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THERMAL DECOMPOSITION AND THERMOFRACTOCHROMATOGRAPHIC STUDIES OF METAL CITRATES

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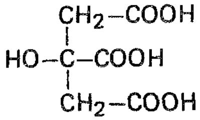
The thermal decomposition and kinetic parameters of thermal decomposition of Mg(II), Ca(II), Al(III), Cr(III), Fe(III), Co(II), Ni(II), Zn(II), Mn(II) and Cd(II) complex salts with citric acid were investigated on the basis of the respective thermal curves. The values of the activation energy (E_a) and reaction order (n) of the thermal decomposition were compared. Thermofractochromatograph constructed in our laboratory complies with the requirements of apparatus for separation, evolution and identification of products formed during the heating of the investigated samples in the temperature range of 293 to 600 K.

Citric acid $C_6H_8O_7 \cdot H_2O$ an acid widely used in the food industry [1–8]. It is a tribasic acid H_3R (formula I) and an optically inactive compound due to the absence of asymmetrical carbon.



$$HO-\overset{\overset{\displaystyle CH_2-COOH}{|}}{\underset{\underset{\displaystyle CH_2-COOH}{|}}{C}}-COOH$$

I. Citric acid H_3R

Its melting point is 153° and its specific gravity is 1.542 g/cm^3 [1]. It dissolves well in water and other polar solvents such as CH_3OH, C_3H_5OH, $(CH_3)_2O$, $(CH_3)_2CO$ etc. Citric acid is produced from glucose with the help of yeasts: Aspergillus niger, Cytromyces pferfferianus or some Penicyllinum [1]. The citric acid producers also use Candida bimundalis, Candida Scottii and other yeasts [7–9]. In commercial manufacturing methods, an important stage is the separation of citric acid in the form of precipitated calcium citrate $Ca_3(C_6H_5O_7)_2$ [10]. It is precipitated in a hot state, thus being easily separable from accompanying tartrates, oxalates and malates.

Metal citrates are often formed in natural systems [9], in various conversions and in processes of food manufacture [1, 2, 8]. In the food industry many processes occurring at elevated temperatures are associated with the decomposition of the metal citrates formed. It is, then, interesting to study the mechanism and stages of decomposition [11–18] of such compounds. The present paper includes the results of studies on the decomposition of citrates of metals such as: Mg(II), Al(III), Ca(II), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II). Most of the compounds were prepared by the methods given by Supniewski [10].

Experimental

Analar citric acid $C_6H_8O_7 \cdot H_2O$ (Fabryka Kwasu Cytrynowego, Zgierz, Poland) with m. p. 154.9° and analar nitrates of suitable metals (POCh, Gliwice) were used for the investigations. The prepared citrates and some of their physical properties are given in Table 1, while the results of the crystalline water determination, and the analytical data, allowing to find out the complexes composition, in Table 2. It follows from the data that the number of water molecules in the prepared compounds varies from 1 to 10.

Thermal curves were taken for these compounds using a 1000/1500 Paulik–Paulik–Erdey Derivatograph (MOM, Budapest) in static air atmosphere, using weighed

Table 1 Some characteristic data of the complexes

Complex	Color	Melting point, K
$Mg_3(C_6H_5O_7)_2 \cdot 4\,H_2O$	White	568
$Al(C_6H_5O_7) \cdot 4\,H_2O$	White	518
$Ca_3(C_6H_5O_7)_2 \cdot 4\,H_2O$	White	528
$Cr(C_6H_5O_7) \cdot 6\,H_2O$	Violet	498
$Mn_3(C_6H_5O_7)_2 \cdot 9\,H_2O$	Pale pink	518
$Fe(C_6H_5O_7) \cdot 3\,H_2O$	Brown	573
$Co_3(C_6H_5O_7)_2 \cdot 8\,H_2O$	Pink	523
$Ni_3(C_6H_5O_7)_2 \cdot 10\,H_2O$	Green	529
$Cu_3(C_6H_5O_7)_2 \cdot 5\,H_2O$	Bluish green	503
$Zn_3(C_6H_5O_7)_2 \cdot H_2O$	White	643

Table 2 Analytical data of the complexes

Complex	H_2O %		Metal %		C %		H %	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$Mg_3(C_6H_5O_7)_2 \cdot 4\,H_2O$	13.77	13.59	16.16	16.21	31.94	31.82	2.23	2.15
$Al(C_6H_5O_7) \cdot 4\,H_2O$	25.01	25.26	12.48	12.50	33.36	33.20	2.28	2.19
$Ca_3(C_6H_5O_7)_2 \cdot 4\,H_2O$	12.63	12.59	24.13	24.20	28.92	28.80	2.20	2.15
$Cr(C_6H_5O_7) \cdot 6\,H_2O$	30.95	30.88	21.56	21.70	29.88	29.79	2.08	2.03
$Mn_3(C_6H_5O_7)_2 \cdot 9\,H_2O$	22.99	23.01	30.35	30.42	26.54	26.50	1.85	1.75
$Fe(C_6H_5O_7) \cdot 3\,H_2O$	18.07	18.10	22.80	22.95	29.42	29.15	2.09	2.00
$Co_3(C_6H_5O_7)_2 \cdot 8\,H_2O$	20.61	20.45	31.87	31.99	25.98	25.78	1.81	1.96
$Ni_3(C_6H_5O_7)_2 \cdot 10\,H_2O$	24.51	24.59	31.77	32.00	26.00	25.98	1.81	1.76
$Cu_3(C_6H_5O_7)_2 \cdot 5\,H_2O$	13.67	13.80	33.51	33.87	25.34	25.29	1.77	1.60
$Zn_3(C_6H_5O_7)_2 \cdot H_2O$	3.04	2.85	34.15	34.01	25.09	24.98	1.74	1.50

portions of 500 mg. Other conditions were as follows: temperature range 20–1000°, heating rate 5 deg/min., DTA sensitivity 1/5, the recorder tape rate 1 mm/min.

Thermofractochromatograms of the samples were made using a thermofractochromatograph of our own construction described in paper [19]. The apparatus allows to carry out the investigations under non-isothermal conditions. A 2.00 mg sample, placed in an open glass tube is heated in an oven with precisely controlled temperature increase. The evaporating compounds in a neutral gas carrier are deposited directly into a thin-layer chromatography plate moving at a constant rate along the plane perpendicular to the capillary outlet of the tube (Fig. 1). This method provides a fractional separation of volatile compounds according to their temperatures of evaporation, sublimation, melting, boiling etc. These experiments were carried out under the dynamic atmosphere of argon within the temperature range of 20–600° at a heating rate of 15 deg/min. The thin-layer chromatography plates were of Merck, type DC – Alufolien Kieselgel (ohne Fluoreszenzindicator). The development of chromatograms was carried out according to the procedure given in monographs [20, 21].

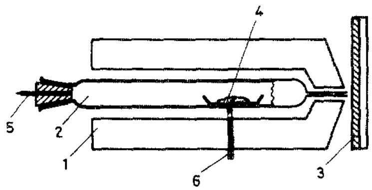


Fig. 1 Thermofractochromatograph. 1 – oven, 2 – glass tube, 3 – thin-layer chromatography plate, 4 – sample, 5 – carrier gas, 6 – thermocouple

Results and discussion

Figure 2 shows the TG, DTG and DTA curves of citric acid and Figures 3 from a to b illustrate the curves of 2 metal citrates investigated in static air atmosphere. The thermal decomposition data obtained from the chromatograms and characterizing the decomposition stages from 333 to 1073 K are shown in Table 3. It can be seen from the data that the thermal decomposition of the investigated metal citrates occurs in four or five stages with the first stage being associated with the sample dehydration.

E.g. the thermal decomposition of calcium citrate takes place in the following five stages:

$$Ca_3(C_6H_5O_7)_2 \cdot 4\,H_2O \xrightarrow{353-393\ K} Ca_3(C_6H_5O_7)_2 \cdot 2\,H_2O + 2\,H_2O \quad (1)$$

$$Ca_3(C_6H_5O_7)_2 \cdot 2\,H_2O \xrightarrow{393-433\ K} Ca_3(C_6H_5O_7)_2 + 2\,H_2O \quad (2)$$

$$Ca_3(C_6H_5O_7)_2 \xrightarrow{483-623\ K} Ca_3(C_6H_3O_6)_2 + 2\,H_2O \quad (3)$$

$$Ca_3(C_6H_3O_6)_2 + 9\,O_2 \xrightarrow{623-893\text{ K}} 3\,CaCO_3 + 3\,H_2O + 9\,CO_2 \tag{4}$$

$$CaCO_3 \xrightarrow{893-1037\text{ K}} CaO + CO_2 \tag{5}$$

with the formation of anhydrous salt, then calcium aconitinate, calcium carbonate and finally calcium oxide and carbon dioxide. The products were identified by chemical methods, performing suitable quantitative determinations of Ca^{2+} and CO_2 [6, 16, 17, 19].

Based on the obtained TG, DTG and T curves, the following kinetic parameters of the dehydration process were found: activation energy E_a, frequency factor A and reaction order n.

By a graphical way, the Arrhenius equation [4, 5, 18] was solved for dm/dt:

$$\frac{dm}{dt} = Ac^n \exp\left(-\frac{E_a}{RT}\right) \tag{1}$$

and the logarithmic form of this equation was used:

$$\log \frac{dm}{dt} = \log A + n \log c - \frac{E_a}{RT} \log c \tag{2}$$

From the thermal curves were taken: dm/dt – the distance of DTG curve from the basic line in mm; Δm – mass loss in mg. The value of the conversion degree c was calculated from Eq. (3):

$$c = \frac{\Delta m_\infty - \Delta m}{\Delta m_\infty} \tag{3}$$

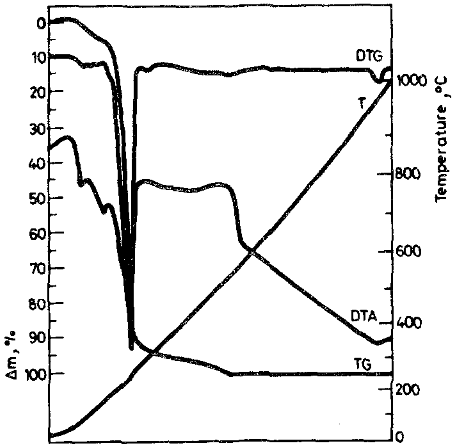


Fig. 2 Simultaneous TG DTG, DTA and T curves of citric acid $C_6H_8O_7 \cdot H_2O$ in static air atmosphere: $m_0 = 500$ mg, DTA = 1/5, $u = 5$ mm/min; $\beta = 2.5$ K/min

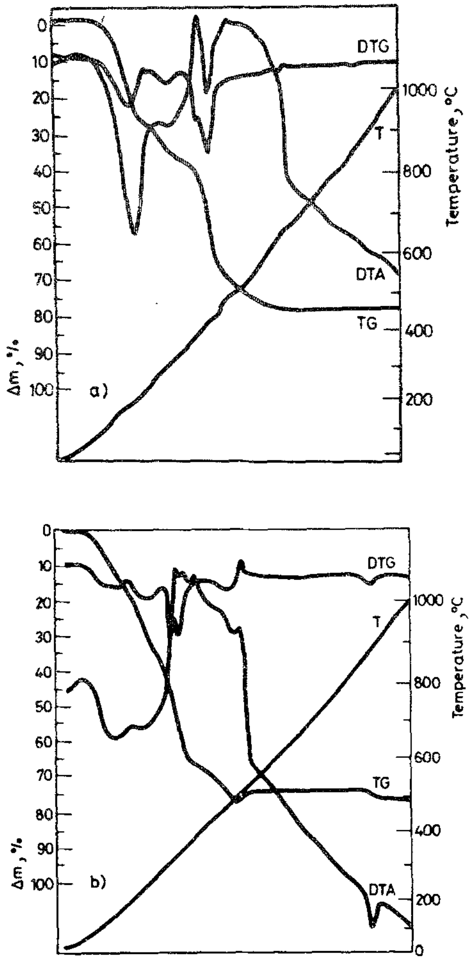


Fig. 3 Simultaneous TG, DTG, DTA and T curves of metal citrates in static air atmosphere: a – $Mg_3(C_6H_5O_7)_2 \cdot 4H_2O$; b – $Co_3(C_6H_5O_7)_2 \cdot 8H_2O$; $m_0 = 500$ mg, TG = 500 mg, DTG = 1/5, DTA = 1/5, $u = 1$ mm/min, $\beta = 5$ K/min

where Δm_∞ is the maximal mass loss in the given stage, and Δm mass loss at the given point of conversion in mg.

The data of corresponding compounds and calculated degree of conversion c and $1/T$ were used to make a plot of $\log dm/dt = f(1/T)$ as shown in Fig. 4. The linear part of the plot (Fig. 4) allows to calculate the slope as $\mathrm{tg}\,\alpha$, and then, activation energy E_a from Eq. (4):

$$E_a = 2.303\,R\,\mathrm{tg}\,\alpha \tag{4}$$

Table 3 Experimental data characterizing the stages of thermal decomposition of citric acid and metal citrates

Compound	Temperature ranges, K	Effect type	Weight loss, %
$C_6H_8O_7 \cdot H_2O$	333–383	endo	4.5
	383–423	endo	4.0
	423–513	endo	79.5
	513–803	exo	11.9
$Mg_3(C_6H_5O_7)_2 \cdot 4\,H_2O$	373–423	endo	12.1
	423–493	exo	17.0
	495–613	endo	6.2
	613–974	endo	21.1
$Ca_3(C_6H_5O_7)_2 \cdot 4\,H_2O$	353–393	endo	6.0
	393–433	endo	7.7
	483–623	exo	4.0
	623–893	endo	30.8
	893–1073	exo	24.0
$Al(C_6H_5O_7) \cdot 4\,H_2O$	333–383	endo	7.1
	383–443	endo	21.0
	453–553	exo	5.0
	553–903	endo	45.0
$Cr(C_6H_5O_7) \cdot 6\,H_2O$	343–380	endo	12.1
	383–423	endo	16.0
	423–503	endo	5.1
	503–583	exo	11.0
	583–943	endo	33.0
$Fe(C_6H_5O_7) \cdot 3\,H_2O$	343–383	endo	3.0
	383–423	endo	18.1
	423–483	exo	22.0
	493–763	endo	25.1
$Mn_3(C_6H_5O_7)_2 \cdot 9\,H_2O$	343–383	endo	2.0
	383–443	endo	19.0
	443–503	endo	5.1
	503–833	endo	44.0
$Co_3(C_6H_5O_7)_2 \cdot 8\,H_2O$	333–383	endo	5.0
	403–423	endo	17.1
	423–503	endo	10.0
	533–753	endo	42.2
	753–833	endo	2.0
$Ni_3(C_6H_5O_7)_2 \cdot 10\,H_2O$	333–383	endo	5.0
	383–433	endo	12.1
	433–553	exo	20.0
	553–783	endo	40.0
	1153–1183	endo	1.3
$Zn_3(C_6H_5O_7)_2 \cdot H_2O$	343–383	endo	2.0
	383–583	exo	18.1
	583–813	endo	40.0
$Cu_3(C_6H_5O_7)_2 \cdot 5\,H_2O$	343–383	endo	8.1
	383–423	endo	6.0
	423–593	endo	59.0

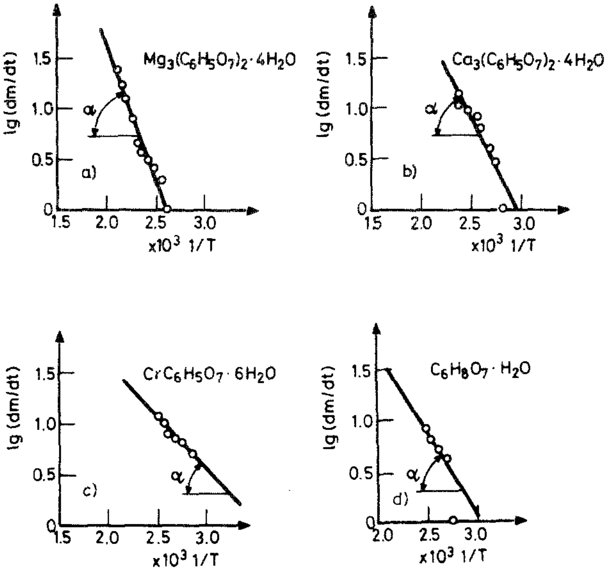


Fig. 4 Graphic determination of the activation energy E_a the dehydration reaction of metal citrates from plots of log (dm/dt) vs. $1/T$ [4, 5, 19, 22]

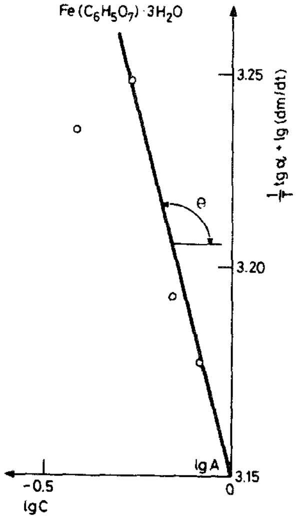


Fig. 5 Graphic determination of the valocity constant $'k$ the dehydration reaction of iron(III) citrate from plots $1/T$ tg α + log dm/dt vs. log c [4, 5, 19, 22]

Knowing the value of E_a, Eq. (5) was drawn:

$$\log \frac{dm}{dt} + \frac{E}{RT} \log c = f(\log c) \tag{5}$$

Table 4 Kinetic parameters E_a, n, A and k of the first partial process of the decomposition of metal complexes with citric acid during heat treatment in static air atmosphere

Compound formula	Activation energy E_a, kJ/mol	Order of reaction, n	Value of A	Velocity constant k of reaction in temp. 290 K, s^{-1}
$Zn_3(C_6H_5O_7)_2 \cdot H_2O$	44.1	0.6	$1.2 \cdot 10^8$	$8.6 \cdot 10^{-1}$
$Mn_3(C_6H_5O_7)_2 \cdot 9\,H_2O$	84.4	0.9	$1.1 \cdot 10^9$	$4.3 \cdot 10^{-2}$
$Cu_3(C_6H_5O_7)_2 \cdot 5\,H_2O$	69.9	0.6	$3.9 \cdot 10^9$	$2.1 \cdot 10^{-2}$
$Co_3(C_6H_5O_7)_2 \cdot 8\,H_2O$	54.9	1.3	$1.0 \cdot 10^9$	$7.1 \cdot 10^{-2}$
$Fe(C_6H_5O_7) \cdot 3\,H_2O$	49.0	1.4	$3.2 \cdot 10^8$	$5.5 \cdot 10^{-2}$
$Cr(C_6H_5O_7) \cdot 6\,H_2O$	59.1	1.0	$1.6 \cdot 10^9$	$6.6 \cdot 10^{-2}$
$Ni_3(C_6H_5O_7)_2 \cdot 10\,H_2O$	65.0	0.8	$2.3 \cdot 10^9$	$1.2 \cdot 10^{-2}$
$Al(C_6H_5O_7) \cdot 4\,H_2O$	70.3	0.7	$3.1 \cdot 10^{10}$	$9.8 \cdot 10^{-2}$
$Mg_3(C_6H_5O_7)_2 \cdot 4\,H_2O$	72.4	0.8	$5.3 \cdot 10^{10}$	$8.4 \cdot 10^{-2}$
$Ca_3(C_6H_5O_7)_2 \cdot 4\,H_2O$	76.1	1.2	$4.2 \cdot 10^{10}$	$7.8 \cdot 10^{-2}$

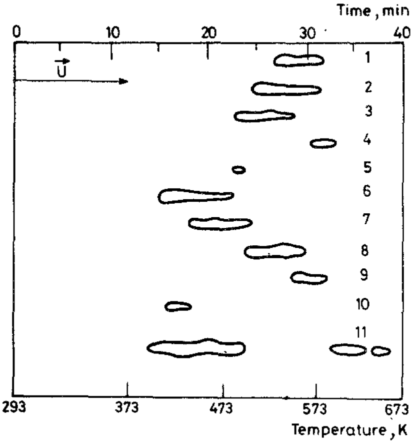


Fig. 6 Spots on chromatographic plates occurring during the condensation of vapours evolving from the capillary in the thermofractophic process

The slope of the obtained straight line in Fig. 5 is equal to the reaction order n. The abscissa is equal to log A. Table 4 shows the obtained numerical values of kinetic parameters such as activation energy E_a, reaction order n, coefficient A and rate constant k at 293 K.

The thermofractochromatograms of the investigated compounds obtained in the dynamic atmosphere of argon are illustrated in Fig. 6. Table 5 contains the values of sublimation heat of the investigated compounds. The molar heat of sublimation of

Table 5 Molar heat of sublimation (Q) of metal citrates found from the thermofractochromatographic data

Metal citrate	T_n, K the temperature at which a spot appears on the plate	Q, kJ/mol
$Mg_3(C_6H_5O_7)_2 \cdot 4\,H_2O$	543.5	48.5
$Al(C_6H_5O_7) \cdot 4\,H_2O$	513.2	46.0
$Ca_3(C_6H_5O_7)_2 \cdot 4\,H_2O$	498.8	44.7
$Cr(C_6H_5O_7) \cdot 6\,H_2O$	583.2	52.3
$Mn_3(C_6H_5O_7)_2 \cdot 9\,H_2O$	497.1	44.6
$Fe(C_6H_5O_7) \cdot 3\,H_2O$	478.0	37.5
$Co_3(C_6H_5O_7)_2 \cdot 8\,H_2O$	443.9	39.7
$Ni_3(C_6H_5O_7)_2 \cdot 10\,H_2O$	508.3	45.5
$Cu_3(C_6H_5O_7)_2 \cdot 5\,H_2O$	558.4	50.0
$Zn_3(C_6H_5O_7)_2 \cdot H_2O$	433.1	38.0

magnesium citrate 48.5 kJ/mol was treated here as a standard [19]. This table includes also the values of T_n, i.e. the temperature at which a spot appears on the plate. Assuming T_n as a volatility criterion, one can state that the volatility of the citrates under investigation decreases in the order:

$$Zn > Al > Ni > Co > Fe > Mg > Cu > Mn > Ca > Cr$$

* * *

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Zusammenfassung — Die thermische Zersetzung von Komplexsalzen von Mg(II), Ca(II), Al(III), Cr(III), Fe(III), Co(II), Ni(II), Zn(II), Mn(II) und Cd(II) mit Citronensäure wurde untersucht. Die kinetischen Parameter der einzelnen Zersetzungsreaktionen wurden durch Analyse der betreffenden thermischen Kurven ermittelt und die Aktivierungsenergien (E_a) und Reaktionsordnungen (n) verglichen. Ein im Laboratorium der Autoren konstruierter Thermofractochromatograph wird den Anforderungen an eine Apparatur zur Trennung, Freisetzung und Identifizierung der beim Erhitzen der untersuchten Verbindungen im Temperaturbereich von 293—600 K gebildeten Produkte gerecht.

Резюме — Термическое разложение и кинетические параметры реакций разложения комплексов двухвалентных магния, кальция, кобальта, никеля, цинка, марганца, кадмия и трехвалентных алюминия, хрома и железа с лимонной кислотой были исследованы на основе их соответствующих термических кривых. Сопоставлены значения энергии активации (E_a) и порядок (n) реакции термического разложения. Сконтруированный в лаборатории авторов термофрактохроматограф, удовлетворяет требованиям, предъявляемым к аппаратуре для разделения, выделения и идентификации продуктов, образующихся при нагревании исследованных образцов в области температур 293—600 K.