

# PHOTOSTIMULATED EXOELECTRON EMISSION DURING THERMAL DECOMPOSITION OF NON-METALLIC NICKEL COMPOUNDS

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Investigations concerned the temperature-dependence of the intensity of photostimulated emission of exoelectrons from nickel compounds ( $\text{NiO}$ ,  $\text{Ni}_2\text{O}_3$ ,  $\text{Ni}_3\text{O}_4$ ,  $\text{NiCO}_3$ ,  $\text{Ni(OH)}_2$ ,  $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NiCO}_3(\text{NiOH})_2 \cdot n\text{H}_2\text{O}$ ). The  $\frac{N}{t} = f(T)$  curves were found to have maxima at points corresponding to the temperatures of decomposition or phase transitions of the examined substances. These results, confirmed by X-ray analyses, point to the possibility of employing the phenomenon of photostimulated exoelectron emission in research on the kinetics of the thermal decomposition of chemical compounds. It may also be used in the identification of solid decomposition products.

## 1. Introduction

Kramer [1,2] was the first to notice the possibility of applying the phenomenon of exoelectron emission to studies on the kinetics of thermal decomposition of chemical compounds. By analyzing the dependence of the intensity of photo- and thermo-stimulated emission of exoelectrons from carbonates and hydroxides upon the temperature at which samples were annealed before excitation with X-rays, he revealed that there appeared a maximum in the  $\frac{N}{t} = f(T_{\text{annealing}})$  curves at points corresponding to the temperatures of decomposition of the examined substances. The results of Kramer soon found confirmation in the research by Hanle and coworkers [3, 4].

The method of determining the decomposition temperatures of chemical compounds proposed by Kramer has several drawbacks. Among other things, the samples have to be irradiated with X-rays before measurements, and the method requires very time-consuming repeated measurements of emission from samples annealed at various temperature which constitute the basis for plotting a curve depicting the dependence of the rate

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of the decomposition reaction upon sample temperature. The need arose, therefore, to develop another version of the exoemission method which would eliminate the necessity of sample irradiation prior to measurement and would shorten the measurement cycle.

The results of researches carried out by Sujak, Górecki and Biernacki [5-8] hitherto in the field of photostimulated exoelectron emission during phase transitions in solids suggested that maxima should also appear in the photostimulated exoelectron emission intensity *versus* temperature curves for unexcited samples at points characteristic for the reaction of thermal decomposition of compounds. The fact that the shape of the  $\frac{N}{t} = f(T)$  curves is a characteristic feature of any examined substance additionally indicated the possibility of utilizing the phenomenon in mention for identifying the solid decomposition products. In order to check these presumptions, the photostimulated exoelectron emission during the decomposition reaction of nickel compounds has been studied.

## 2. Experimental conditions and sample preparation

Measurements of the temperature-dependence of the intensity of photostimulated exoelectron emission were accomplished with the use of the apparatus described in detail in an earlier study [7]. The detector was an open point counter with saturated ethanol quenching vapour. Throughout the measurement the sample surface was illuminated by the radiation of a quartz lamp with a Q-400 burner. The fixed heating rate of the samples was 50 K/min. Prior to measurement the samples were not submitted to any forms of action stimulating emission (irradiation, deformation).

Measurements of the temperature-dependence of the intensity of photostimulated exoelectron emission were carried out on powders of the following nickel compounds: 1. nickelous oxide NiO, pure; 2. nickelic oxide Ni<sub>2</sub>O<sub>3</sub>, pure; 3. nickelonickelic oxide Ni<sub>3</sub>O<sub>4</sub>, pure; 4. nickel carbonate NiCO<sub>3</sub>, pure; 5. basic nickel carbonate NiCO<sub>3</sub>(NiOH)<sub>2</sub> · nH<sub>2</sub>O, pure; 6. nickel nitrate Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, analytically pure; 7. nickelous hydroxide Ni(OH)<sub>2</sub>.

The nickelous hydroxide was obtained from an aqueous solution of nickelous chloride by treating it with potassium hydroxide KOH. The precipitated sediment Ni(OH)<sub>2</sub> was filtered off through filter paper, rinsed and dried in a stream of warm air.

The nickelous oxide NiO was produced by Riedel und de Haen AG Seelze, Hannover; the manufacturer of the other reagents was Polish Chemical Reagents in Gliwice.

Control X-ray analyses were carried out at Institute of Heavy Organic Synthesis in Blachownia Śląska by means of a TUR 60 camera (Cu K<sub>α</sub> radiation, 40 kV, 18 mA).

## 3. Results of measurements

The curve of the temperature-dependence of the intensity of photostimulated emission of electrons from the nickel oxides are shown in Fig. 1. Only the  $\frac{N}{t} = f(T)$  curve for nickelous oxide NiO exhibits a distinct maximum in the vicinity of 520 K, *i. e.*, near the

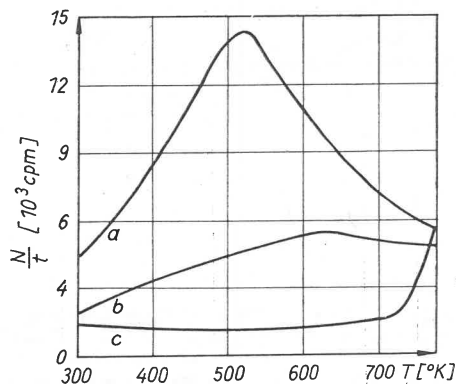


Fig. 1. Curves of the temperature-dependence of the intensity of photostimulated exoelectron emission from nickel oxides; *a* - NiO, *b* - Ni<sub>2</sub>O<sub>3</sub>, *c* - Ni<sub>3</sub>O<sub>4</sub>

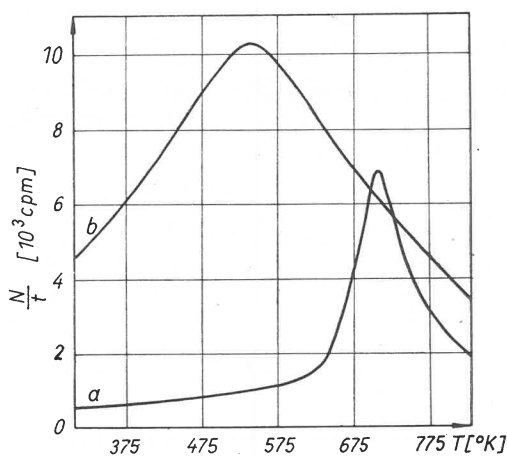


Fig. 2. Curves of the temperature-dependence of the intensity of photostimulated exoelectron emission from NiCO<sub>3</sub>; *a* - first sample heating, *b* - second heating of the same sample

Néel point of this substance. The intensity *versus* temperature curves for the various nickel oxides distinctly differ from one another. Repeated exoelectron emission measurements with the same sample demonstrated that the shape of the  $\frac{N}{t} = f(T)$  curve remains unchanged.

In the photostimulated exoelectron emission intensity *versus* temperature curve for nickel carbonate NiCO<sub>3</sub> (Fig. 2) there is a maximum in the vicinity of 700 K. Repeated heating of the same sample gave a curve with a maximum in the vicinity of 520 K, very similar in shape to that of the curve of the temperature-dependence of photostimulated exoemission from NiO.

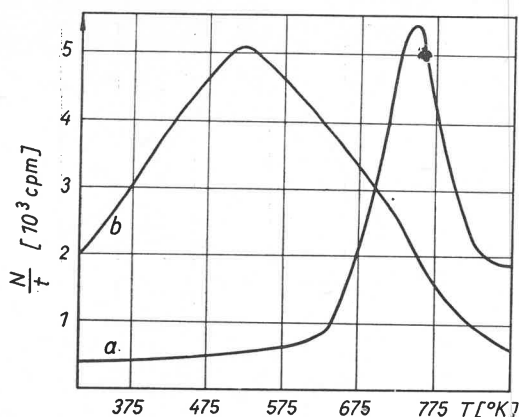


Fig. 3. Curves of the temperature-dependence of the intensity of photostimulated exoelectron emission from basic nickel carbonate; *a* – first sample heating, *b* – second heating of the same sample

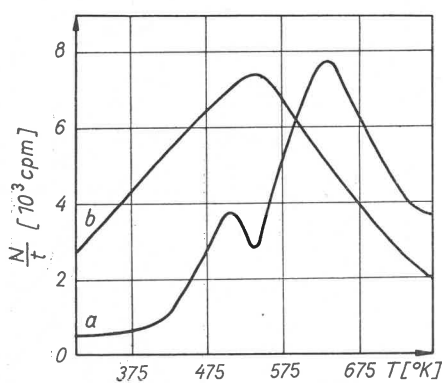


Fig. 4. Temperature-dependence of the intensity of photostimulated exoelectron emission from  $\text{Ni}(\text{OH})_2$ ; *a* – first sample heating, *b* – second heating of the same sample

Figure 3 presents the  $\frac{N}{t} = f(T)$  curves obtained during two successive heatings of the same sample of basic nickel carbonate. The first measurement yielded a curve with a peak around 750 K, whereas the curve obtained from the second measurement of emission from the same sample, just as in the case of  $\text{NiCO}_3$ , runs like the  $\frac{N}{t} = f(T)$  curve for nickelous oxide NiO.

Figure 4 shows the analogous results of measurements for nickelous hydroxide  $\text{Ni}(\text{OH})_2$ . The curve of the first heating cycle shows two distinct maxima in the vicinity of the temperatures 500 K and 630 K. Heating the same sample for the second time gave a curve with a broad maximum near 520 K, hence, like the  $\frac{N}{t} = f(T)$  curve for nickelous oxide.

In all of the cases discussed thus far it was necessary, in order to be able to observe emission, to have the sample illuminated with UV light during measurement and to generate a field between the sample and counter which accelerated and steered negatively charged particles into the active volume of the counter. The course of studies on the exoelectron emission from hydrated nickel nitrate is somewhat more intricate. During the first heating of the sample of this compound photostimulation yielded a curve with maxima at temperatu-

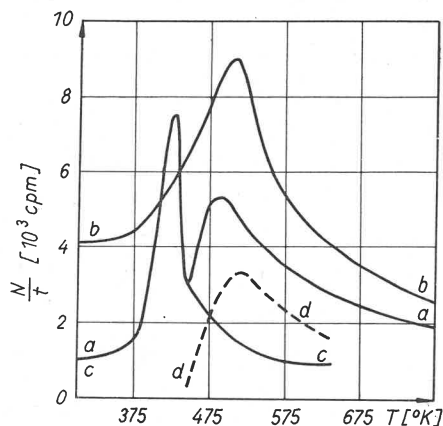


Fig. 5. Temperature-dependence of emission from nickelous nitrate hydrate; *a* – first sample heating, *b* – second heating of the same sample (with photostimulation), *c* – first heating without photostimulation and accelerating voltage; *d* – curve obtained by subtracting curve *c* from curve *a*

res of 425 K and 490 K. It was found, however, that the counter records an increased counting rate also without photostimulation and even in the presence of a field retarding the negatively charged particles. Then a curve with a maximum near 425 K is obtained. To observe exoelectron emission in the second heating cycle of the nickel nitrate sample, however, it is necessary to apply photostimulation and an accelerating field. An  $\frac{N}{t} = f(T)$  curve similar to the one for NiO is then obtained (Fig. 5).

#### 4. Discussion

As had been demonstrated by earlier studies [6, 7], the maximum in the temperature response of photostimulated exoelectron emission from nickelous oxide NiO should be assigned to the magnetic phase transition of this substance at the Néel point (520 K). None the less, the large width of this peak attracts some attention. There are two probable reasons for this effect. One is the fact that when powder samples are used different parts of them become heated at different rates. Because of this, various parts of the examined sample attain a certain temperature at different times, what with the applied measuring technique, shows up as a broadening of the maximum corresponding to the phase transition. The other cause of the peak broadening may be the proximity of the points of two

different phase transitions occurring in NiO ( $T_{\alpha-\beta} = 470$  K, Néel point 520 K). Both of these transitions may be accompanied by enhanced exoelectron emission. The aggregate of the emission effects accompanying both of these transitions gives in result the recorded  $\frac{N}{t} = f(T)$  curve, being the envelope of two indifferentiable exoemission maxima.

The monotonic shape of the curves of photostimulated exoelectron emission intensity against temperature for  $\text{Ni}_2\text{O}_3$  and  $\text{Ni}_3\text{O}_4$  is proof that within the range of temperatures examined there are no phase transitions in these compounds.

It appears that the clear differentiation of the curves of the temperature-dependence of the intensity of photostimulated exoelectron emission from various nickel oxides may be employed as a tool for their identification.

Thermal decomposition of nickel carbonate (at 670 K), nickel hydroxide (at 630 K) and nickel nitrate (at 410 K) is one of the commonly used methods of obtaining nickelous oxide NiO [9]. This gives rise to the supposition that emission effects observed during the heating of these substances are associated with the reaction of decomposition of the examined compounds. The similarity of the  $\frac{N}{t} = f(T)$  curves obtained by repeated heating of the samples with the exoemission intensity *versus* temperature curve for nickelous oxide leads to the presumption that the examined substance becomes decomposed entirely during the first measurement and nickelous oxide is produced; hence, only exoemission from NiO is observed during a repeated measurement.

To check this hypothesis, *X*-ray patterns of the powders of the examined substances were recorded when heated to the temperature at which exoemission began to rise and of the analogous samples heated to temperatures exceeding that of the peak in the  $\frac{N}{t} = f(T)$  curve. The samples were heated for *X*-ray analysis in exactly the same way as during exoemission measurements and at the same rate of 50 K/min. The obtained *X*-ray patterns were compared with those for nickelous oxide NiO produced by Riedel und de Haen AG Seelze.

The confrontation of the *X*-ray patterns of  $\text{NiCO}_3$  powders heated to various temperatures with that of NiO (Fig. 6) proves that in the 600 K to 770 K temperature range the nickelous carbonate decomposed to produce nickelous oxide NiO. In this same range the exoelectron emission is intensified. Maximum intensity of this emission is at 700 K. It may be assumed, therefore, that the observed emission is associated with the decomposition of  $\text{NiCO}_3$ , while the position of the maximum in the  $\frac{N}{t} = f(T)$  curve corresponds to the maximum decomposition rate (at the applied rate of temperature changes). This result is in satisfactory agreement with the literature data regarding the temperature of nickelous carbonate decomposition (670 K, see [9, 10]).

The comparison of the *X*-ray patterns of powders of basic nickel carbonate and nickelous oxide (Fig. 7) shows that the decomposition of  $\text{NiCO}_3(\text{NiOH})_2 \cdot n\text{H}_2\text{O}$  with the production of NiO takes place within the range of temperatures from 620 K to 800 K.

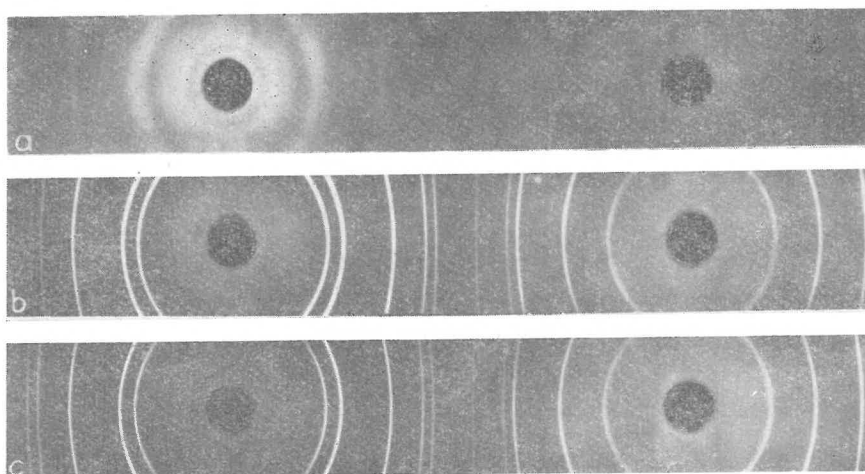


Fig. 6. X-ray patterns of powders of: a – nickelous nitrate heated to 600 K, b – nickelous nitrate heated to 770 K, c – nickelous oxide NiO, pure

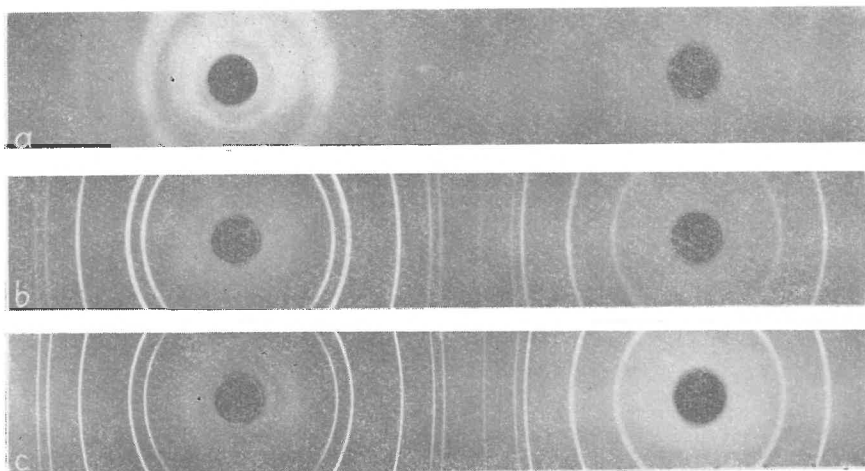


Fig. 7. X-ray patterns of powders of: a – basic nickel carbonate heated to 620 K, b – basic nickel carbonate heated to 800 K, c – nickelous oxide NiO, pure

This permits the exoelectron emission observed in this temperature range to be interpreted as an effect associated with the decomposition reaction. Unfortunately, the lack of literature data regarding the decomposition temperature of this compound makes a complete comparison impossible.

Data in the literature [9, 10] state that the decomposition of nickelous hydroxide occurs in two stages. The first stage occurs in the vicinity of 500 K, the other at 630 K. These values are in excellent agreement with the temperatures of the maxima in the  $\frac{N}{t} = f(T)$  curves for nickelous hydroxide (Fig. 4). This conformity, backed by the com-

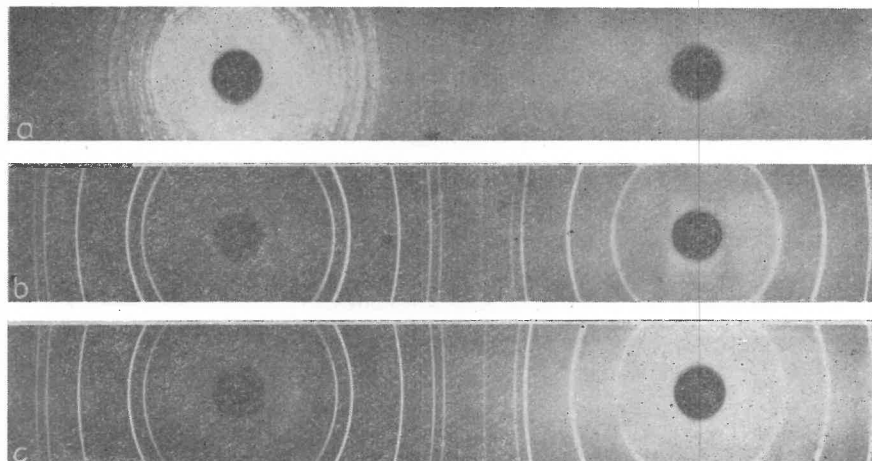


Fig. 8. X-ray patterns of powders of: a – nickelous hydroxide heated to 420 K, b – nickelous hydroxide heated to 720 K, c – nickelous oxide NiO, pure

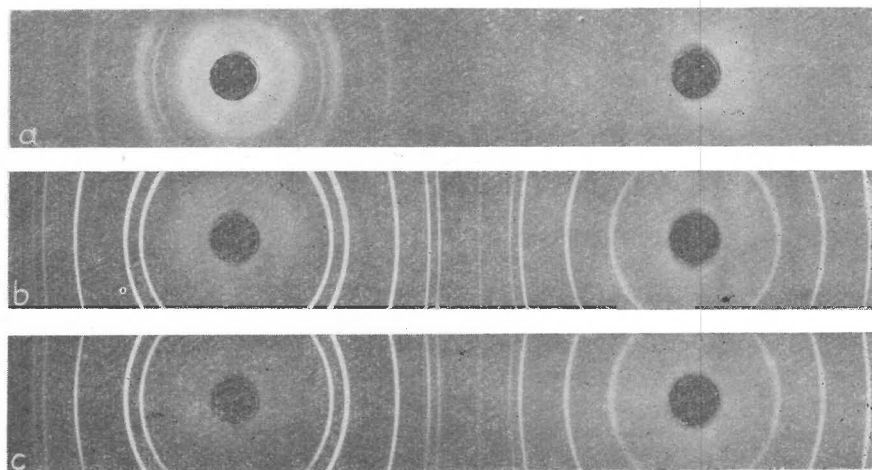


Fig. 9. X-ray patterns of powders of: a – nickelous nitrate heated to 350 K, b – nickelous nitrate heated to 450 K, c – nickelous oxide NiO, pure

parison of the X-ray patterns for  $\text{Ni}(\text{OH})_2$  and NiO (Fig. 8), corroborates the hypothesis relating the effects in mention with the decomposition reaction.

When nickelous nitrate  $\text{Ni}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$  is heated the crystallization water is released and the compound then decomposes with NiO as a product [9, 10]. In this situation the emission maximum appearing even when an electric field retarding negatively charged particles is present should be looked at as a reaction of the counter to water vapour molecules liberated from the sample during decomposition which get into the active volume of the counter [11, 12]. The X-ray patterns compared in Fig. 9 show that after the nitrate is heated to over 450 K only NiO remains. The maximum of exoelectron



emission intensity in the vicinity of 490 K (or in principle near 520 K once the curve corresponding to the reaction of the counter to the water vapour molecules is subtracted) should be related to the phase transition of the newly formed nickelous oxide. All the more so that to reveal this maximum it is necessary to illuminate the sample surface with UV radiation. The maximum observed when the same sample is reheated should be interpreted along the same lines.

It is surprising that the counter does not appear to react to water released during the decomposition of nickelous hydroxide and basic nickel carbonate. Perhaps this is because the quantity of water released in these case is much smaller than in the case of the nitrate, what is not without significance at the sample-to-counter distance applied here (2 cm).

### 5. Conclusions

The results presented in the foregoing show that the method of photostimulated exoelectron emission may be successfully employed not only for studying the kinetics of the decomposition of chemical compounds, but also for identifying solid decomposition products. Virtues of the proposed method, as compared with traditional ones, are the simplicity of sample preparation and the rapidity of measurements.

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