Simultaneous determination of potassium and caesium by the decomposition of nitritocuprates(II) of the lead group

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Abstract

A method for simultaneous determination of potassium and caesium has been developed. The method involves quantitative precipitation of $K_2Pb[Cu(NO_2)_6]$ and $Cs_2Pb[Cu(NO_2)_6]$, and then thermal decomposition at $400°C$ and determination of the loss in mass or the amount of nitrogen oxides released. The results of the analysis are calculated on the basis of calibration curves for the loss in mass or conductivity, determined through the decomposition of standard samples.

Keywords: Conductivity; DTA; DTG; Methodology; Nitritocuprate; Nitrogen oxide; TG

1. Introduction

The elements of the potassium group form sparingly soluble nitritocuprates of the lead group of general formula $M_2Pb[Cu(NO_2)_6]$, and of the strontium group of general formula $M_2Sr[Cu(NO_2)_6]$ (where M is NH_4, K, Rb, Cs) [1]. Nitritocuprates of the strontium group are applied for determination of caesium and rubidium by complexometric methods [2,3]. In the present work the determination of potassium or caesium, or the simultaneous determination of potassium and caesium, involves precipitation of sparingly soluble lead–potassium and lead–caesium nitritocuprates(II) at $400°C$ in a specially constructed apparatus [4]. This allows simultaneous recording of the loss in mass and the change in the

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conductivity of the solution which absorbs the released nitrogen oxides as a function of the linear increase in temperature [5]. On the basis of the determined mass of the precipitates, the value of the loss in mass, the change in conductivity, and the previously prepared calibration curves for the loss in mass and for the change in conductivity of the absorbing solution, it is possible to calculate the content of these cations in the mixture under investigation.

2. Experimental

Standard solutions of potassium and caesium were prepared separately by dissolving 103.42 g of analytical reagent KNO_3 (POCh Gliwice) in distilled water made up to 1 dm^3, and 5.58 g of $CsNO_3$ (BDH Chemicals Ltd., Poole) in distilled water made up to 100 cm^3. The K and Cs contents were determined by the perchlorate method.

The precipitating reagent was prepared immediately before use by dissolving 21 g of $NaNO_3$, 12 g of $Cu(NO_3)_2 \cdot 3H_2O$ and 15 g of $Pb(NO_3)_2$ in 50 cm^3 of distilled water.

An OD-102 type derivatograph (MOM Budapest) was used: the compounds were decomposed in air; temperature range $20-1000°C$; heating rate $5°C$ min^{-1}; sample mass, 100 mg; TG sensitivity, 100 mg; DTG and DTA sensitivity, 1/10.

A specially constructed apparatus for simultaneous recording of the loss in mass and the changes in conductivity of the absorbing solution consisted of: a thermobalance, a heating furnace with thermocouple, a nitric oxides absorber, a conductometer with a universal graphite electrode, a line temperature programmer, a digital millivoltmeter, a thermoscope, MD WO-004 operational amplifiers, two XY recording devices, a computer, an analog interface, a highly stabilized d.c. feeder, an autotransformer, a vacuum pump, a peristaltic pump, and Schot crucibles (Fig. 1).

The thermobalance was made of an LB-1050/2 analytical balance manufactured in Hungary, in which the maximum loss in mass is 100 mg. A quartz beam of the thermobalance (22), with a porcelain tray (4) at the end, is attached to the vibration damper of the front scale pan (5). On the porcelain tray is placed a crucible containing the precipitate, and a cylindrical furnace (3) is slid down over it. The chromel–alumel contact of the thermocouple (6) is placed in the furnace, just beneath the crucible containing the precipitate. The system recording the mass losses is installed in the thermobalance. The light beam formed by a system of lenses (8) is extinguished or exposed by a diaphragm (9) as the balance works during the course of the thermal decomposition. The amount of light falling on the photocell (10) is proportional to the location of the beam of the scale, and thus to the loss in mass of the crucible containing the precipitate. Electric signals from the photocell, the programmer of the rise in temperature in the furnace (PG) and the conductometer (KD) are transmitted simultaneously to the $X-Y$ recorder and to the computer. Gases from the furnace (3) are sent to the coil of the absorber (13). The carrier gas (air), which causes constant motion of the liquid in the absorber
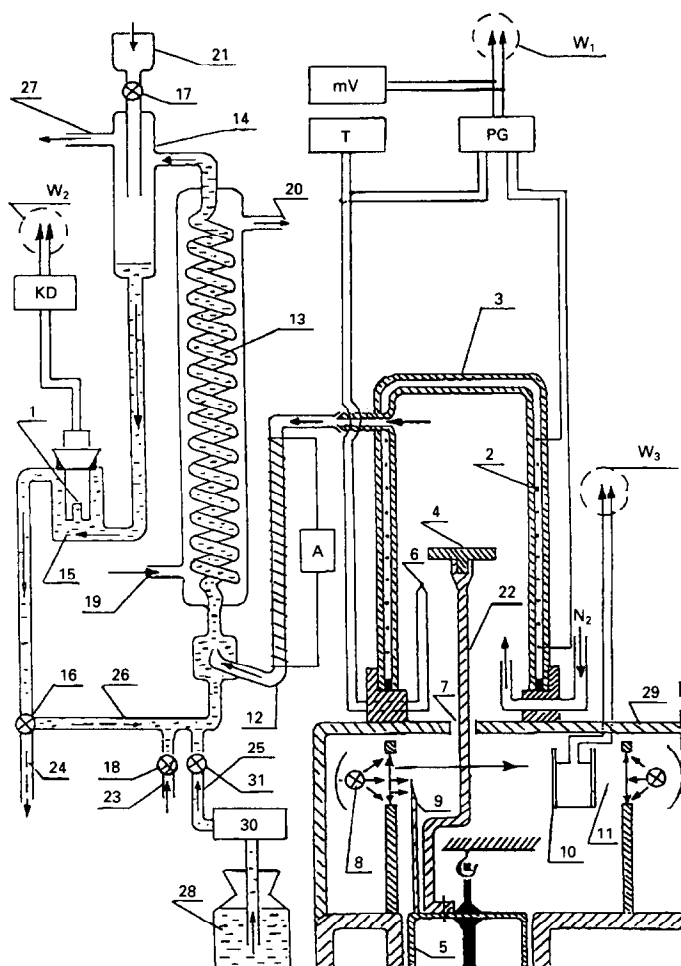
Fig. 1. Apparatus for thermal decomposition (see text).

and the furnace after the absorption of the determined gases in 0.01 M l^{-1} NaOH solution, is separated from the liquid in the chamber (14). The conductivity cell with the measuring graphite electrode built into the absorber system enables continuous recording of the changes in the conductivity of the absorbing solution.

2.1. Thermal decomposition of nitritocuprates(II)

The thermal analysis of $K_2Pb[Cu(NO_2)_6]$ and $Cs_2Pb[Cu(NO_2)_6]$ was carried out using the derivatograph and the apparatus for simultaneous recording of TG curves and changes in conductivity. Thermal curves of $K_2Pb[Cu(NO_2)_6]$ and $Cs_2Pb[Cu(NO_2)_6]$ are presented in Figs. 2 and 3. The common characteristics of the potassium and caesium complexes are the presence of a flat section on the TG and
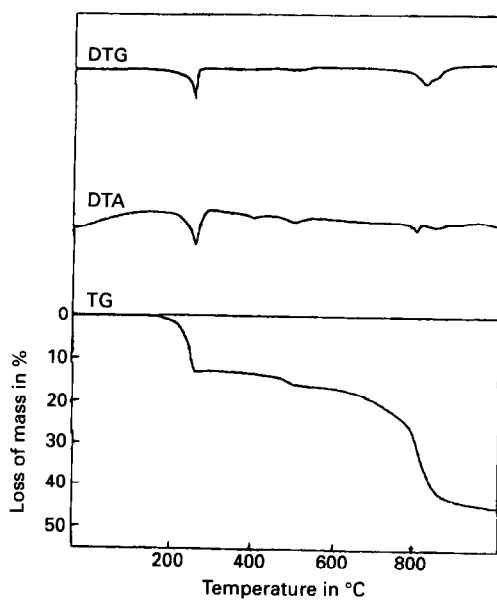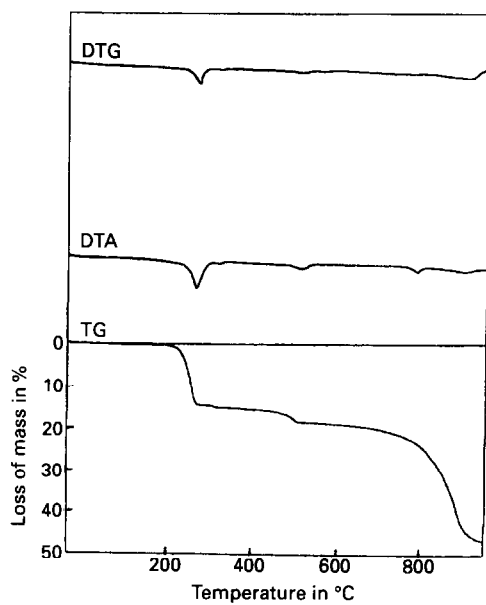
Fig. 2. Thermal curves of $Cs_2Pb[Cu(NO_2)_6]$.

Fig. 3. Thermal curves of $K_2Pb[Cu(NO_2)_6]$.

Table 1
Experimental data obtained from thermal curves

Compound	Stage 1			Stage 2		
	Initial temp. of decomp. in °C	Final temp. of decomp. in °C	Mass loss in %	Initial temp. of decomp. in °C	Final temp. of decomp. in °C	Mass loss in %
K_2L	205	237	19.16	540	880	25.77
Cs_2L	220	280	14.16	630	850	28.13

L is $Pb[Cu(NO_2)_6]^{2-}$.

DTA curves over the range 237–540°C for $K_2Pb[Cu(NO_2)_6]$, and 280–630°C $Cs_2Pb[Cu(NO_2)_6]$. Thus the section between 280 and 470°C is flat for both compounds. The experimental data obtained on the basis of the thermal curves determined using the derivatograph are listed in Table 1.

The curves illustrating the loss in mass of the nitritocuprates(II) and the curves of the change in conductivity related to temperature, obtained using the apparatus for simultaneous recording of mass losses and conductivity changes, are presented in Fig. 4. The maximum of the peak of the conductivity change of the absorbing
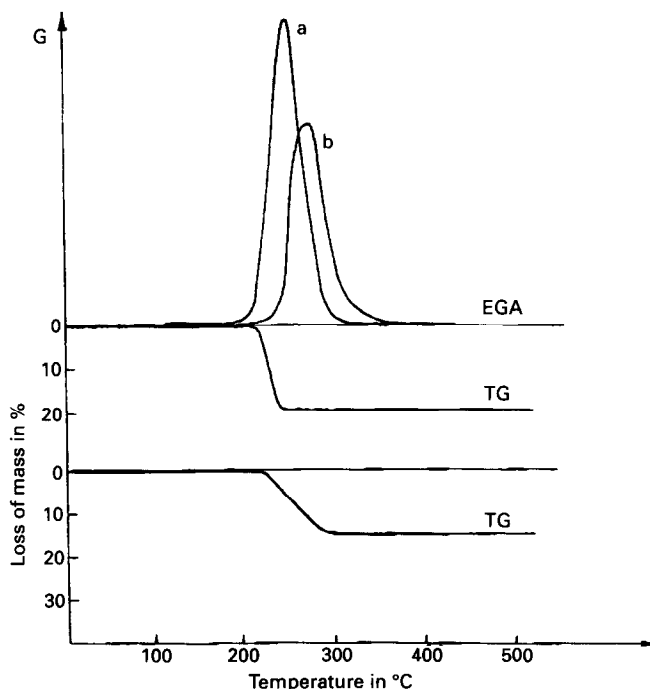

Fig. 4. Conductivity change curves and corresponding mass losses: curve a, $K_2Pb[Cu(NO_2)_6]$; curve b, $Cs_2Pb[Cu(NO_2)_6]$.

solution corresponds with the first stage of the thermal decomposition of the potassium complex which begins at 252°C, and of the caesium complex beginning at 274°C. The evolution of nitric oxides from these compounds is completed at 350°C, a temperature slightly higher than that indicated by the maximum of the mass loss in the TG curve for the caesium and potassium complexes. This is caused by the time necessary for complete absorption of previously evolved nitric oxides, accompanied by a simultaneous increase in temperature during the thermal decomposition of the compounds. On the basis of thermal, chemical and X-ray analyses of the solid products of decomposition and the analyses of gaseous products performed in the present work (absorption of the gases released in the sodium hydroxide and potassium permanganate solution), it was found that the thermal decomposition of the nitritocuprates of the lead group at 300°C proceeds in accordance with the reaction [6]

$$2M_2Pb[Cu(NO_2)_6] + O_2 \rightarrow 4MNO_2 + PbO + Pb(NO_3)_2 + 2CuO + 3N_2O_3$$
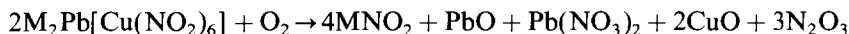
2.2. Determination of potassium and caesium on the basis of the loss in mass

Nitric acid (1 + 4) was added dropwise to the solution containing the potassium and caesium salts until the solution was strongly acidic. The solution was evaporated to dryness on a water bath, and the residue dissolved in a few cm^3 of water;
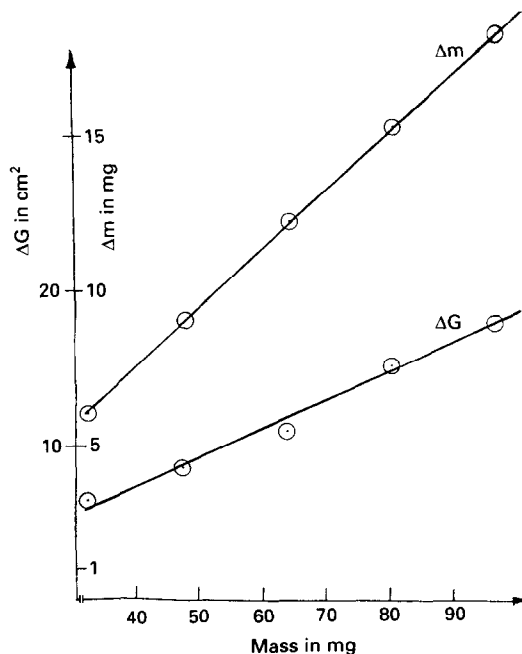

Fig. 5. Relation between the mass of the sample (potassium complex) and the loss in mass and change in conductivity.

10 cm³ of the precipitating agent was added for each 100 cm³ of each of the cations (K⁺, Cs⁺) to precipitate the nitritocuprate(II). The solution was cooled to 10°C for one hour and filtered through the Schot crucible. The precipitate was washed with 20 cm³ of methanol and dried at 70°C to constant mass.

2.3. Calibration curves

The calibration curves, $\Delta m = f(m)$ and $\Delta G = f(m)$ (where Δm is the loss in mass of the precipitate at 400°C, m is the mass of potassium or caesium and ΔG is the change in conductivity of the absorbing solution) for the caesium and potassium complexes were obtained by precipitation from standard solution, where the concentration of potassium in the solution was 0.4007 mg ml⁻¹, and the concentration of caesium was 0.3800 mg ml⁻¹.

From the increasing amounts of solutions (2, 4, 6, 8, 10 ml) diluted 100-fold, lead–potassium and lead–caesium nitritocuprates(II) were precipitated according to the described procedure. Then the quantitatively precipitated sales were thermally decomposed at 400°C, the loss in mass and changes in the conductivity of the 0.01 mol l⁻¹ NaOH solution being recorded (Figs. 5 and 6).

The caesium and potassium present in the solutions were determined by the same procedure as that used for obtaining the calibration curves.
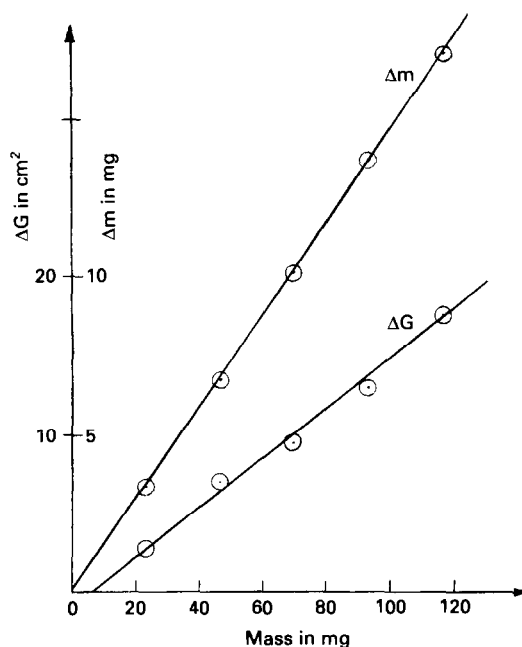

Fig. 6. Relation between the mass of the sample (caesium complex) and the loss in mass and change in conductivity.

3. Calculation of results

3.1. Determination of caesium and potassium on the basis of the loss in mass

The loss in mass of the mixture of lead–caesium and lead–potassium nitrito-cuprates(II) must fall between the mean loss of the mass of the potassium complex and the mean loss of the mass of the caesium complex. Therefore, the obtained experimental points for the mixture of the complexes are situated between the calibration lines of the potassium and the caesium compounds. The equations to calculate the content of both elements in the mixture on the basis of the mass loss in the course of thermal decomposition take the form

$$X_{K_2PbL} = \frac{\Delta m - a_1 m_0 - b_1}{(a_2 - a_1)m_0 + b_2 - b_1} m_0$$

where X_{K_2PbL} is the mass fraction expressing the content of the potassium compound in the mixture, L is $[Cu(NO_2)_6]^{3-}$, m_0 the mass of the mixture precipitate, Δm the loss in mass of the mixture, m_K and m_{Cs} the mass of potassium and caesium in the sample, and a_1, a_2, b_1, b_2 the slopes of the calibration lines. The equation of the calibration lines is $\Delta m = a_1 m_0 + b_1$. For the potassium compound: $\Delta m_2 = 0.19029m_0 + 0.02985$; and for the caesium compound: $\Delta m_1 = 0.14615m_0 + 0.07308$.

The content of the individual alkali metals was determined from the following equations

$$m_K = X_{K_2PbL}\, m_0\, 0.12513$$

$$m_{Cs} = (1 - X_{Cs_2PbL})m_0\, 0.32712$$

The results of the determination of potassium and caesium in the solution are presented in Table 2.

Table 2
Results of determination of potassium and caesium in the mixtures on the basis of the loss in the mass of sample

No.	Amount taken		Amount determined		Difference in %	
	K in mg	Cs in mg	K in mg	Cs in mg	K	Cs
1	2.00	15.20	1.95	15.36	−2.50	+1.05
2	4.01	7.60	4.12	7.49	+2.74	−1.44
3	8.01	7.60	8.13	7.53	+1.49	−0.92
4	8.01	3.80	8.08	3.72	+0.87	−2.10
5	8.01	2.88	7.92	2.95	−1.12	+2.43
6	10.02	3.80	10.26	3.70	+2.39	−2.63

Table 3
Results of determination of potassium and caesium in the mixtures on the basis of the change in the conductivity of the absorbing solution

No.	Amount taken		Amount determined		Difference in %	
	K in mg	Cs in mg	K in mg	Cs in mg	K	Cs
1	2.00	15.20	1.94	15.37	−3.00	+1.12
2	4.01	7.60	4.10	7.40	+2.24	−2.63
3	8.01	7.60	8.16	7.35	+1.87	−3.28
4	8.01	3.80	8.08	3.68	+0.87	−3.16
5	8.01	2.88	7.82	2.98	−2.37	+3.47
6	10.02	3.80	10.31	3.65	+2.89	−3.94

3.2. Determination of caesium and potassium on the basis of the changes in conductivity

The method of determination of the composition of the mixture of nitrito-cuprates is similar to that based on the loss in mass, but the loss in mass of the mixture is replaced by the value of the area of the peak drawn by the recording device coupled with the conductometer. In this case, the equation takes the form

$$X_{K_2PbL} = \frac{\Delta G - a_1 m_0 - b_3}{(a_4 - a_3)m_0 + b_4 - b_3} m_0$$

where ΔG is the surface of the peak corresponding with the change in conductivity, a_3 and b_3 are the slopes of the calibration lines of conductivity for the caesium compound, and a_4 and b_4 are the slopes of the calibration lines of conductivity for the potassium compound. The equations of the calibration lines are $\Delta G = am_0 + b$. For the potassium compound: $\Delta G_1 = 0.19005m_0 - 0.26365$; for the caesium compound: $\Delta G_2 = 0.15789m_0 - 0.97368$. The results of the determination are presented in Table 3.

4. Discussion

The simultaneous determination of potassium, rubidium, caesium and francium in a solution is generally considered to be difficult due to the high chemical similarity of these cations. The determination of caesium and potassium usually requires separation of these cations, using a selective method for determination of caesium [7] and then determining potassium in the solution [8]. There have been no methods for simultaneous determination of the elements of this group, which are much easier than methods in which separation is necessary. The thermal decomposition of precipitated compounds enables simultaneous determination of the elements. The results obtained on the basis of the value of the loss in mass, where the

Table 4
Statistical evaluation of results of potassium and caesium determination

Cation determined	Determination results in mg	$\bar{x}$ in mg	S_r in %	Confidence interval
K 8.01 mg taken	Mass loss method: 8.30, 8.12 8.18, 8.00, 7.75, 7.90	8.02	2.9	8.02 ± 0.3306
	Conductivity method 8.16, 8.05, 8.25, 7.70, 7.60, 7.90	8.04	3.4	8.04 ± 0.3693
Cs 7.60 mg taken	Mass loss method: 7.50, 7.45, 7.85, 7.75, 7.50, 7.70	7.62	2.1	7.62 ± 0.1716
	Conductivity method: 7.35, 7.90, 7.80, 7.90, 7.52, 7.30	7.63	2.7	7.63 ± 0.2037

determination error did not exceed 2.7% (Table 2), are more precise than those based on the changes in conductivity (Table 3). The analysis does not require an apparatus for continuous recording of both the loss in mass and conductivity (it is necessary only in developing the method).

Complex nitrite salts are especially suitable for developing thermo-analytical methods, as their decomposition temperature is low ($\approx 300°C$). Fig. 4 shows that the evolution of nitrite oxides at about 250°C is intense, which is exhibited by a rapid change in conductivity. The evolution of nitric oxides is completed at 300°C for the potassium compound, and at 350°C in the case of the caesium salt (Fig. 4).

The evolution of nitric oxides is accompanied by a rapid loss in mass which is completed at 250°C (the potassium compound) and 300°C (the caesium compound). The TG curves of the derivatogram demonstrate that the first stage of decomposition is completed at 260°C. The statistical evaluation of the results shows that the precision of the method is good (Table 4). The present work is mainly of methodological value because it gives a basis for developing simultaneous methods for determination of elements by recording the loss of mass and evolved gaseous products using the specially constructed apparatus.

Acknowledgment

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