FACTORS influencing the response of the apparatus for emanation thermal analysis are discussed and the ETA computed curves accounting for the various factors are demonstrated. The influence of inertia of the ETA apparatus is demonstrated on model short time pulses as well as on ETA curves obtained during thermally stimulated inert gas release. Examples of the distortion of ETA curves when using different inert gases are given.

A method for the reconstruction of the true ETA curve, based on the determination of the apparatus response to a "one second model pulse" is suggested. This method has other applications and may be used not only for ETA but also, for example, for evolved gas analysis curves. A practical example of the reconstruction of an ETA curve is given which was obtained with polypropylene foil at the following conditions: heating rate 4°C min⁻¹, the temperature range from -196 to +400°C.
curves 2-5 in Fig. 1. Curve 2 represents the case of a simple time delay resulting in a shift of the pulse in time $t^*$. The true ETA curve can be established by a simple subtraction $(t^* - t_0)$.

When, during the transport of the inert gas pulse from the sample to the detector, some disturbing phenomenon, such as diffusion of the radioactive inert gas into the carrier gas, mixing effects or inert gas adsorption on the walls takes place, the resulting ETA effects are shifted in time and also become asymmetric (Fig. 1, curve 3). When the detector of the radioactive inert gas is very close to the sample cell the shift of the pulse may not be observed and the decreasing slope of the response of the apparatus represents an exponential-like curve (curve 4, Fig. 1). The form of the exponential-like curve depends mainly on the integrating effect of the radioactivity detector.

Fig. 1. Various types of response curves corresponding to the model pulse of inert gas release ("one second pulse"): curve 1-the "one second pulse" of the radioactive inert gas at the input of the measuring system, in time $t_0$; curve 2-the distortion of the apparatus response in time $t^*$ by a simple time shift; curve 3-the distortion of the response caused by mixing effects, adsorption and diffusion of the measured gas in the carrier gas pipe-line; curve 4-the distortion of the response caused only by the integrating effect of the measuring chamber; curve 5-the apparatus response as in curve 4 plus the effect of the "active deposit"; $W_{1/2}$ is the width of the peak-apparatus response to a "one second pulse" measured at the half-height of the peak.

Generally, the influence of the ETA apparatus can be characterized by a time constant $\tau_s$ ($s^{-1}$) which is

$$1/\tau_s = \sum_{i=1}^{n} 1/\tau_i$$

(1)

where $\tau_i$ are the time constants corresponding to the individual elements or factors causing the inertia of the apparatus.

Supposing a satisfactory mixing of the inert gas atoms in the measuring chamber, the number $N(t)$ of the inert gas atoms present in the chamber can be expressed by eqn. (2)

$$dN(t)/dt = F(t) - ZN(t)$$

(2)

where $N(t)$ is the number of inert gas atoms in the measuring chamber, at time $t$, $F(t)$ is the velocity of the inert gas input into the measuring chamber, $Z$ is the total velocity of the inert gas output from the measuring chamber ($Z = \delta V$, $\delta$ being the flow-rate of the carrier gas and $V$ the volume of the measuring chamber).

The solution of eqn. (2) can be expressed by the following formula [4]

$$N(t) = N_0 \exp[-Z(t)] + \int_0^t \exp[-Z(t-\tau)]F(\tau)d\tau$$

(3)

The volume of the measuring chamber is usually chosen by considering the highest attainable sensitivity of the detector. When radon isotopes are measured, optimal conditions for the measuring of alpha-radioactivity of Rn-isotopes are fulfilled when the measuring chamber has the form of a hemisphere of radius 2.5 cm, which is the path of radon alpha-particles in air. However, if inertia is considered the resulting volume of the measuring chamber causes a significant distortion of the inert
gas pulses, and a compromise is usually made to fulfil both conditions for optimum sensitivity and minimum distortion of the ETA curve. Moreover, in the case of the short-lived radionuclide \(^{220}\text{Rn}\) (\(T_{1/2} = 55.6\) s), the radioactive decay of the inert gas affects the efficiency of the detector. The dependence of the total radioactivity of the inert gas measured on the carrier gas flow-rate is demonstrated in Fig. 2(a). The width of the inert gas pulses measured is also significantly influenced by the ratio \(Z\). Supposing that the volume \(V\) of the measuring chamber is constant, then the width of the response to a short model pulse of inert gas is influenced by the carrier gas flow-rate (Fig. 2(b)).

Apart from the inertia of the measuring chamber, there is also inertia of the electronic measuring system, i.e. the counts-rate meter, the printer, plotter or the recorder. However, the time constants \(\tau\) of these parts of the ETA apparatus are much smaller than the time constant of the measuring chamber.

When radon isotopes, e.g. \(^{222}\text{Rn}\), are used for measurement, another factor influencing the form of the ETA curves appears, i.e. the existence of the "active deposit" adsorbed on the walls of the detectors (including long-lived radioisotopes—the products of the radioactive decay of radon \(^{222}\text{Rn}\)). The alpha-radioactivity of these radionuclides is measured simultaneously with the alpha-radioactivity of the inert gas atoms, leading to distortion of the short time pulse (Fig. 1, curve 5). The distorting effect of the active deposit on the form of the ETA curve cannot be resolved analytically.

INFLUENCE OF THE INERTIA OF THE APPARATUS ON THE FORM OF THE ETA CURVES

A. As the first example the release of radioactive inert gas introduced by the adsorption on the surface of a solid sample will be considered. In this case only desorption of the inert gas from the surface takes place during heating of the sample.

The dependence of the diffusion flow \(J(t)\) of the inert gas during the course of heating at a constant rate can be described [5] by eqn. (4)

\[
J(t) = -\frac{\partial c}{\partial t} = c_0 k_0 \exp[-E/RT] \exp\left\{- \frac{k_0}{\kappa} \int_0^{T_o + \kappa} \exp[-E/RT] dt \right\}
\]

where \(c_0\) is the starting concentration of the inert gas in the sample, \(k_0\) is the frequency factor of the adsorption, \(E\) is the activation energy of the inert gas desorption, \(T_o\) is the starting temperature of the sample heating, and \(\kappa\) is the heating rate.

Figure 3 demonstrates the influence of the inertia of the apparatus on the form of the ETA curve for the case of the mechanism of thermally activated inert gas release. The distorting effect of the "active deposit" of \(^{222}\text{Rn}\) decay production on the ETA curve is shown in Fig. 3(a); Fig. 3(b) shows the influence of the parameter \(Z\) on the form of the ETA curves (for \(^{85}\text{Kr}\), which does not yield an active deposit).
The inertia of the apparatus can be characterized by the width \( (W_{1/2}) \) of the response of the very short pulse measured at the half-height of the peak. In Fig. 3(b), curve 1 represents the true, non-disturbed ETA curve, and curves 2 and 3 the disturbed ETA curves corresponding to the widths \( W_{1/2} = 30 \) and \( 60 \) s, respectively. In Fig. 3(c) the same influence of the form of the ETA curves on the Z value for \(^{222}\text{Rn}\), including the effect of the "active deposit", is observed. The normalization of the ETA curves in Figs. 3(b) and 3(c) to the peak height makes direct comparison of the effects possible. As follows from Fig. 3(b), there exists a substantial distortion of the ETA curves when \(^{222}\text{Rn}\) is used, which can be diminished by the choice of a suitable (optimal) value of Z. However, the effect of the "active deposit" cannot be eliminated in this way. The distorting effect of the active deposit does not appear when suitable radionuclides (which decay into non-radioactive nuclides, e.g. \(^{85}\text{Kr}\)) are used, and the effect can be diminished by the application of suitable filters.

B. Another example of ETA curve distortion occurs when radon \(^{220}\text{Rn}\) formed by the radioactive decay of \(^{228}\text{Th}\) and \(^{224}\text{Ra}\) used for labelling the solids is released.

The time dependence of the diffusion flow can be described by eqn. 5 [6]

\[
\frac{J(t)}{C_1 \lambda_1} = \frac{(3/r_0)(D_{df}/\lambda_2)^{1/2}}{\lambda_1 \lambda_2} (5)
\]

where \( C_1 \) is the concentration of the \(^{224}\text{Ra}\) parent isotope for radon, \( \lambda_1 \) is the decay constant of \(^{224}\text{Ra}\), \( r_0 \) is the radius of the grain, \( X_2 \) is the decay constant of \(^{220}\text{Rn}\), \( D_{df} \) is the effective coefficient of radon diffusion; \( D_{df} = D_0 \exp(-E_D/RT) \); \( E_D, D_0 \) are the activation energy and pre-exponential factor of the inert gas diffusion, respectively, \( T \) is the temperature increasing with a constant rate \( (T = T_o + \kappa t) \), and \( \kappa \) is the heating rate.

In our example the diffusion of the inert gas \((^{220}\text{Rn})\) in two independent channels, e.g. via vacancies and interstitials, is assumed. Moreover, we assume that exchange of the inert gas atoms between channels can take place by the so-called "dissociative diffusion mechanism" [7,8]. This mechanism can be formally described by the kinetics of a reaction of the 1st order. In this case, the effective coefficient of the inert gas diffusion, \( D_{ef} \), may be expressed by eqn. (6)

\[
D_{ef} = \frac{(D_1 + KD_2)}{(1 + K)} = \frac{D_{1,0} \exp(-E_1/RT) + K_0 D_{2,0} \exp(-E_2 - E_K/RT)}{1 + K_0 \exp(E_K/RT)} (6)
\]

where \( D_1 \) and \( D_2 \) are the coefficients of the inert gas diffusion in the 1st and 2nd channels, respectively, \( D_{1,0}, D_{2,0} \); \( E_1 \) and \( E_2 \) are the respective pre-exponential factors and activation energies, and \( K \) is the equilibrium constant of the inert gas exchange between the two channels.

In the case of dissociative diffusion of the inert gas in the solid a peak on the ETA curve appears during the heating at constant heating rate. Figure 4 shows the computed ETA curves as influenced by the inertia of the apparatus (the value Z being characterized by the width \( W_{1/2} \) of the response to a "one second pulse", measured at the half-height of the response). It follows from Fig. 4, that the increase of the inertia of the apparatus leads to the distortion of the ETA effect mainly in the high temperature range. For example the shift of the maximum of an ETA effect is proportional to the half-peak width \( W_{1/2} \) of the response, e.g. the 30 s width of the response (curve 2) corresponds to a 30 s shift of the ETA maximum, which represents a shift by 2.5°C when a heating rate of 5°C min\(^{-1}\) is used in the ETA measurement. From Fig. 4 it follows that the distortion becomes more important for larger widths of the response as well as for higher heating rates. Consequently, when the response width does not exceed 30-60 s, heating rates up to 5°C min\(^{-1}\) can be used and the shift of ETA peaks towards higher temperatures may be neglected.
POSSIBILITY OF THE RECONSTRUCTION OF THE TRUE FORM OF THE ETA CURVE

In a previous report [9] the dependence on the parameter Z of the height, width and the position of the symmetric maximum of the "Gauss-like" form were calculated. These dependences can be used to find the true values for the parameters of the ETA effects. However, this is not sufficient for reconstruction of the whole form of the ETA curve. Moreover, this method necessitates knowledge of the volume of the measuring chamber (or the detector itself) and the distribution of the inert gas in the solid sample but does not take into account the processes in the sample cell, in the pipe-lines, in the registration system, etc.

We suggest a more universal method for the reconstruction of the true ETA curve enabling even systematic errors of the measurements, the effect of the "active deposit", etc. to be taken into account. This method is based on the determination of the apparatus response to a short model inert gas pulse. This experimentally determined response curve serves to determine the so-called apparatus function $K(t)$ [10]. Reconstruction of the ETA curve can be achieved by the solution of the Fredholm integral equation of the 1st order.
\[ f(t) = \int K(t-\tau)\varphi(\tau)d\tau \quad (7) \]

where \( f(t) \) is the function (curve) experimentally obtained, \( \varphi(t) \) is the true ETA curve to be found, \( K(t-\tau) \) is the nucleus of the Fredholm equation [10].

When the function \( f(t) \) is fully known from experiment, the solution of eqn. (7) with respect to the function \( \varphi(t) \) represents the "inverse task". It should be noted that a solution of the Fredholm equation of the 1st order cannot be found for each function \( f(t) \). Moreover, because of statistical errors of the measurements it is not possible to find a solution of eqn. (7); a very small variation of the experimental data can cause a considerable variation of function \( \varphi(t) \) [11]. This so-called incorrectly formulated task can be solved only by introducing a condition that eqn. (7) should be taken into account only within the accuracy of the experimental measurements. The approximate solution found under this condition is called the "regulated solution".

The calculations of eqn. (7) were carried out using the computer BESM-6 (USSR) and the solution to the equation was found by the application of the method of one parameter regulation by Tikhonov [11]. A preliminary mathematical experiment was carried out in order to find the conditions of the reconstruction.

PRACTICAL EXAMPLE OF EXPERIMENTAL ETA CURVE RECONSTRUCTION

First, the systematic errors of the apparatus were assessed: a "one second pulse" of radon \(^{222}\)Rn was introduced into the stabilized carrier gas flow in the ETA apparatus and the response function was registered by the measuring system of the apparatus. The form of the response curve is shown in Fig. 1. Secondly, from the results obtained the quadratic matrix \( K(t) \) was formed, every line of the matrix representing the response of the apparatus to the "one second pulse". The matrix \( f(t) \) has the form of one column, being composed of experimental data obtained from the ETA curve registered in the time intervals \( \Delta t = 60 \) s. The matrix \( \varphi(t) \) to be found is a matrix of one column composed of the data of the reconstructed ETA curve.

Fig. 4. Results of the mathematical modelling showing the distortion of the ETA curves for the case of \(^{220}\)Rn release controlled by the mechanism of dissociative diffusion: curve 1-true/non-distorted ETA curve; curves 2, 3 and 4-the responses to curve 1 which can be obtained by an apparatus whose inertia is characterized by the value \( W_{1/2} = 30, 60 \) and \( 90 \) s, respectively; curves 2', 3' and 4'-conditions as in Fig. 3(c). The curves 1-4 were normalized with respect to the starting point of the curves.

Fig. 5. The reconstruction of the experimentally obtained ETA curve of a polypropylene foil in the temperature range -196 to +400°C (heating rate 4°C min\(^{-1}\)) which was labelled with \(^{222}\)Rn: curve 1-the apparatus response to the "one second pulse"; curve 2-the experimentally obtained ETA curve; curve 3-the reconstructed ETA curve.
Figure 5 shows the results of the reconstruction of the ETA curve of a polypropylene film of thickness $\sim 100 \mu m$, labelled by radon $^{222}\text{Rn}$ by a diffusion technique. The ETA curve was measured during heating of the labelled sample at a constant rate of $4^\circ \text{C min}^{-1}$, over the temperature range — 196 to 400$^\circ \text{C}$. As can be seen from curve 1, Fig. 5 which shows apparatus response to the "one second pulse", the apparatus may cause a significant distortion of the ETA curve, in this case mainly due to the rather high value of the time constant $\tau$ of the counts-rate meter. The experimentally obtained ETA curve (Fig. 5, curve 2) exhibits a symmetrical form which could be ascribed to the inert gas release obeying 1st order release kinetics with a spectrum of activation energies.

However, as follows from the reconstructed curve (Fig. 5, curve 3) the true form of the ETA curve is characterized by two effects, the first corresponding to the gas release controlled by 1st order kinetics with a single value for activation energy of 84 kJ mol$^{-1}$. The second effect corresponds to the diffusion release with an activation energy of 126 kJ mol$^{-1}$. On the basis of the reconstructed (true) ETA curve it can be stated that in the polypropylene foil sample, which has been prepared under a pressure of 100 atmospheres, radon atoms are situated in both amorphous and crystalline phases. These phases are characterized by different diffusion resistances, 84 and 126 kJ mol$^{-1}$ respectively. From the amount of inert gas release in the respective release processes it followed that in the amorphous phase about 80% of Rn, and in the crystalline phase about 20% of radon can be found.

CONCLUSION

The reconstruction of the true form of the ETA curves gives the possibility of a more precise evaluation of the experimental data. The suggested method of the reconstruction enabled us to obtain the corrected ETA curve and to reduce all types of distortion of the curves including the "active deposit effect". The method can be used in any gas flow or dynamic vacuum arrangement of the ETA apparatus. Moreover, it can be used for ETA curves but also for example for curves of Evolved Gas Analysis when gaseous products of chemical reactions are detected and analyzed.

However, it should be pointed out that the reconstruction of the true ETA (EGA) curve is a complex task and that the apparatus and experimental conditions should be chosen to ensure that a large distortion of the experimental curves does not occur. With commercial apparatus for ETA by NETZSCH (FRG) where the volume of the measuring chamber is 10 cm$^3$, and the distance of the measuring chamber from the sample is 20 cm, this condition is fulfilled when the flow-rate of the barrier gas is approx. 50 cm$^3$ min$^{-1}$ and the heating rate is lower than 5$^\circ \text{C min}^{-1}$.

ACKNOWLEDGEMENT

The authors would like to thank Mrs. F. Hrdlickova, Nuclear Research Institute, Rez, for careful typing of the manuscript, and Mrs. J. Halkova, Prague, for drawings.

REFERENCES

5  G. Carter, Vacuum, 12 (1962) 245.
9  A.M. Pankov and V.A. Ruban, Radiokhimiya, 8 (1966) 232.