

Special Review

EMANATION THERMAL ANALYSIS: THE PRESENT STATE AND PERSPECTIVES

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The principles of emanation thermal analysis, a method by means of which information about solid state and its changes are given. The method is based on measuring the release of radioactive inert gases at various temperatures from solids previously labelled. The techniques used for labelling the samples are reviewed and the apparatus is described. Examples of recent application of emanation thermal analysis in solid state chemistry, materials science and technology, corrosion studies, heterogeneous catalysis as well as in analytical chemistry are given. The perspectives of the method are outlined.

Emanation thermal analysis [1] is the method by means of which information about the solid state and its changes is obtained on the basis of inert gas release from solids, measured at various temperatures. This definition has been approved [2] by the International Confederation for Thermal Analysis.

Inert gas atoms are used as trace indicators of the solid state and its changes. The inert gases do not react with the solid, in which they were incorporated in trace amounts before the measurement. The inert gas release measured is controlled by physico-chemical processes in the solid studied. Structural changes, interaction of the solid sample with the surrounding medium, or the establishing of chemical equilibrium of reactions which take place in solids, bring about microscopical processes followed by inert gas release.

Labelling of solids

In most cases, the solids investigated by emanation thermal analysis do not contain inert gas, and therefore it is necessary to label the solid with inert gas to allow the subsequent measurement of gas release from the sample.

Different inert gases can be incorporated into solids by various methods [1]. The classical emanation technique uses natural radioactive gases (radon isotopes emanation). In this technique, during preparation of the solid the inert gas is usually incorporated by coprecipitation of trace amounts (e.g. 10^4 counts \cdot s $^{-1}$ /g of substance) of the parent isotope of the gas (e.g. ^{228}Th and/or ^{224}Ra) from a solution. When it is impossible to introduce the parent isotope into the solid in the course of its preparation, the sample to be measured is impregnated with a

solution containing ^{228}Th and ^{224}Ra nuclides. The inert radioactive gas is formed in the substance as a consequence of radioactive disintegration, $^{228}\text{Th} \xrightarrow{\alpha} ^{224}\text{Ra} \xrightarrow{\alpha} ^{220}\text{Rn} \xrightarrow{\alpha}$, and does not react with the substance.

Other methods of sample labelling are based on the introduction of the gas itself into solids (i.e. without its parent isotope). The following techniques are used:

1. *Recoil energy of nuclear reactions:*

Alpha decay (e.g. $^{226}\text{Ra} \xrightarrow{\alpha} ^{222}\text{Rn}$)

Beta decay (e.g. $^{83}\text{Se} \xrightarrow{-\beta} ^{83}\text{Br} \xrightarrow{-\beta} ^{83}\text{Kr}$

$^{133}\text{Te} \xrightarrow{-\beta} ^{133}\text{I} \xrightarrow{-\beta} ^{133}\text{Xe}$)

The energy of inert gas atoms produced by disintegration can be used to incorporate them into substances; parent isotopes are usually adsorbed on the sample surface.

Neutron-activated reactions ((n, α) , (n, p) , (n, γ) , $(n, \text{fission})$)

Solids are irradiated by neutrons in a nuclear reactor, and the inert gases Ar, Kr and Xe are produced, as shown in Table 1. This technique can be used, for example, for labelling alkaline or alkaline-earth substances. The nuclear fission process has been used to incorporate nuclear fission products ^{133}Xe and ^{85}Kr into solids.

2. *Accelerated inert gas ion introduction:* The result is the volume or surface labelling of the solid concerned, which is dependent on the energy of ion bombardment and the inert gas used.

3. *Diffusion process at a higher temperature and pressure in an inert gas atmosphere:* ^{85}Kr is mostly used for this purpose and is incorporated into the crystalline lattice. Over 200 different solids (elements, alloys, and inorganic and organic compounds) have been "kryptonated" at elevated temperature and ^{85}Kr pressure.

4. *Crystallization of solids from melts or sublimation of solids in an atmosphere of radioactive gas:* Both these techniques have mainly been used for the preparation of labelled solids which form clathrates with inert gases, e.g. quinone, hydroquinone, β -naphthol, etc.

All of these techniques for labelling solids with inert radioactive gases yield products in which the incorporated inert gas is more or less stable. Inert gas atoms are situated in substituting or interstitial positions in the lattice. The method used for labelling is determined by the character of the solid and the purpose of the subsequent inert gas release measurement.

Inert gas release from solids

Inert gas incorporated into a solid can be liberated as a result of chemical reaction, physical transformation or of damage to the crystalline state, inert gas diffusion, and the recoil of inert gas atoms. We will first analyze inert gas release

from solids when no chemical or physical transformation takes place within the solid in the temperature region considered.

The gas release is dependent on the technique used for sample labelling, i.e. whether inert gas itself or its parent nuclide has been introduced into the solid, and on the distribution of the gas or parent nuclide.

If the inert gas is formed by radioactive decay of its parent nuclide within a solid labelled by the emanation technique, the gas atom may escape from the solid in one of the following ways (see Fig. 1). When the parent atom lies close to the surface of the grain of solid, the recoil energy (of the order of 100 keV)

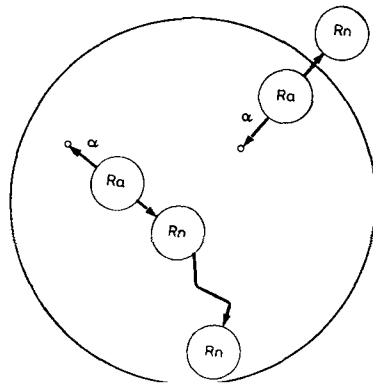


Fig. 1. The recoil and diffusion processes of inert gas release from a spherical grain

which the inert gas atom gains during the decay of the parent may be sufficient to eject it from the solid, or it may still escape by diffusion before it decays.

According to the theories of both the recoil and the diffusion processes [3], the release rate of the inert gas emanation from a grain of the solid is given by Eq. (1):

$$E = E_r + E_d = (r_0/4)(S/M)\rho + (D/\lambda)^{1/2} \cdot (S/M)\rho \quad (1)$$

where E_r is the part of the emanation release due to recoil, E_d is the diffusion part of the released emanation atoms, r_0 is the range of recoiling atoms, S is the surface area, M is the grain mass, ρ is density, and λ is the decay constant of emanation. The term E_r is temperature-independent and at room temperature is usually greater than E_d for the solids in which the diffusion coefficient of the inert gas is small. At elevated temperatures, E_d rises because

$$D = D_0 \exp(-\Delta H/RT) \quad (2)$$

where D_0 is a preexponential term, ΔH is the activation enthalpy of diffusion of emanation in the solid, R is the gas constant, and T is the absolute temperature.

Therefore, E_d could be evaluated from E total and E_r , which is obtained as a value of E measured at a low enough temperature:

$$E_d = E - E_r$$

When inert gas has been incorporated into a solid without its parent nuclide, the inert gas can be released by various diffusion processes, depending on the diffusion mechanisms. A number of equations have been proposed for these processes [1, 4].

All the theoretical considerations are valid, assuming that no chemical or physical transformation takes place in the solid during heat treatment. If a change in the structure or surface of the solid takes place, however, discontinuities occur in the ETA curve.

Measurement of inert gas release

Generally, it is possible to measure either the radioactivity of the gas remaining in the solid or the quantity of the gas released.

The ETA apparatus consists in general of several components, ensuring inert gas detection, sample heating and temperature control and measurement, carrier gas supply with flow stabilization and measurement, and measurement of complementary parameters. The inert gas released from the sample is carried by a carrier gas (air, nitrogen, etc.) from the reaction vessel (situated in the furnace) into the inert gas radioactivity measuring chamber. To measure the α -activity of Rn, a scintillation counter, an ionization chamber or semiconductor detectors connected to a counts-rate meter can be used. All β -activity measurements (Kr, Xe, Ar) are made with Geiger-Müller (GM) tubes. Gamma-active gases can be measured with a γ -spectrometer. Figure 2 shows the scheme of the ETA apparatus.

To ensure optimum conditions for a direct comparison of ETA data with results obtained by other thermoanalytical methods, devices providing simultaneous measurement of several other parameters, such as DTA, dilatometry, thermogravimetry and EGA, have been constructed [1]. A fully automated apparatus [5] for simultaneous measurements of ETA with DTA, TG, EGA and dilatometry, respectively, has been commercially developed by NETZSCH, West Germany. The ETA-DTA apparatus of NETZSCH is shown in Fig. 3.

Radiation safety of ETA measurements

Throughout the years that ETA has been used, there has been some question about the biological hazards of the radioactive inert gases used for labelling solids. In the interest of safety, the labelling of samples should be performed in a specially equipped laboratory certified for work with radioactive isotopes. The ETA apparatus itself can be installed in any chemical or physical laboratory equipped with a digestory exhaust. Since ETA is a micromethod, the sample amount used for a measurement is small, usually about 10–100 mg. Furthermore, the radioactive inert gas, after dilution by the carrier gas, does not represent a biological hazard.

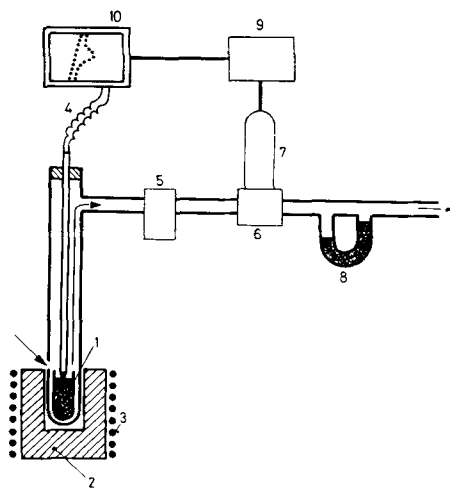


Fig. 2. Scheme of the ETA apparatus: 1 — labelled sample, 2 — metal block, 3 — furnace, 4 — thermocouple, 5 — freezing trap, 6 — measuring chamber, 7 — photomultiplier, 8 — flow-rate meter, 9 — counts-rate meter, 10 — multichannel recorder

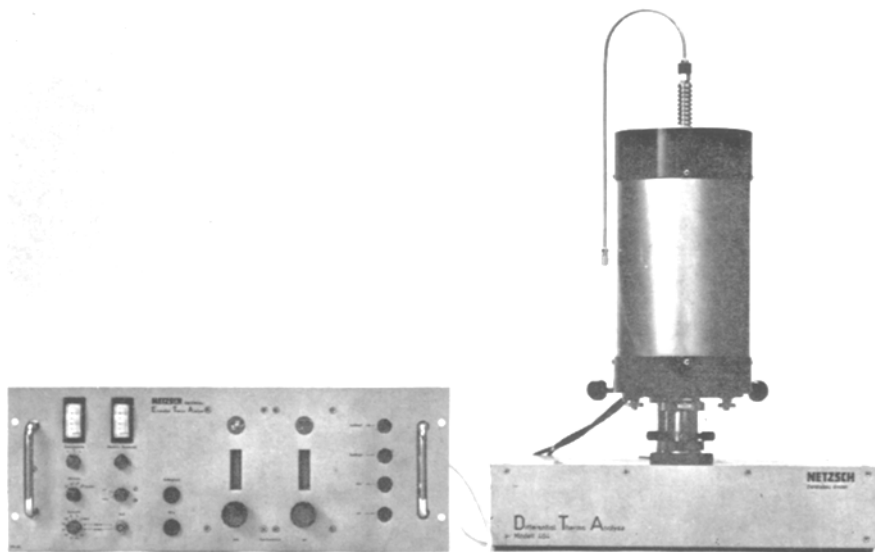


Fig. 3. General view of commercial Netzsch device for simultaneous ETA-DTA

Information from ETA measurements

Two types of information can be obtained from the ETA measurement. First, indirect information about processes taking place in the solid. Any process proceeding within a solid and leading to a change either in the surface to volume ratio or in the diffusivity of the emanation atoms becomes indirectly observable from the measurement of the emanation release rate. This is the basis of the numerous qualitative applications of ETA to the study of solid-state processes, such as aging, recrystallization, modification changes, dissociation, solid-state reactions, etc.

Due to the complexity of the release processes, supplementary information about the studied solid is usually necessary for the correct evaluation of ETA curves. Methods such as DTA, TG, dilatometry, X-ray analysis, etc. are frequently employed. To provide this indirect, valuable information, the choice of the incorporation technique is directed by the aim of the measurement. Should information about changes in the surface layers of the solid be obtained, a surface distribution of the inert gas is advantageous.

Secondly, from emanation release rate measurements, it is possible to obtain direct information about specific surface or diffusion parameters of the inert gas in the solid. The experimental conditions must be maintained so that the state of radioactive equilibrium is not destroyed during the measurement of the emanation release rate. For this information the question of labelling of samples becomes extremely important, since any theoretical approach starts with the assumption of some well-defined distribution of the immediate parent of emanation throughout the solid.

The evaluation of the diffusion coefficient D and the activation enthalpy ΔH of diffusion of emanation makes possible the quantitative estimation of factors influencing the diffusion parameters of the solid, such as non-equilibrium defects, non-stoichiometry, presence of impurities, etc. The inert gas diffusion characteristics, D and ΔH of the solid, provide valuable information on the properties of the solid and its state. In the low-temperature range, where $T < \tau$, the diffusion characteristics usually reflect a non-equilibrium state of the lattice; in the high-temperature range, where $T > \tau$, an equilibrium state of the lattice is described.

From the plot of $\log E_D$ vs. $1/T$ obtained during the heating or cooling of the sample, the Tammann temperature can be estimated. The temperature τ , estimated from the ETA cooling curve of the sample, indicates the temperature at which the defect equilibrium achieved by previous heating is being frozen. In addition, other phenomena connected with changes of the mobility of the inert gas atoms in the solid can be indicated by means of the ETA curves.

Applications

As shown in Eq. (1), variation in the rate of release of emanation from solids indirectly reflects all processes associated with changes in the surface area or in the conditions for inert gas diffusion in solids. These include solid-state processes,

such as various solid-state interactions, thermal decomposition, modification transitions, conversions of amorphous structures into crystalline ones, changes in lattice ordering and in defect concentration of the solids, sintering and aging of precipitates, etc. ETA gives valuable information on solids and their changes which would be difficult to obtain by other methods. It has found numerous applications in solid-state chemistry, catalysis, ceramics and materials science, powder metallurgy, chemical technology, testing of building materials, polymer science, geological sciences, and analytical chemistry.

Emanation thermal analysis has been widely applied to the characterization of powders [6, 7], gelous materials [8], glasses [9, 10] and crystalline solids [11–14]. The active states of solids [7] and their degree of disorder have been evaluated by ETA. Investigation of multicomponent systems [15, 16] by ETA has been especially advantageous in the case of poorly crystalline or amorphous solids, where commonly used methods, such as X-ray patterns, do not provide satisfactory results.

ETA has been used for the investigation of the solid-state processes taking place during heating or cooling of samples, such as phase changes, thermal decomposition [17, 18], melting [19] and solid-gas and solid-liquid interactions [20, 21].

The possibility of obtaining continuous information about the development of the surface area of solids and the changes in their structure enabled us to use ETA for the study of kinetics of sintering and related phenomena [22, 23]. ETA has been successfully applied to investigate the behaviour of materials directly during the process of their treatment under the conditions required by technology. The characterization of the intermediate products has been made at the same time. In this way ETA enabled us to provide the operative control of the industrial processes. This has been proved by the investigation of the processes of fabrication of ferrites [24] from initial oxide powders and the processes of preparation of ceramic nuclear fuels [25] by high-temperature treatment in the required atmosphere. Various applications of ETA have been reviewed by the author elsewhere [1, 26]. Some recent applications of ETA are given below.

1. Application to ceramics and materials science and technology

Testing of the active states of solids

The diffusion emanation release rate E_D measured at temperatures where surface and grain boundary diffusion are the controlling factors makes characterization of the texture and morphology possible.

Figure 4 shows the ETA curves of α - Fe_2O_3 measured during cooling at a linear rate of 2.5 Kmin^{-1} . Ferric oxide samples differing in the morphology were prepared by heating Fe(III) hydroxide [27] to 350, 410 and 530°. The ETA curve corresponding to a dispersed sample with a more developed texture lies higher than that of a sample with a less developed texture, mainly because of the smaller mean grain

size causing increased E_D and E_R . Use of the ETA cooling curve has been proposed for the characterization of material preheated to temperatures where annealing of the textural defects occurred. Since the inert gas diffusion in the "low-temperature range" is controlled by the texture defects (grain boundaries, dislocations and other non-equilibrium defects), the activation energy of inert gas diffusion in this temperature range can be used as a parameter characterizing the active state of the dispersed solid. The ΔH values evaluated from the slopes of the $\log E_D = f(1/T)$ plots in Fig. 4 equal 25, 35 and 55 kJ mole⁻¹ (i.e. 5.9, 8.34 and 13.1 kcal mole⁻¹) for ferric oxide samples preheated to 350, 410 and 530°, respectively.

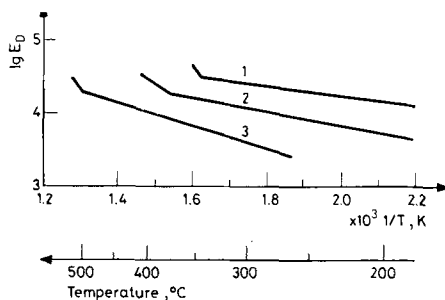


Fig. 4. Plot of $\log E_d$ vs. $1/T$ for ferric oxide (ex-hydroxide) obtained during cooling samples pre-heated to 350 (curve 1), 410 (curve 2) and 530° (curve 3)

Figure 5a, b shows ETA curves of ferric oxide samples prepared by the heating of various iron salts (Mohr's salt, iron(II)sulphate, iron(II)oxalate and iron(II, III)carbonate) to 1100°. Values of activation enthalpies for the diffusion of emanation [7] $\Delta H = 46.06, 79.6, 117.2$ and 125.6 kJ mole⁻¹, respectively, were determined in the temperature range between 600 and 750°. These values express quantitatively the influence of the non-equilibrium defects on the active state of the ferric oxide.

The reason for the different behaviours of the ferric oxide samples with various histories (expressed in their reactivity, solubility in acids, catalytic activity) was named structural memory by Hedvall [28]. According to Hedvall [26] "the structure of the salt remained in the structure of the ferric oxide sample until the mobility of the crystal lattice increased to such a degree that the equilibrium state in the lattice was reached".

Appreciable alterations of the active state of a solid may occur as a result of deviations from stoichiometry. The diffusion emanating power, E_D , of a number of solid proved to be dependent on non-stoichiometry. Even if chemical analysis is not sensitive enough to detect the degree of non-stoichiometry, emanation release measurements still point towards it. For example, when heated in a reducing atmosphere, titania (TiO_2) may lose oxygen and form a solid of formula $\text{Ti}_{1-2x}^{4+} \text{Ti}_{2x}^{3+} \text{O}_{2-x}^{2-} (\text{A.V.})_x$, where (A.V.) is an anion vacancy. The difference in the

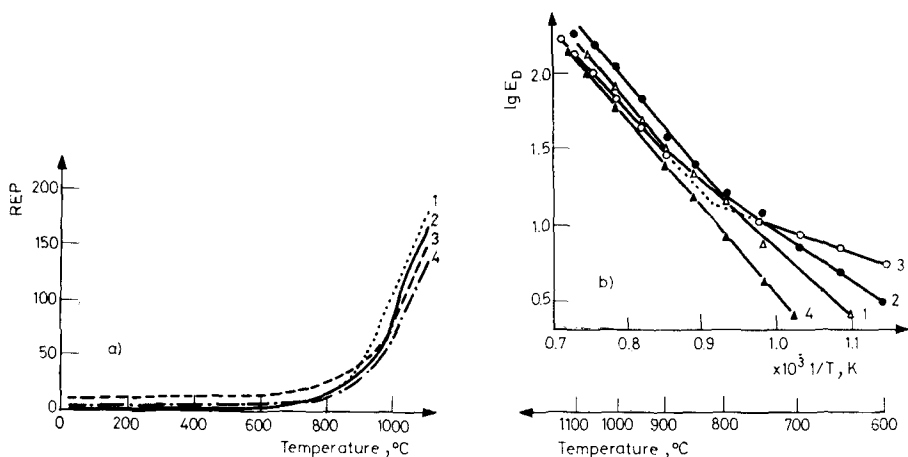


Fig. 5. ETA curves of ferric oxide samples prepared by heating various iron salts to 1100° : iron(II, III) carbonate (curve 1), iron(II) sulphate (curve 2), Mohr's salt (curve 3), and iron(II) oxalate (curve 4); (a) as dependence of E vs. T ; (b) as dependence of $\log E_d$ vs. $1/T$

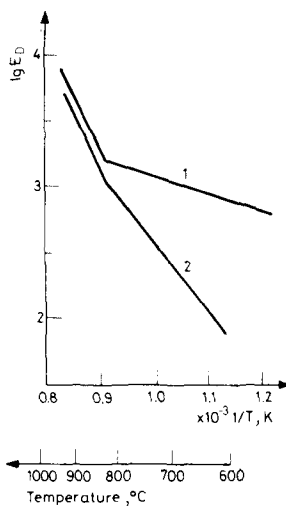


Fig. 6. The $\log E_d-1/T$ relationship obtained during cooling of TiO_2 (curve 2) and TiO_{2-x} (curve 1)

active state of the solid due to the non-stoichiometry of TiO_2 (annealed to 1100° in air) and of TiO_{2-x} (annealed to 1100° in nitrogen) is illustrated in Fig. 6. The $\log E_D$ vs. $1/T$ relationship is shown here by curves 1 and 2, corresponding to samples cooled in nitrogen and air, respectively. The values of the activation enthalpy, ΔH , within the temperature range $600-850^{\circ}$ are $50.2 \text{ kJ mole}^{-1}$ and

213.5 kJ mole⁻¹ (12 and 51 kcal mole⁻¹). The increase of the ΔH value for TiO₂ is ascribed [29] to the decreased concentration of anion vacancies [A.V.].

Testing of reactivities of powders

A method has been proposed [30, 31] for estimating the reactivity of ferric oxide in the solid-state reaction between ZnO and Fe₂O₃. The method consists in measuring the emanation release rate during heating of the reaction mixture, where one component at least has to be labelled with ²²⁸Th.

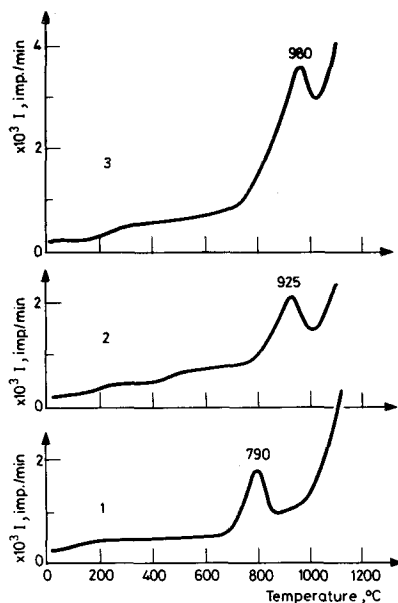


Fig. 7. ETA curves of ZnO—Fe₂O₃ reaction mixtures, where various Fe₂O₃ components were prepared by heating iron(II, III) carbonate to various temperatures: 700 (curve 1), 900 (curve 2) and 1100° (curve 3)

The labelled component (ZnO in this case) is mixed in a stoichiometric ratio (1 : 1) with the component to be tested (Fe₂O₃ in this case) and the homogenized mixture is heated to 1100° at a constant rate of 10 K min⁻¹. The ETA curves of the mixtures containing different types of ferric oxide exhibited the differences between the initial surface stage and the volume stage of the solid-state reaction of ZnO + Fe₂O₃. The temperature of the most pronounced peak in the ETA curves (see Fig. 7), i.e. the start of the slowing-down of the emanation release rate after zinc ferrite formation, was proposed as a characteristic parameter for testing the ability of ferric oxide to react with ZnO. The higher the temperature of the peak, the lower the reactivity of the ferric oxide. In this way, a true picture of the reactivity of ferric oxide relevant to the solid-state reaction with ZnO has been obtained.

Table 1

Neutron activated nuclear reactions (n, α) and (n, γ) leading to inert gas production

n, p		n, α	
Li	He ⁶	Be	He ⁶
Na	Ne ²³	Mg	Ne ²³
K	Ar ³⁹ _{260a} Ar ⁴¹ _{1,8h}	Ca	Ar ³⁷ _{34,3d} Ar ⁴¹ _{1,8h}
Rb	Kr ^{85m} _{4,4h} Kr ⁸⁷ _{73m}	Sr	Kr ^{85m} _{4,4h}
Cs	Xe ^{133m} _{2,3d} Xe ¹³³ _{5,3c}	Ba	Xe ¹³⁵ _{9,2h} Xe ¹³³ _{5,3d}
Fr		Ra	

Table 2 lists the reactivity characteristics of ferric oxide samples prepared by thermal decomposition of iron(II, III)carbonate (see Fig. 7) and of three commercial ferric oxide samples, denoted "D.F.", "P.P.G." and "Č.D.A." (made in the U.S.S.R.). By comparing the ETA results obtained and the specific surface areas, we can see that ferric oxide (ex-carbonate) loses its reactivity with a decreasing surface area. Of the commercial ferric oxides, sample "D.F." exhibits the highest reactivity, even though its surface area is relatively low (3.8 m² g⁻¹). The reactivities of the three commercial ferric oxide samples decrease in the sequence: "D.F.", "P.P.G.", "Č.D.A."

No dependence was found between the reactivities and specific surface areas of these commercial samples [31].

Sinterability and kinetics of sintering

The ETA heating curves reflect in a sensitive manner any surface area change and recrystallization of solids. As sintering, or more exactly its initial stage, is usually connected with these processes, ETA can be employed to estimate the sinterability of materials.

Table 2

Comparing reactivity characteristics of ferric oxide samples

Sample	Fe ₂ O ₃ (ex-carbonate) heated to °C			commercial samples		
	700	900	1100	"DF"	"PPG"	"ČDA"
Specific surface area, m ² g ⁻¹	5.9	0.9	0.3	3.8	14.8	7.8
Effect on ETA-curve, °C	790	925	980	720	880	920

Figure 8 shows the time-dependence of the emanation release rate E measured during isothermal treatment of thoria [32] (ThO_2) at 705, 735, 780 and 825°.

As $E_D = K_2 S$, where $K_2 = (D/\lambda)^{1/2} \rho$, and S is the effective surface area, the following kinetic law has been proposed for the first stage of thoria sintering:

$$\log S = n \log t + \text{const.} \quad (2)$$

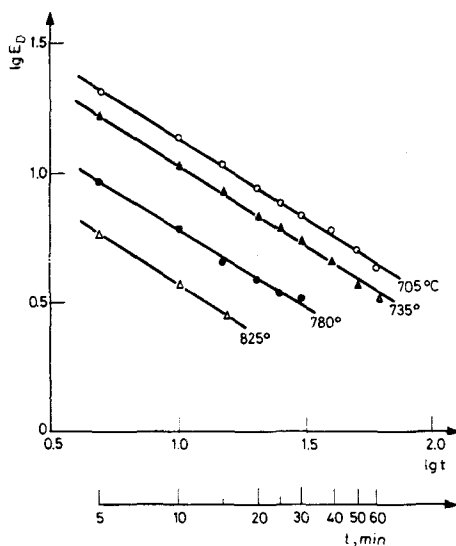


Fig. 8. $\log E_D$ vs. \log (time) dependences for thorium oxide powder (ex-oxalate) obtained during isothermal treatment in air at temperatures 705, 735, 780 and 825°

The result obtained permitted the author [32] to make the conclusion that the sintering of the sample studied in the respective temperature range is controlled by a single mechanism. The effective surface area used in Eq. (2) can differ from the surface area determined by adsorption methods. This value resulting from the slowing-down of emanation release at the given temperature, involves information about the state of the active surface controlling the initial sintering stages. The effective surface area reflected by measurement of the diffusion emanation release rate is therefore more convenient to describe the powder behaviour during the first stages of sintering than the surface area measured by an adsorption method. ETA makes it possible to follow directly the changes in the active surface, including its annealing, and to evaluate quantitatively the kinetics of these changes [22, 23, 32].

2. Characterization of technological processes and their intermediate and final products

Calcination and firing of oxide mixtures for ferrite production

Figure 9 shows ETA curves of two samples of $\text{ZnO}-\text{Fe}_2\text{O}_3$ mixture tested during calcination up to 1100° in air. Both samples were prepared by mixing ZnO and Fe_2O_3 in the same way; various Fe_2O_3 specimens were used as delivered by the producer (Bayer A. G.). No difference was found in the surface areas of the two ferric oxide samples and their reactivities were declared by the producer

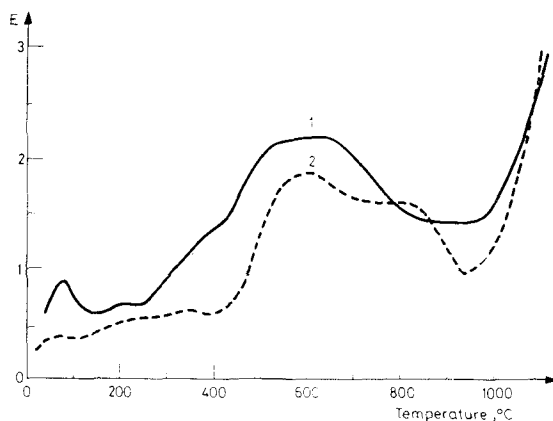


Fig. 9. ETA curves of two samples of $\text{ZnO}-\text{Fe}_2\text{O}_3$ reaction mixture measured during calcination at constant heating rate 10°min^{-1} in air

to be identical. However, differences in behaviour of the $\text{ZnO}-\text{Fe}_2\text{O}_3$ mixtures were indicated by ETA during heating up to 1100° , as shown in Fig. 9.

In the temperature range $600-950^\circ$ the Zn-ferrite formed undergoes a structural rearrangement, as indicated by slowing-down of emanation release. This process takes place in different ways in the two reaction mixtures.

The firing of the Zn-ferrite pre-calcined samples, carried out by heating to 1300° with subsequent isothermal treatment at 1300° lasting 3 hours, was followed by ETA in an atmosphere of nitrogen containing 10% of oxygen, as required by the technology. Figure 10 shows ETA curves of samples of the two ferrite mixtures, which exhibit differences. This dynamic characterization of the intermediate product of ferrite production agrees well with density measurements and the technological tests performed.

The above example demonstrated the ability of ETA to distinguish the reactivities and thermal behaviours of oxide mixtures for ferrite production, directly under the conditions required by the technology. From the differences in thermal behaviours of the samples tested, the suitability of the raw materials for ferrite

production has been estimated. The ETA data can also be used for optimization of the technology from the viewpoint of the production of ferrites with the required properties.

Preparations of urania spheres as nuclear fuel material

Figure 11 shows the ETA curves of dried uranyl gel spheres, measured on heating up to 1200 or 1300° in argon containing 5% of hydrogen. The recrystallization of very fine crystallites of the initially gelous sample, taking place in the temperature range 600–900°, is indicated by the slowing-down of the emanation release. At 1250° where the abrupt decrease of the emanation release rate E starts, the

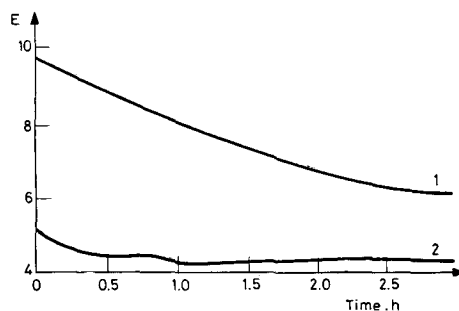


Fig. 10. ETA curves of two samples of pre-calcined Zn-ferrites (see Fig. 9) measured during firing at 1300° in nitrogen + 10% oxygen

structural rearrangement (sintering) of the urania attained a stage causing the decrease of the radon diffusion rate in the sample.

Moreover, during the isothermal treatment of the sample at 1200° (curve 2, Fig. 11, right side) a decrease of E was not observed, whereas during its isothermal treatment at 1300° the decrease of the emanation release rate takes place (curve 1, Fig. 11, right side). The great difference in the behaviours of dried uranyl gel samples during heating at 1200 and 1300°, indicative of the sintering process, was confirmed by density measurements.

ETA is preferable to other methods. TG and DTA do not provide any information about the behaviour of the material when treated above 600° and therm dilatometry indicates only processes accompanied by dimension changes. Continuous measurements of the emanation release rate when the solid is heated in the required gas media makes it possible to distinguish the quality of the intermediate products for urania spheres. The course of ETA curves during recrystallization or sintering, measured under isothermal heating, can be used for characterization of the sample.

ETA represents a means of objective characterization of intermediate solid phases, and is advantageous with poorly crystalline, gelous or amorphous materials, where X-ray patterns do not provide satisfactory results. ETA has been

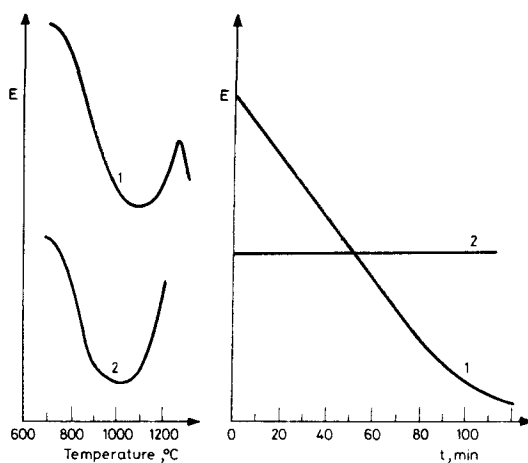


Fig. 11. ETA curves of uranyl gel spheres measured during heating in argon + 5% hydrogen at the constant rate of $5^{\circ} \text{ min}^{-1}$ (on the left) to 1300 (curve 1) and 1200° (curve 2) with subsequent isothermal heating at the respective temperatures (on the right)

suggested [25] as a simple and rapid method for operative control of the intermediate products for uranium nuclear fuel.

3. Testing of building materials

Characterization of cement hydration processes

It was recently shown [33, 34] that ETA yields valuable information about processes taking place during the setting and hardening of cement paste. Figure 12 shows the time-dependence of the emanation rate (curve 1), the evolution of

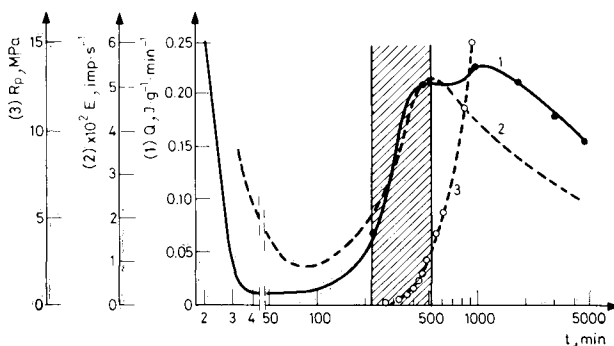


Fig. 12. Characterization of the hydration of cement (PC-400) at 20° in air by ETA (curve 1), calorimetry (curve 2) and penetration resistance of the cement paste (curve 3)

the hydration heat (curve 2) and the penetration resistance (curve 3) of a cement paste (PC-400) during its setting and hardening at 20° in air.

Various stages of the cement hydration process can be distinguished in the ETA curve [33] (Fig. 12, curve 1). In the first hydration stage, which takes place immediately after the addition of water to the cement sample, an intense increase in E takes place, reflecting the interaction of the water with the cement. The slowing-down of the increase in E indicates the formation on the cement grain surfaces of a layer of hydration products, which causes the slowing-down of the hydration process. The curves of ETA (curve 1) and calorimetry (curve 2) are similar in this time interval.

The following induction period is characterized by a low value of E . In this period the hydration rate is negligible. The beginning of the setting period is indicated by an intense increase of E . The recrystallization of the hydration products on the surface of the cement grains takes place and the hydration of the cement proceeds as indicated by the calorimetry measurement (curve 2). By ETA (curve 1) it is possible to determine the time interval where recrystallization of the C-S-H gels formed during hydration starts. The recrystallization is indicated by the slowing-down of the rise in E , accompanied by the increase of the penetration resistance of the cement paste (curve 3). The onset and the end of the setting period, determined by the standard Vicat test, are indicated in Fig. 12 by the hatched area. ETA has been recommended [33] as a suitable method for investigation of cement hydration and the influence of additives [34] and temperature [33] on this process. As shown in Fig. 13, the influence of an increase in temperature on the cement hydration process is reflected very sensitively by the ETA curves.

Chemical endurance of hardened cement paste

The application of emanation thermal analysis for this purpose consists in the continuous measurement of the emanation release rate from a sample put in contact with a corrosive medium. The chemical endurance of the tested material towards the aggressive medium in given concentration is evaluated [35] from the time-dependence of the emanation release rate.

Figure 14 shows the time-dependence of the emanation release rates of two specimens of hardened cement paste put into contact with 0.2 or 1.0% nitric acid solution. The two samples tested differed in the water/cement ratio of the cement paste used in their preparation. It follows from Fig. 14 that the sample with the lower w/c ratio and lower porosity is characterized by a higher chemical endurance towards nitric acid.

Due to the extraordinary sensitivity of radioactive indicators to the chemical changes which occur in a sample, the difference in chemical endurance of materials can be estimated within a few minutes (instead of several months or years when common methods are used). The emanation method makes it possible to evaluate the endurance of mortars, hardened cement paste and other building materials towards both liquid and gaseous aggressive media.

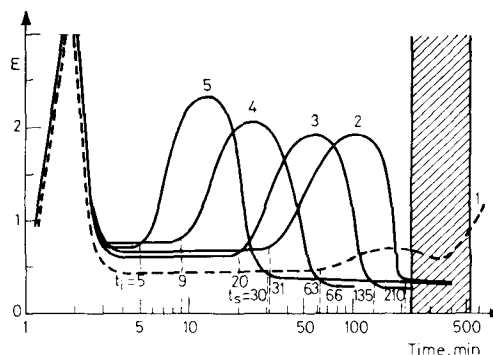


Fig. 13. ETA curves of cement paste (SPC-325) during hydration at various temperatures: 20, 35, 45, 65 and 85° (curves 1–5, resp.)

4. Reduction and oxidation of solids. Corrosion study

ETA has also been applied to the investigation of reduction and oxidation of solids. The reaction $\text{NiO} + \text{H}_2 \rightarrow \text{Ni} + \text{H}_2\text{O}$ was investigated by Quet *et al.* [20]. The reaction kinetics can be followed by means of ^{222}Rn released from labelled NiO. During heating in hydrogen atmosphere, a peak appears in the ETA curve at temperatures between 230 to 300° (see Fig. 15a). A similar peak of water release was simultaneously recorded by a katharometer. In the kinetic study, (Fig. 15b), NiO was heated isothermally at various temperatures in this range and the heights of the water peaks were proportional to the maximum rate $(d\alpha/dt)_{\text{max}}$ of the solid-gas reaction (where α is the degree of transformation in time t). Analogously,

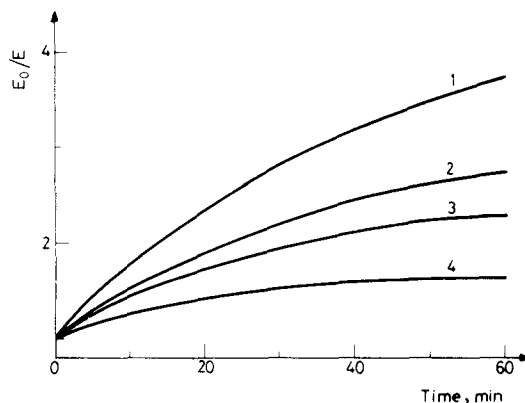


Fig. 14. Testing endurance of hardened cement paste towards nitric acid. Time dependences of emanation rate E for two samples measured in nitric acid solutions of 0.2% (curves 1, 2) and 1% (curves 3, 4). Curves 1 and 2' correspond to sample $w/c = 0.55$ curves 3 and 4 correspond to sample $w/c = 0.27$

the heights of the maxima of the ETA isotherms were considered proportional to the maximum rate of radon release $(dF/dt)_{\max}$ at the given temperatures. Figure 15b shows the peak heights of the ETA isotherms, as well as the peak heights of water release in the isotherms (measured simultaneously at several temperatures between 230 and 300°), plotted on a logarithmic scale against $1/T$. The similarity of the plots $\lg (dF/dt)_{\max} = f(1/T)$ and $\lg (d\alpha/dt)_{\max} = f(1/T)$ showed that ETA can be successfully used for the kinetic study of this solid-gas reaction. The apparent activation energy of the reaction, evaluated from the slopes of both plots in Fig. 15b, is $117.2 \text{ kJ mole}^{-1}$ ($28 \text{ kcal mole}^{-1}$).

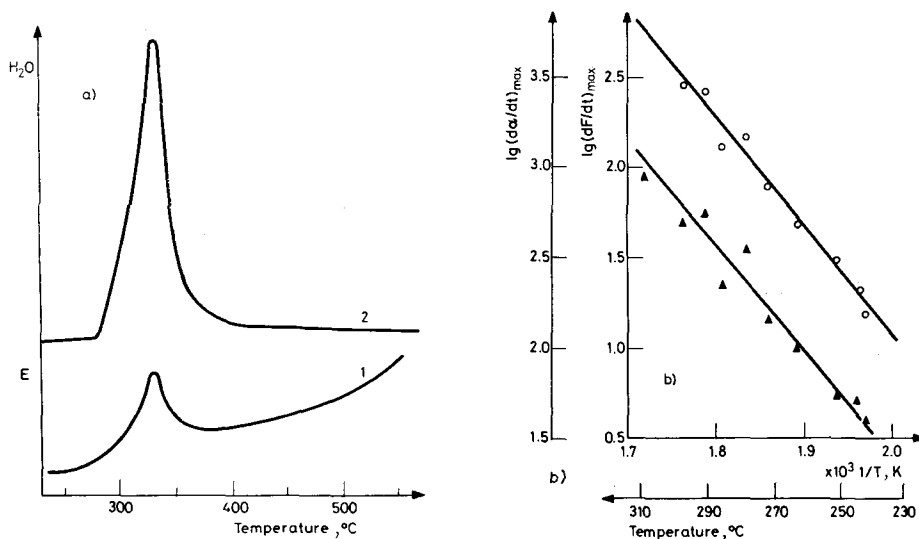


Fig. 15. a: ETA (curve 1) and water release (curve 2) during heating of NiO in hydrogen. Heating rate 5° min^{-1} ; b: Kinetic study of NiO reduction by hydrogen in the temperature range between 230 and 300°

The application of ETA is especially advantageous for the study of gas-solid reactions involving industrial gases such as hydrocarbons, where the gaseous products of reaction are difficult to detect.

The surface oxidation of metallic copper labelled with ^{85}Kr was studied by Chleck *et al.* [36] and the reaction rate, reaction order, concentration and temperature-dependence were all determined. The loss of ^{85}Kr was shown to be directly proportional to the rate of the oxidation process taking place on the metal surface. The measurement of the inert gas released, as well as the residual ^{85}Kr activity in the sample, can be used for this investigation. Figure 16 shows results of the experiments by Chleck *et al.* [36]. The percentage loss of the ^{85}Kr activity of the copper labelled, expressed as $d(N_i/N_0)/dt$, was found to be linearly dependent on the log of the oxygen concentration over the range 10^{-2} to 10^4 ppm O_2 . From

the Arrhenius dependence, $\log d(N_i/N_0)/dt$ vs. $1/T$, the reaction order was determined.

Matzke [37] used ^{133}Xe -release measurements to establish the temperature-dependence of the growth of oxide layers on stainless steel, Ti, Ni, Cu and α -brass, 40 keV – Xe ion bombardment being used to label the metals.

Radioactive inert gases can be used for the study of corrosion processes that cause changes in the surface or damage the solid studied. The technique for the investigation of the corrosion of solids by liquids and gases is based on measurement of the ^{85}Kr loss of the labelled solid after its exposure to the corrosive

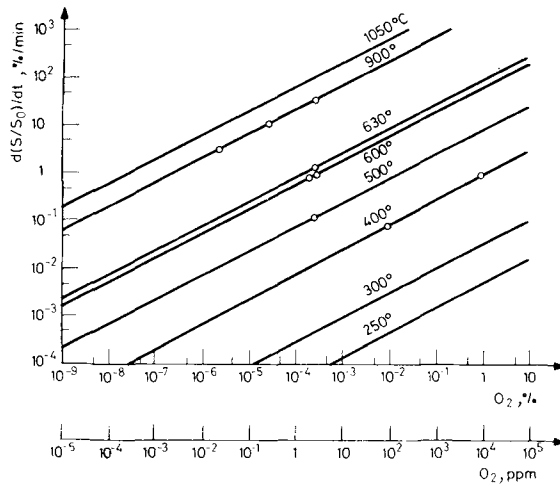


Fig. 16. Inert gas release kinetics of kryptonated Cu as response to oxygen as various temperatures

medium [38]. This technique permits the rapid determination of extremely low corrosion rates. Current methods used to evaluate anticorrosion or protective agents are generally unreliable and in many cases take several months to complete. ETA, using samples labelled with ^{85}Kr , enables one to carry out such investigations in a reliable and simple way. Corrosion imperceptible to the human eye can be demonstrated by this method within several hours.

5. Application to heterogeneous catalysis

A special group of solid-gas reactions are catalytic reactions taking place on solid surfaces. Figure 17 shows emanation release rates and temperatures of ZrO_2 and MgO catalysts [21] during their interaction with acetone vapour added to a nitrogen stream. It may be seen from Fig. 17 that acetone vapour has different effects on the emanation release rates of ZrO_2 and MgO heated to 300 and 400°, respectively. With ZrO_2 the interaction leads to a decrease of the emanation release

rate, and with MgO to its increase. The different characters of the ETA response was explained by Zhabrova *et al.* [21] as being due to the different characters of the catalytic interactions. The increase of the MgO emanation release rate during the reaction of acetone is thought to be accompanied by a partial decomposition of the acetone. The subsequent flow of pure nitrogen leads to a decrease of the emanation release rate of the MgO catalyst. The regeneration of the catalyst in the air is accompanied by the increase of both the emanation release rate and the temperature of the catalyst surface layer.

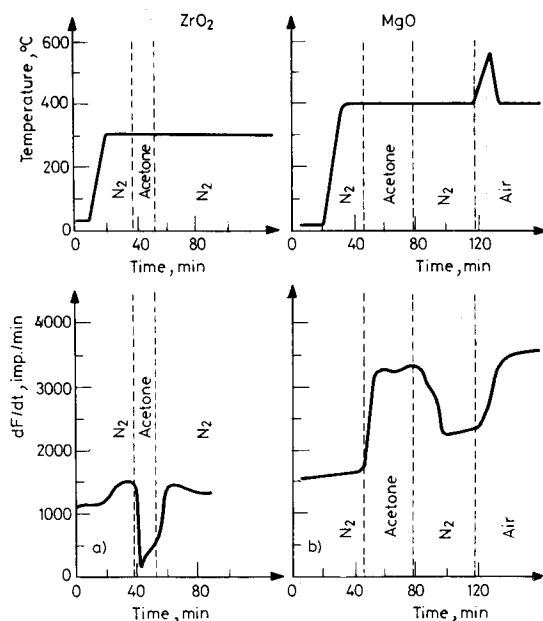


Fig. 17. Emanation release rate (dF/dt) and temperature measured during interaction of ZrO₂ (a) and MgO (b) with acetone vapour at 300 and 400°, respectively

The release of inert gas was also observed by Jech [39] when a hydrogen-oxygen mixture was allowed to react on a Pt-foil labelled with ²²²Rn. The increased rate of radon release during the first stage of the catalytic reaction on Pt-foil was assumed to be due to the reduction of the chemisorbed oxygen, which is the first step of catalytic hydrogen oxidation. The ETA measurements carried out by Bekman *et al.* [40], in the course of various catalytic reactions, supported the theoretical considerations about the selectivity of the active centres on the catalyst surface.

6. Polymers and organic substances

The application of ETA has also yielded valuable information in the investigation of polymers. The thermal behaviours of polyethylene, polymethylmethacrylate and other polymers treated in various ways, including irradiation by

gamma-rays, have been studied [41, 42]. The diffusion properties of some organic solids [43] and polymers [44] have been determined on the basis of inert gas diffusion. The diffusion properties of the barium salts of phthalic, isophthalic, and terephthalic acids, determined by ETA, showed differences in solids composed of molecules exhibiting positional isomerism [43]. Progressively rising emanation release rates have been reported for barium salts of long-chain monocarboxylic fatty acids.

7. Application in analytical chemistry

In analytical chemistry, the basic assumption for the use of solids labelled with inert radioactive gases (usually ^{85}Kr) is that when the solid enters into chemical reaction the crystalline lattice will be destroyed and the radioactive krypton will

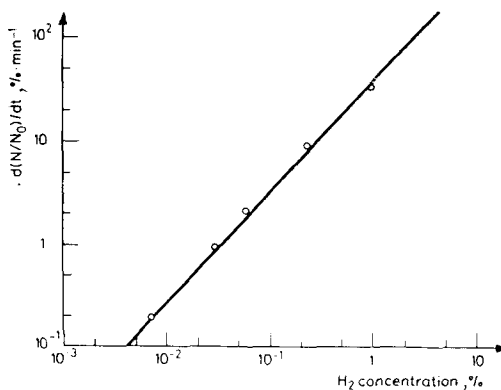


Fig. 18. Dependence of ^{85}Kr release rate of PtO_2 on various concentrations of hydrogen in nitrogen measured at room temperature

be released. The only requirement is that the solid react with the species of interest. In the course of a chemical reaction, the release rate of ^{85}Kr should be proportional to the reaction rate, and this reaction rate is a measure of the concentration of the component to be determined. The quantitative determination can be made by using a calibration curve, comparing with a standard, or using a device calibrated with a previous standard, etc.

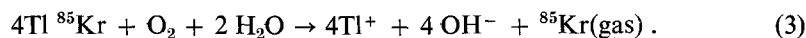
Methods have been proposed [45, 46] for the determination of gaseous components and traces of impurities in air, e.g. ozone, oxygen, SO_2 , F_2 , Cl_2 , NO , NO_2 , amines, and gaseous hydrogen. Some of the methods have already been used for the determination of these components in the atmospheres of other planets, e.g. Mars and Venus. They are also of great importance in the determination of pollutants found in hazardous workplaces.

As an example of gas analysis via radioactive krypton as an indicator, mention may be made of the measurement of hydrogen by means of kryptonated PtO_2 . Figure 18 shows the response of kryptonated PtO_2 to hydrogen at room tempera-

ture and in a nitrogen atmosphere [45]. In the Trace Lab Research Laboratories (Panametrics), U.S.A., two types of apparatus have been developed for the determination of oxidizing and reducing impurities in concentrations of the order of parts per million in the atmosphere.

In addition to gas analysis using solids labelled with radioactive inert gases, determinations in solutions can also be accomplished. To determine trace water in organic liquids, kryptonated CaC_2 has been used as a labelled solid and the activity of the ^{85}Kr released has been measured. For 0.25–2.0% H_2O in methyl alcohol, the activity of the ^{85}Kr released is directly proportional to the amount of water.

The determination of oxygen dissolved in water or other liquids is a difficult analytical problem. However, thallium labelled with ^{85}Kr can be used [45]. The determination is based on the reaction:



The decrease in radioactivity of the labelled thallium in distilled water is linear with the concentration of oxygen dissolved down to the lowest concentration of 0.3 ppm measured.

A special application of solids labelled with radioactive inert gas has been found in radiometric titrations [45].

Perspectives of the method

Emanation thermal analysis has become an important tool in basic research, as well as in the solution of practical problems of chemical technology, metallurgy, production of plastics and pharmaceuticals, nuclear science and technology, environmental research, cosmochemistry, etc. The recently increased interest in the radiometric emanation methods, i.e. emanation thermal analysis, is due to their high versatility and sensitivity in comparison with other chemical and physical methods.

Applications of radioactive inert gas offer some new possibilities in analytical chemistry and solid-state chemistry and have improved the possibilities in the thermal analysis of solids. The radiometric emanation methods have been used in determination of toxic pollutants in the atmosphere of hazardous workplaces and geographic regions, in waste liquids, in the water of rivers and seas, and in biological materials.

The increasing interest in ETA is characterized by the number of papers dealing with the applications of this method. Emanation thermal analysis has experienced a renaissance in the post-war years. Between 1950 and 1960 the number of papers was 215, between 1960 and 1970 it was 930, and the number published since 1970 exceeds 1200.

The improved measuring apparatus and the current, actual problems of science and technology have all contributed to the renewed interest and usefulness of emanation thermal analysis. Easy automation of the radioactive inert gas measurement promises this method a bright future.

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RÉSUMÉ — On donne le principe de l'analyse thermique par émanation, méthode fournissant des renseignements sur l'état des solides et son changement par mesure du départ des gaz rares radioactifs des solides marqués. On donne un résumé des méthodes de marquage des échantillons ainsi que de l'appareillage. On présente quelques exemples d'utilisation de la méthode dans le domaine de la chimie des solides, de la science et de la technologie des matériaux, des études de corrosion, de la catalyse hétérogène ainsi que de la chimie analytique. Les perspectives de la méthode d'analyse thermique par émanation sont indiquées.

ZUSAMMENFASSUNG — Es werden die Grundlagen der Emanationsthermoanalyse beschrieben, einer Methode zur Gewinnung von Informationen über den Zustand der Festkörper und seine Änderungen. Die Methode beruht auf der Messung freigesetzter radioaktiver inerte Gase aus vorher markierten Proben. Es wird eine Übersicht der zur Markierung der Proben verwendeten Verfahren sowie eine Beschreibung des ETA-Gerätes gegeben. Beispiele der neuesten Anwendungen der Emanationsthermoanalyse in der Festkörperchemie, der Materialkunde und Technologie, der Korrosionslehre, der heterogenen Katalyse sowie in der analytischen Chemie unterstreichen die Vielseitigkeit dieser Methode. Perspektiven der Anwendung der Methode werden gezeigt.

Резюме — Представлены основы эманационного термического анализа, посредством которого может быть получена информация о твердом теле и его изменениях. Метод основан на измерении выделяющихся при различных температурах радиоактивных инертных газов из предварительно меченных твердых тел. Представлен обзор методов мечения образцов и описана соответствующая аппаратура. Показаны примеры недавнего применения эманационного термического анализа в химии твердого тела, материаловедении и технологии, исследовании коррозии, гетерогенном катализе, а также в аналитической химии. Перспективными является использование этого метода вне линии с ЭВМ.