

## THERMAL DECOMPOSITION OF SOME HEAVY AND TRANSITION METAL BENZENESULPHONATES

T. MEISEL, Cs. MÉLYKÚTI and Z. HALMOS

*Institute for General and Analytical Chemistry,  
Technical University of Budapest, Hungary*

(Received September 8, 1975)

The thermal behaviours of Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II), Pb(II), and VO(II) benzenesulphonates were studied by simultaneous thermoanalytical methods (DTA, TG, DTG, EGA). The measurements were at times supplemented by X-ray analysis of the decomposition products, as well as by chemical analysis. The decomposition processes of samples were carried out in oxygen, in air and in nitrogen atmospheres. The effect of the atmosphere on the decomposition was studied primarily with regard to the reaction paths of the sulphur content of compounds investigated. The possibility of quantitative analysis of these salts was studied from the aspects of both residues and the sulphur oxide products.

No data are available in the literature as regards the thermal analysis of the benzenesulphonates of the ions mentioned above. We recently reported some results [1–4] on the thermal decompositions of the alkali metal and alkaline-earth metal benzenesulphonates. In the latter salts a nucleophilic exchange reaction is well known to occur between the sulphonic and hydroxyl groups as a “fusion reaction” in the presence of base. This reaction is used for technological purposes. It is accompanied by a great number of side-reactions, which become predominant, if the salts are exposed to thermal degradation alone. Thus depending on the effect of the atmosphere applied volatile products are formed, e.g. sulphur oxides, benzene, thiophenol, diphenil oxides and others, the residue containing alkali metal sulphides and sulphates, and carbon black. It was observed that in an inert atmosphere the reaction between carbon black and sulphate, producing sulphide is significant [4].

For the purpose of quantitative analysis it was important to determine the yields of sulphur oxide in the decomposition, and the conditions which have to be used to obtain a residue suitable for stoichiometric calculations. The yield of sulphur dioxide is reasonable according to Siggia [5]. His experiments indicated that the pyrolysis of arylsulphonic acids and their salts yield sulphur dioxide quantitatively in a reducing atmosphere, and the product can be measured easily by G. C. methods. It was therefore interesting to know whether similar results can be obtained or not in the case of the salts examined. It was also interesting to investigate the influence of different metal ions on the decomposition.

## Experimental

### *Preparation of samples*

The compounds examined were prepared by reactions between carefully purified benzenesulphonic acid and appropriate metal hydroxides or carbonates. In some cases the reaction between barium benzenesulphonate and the metal sulphates seemed to be advantageous for preparation. The compounds were recrystallized. Their metal contents were determined by complexometry (Cd(II), Zn(II), Pb(II), Co(II), Ni(II), Mn(II), by permanganometry (Fe(II), Fe(III), VO(II)), by iodometry (Cu(II)) and by argentometry (Ag(I)). Our analyses showed that the metal salts were pure, and had stoichiometric compositions.

### *The methods of investigation*

Measurements were carried out by means of a derivatograph fitted with a thermogastitrimetric accessory (TGT, DTGT) [6, 7]. The sample mass was 100–200 mg, the heating rate 5°/min and platinum crucible was used. The gas flow rate was 30 l/h with a suction rate 15 l/h. The relative standard deviations of sulphur oxide analysis by this method were about 2–3%. The individual residues of the decompositions were identified by means of an X-ray apparatus. The sulphide contents of the residues were determined by iodometry. Sulphate content was analyzed by conductometry, using barium acetate solution. The amount of water of crystallization was checked by the Karl-Fischer method, although for some of the salts investigated there are theoretical limitations to the application of this method.

## Results and discussion

Some of the thermoanalytical curves obtained simultaneously are presented in Figs 1 and 2.

The following data and conclusions resulted from evaluation of thermoanalytical curves obtained for simultaneous reactions. The water of crystallization content determined from the TG and DTG curves is equal to that measured by direct water determination, except in the case of the copper and vanadyl derivatives. The results obtained by TG are relatively close to the data available in the literature [8], except in the cases of the iron(III) and cobalt(II) salts [8]. This difference is probably caused by the different drying and pretreatments. Only the silver (318–320°), lead (220°), and iron(III) (310–325°) salts transformed into molten phases under the applied circumstances; the others decomposed directly in the solid state.

Silver and lead benzenesulphonates exhibit reversible polymorphic transitions between room and decomposition temperatures. The thermal decompositions revealed two stages in the case of measurements in a nitrogen atmosphere. The

first stage is thermal degradation (the evolution of organic compounds), accompanied by the formation of a significant quantity of carbon black and sulphur oxides, while in the second stage a reaction takes place between the carbon black and the inorganic sulphur-containing residue. A large amount of sulphur dioxide is produced during the first reaction. The release of sulphur dioxide takes place at times in one step, and in other cases in two or more steps, but these are not essentially separated from each other.

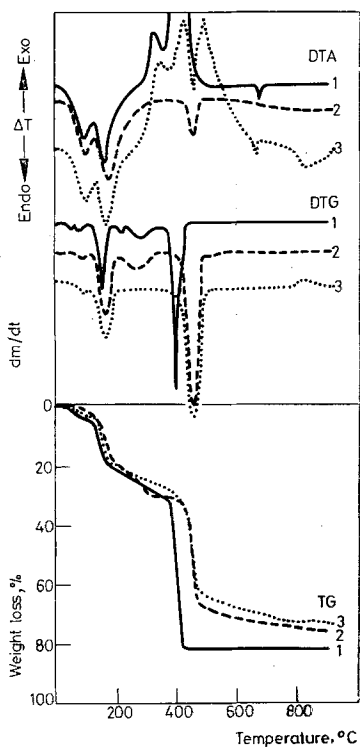


Fig. 1. Complex thermoanalytical curves of vanadyl(II) benzenesulphonate(VO)  $(C_6H_5SO_3)_2$ , in oxygen (1), nitrogen (2), and air (3) atmospheres

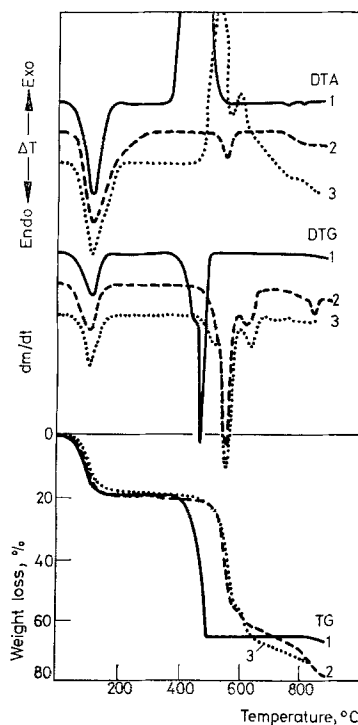


Fig. 2. Complex thermoanalytical curves of cadmium(II) benzenesulphonate  $Cd (C_6H_5SO_3)_2 \cdot 5.5H_2O$ , in oxygen (1), nitrogen (2) and air (3) atmospheres

When the zinc salt was heated over  $1000^\circ$ , a small amount of sulphur dioxide was produced. This is related to the fact that the main decomposition process was combined with the formation of sulphite and/or sulphate.

The release of sulphur dioxide was followed by thermogastitrimetry in conjunction with the derivatograph. Some examples of the results are given in Figs 3–5.

Table 1

The amount of sulphur oxide liberated during decomposition in oxygen and nitrogen atmospheres, and the sulphide and sulphite contents of the residue

Benzenesulphonate	Sulphur content measured during decomposition				
	in O <sub>2</sub> atm.	in N <sub>2</sub> atmosphere			
	by titration, %	by titration, %	as S <sup>2-</sup> , %	as SO <sub>3</sub> <sup>2-</sup> , %	total S cont., %
Vanadyl(II)	93.55	56.9	—	—	56.9
Manganese(II)	91.85	37.6	—	—	37.6
Iron(II)	85.34	40.0	—	—	40.0
Iron(III)	65.75	53.0	10.89	8.6	72.45
Cobalt(II)	96.6	54.6	—	—	54.6
Nickel(II)	98.0	62.0	7.0	—	69.0
Copper(II)	79.24	80.1	—	—	80.1
Zinc(II)	93.53	84.5	—	—	84.5
Silver(I)	89.31	97.4	—	—	97.4
Cadmium(II)	39.6	82.6	17.2	—	99.8
Lead(II)	63.7	31.6	23.49	—	55.09

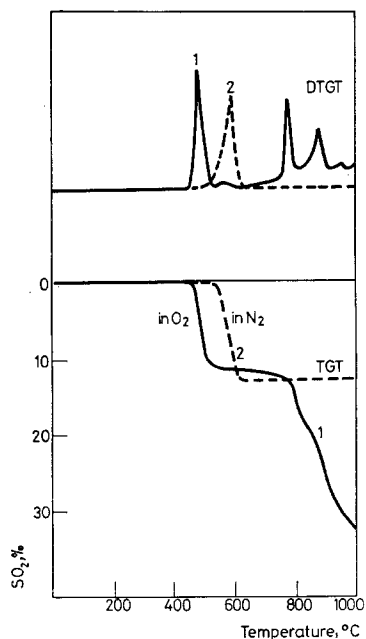


Fig. 3. Thermogravimetric (TGT) and derivative thermogravimetric (DTGT) curves of manganese(II) benzenesulphonate  $\text{Mn}(\text{C}_6\text{H}_5\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$ , in nitrogen (1) and oxygen (2) atmospheres

In order to determine the sulphide contents of the residues of the salts in an inert atmosphere, the sulphide was liberated with a mineral acid in the form of hydrogen sulphide and this was measured. The sulphide contents could be detected in the case of iron(III), nickel(II) and lead(II) salts, as can be seen in Fig. 6 and Table 1.

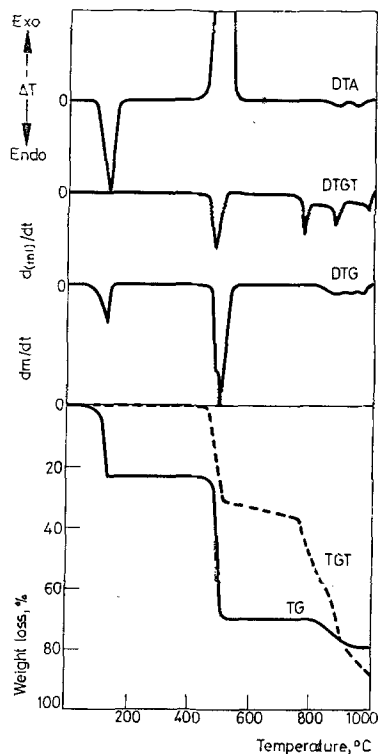


Fig. 4. Thermoanalytical (DTA, TG, DTG, TGT, DTGT) curves of manganese(II) benzenesulphonate  $\text{Mn}(\text{C}_6\text{H}_5\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$ , in oxygen atmosphere

The application of an oxygen atmosphere significantly modified the shapes of the complex thermoanalytical curves. The characteristics of the dehydration of the salts remained the same as in a nitrogen atmosphere. However, the temperatures of the main degradation reactions, i.e. the initial, peak, and final temperatures, were shifted considerably towards lower temperatures. The temperature ranges of the decomposition reactions are listed in Table 2. Obviously, the exothermic character of the DTA curves during the decomposition becomes predominant in an oxygen atmosphere. The decompositions were very violent, and therefore the temperature of the sample occasionally surpassed the program by 20–90°. The decomposition took place very sharply, within a very narrow temperature range.

Table 2

The temperature ranges of the decompositions and upper limits of temperature investigations

Benzenesulphonate	Decomposition temperature, °C in O <sub>2</sub> atm.			Decomposition temperature, °C in N <sub>2</sub> atm.		
	step 1	step 2	Upper tempera- ture limit	step 1	step 2	Final temp.
Vanadyl(II)	180–380 380–420		920	380–480	480–824	824
Manganese(II)	440–540	800–970	1020	500–630	630–918	918
Iron(II)	310–370	560–690	925	440–590	590–935	935
Iron(III)	210–350	580–710	895	310–400		
				435–720	720–880	880
Cobalt(II)	250–380	730–880	980	530–590	590–890	890
Nickel(II)	385–470	720–835	945	460–600	600–940	940
Zinc(II)	230–380					
	380–560	640–870	985	440–590	590–1022	1022
Silver(I)	350–480	—	600	330–460	460–602	602
Cadmium(II)	370–450	780–850	850	470–660	660–870	870
Copper(II)	280–340					
	340–430	600–760	875	280–410	410–870	870
Lead(II)	420–520	—	630	460–540	540–630	630

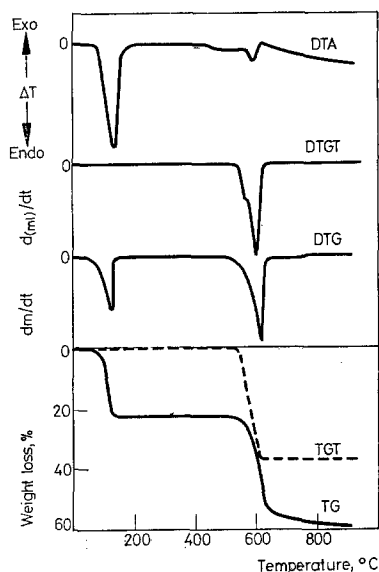
Fig. 5. Thermoanalytical (DTA, TG, DTG and TGT, DTGT) curves of manganese(II) benzenesulphonate  $Mn(C_6H_5SO_3)_2 \cdot 6H_2O$ , in nitrogen atmosphere

Table 3

The sulphur liberated in the form of sulphur oxide during the main and the second decomposition, measured in an oxygen atmosphere. The nature of the residue is also indicated

Benzenesulphonate	Main decomposition in O <sub>2</sub> atm			Second decomposition in O <sub>2</sub> atm		
	Up to temperature, °C	Liberated sulphur, as % of theoretical	Residue measured by X-ray	Up to temperature, °C	Liberated sulphur, as % of theoretical	Residue measured by X-ray
Vanadyl(II)	650	85.2	V <sub>2</sub> O <sub>5</sub>	—	8.35	—
Manganese(II)	600	37.0	MnS <sub>0.6</sub> O <sub>3</sub>	1020	54.85	γ-Mn <sub>2</sub> O <sub>3</sub> MnO · Mn <sub>2</sub> O <sub>3</sub>
Iron(II)	510	54.6	FeSO <sub>4</sub> α-Fe <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub>	925	30.74	α-Fe <sub>2</sub> O <sub>3</sub> Fe <sub>3</sub> O <sub>4</sub>
Iron(III)	480	54.8	Fe <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	895	10.95	Fe <sub>3</sub> O <sub>4</sub> α-Fe <sub>2</sub> O <sub>3</sub>
Cobalt(II)	510	27.5	α-CoSO <sub>4</sub>	980	69.1	Co <sub>3</sub> O <sub>4</sub> CoO
Nickel(II)	545	15.58	NiSO <sub>4</sub>	945	82.42	NiO
Copper(II)	500	52.6	CuO CuSO <sub>4</sub>	875	27.64	CuO CuSO <sub>4</sub>
Zinc(II)	578	34.99	ZnO ZnO · 2ZnSO <sub>4</sub>	985	58.54	ZnO
Silver(I)	600	87.6	Ag	—	—	—
Cadmium(II)	540	37.7	CdSO <sub>4</sub>	850	1.88	CdO CdSO <sub>4</sub>
Lead(II)	630	63.7	PbO · PbSO <sub>4</sub>	—	—	—

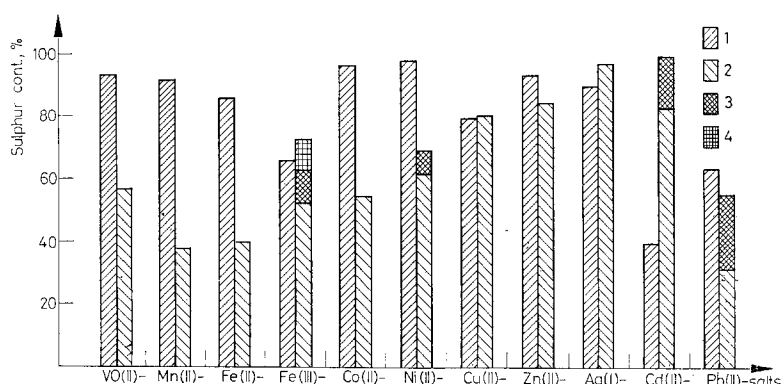


Fig. 6. Sulphur contents of the benzenesulphonates of transition metal ions, measured during their decompositions, under conditions indicated. 1. S content measured in O<sub>2</sub> as SO<sub>2</sub>; 2. S content determined by titration in N<sub>2</sub> as SO<sub>2</sub>; 3. S<sup>2-</sup> amount measured during decomposition in N<sub>2</sub>; 4. SO<sub>3</sub><sup>2-</sup> amount measured during decomposition in N<sub>2</sub>

The reaction was accompanied by sulphur oxide evolution, which was measured quantitatively (see Figs 3–5). The main decomposition was separated from the second one; it was shown by a smaller or larger plateau in the TG curve. The second reaction can be observed in most cases, and is due to the thermal degradation of metal sulphate formed during the previous reaction. The silver salt is an exception, because silver metal was formed during its thermal decomposition, even in an oxygen atmosphere, and only a very small amount of sulphate could be measured conductometrically. In the course of decomposition of vanadyl salts, vanadium pentoxide was formed directly. Tables 3 and 4 contain all the data

Table 4

The sulphur liberated in the form of sulphur oxide during the main and the second decomposition, measured in a nitrogen atmosphere. The nature of the residue is also indicated

Benzenesulphonate	Sulphur measured during decomposition in N <sub>2</sub> atmosphere		Upper temperature limit	Residue measured by X-ray
	main decomp., %	second decomp., %		
Vanadyl(II)	48.73	8.07	824	
Manganese(II)	37.5	—	918	
Iron(II)	38.75	1.25	935	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>
Iron(III)	51.98	1.02	880	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> ; S <sup>2-</sup> ; SO <sub>3</sub> <sup>2-</sup> ; C
Cobalt(II)	53.0	1.6	890	CoO + C
Nickel(II)	60.8	1.2	940	NiO; NiS; C
Copper(II)	80.1	—	870	CuO
Zinc(II)	76.36	8.14	1022	ZnO
Silver(I)	97.4	—	602	Ag; C
Cadmium(II)	81.33	1.27	870	CdS; C
Lead(II)	30.1	1.5	630	PbS; C

concerning the formation of sulphur oxides. The residues were identified by X-ray measurements. It can be clearly recognized that the sulphur content of the compounds was not converted quantitatively to sulphur dioxide. This is due to the formation of compounds containing sulphur in the course of thermal decompositions, for example thianthrene, thiophenol, diphenyl sulphide etc. Analysis of the salts based on the determination of sulphur oxide can therefore not give correct results. However, the weight stability of sulphate derivative formed in an oxygen atmosphere after the main decomposition, offers a possibility of quantitative determination, at least theoretically, for most of the compounds investigated. It has also to be considered that the formation of sulphate needs only half the sulphur content of the benzenesulphonates. The situation concerning the compositions of the residues is summarized in Table 5.



Table 5

The measured and calculated weight residues of the metal benzenesulphonates

Benzenesulphonate	Measured residue, %		Calculated metal sulphate, %	Calculated metal oxide, %	Calculated metal, %
	step 1	step 2			
Vanadyl(II)	17.0	—	—	18.9 (V <sub>2</sub> O <sub>5</sub> )	—
Manganese(II)	30.0	20.0	32.0 (MnSO <sub>4</sub> )	16.5 (Mn <sub>2</sub> O <sub>3</sub> )	—
Iron(II)	25.5	17.0	31.8 (FeSO <sub>4</sub> )	16.7 (Fe <sub>2</sub> O <sub>3</sub> )	—
Iron(III)	34.8	29.2	34.3 [Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ]	13.7 (Fe <sub>2</sub> O <sub>3</sub> )	—
Cobalt(II)	34.0	15.0	32.1 (CoSO <sub>4</sub> )	15.55 (CoO)	—
Nickel(II)	32.0	15.8	32.1 (NiSO <sub>4</sub> )	15.5 (NiO)	—
Copper(II)	20.0	16.0	32.8 (CuSO <sub>4</sub> )	16.4 (CuO)	—
Zinc(II)	33.0	18.5	33.1 (ZnSO <sub>4</sub> )	16.7 (ZnO)	—
Silver(I)	42.4	—	—	—	40.6
Cadmium(II)	34.0	32.8	39.6 (CdSO <sub>4</sub> )	24.4 (CdO)	—
Lead(II)	50.0	—	49.5 (PbO · · PbSO <sub>4</sub> )	—	—

It can be observed that, during the main decomposition, a quantitative conversion to sulphate resulted only in the case of the Fe(III), Ni(II) and Zn(II) salt; Pb(II) gave a residue of oxide-sulphate (PbO.PbSO<sub>4</sub>). The residues of the other compounds were a mixture of metal oxide and sulphate. The Ag salt is an exception, as mentioned earlier. The metal sulphates decomposed into metal oxides at higher temperatures, depending on the nature of the cations (see Table 5.). It should be pointed out that in the case of the majority of the compounds investigated the thermal behaviour in air was quite different from that in pure oxygen. The shapes of the thermoanalytical curves were found to be similar to those in an inert atmosphere, rather than to those in oxygen, because of the local and periodical lack of oxygen.

### References

1. S. GÁL, T. MEISEL, Z. HALMOS and L. ERDEY, *Mikrochim. Acta*, 4–5 (1966) 903.
2. T. MEISEL, S. GÁL, Z. HALMOS and L. ERDEY, *Mikrochim. Acta*, 1 (1967) 31.
3. Z. HALMOS, T. MEISEL, L. ERDEY, *Proc. 3rd Anal. Chem. Conf. Budapest*, 2 (1970) 249.
4. Z. HALMOS, Thesis, Technical University of Budapest 1970.
5. S. SIGGIA, *Anal. Chem.*, 42 (1970) 1719.
6. F. PAULIK, J. PAULIK, L. ERDEY, *Z. Anal. Chem.*, 160 (1958) 241.
7. F. PAULIK, J. PAULIK and L. ERDEY, *Mikrochim. Acta*, (1966) 886.
8. *Beilsteins Handbuch der Organischen Chemie*, 11 (1928) 28.

RÉSUMÉ — On a étudié par ATD, TG, TGD et AGE simultanées le comportement thermique des benzène-sulfonates de Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II), Pb(II) et VO(II). Occasionnellement, on a complété ces résultats par analyse aux rayons X et par analyse chimique. On a étudié l'effet de l'atmosphère (oxygène, air et azote) sur la décomposition, surtout du point de vue des processus réactionnels liés à la teneur en soufre des composés. On a étudié la possibilité d'une analyse quantitative de ces sels à partir des résidus ainsi qu'à partir des oxydes de soufre.

ZUSAMMENFASSUNG — Das thermische Verhalten von Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II), Pb(II) und VO(II)-benzolsulfonaten wurde durch simultane thermoanalytische Methoden (DTA, TG, DTG, EGA) untersucht. Gelegentlich wurden die Messungen durch Röntgenanalyse der Zersetzungsprodukte sowie durch chemische Analyse ergänzt. Die Zersetzungsvorgänge der Proben wurden in Sauerstoff, Luft und Stickstoffatmosphäre durchgeführt. Die Wirkung der Atmosphäre auf die Zersetzung wurde untersucht, mit besonderer Berücksichtigung der Reaktionen entsprechend dem Schwefelgehalt der geprüften Verbindungen. Die Möglichkeit der quantitativen Analyse dieser Salze wurde nach den Resten und den Schwefeloxid-Produkten untersucht.

Резюме — Термическое поведение бензол-сульфонатов Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II), Pb(II) и VO(II) было изучено совместными термоаналитическими методами (ДТА, ТГ, ДТГ и ЭГА). Измерения были дополнены как химическим анализом, так и рентгеноструктурным анализом продуктов разложения. Процессы разложения образцов были выполнены в атмосфере кислорода, воздуха и азота. Было изучено влияние атмосферы на разложение относительно направлений реакций всех исследованных серосодержащих соединений. Изучена возможность количественного анализа этих солей, исходя соответственно из остатков и окислов серы.