ANALYSIS OF NORMALIZED — CHARACTERISTIC CURVES AND DETERMINATION OF THE GRANULOMETRIC STATE OF DISSOLVED URANIUM DIOXIDES

F.Melichar[a] and L.Neumann[b]

[a] *Institute of Nuclear Research, 250 68 Prague - Řež and*
[b] *Department of Technology of Nuclear Fuels and Radiochemistry,*
Prague Institute of Chemical Technology, 166 28 Prague 6

Methods are presented for the analysis of normalized — characteristic curves, which make it possible to determine the granulometric composition of a dissolved polydispersion — the cumulative mass distribution of particles — as a function of the relative particle size. If the size of the largest particle in the dissolved polydispersion is known, these methods enable one to determine the dependence of cumulative mass ratios of particles on their absolute sizes. In the inverse method of the geometrical model for determining the granulometric composition of a dissolved polydispersion, the polydispersion is represented by a finite number of monodispersions. An exact analysis of normalized — characteristic equations leads to the Akselrud dissolution model. In contrast to the other two methods, this one makes it possible to determine the granulometric composition for an arbitrary number of particle sizes. The method of granulometric atlas is a method for estimation of the granulometric composition of a dissolved polydisperion and it is based on a comparison of a normalized — characteristic curve for an unknown granulometric composition with an atlas of normalized-characteristic curves for selected granulometric spectra of polydispersions.

In a previous paper[8], methods have been described for evaluating the course of normalized — characteristic curves which determine the granulometric state of a dissolved polydisperse solid. Simultaneously, selected experimental conditions of dissolution have been described and complete physico-chemical characteristics of the dissolved polydispersion of uranium dioxide has been given.

For an actual determination of the granulometric state of a dissolved polydisperse solid, three different methods of the analysis of normalized — characteristic curves of corresponding polydispersions were further proposed and verified: *a*) the method of inverse geometrical model, *b*) the method by the Akselrud model[1] and *c*) the method of granulometric atlas.

The Method of Inverse Geometrical Model

For determining the granulometric composition of a dissolved polydispersion, the principle of the method of geometrical model was employed[2], which is being used in solutions of the dissolution kinetics of polydisperse solids.

The normalized dissolution curve was approximated in our modified model by the equation

$$F(\tau) = \sum_{i=1}^{i=n} m[z_i(0)] \, f[\tau_i(\tau)] \,, \qquad (1)$$

where n is the number of granulometric classes of the geometrical model and $m[z_i(0)]$ is the required relative mass of the particle fraction with the characteristic size $x_i(0)$ at time $t = 0$; this size was expressed through its relative value $z_i(0) = x_i(0)/x_n(0)$ with respect to the largest particle $x_n(0)$ in this selected model. In contrast to this, the original model starts from a constant mass ratio in a class, $m[z_i(0)] = \text{const.}$, and the size of the characteristic particle, $z_i(0)$, must be determined. On evaluating the functional relation $f[\tau_i(\tau)]$, *i.e.* substituting values of the particle age and corresponding dissolved fractions of the polydispersion into this relation, a set of equations can be obtained which on solution yields values of mass ratios corresponding to selected relative sizes of the particles.

If the following condition for the relative mass of the polydispersion is satisfied

$$\sum_{i=1}^{i=n} m[z_i(0)] = 1 \,, \qquad (2)$$

then the granulometric composition of the dissolved polydispersion is described in this inverse geometrical model by the relative particle size $z_1(0) - z_n(0)$, $z_n(0) = 1$ and by the relative mass of model particles $m[z_i(0)]$. An equidistant division of the set of values z_1 and z_n is not necessary. If the size of the largest particle in the model polydispersion or another close to it is known, absolute values of particle sizes may be calculated.

For a selected series of ages of the largest model particle determined from the normalized − characteristic dissolution curve of the corresponding polydispersion, the analytical form of the functional relation $f[\tau_i(\tau)]$ is obtained by finding ages of remaining particles in the selected granulometric model

$$\tau_i(\tau) = \tau/z_i(0) \,. \qquad (3)$$

According to a preliminarily estimated shape of the particles, the function $f[\tau_i(\tau)]$, which represents the dissolved fraction of the corresponding part of the model, is given for spherical particles by the equation

$$f[\tau_i(\tau)] = 1 - (1 - \tau)^3 = \tau^3 - 3\tau^2 + 3\tau \qquad (4)$$

for fibrillar disperse particles whose shape may be approximated by a rod by

$$f[\tau_i(\tau)] = 1 - (1 - \tau)^2 = 2\tau - \tau^2 \qquad (5)$$

and for laminar disperse particles which may be approximated by a slab by

$$f[\tau_i(\tau)] = \tau . \qquad (6)$$

The corresponding analytical functional relation $(4)-(6)$ substituted into Eq. (1) represents for p $[\tau, F(\tau)]$ pairs of values of the normalized dissolution curve a set of equations with n unknowns which may be solved by the least squares method and wherefrom relative masses of individual classes $m[z_i(0)]$ of the granulometric model may be determined which correspond to selected relative sizes of particles in this model.

Computations according to this method were performed an a Gier computer[3] for $p = 28$ and $n = 4$. The analysis was performed with normalized − characteristic dissolution curves of dissolved uranium dioxides corresponding to 1st−3rd-order polynomials. Relative mass ratios of classes $m[z_i(0)]$ were calculated for relative particle sizes $z_1(0) = 0.25$, $z_2(0) = 0.50$, $z_3(0) = 0.75$, $z_4(0) = 1$ and they are represented graphically as cumulative mass ratios of dissolved polydispersions on Fig. 1.

The order of the polynomial used for calculation of the granulometric composition was not highest for which the obtained results possessed still any physical meaning. The values in Table I are mean values calculated from a series of experiments performed in the range of $375-510$ mV and at 5 or 10°C. Absolute values of particle sizes were determined from the value of $x_n(0)$ which was selected as the largest particle in the geometrical model of the polydispersion suggested by microscopical analysis of corresponding oxides.

It obviously follows from the given results that courses of the normalized − characteristic curves described by first to third-order polynomials differ only in the regions of finest particles of the granulometric spectrum. The maximum absolute
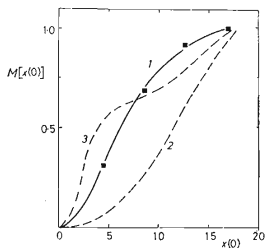

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Granulometric Analysis of J−2 UO_2 by the Inverse Geometrical Model (1), Microscopical Analysis, (2), Sedimentation Analysis (3) $x(0)$ in μm.

deviation in the cumulative mass ratio of the fraction with the size $z_1(0) = 0.25$ is 9% for a first to third-order polynomial, but it amounts to only 3% for $z_2(0) = 0.50$. Simultaneously, the number of solutions which possess some physical meaning decreases with increasing order of the polynomial. Except for the beginning and tail of the granulometric spectrum, this method yields rather high values of cumulative mass ratios in comparison with results of the microscopical analysis. The resulting granulometric spectrum approximates therefore better the primary dispersion than the secondary one determined by the microscopical analysis.

A comparison of results of this method with the sedimentation analysis shows that the former yields higher values of cumulative mass fractions in the range of the relative particle size $z_i(0) \sim 0.40-1.00$, whereas at the beginning of the granulometric spectrum the reverse is true. Most probably this is due to a higher degree of separation of particle agglomerates during the sedimentation analysis than in the case of the dissolution process.

Simultaneously, the possibility was examined of increasing the number of selected granulometric classes to $n = 6-10$. In this case, however, results of the analysis of normalized curves possessed no physical meaning due to negative values of $m[z_i(0)]$.

TABLE I

Granulometric Composition of Uranium Dioxides Determined by the Inverse Geometrical Model

UO$_2$	$x_i(0),/\mu m$				RRS-function[a]	
	$M[x_i(0)]$				x', μm	w
J-2	4·31	8·63	12·94	17·25	7·7	1·85
	0·3135	0·6729	0·9017	0·9970		
J-5	4·18	8·35	12·53	16·70	7·5	2·0
	0·3570	0·6491	0·9165	0·9982		
J-2-7,5[b]	4·31	8·63	12·94	17·25	8·0	1·94
	0·3368	0·6641	0·9090	0·9984		
J-2-15[b]	4·31	8·63	12·94	17·25	8·0	1·44
	0·3486	0·6529	0·9159	0·9976		
J-2-30[b]	4·31	8·63	12·94	17·253	8·0	1·94
	0·2941	0·6926	0·8918	0·9984		
J-18	4·23	8·46	12·69	17·92	7·6	1·98
	0·3098	0·6877	0·9064	0·9931		

[a] Rosin–Rammler–Sperlinger function. [b] Thermally treated UO$_2$ (cf. the Experimental Part in the previous communication).

The Method Using the Akselrud Model

This method is based on determining parameters in the mass distribution function of the dissolved polydispersion which is included implicitly in the normalized — characteristic equation. It may be derived from the Akselrud model[1], in which, however, the dimensionless time of dissolution τ_A differs from the particle age τ used in our work. These two quantities are related through

$$\tau = \tau_A \, \overline{x(0)}/x_n(0) .\tag{7}$$

After introducing τ, the undissolved fraction of the polydispersion is expressed by[2]:

$$1 - F(\tau) = \int_{x_m(0).\tau}^{x_m(0)} \left(1 - \tau \, \frac{x_m(0)}{x(0)} \right)^3 m[x(0)] \, dx(0) .\tag{8}$$

After further substitution, rearrangement, and differentiation according to the method proposed by Akselrud, the following expression was derived for the 4th-order derivative of the normalized — characteristic curve (equation):

$$d^4[1 - F(\tau)]/d\tau^4 = 6\Phi(\tau)/\tau^3 ,\tag{9}$$

in which the function $\Phi(\tau)$ represents the mass distribution function of particles with respect to their sizes and expressed in relative units of the particle age.

If the size of the largest particle in the polydispersion, $x_m(0)$, or of some other close to it is known, the absolute size of the particles may be found from the relation

$$x_i(0) = x_m(0) \left(1 - \tau_i \right)\tag{10}$$

and the cumulative ratios of the polydispersion are given by

$$M[x_i(0)] = \Big[\sum_{i=1}^{i=p} \Phi(\tau_i) \Big] \Big[\sum_{i=1}^{n} \Phi(\tau_i) \Big]^{-1} .\tag{11}$$

The absolute size $x_i(0)$ was again determined on the assumption that the largest particle in the polydispersion $x_m(0)$ is that with the characteristic size $x_n(0)$, *i.e.* the largest particle of the granulometric model according to the microscopical analysis.

The differentiation of the normalized — characteristic equation $[1 - F(\tau)]$ approximated by a first to third-order polynomial was performed on a Gier computer[4] for 28 selected values of τ so that the resulting cumulative ratios may cover the entire granulometric spectrum of the polydispersion.

The calculation of the granulometric composition from the normalized — characteristic equation approximated by a polynomial was performed for a highest order

of the polynomial whose 4th-order derivative would exhibit a smooth course, *i.e.* which would not reflect the experimental error in the measured quantity $F(\tau)$. The resulting granulometric spectrum of the sample was found by analyzing the normalized — characteristic curve determined at different experimental conditions.

Table II gives only mean values of quartiles and mean median diameters of remaining samples. The whole resulting granulometric spectrum is outlined in Fig. 2.

The granulometric composition of uranium dioxides determined by this method differs considerably from that provided by the microscopical analysis in the range

TABLE II

Granulometric Composition of Uranium Dioxides Determined by the Akselrud Model

UO$_2$	Quartiles and median diameters, μm			RRS-function[a]	
	$x_{25,3}$	$x_{50,3}$	$x_{75,3}$	x', μm	w
J-2	7·90	8·89	12·19	11·13	3·97
J-5	8·12	10·35	12·36	11·13	3·80
J-2-7·5	8·14	9·95	12·27	11·15	3·63
J-2-15	8·17	9·79	12·45	11·50	3·59
J-2-30	8·00	9·69	11·87	10·97	3·54
J-18	7·96	9·45	11·88	10·76	3·57

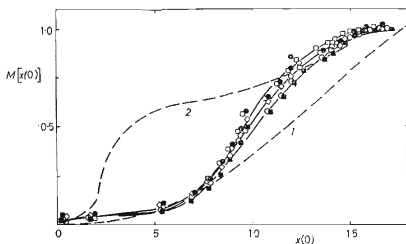[a] Rosin–Rammler–Sperlinger function.

FIG. 2

Granulometric Analysis of J—2 UO$_2$ by the Akselrud Model at 5°C
○ 420, ■ 450, ◊ 470, □ 490, ● 510 mV. *1* microscopical, *2* sedimentation analysis; $x(0)$ in μm.

of the relative particle sizes $z_i = 0.30 - 1.00$, where the cumulative mass ratios are higher than in the microscopical method. The resulting granulometric spectra differ from those found by the sedimentation analysis mainly in the range of the relative particle sizes $z_i = 0 - 0.75$; in this interval, the values of the cumulative mass ratios determined from the dissolution data are clearly lower than those obtained from the sedimentation analysis.

Differences between values of cumulative mass ratios determined by this method and by the other ones are obviously affected by the accuracy of the computed derivative $d[1 - F(\tau)]/d\tau$, which decreases with increasing order of the derivative in the vicinity of 0 and 1. This method may be therefore used for such polydispersions whose experimentally determined normalized − characteristic curve displays a not too steep course. In that case values of the derivatives in the initial and final intervals of τ do not reach extreme values, which corresponds to the granulometric spectrum with a sufficiently high degree of dispersity.

The Method of the Granulometric Atlas

In this method, experimentally determined dissolution curves are compared with a set of standard normalized − characteristic curves computed by the method of the geometrical model for selected granulometric spectra.

Granulometric standards of the polydispersion were found from four pairs of relative particle sizes $z_1(0) - z_4(0)$ and corresponding mass ratios $m[z_1(0)] - m[z_4(0)]$. Relative mass ratios were determined for 9 combinations A − I by selecting series of values 0.05; 0.10; 0.15; 0.20; 0.26; 0.30 for $m[z_1(0)]$ and $m[z_2(0)]$, 0.10; 0.15; 0.25; 0.26; 0.30; 0.40; 0.50 for $m[z_3(0)]$ and 0.10; 0.20; 0.25; 0.55; 0.70; 0.85 for $m[z_4(0)]$. The sum of selected relative mass ratios in the corresponding combination satisfied always the condition

$$\sum_{i=1}^{i=4} m[z_i(0)] = 1 .$$

A total of 78 combinations of numbers 0.1; 0.2; 0.34 ... 1.0 was selected for the relative particle size so that the relation $z_4(0) = 1 > z_3(0) > z_2(0) > z_1(0)$ may always hold. This gave rise to a set of granulometric spectra − the granulometric atlas − in which the individual spectra were denoted by combinations 1A − 78I and for which the corresponding normalized − characteristic curves were also found. The total amount of selected values of the particle age employed for determining the normalized − characteristic equations was 45. Values of $F(\tau_i)$ for $i \in \langle 1.45 \rangle$ were tabulated by finding and noting, for a given value of τ_i, the corresponding compositions of the polydispersion whose dissolved fractions were in the selected interval of values $F''(\tau_i) - F'(\tau_i) = 0.005$.

With the help of this "key", a suitable granulometric composition of the polydispersion was assigned to the experimentally determined normalized − characteristic curve so that the corresponding tabulated normalized curve may agree with the experimental one in a maximum number of points with coordinates τ, $F(\tau)$.

As a criterion of agreement between these curves, the "relative number of coinciding points" of compared curves was selected, which was defined as the ratio of the number of coinciding points and the total number p of pairs $[\tau, F(\tau)]$ of the experimental normalized − characteristic curve $(p = 28)$.

As a further criterion B of identity of the tabulated and experimental normalized − characteristic curves, the mean quadratic deviation g was chosen, which is equal to

$$g = \Big\{ \sum_{j=1}^{j=p} \big[F(\tau_j)_{exp} - F(\tau_j)_{tab} \big]^2 \Big\}^{1/2} \big[p(p-1) \big]^{-1/2} . \qquad (12)$$

This method was verified for normalized − characteristic curves of dissolved uranium dioxides (Table III). The results of this method were evaluated on a Gier computer[5] by comparing the corresponding experimental normalized curve with the atlas of tabulated normalized curves. The resulting granulometric composition of the given polydispersion was determined by evaluating all normalized − characteristic curves obtained at different experimental conditions (temperature, redox potential). It represents a granulometric spectrum which, for a given polynomial order of the normalized − characteristic curves and given accuracy, may be assigned with the highest probability (in Tables denoted as "Probability") to the corresponding polydispersion.

TABLE III

Granulometric Composition of Uranium Dioxides Determined by the "Atlas Method" (with the highest probability)

UO_2	crit/%[a]		$x_i(0)$, μm/$M[x_i(0)]$			
J-2	A/50	3·4/0·20	8·6/0·50	10·3/0·90	17·2/1·00
J-2	B/33	5·2/0·25	6·9/0·50	8·6/0·75	17·2/1·00
J-5	A/40	3·4/0·20	5·0/0·50	10·0/0·80	16·7/1·00
J-5	B/40	3·4/0·20	5·0/0·50	11·7/0·80	16·7/1·00
J-18	A/66·6	8·4/0·20	8·5/0·50	10·1/0·90	16·9/1·00
J-18	B/66·6	5·0/0·30	6·8/0·60	11·8/0·90	16·9/1·00

[a] Criterion A or B for the given probability level.

The magnitude of particles of the selected granulometric spectrum is again in absolute particle sizes, where the particle with the size $x_m(0)$ was taken as the largest particle in the geometrical model $x_n(0)$.
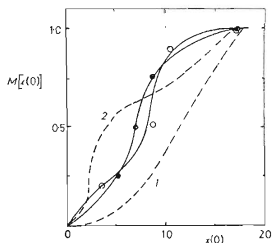

FIG. 3

Granulometric Analysis of $J-2\ UO_2$ by the Granulometric Atlas Method According to the Criterion A — ● and B — ○

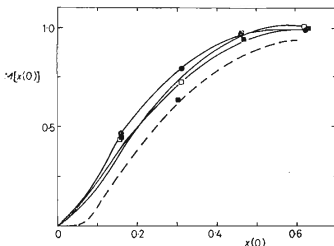*1* Microscopical, *2* sedimentation analysis; $x(0)$ in μm.

FIG. 4

Granulometric Analysis of Kieserite by the Inverse Geometrical Model

Dashed curve — mesh analysis, ■ ($u = 2$) and □ ($u = 3$) — dissolution analysis, ● original granulometry; $x(0)$ in μm.
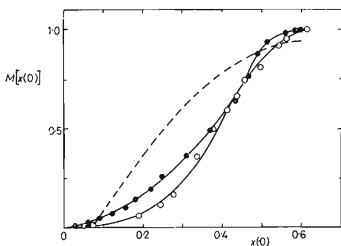

FIG. 5

Granulometric Analysis of Kieserite by the Akselrud Model

Dashed curve — mesh analysis, ○ dissolution analysis ($u = 2$), ● original granulometry; $x(0)$ in μm.
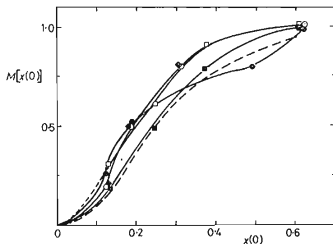

FIG. 6

Granulometric Analysis of Kieserite by the Granulometric Atlas Method

Dashed curve — mesh analysis, dissolution data: ○ $u = 2$, crit. A, □ $u = 3$, crit. A, ● $u = 2$, crit. B, ■ $u = 3$, crit. B; ♦ original granulometry; $x(0)$ in μm.

It obviously follows from results obtained by this method (Fig. 3) of analysis of normalized — characteristic curves that it does not yield quite unambiguous results for all experimental data. The reason is in the too finely spaced "granulometric atlas" of normalized curves, which, due to the error in the experimental normalized curve, determines the required granulometric composition with a low probability. Simultaneously, the probability that the determination of the granulometric type of the dissolved polydispersion is unambiguous decreases with increasing order of the polynomial in the normalized — characteristic curve. The resulting granulometric spectra resemble closely those obtained from the granulometric analysis by the inverse geometrical model. We may again say that cumulative ratios of particle masses determined by this method are, in comparison with results of the microscopical analysis, higher in the whole interval of particle sizes except for its beginning and end. This method yields values of cumulative mass ratios which are lower than those provided by the sedimentation analysis for particles smaller than approximately 8 μm, whereas for larger particles this relation is reverse.

Further Verification for Particle Sizes up to 0·1 mm

The proposed methods were further verified on a kieserite polydispersion whose normalized — characteristic curves were determined from original experimental data[6].

In determining the normalized — characteristic equations, the basic condition for the calculation of the total dissolution time, namely that the linear rate of dissolution is constant during the dissolution process, was satisfied.

The results of the granulometric analyses of kieserite by the inverse geometrical model, by the Akselrud model and by the granulometric atlas method are illustrated on Figs 4—6. For determining the granulometric state of the dissolved polydispersion, the normalized — characteristic equation[6,7] obtained from the original granulometric analysis was employed in the form

$$1 - F(\tau) = Q_0 - Q_1 \exp\left(-q_1\tau\right), \tag{13}$$

with q, Q being constants.

The results of the granulometric analysis also confirmed the applicability of this method to polydispersions with particle size up to 0·7 mm, even though for the comparison of the resulting granulometric spectra only results of the mesh analysis were available. In this case the Akselrud method again yields values of the cumulative mass ratios of corresponding particle sizes which are lower than those obtained from the inverse geometrical or granulometric atlas methods except for the beginning and end of the granulometric spectrum.

In the inverse geometrical and granulometric atlas methods, a higher degree of deagglomeration of particles is observed than it would correspond to the granulometric spectrum found by the mesh analysis.

The tested methods for determining the granulometric composition of a dissolved polydispersion may be thus considered as a further extension of existing methods of granulometric analysis. They are suitable for particle sizes in the range $1-700\ \mu m$. They may be applied to materials soluble in different solvents and whose soluble component can be determined easily by an analytical method.

In technological practice they might be employed if other methods of granulometric analysis of the polydispersion, *e.g.* in the case of a polydispersion from the hydrometalurgical process, could not be used. The main advantage of these methods is in the fact that they can produce the distribution of the dissolved component of the polydispersion.

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