quantities Δr_i, are taken with their algebraic signs. Hence, the actual absolute error $|\Delta Q|$ represents the absolute value of the algebraic sum of the terms $(\partial f/\partial r_i)\Delta r_i$. Because the values of Δr_i are usually known, but not their signs, there is a convention in the theory of calculating the so-called maximal absolute (MA) error ΔQ, defined by the expression

$$\Delta Q = \sum_{i=1}^{n} \left|\frac{\partial f}{\partial r_i}\right| |\Delta r_i| \tag{A2}$$

Comparing eqns. A1 and A2, it becomes evident that

$$\left|\sum_{i=1}^{n} \frac{\partial f}{\partial r_i} \Delta r_i\right| \leqslant \sum_{i=1}^{n} \left|\frac{\partial f}{\partial r_i}\right| |\Delta r_i| \tag{A3}$$

i.e.,

$$|\Delta Q| \leqslant \Delta Q \tag{A4}$$

The inequality eqn. A4 guarantees that the actual absolute error $|\Delta Q|$ of calculating Q does not exceed the MA error $\Delta Q$of the same quantity. Analogously, the maximal relative (MR) error of Q is defined as

$$\delta Q = \sum_{i=1}^{n} \left| \frac{\partial \ln f}{\partial r_i} \right| |\Delta r_i| \tag{A5}$$

In this paper, eqns. A2 and A5 were applied in evaluating the corresponding maximal errors of the quantities listed in Table II. The values obtained give us an idea of how large the errors of the calculated quantities might be. Certainly, however, the actual errors appear most frequently to be considerably lower than the maximal values. Evidence for this statement is given by the data presented in Table III.

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